Review

Why Alkaline Activation – 60 Years of the Theory and Practice of Alkali-Activated Materials

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Abstract

Sixty years ago, just the idea of the presence of free alkalis in a cement matrix was considered by ordinary Portland cement people to be absurd, and this was a basic postulate accepted in cement chemistry. In 1957, a scientist from Kyiv, Ukraine (then, USSR), Victor Glukhovsky, put forward an assumption that was taken as a basis for development and realization of a principally new class of cementitious materials, which first appeared under the name of “alkaline cements” (nowadays also known under the general name of “alkali-activated cements”). The validity of these ideas is confirmed by more than 60 years of evolutionary development and vast experience collected from the practical use of these new materials in a variety of large-scale applications. The present review covers theoretical views on the role played by alkali in the formation of cement stone structure. Examples of compositional build-up of alkali-activated cementitious materials as a function of the quantity of the alkali and type of aluminosilicate component are reported, as well as the findings of analysis of alkali-activated cement concrete structures.

Keywords: Alkaline activation, aluminosilicate, cement, concrete, durability, hydration products, terminology

I. Introduction

Alkali metal compounds were excluded from traditional hydraulic cement components on account of their high solubility. At the same time, studies undertaken to reveal reasons for the excellent durability of ancient cements together with the data collected on the stability and composition of natural minerals testified that this opinion was not correct.

According to data reported in references 1–7, excellent durability of the ancient concrete structures was attributed to the considerably greater quantities of alkali metal compounds contained in ancient cements compared to in contemporary Portland cements. This was found to result in the formation of a cement stone structure of alkaline aluminosilicate hydrate compounds – analogs of natural zeolites along with calcium silicate hydrates. At the same time, a strategy of global sustainable development predetermined the actions to be taken by the building materials industry, in particular by the cement industry.

Ordinary Portland cement has proven to be an excellent building material, and concretes based on this exhibit good physico-mechanical properties and durability. However, when Portland cement is exposed to extreme service conditions (high/low temperature, corrosive environments, radiation, etc.), its drawbacks become apparent, resulting in poor performance. These drawbacks can be attributed to the metastability of Portland cement hydration products resulting from conversion of high-basicity calcium hydrate in the low basicity of C$_2$SH into CSH(B), relatively high solubility of the hydration products, and low corrosion resistance in the presence of C$_2$SH$_2$ and 3CaO·Al$_2$O$_3$·3CaSO$_4$·31H$_2$O. Above all, the production of Portland cement is associated with high consumption of energy (7500 J/t), high carbon dioxide (CO$_2$) emissions (0.5 metric t/t) and the depletion of natural resources.

That is why the cement science should move in the direction of cement alternatives to OPCs.

One such cement that appeared in the field over 60 years ago is a class of alkaline or alkali-activated cements (AACs). This paper covers the theoretical principles laid down in the creation of these cements, history and experience collected from large-scale applications.

II. Historical Aspects and Overview

First data about the possibility of producing a binder material from granulated blast-furnace slag and caustic soda in combination with slaked lime go back to 1895 8. Later, in the 1930s, H. Kühl reported studies on the setting behavior of mixtures of ground slag and a solution of caustic potash 9. R. Feret reported on the necessity to study slags as a cement component 10. In 1940, A. Purdon reported on the results of first extensive laboratory studies on cements without OPC clinker, consisting of slag and caustic alkalis produced with a base and an alkaline salt 11.

Later, in 1957, a Soviet Union scientist Victor Glukhovsky 12 was the first to discover the possibility of making binding materials using low-basicity calcium or calcium-free aluminosilicates (clays) and solutions of alkali metals. He called these binders “soil cements”
and “soil silicates” in order to reflect their similarity to natural minerals. Depending on the composition of their constituent materials, the AACs were divided into two groups: alkaline (Me \(_2\)O-MeO-\(_3\)SiO\(_2\)-H\(_2\)O) and alkaline-alkaline earth (Me\(_2\)O-MeO-\(_3\)SiO\(_2\)-H\(_2\)O). As a result, a variety of AACs have been formulated from metallurgical slags, clays, aluminosilicate rocks, fuel ashes and other constituents. Extensive research and development of AACs and ACC-based concretes have been initiated since those times. In particular, Trief cements and F-cements from Scandinavian countries (Forss) and alkali-activated blended cements are more recent examples (J. Davidovits, D. Roy and M. Silsbee).

In the 1980s, J. Davidovits \(^13\) published his results on making binders by mixing alkalis with a burnt mixture of kaolinite, limestone and dolomite. He called these binders “geopolymers” because their structure was similar to polymers. He has also registered several trademarks similar to Pyrament, Geopolycem and Geopolymite. These binders “geopolymers” because their structure was similar to polymers. He has also registered several trademarks similar to Pyrament, Geopolycem and Geopolymite. These materials belong to the alkaline binding system Me\(_2\)O-MeO-\(_3\)SiO\(_2\)-H\(_2\)O, as proposed by V. Glukhovsky.

In 1986, P. Krivenko published the results of his research on the principles of regulation of technological and physical-mechanical properties of AACs and ACC concretes \(^14\).

R. Malek, D. Roy et al. \(^15\) identified the alkali-activated cement-type materials as a matrix formed in the solidification of certain radioactive wastes, while D. Roy and C. Langton \(^16\) showed some analogies of such materials with ancient concretes.

P. Krivenko \(^17\) further showed that alkalies and alkali metal salts, similar to silicates, aluminates and aluminosilicates, enter into reaction in an alkaline aqueous medium under conditions of high alkali concentration. 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 in ambient (normal) conditions with the formation of water-resistant alkali or alkaline-alkaline earth aluminosilicate hydrates, which are analogs of natural zeolites and micas.

III. Why Alkaline Activation?

Alkalies play an important role in the processes of artificial stone formation taking place in nature, they are found in concrete of ancient structures and are contained in contemporary cements.

Less than a century ago, just the idea of the presence of free alkali in a cement composition was considered absurd by cement specialists and this was a basic postulate of the fundamentals for exhibiting hydraulic properties based on mineral systems. The alkali metal compounds were excluded from components of traditional hydraulic cementitious systems because of their high solubility.

At the same time, extensive studies undertaken to reveal reasons for the excellent durability of ancient concrete structures in combination with data collected on the stability and composition of natural mineral formations testified that this postulate was not correct.

V. Glukhovsky made an assumption (and this was a revolutionary discovery in cement science) that compounds of alkali metals (Li, Na, K, Rb, Cs) – the elements of the first group of the periodic table – exhibited hydraulic binding properties similar to those of alkaline earth metals (Mg, Ca, Sr, Ba) – the elements of the second group.

The idea to use these compounds as cementitious systems was, first of all, based on collected geological data that sodium- potassium- and calcium aluminosilicate compounds, which are known to have higher stability and resistance to atmospheric reagents, are present in the earth’s crust. Secondly, this idea was based on experimental observation that proved that alkali metal 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-alkaline earth aluminosilicate hydration products that were analogs of natural minerals of the zeolite and mica types \(^18\).

(1) Alkalies in nature

Based on geological data, the earth’s crust contains a large number of calcium, sodium or calcium-sodium aluminosilicate formations \(^19\).

Some sedimentary, stone-like rock formation processes take place under temperatures and pressures close to those used in the production of materials from hydraulic cements and, hence, can be simulated in the building materials industry. For example, zeolites of sedimentary origin, such as analcime Na[Al\(_2\)Si\(_2\)O\(_6\)]H\(_2\)O, phillipite (K\(_2\), Ca) [Al\(_2\)Si\(_2\)O\(_12\)].4H\(_2\)O, mordenite (Ca, Na\(_2\), K\(_2\)) [Al\(_2\)Si\(_2\)O\(_22\)]6H\(_2\)O, natrolite Na\(_2\) [Al\(_2\)Si\(_3\)O\(_10\)].2H\(_2\)O, scolecite Ca[Al\(_2\)Si\(_2\)O\(_10\)].2H\(_2\)O and other zeolites occur in residual soil as a result of low-temperature hydrothermal reactions. Analcime, for instance, is formed at the bottom of sea basins at temperatures below 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 that type of zeolite depends upon the chemical composition of the hydrothermal solutions. For example, chiefly calcium varieties are known to occur in rich-calcium solutions. With the increase in concentrations of alkalies, the alkaline earth cations are partially or completely replaced by sodium or potassium, resulting in the formation of zeolites of the alkaline and alkaline-alkaline earth composition.

Analysis of data on sedimentation processes showed that chemical decomposition of rocks under the action of alkaline solutions depended upon their chemical and constituent compositions. Hydrated aluminosilicates: muscovite, sericite, zeolites, etc. are the products of chemical decomposition of widely found rocks of alkaline and alkaline-alkaline earth aluminosilicate compositions, such as plagioclases and sodium-potassium feldspars. The most characteristic process of decomposition of plagioclases (alkaline-alkaline earth aluminosilicate hydrates) is the process of sericitization – a replacement of plagioclases by muscovite; that is a conversion of anhydrous aluminosilicates containing anorthite into alkaline aluminosilicate hydrates.

Finally, as a result of interaction of the feldspar (R\(_2\)O·Al\(_2\)O\(_3\)·6SiO\(_2\)·nH\(_2\)O) with water, two reactions that can
be schematically represented as shown below can take place (with approximation):

\[
0.33(\text{R}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot n\text{H}_2\text{O}) + 0.67(\text{R}_2\text{O} \cdot 6\text{SiO}_2 \cdot x\text{H}_2\text{O}) \rightarrow (1)
\]

\[
\text{R}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 2\text{SiO}_2 \cdot (n-2)\text{H}_2\text{O}.
\]

Their essence can be explained as hydration of the anhydrous alkaline aluminosilicates and formation of hydrates, including aluminosilicates of the muscovite or analcime type. This process is similar to the process in Portland cement hydration. An assumption can be proposed that it may take place during hardening of the alkaline and alkaline-alkaline earth cementitious systems 19.

According to their solubility in the weathering zone, the elements of alkali metal and alkaline earth metals can be arranged as follows: calcium (with the highest solubility), sodium and magnesium and, lastly, potassium. For example, potassium feldspars tend to decompose more slowly than the calcium and sodium ones, of which albite was found to be the most stable mineral. For plagioclases, an inverse relationship of resistance of the minerals to the quantity of the anorthite component occurs: the calcium plagioclases decompose at faster rates.

Alkaline aluminosilicate hydrates such as muscovite and paragonite exhibit increased resistance to weathering compared to calcium hydrates. These data provide proof of the higher durability of the AAC hydration products containing hydrated sodium and potassium aluminosilicates. A trend to reduce the basicity of hydration products compared to initial unhydrated minerals is also a proof of the analogy between the processes taking place in nature and man-made conditions to produce alkaline and alkaline-alkaline earth aluminosilicate compositions. In the general case, these processes have the following basic stages connected with changes in alkalinity of the environment: hydration of alkali metal and alkaline earth metals, and partial replacement of alkalies and alkaline earth metals. With hydration of alkali metal and alkaline earth metals, and particularly replacement of alkalis and alkaline earth metals by circulating overheated aqueous solutions. They are reflected in the removal or binding of alkalies, crystallization of zeolites, hydromicas, micas, which under conditions of thermal metamorphism tend to recrystallize later into albite, orthoclase, feldspatoids and others.

Among a variety of phases that are formed, the zoite-like Na-K-Ca aluminosilicate phases are the most resistant to carbonation and to lowering of alkalinity of the pore liquid. At values \(7 < p\text{H} < 9\) they replace such phases as, for example, calcium silicate hydrates \(\text{Ca}_2\text{SiO}_3\text{O}_5\cdot5\text{H}_2\text{O}, (\text{CaO})_{0.833}\text{SiO}_2\cdot(\text{H}_2\text{O})_{1.333},\) tacharanite (clinoptilolomite) \(\text{Ca}_{12}\text{Al}_2\text{Si}_{18}\text{O}_{35}(\text{OH})_{36},\) apophyllite \(\text{KCa}_4(\text{Si}_6\text{O}_{10})_2\text{OH} \cdot 8\text{H}_2\text{O},\) etc.

Worth mentioning is that a specific feature of the metamorphism stage is the higher pressures compared to those used in the production of building materials, which is why simulating this process in practice is a complicated matter. However, the work conducted by the scientific school in Kiev suggested simulation based on the use of aluminosilicate substances of metastable structure and active alkali metal non-silicate or silicate compounds in quantities required for the synthesis of alkaline aluminosilicate hydrates. Similar processes could be simulated in large volumes and under curing regimes (temperatures and humidity) used in the production of traditional Portland cement concretes.

By summarizing the above, a conclusion could be drawn that in the earth’s crust and on its surface, continuous stage-by-stage polymerization and depolymerization processes of silicate substances take place and are accompanied by mutual conversions of hydrated into unhydrated mineral systems and vice versa. They progress mainly with participation of the alkali metal and alkaline earth metal oxides, resulting, similar to the processes of hydration and hardening of cementitious building materials, in the synthesis of stone-like hydration products. These data could be a prerequisite for the synthesis of analogs of natural aqueous sodium-potassium-calcium minerals based on hydration of alkaline-alkaline earth cementitious systems. These are: alkaline-alkaline earth cements, which in the general case may contain slags, intrusive and effusive rocks, clay minerals, silica, etc. In the process of interaction of these substances with alkali metal hydroxides, the processes of formation of minerals in the earth’s crust and stone-like rocks are replicated.

(2) Modeling of rock – mineral formation processes

A scheme of the formation of sedimentary rocks based on rock weathering processes was adopted for modeling 19.

It was established that alkali metal hydroxides and salts of alkali metals produce in an aqueous medium an alkaline reaction, under conditions of their high concentrations, and enter into interaction with clay minerals (Fig. 1) 20, metakaolin 21, fly ash (Fig. 2) 22, granulated blast-furnace slag (Fig. 3) 18, with the formation of water-resistant, alkaline and alkaline-alkaline earth aluminosilicate hydration products that are similar to minerals of the zeolite and mica-types, along with calcium silicate hydrates.
Fig. 1: Formation of various zeolites based on clays and sodium carbonate (a) and potassium carbonate (b).\textsuperscript{20}

Fig. 2: AAC (source of aluminosilicate): metakaolin, fly ash 1, 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.\textsuperscript{22}
Results of this study suggested that the basic composition of the AAC hydration products depending upon the type of the alkaline activator are:

I – (mixing liquid – water $H_2O$) – $RO-SiO_2-H_2O$;

II – (alkaline activator as “mixing liquid” – alkali metal hydroxides) – $RO-SiO_2-H_2O$, $R_2O-Al_2O_3-SiO_2-H_2O$;

III – (alkaline activator as “mixing liquid” – alkaline earth metal hydroxides) – $RO-SiO_2-H_2O$;

IV – (alkaline activator as “mixing liquid” – alkaline carbonates) – $RO-SiO_2-H_2O$, $R_2O-Al_2O_3-SiO_2-H_2O$;

V – (alkaline activator as “mixing liquid” – alkaline earth metal carbonates) – $RO-SiO_2H_2O$;

where: $RO$ – $CaO$, $SrO$, $BaO$, $MgO$ and $R_2O$ – $K_2O$, $Na_2O$, $Li_2O$.

![Fig. 3: Compressive strengths of AAC vs type of alkaline activator and curing conditions.](image)

The studies led to the following conclusions:

- Physico-chemical processes taking place during hardening of conventional calcium-based cementitious building materials are similar to those of the chemical weathering of rocks and formation of the structure of stone-like substances of sedimentary and metamorphic origin. These processes take place at different rates, since the starting materials vary in basicity and physical state;

- Hydration processes in calcium-based cements, owing to a higher basicity and metastability of constituent minerals, take place more actively compared to those of alkaline rocks of stable structure. Their hydration products are water-resistant silicate and aluminate hydrates, as well as soluble hydroxide of calcium;

- Acceleration of these processes both in natural rocks and artificial alkaline and alkaline-alkaline earth aluminosilicates, which are similar in composition, in order to reach upper limits under which they can be used in a form of hydraulic cementitious materials, can be done by converting a substance from a stable crystalline state into a more active metastable state, including a glassy state, as well as when necessary, with the introduction of alkaline oxides or alkali metal hydroxides from the outside. As a result, hydration processes of high-basic alkaline substances will be similar in their character to natural processes of formation of stone-like sediments of the feldspar and nepheline rocks, and in activity similar to OPCs. Hydration processes of low-basic or alkali-free substances are similar in their character to natural processes of step-by-step conversion of pozzolana, lime-clay, lime-slag and slag (Portland) cements;

- Hydrated high- and low-basic substances are similar to natural mineral formations: water-resistant aluminosilicates – to micas, zeolites and low-basic calcium silicate hydrates, as well as to soluble hydroxides or silicates of sodium and potassium.

(3) **Specific features of alkaline activation**

Known in the art is that processes revealing an ability to hydrate by traditional aluminosilicate cements are attributed to the possibility to transform the aluminum-silicon-oxygen tetrahedra to a discrete state. Their hydrates (sols) are capable of polycondensation with the formation of gels – colloidal solutions and, finally, crystalline formations. The dissolution process is the breaking up of ionic (Ca-O) and covalent (Si-O-Si, Al-O-Al and Al-O-Si) bonds. The higher degree of ionicity of the bonds, the easier the substance is hydrated by water. In the case of Portland cement, this takes place at the expense of blocking a discrete state of $SiO_2$ by a Ca-ion (for example, $CaSi_2$, $CaS_3$). In this state, due to protonization of the Ca-O bond, an autocatalytic destruction of a mineral occurs when it is mixed with water, with the formation of hydrated tetrahedra [$SiO_4$]$^{6-}$ and [$AlO_4$]$^{5-}$ as well as, according to $Na_2Si_4O_9$, $Ca(OH)_2$ or $Ca(H_2O)_2(OH)$.

When water is mixed with minerals having a low degree of bond ionicity, such as CS, the ionic force of water ($pH = 7$) is not enough, because covalent bonds that require a different mechanism to break them prevail in the CS, for example, complexing while hydrating (similar to the conversion of $SiO_2$ into its hydrated forms). This is achieved by changing the ionic force of the mixing medium with the introduction of ions with good electron donor properties, such as ions of alkali metals, which increase the pH of the mixing medium.

Just this idea was put forward in 1957 by V. Glukhovsky when he proposed using compounds of alkali metals – the elements of the first group of the periodic table, such as, for example, $Na(K)_2CO_3$, $Na(K)OH$, $N(K)C_2O_3SiO_2nH_2O$. Based on in-depth analysis of mineral formation processes taking place in nature and the role played by alkali metal compounds in these processes, a “kaolinite ($OH$)$_4Al_2(Si_2O_5) + 2NaOH” system was chosen as a model system for the first stage.

The studies showed that under normal conditions, the process of synthesis of alkaline aluminosilicate compounds takes place very slowly over time, which is not compatible with process regimes in the production of building materials. At the same time, it was concluded...
that the most widely found in nature are mixed alkaline-alkaline earth aluminosilicate hydrates. All this allowed the assumption that the elements of the second group of the periodic table (Ca$^{2+}$, Mg$^{2+}$, etc.) could be taken as catalysts for the formation of zeolite-like compounds.

The incorporation of alkali metal compounds in the cement composition in much larger quantities than were allowed, in compliance with the principles of compositional build-up of traditional cements based on calcium and magnesium compounds, suggested an assumption that alkali metal compounds act not only as activators of hardening, but also as self-functioning components for the binding system Me$_2$O-MeO-Me$_2$O$_3$-SiO$_2$-H$_2$O, the main structure-forming products of which were low-basic calcium silicate hydrates and zeolite-like products. Low basicity of the hydration products is attributed to specific features of the structure-forming processes taking place in the case of the alkali-activated slag cements. Thus, hydrolytic destruction of the solid low-basic phase is caused first of all by the breaking of the covalent bonds Si-O-Si, Me$_3$+-O-Me$_3$+, Si-O-Me$_3$+ according to the following scheme:

$$\text{Si-O-Si} \leftrightarrow [\text{Si-O-Si}]^n \leftrightarrow \text{Si-OH} + \text{Si-O-}$$

with the protonization of the Me$_2$+–O ionic bonds taking place in parallel, as known to occur in highly basic systems 14, 17.

At the initial stage of breaking of covalent bonds in the alkaline medium with $9 < \text{pH} < 12$, the OH$^-$ and Na$^+$ ions play a key role. However, according to views on the mechanism under which the Si-O-Si bonds break 26, with the increase in degree of silicon atom surface hydroxylation up to 2...3 hydroxyl units, its electron donor-acceptor properties tend to increase. This increases the probability of participation of water molecules in the destruction of the Si-O-Si bonds. In this case the probability of formation of the intermediate complex compounds, which decompose under the following scheme, is higher:

$$\text{Me}_2\text{O-MeO-Me}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$$

$$\text{Si-O-Si} \leftrightarrow [\text{Si-O-Si}]^n \leftrightarrow \text{Si-OH} + \text{Si-O-}$$

Similar polarizing action is rendered by the OH$^-$ ions on the aluminosiloxane bond Al-O-Si. According to coordination theory 27, aluminates in an alkaline solution are present in the form of complex anions: Al(OH)$_4^-$, Al(OH)$_5^{2-}$, Al(OH)$_6^{3-}$, the existence of which is dependent on the pH of the mixing medium. Owing to amphotericity of polyvalent metals, the formation of gel of aluminohydrate has specific features that depend on the pH of the mixing medium.

In general, the reversible process of polycondensation (destruction of the solid phase aluminate constituent) can be described, according to 28, by the following equation:

$$[\text{Al(H}_2\text{O)}_6^{3-}]^n \leftrightarrow \text{OH}^+ \rightarrow [\text{Al(H}_2\text{O})_6^{3-}(\text{OH})_2] \leftrightarrow \text{OH}^+ \rightarrow [\text{Al(OH)}_3]^{n-} \rightarrow [\text{Al(OH)}_3]$$

This equation, according to Pleiffer’s theory 27, 28, reflects the amphoteric nature of aluminum. However, in compliance with the views on the polymeric nature of its (aluminum) hydroxide, it is supplemented by the following equation of reaction 23:

$$n[\text{Al}(\text{H}_2\text{O})_3^{4-}] \leftrightarrow [\text{Al(OH)}_3]_n + n\text{H}_2\text{O}.$$ (5)

Iron reveals its amorphous properties during conversion Fe$^{2+} \rightarrow$ Fe$^{3+}$ and change of structural coordination from four-fold into six-fold coordination, which can be done in alkaline conditions.

Iron and aluminum hydroxides can act in the process of coagulation structure formation both as cation and anion constituents, thus promoting accelerated removal of hydroxysols into a solid phase and intensification of the processes of hardening.

The Si-O$^-$ anions that occur in the breaking of the Si-O-Si bonds are less capable of complexing compared to hydroxylated atoms of silicon, thus retarding the process of hydration. A negative charge of the oxygen atom pre-determines the increase of electron density in the silicon atom due to more intensive $\psi_e$–$\psi_d$–interaction and results in weakening of its electron acceptor properties. Furthermore, the Si-O$^-$ anions can participate in a reverse reaction – polycondensation, thus decelerating breaking of the Si-O-Si bonds.

However, in the presence of cations of alkali metals (Me$^+$) this does not happen, since these cations neutralize the Si-O$^-$ anions. The occurrence of the Si-O$^-$/Na$^+$ type bonds will impede a reverse reaction of the formation of the siloxane bond; the Si-O$^-$ anions are removed from the reaction and enter the colloid phase. Subsequently, the alkaline silicates that are formed can, evidently, enter into cation-exchange reactions with ions of the alkaline earth (Me$^{2+}$) present in the solid phase, and, first of all, with the Ca$^{2+}$ cations under the following scheme:

$$\text{Si-O}^- + \text{Na}^+ \leftrightarrow \text{Si-O-Na},$$ (6)

and afterwards under the following scheme:

$$\text{Si-O-Na}^+ \text{OH}^- \leftrightarrow \text{Si-O-Na-OH},$$
$$\text{Si-O-Na-OH} + \text{Ca}^{2+} \leftrightarrow \text{Si-O-Ca-OH} + \text{Na}^+.$$ (7)

In a similar way, the products of destruction with participation of complex anions are: Al(OH)$_4^-$, Al(OH)$_5^{2-}$, Al(OH)$_6^{3-}$ as the aqua complexes Si-O-Al-OH-Ca-OH are removed.

Thus, an alkaline cation promoting the course of hydrolytic destruction of the low-active, low-basic phases acts in the early stages of structure formation as a catalyst of destruction. Later, as far as the condensation processes proceed, it takes an active part as a co-partner of Ca$^{2+}$ and Mg$^{2+}$ in the structure formation processes. Thus it facilitates its modification due to formation of the alkaline and alkaline-alkaline earth aluminosilicate hydrates that are morphologically homogeneous with low-basic calcium- magnesium silicate hydrate phases.

It is important to note that the structural representative of C-N-A-S-H gel in AACs (C-A-S-H[Na, 2H]) has the
highest bulk modulus value, and this information, combined with the formation energy and bond strength data provide evidence that these alternative cements may be as stable as the C-S-H gel in OPC paste. This is consistent with a previous study that reported an increase in the bulk modulus value as the Ca/Si ratio was lowered.

**Principles of compositional build-up of the alkali-activated cements**

Simulation of naturally occurring processes of conversion of hydrated aluminosilicates into anhydrous ones allowed the development of cementitious material systems. Their hydration products are capable of changing their chemical composition and crystal lattice from hydrous to anhydrous, depending on the temperatures under which the concretes will be in service.

As a result, an idea for creating cementitious materials was transformed according to the following:

**OLD** scheme (Portland cement, high-alumina cement)

\[
\begin{align*}
RO-SiO_2 &+ RO-Al_2O_3 + H_2O \\
&\rightarrow RO-SiO_2-H_2O \quad RO-Al_2O_3-H_2O
\end{align*}
\]

**NEW** scheme (alkali-activated cement)

\[
\begin{align*}
Al_2O_3-SiO_2 &+ R_2O + H_2O \\
&\rightarrow R_2O-Al_2O_3-SiO_2-H_2O
\end{align*}
\]

where RO = Mg(Ca)O, R_2O(Na, K)_2O.

The following postulates have been laid down to describe their formation:

- alkalis act not only as activators but as structure-forming elements included in the formed phases as well;
- phases of the hydration products being formed are characteristic of the presence of R_2O-Al_2O_3-SiO_2-H_2O and R_2O-CaO-Al_2O_3-SiO_2-H_2O as well as RO-SiO_2-H_2O;
- quantities of alkalis to be added are caused by the necessity to meet a stoichiometric composition/stoichiometry requirement of the alkaline and alkaline-earth aluminosilicate hydrates analogous to natural zeolites.

A classification proposed by P. Krivenko is based on the characteristic features of products of hydration and hardening of the alkali-activated cements, the “edge” variants of which may be represented by the compounds of two types, these are: alkaline aluminosilicate hydrates of the R_2O-Al_2O_3-SiO_2-H_2O system and alkaline earth metal silicate hydrates CaO-SiO_2-H_2O. A variety of mixed alkaline-alkaline earth aluminosilicate hydrates may fall within these ranges. Phase composition of the hydration products of the AAC stone is determined by the starting constituent materials. On the basis of a knowledge of these principles, the required properties can be achieved by selection of appropriate starting constituent materials.

### Table 1: Mineralogical composition of the cement hydration products vs type of starting aluminosilicate constituent.

<table>
<thead>
<tr>
<th>Cement type</th>
<th>Initial solid phase</th>
<th>Alkali content (calculated as R_2O, %)</th>
<th>Hydration product</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>OPC clinker</td>
<td>&lt;0.6</td>
<td>0% 100%</td>
</tr>
<tr>
<td>Alkaline OPC</td>
<td>OPC clinker+ R_2O</td>
<td>1-5</td>
<td></td>
</tr>
<tr>
<td>Blended alkaline OPC</td>
<td>OPC clinker+ additive (slag, ash, basalt, red mud) + Me_2O</td>
<td>2-5</td>
<td></td>
</tr>
<tr>
<td>Alkali-activated slag cement</td>
<td>Metallurgical slag+ R_2O</td>
<td>4-8</td>
<td></td>
</tr>
<tr>
<td>Alkali-activated ash cement</td>
<td>Ash - product of coal combustion</td>
<td>5-10</td>
<td></td>
</tr>
<tr>
<td>Geocement</td>
<td>Clay+ R_2O</td>
<td>10-20</td>
<td></td>
</tr>
</tbody>
</table>

V. Glukhovsky proposed dividing cements into two types: alkaline and alkaline-earth aluminosilicate hydrates. Later, they were divided into three types:

- high-calcium alkali-activated cements
- low-calcium alkali-activated cements
- hybrid alkali-activated cements

**High-calcium alkali-activated cements**

Alkali-activated Portland and alkali-activated slag cements can be representatives of this alkali-activated cement model. Contents of SiO_2+CaO are over 70 mass%, and content of Al_2O_3 is less than 20 mass%. The main reaction product in this case is C-S-H, which is formed at early stages of hydration. The alkaline N-A-S-H as well as C-N-A-S-H, as a result of the slower crystallization process in these cements, occur at the later stages.

Moreover, high pH-values of the medium in which the hydration process takes place tend to block a transfer of the Ca-ions into solution, this is an explanation of the absence of Ca(OH)_2 and the fact that the basicity of the resulting calcium silicate hydrate, as a rule, exceeds 1.4.

R. Myers et al. have developed a structural model to describe these gels based on the constraints inherent in the cross-linked and non-cross-linked structures of different tobermorite-like units (Fig. 4). This model enables a calculation of the chain length, Al/Si ratio and degree of cross linking for these more complex structures that cannot be fully described by standard models for non-cross linked tobermorite-like C-S-H gels.

Recent studies have also revealed that it is possible that some of the chemically bound Ca^{2+} in C-A-S-H is replaced by Na^+, leading to the formation of a C-(N)-A-S-H inner type gel in both NaOH-activated and silicate-activated slag cements C-(N)-A-S-H type gels. These have also been observed in the interfacial transition zone between siliceous aggregates and silicate-activated slag cements, having a lower Ca/Si ratio than is observed in the binding gel formed in the bulk region.
(b) **Low-calcium alkali-activated cements.**

The representatives of this alkali-activated cement model are the alkali-activated cements in which clays or type F ashes with low CaO content are used as an aluminosilicate raw material. The model of the structure formation process was described by V. Glukhovsky\(^\text{18}\) and further developed in other works\(^\text{14, 20 – 22, 33, 39 – 41}\). The main reaction product formed in this case is a three-dimensional, inorganic alkaline polymer N-A-S-H or “geopolymer”, which can be regarded as a zeolite precursor (Fig. 3)\(^\text{31}\).

The structure of the gels forming in the alkaline activation of low-calcium aluminosilicate materials differs substantially from the structure of the gels formed in the activation of calcium-rich cements. These (N-A-S-H) gels are characterized by a three-dimensional (3D) structure in which the Si is found in a variety of environments, with a predominance of (Q\(^4\)) and (nAl) (n = 0, 1, 2, 3 or 4) units (Fig. 5)\(^\text{42, 43}\).

(c) **Intermediate calcium alkali-activated cements – hybrid cements**

The compositional build-up of the hybrid alkali-activated cements often requires the use of starting constituent materials with various contents of Ca\(^{+2}\) and Al\(^{+3}\), such as for example, OPC+slag (ggbs)+fly ash, slag (ggbs)+kaolin (metakaolin) OPC+fly ash, slag (ggbs)+fly ash, slag (ggbs)+red mud, etc. Contents of Al\(_2\)O\(_3\) in these cements are higher than 20\%\(^\text{44, 45}\).

The reaction products precipitating as a result of hybrid cement hydration are very complex and comprise a mix of cementitious gels, including C-A-S-H (containing sodium) and (N, C)-A-S-H (high-calcium-content N-A-S-H gels) ones. The following is a description of the most significant features of the aforementioned procedures and the activation reactions governing each.

In an initial attempt at determining the compatibility of [N-A-S-H]-[C-A-S-H] gels, the possibility of co-precipitating the two cementitious gels in a sol-gel process was studied\(^\text{46, 47}\). The laboratory reagents were a sodium silicate (source of silicon), calcium nitrate (source of calcium) and aluminum nitrate (source of aluminum) solutions. The alkalinity of the medium was controlled with a NaOH solution. The synthesis parameters analyzed were pH and the initial Si/Al and Ca/Si ratios. The resulting synthetic gels were characterized with XRD, TEM/EDX and NMR. The findings showed that the type of products formed and their characteristics depended heavily on the pH in the synthesis medium and the initial Ca/Si and Si/Al ratios. While a medium-high lime content favored the formation of C-A-S-H gels, the presence of a high alumina and silica content led to the formation of an N-C-A-S-H gel.

Very recently, the same group of authors\(^\text{48}\) proposed a tentative phase diagram for the Na\(_2\)O-CaO-Al\(_2\)O\(_3\)-SiO\(_2\) system at 25 °C, based on a series of solution/precipitation studies. At pH values relevant to cement, the predominant phase was a solid solution designated C-A-S-H with compositional ranges of 0.72 < CaO/SiO\(_2\) < 1.94 and 0 < Al\(_2\)O\(_3\) /SiO\(_2\) < 0.1. The Na\(_2\)O content in this and related CaO-rich phases was negligible, all phases being assumed to be water-saturated.

A gel denominated N-A-S-H, exhibiting a three-dimensional structure, was also observed in this system. In the presence of Ca, however, it was only found to be stable at low pH values (< 12). At high values (> 12), the presence of Ca favored C-A-S-H formation to the detriment of N-A-S-H. At low pH, this phase behaved like a zeolite and an ion exchange process was observed in which the Na\(^+\) was replaced by Ca\(^{2+}\) until the stone of the latter was completely depleted.
A study was conducted on the compatibility between cementitious gels by directly mixing pre-synthesized C-S-H or C-A-S-H with N-A-S-H. Based on the observation that the two gels inter-react under these conditions, it was predicted that N-A-S-H would gradually degrade to C-A-S-H until the C-A-S-H reached a composition reflecting its minimum CaO/SiO₂ and maximum Al₂O₃/SiO₂ ratios. In the resulting mixture, the remaining N-A-S-H and C-A-S-H gels would be in equilibrium.

These hybrid materials can be divided into two groups. Group A includes materials having a low Portland cement clinker content and a high proportion (over 70%) of mineral additions. Examples are: OPC+slag (ggbs), OPC+fly ash, OPC+slag (ggbs)+fly ash. Group B comprises blends without Portland cement: slag (ggbs)+fly ash, phosphorous slag+granulated blast furnace slag (ggbs)+fly ash and similar.

The reaction products precipitating as a result of hybrid cement hydration are very complex, comprising a mix of cementitious gels, including C-A-S-H (containing sodium) and (N, C)-A-S-H (high-calcium-content N-A-S-H gels) gels.

V. Terminology

Taking into account a similarity of rock formation in nature and artificial stone formation in the production of building materials, back in 1957, V. Glukhovsky proposed the name “soil cements” for this new class of cements and materials. Back in 1957, V. Glukhovsky proposed the name “soil cements” for this new class of cements and materials. The name of an artificial stone. The rate of structure formation processes is determined by ratios between basic constituent oxides in the Me₂O-MeO-Me₂O₃-SiO₂ system, and conditions under which the synthesis takes place. At the first stage, the alkaline cations Me⁺ act as a catalyst of destruction of the Si-O-Si, Al-O-Al and Si-O-Al bonds. At the second stage, they participate as co-partners of the cations Me²⁺ in the formation of the alkaline or alkaline-alkaline earth aluminosilicate hydrates similar to natural zeolites.

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