

Progress in Cement Science - Why Alkaline Activation?

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Summary. Fifty years ago just an idea of the presence of free alkalis in a cement matrix was considered by the ordinary portland cement (OPC) people as an absurd one and this was a basic postulate accepted in the chemistry of cements. In 1957 a scientist from Ukraine (USSR) Victor Glukhovsky put forward an assumption which was taken as a base for development and bringing into practice of construction a principally new class of cementitious materials which first appeared in the art under a name of “alkaline cements” (now also known under a general name of “alkali-activated cements (AAC)”). A validity of these ideas is confirmed by more than 50 years of evolutionary development and vast experience collected from practical use of new materials in a variety of large-scale applications. A present review covers theoretical views on role played by alkali in cement stone structure formation. Examples of compositional build-up of the alkali- activated cementitious materials as a function of quantity of alkali and type of aluminosilicate component are reported as well as the results of inspection taken over the AAC concrete structures made with these cements.

Key words: alkali- activated, aluminosilicate, cements, durability, hydration products.

INTRODUCTION

The alkali metal compounds were excluded from traditional hydraulic cement constituents due to their high solubility. At the same time, the studies held in order to reveal the reasons for excellent durability of ancient cements together with the data collected on stability and composition of natural mineral formations testified that this postulate was not correct.

According to the data reported in [1-7], excellent durability of the ancient structures is attributed to considerably greater quantities of the alkali metal compounds contained in the ancient cements compared to contemporary portland cements. This was found to result in the formation of alkaline hydroaluminosilicate compounds- analogous to natural zeolites in a cement stone structure along with the calcium hydrosilicates.

A strategy of sustainable development predetermines actions to be taken by the industry of building materials and, in particular, by cement industry.

The OPC-based cements are not able to meet today's requirements due to:

- not high enough physico- mechanical properties and required durability resulted from low- effective strength of the OPC stone:
- metastability of the hydration products resulted from transformation of C_2SH into $CSH(B)$,
- relatively high solubility of the phases,
- low corrosion resistance in the presence of $Ca(OH)_2$ and $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$,
- high consumption of energy (7500 J/1t),
- high carbon dioxide emissions (0.5 metric t CO_2 /1t OPC),
- depletion of natural resources.

That's why the cement science should evolve in the direction of the cements alter-

native to OPC. One of such cement that appeared in the art 50 years ago is an alkaline cement with a number of building products made from it. This paper covers theoretical principles laid down in the creation of these cements, history and experience collected from large-scale application.

HISTORICAL ASPECTS AND OVERVIEW

First attempts to use an alkali in cementitious materials goes back to 1930s, when H.Kühl reported [8] about his studies on setting behaviour of the mixtures of ground slag and solution of caustic potash. R.Feret [10] reported on necessity of study to be taken on slags as cement constituent. In 1940, A.O. Purdon [19] reported on the results of first extensive laboratory study on the cements without OPC clinker consisting of the slag and caustic soda and the slag and caustic alkalis produced by a base and an alkaline salt. Important historic developments of the alkali-activated cements (AAC) are summarized in Table 1.

Later, in 1957 Victor Glukhovsky [12] was the first who discovered the possibility of making binding materials using low basic calcium or calcium-free aluminosilicate (clays) and solutions of alkali metals. He called these binders “soil cements” and the corresponding concretes “soil silicates”. Depending on the composition of starting materials, the binders can be divided into two groups: alkaline binding system $\text{Me}_2\text{O}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and alkaline-earth alkali binding system $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Also, a variety of the alkaline binders which used other metallurgical slags, clays, aluminosilicate rocks, fuel ashes and other constituents have been proposed. Extensive researches and developments on alkali-activated cements (AAC) and AAC-based concrete started since then. Trief cements and F-cements from the Scandinavian countries (Forss 1983a, 1983b) and alkali-activated blended cements are more recent examples (Davidovits, 1988, Roy and Silsbee, 1992).

In 1981 Josef Davidovits [13] from France published his results on making binders by mixing alkalis with burnt mixture of kaolinite, limestone and dolomite. He called these binders “geopolymer” for their polymeric structure. He also registered several trademarks such as Pyrament, Geopolycem and Geopolymite. These materials belong to the alkaline binding system $\text{Me}_2\text{O}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, as was discovered by Victor Glukhovsky.

In 1986 Pavel Krivenko published the results of his research on principles of regulation of technological and physico-mechanical properties of the AAC and ACC concretes in order to achieve the required properties [14].

Malek and Roy at al. [15] identified alkali-activated cement type materials as the matrix formed in the solidification of certain radioactive wastes, while Roy and Langton [16] showed some analogies of such materials with ancient concretes.

Table 1. Important historic developments of the AAC

Year	Name	Country	Work/impact
1930	Kühl	Germany	Investigated setting behaviour of slags in the presence of caustic potash
1937	Chassevent	unknown	Measured reactivity of slags using caustic potash and soda solution.
1940	Purdon	Belgium	Investigated clinker-free cements consisting of slag and caustic soda or slag and caustic alkalis produced by a base and an alkaline salt.
1957	Glukhovsky	USSR	Synthesized binders using hydrous and anhydrous aluminosilicates (glassy rocks, clays, metallurgical slags, etc.) and alkalis, proposed $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ cementitious system, and called the binder “soil cement”.
1981	Davidovich	France	Mixed alkalis with a burnt mixture of kaolinite, limestone and dolomite, and used several trademarks such as Geopolymer, Pyrament, Geopolycem, Geopolymite.
1986	Krivenko	USSR	Developed principles of regulation of properties of the system $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{Al}_2\text{O}_3$ Proposed name “alkaline cements” and its particular case- “geocement”

Pavel Krivenko [17] further showed that alkalis and alkali metal salts similar to silicates, aluminates, and aluminosilicates enter

into reaction in the alkaline aqueous medium under condition that alkali concentration is sufficient. Such interaction takes place with clay minerals, aluminosilicate glasses of natural and artificial origin, in which calcium is absent, as well as with calcium-based cementitious systems under natural condition with the formation of water-resistant alkali or alkali-alkaline-earth hydroaluminosilicates, which are analogous to natural zeolites and micas.

Kiev National University of Civil Engineering and Architecture organized two international conferences on alkali-activated cements and concretes in 1994 and 1999 in Kiev, Ukraine [Krivenko, 1994, 1999] and the third conference was held in 2007 in Prague, Czech Republic (sponsored by the EU, Government of the Czech Republic and the City Government of Prague). Professor Josef Davidovits from France organized three international conferences on geopolymer in 1988, 1999 and 2007. Professor Jannie van Deventer from the University of Melbourne, Australia, organized the conference on geopolymer in 2002. The fourth international conference and a workshop on geopolymer were held in France and Australia, respectively, in 2005.

WHY ALKALI ACTIVATION?

The alkalis are known to play an important role in the processes of artificial stone synthesis which take place in nature, are found in the concrete of ancient structures and are contained in contemporary cements.

Less than a century ago just an idea of presence of free alkali in a cement composition was considered by cement people as absurd one and this was a basic postulate of fundamentals of exhibiting hydraulic properties by mineral systems. The alkali metal compounds were excluded from traditional hydraulic cements because of their high solubility.

At the same time, the studies held to reveal the reasons explaining excellent durability of the ancient concretes in combination with the data collected on stability and com-

position of natural mineral formations testified that this postulate was not correct.

Professor Glukhovsky has made a discovery that compounds of alkali metals (Li, Na, K, Rb, Cs) - the elements of the first group of the Periodic Table- exhibit hydraulic binding properties similar to those of the alkali earth metals (Mg, Ca, Sr, Ba)- the elements of the second group.

The idea itself of using these systems as cementitious ones was based, first of all, on collected geological data that sodium- potassium- calcium aluminosilicate compounds, which are known to have the higher stability and resistance to atmospheric reagents, are present in the Earth crust. Secondly, this idea was based on the results of experimental studies which proved that alkali hydroxides and salts of alkali metals entered into interaction with clay minerals, aluminosilicate glasses and crystalline substances of natural and artificial origin with the formation of water resistant alkaline and alkaline- alkali-earth aluminosilicate hydration products that were analogous to natural minerals of the zeolite and mica types.

ALKALIS IN NATURE

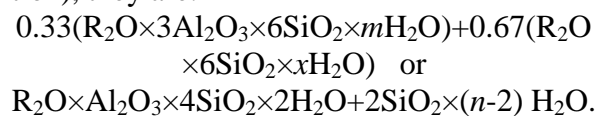
Geological data on conditions under which sedimentary and metamorphic silicate rocks occur and on constituent composition of basic rock-forming minerals along with the above reported data can serve as a theoretical substantiation of a possibility to produce and use in practice of construction of the concretes made using alkali metal compounds along with those made using only calcium compounds.

Some of the processes of formation of the sedimentary stone-like rocks take place under temperatures and pressures close to those which take place in production of materials of hydraulic hardening and, hence, can be simulated in the building materials industry. For example, zeolites of sedimentary origin, such as analcime $\text{Na}[\text{AlSi}_2\text{O}_6] \cdot \text{H}_2\text{O}$, phillipsite (K_2 , Ca) $[\text{Al}_2\text{SiO}_{12}] \times 4.5\text{H}_2\text{O}$, mordenite (Ca, Na₂, K₂) $[\text{Al}_2\text{Si}_9\text{O}_{22}] \times 6\text{H}_2\text{O}$, natrolite $\text{Na}_2 [\text{Al}_2\text{Si}_3\text{O}_{10}] \times 2\text{H}_2\text{O}$ scolecite $\text{Ca} [\text{Al}_2\text{Si}_3\text{O}_{10}] \times 2\text{H}_2\text{O}$ and other occur in the residual soil as a result of low-temperature

hydrothermal reactions. So, analcime is formed on the bottom of sea basins at a temperature lower than 30 °C as a result of interaction between volcanic ash which decomposes into a silicic acid and alumina and alkali metal salt dissolved in water. An occurrence of this or other type of zeolites depends upon chemical composition of the hydrothermal solutions. For example, in the rich-calcium solutions mainly calcium varieties are known to occur and with increase in concentration of the alkalis the alkali- earth cations are partially or completely replaced with sodium or potassium resulting in the formation of zeolites of alkaline and alkaline-alkali-earth composition.

Analysis of the data on sedimentation processes indicates that chemical decomposition of the rocks under action of alkaline solutions is a reason of their chemical and constituent compositions. Hydroaluminosilicates: muscovite, sericite, zeolites, etc. are the products of chemical decomposition of the widely spread rocks of alkaline and alkaline- alkali- earth aluminosilicate compositions such as plagioclases and sodium- potassium feldspars/ The most characteristic process of decomposition of the plagioclases (alkaline- alkali-earth hydration products) is a process of sericitization- a replacement of plagioclases with muscovite, that is a conversion of anhydrous aluminosilicates containing anorthite into hydrous alkaline aluminosilicates.

Finally, as a result of interaction of the feldspar $R_2O \cdot Al_2O_3 \cdot 6SiO_2 \cdot nH_2O$ with water two reactions may take place which can be schematically represented (with approximation), they are:



Their essence can be explained as hydration of the anhydrous alkaline aluminosilicate and formation of a system of hydrates, including an aluminosilicate of the muscovite or analcime type. In its essence this process is similar to the process of portland clinker minerals hydration and an assumption can be put forward that it may take place and under

hardening of the alkaline and alkaline- alkali-earth cementitious systems [18].

According to their flowability in the zone of weathering the alkaline elements can be arranged as the following: calcium (with the highest flowability), sodium and magnesium and at last potassium. For example, potassium feldspars tend to decompose slower than the calcium and sodium ones, out of which an albite was found to be the most stable mineral. For plagioclases, an inverse relationship of resistance of the minerals upon quantity of the anorthite component: the calcium plagioclases decompose with a greater rate.

The alkaline hydrates such as muscovite and paragonite feature the increased resistance to weathering compared to the calcium ones.

These data provide evidence of durability of the AAC hydration products containing sodium and potassium hydroaluminosilicates. A tend to reduce a basicity of the hydration products compared to initial anhydrous minerals in cements used in construction also is a proof of analogy between the processes taking place in natural and man-made substances of alkaline and alkaline- alkali-earth aluminosilicate compositions. In general case these processes have such basic stages connected with changes in an alkalinity of the environment: hydration of the alkali metal and alkali-earth metals, partial replacement of the alkalis and alkali- earth metals. With the ions of hydrogen or hydroxon, the occurrence of the less alkaline almost not dissoluble hydroaluminosilicates of the $R_2O \times (1 - 3) Al_2O_3 \times (2 - 6) \times nH_2O$ type and low basic alkali-earth hydrosilicates of the $RO \times SiO_2 \times nH_2O$ type as well as soluble hydrates of the $R(OH)_2$; ROH ; $R_2O \times SiO_2 \times nH_2O \times Al_2O_3 \times nH_2O$ type in amorphous or submicrocrystalline state.

Under conditions of low temperature hydrothermal metamorphism which occurs in the Earth crust at relatively low temperatures and pressures, the processes of transformation of the rocks are accompanied also by hydration of the feldspar minerals and formation of water resistant and not water resistant alkaline hydration products. In their essence

and orientation they are similar to the processes taking place in the zone of accumulation of the sediments and to the hydration processes of building cements. Side by side with this the aqueous non-alkaline or low in alkali substances convert into more basic ones, for example, clay minerals- into zeolites, hydromicas- into micas, etc., similar to that taking place under conditions of autoclave treatment- a low basic hydrosilicate is formed from lime-siliceous mixtures and tricalcium hydrosilicate- from a mixture of β - C_2S and lime. In both cases the natural processes of metamorphism lead to changes in the mineral hydration products as a result of bringing or loss/removal of the alkaline substances by circulating overheated aqueous solutions. They are reflected in removal or binding of the alkalis, crystallization of the zeolites, hydromicas, micas, which under conditions of thermal metamorphism later recrystallize in albite, orthoclase, feldspathoids, etc.

Worthy mentioning is the fact that a specific feature of the metamorphism stage is more higher pressures compared to those used in the building materials production that is why simulation of this process is complicated. However, the works of the scientists of the Scientific Research Institute of Binders and Materials (Kiev, Ukraine) suggested to establish that by using the aluminosilicate substances of metastable structure and active alkali metal non-silicate or silicate compounds in quantities required for synthesis of the alkaline hydroaluminosilicates, similar processes might be simulated in the larger volumes and under curing regimes (temperatures and humidity) used in the production of traditional concretes.

By summarizing the above a conclusion may be drawn that in the Earth crust and on its surface the continuous stage-by-stage condensation and dispergation processes of the silicate substances accompanied by mutual transformations of hydrous and anhydrous mineral systems, take place and they flow mainly with participation of the alkaline and alkali-earth oxides resulting, similar to processes of hydration and hardening of the building cements, in synthesis of stone-like

hydration products. These data serve as a prerequisite for the synthesis of analogs to natural aqueous sodium- potassium-calcium minerals through hydration of alkaline- alkali-earth systems, they are: alkaline- alkali-earth cement concretes which contain in general case: slags, intrusive and effusive rocks, clay minerals, silica, etc. In the process of interaction of these substances with alkali hydroxides, the processes of formation of the minerals of the Earth crust and stone-like rocks.

MODELLING OF ROCK- MINERAL FORMATION PROCESSES

Taken as a base for modeling was a scheme of formation of sedimentary rocks based on rock weathering products [18].

It was established that alkali hydroxides and salts of alkali metals producing in a aqueous medium an alkaline reaction, under condition of their high concentration, come into interaction with the clay minerals (Fig. 1, 2), aluminosilicate glasses (Fig. 3, 4) with the formation of water resistant alkaline and alkaline-alkali-earth aluminosilicate new hydration products like minerals of zeolite and mica types.

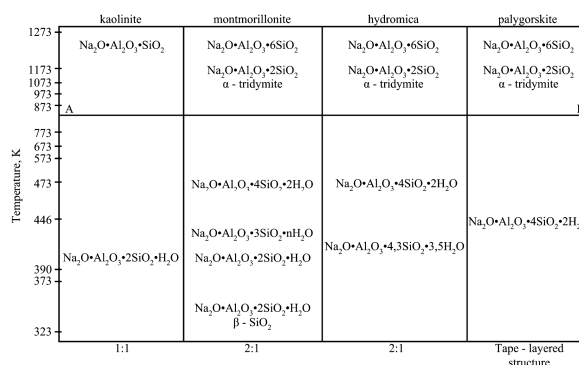


Fig. 1. Conditions of formation of various zeolites based on clays and sodium carbonate

The study results suggested concluding that basic composition of the cement stone hydration products depended upon type of the alkaline activator/admixture/used:

- I – (addition – H_2O) – $RO-SiO_2-H_2O$,
- II – (addition – hydroxides of alkali metal) – $RO-SiO_2-H_2O$, $R_2O-Al_2O_3-SiO_2-H_2O$, $R_2O-RO-Al_2O_3-SiO_2-H_2O$,

III – (addition – hydroxides of alkali earth metal) – $\text{RO-SiO}_2\text{-H}_2\text{O}$,
 IV – (addition – carbonates of alkali metal) – $\text{RO-SiO}_2\text{-H}_2\text{O}$, $\text{R}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, $\text{R}_2\text{O-RO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$,
 V – (addition – carbonates of alkali earth metal) – $\text{RO-SiO}_2\text{-H}_2\text{O}$,
 where: RO – CaO, SrO, BaO, MgO; R_2O – K_2O , Na_2O , Li_2O .

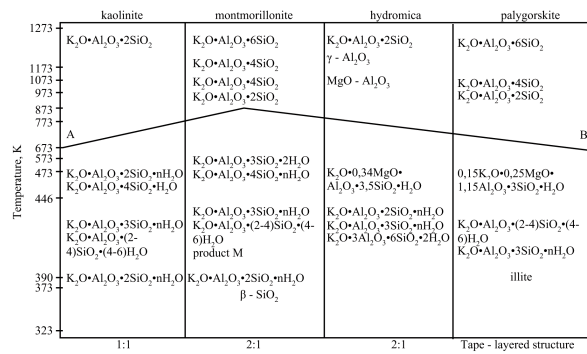


Fig. 2. Conditions of formation of various zeolites based on clays and potassium carbonate

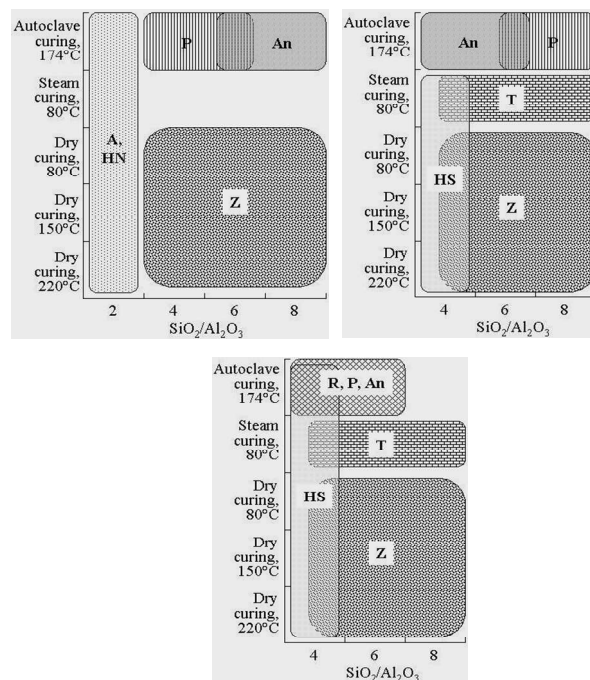


Fig. 3. Geocement composition (source of aluminosilicate):

a – metakaolin, b – fly ash 1, c – fly ash 2 vs curing conditions and hydration products. An – analcime, A – zeolite Na-A, P – zeolite P, R – zeolite R, HN – nepheline hydrate, HS – hydroxysodalite, Z – trona, T – sodium carbonate hydrate

The studies held allowed to draw the following conclusions:

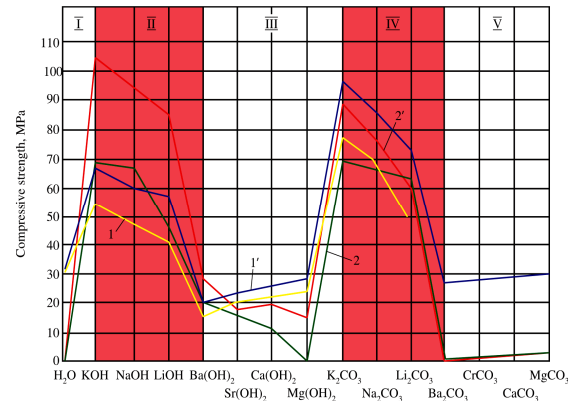


Fig. 4. Compressive strength of the AAC compositions vs type of alkaline activator and composition of hydration products:

1 and 1* – slag with $\text{Mb}=1.13$ ($\text{Al}_2\text{O}_3=6.75\%$), 2 and 2* – slag with $\text{Mb}=0.85$ ($\text{Al}_2\text{O}_3=15.85\%$), 1 and 2 – steam-cured specimens ($T=90\pm5^\circ\text{C}$, 3+7+2 hrs.), 1* and 2* – specimens cured in autoclave ($T=173^\circ\text{C}$; 3+7+2 hrs)

- physico- chemical processes taking place during hardening of the conventional building calcium-based cementitious materials are similar to those of chemical weathering of rocks and formation of structure of the stone-like substances of sedimentary and metamorphous origin,
- being similar in essence, these processes take place at different rate, since starting materials vary in basicity and physical state,
- hydration processes in the calcium-based cements due to a higher basicity and metastability of the constituent minerals take place more actively compared to those of the alkaline rocks of stable structure; their hydration products are water resistant hydrosilicates and aluminates as well as soluble hydroxide of calcium,
- acceleration of these processes both in natural rocks and artificial alkaline and alkaline- alkali-earth aluminosilicates which are similar in composition up to the limits, under which they can be used in a form of hydraulic cementitious materials can be done through conversion of a substance from a stable crystalline state into more active metastable one, including

a glassy one, and, when necessary, by introduction of the alkaline oxides or hydroxides from outside. As a result, the hydration processes of high-basic alkaline substances will be similar in their character to natural processes of formation of the stone-like sediments of feldspar and nepheline rocks, and in activity – to portland cements. The hydration processes of low-basic or alkali-free substances in their character will be similar to natural processes of step-by-step conversion of pozzolana, lime-clay, lime- slag and slag (portland) cements,

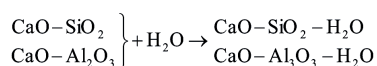
hydration products of high- basic and low-basic substances are similar to natural mineral formations are water- resistant hydroaluminosilicates- micas, zeolites and low-basic calcium hydrosilicates, as well as soluble hydroxides or silicates of sodium and potassium.

ALKALI- ACTIVATED CEMENTS

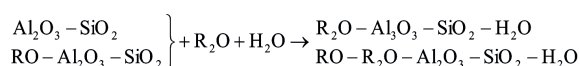
Simulation of the naturally occurring processes of transformation of the hydrous aluminosilicates into anhydrous ones allowed to develop systems of binding materials, the hydration products of which are capable to change their chemical composition and crystal lattice from hydrous to anhydrous one depending upon temperature curing conditions under which the concretes will be in service.

As a result, an idea of creation of cementitious materials was transformed as the following:

“OLD” scheme (OPC), high-alumina cement)



“NEW” scheme (alkali- activated cement)(AAC)



where R- Na, K, Li, Rb, Cs.

PRINCIPLES OF COMPOSITIONAL BUILD-UP OF THE ALKALI-ACTIVATED CEMENTS

The following postulates have been laid down in their creation:

- alkalis act not only as activators but as structure- forming elements included into the formed phases as well,
- the formed hydration products phases are characteristic of the presence of new formations of the $\text{R}_2\text{O-Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{R}_2\text{O-CaO-Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ types;
- quantities of alkalis to be introduced are caused by a necessity to meet a stoichiometric composition/ stoichiometry requirement/ of the alkaline and alkaline-alkali-earth hydroaluminosilicates analogous to natural zeolites.

In compliance with these principles the alkali content of the cement will be determined by an Al_2O_3 content of the aluminosilicate component (Fig. 5).

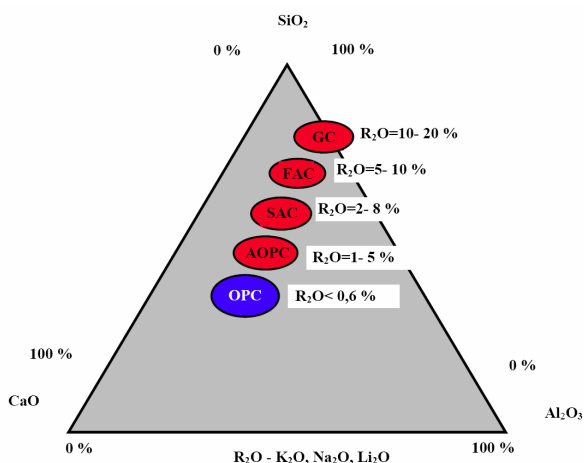


Fig. 5. Comparative chemical analysis of different types of OPC and AAC.

Abbreviations: **OPC**- ordinary Portland cement, **AOPC** – alkali- activated ordinary Portland cement, **SAC** – slag alkali- activated cement, **FAC** – ash alkali- activated cement, **GC** – geocement

The introduction into a cement composition of the alkali metal compounds in much larger quantities than was allowed in compliance with the principles of compositional build-up of the traditional cements based on

calcium and magnesium compounds suggested to consider that the alkali metal compounds acted not only as activators of hardening but as self-functioning components of the binding system $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, the main structure-forming products of which were low-basic calcium hydrosilicates and zeolite-like products. A low basicity of the hydration products is attributed to specific features of the structure-forming processes taking place in case of the slag alkali-activated cements, namely: a hydrolytic destruction of the solid phase of the low-basic phases is caused, first of all, by the break of the covalent bonds $\text{Si}-\text{O}-\text{Si}$, $\text{Me}^{3+}-\text{O}-\text{Me}^{3+}$, $\text{Si}-\text{O}-\text{Me}^{3+}$ according to a scheme $\equiv\text{Si}-\text{O}-\text{Si}\equiv \leftrightarrow [\equiv\text{Si}-\text{O}-\text{Si}\equiv]^- \leftrightarrow \equiv\text{Si}-\text{OH} + \equiv\text{Si}-\text{O}^-$ with protonization of the ion $\text{Me}^{2+}-\text{O}$ bonds taking place in parallel, as it is known to happen in the high-basic systems [14].

An alkaline cation promoting flow of hydrolytic destruction of the low-active low-basic phases acts at early stages of structure formation as a catalyst of destruction. Later, as far as the condensation processes evolve, it takes an active part as a co-partner of Ca^{2+} and Mg^{2+} in the structure formation processes, thus facilitating its modification due to formation of the alkaline and alkaline-alkali-earth hydroaluminosilicates that are morphologically homogeneous with the low-basic calcium- magnesium hydrosilicate phases.

At early stages of hydration and hardening (for example, of the slag alkali-activated cements), the structure formation is caused, mainly, by the formation and crystallization of the low- basic hydrosilicates and hydrogarnets. The alkaline and alkali- earth hydroaluminosilicates, as a result of their slower crystallization, occur at the later stages. Being formed, mainly, in the pore space, they fill it and promote strong crystallization contacts with the primary phases to occur, as well as initiate the formation of more homogeneous and dense structure.

Besides, high pH-values of the medium at which the hydration process takes place tend to block a transfer of the Ca-ions into solution, thus explaining the absence of $\text{Ca}(\text{OH})_2$ and the fact that the resulted calcium hy-

drosilicate has, as a rule, a basicity exceeding 1.

CLASSIFICATION

A classification proposed in [19] is based on the characteristic features of the products of hydration and hardening of the alkali-activated cements, the “edge” variants of which may be represented by the compounds of two types: alkaline hydroaluminosilicates of the system $\text{R}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and earth metal hydrosilicates.

A variety of blended alkaline- alkali- earth hydroaluminosilicates may fall within these ranges. A phase composition of the hydration products of a cement stone is determined by a kind of starting raw material (Table 2). Depending upon these starting materials the best application of the alkali- activated cements is to be chosen (Fig. 6).

Table 2. Mineralogical composition of the cement hydration products vs type of starting aluminosilicate component

Cement type	Initial solid phase	Alkali content, R_2O , %	Hydration product
OPC	OPC clinker	< 0.6	
Alkaline OPC	OPC clinker+ R_2O	1-5	
Blended alkaline OPC	OPC clinker+ additive (slag, ash, basalt)+ Me_2O	2-5	
Slag alkali-activated cement	Metallurgical slag+ R_2O	4-8	
Ash alkali-activated cement	Ash - product of coal combustion	5-10	
Geocement	Clay+ R_2O	10-20	

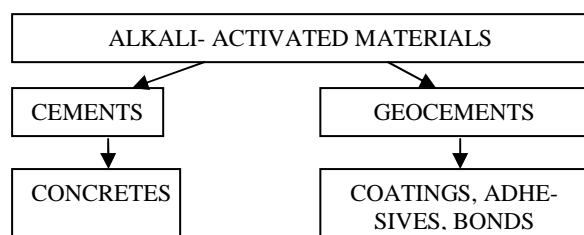


Fig. 6. Fields of application of the alkali-activated cementitious materials

INDUSTRIAL USES

The experience from the small- and large scale industrial uses of the alkali- activated cements gained starting the 1960s in construction (hydropower engineering, road, agricultural, industrial, civil engineering, mining, etc.) gave proofs to high performance properties of the concretes on them. The use of the alkali- activated cement- based materials was found to be especially effective one for specially intended use in many fields besides construction [20].

Below are given some fields of the manufacture and use of the alkali- activated aluminosilicates.

EFFICIENCY

More than 50 years passed since the alkali- activated cements appeared in the field and their efficiency and potential have been proved by extensive researches held not only in the Soviet Union but in many countries over the world: Poland, Finland, The Netherlands, Germany, Czech Republic, Romania, Slovak Republic, Bulgaria, Japan, China, USA, Canada, India, Brazil, Spain, the UK. The experience collected for this period of commercial- scale manufacture and use of structures and articles made from the slag alkali- activated cement concretes in various fields of construction testifies to their higher service properties as compared with those of Portland cement concretes (Table 3).

These materials were found to be the most highly effective ones when used in extremely severe conditions as well as in non- civil engineering fields (Fig. 7). Moreover, compared to traditional cements, the AAC possess polyfunctional properties and can be successfully used as high strength, quick

hardening, corrosion resistant, frost resistant, heat- and fire resistant and low exothermal cements [21].

Table 3. Properties of different cements

Cement type	Early strength	Durability	Chemical resistance
Portland cement	++	++	+
Blended cement	+	+++	++
High alumina cement	+++	+	+++
High sulphate cement	+	++	+++
Alkali-activated cement	+++	+++	+++
Sulphoaluminate cement	+++	++	+++

TECHNOLOGY

More than 50 years practical experience of the Kiev school is connected with a manufacturing technology under which the alkaline activator was introduced into a concrete in a form of aqueous solution- so-called CONCRETE technology. Now there are two technologies, they are:

So-called “concrete” technology– under which all raw materials, they are: aluminosilicate component, alkaline activator and modifying additives/admixtures are introduced in a dry form or in a form of solution during mixing concrete ingredients similar to conventional concrete technology [22].

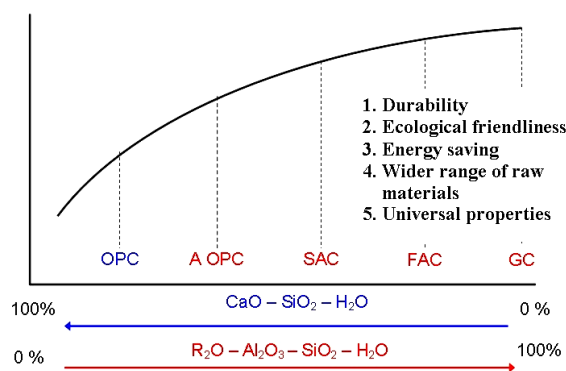


Fig. 7. Benefits of the AAC as compared to OPC-based cements

So-called “cement” (all-in-one) technology– under which all raw materials: aluminosilicate component, alkaline activator and modifying additives/admixtures are ground together and packed in bags for further use similar to other know-in-the-art cements for

the use in concrete under traditional OPC-based concrete technology (Fig. 8). This scheme in general features is given below. As to required equipment- *the best available techniques* (BET) can be successfully explored in it.

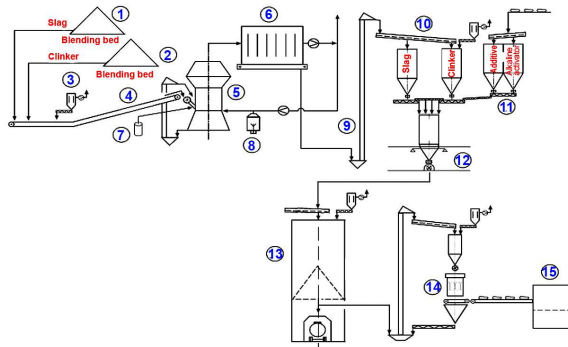


Fig. 8. “Cement” technology for the ACC manufacture. 1 – blending bed for slag, 2 – blending bed for clinker, 3 – dust collector, 4 – belt conveyor, 5 – vertical roller mill, 6 – fabric filter, 7 – metering equipment for water repellent, 8 – heat generator for drying, 9 – elevator, 10 – silos for cement constituents, 11 – bunker for additives/admixtures and alkaline activator, 12 – mixer for dry cement constituents, 13 – ready product storage silo, 14 – packer for bags, 15 – palletizer

STANDARDISATION AND TEST PROCEDURES

In order to bring a newly developed product into a commercial-scale production it should pass all standardisation procedure according to national rules. In the former USSR, the commercialization of the ACCs was possible through its full-scale standardisation: a variety of national and industry standards have been issued [23]. As a result, the AACs were officially approved by the governmental bodies of the USSR for the use in construction for all structures along with OPC (Fig.9).

The latest achievement in standardisation of the ACCs is a newly issued national standard of Ukraine covering some ACC types [24]. Similar to the EN-196, the standard specifies only strength classes and compressive strength after 2, 7 and 28 days. In composition and strength at an age of 28 days the ACCs are classified as the following:



Fig. 9. The first residential house made without nay OPC from alkali- activated cement concrete (Lipetsk, Russian Federation)

slag alkaline cement, alkaline Portland cement, alkaline pozzolana cement, alkaline slag Portland cement, alkaline composite cement, which differ in combination of such aluminosilicate component as granulated blast furnace slag, OPC clinker, ashes from coal combustion, and basalt taken in combination with the alkaline activator (Table 4). Compressive strength classes under the standard are: 300, 400, 400R, 500, 500R, 600, 600R, 700, 800, 900, 1000. The standard is applicable to making concretes for common application.

Determination of mechanical and physical properties of the AACs is carried out in compliance with Ukrainian standard DSTU B V 2.7-24-95 and US standard ASTM C 109/C 109M. According to these standards, a water to cement ratio (W/C) is to be chosen to provide a flow value (measured on cone) = 106 – 115 mm. In case of using these test methods according to EN standards (EN 196-1, 196-3, and 196-6, under which the W/C is restricted to a value of 0.5), the following amendments should be introduced: in determination of flowability of the cement/sand mortar the alkaline solution/ solid constituents or water/ solid constituents ratio should be chosen ex-

Table 4. Cement types according to National Standard of Ukraine DSTU B V.2.7-181:2009 “Alkaline Cements”

Cement type		Designation	Content, % by mass				
			Aluminosilicate constituent				Alkali metal compounds (sodium or potassium)
			Granulated blast-furnace slag	OPC clinker	Fly ash	Basalt	
ACEM I	Slag alkaline cement	ACEM I	90-100	0-10	-	-	1.5-12
	Slag alkaline cement with additive of fly ash	ACEM I -3	55-90	0-10	10-35	-	1.5-12
ACEM II	Alkaline portland cement	ACEM II	-	100	-	-	1.5-12
ACEM III	Alkaline pozzolana cement	ACEM III-3	←-----→		36-80	-	1.5-12
		ACEM III-B			-	36-80	
ACEM IV	Alkaline slag portland cement	ACEM IV	36-89	11-64	-	-	1.5-12
ACEM V	Alkaline composite cement	ACEM V	30-50	5-10	40-65	-	1.5-12

perimentally in such a way that to provide the flow values between 160-180 mm.

CONCLUSIONS

Now Ukraine has all normative documentation required for a large-scale application of the alkali-activated cementitious materials into practice of construction.

In order to bring this technology into a large-scale world-wide application, the RILEM Technical Committee “Alkali Activated Materials” was organized in 2007 (www.rilem.net). Its tasks are: to collect and summarize the experience on raw materials; cements; concretes; structures; production; test procedures; durability; intended use and to develop basic recommendations on preparation of performance-based specification for cast-in-place alkali-activated cements and concretes.

The results of this work are expected to allow to develop and approve national and international standards for the alkali-activated materials.

REFERENCES

1. **Malinowski R. 1982.** Ancient mortars and concretes: aspect of their durability. History of Technology, Nr 7, 9-101.
2. **Malinowski R., Stalkine A., Ben Yair M. 1961.** Durability of Roman mortars and concretes for hydraulic structures at Caesarea and Tiberias. Proceed. Int. Symp. On Durability of Concrete, Prague, 1-14.
3. **Malinowski R. 1979.** Concrete and mortars in ancient aqueducts, Concrete International, Nr 1, 66-67.
4. **Malinowski R. 1979.** Betontechnische Problemlösung bei antiken Wasserbauten. Leichtweiss Institut, Braunschweig, Germany, Mitteilungeng, Nr 64, 7-12.
5. **Langdon C. A., Roy D. M. 1984.** Longevity of borehole and shaft sealing materials: characterization of ancient cement-based building materials. Materials Research Society Symposium Proceedings, Nr 26, 546-549.
6. **Davidovich J. 1988.** Ancient and modern concretes: what is the real difference? Concrete International, Nr 9, 23-29.
7. **Glukhovsky V. D. 1989.** Ancient, Modern and Future Concretes, Proceed. 2nd International Seminar, Gothenburg, Sweden, 53-62.
8. **Kühl H. 1930.** Zementchemie, Berlin, Germany: Verlag Technik, Band III; 1958 or Zement 19.
9. **Chasserent L. 1937.** 17 me Congr. De Chim.
10. **Feret R. 1939.** Slags for the manufacture of cement. Rev. Mater. Constr. Tr. Publications, 1-145.
11. **Purdon A. 1940.** The action of alkalis on blast furnace slag. Journal of the Society of Chemical Industry, Nr 59, 191-202.
12. **Glukhovsky V.D. 1957.** Soil silicate-based products and structures. Kiev, USSR: Gostroiizdat Publish.
13. **Davidovich J.** Synthetic mineral polymer compound of the silicoaluminates family and preparation progress, US Patent, 4, 472,199.
14. **Krivenko P. 1986.** Synthesis of cementitious materials of the $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system with required properties, DSc(Eng) Degree Thesis, Kiev, USSR: KISI Publish.
15. **Malek R.I., Licastro P.H., Roy D.M., Langton C.A. 1986.** Slag cement-low level radioactive waste forms at Savannah River Plant. Ceramic Bulletin; Nr 65, 1578-1583.

16. **Langton C.A., Roy D.M. 1984.** Longevity of bore hole and shaft sealing materials, characterization of ancient cement-blast building materials. Scientific Basis of Nuclear Waste Management, Nr 26, 543-549.
17. **Krivenko P.V. 1995.** Special slag alkaline cements. Kiev, USSR: Budivel'nyk Publisher.
18. **Ginzburg I.J., Rukavishikova I.A. 1951.** Minerals of the ancient zone of weathering of the Ural Mountains, Moscow, USSR.
19. **Krivenko P.V. 1997.** Alkaline cements: terminology, classification, aspects of durability. Proceed 10th Congress on the Chemistry of Cements, Sweden, 4 iv 046.
20. **Efremov A.N., Krivenko P.V. 2008.** Fire-resistant concretes from alkaline cements with the higher thermo- mechanical properties. Makeevka, Ukraine, DonNASA Publish.
21. **Krivenko P.V., Pushkaryeva E.K. 1993.** Durability of slag alkaline cement concretes. Kiev, Ukraine, Budivel'nyk Publish.
22. **Glukhovsky V. D., Krivenko P.V. at al. 1988.** Manufacture of concretes and structures from slag alkaline binders. Kiev, Ukraine, Budivel'nyk Publish.
23. **Shi C., Krivenko P., Roy D. 2006.** Alkali-activated cements and concretes. London: Taylor and Francis.
24. **National Standard of Ukraine DSTU B V.2.7-181:2009. 2009.** "Alkaline Cements".

СПИРАЛЬНЫЙ СПОСОБ ДОБЫЧИ КОНКРЕЦИЙ СО ДНА АКВАТОРИЙ

Аннотация. В связи с имеющими место в настоящее время энергетическими, экономическими и экологическими проблемами прогресс в науке о цементе приобретает актуальное значение.

С 1957 года Киевская научная школа развивает новое направление в цементоведении, основанное на установленных профессором В.Д. Глуховским закономерностях проявления вяжущих свойств соединениями I-й группы периодической системы элементов. Результатом этой работы явилось создание принципиально новых цементов, в которых соединения щелочных металлов выступают не в роли активаторов, как их использовали ранее, а в роли структурообразующих элементов, формируя фазовый состав цементного камня новообразованиями типа щелочных и смешанных щелочно-щелочноземельных гидроалюмосиликатов, которые являются аналогами природных цеолитов.

Эффективность таких цементов подтверждена более чем 50-летним опытом их изучения, производства и применения.

Ключевые слова: щелочеактивированные, алюмосиликаты, цементы, долговечность, продукты гидратации.