

ALKALI ACTIVATED MATERIALS OR GEOPOLYMERS?

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The paper presents an overview of the state-of-the-art on the alkali activated materials since 1973 in Department of Glass and Ceramics in Prague. Properties of alkali activated materials in comparison with standard Portland cement are discussed.

INTRODUCTION

Alkalis (Na, K) bring about problems in the technology of Portland cement and concrete. These troubles can be characterized as problems in the clinker production and the formation of undesirable silicate and aluminous phases of the type $KC_{12}S_{23}$, NC_8A_3 . However, the alkali-silica reaction in the concrete that is accompanied by expansion represents the major source of problems. Such problems call for a strict limitation of the alkali content in the cement to values amounting to 0.6 percent and less (expressed as Na_2O). On the other hand, however, soluble alkali compounds speed up the hydration process of hydraulic and latently hydraulic substances thus facilitating the formation of new hydration phases as this was shown by Purdon [1] in his work from 1940. In 1959 Gluchovskij [2] demonstrated in his book "Gruntosilikaty" (Figure 1) the possibility of preparing new materials by means of the reaction of aluminosilicate raw materials (slags, fly ashes, clay materials) with alkaline compounds (carbonates, hydroxides, silicates).

The possibilities resulting from the use of the alkali activation of aluminosilicate materials were later investigated by a variety of workers. At present, the data base in Chemical Abstracts includes more than 1 800 original papers devoted to this topic. Furthermore, a series of congresses dealing with alkali activated materials [3-10] took place since 1978.

The Institute of Glass and Ceramics ICT Prague has been investigating the problems associated with the alkali activation since 1973. The attention has been focused on processes of alkali activation of Portland cements, ground Portland cement clinker, blast-furnace slags, kaolinite materials and other inorganic wastes. The investigation into high strength gypsum-free Portland cements (alkali-activated) lasted several years and

eventually ended successfully with an industrial viability stage [11-13]. Our present day attention focuses on alkali activation processes of fly ashes occurring during the combustion of brown and bituminous types of coal.



Figure 1. V.D. Gluchovskij: *Book Gruntosilikaty*, Kijev 1959.

Fly ash wastes represent a considerable environmental problem in the Czech Republic because more than 10 million tons are rejected annually with the majority of this amount being disposed of on disposal sites.

ALKALI ACTIVATION

Alkali activation of alumino-silicate materials represents a complex process that has not been described to the full yet. The reaction of alumino-silicate materials in a strong alkaline environment results, first of all, in a breakdown of Si–O–Si bonds; later, new phases arise and the mechanism of their formation seems to be a process that includes a solution ("synthesis via solution"). The penetration of Al atoms into the original Si–O–Si structure represents a substantial feature of this reaction. Alumino-silicate gels (zeolite precursors) are mostly formed. Their composition can be characterized by the formula $M_n[-(Si-O)_z-Al-O]_n \cdot wH_2O$. The C–S–H and C–A–H phases may also be originated in dependence on the composition of the starting materials and the conditions of the reaction. Even secondary H_2O may be formed during these (poly-condensation) reactions.

Amorphous (gel-like) or partially amorphous or crystalline substances may be originated in dependence on the character of starting raw materials and on the conditions of the reaction. The concentration of the solid matter plays a substantial role in the process of alkali activation. Mostly crystalline zeolite-type products (analcime, hydro-sodalite and other) are formed in extremely diluted suspensions ($w > 1 \dots 10$). Therefore, the above process is used for the synthesis of manmade zeolites as this is corroborated by numerous publications. Predominantly amorphous products are originated at higher concentrations of the solid phase in the suspension ($w < 1$).

It was for the above amorphous bodies that Davidovits [14] proposed a terminology of poly-sialates by taking into consideration the Si-to-Al ratio (Figure 2).

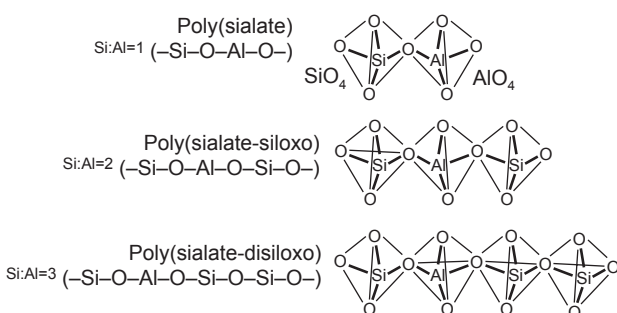


Figure 2. Davidovits terminology.

In 1976 to 1979 Davidovits [15] coined a new term "geopolymer" (almost 20 years after the Gluchovskij's term "gruntosilikat", "gruntocement-geocement").

Davidovits defines the material as follows: "The geopolymer is a material originated by inorganic polycondensation, i.e. by so-called "geopolymerization" (in result of the alkali activation of alumino-silicate materials -our note).

A three-dimensional alumino-silicate network characterized by the empirical formula $Na,K_n \{-(Si-O)_z-Al-O\}_n \cdot wH_2O$ where M is K, Na or Ca atom, n - the degree of poly-condensation, z - 1, 2, 3 or more than 3 is formed. The network is configured of SiO_4 and AlO_4 tetrahedrons united together by oxygen bridges. Chains or rings united by Si–O–Al bridges are formed. Positive ions (Na^+ , K^+ , Ca^{++}) must compensate the negative charge of Al that is present in the coordination 4.

CONCEPTION OF GEOPOLYMERS

Based on his research work Davidovits [16] elaborated a structural model of the geopolymer (in this case, the model was designed for a poly-sialate - silox type formed by alkali activation of meta-kaolin). In his model he assumed an essentially monolithic polymer similar to organic polymers. (Figure 3).

Further progress in the investigation into the microstructure of the products of alkali activation (geopolymerization) and, in particular, the results obtained by using the methods of thermal analysis, mercury porosimetry, data obtained by measurement of BET isothermal curves and MAS NMR spectroscopy (Si, Al and especially Na) permitted a certain revision of this conception. Based on the above results Barbosa [17] proposed a modified model (Figure 4). Geopolymer materials are similar to vitreous bodies - the NMR spectra of alumino-silicate glasses and those of geopolymers are similar. Both materials exhibit the same three-dimensional arrangement. However, there is no water present in the glass structure, and the glass is practically without pores (Figure 5).

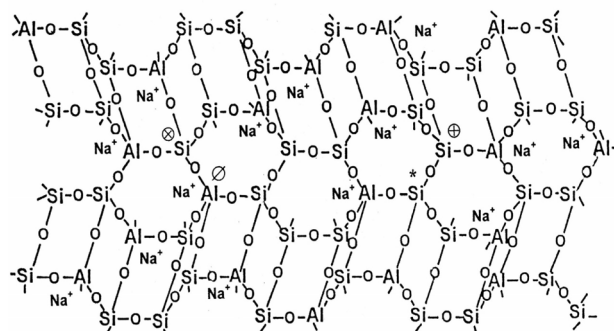


Figure 3. Davidovits model of geopolymer structure [16,18].

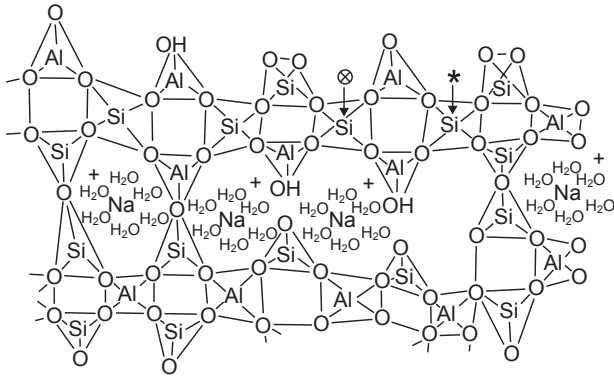


Figure 4. Barboza model of geopolymer structure [17].

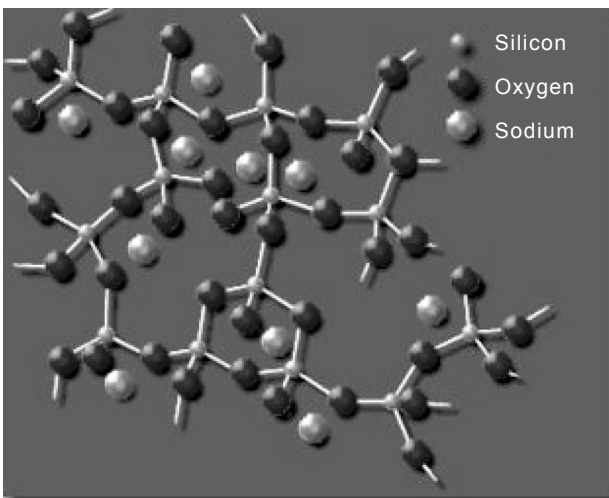


Figure 5. Structure of glass.

There is also a certain similarity between the geopolymer materials and the Portland cement because both materials are resistant to the action of water after their hardening. Therefore, they behave like a hydraulic binder. The hardened Portland cement is also a porous material with pores ranging from nanometers to micrometers. In contrast to the geopolymer, the Portland cement contains not only amorphous hydrates but also the crystalline ones ($\text{Ca}(\text{OH})_2$, ettringite, etc.). There is $\text{Ca}(\text{OH})_2$ present in the pores of hardened Portland cement and the surface is coated by a thin layer of CaCO_3 (because of the carbonate formation). The water is used ("consumed") for the hydrate formation during the hardening of the Portland cement whereas it stays in the structure during the geopolymer hardening (water serves predominantly as a "carrier" of the alkali activating agent).

The results published up to now (they are in full agreement with our data) give the possibility to declare that a geopolymer material (on the basis of fly ashes, metakaolin):

- does not possess any monolithic structure of the polysialate - silox type,

- the alkali cation (Na, K) is present in the structure in a solvated form; furthermore, it is bonded more weakly than in the crystalline structure of zeolites (this fact represents a potential danger as regards the efflorescence occurrence),
- is rather characterized by a random three-dimensional arrangement,
- represents a porous body with pores ranging from nanometers to micrometers,
- contains water in pores and in the gel;
- the water plays only a role of a carrier of the alkali activating agent and that of a "rheological" water;
- crystalline and amorphous hydrates occur only rarely and only if a slag or Ca-containing material is present.

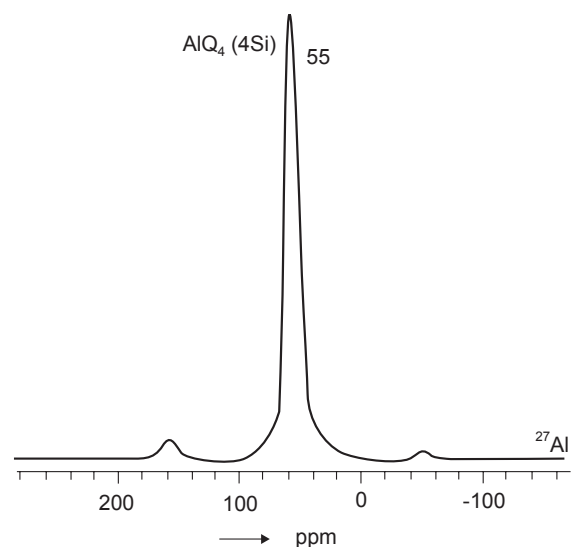
Hence, what is a geopolymer?

Davidovits says [16, 18]: "... the ^{27}Al NMR spectra of the product must exhibit a peak only at about 55 ppm. Al may be present in the product structure only and exclusively in the coordination 4..." (Figure 6).

If it is not so, the product may not be called a geopolymer but only an alkali activated material ..."

This very strictly formulated definition satisfies essentially only the materials obtained by alkali activation of pure metakaolin. There is a variety of question marks coming to mind when the materials originated by alkali activation (geopolymerization) are analyzed and classified:

- Do the materials obtained on the basis of other raw materials than metakaolin belong to geopolymers too?
- Can also the materials that contain Al in the coordination six, eg unreacted mullite residues (fly ashes) be regarded as geopolymers?

Figure 6. NMR MAS ^{27}Al of "true", "genuine" geopolymer [16,18].

- Can the materials that also contain the C–S–H phase (in the case of slags or clinker) be called geopolymers, too?
- Can the materials formed only at a temperature of 20°C or during a hydrothermal synthesis or at a higher temperature be called geopolymers?
- Can the materials that also contain B and P atoms in addition to Si and Al atoms be classified as geopolymers (Figure 7)?

A scientific discussion on the above topics is necessary.

What do have alkali-activated aluminosilicate materials in common?

The presence of the $\text{Na}_n\text{K}_m\{-(\text{Si-O})_z\text{-Al-O}\}_n \cdot n\text{H}_2\text{O}$ phase. How should we call this phase?

An N–S–A–H or K–S–A–H phase (as would be customary among the cement scientists)?

Or a zeolite-like phase (Gluchovskii)? (analogy to the tobermorite-like phase, the C–S–H phase today).

Or shouldn't we rather use a quite different denomination: polymer silicate, inorganic polymer concrete?

If we forget the strict definition of the geopolymer formulated by Davidovits (related to pure metakaolin) we shall reach a new very large group of inorganic binders with substantial ecological and energetic potentials as well as the binders with properties that have not been described yet. Then, such materials could be defined in accordance with the starting raw materials, e.g.:

geopolymer on the fly ash basis

geopolymer on the metakaolin basis etc.

If the geopolymers are conceptualized as a large group of binders, then significant differences in the product character and composition can be found during the alkali activation of various alumino-silicate raw materials (Figure 8).

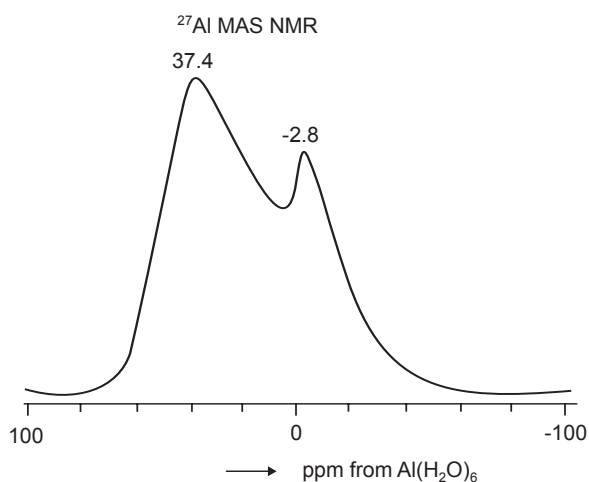


Figure 7. INMR MAS ^{27}Al of geopolymer containing P [21].

There are visible trends that can be observed in the series starting with clinker, slags, fly ashes and ending with kaolinitic materials:

- The necessity to increase the Na_2O content in the alkali activating agent is obvious.
- Stronger activating agents (alkali carbonate, alkali silicate, respectively alkali hydroxide) must be used.
- The content in the $\text{M}_n\{-(\text{Si-O})_z\text{-Al-O}\}_n \cdot n\text{H}_2\text{O}$ phase increases.
- The Ca content in the product drops and, hence, also the content of the C–S–H and C–A–H phase decreases.

Therefore, two phases co-exist one along another in geopolymer materials the $\text{M}_n\{-(\text{Si-O})_z\text{-Al-O}\}_n \cdot n\text{H}_2\text{O}$ phase having the character of a zeolite and the C–S–H phase, respectively the C–A–H phase. This coexistence affects the properties of geopolymer materials and we may state that the highest values of strength (up to 160 MPa compression strength) could be achieved in geopolymer materials that exhibited the coexistence of both types of phases.

The results of system analyses [19] of a wide range of aluminosilicate raw materials used for the preparation of geopolymers show that metakaolin occupies the top position as regards the consumption of energy, environmental impacts and cost (the cost/benefit factor amounting to 7-8); slags and ceramic waste are less demanding and the fly ashes (the cost/benefit factor amounting to 0.5) are the least demanding raw materials. The cost/benefit factor of the Portland cement (1.2) was determined in the same way.

Acknowledgement

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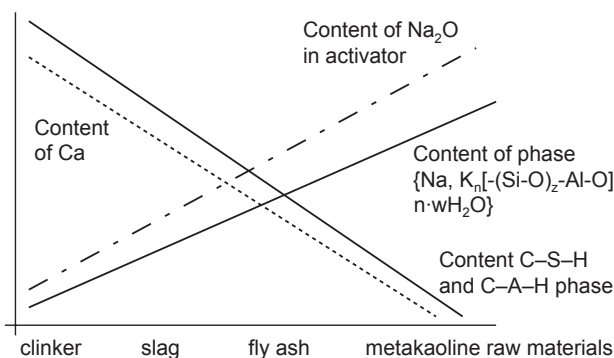


Figure 8. Composition of various alkali activated materials.

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ALKALICKY AKTIVOVANÉ MATERIÁLY
NEBO GEOPOLYMERŮ?

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V přednášce je uveden přehled o výzkumné činnosti a výsledcích dosažených v oblasti alkalicky aktivovaných materiálů od roku 1973. Jsou diskutovány terminologické otázky a klasifikace alkalicky aktivovaných materiálů - geopolymérů. Jsou také diskutovány mikrostrukturální modely geopolymérů.