Review of practical applications of alkali-activated systems in construction

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Abstract. This paper reviews the possibilities of using alkali-activated systems in building industry. The history of research of alkali-activated systems and practical applications of these binders in building industry are summarized. This article shows where the evolution of these systems should be directed.

1. Introduction
Alkali-activated materials represent a group of alternative inorganic binders, where binder component consists of aluminosilicates and alkaline activators [1]. Wider interest in research and practical use of these systems in building industry is registered in the last 15 years.

Opportunity to use in production of these composites based on waste materials from various industrial sectors and also the excellent properties of the final product make this group of binders, suitable ecological alternative to Portland cements.

This paper summarizes the basic directions of the possible application of alkali-activated materials, primarily in the field of construction.

2. Materials used for alkaline activation
For alkaline activation, as binder are used latent hydraulic substances or pozzolans. Hydraulicity of these binders takes shape when a suitable activator is added with indispensable quantity of water. Binders are based on natural or technogenic origin, the most commonly used, are blast furnace slag, fly ash, metakaolin and also natural pozzolans [2].

The function of activator is performed by hydroxides, silicates, or carbonates of alkali metals. The final structure and properties of alkali-activated systems depend primarily on used raw materials, the ratio of particular components, type of aggregate, method of preparation and storage conditions. The diversity of the final products is increased in effort to prepare various binders of specific properties by using mixture of many materials as a raw material [1,2,3].

The best results of strength and durability were reached by alkali activated systems based on blast furnace slag. Composites based on alkali-activation of metakaolin reach low strengths, but the final materials are highly external influences resistant, especially resistant to frost, aggressive substances and high temperatures. Fly ash-based geopolymers reach lower durability, in comparison to metakaolin-based geopolymers, but generally achieve higher strength [1].

3. History of alkali activation research and application
Probably the first use of alkali-activated systems belongs to antiquity, is discussed its particular use in construction of the pyramids in Egypt and the ziggurats of Mesopotamia. There are also speculations
about the use of alkali-activated systems by civilizations in Central and South America and many centuries later in relationship with the buildings of ancient Rome. Based on information about these advanced cultures, economic situation, geographical location and according to the results of chemical analyzes of preserved structures we suggest that people were able to produce these materials [6].

Current research has been started in the first half of the 20th century. One of the first reported use of alkali-activated materials in the industry was application of the mixture based on kaolin and sodium carbonate at 150 °C in a ceramic factory Olsen in 1934 [7]. In the 1930s research of suitability sodium hydroxide and potassium hydroxide for use with blast furnace slag as possible ingredients of Portland cements was conducted. During the research of the systems Purdon found, that the addition of alkali generates new, fast-hardening binder [8, 9].

In the 1950s, professor Gluchovskij led research of alkali activated slag in Ukraine, during the 1960s and the 1970s he contributed significantly to the identification of solidified products. The research revealed that the components react together to form zeolites. Concrete based on alkali activated slag called the "grunctocements" and described it in the book "Gruntosilikaty" published in 1959. In 1969, Gluchovskij acquired the first patent for the preparation of these materials [10]. In the follow to his research a first building was built in the 1960s in Ukraine. The building was built of prefabricated blocks prepared according to his recipe. Clays were substituted by blast furnace slag, prepared concrete was called slag-alkali, and it was used in the construction of sewers and other, by external influences highly stressed structures [7].

"Trief Cements" (alkali-activated slagcements) were, due to the generation of smaller hydration heat used in the 1950s mainly in the massive structures construction [9].

The nowadays first practical use of alkali-activated system for construction is known from the 60s of the last century. In Ukraine, the building was built of blocks made of recipe Professor Gluchovskij [1].

In 1953 alkali-activated systems were researched by the U.S. Army, the alkaline activation was carried out by mixing of 1.5 % NaCl, 1.5 % NaOH and 97 % ground slag [9].

From the 1960s sewer systems, roads and breakwaters were built of alkali-slag concretes in Russia, Poland, Finland, USA, Canada and later also in Spain, Germany and other countries [7].

In the 1970s alkali-activated systems were also studied by French scientists Besson Cailler and Henin, in 1969 the result of their work was the synthesis of various kaolinitic materials in concentrated sodium hydroxide solution at a temperature of 100 °C [10].

Then building products were fire-resistant wood chipboard designed the 1972 by Legrand. These were formed by a wood core encased with alkali-activated material. [10].

In 1972, a team of scientists Davidovics and Latapie prepared mixture for the production of water-resistant ceramic tiles. These were produced at temperatures lower than 450 °C [11].

In the years 1977 - 1982 L.T.G.S. technology were created. It is a procedure where the kaolinite ceramic paste achieved in an alkaline environment high strength and water resistance [10].

In the 1970s team of Davidovits and Legrand developed technology based on geosynthesis. Joseph Davidovits, claiming to be the discoverer of geopolymerization, he used for alkali activated materials based on kaolin as the first term “geopolymer” in 1978 [11].

In 1983, the U.S. developed high strength geopolymer cement PYRAMENT™. It was made of Portland cement, fly ash, metakaolin, ground slag, and potassium carbonate. This cement was used to airport runways repair. PYRAMENT™ achieved high initial strength of about 20 MPa after 4 hours of hardening, after 28 days were measured strength in the range of 70 to 100 MPa [10].

In 1983, Foss developed F-cement in Finland, low-porosity cement designed for industrial applications with a rapid increase in strength. It was based on alkaline activation of slag or fly ash. F-cement contains as a superplasticizer a sulphonated polyelectrolyte, which in this type of concrete allowed to achieve optimal consistency even with minimal water coefficient [12].

In 1984, Langton and Roy examined specimens of mortar and plaster from ancient Greece, because of their high resistance. According to their findings, they divided the composite matrices into five groups, which are divided according to the content occurrence of individual hydraulic aluminosilicate
and pozzolanese mastics. In the framework of this research it was found, that the mineralogy of the matrix, the particle size, the porosity, the dosage and the type of aggregate, as well as the method of deposition and the surrounding conditions, therefore the same factors that affect life of materials based on Portland cement, have also a crucial influence on the extremely long lifetime of these new type materials [13].

In 1986, Krivenko described the mechanism that controls the process of forming the structure of the alkali-activated mass, dividing the links into two main categories. In the first case, the alkali component is a monovalent cation of Na\(^+\) or K\(^+\), and in the latter case, the divalent Ca\(^{2+}\) cation is in the alkaline component. In general, these binder systems can be divided into the following two groups according to the theory:

\[
\begin{align*}
\text{Me}_2\text{O} &- \text{Me}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O} \\
\text{Me}_2\text{O} &- \text{MeO} - \text{Me}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O} \quad [14,15]
\end{align*}
\]

In 1986, Malek and colleagues proposed slag-concrete for the disposal of radioactive salt (generated by crystallization of waste sludge) from the Savannah River area of South Carolina by placing this material in artificial ditches. The material capture matrix must have the required properties, in particular the minimum permeability of toxic substances to the environment. Therefore, a mixture of ash with granulated slag was proposed, variants of this mixture were tested using Portland cement and the variant without addition, and the data were compared with other formulations (based on a different type of ash, without slag, etc.) [16,17].

In 1989, in the Russian city of Lipetsk a twenty-floor house was built of alkali-slag concrete, without Portland cement [28].

Since the 1990s, the number of research studies dealing with alkali-activated systems has grown considerably. As a representative of this era, in addition to the ongoing experiments of the aforementioned scientists (Gluchovsky, Davidovits, Krivenko, Roy), it is possible to mention, for example, the results of Professor Brandštetr’s team, whose research focuses on the preparation of composites using waste materials, blast furnace slag, and the use of ash in non-cement mixtures. Furthermore, the team of prof. Paloma, which deals with alkali activation of fly ash, including observation and description of the resulting microstructure, as well as the Provis - Deventer team, dealing with, among others, the industrial use of alkaline activated materials [15].

From the point of view of practical use in recent years, the following applications of alkali-activated materials can be mentioned.

In Australia, in Brisbane, the first house was constructed for Queensland University, in which a geopolymer concrete was used. The four-storey building is built of prefabricated buildings. From the alkaline activated blast furnace slag and ash composite, 33 prefabricated ceiling panels were used [18].

The largest project for the use of alkali-activated material is the construction of the Brisbane West Wellcamp Airport in 2014, with the implementation of 40,000 cubic meters of geopolymer concrete. The material was used during construction for its high strength, low shrinkage and good workability. Geopolymer concrete was applied in a layer of 435 mm thickness [19].

Another example of the application of alkaline activated systems in building practice is E-Crete™. This is concrete prepared on the basis of fly ashes from coal combustion in power plants and blast furnace slag. E-Crete™ is a product of the Australian company Zeobond Group, which offers it in the form of both the concrete and prefabricated parts [22].

In Australia, "geopolymer concrete" is also produced, called Earth Friendly Concrete (EFC). It is a composite based on a combination of blast furnace slag and fly ash, wherein alkaline activation takes place at elevated temperatures using alkali in solid or liquid form. Various types of prefabricated components are produced from the given material, for example their use in tunneling and sewerage segments, using their high resistance to aggressive environments [21].
4. Alkali activation research in Czech Republic

In the Czech Republic research of alkali activated materials for construction first began professor Brandšteť in the 1960s in Brno University of Technology [4,5,7].

From the 1970s alkali activation was researched by the Department of Glass and Ceramics, Institute of Chemical Technology in Prague, later in cooperation with the Faculty of Civil Engineering, CTU in Prague [22].

In 1979 a team of CTU and University of Chemistry and Technology Prague formulated the principles of preparation no-gypsum Portland cement, called "BS cement". This is made of Portland cement, or slag, alkaline salt and anioactive surfactant. Final product is rapidly hardening cement. It hardens at temperatures as low as -30 °C and it is resistant to high temperatures up to 1200 °C. The maximum measured compressive strengths reach values up to 245 MPa. BS cement was in 1989 experimentally applied to industrially produced building materials, concretes reached strengths of 100 MPa [22].

In the 90th years, the Department of Glass and Ceramics at University of Chemistry and Technology Prague researched geopolymers based on metallurgical slags and fly ashes. The final product contained a mixture of fly ash and slag reached compressive strengths up to about 170 MPa. In 2002 a cement-free geopolymer concrete based on fly ash - POPbeton® was prepared. This material achieved compressive strengths up to 60 MPa, it is resistant to salts and high temperatures. The main advantage of this product is the use of waste material [22].

Research of Institute of Rock Structure and Mechanics ASCR, v.v.i. Prague is focused on potential use of geopolymers in disposal of radioactive and hazardous waste and for the fireproof, sound and thermal insulating materials preparation [24].

The Institute of Chemical Technology in Prague deals with the technology of alkali-activated mortars and concretes preparation in dependence on the final use of the product. The research is also focused on finding the optimal composition of the activator, the determination of micromechanical properties using nanointendance, a detailed description of the mechanisms of alkaline activation, achieving the required properties for each type of mixture, fixation of heavy metals in the polymer matrix, determination of the extracts of fly ash geopolymer, chemical resistance in strongly acidic and alkaline mediums, geopolymer adhesion to concrete reinforcement [22].

Institute of Industrial Ceramics FMME VSB - TUO studies the use of secondary metallurgy slags in application of alkali-activated systems [2,3].

Since 2008 alkali-activated materials has been researched also by Faculty of Civil Engineering, VSB-TU Ostrava. For the possible use of these systems in the construction industry were tested alkali activated blast furnace slags with fillers based on various types of construction and mining waste. Research is also focused on the preparation of thermal insulation alkali-activated building materials, compressed geopolymer mixtures and development of protective layers [20,23,25-27].

In cooperation with building companies (Prefa Troubelice, a.s., ŽPSV, a.s., etc.), practical applications are being carried out in the construction industry, the possibilities of using these systems in elements of transport structures, fine-grained mixtures, facade elements and prefabricated elements are tested.

An example of practical application of alkali-activated systems is alkali activated binder Baucis, a raw material based on kaolinite. This binder is produced by Ceske lupkove zavody. It is produced by the controlled heat treatment of kaolin and shale. After mixing the binder with water and alkali silicates, material chemically and structurally similar to natural rock is prepared. Firing temperature of this material is 750 °C, it hardens rapidly, 40-50 % of the final strength is achieved after 1 day and 90 % strength is reached in 7-14 days. The binder is suitable for fire-resistant products, and may be exposed to temperatures up to 1200 °C [29].

With the support of the Czech Development Agency are in the short-run lines produced various prototypes of products of alkaline activation, imitating various materials, such as bricks, stone, wood and metals [10].
Another example of the alkali-activated system used in practice is the binder Geopol®. This technology of SAND TEAM Ltd. is prepared for the production of molds and cores for ferrous and non-ferrous metals casting. The advantage of the technology is the possibility of the used materials recycling, the minimum mechanical abrasion, good workability and good binder properties at a very low dosage of binder [30]. The company is applying cast molds based on alkali activation especially in the U.S. where growing pressures on environmental protection [31].

5. Perspective
Alkali-activated materials have considerable potential for use not only in the building industry. Their widespread use in building practice prevents in particular the need for considerable technological discipline during the alkaline activation process, the failure of which ultimately leads to significant fluctuations in the values of the monitored parameters.

The wider application of alkali-activated systems is obstructed also by the absence of standards for testing, the use of liquid activators in the manufacture and the conservative attitudes. Builders are afraid of the use of non-traditional binding systems. Due to the requirements of sustainable development and conservation of mineral resources, however, we can expect in a relatively short period, a boom in the market of products based on alkali-activated systems.

6. Conclusion
This paper was prepared to summarize the historical and current scientific results and practical applications in the field of alkali-activated systems. Alkali-activated materials form a group of inorganic binders. The properties of these materials are verified in many experiments and represent a promising set of alternative masses. At present, they are used rather marginally in construction practice, but in the future they can be expected to expand into many sectors of the construction industry.

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