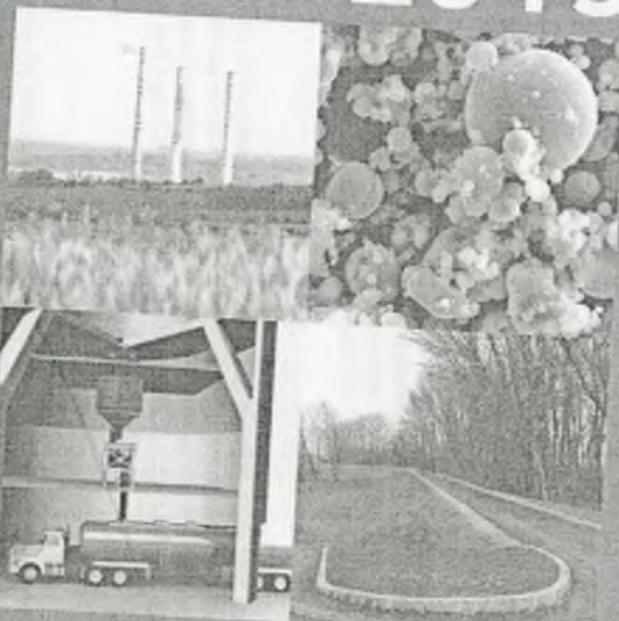


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# HYBRIDNÍ ALKALICKÁ POJIVA NA POPÍLKOVÉ BÁZI

## HYBRID FLY ASH BASED ALKALI ACTIVATED CEMENTS

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**Klíčová slova:** popílek, alkalicky aktivované materiály,

**Keywords:** fly ash, alkali activated materials

**Anotace:**

Alkalická aktivace je jedním z nejperspektivnějších způsobů, jak vytvořit velký objem popílkových cementů. Hlavní fáze struktury v takových «hybridních» systémech jsou směsi N-A-S-H a nové formace N-C-A-S-H. Přísspěvek ukazuje rozdíly ve struktuře tvorby alkalicky aktivovaných cementů obsahující popílky s vysokým a nízkým obsahem Ca. V článku jsou uvedeny vhodné aplikace.

**Anotation:**

Alkaline activation is one of the most perspective ways for creating very high volumes fly ash cements. The main phases of structure in such "hybrid" systems are represented by mixes N-A-S-H and N-C-A-S-H new formations. The paper is showing differences in structure formation and properties of low-Ca and high-Ca-containing fly ash alkali activated cements. Appropriate applications are shown.

## 1 INTRODUCTION

concept of "High Volume Fly Ash Concrete" (HVFA) [1] allows changing a role played by fly ash in the cementitious system from a "supplementary" to a "basic" material. A content of the fly ash may be improved by applying activation methods. Development of the alkali-activated cements [2] allowed proposing other approaches based on the use of alkali metal compounds. Specific features of structure formation processes in the alkaline cements are determined to a large extent by a type of the binding system; it was reflected in the classification [3]. The alkaline aluminosilicate systems (R-A-S-H, where R is Na or K) were classified as the first class called "geocements" with main reaction products represented by 3d-polymeric compounds which have analogies in nature (zeolites, etc.). These zeolite-like products provide for a variety of unique special properties such as heat-, fire- and acid resistance, adhesion and ability to bind hazardous elements, etc. [4, 5]. The calcium compounds are present here in small quantities, thus playing a supplementary role.

On the contrary to the first class, low basic calcium silicate hydrates are the main reaction products in the second class of the alkaline cements (R-C-A-S-H). 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<sub>2</sub> emission. The Geocements, in turn, can not be considered as an alternative to the OPC because of relatively high price; however they are more promising systems for creating special building composite materials.

These specific features predetermined differences in the approaches to the alkaline activation of fly ash depending upon purpose of cementitious materials. An alkaline activation without introduction of calcium compounds is used for development of the HVFA of special application, in particular for making heat resistant materials, matrices for immobilization of radioactive wastes, etc. Incorporation rate of the fly ash in these systems may exceed 90%, however these binders are capable to harden only at elevated temperatures (40-150°C) and are rather expensive materials. At the same time, the mixed fly ash alkaline cements (class II) may become an essential alternative to traditional ones, not inferior to the last in basic properties, even with the fly ash content up to 70% [6-12]. Such hybrid systems has mix compositions of new formations R-A-S-H + R-C-A-S-H + C-S-H that make it possible to obtain increased service and special properties of such materials.

Thus, two different alkaline fly ash cements are elaborated: the first one is calcium free, and the second one with CaO content of over 20% (hybrid cement). In such way, the question is what is the role of Ca-containing additives added to alkali activated fly ashes and how does this kind of modification influence structure and properties of that material.

## 2. EXPERIMENTAL

A typical class F fly ash from a Ukrainian power plant was used (chemical composition is shown in Table 1), with Blaine specific surface of 350 m<sup>2</sup>/kg. Water glass (soluble sodium silicate with a silicate modulus of 2.8 and a density of 1350 kg/m<sup>3</sup>) was used as the main alkaline activator. In order to obtain the necessary Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of the alkaline solution, waterglass was adjusted by additions of dry NaOH. Calculation of initial mixtures compositions was carried in order to obtain a model composition Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>·xH<sub>2</sub>O, water/solid ratio (W/S) was 0.2. There were three different Ca-containing additives used, with their quantity of 0, 1 2.5, 5 and 10% by mass:

- type I OPC, with a compressive strength of 50 MPa measured by a standard method;
- grinded (550 m<sup>2</sup>/kg) blast furnace slag from Mariupil plant,
- high-alumina cement, with a compressive strength of 50 MPa.

Table 1 Chemical compositions of fly ash

Material	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	L.O.I.
Fly ash	50,94	24,56	13,25	2,86	1,98		0,69	2,69	1,64
Type I OPC (C)	23,40	5,17	4,12	64,13	0,88	0,55	0,41	0,33	0,20
Blast furnace slag(B)	40,00	5,91	0,32	46,98	5,87	1,62			
Alumina cement (L)	7,6	56,8	2,6	30,6	2,4				

"Hot moulding" technology was used to prevent quick setting, and moulds once prepared were covered by a plastic film to prevent water evaporation and then were cured in accordance with one of the three curing conditions:

"curing in a covered mould": covered moulds were introduced into the oven at the temperature of 85°C for 8 hours;

"autoclave curing": covered moulds were first introduced into the oven at the temperature of 85°C until set and after then dismoulded samples were cured in autoclave at the isothermal temperature of 174°C and pressure of 0.8 MPa;

"steam curing": covered moulds were first introduced into the oven at the temperature of 85°C until set and after then demoulded samples were cured at the atmosphere pressure in a media with 100% humidity at the isothermal temperature of 85°C.

Time of isothermal conditioning was kept equal to 6 hours in all the curing conditions. Strength properties in paste were determined at 1 day age after curing using samples of 2×2×2 cm in size. Peculiarities of microstructure were studied using XRD and mercury porosimetry. Leaching studies for Na and Pb was studied in accordance to EDV-S4 method: 100 of samples 2-4 mm in size were shaken in 500 ml of distilled water during 24 hours at room temperature, and then a leachate was analyzed using ICP technique.

Corrosion resistance was tasted in accordance to standard methods: the samples of the standard mortar 10×10×60 cm in size, were held in water during 14 days, after that they were placed in a 5% solution of sodium sulfate or chloride. After keeping the samples in the solutions during 3 months, mechanical strength was tested. Corrosion resistance coefficient was calculated as a ratio between the mechanical strength of the samples kept in a salt solution to the strength of the ones kept the same time under the water

### 3. RESULTS AND DISCUSSION

#### 3.1 MECHANICAL STRENGTH

First of all, peculiarities of influence of additives depend greatly on curing conditions (fig. 1). Compressive strength in a general way tends to increase with increasing of Ca content when autoclave or steam curing were applied; however no strength growth was observed for Ca-containing pastes after curing in a covered mould. This may be explained when taking into account three ideas:

two different groups of phases are responsible for strength development in the mixed sodium-calcium system: N-A-S-H gel (with inclusions of crystalline zeolites) and N-C-A-S-H-gel;

the best strength values for "pure" mixed alkaline fly ashes are fixed after curing in a covered mould;

conversely, it is well known that the best curing conditions for calcium silicate hydrates are steam or autoclave curing.

Thus, at steam curing conditions, the higher calcium content, the higher compressive strength because N-A-S-H structure remains strong and an amount of C-S-H gel seems to growing; these two structures coincides well thus influencing additively to the strength values (fig. 1 c). During autoclave curing, some degradation of a zeolite-based microstructure takes place at calcium content within 1 .5% due to some inhibition of zeolite gel synthesis; it results in some strength decline (fig. 1 a). When calcium content is superior 5%, C-S-H structure becomes playing important role and the strength values are growing; this process is more intensive when OPC additive is used. Finally, curing in a covered mould is not an appropriate condition for synthesis of C-S-H phase and this fact alongside with some probable degradation of N-A-S-H phase at increased calcium content may result in some strength decline (fig. 1 b).

Comparing different additives between themselves, it is to be noted that Portland and alumina cements gave better results from the point of view of mechanical strength compared with blast furnace slag; the system seemed to be low sensible to the contact of the last one.

Thus, the role of Ca-containing additive depends greatly on the type of curing condition. At water-intensive curing such as steam or autoclave curing, an increasing amount of calcium-containing additives generally makes for increasing compressive strength because of coinciding of N-A-S-H and C-S-H phases; the higher their overall amount, the higher compressive strength. These additives also enrich the system with aluminum making for improved hydroxysodalite synthesis. However Ca-additives do not improve mechanical strength when curing in a covered mould is applied.

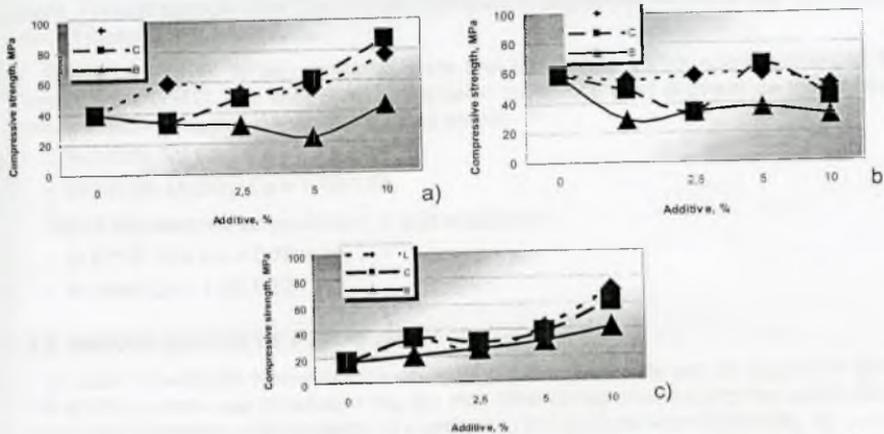


Figure 1 Compressive strength of alkali activated fly ash as a function of thermal curing conditions (a autoclave curing, b curing in a covered mould, c steam curing) and Ca-containing additive (L alumina cement, C OPC, B blast furnace slag)

### 3.2 XRD STUDIES

Fig. 2 shows XRD patterns of alkali activated fly ash filled with different Ca-containing additives, after different types of curing. Generally, there were three groups of crystalline phases identified:

zeolites: hydroxysodalite, Na-chabazite (herchelite and zeolite P<sup>+</sup> products of carbonation of alkalis: Na<sub>2</sub>O·H<sub>2</sub>O;

Ca-containing phase with main peak at 0.306 nm. This peak is probably belongs to calcium carbonate, however it coincides with the main peak belonged to crystalline calcium silicate hydrates (xonotlite, hyrolite also supposed to appear in this system.

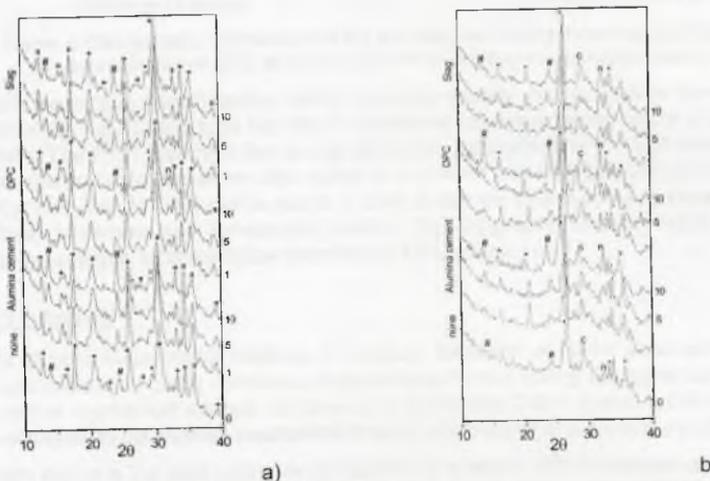


Figure 1 XRD patterns of alkali activated fly ash modified with different Ca-containing additives, after autoclave curing (a) and steam curing (b).

# hydroxysodalite, + Na-chabazite, c calcium carbonate, n sodium carbonate hydrate, quartz and mullite from fly ash composition

Peculiarities of phase composition depend on curing type. Autoclave curing results in intensive synthesis of zeolite products (mainly Na-chabazite with some quantities of hydroxysodalite), whereas other types of curing only lead to appearance of less intensive synthesis of hydroxysodalite. Depending on amount of a Ca-containing additive, an increasing of content of Ca-containing additive leads to:

- slight improving of synthesis of calcium carbonate due to increasing of overall amount of calcium oxide in the system;

- significant improving of synthesis of hydroxysodalite. The reason is that all the studied additives enrich the system with aluminum oxide as well and this is essential for synthesis of that Al-rich phase;

- slight decreasing of amount of Na-chabazite (after autoclave curing).

Depending on type of an additive used, alumina cement creates the best conditions for hydroxysodalite synthesis (due to the highest alumina content). It is to be mentioned that XRD does not give complete information about microstructure of studied systems because it does not reveal the role of an amorphous phase played in structure formation.

### 3.3 LEACHING OF SODIUM

After curing, a leaching test under EDV-S4 method was also used for the samples, and then a concentration of sodium in the leachate was analyzed using ICP method (fig. 3). This index is of a big importance for alkali activated materials: the higher concentration of alkalis in the leachate, the lower value of alkalis bounded, and the higher probability of durability problems exists.

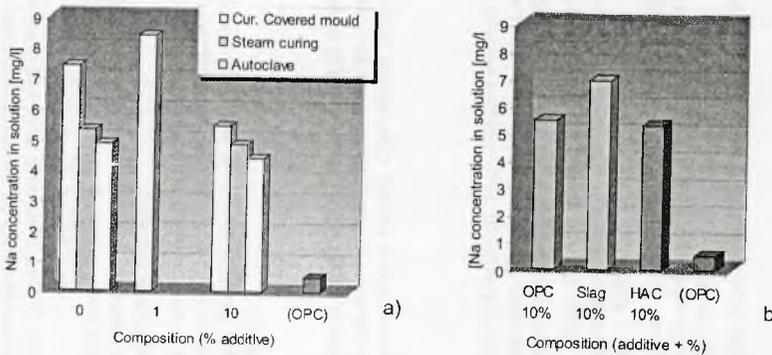


Figure 3: Concentration of sodium in the leachate, depending on curing conditions and concentration of OPC additive (a), and depending on additive type (b)

It was founded that the most important factor affecting rate of bonded alkalis is a curing condition: the highest level of bonding is achieved after autoclave curing, and the lowest one is fixed after curing in a covered mould. Therefore, a water-intensive curing is a key for improving rate of bonded alkalis and activation reaction in general. Concentration of calcium in the mix is also important since alkalis become being bounded better at higher additive's content. It is to be noted that the difference in free alkali concentration reduces at higher calcium concentration. However it was founded that the type of Ca-containing additive does not influence greatly to the rate of bonding alkalis (fig. 3b).

### 3.4 CORROSION RESISTANCE

Corrosion resistance is the function of microstructure. Far as the fly ash cements do not contain free lime and represented mainly by high-silica calcium silicate hydrates, these cements were presupposed to have high corrosion resistance. It is seen from the results (coefficient of corrosion resistance in sodium sulfate 0.98, in sodium chloride 0.98), alkaline fly ash cements are resistant

ones. Flexural strength after three month of keeping in aggressive medias is only 1-2% lower than one of those kept in pure water

Based on alkaline fly ash concretes were also founded to be corrosion-resistant in mineral salts medias [7-12]. The coefficient of corrosion resistance (Ca) depends on the solution and concentration of aggressive media as listed below:

In 3-10%  $\text{Na}_2\text{SO}_4$ . Ca = 1.19-1.48;

In 1.5-5%  $\text{MgSO}_4$ . Ca = 1.19-1.51

Also it was determined coefficient of acid resistance:

In 0.1-N HCl: Ca = 0.78-1.15;

In urea: Ca = 1.09-1.12.

### 3.5 IMMOBILIZATION OF PLUMBUM

In order to evaluate immobilization ability of alkali activated fly ash as regards to plumbum, 1% of Pb by mass was introduced into the mix. After curing and leaching test under the above mentioned procedure, concentration of plumbum in the leachate was studied (fig. 4).

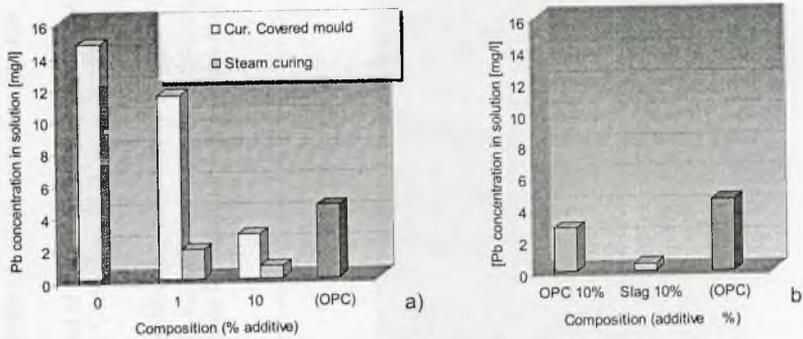


Figure 4: Concentration of plumbum in the leachate, depending on curing conditions and concentration of OPC admixture (a), and depending on admixture type (b)

It is easily seen that immobilization ability decrease greatly with increasing concentration of OPC additive (fig. 4a). Curing type has also a significant influence: steam curing gives 3-7 times better results. The most important fact is that plumbum immobilization in alkali activated fly ash matrix after steam curing as well as after curing in a covered mould at additive content of 10% is rather better than that of OPC matrix (up to 6 times better for steam-cured mixture with 10% of OPC additive). Moreover blast furnace slag additive (fig. 4b) gives even better result: in this case, immobilization ability is 10 times better than that of OPC paste.

## 4 CONCLUSIONS

- 1 Role of calcium-containing additives in structure formation of hybrid alkali activated fly ash cement depend on curing conditions. At steam or autoclave curing, the higher calcium content, the higher mechanical strength because of N-A-S-H and C-S-H phases coincided. However Ca-additives do not improve mechanical strength when curing in a covered mould is applied.
2. Steam curing is the best curing mode applied to systems with increased calcium content. low strength of Ca-free alkali activated fly ashes is caused by large pores (0.5 - 2.5 mkm) formed. In turn, curing in a covered mould is the best for Ca-free systems.
3. Selecting an appropriate percentage of a Ca-containing additive, it is possible to obtain hybrid alkali activated fly ash compositions with compressive strength of 60-80 MPa in paste after any curing condition.

4. The higher concentration of calcium-containing additive, the better rate of bounded sodium in the matrix. Water-intensive curing modes such as steam or autoclave curing give better results in this respect, too. However type of admixture does not influence greatly on the rate of bounded alkalis.
5. Hybrid fly ash based alkali activated cement seems to be perspective material to obtain concretes and coatings with high corrosion resistance because of high coefficient of corrosion resistance in different aggressive medias.
6. Ca-modified alkali activated hybrid fly ash cements were found to be perspective systems for fixing of plumbum since the give up to 10 times better immobilization ability comparing to OPC paste. The best results were fixed for steam- or autoclave-cured mixes with blast furnace slag additive of 10% by mass.

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