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Directed synthesis of alkaline aluminosilicate minerals in a geocement matrix

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Abstract Geocements were created in accordance with a hypothesis put forward by Prof. V. Glukhovsky that the structure formation processes in the alkaline aluminosilicate binders corresponded to geological transformations of aluminosilicate minerals taking place in nature. At low temperatures, a type of hydration products depends on curing conditions and mix composition. An autoclave curing allows for an intensive synthesis of a well-crystallized zeolite structure, whereas other types of curing result in the formation of an amorphous structure with crystalline inclusions represented mainly by hydroxysodalite. On the contrary to this, after curing at high temperatures, a formation of nepheline, albite or α-cristobalite depends exclusively on the firing temperature and initial geocement composition.

Mechanical strength of the geocements may reach 88.5 MPa after low temperature curing and 88.7 MPa after firing at 800 °C. Optimal thermo-mechanical properties of the metakaolin- and fly ash-based geocements may be reached in compositions with a microstructure represented by an average amount of thermostable zeolites, since just these phases are characterized by a smooth dehydration and subsequent re-crystallization into stable anhydrous alkaline aluminosilicates without destruction of a framework. Directed regulation of structure formation at low temperatures is a key question in obtaining a wide range of special materials such as acid-resistant, high-strength, quick hardening, with low leach rates, high adhesion, etc. At the same time, a structure formation at high temperatures is important with regard to creation of heat- and fire-resistant composite materials. Synthesis of analogies to natural aluminosilicate minerals ensures also high durability.

Introduction

The nature is known to be the best judge of durability and nothing is more durable than natural minerals. This should be taken into account when durability becomes a corner stone in developing new cements. However, a phase composition of the ordinary Portland cement (OPC) is represented by the compounds not having analogies to natural minerals. This results in some problems connected with durability of OPC concretes, which are currently discussed. At the same time, an excellent durability of ancient cements is believed to be explained by peculiarities of their chemical composition (that is, by the increased content of alkalis), which lead to formation of the analogies to natural zeolites in the reaction products of such cements [1–3]. Glukhovsky [4–6] was the first who assumed that, since the geological process of transformations of some volcanic rocks into zeolites takes place during formation of the sedimentary rocks at low temperatures and pressure, it might be modelled and carried out in the cementitious systems.

The alkalis play an important role in mutual transformations of minerals in the earth crust. It should

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be also mentioned that the alkaline aluminosilicates (first of all, feldspars [5]) are known to be stable and durable compared to the calcium ones. Predominance of one or another mineral may be taken as an index of the mineral's durability. The zeolites, natural alkaline or alkali-earth hydrated aluminosilicates with a porous structure of framework, are supposed to be one of the most important groups of the sedimentary minerals. Usually, they are formed as a result of transformation of the aluminosilicate volcanic rocks in the presence of alkaline solutions at low temperatures (below 200–300 °C, depending on a zeolite type). The increase in temperature to 400 °C promotes their re-crystallization into more stable high-silica structures (first of all, analcime) and then, into secondary feldspars which are the dominant minerals of the earth crust. In particular, transformation of a primary volcanic glass in the salt lakes or open hydrological formations may be represented as follows [7–9].

$$\text{Volcanic vitreous rock} \xrightarrow{20\text{–}200\,\mathrm{C}} \text{Various zeolites (low-silica)} \xrightarrow{\text{up to } 300\,\mathrm{C}} \text{Analcime} \xrightarrow{\text{over } 300\,\mathrm{C}} \text{Feldspars}$$

It can be clearly seen that all these transformations take place at relatively low temperatures, which may be modelled in the process of hardening of the cementitious systems. Since the geological processes require a lot of time in real natural conditions, these processes should be accelerated in the construction industry by applying high-intensive technologies such as easily reactive starting materials, high initial alkalinity, high curing temperatures, etc. A directed synthesis of the alkaline aluminosilicate minerals in the phase composition of such cementitious systems may ensure an excellent durability of an artificial stone formed side by side with a set of new useful properties since the structures and properties of the zeolites vary within a wide range.

According to the above hypothesis, the alkaline aluminosilicate cementitious systems (called first as the ''soil silicates'') appeared in the field [3–6, 10]. Later, a lot of studies held in different countries showed a possibility to obtain a variety of cements in the system R_2O–Al_2O_3–SiO_2–H_2O using different starting materials. The structure formation process of these cementitious materials is considered to be a complex of destruction–condensation conversions including: (I) destruction of an initial solid phase into certain units of instable structure, (II) their contact interaction resulted in the formation of coagulated thixotropic structures leading to (III) creation of the condensation/crystallization structure of the hydrated products [10]. In the 70th, Professor Davidovits suggested to use a term ''geopolymerization'' [11] in order to describe a process of polycondensation of the alkaline aluminosilicate cementitious systems into an artificial stone with a 3d-polymeric structure similar in a general way to that of natural zeolites.

As far as a family of the alkali activated, cements was growing and various starting materials and cementitious systems were tried and used in them, a classification of the alkaline cements was proposed in 1991. This classification is based on a phase composition of the hydration products [12]. The alkaline aluminosilicate systems (R–A–S–H, where R– Na or K) were classified as the first class called ''geocements'' (a term introduced to underline a similarity of their structure formation processes and geological processes taking place in nature), with main hydration products represented by 3d-polymeric compounds, which have analogies in nature (zeolites, etc.). These zeolite-like hydration products provide for a variety of unique special properties of the materials such as heat-, fire- and acid resistance, adhesion and ability to bind hazardous elements, etc. [11, 13]. The calcium compounds are present in this first class in small quantities, thus playing a supplementary role.

On the contrary to the first class, low basic calcium silicate hydrates are the main hydration products in the second class of the alkaline cements (R–C–A–S–H), which includes, in particular, the alkali activated slags and alkaline portland cements. The calcium-free alkaline aluminosilicates appear usually as supplementary phases in these cements, because a synthesis of the C–S–H gel from the thermodynamic point of view is more preferable at high contents of calcium compounds. Thus, geopolymerization plays a supplementary role in the structure formation and genesis of strength of these cements. Taking into account the improved service properties and high volume of industrial wastes utilized in these systems, the alkaline cements of the second class are expected to become an important alternative to the OPC, especially in view of the problem of creating a new generation of cements with low CO_2

emission. The geocements cannot be considered as an alternative to the OPC due to relatively high price, however, they are much more promising systems for creating special building composite materials.

Main selection criteria for the geocement starting materials are: high contents of silica and alumina along with a low (<5%) content of calcium oxide, which inhibits the zeolite synthesis [7–9]. Among many other starting materials capable to geopolymerization [5, 14], a metakaolin and fly ash are considered to be the most suitable ones. The metakaolin-based cementitious materials are simpler from the point of view of their processing, whereas the fly ash-based ones are cheaper and more favourable from an ecological point of view [15–18]. The most important factors affecting peculiarities of a phase composition and, correspondingly, properties of the geocements are: (1) curing conditions and (2) type and concentration of alkaline solution (which determine in fact the ratios between main oxides, Na_2O/Al_2O_3 and SiO_2/Al_2O_3) as well as a water to solid (W/S) ratio [5, 11, 13–21].

The majority of researchers [11, 14, 16, 17] concluded that an amorphous structure of the geocement/geopolymer artificial stone synthesized was preferable in order to achieve optimal mechanical strength. However, a crystalline or semi-crystalline structure seems to be more suitable for some special applications. In particular, as crystals are more resistant to acid attack or to thermal shock, the improved crystallinity of the artificial stone is expected to be more resistant to the above mentioned factors [19, 20]. Moreover, since the zeolite family is extremely diverse, different zeolites, once synthesized in the geocement composition, are thought to secure different target properties. In particular, as it was reported in [22], the metakaolin-based geocements in which the analcime is formed as a hydration product are suitable for making low-temperature ceramic materials; the zeolite P ensures high strength within the temperature range of 20–250 °C; the zeolites R, NaX, NaY provide for stability of mechanical strength during heating up to 800 °C. That is why properties of the geocements should be studied versus peculiarities of microstructure (phase composition, crystallinity, etc.).

A main target of this study was to reveal the interrelation between a sodium-based geocement mix composition, curing conditions, peculiarities of microstructure and properties in order to demonstrate how a directed synthesis of the aluminosilicate minerals in the geocement matrix gives an opportunity to regulate the structure formation process and features. As an example, a role of phase composition and crystallinity was analysed from the point of view of reaching a high heat resistance.

Experimental

Two different aluminosilicate components were studied in this research: a traditional metakaolin and type F fly ashes (380 m^2/kg) of different origin (Table 1). Water glass with a silicate modulus of 2.8 and density of 1400 kg/m^3 was used as main alkaline component; sodium hydroxide and silica fume were used in some cases to adjust the geocement mix composition. When studying the heat resistance, a ground chamotte (410 m^2/kg) was used as a heat-resistant filler only in the studies held at high temperatures. After a preliminary curing in an air tight mould at 80 °C until setting, the samples were then cured for 6 h under one out of 5 possible regimes: autoclave curing at 174 °C, steam curing at 80 °C, and dry curing at 80, 150 and 220 °C. In order to study the structure formation process at high temperatures, a part of the samples was then cured in an oven at 800 °C for 4 h. Mechanical properties determined on the specimens of size 2 × 2 × 2 cm were compared with the results of phase composition studied by means of XRD and DTA methods.

The mix compositions were designed with taking into account both previously obtained results and

Table 1 Chemical composition of starting materials

Constituent	Chemical composition (% by mass)											In total
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	R_2O	P_2O_5	LOI	
Kaolinclay	48.17	0.62	36.33	0.36	–	–	0.30	0.62	–	–	13.63	100.03
Fly ash 1	50.27	1.20	23.55	9.60	0.70	0.15	1.75	2.30	3.24	0.45	6.05	100.06
Fly ash 2	48.20	0.89	19.65	4.50	3.15	0.11	1.36	2.18	3.82	0.02	16.02	99.92
Silica fume	87.40	–	0.20	0.14	–	–	0.50	2.10	4.75	–	4.70	99.96
Chamotte	60.2	–	35.3	0.8	–	–	0.31	0.29	2.13	–	0.22	99.25

Table 2 Initial geocement mix compositions

Aluminosilicate component	Mix No.	Molar ratio		
		Na_2O/Al_2O_3	SiO_2/Al_2O_3	H_2O/Al_2O_3[a]
Metakaolin	1	1.0	2.0	9.5
	2	1.0	4.0	10.0
	3	1.0	6.0	15.0
	4	1.0	8.0	20.0
Fly Ash 1	5	1.0	4.0	7.0
	6	1.0	6.0	10.5
	7	1.0	8.0	16.5

theoretical data on synthesis of zeolites in a geological formation and chemical industry. On the contrary to a traditional approach, under which changes in a pH-value and fly ash/solution ratio are taken as variables, a method applied in this study was based on a ratio between main oxides (mainly SiO_2/Al_2O_3) in a reacting mix; it makes easier the understanding of the structure formation process in connection with peculiarities of a microstructure synthesized.

Results and discussion

Phase composition of the geocements after hydration (low temperature curing)

Ten mix compositions were chosen for this study, divided according to a type of aluminosilicate component and the ratio between main oxides (Table 2). Each mix composition was cured under 1 of 5 regimes mentioned above. The XRD and DTA results allowed to identify the fields of crystallization of the geocement-based hydration products (Fig. 1).

The results obtained allowed to make a conclusion about a principal similarity of the phase composition of the hydration products of the metakaolin- and fly ash-based geocements. Thus, a phase composition of the autoclaved fly ash-based geocements is represented mainly by the analcime, zeolite P and zeolite R. It correlates well with the results obtained using model systems [7, 8] and with the data of previous studies held on the metakaolin-based geocements [19].

Being dependent on high content of the caustic soda due to peculiarities of the mix formulations, a synthesis of hydroxysodalite in steam cured and dry cured fly ash-based compositions with $SiO_2/Al_2O_3 = 4$ correlates well with the results obtained on similar systems with high alkali concentrations and normal pressure of treatment [7, 8, 15]. When using the low-alkali compositions with $SiO_2/Al_2O_3 = 6...8$ simultaneously with a low-intensity treatment such as steam or dry curing, the accepted exposition time is not enough for the zeolite crystallization. However, the DTA patterns allowed to assume the formation of a 3d-aluminosilicate gel.

The rate of zeolite formation measured by a height of the XRD peaks was much higher in the fly ash-based geocements compared to that in the metakaolin-based ones. Besides, the application of the fly ash 1 made for a synthesis of rather large amounts of plain zeolite-like products, whereas the application of the less pure fly ash 2 resulted in the formation of the more diverse composition of less crystallized zeolites.

After dry curing of both metakaolin- and fly ash-based geocements, irrespective of a composition, the weak XRD peaks (0.493, 0.323, 0.308, 0.264, 0.245,

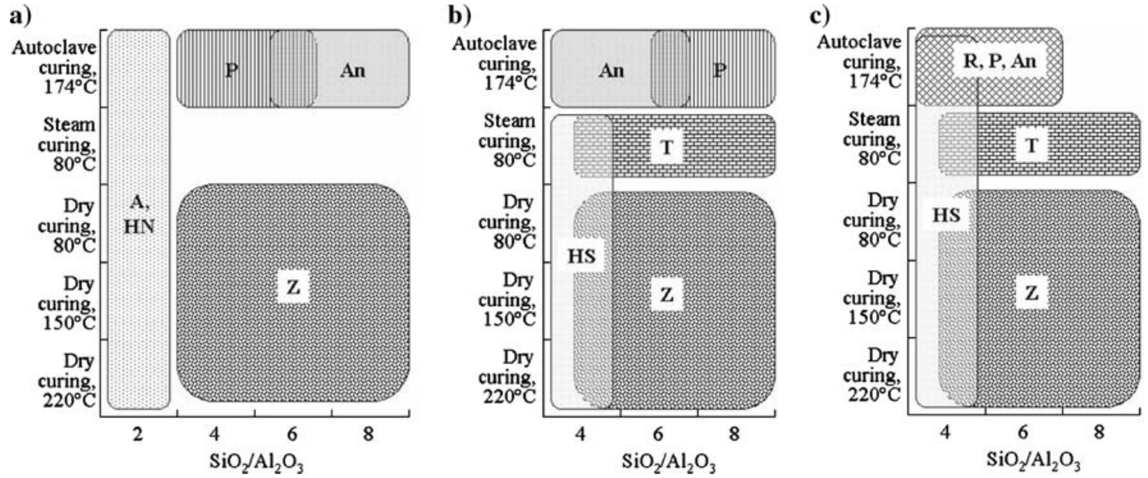


Fig. 1 Composition of hydration products versus the geocement compositions (aluminosilicate component: (**a**) metakaolin, (**b**) fly ash 1, (**c**) fly ash 2) and curing conditions. An—analcime, A—zeolite Na–A, P—zeolite P, R—zeolite R, HN—nepheline hydrate, HS—hydroxysodalite; Z—trona, T—sodium carbonate hydrate

0.211 and 0.204 nm) were fixed. This minor phase was marked at first as a ''phase Z'' [18], but recent studies on carbonation finally showed that these peaks could be identified as a mineral trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, JCPDS # 29-1447, 75-1195, 76-0739, 76-1105, 78-1064). In case of steam curing, another minor phase with main peaks (0.276, 0.237 nm) was synthesized, at first it was identified by mistake as a ''tobermorite gel'' [18], but in fact, these peaks indicate the formation of another sodium carbonate, $Na_2CO_3 \cdot H_2O$ (JCPDS # 08-0037, 70-0845, 70-2148, 76-0910). The reason for carbonation is an insufficient rate of sodium bound into insoluble zeolite-like products. Recent studies have also shown that these two phases may coexist sometimes, although a synthesis of the trona tended to increase at the higher initial W/S ratio, and a synthesis of the sodium carbonate hydrate took place only in the mixes with low W/S ratio and with the increased alkalinity under hydrothermal conditions (steam curing, curing in an air tight mould). It means that these two phases appeared under a different mechanism. Further investigations on the carbonation are required as these two carbonate phases mentioned above have different chemical properties and, according to the preliminary results, the formation of the sodium carbonate hydrate is undesirable from the point of view of durability.

Phase composition of the geocements after dehydration (high temperature curing)

After a low temperature treatment, the geocement samples (Table 2) were fired at 800 °C to study a phase composition of the dehydration products. On the contrary to the phase composition after hydration which is dependent above all on a type of low temperature curing, the phase composition after dehydration depends only on the geocement composition and does not depend on the type of the preliminary low temperature curing. Thus, a phase composition of the geocements with $SiO_2/Al_2O_3 = 4$, irrespective of the type of preliminary low temperature curing, is represented by a nepheline. The degree of crystallization of the crystalline products formed does not depend on the type of preliminary low temperature curing as well, and with other conditions being equal depends on a type of the aluminosilicate component: a maximal value was observed when the metakaolin, the most chemically pure component, was used. The impurities from the fly ash resulted in the reduced content of the anhydrous aluminosilicates formed and in the formation of some additional amount of a hematite Fe_2O_3.

In studying the influence of the geocement mix composition on phase composition after its dehydration, it was determined that a correlation exists between the SiO_2/Al_2O_3 molar ratio in the initial geocements and their dehydration products (Table 3). With increase in this ratio from 2 to 8, the dehydration products change in the direction as follows: nepheline ($Na_2O–Al_2O_3–2SiO_2$)–albite ($Na_2O–Al_2O_3–6SiO_2$)–α-cristobalite (SiO_2). This tendency generally coincides well with the results obtained on the model systems of the alkaline aluminosilicate cementitious materials [24]. Thus, a phase composition of the geocements with $SiO_2/Al_2O_3 = 2...4$, irrespective of a type of the aluminosilicate component used, is represented by a feldspathoid nepheline ($SiO_2/Al_2O_3 = 2$ in the aluminosilicate framework). It should be mentioned that a quantity of the synthesized nepheline measured by the XRD method was found to reach a maximum degree in case when the stoichiometric nepheline composition was used. The increase in the SiO_2/Al_2O_3 ratio up to 6...8 in the metakaolin-based geocements resulted in crystallization of the amorphous silica into the α-cristobalite ($d = 0.411$; 0.252; 0.206; 0.163 nm). It coincides with the data of hydrothermal chemistry [8] on the crystallization of amorphous silica in the alkaline systems through a metastable phase (cristobalite) instead of a stable one (quartz), in accordance with the Ostwald rule on successive transformations. The speed of cristobalite formation tends to increase sharply with increase in the amorphous silica content; it testifies to insufficient reaction of the amorphous silica introduced in a form of the silica fume in comparison

Table 3 Correlation between SiO_2/Al_2O_3 molar ratio of initial geocements and their products of dehydration (high temperature structure formation)

Aluminosilicate component	SiO_2/Al_2O_3 molar ratio	
	Initial geocements	Products of dehydration (corresponding phase)
Metakaolin	2	**2 (nepheline)**
	4	**2 (nepheline)**
	6	**∞ (cristobalite)**, 2 (nepheline)
	8	**∞ (cristobalite)**, 2 (nepheline)
Fly ash	4	**2 (nepheline)**
	6	**6 (albite)**, 2 (nepheline)
	8	**∞ (cristobalite)**, 2 (nepheline)

Dominating phases are given in bold

with that introduced in a form of the soluble sodium silicate (water glass).

In contrast to the metakaolin-based geocements, an increase in the SiO_2/Al_2O_3 ratio in the fly ash-based composition up to six results in the formation of the high-silica feldspar albite side by side with the smaller amounts of the nepheline. The formation of the albite in this case is explained by high contents of impurities, which can also be regarded as oxides-mineralizers. Additionally, the albite formation may also depend on the peculiarities of kinetic of alkaline dissolution of silica and alumina from the initial metakaolin and fly ash. With increase in the SiO_2/Al_2O_3 ratio up to 8, the composition of the dehydrated products of the fly ash-based geocements tends to become similar to that of the metakaolin-based one, but a quantity of the cristobalite is smaller than that in the metakaolin-based compositions. This may depend on some quantities of the silica contained in the fly ash-based compositions in a form of non-active compounds such as quartz and mullite, which decrease the real SiO_2/Al_2O_3 ratio in the fly ash-based systems.

A temperature of crystallization of the anhydrous aluminosilicates depends on the initial composition, and first of all, on the alkali content. In the alkali-rich systems they appears in the limited amounts at 600 °C, whereas in the low-alkali compositions the crystallization begins only at 1000 °C. These results coincide in general with the earlier results from the alkaline activation of various clays [24] which showed that a phase composition of the alkaline aluminosilicates synthesized might also be regulated by changing a temperature of high-thermal curing. Thus, independently on a clay type and type of preliminary low-thermal curing, a nepheline was found to be a main product of the system ‘‘clay + sodium alkaline component’’ after firing at 750–900 °C, and an albite appeared after firing at 900–1000 °C.

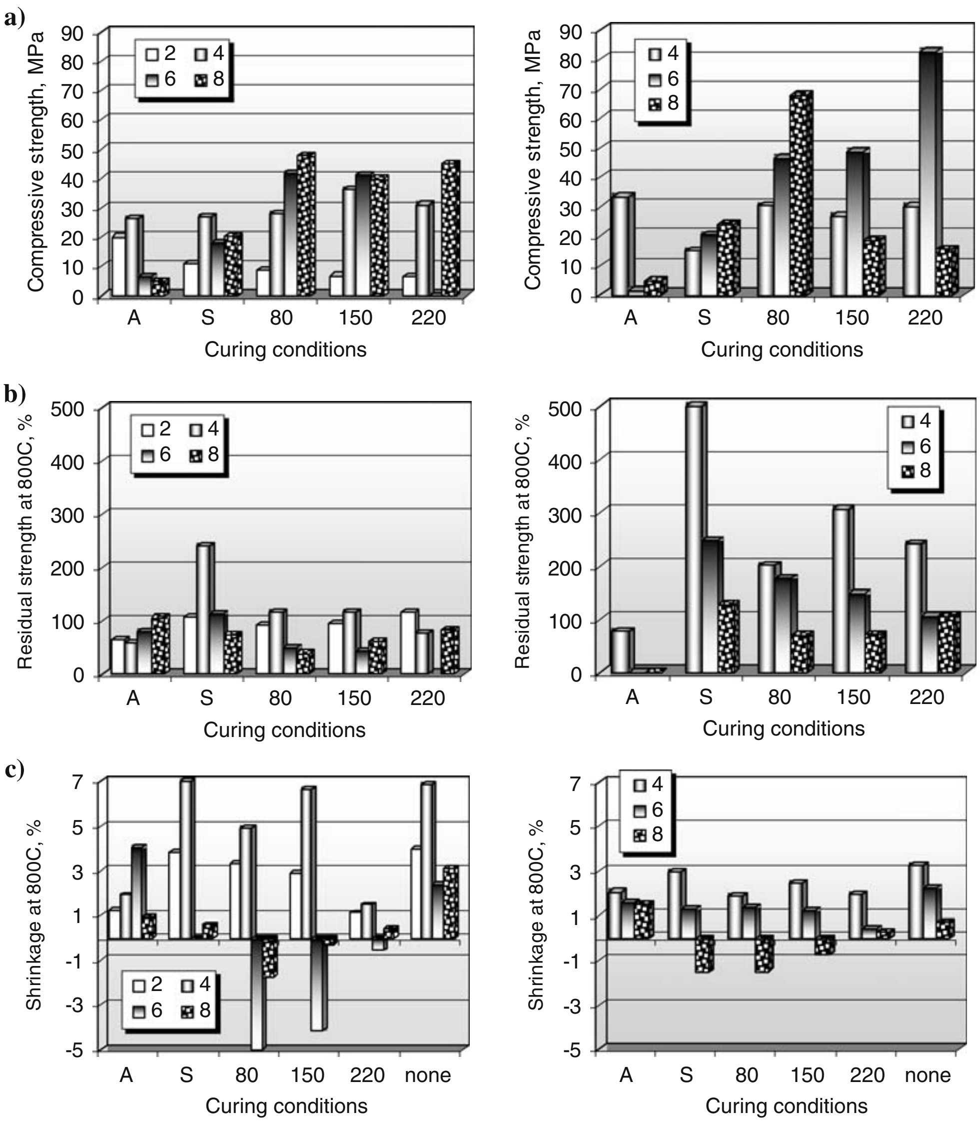
Similar results were also obtained in the potassium (KOH)- and calcium (OPC clinker)-modified geocements, in which a leucite (a potassium feldspathoid) and labradorite (a sodium–calcium feldspar) were found to be the main phases after firing. This mixed compound composition, N–K–C–A–S–H, had an amorphous structure after firing at 800 °C, whereas strong XRD peaks of leucite and labradorite were identified after firing at 1000 °C. A temperature of their crystallization measured by a DTA method was of about 900 °C. Being fired at 1300 °C, the system demonstrates redistribution of shares of the products mentioned, in accordance with their thermodynamic stability at this temperature: a quantity of the labradorite increases, whereas that of the leucite decreases.

Interrelation between mix proportion, phase composition after hydration and dehydration and properties of the geocement-based heat-resistant composite materials

The heat-resistant composite materials require a stability of volume changes within a wide temperature range. The study held allowed to show that a shrinkage/expansion process during heating should be regulated by a selection of optimal geocement mix composition side by side with the addition of a heat-resistant filler. A chamotte was found to be the rational one [22]. The study of interrelation between a mix composition, curing conditions, phase composition of microstructure and properties of the geocement-based artificial stone was carried out on the compositions modified by the ground chamotte taken in a quantity of 1:1 by mass (Fig. 2). Additionally, an interrelation between a relative intensity of the crystalline phases formation and key properties was studied: the maximum height of peak in the XRD patterns in this experiment (fixed for the analcime’s main peak at 0.343 nm in the XRD pattern of the autoclaved fly ash 1-based geocement with $SiO_2/Al_2O_3 = 4$) was taken as 100%.

It was revealed that optimal thermo-mechanical properties such as high density and mechanical strength along with low contraction after firing was achieved in the mixes with a microstructure composition presented by an average amount (from 2.5 to 10%) of the thermostable zeolite-like products such as analcime, hydroxysodalite and zeolite R. These phases are characterized by a smooth dehydration and subsequent re-crystallization into stable anhydrous alkaline aluminosilicates such as nepheline and albite (Table 3) without destruction of the aluminosilicate framework [20]. High intensity of the crystal formation (higher than 10%) in the autoclave-cured compositions as well as insufficient rate of crystallization of the high-silica geocements (from 0 to 2.5%) was found to result in a sharp deterioration of service properties. In case of a high-crystalline structure, it may be caused by the increase in stresses in the already hardened cement stone during intensive re-crystallization taking place at high temperature. At the same time, in case of low-crystalline structure it is caused by the absence of a hard crystalline framework. Heat resistance of the fly ash-based geocements is higher than that of the metakaolin-based ones.

Fig 2 Compressive strength (**a**), residual strength after firing (**b**) and shrinkage after firing at 800 °C (**c**) VS geocement composition and curing conditions. The geocements were modified by ground chamotte taken in a quantity of 1:1 by mass. Negative values in the diagrams of shrinkage correspond to expansion of the specimens



Experience of application of the geocement-based heat resistant materials

The composite materials in the system "geocement—heat resistant filler" had setting time at 80 °C up to 4 h, compressive strength after low-temperature treatment up to 88.5 MPa, compressive strength after firing at 800 °C up to 88.7 MPa, residual strength after firing up to 245% and contraction after firing up to 4.2%. The designed compositions were used for development of a wide range of non-fired heat-resistant composite materials. In particular, a heat-resistant aerated concrete with a maximal use temperature of 800 °C was developed using the fly ash-based geocements and an aluminium powder as a gas producing agent [20, 25]. This material was intended for thermal insulation of high-temperature equipment, such as furnaces, conduits, chimneys, boilers, fireplaces, etc. The development of process parameters and mix proportions allowed to produce the heat-resistant aerated concretes of density varying between 300 and 1200 kg/m^3, compressive strength up to 16 MPa, thermal resistance up to 34 cycles in the air, residual strength after firing at 800 °C of 75...537% and shrinkage of 0.94...1.97%. The manufacture of this material does not require high temperatures, and thus its manufacture is cheaper, more energy saving and environmentally friendly in comparison with the manufacture of traditional lightweight refractory materials.

In order to launch a commercial scale application of this material as heat insulation of a furnace lining at the glassware plant (Kiev, Ukraine), the geocement-based heat-resistant adhesive was developed. Using this adhesive, the materials may be glued at ambient or

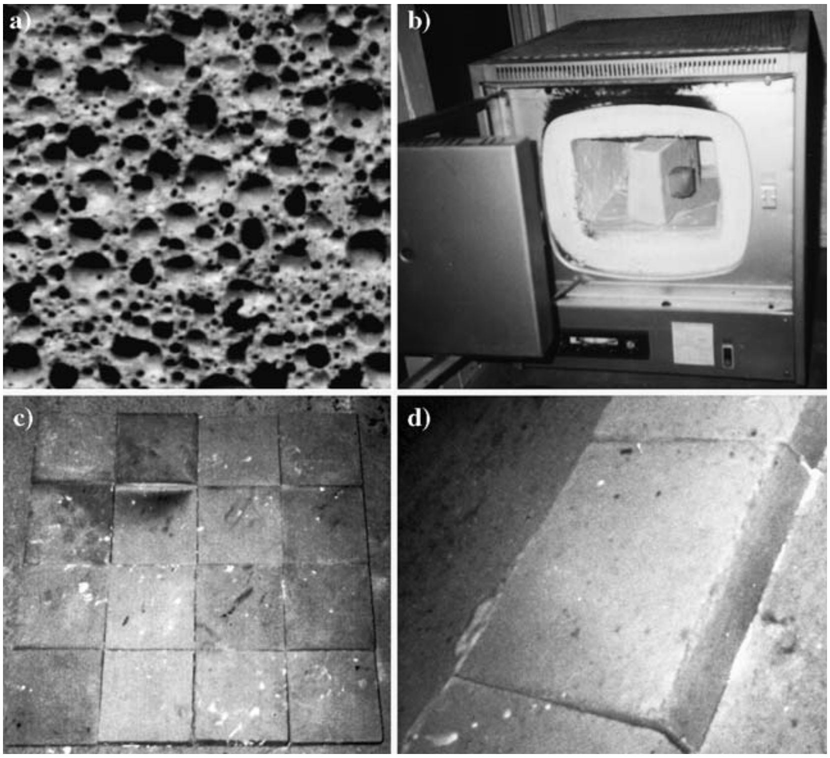


Fig. 3 Pilot-scale application of the geocement-based heat resistant aerated concrete: structure of the heat-resistant aerated concrete (**a**); testing of heat-resistant adhesive in a laboratory oven (**b**); fragments of a glassware furnace lining insulated with the developed material (**c**, **d**)

increased temperatures and the adhesive maintains its high adhesion after heating up to 1000 °C and cooling. Thus, lightweight (600 kg/m^3) heat-resistant tiles $40 \times 40 \times 4$ cm in size made from the elaborated aerated concrete were glued directly to a hot furnace surface (up to 700 °C) without interruption of the furnace operation (Fig. 3). After six months in service, no destruction of the heat resistant aerated concrete products was visualized.

Conclusions

The analogies to natural aluminosilicate materials may be synthesized in the phase composition of the geocements—the hydraulic cementitious materials of the system Na_2O–Al_2O_3–SiO_2–H_2O. The zeolites in a crystalline or semi-crystalline state were found to appear after hydrothermal treatment at temperatures up to 250 °C, whereas the feldspathoids and feldspars appear after high temperature treatment (750...1300 °C). The structure formation and properties of the zeolite-based geocements at low temperatures may be regulated by changing curing conditions, type and concentration of the alkaline solution as well as the solution to solid ratio. However, at high temperatures, the only significant factors affecting a phase composition and properties are an initial geocement composition as well as temperature of firing. A directed regulation of the low temperature structure formation is a key allowing to obtain a wide range of special materials such as acid-resistant, high-strength, quick hardening, with low leach rates, adhesives, etc. depending on a type of zeolite-like structure synthesized. In the meanwhile, regulation of the high-temperature structure formation is important in order to create heat- and fire-resistant composite materials. In particular, this approach was applied to create heat resistant aerated concretes for high-thermal insulation. A synthesis of analogies to natural aluminosilicate minerals also promotes for high durability of a matrix. Since the structure formation of the geocement-based heat-resistant composite materials is supported by the smooth dehydration and subsequent re-crystallisation of the hydrated products into stable anhydrous alkaline aluminosilicates, these materials resemble the chemically bonded ceramics [26] in terms of prevalence of strong covalent bonds within the aluminosilicate framework, low temperature of formation and excellent properties.

References

1. Malinowski R (1979) Concrete Int: Design Construct 1:66
2. Davidovits J (1987) Concrete Int: Design Construct 9(12):23
3. Krivenko P (1999) Proceedings of the 2nd International Conference in ‘‘Alkaline Cements and Concretes’’, Kyiv, pp 3–43

4. Glukhovsky V (1959) Soil silicates, Gosstroyizdat USSR, Kiev (in Russian)
5. Glukhovsky V (1967) Soil silicate articles and constructions, Budivelnik, Kiev (in Ukrainian)
6. Glukhovsky V (1989) Proceedings of the international seminar on ‘‘Durability of Concrete’’, Götheborg, pp 53–62
7. Breck D (1974) Zeolite molecular sieves. J. Wiley & Sons, New York
8. Barrer R (1982) Hydrothermal chemistry of zeolites. Academic Press, London
9. Dyer A (1988) An introduction to zeolite molecular sieves. J. Wiley & Sons, New York
10. Krivenko P (1994) Proceedings of the 1st international conference in ‘‘Alkaline Cements and Concretes’’, Kyiv, pp 11–129
11. Davidovits J (1988) Proceedings of the 1st European conference on soft mineralurgy ‘‘Geopolymer’ 88’’, Saint-Quentin, pp 25–48
12. Krivenko P (1997) Proceedings of the tenth international congress on the chemistry of cement, Götheborg, pp 4iv046–4iv050
13. Krivenko P (ed) (1999) Alkaline cements and concretes: proceedings of the 2nd international conference on alkaline cements and concretes. Oranta Ltd, Kyiv
14. Xu H, Van Deventer J (1999) Proceedings of the second international conference on geopolymers ‘‘Geopolymer’ 99’’, Saint-Quentin, pp 43–64
15. Krivenko P, Skurchinskaya J (1991) Proceedings of the international conference on the utilization of fly ash and other coal combustion by-products, Shanghai, pp 64-1–64-7
16. Van Jaarsveld J, Van Deventer J (1999) Ind Eng Chem Res 38:3932
17. Palomo A, Fernández-Jiménez A (2003) Proceedings of the 11th international congress on the chemistry of cement, Durban, pp 1332–1340
18. Krivenko P, Kovalchuk G (2002) Innovations and developments in concrete materials and construction: proceedings of the international conference on ‘‘Challenges of Concrete Construction’’, Dundee, pp 123–132
19. Popel G (1999) Proceedings of the 2nd international conference on alkaline cements and concretes, Kyiv, pp 208–219
20. Kovalchuk G (2002) Heat resistant gas concrete based on alkaline aluminosilicate binder. PhD Thesis, Kyiv (in Ukrainian)
21. Palomo A, Fernández-Jiménez A, Kovalchuk G (2005) Proceedings of the international symposium on ‘‘Non-Traditional Cement and Concrete II’’, Brno, pp 1–12
22. Gonchar V (2000) Abrasive and thermoresistant composite materials based on alkaline aluminosilicate binders. PhD Thesis, Kyiv (in Ukrainian)
23. Quepol X et al (1997) Environ Sci Technol 31:2527
24. Skurchinskaya J (1994) Proceedings of the 1st international conference on alkaline cements and concretes, Kiev, pp 271–298
25. Krivenko P, Kovalchuk G, Kovalchuk O (2005) Proceedings of the international congress ‘‘Global Construction: Ultimate Concrete Opportunities’’, Dundee
26. Roy D (1987) Science 235:651