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POSSIBLE APLICATIONS OF ALKALI-ACTIVATED SYSTEMS IN CONSTRUCITON

MOŽNOSTI APLIKACE ALKALICKY AKTIVOVANÝCH SYSTÉMŮ VE STAVEBNICTVÍ

Abstract

This paper deals with the possibilities of using alkali-activated systems in construction. This article summarizes the advantages and disadvantages of geopolymer in comparison to Portland cement, summarizes research and practical applications of alkali-activated materials in our country and abroad, and provides an overview of directions where these alternative inorganic binders can be in the future very well applied.

Keywords

Alkali-activated system, geopolymer, binder.

Abstrakt

Příspěvek se zabývá možnostmi využití alkalicky aktivovaných systémů ve stavebnictví. Článek shrnuje výhody a nevýhody geopolymerů v porovnání s portlandskými cementy, rekapituluje výzkumy a praktické aplikace alkalicky aktivovaných systémů u nás i v zahraničí a nabízí přehled směrů, ve kterých se mohou tato alternativní anorganická pojiva v budoucnosti velmi dobře uplatnit.

Klíčová slova

Alkalicky aktivovaný systém, geopolymer, pojivo.

1 INTRODUCTION

Alkali-activated materials, also known as geopolymers, represent a group of alternative inorganic binders. Geopolymers are involved composites, where binder component consists of aluminosilicates and alkaline activators [1]. Wide interest in research and practical use of geopolymers in construction are registered especially in the last 10-15 years. Opportunity to use in production of geopolymer 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.

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2 MATERIALS SUITABLE FOR ALKALINE ACTIVATION

To alkali-activated systems preparation are as binders used latent hydraulic substances or pozzolans. Hydraulicity of these binders takes shape when a suitable activator is added with indispensable quantity of a water. Binders are based on natural or technogenic origin, the most commonly used, is 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 [1]. The final structure and the resultant 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 [1, 2, 3].

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. The final products are materials known as alkali-activated cements, inorganic polymer concretes, geocements, hydroceramics, or alkali bound ceramics [2].

Generally, the best results of strength and durability were reached by alkali activated systems based on blast furnace slag [1]. Because of its frequent use in the cement industry, slag is becoming scarce material and so efforts to use slag in alkali-activated systems in a minimum amount are intensified, while maintaining the desired properties of the final products. Finely ground granulated blast furnace slag is, used in the construction industry particularly as a suitable substitution of Portland cement in the production of cement concrete, or as a component in the production of blended cements. The results of experimental research dealing with up to 100 % weight replacement of Portland cement by finely ground blast furnace slag in the manufacture of cement concrete are described in [4].

Alkali-activated metakaolin-based systems reach low strength, but the final materials are highly external influences resistant, especially resistant to frost, aggressive substances and high temperatures [1].

Ash-based geopolymers reach lower durability, in comparision to metakaolin-based geopolymers, but generally achieve higher strength [1]. According to the study Materials suitable for geopolymers [1] in terms of relative energy-consumption factor, that takes account into the economic and environmental impacts of materials, fly ashes from lignite and hard coal were appointed as the most suitable resource. Fly ash is a waste incineration product, there is no other treatment needed for it´s further conversion into alkali-activated mixtures. In contrast, the least suitable for geopolymer preparation was metakaolin referred according to this study. This is especially becaused of the prior calcination necessity at temperatures around 600-850 ° C [1, 5].

3 DIFFERENCES BETWEEN GEOPOLYMERS AND CEMENTS

Basic differences between alkali-activated systems and products of Portland cement hydration also cause different final properties.

If the product of Portland cement hydration is CSH gel and $Ca(OH)_2$, then the alkaline activation of granulated blast-furnace slag forms primarily CSH gels and a zeolitic phases to a small extent as well. In contrast, geopolymers based on metakaolin and fly ash consists mostly of the zeolitic phase type ($Na, K_n\{- (Si\text{-}O)_z\text{-}Al\text{-}O\}_n.wH_2O$) [1, 3].

The essential difference in results of hydration processes is the fact that alkali-activated system products do not contain Portlandit, that is the weakest component of hydrated Portland cement in the composite system. Due to the variability of used raw materials there are several different types of final products in the geopolymer mixture [2]. Based on research of the dependence of amount and type of hydration products on the type of raw material and the activator amount is clear that since the clinker through slag, fly ash to metakaolin it is necessary to increase the amount of Na_2O in the alkali activator, and to use hydroxides and silicates instead of carbonates [1].

The advantage of alkali-activated materials opposite to cements is especially fact, that these materials are amiable to the environment. Not only because the alkaline activation does not produce any carbon dioxide, but the most positive is the fact that, as major raw materials are primarily waste industrial materials such as blast furnace slags or fly ashes used. The usage of secondary products saves mineral reserves. By using alkali-activated systems energy-wastefull burning of limestone, the basic raw material for Portland clinker production, is eliminated.

An important advantage of these systems is the ability to use lower quality, concrete unsuitable aggregates, such as aggregates with high proportion of fine particles from quarries, mines and tailings. Research proved that in alkali-activated systems also wastes such as recycled concrete and brick, stone or slag aggregate can be applied [6].

It was proved that the alkali-activated system is able to hold heavy metals and radioactive waste in its structure, without morphology mutation of the system or hardening processes affecting as in cements. Based on the results of heavy metals leaching were alkali activated materials with zeolitic structure accepted as a suitable matrix for the fixation of heavy metals [7].

Alkali-activated systems are in comparison with conventional cements extremely resistant to aggressive substances of the external environment, to sea water or sludge. This corrosion resistance is brouhgt about the compact microstructure, minimum porosity and a presence of zeolitic phases, that in practical use ranks geopolymers among the materials applicable to sewer systems, breakwaters and bridge piers. [8]

Slag-alkali concretes achieve 15 % lower thermal conductivity than concrete based on Portland clinker. Because of low icing of alkaline mixture it can be used for concreting at low temperatures up to -30 °C [9]. It was also demonstrated high consistency of alkali-activated systems with steel, which is advantageous in reinforced concrete [9]. For geopolymers preparation no special equipment is required, current devices used in concrete production are quite sufficient. Other advantages of alkali activated materials are minimal contraction, waterproofing and fire resistance [10]. Geopolymers hydration heat is about a third to a half less than Portland cement hydravion heat [9], that allows the production of massive structural elements. A positive aspect is also a high inceptive strengths, the compressive strength after 2-4 hours after the beginning of the solidification range 10 – 25 MPa.

Geopolymer disadvantage, in comparison to Portland cement, is the usage of caustics in geopolymer production, this problem can be solved by using metasilicate, dry activator, that added to the mixture, then only water is needed for mixture irrigation to start hydration reactions. Further problem is the high cost of activators (particularly potassium water glass, which rate is approximately three times higher than for sodium water glass), this may be solved by, the use of alkaline industrial wastes. The biggest obstacle for geopolymers use seems to be extremely short time of setting and hardening. This can be partially extended by using retarders, the most proven are phosphates and borates in slag-alkali concretes and Rudal (sodium silicate and sodium aluminate solution) in geopolymers made of fly ash, slag and metakaolin [9].

4 PAST AND PRESENT OF GEOPOLYMER RESEARCH

The first use of alkali-activated systems probably belongs to antiquity, argued is its particular use in construction of the pyramids in Egypt and the ziggurats of Mesopotamia. In relationship with the use of alkali-activated systems there are also speculations about 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 [11].

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 [12]. In the 30th 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 Belgian scientist Purdon found, that the addition of alkali generates new, fast-hardening binder [13].

Alkali-activated slagcements called "Trief Cements" were, due to the generation of smaller hydration heat used in the 50th years mainly for the massive structures construction [14]. In 1953 geopolymers 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 [14].

In the 50th, research of alkali activated slag in Ukraine led professor Gluchovskij, who during the 60th and the 70th contributed significantly to the identification of products solidification. The research revealed that the components react together to form zeolites. Concrete based on alkali activated slag called the "gruntocements" and described it in the book "Gruntosilikaty" published in 1959. In 1969, Gluchovskij acquired the first patent for the preparation of these materials [15]. In follow to his research a first building was built in the 60th in Ukraine, the building was built of prefabricated blocks prepared according to his recipe. Then clays were substituted by blast furnace slag, this concrete was called slag-alkali, and was used in the construction of sewers and other, highly environmentaly stressed structures [12].

In the 70th geopolymers 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 [15].

In 1972, a team of scientists Davidovics and Latapie prepared mixture for the production of water-resistant ceramic tiles, these tiles were produced at temperatures lower than 450 ° C. [16] In the 70th 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 [16]. Although that his definition of geopolymer responds just the system, where only pure metakaolin as a binder is used, as geopolymers are simplify titled all alkali activated materials, regardless of used raw materials.

In the Czech Republic research of alkali activated materials for construction first began in the 60th professor Brandštetr in BUT [8, 9, 12].

From the first half of the 70th geopolymers were researched also 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 [17, 18]. In 1979 a team of CTU and ICT formulated the principles of preparation no-gypsum Portland cement, known as "BS cement", which is made of Portland cement, or slag, alkaline salt and anioactive surfactant. Final product is a rapidly hardening cement, it hardens at temperatures as low as -30 °C and it is resistant to high temperatures up to 1200 °C, and 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 [18]. In the 90th years, the Department of Glass and Ceramics at ICT 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 [17]. This material achieved compressive strengths up to 60 MPa, it is resistant to salts (Na_2SO_4, NaCl, $MgSO_4$) and high temperatures. The main advantage of this product is, the use of waste material for concrete manufacture. Nowadays the technology of POPbeton® is optimized and further material properties of the concrete are examined, for example the adhesion to various materials, the influence of additives and admixtures on concrete properties, durability of concrete in various ways of stress, or expansion behavior of POPbeton® in normal year intervals and in critical temperatures [17].

Research since 2003 at the Institute of Chemical Technology in Prague deal with the technology of geopolymerous mortars and concretes preparation in dependence on the final use of the product. This 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 [17].

Institute of Industrial Ceramics FMME VSB - TUO solves in alkali-activated systems the problem of secondary metallurgy slag application, especially the ladle furnace slag application. Long-term research of geopolymers deals with changes of properties in dependance on warming and used activator. Currently is on the faculty solved also the possibility of using dry activators, solid water glass [2, 3].

Institute of Rock Structure and Mechanics ASCR, v.v.i. Prague, led by Assoc. Straka focuses on potential use of geopolymers in disposal of radioactive and hazardous waste and for the fireproof, sound and thermal insulating materials preparation. In 2005 group of workers from the Department of geopolymer chemistry introduced a material called Benit, a fly ash geopolymer. Its advantage is the possibility of use low quality aggregates, unusable for concrete and also the possibility of use a seawater as a mixing water, without negative impact on final strength [19].

Research Institute of Inorganic Chemistry, Usti nad Labem deals with the properties and methods of preparing a two-part geopolymer binder, that consists of a metakaolin and finely ground granulated blast furnace slag, and second, a liquid component is made of water and sodium alkali activator [20]. There were also, under the leadership of Ing. Koutník, produced materials for reconstruction of historical monuments, based on kaolinitic clays and claystones, abundant raw materials in the Czech Republic [21, 22, 23].

Since 2004, in the research of geopolymers is also involved The Czech Development Agency, o.p.s. Its main objective is to promote the technology, research support and geopolymers in construction practice implementation [15].

At the Faculty of Civil Engineering, VSB-TU Ostrava geopolymers are researched since 2008. 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 waste (recycled brick and concrete) and (Fig. 1) mining waste (chippings and waste sand from kaolin washing). Research is currently focused on the preparation of thermal insulation alkali-activated building materials, compressed geopolymer mixtures and development of protective geopolymer layers [24, 25, 26].

Fig. 1: Detail of stone sculptures copy, that was created by stomping of geopolymer mixture based on blast furnace slag, metakaolin and waste sand from kaolin washing [24]

5 HISTORY OF GEOPOLYMER APPLICATION

The first practical use of geopolymers for construction is known from the 60s 20th century. In Ukraine, the building was built of blocks made of recipe Professor Gluchovskij (Fig. 2 [1]).

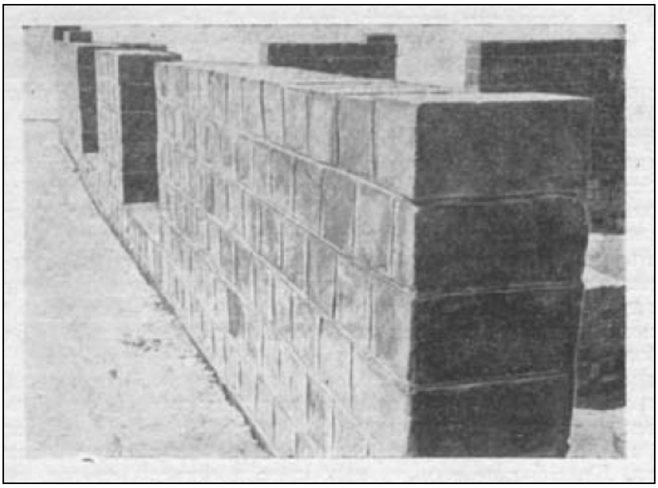

Fig. 2: Construction of gruntocements blocks [1]

From the 60th sewer systems, roads and breakwaters were built of alkali-slag concretes in Russia, Poland, Finland, USA, Canada, the U. S. and later also in Spain, Germany and other countries [12].

Other building products were fire-resistant wood chipboard designed the 1972 by Legrand, these were formed by a wood core encased with a geopolymerous material. The factory products, however, due to the change of works policy were not produced [15]. 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 [15].

In the years 1979 - 1995 in France were developed technologies of geopolymer binder production. For example foamed geopolymer materials, or liquid binders were reached [16].

In 1983, the U. S. developed high strength geopolymer cement PYRAMENT^{TM}. It was made of Portland cement, fly ash, metakaolin, ground slag, and potassium carbonate. This cement was used to airport runways repair. PYRAMENT^{TM} 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 [15].

In 1989, in the Russian city of Lipetsk a twenty-floor house was built of alkali-slag concrete, without Portland cement [27].

6 CURRENT GEOPOLYMER APPLICATION IN THE CZECH REPUBLIC

At present, in the Czech Republic there are produced geopolymers or materials designed specifically for it´s production.

An example of practical application of alkali-activated systems is geopolymer binder Baucis produced by Ceske lupkove zavody a.s., a raw material based on kaolinite. Baucis 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 cement is 750 °C. Material hardens rapidly, 40-50 % of the final strength is achieved after 1 day and 90% strength is reached after 7-14 days. The binder is suitable for fire-resistant products, and may be exposed to temperatures up to 1200 °C [28].

Another example of the geopolymer system use 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 (Fig. 3). 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 [29]. The company is applying cast molds based on geopolymers especially in the U. S. where growing pressures on environmental protection [30].

Fig. 3: Part of molds for bronze casting [30]

With the support of the Czech Development Agency are in the short-run lines produced various prototypes of geopolymer products, imitating various materials, such as bricks (Fig. 4), stone and even wood (Fig. 5 and 6) and metals (Fig. 7) [15].

Fig. 4: Prototype of geopolymer brick imitation [15]

Fig. 5: Prototype of geopolymer wood imitation [15]

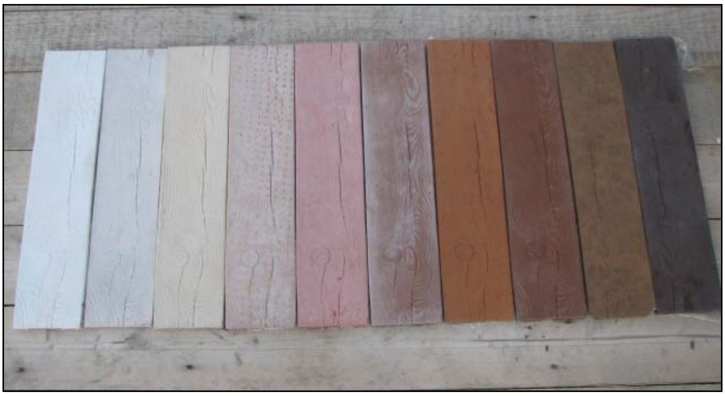

Fig. 6: Prototypes of geopolymer wood imitation - color scale [15]

Fig. 7: Prototype of geopolymer brass imitation [15]

7 PERSPECTIVE

Based on the above facts can be stated, that although geopolymers have a recent history of less than a hundred years, and are currently still relatively little known, geopolymer represent in many ways the future of construction and other industries.

To wider application obstructs absence of standards for geopolymer testing, the use of liquid caustics in the manufacture and the conservative mentality of builders, who resist 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.

8 CONCLUSION

The aim of this paper was to summarize the historical and current scientific results and practical applications in the field of alkali-activated systems.

Alkali activated materials are a large group of inorganic binders with different properties depending on the feedstock. Extending of the use of geopolymers is desirable, because waste materials and nonstandard aggregates can be used in geopolymer manufacturing. Properties of these materials has been tested in many studies and represent a unique incentive for expansion of alkali-activated systems to the construction practice in a much greater extent than they currently are.

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