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ECO-FRIENDLY BINDERS BASED ON FLY ASH

Annemarie PURI, Alina BĂDĂNOIU* and Georgeta VOICU

University POLITEHNICA from Bucharest
Faculty of Applied Chemistry and Materials Science
PO-Box 12-134, Bucharest, Romania

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The paper presents data on the synthesis, interaction processes and properties of alkaline cements based on fly ash. This type of binders consists in a solid compound - a mixture of fly ash and lime and an activator solution - sodium silicate with/without sodium hydroxide or sulfates (Na_2SO_4 and $CaSO_4$).

The fly ash-sodium silicate-lime system has binding properties at room temperature. The presence in the system of sodium silicate determines the dissolution of the aluminosilicate structures form the fly ash, and facilitate the binding of $Ca(OH)_2$ in calcium silicate hydrates (C-S-H) phases, with positive influence on the developed compressive strength. The increase of the binding system's basicity when using NaOH addition, increases furthermore the hardening processes rate and consequently the compressive strength values.

The use of small amounts of sodium or calcium sulfate has a positive effect on the mechanical strength development most probably due to the formation of ettringite ($3CaO.Al_2O_3.3CaSO_4.31H_2O$).

INTRODUCTION

An important reduction of the CO_2 emissions generated during the portland cement manufacture process can be achieved by the replacement of the portland clinker with supplementary cementitious materials (SCM). One of the most used SCM material is fly ash and in the last century, countless research works regarding the fly ash blended cement were published. In this type of cement the hardening process at early ages consists mainly in the hydration of the portland cement, therefore the fly ash cements have lower early strengths compared with the portland cement.[1-4]

The fly ash reactivity vs. $Ca(OH)_2$, released during the cement or lime hydration process, is influenced by its oxide, mineralogical and phase composition as well as its grain size distribution.[1-5]

Several studies provide information regarding the chemical activation of the fly ash – $Ca(OH)_2$ reaction, also called "pozzolanic reaction", in order to permit the increase of the fly ash content in the blended portland cements without a major negative impact on the early strength or even more in the attempt to produce clinker free binders.[6-11]

The use of Na_2SO_4, $CaCl_2.2H_2O$ or $CaSO_4.0.5H_2O$ admixtures to fly ash-lime (80-20) systems, associated with the hydrothermal curing at 50^oC, lead to important increases of the mechanical strengths. Still the mechanical strengths of these binders after 28 days of hardening were small – 13-15 MPa.[6,7]

The chemical activation of class F fly ashes (with less than 10% CaO content) with sodium or potassium silicates with/without hydroxides (NaOH or KOH) admixtures, can lead to the hardening of this system even at the normal temperature.[9-11] The increase of the fly ash specific surface area as well as the reduction of the silicate module "n" ($M_2O.nSiO_2$, M=Na or K) or the increase of the curing medium temperature have a positive effect on the mechanical properties.

In this paper the hydration and hardening processes of fly ash-lime-admixtures (sodium silicate, NaOH, Na_2SO_4, $CaSO_4$) – water systems are studied. The influence of the NaOH content (present in the system as admixture or formed "in situ" by the sodium silicate hydrolysis) on the pozzolanic reaction speed and hardening process was also assessed.

* Corresponding author: a.badanoiu@oxy.pub.ro

EXPERIMENTAL

Materials

The experiments performed in this study were conducted on the following materials: i) class F fly ash with the chemical composition and some properties listed in table 1. The XRD analysis of the fly ash shows the presence of a high amount of vitreous phase as well as small amounts of crystalline compounds – quartz and mullite; ii) lime with 81% CaO and small amounts of $CaCO_3$ as main impurity; iii) 48.5% sodium silicate (water glass) aqueous solution with n=5.2; iv) reagent grade NaOH, dosed as solid material and solved in the mix water; v) reagent grade calcium sulfate - $CaSO_4.2H_2O$ and sodium sulfate - $Na_2SO_4.10H_2O$.

Table 1

Chemical composition and physic properties of the fly ash

Characteristics	Values
L.O.I. (%)	0.49
SiO_2 (%)	55.39
Al_2O_3 (%)	26.55
Fe_2O_3 (%)	8.89
CaO (%)	2.24
MgO (%)	1.79
SO_3 (%)	0.21
Na_2O (%)	0.71
K_2O (%)	2.20
TiO_2 (%)	0.88
Density (g/cm³)	2.16
Specific surface area (cm²/g)	5530

Methods

The solid compounds (fly ash, lime and calcium sulfate) were mixed in a planetary mill for 15 minutes. The activator admixtures (sodium silicate, NaOH, $Na_2SO_4.10H_2O$) were solved in the mixing water.

The hydration processes were assessed by chemical analysis of Ca^{2+} content in suspensions with solid/liquid ratio of 1/100 vs. time. The XRD and themogravimetry (TG, DTG) analysis were performed on pastes (liquid/solid=0.4) after 3, 7 and 28 days of hydration with a SHIMADZU XRD 6000 diffractometer, using Ni-filtered CuKα radiation (λ=1.5418 Å) and SHIMADZU DTG-TA 51H with a heating speed of 10°C/min.

Mechanical strengths were assessed on mortar specimens (15x15x60 mm^3) with binder/aggregate ratio=1/3 and variable water/binder ratios values. The aggregate was sand prepared according to the EN 196-1 standard. The mortar samples were hardened at normal temperature in humid atmosphere (R.H.85%) the first 3 days and in water up to the testing time. The compressive strength tests were performed on a TONINDUSTRIE testing machine, after 3, 7, 28 and 60 days of hardening.

RESULTS AND DISCUSSION

1. Interaction processes in fly ash-lime-sodium silicate (NaOH, sulfates) – water systems

The presence in the fly ash-lime-water system of the sodium silicate (which in aqueous solution hydrolyse and forms NaOH and $Si(OH)_4$)[12] or of the sodium hydroxide, leads to the attack of Si-O-Si and Si-O-Al bonds from the fly ash network and alkaline aluminate and silicate hydrates are formed.[8-11] According to Xie and Xi,[9] these hydrates can subsequently hydrolyse forming reactive silicic acid and releasing NaOH. The process continues and the silicic acid polycondensate and forms an amorphous binding matrix which, together with sodium silicate includes the non reacted fly ash grains. The main disadvantage of this type of binder consists in its reduced stability vs. water, due to the presence of sodium silicate in the hardened matrix.[9]

According to Palomo *et. al.*[10] in ordinary portland cement –fly ash systems activated with NaOH-water glass solutions, the hardening products formed are N-A-S-H gel and C-S-H gel from portland cement hydration process or even from the reaction between the calcium in the cement and soluble silica from the alkaline solution. Coexistence of both gels was also observed in other systems such as metakaolin-slag-alkaline activator,[13] metakaolin-$Ca(OH)_2$-alkaline activator[14,15] and fly ash-$Ca(OH)_2$- alkaline activator.[16] The formation of C-S-H gel and geopolymers depends on many factors such as the crystalinity and thermal history of calcium silicate sources, the ratio between the aluminosilicate and calcium source and the alkalinity of alkali activators.[8,17] At low alkalinity (corresponding to the experimental conditions in this work) the calcium dissolved from the calcium source forms C-S-H gel in conjunction with geopolymeric gel.[10] Therefore the reduction of the CaO content in the fly ash-lime–water system can provide direct information regarding the pozzolanic reaction kinetic.

The Ca^{2+} consumption due to the pozzolanic reaction with the fly ash (figure 1), is influenced by the nature of the Na^{+} source: i) the rate of Ca^{2+} consumption is quasi-similar in the sample E5N (with 5% NaOH) and E5S (with 5% $Na_2O.nSiO_2$ – corresponding to aprox. 1.1% NaOH); ii) the Ca^{2+} consumption is higher in E10S sample (with 10%$Na_2O.nSiO_2$ – corresponding to aprox. 2.2% NaOH).

These data suggests a higher speed of the reaction of calcium ions with silicic acid (resulted from the water glass hydrolysis) as compared with the dissolution of aluminosilicates, from the fly ash, in the alkaline solution. The data also are in good agreement with Palomo model[8, 10] according to which at the activation of aluminosilicate materials with a mild alkaline solution the main reaction product is C-S-H, opposite to the case of Al_2O_3 and SiO_2 containing materials, activated with high alkaline solutions in which the final product is a geopolymer (chains or networks of mineral molecules linked with covalent bonds).

An interesting aspect was noticed when 4.2% Na_2SO_4 (corresponding to 2.36% NaOH) was added in the system with 5% sodium silicate (E5SNs) - after the first 24 h the rate of the consumption process of Ca ions increases. A quasi-similar behaviour was noticed also for the sample E5NCs with 5% NaOH and 5% $CaSO_4$.

The data obtained by TG and DTG analysis (figure 2) confirms the consumption of $Ca(OH)_2$ in pastes (figure 3), process assesed also by chemical dosage of Ca^{2+} ions in suspensions.

The high speed of the Ca ions consumption process in the compositions with $CaSO_4$ or Na_2SO_4 ($Ca(OH)_2 + Na_2SO_4 \rightarrow$ $\mathbf{CaSO_4}$ $+ NaOH$) is explained by the ettringite - $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4.32H_2O$ formation trough the reaction of $CaSO_4$ and aluminates from the fly ash (figure 4). The ettringite formation - compound with a high amount of water molecules in it's network, may contribute to the reduction of the free water in the binder matrix – see the good correlation between the ettringite quantity in samples and the amount of bound water in hydrates (assessed by TG) - figure 5.

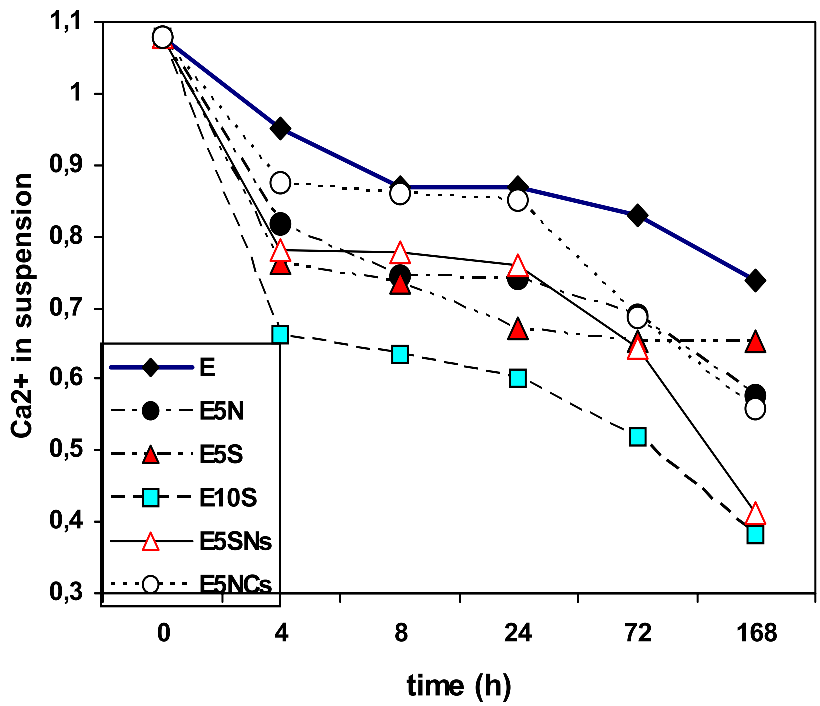

Fig. 1 – Ca^{2+} concentration in suspensions vs. time for: **E** – fly ash+ 20% lime; **E5S** - fly ash+ 20% lime + 5% sodium silicate; **E10S** - fly ash+ 20% lime + 10% sodium silicate; **E5N** - fly ash+ 20% lime + 5%NaOH; **E5SNs** - fly ash+ 20% lime + 5% sodium silicate + 4.2% Na_2SO_4; **E5NCs** - fly ash+ 20% lime + 5% NaOH and 5% $CaSO_4$.

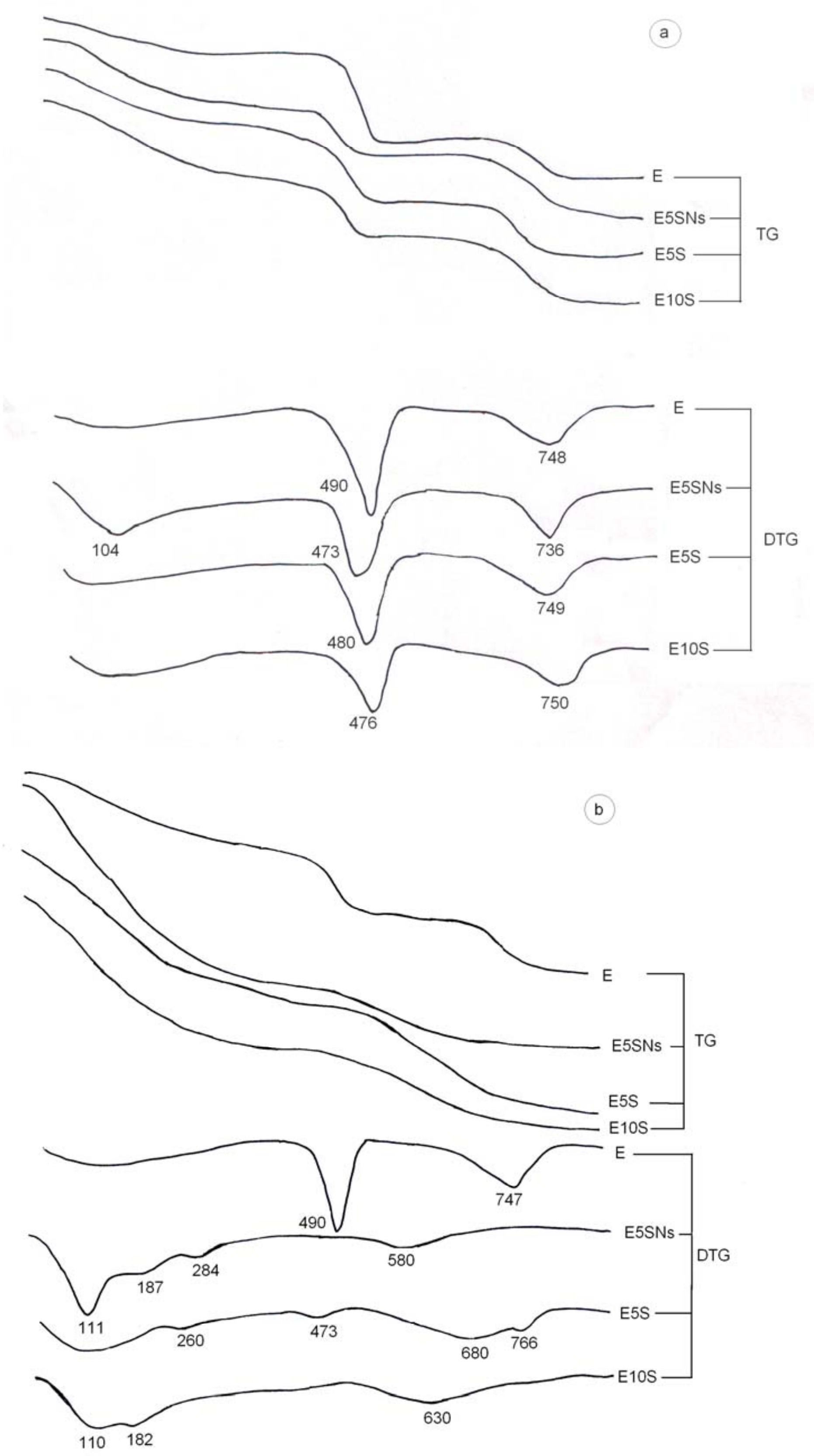

Fig. 2 – TG and DTG curves of the pastes cured for 3 days (a) and 28 days (b). **E** – fly ash+ 20% lime; **E5S** - fly ash+ 20% lime + 5% sodium silicate; **E10S** - fly ash+ 20% lime + 10% sodium silicate; **E5SNs** - fly ash+ 20% lime + 5% sodium silicate + 4.2% Na_2SO_4.

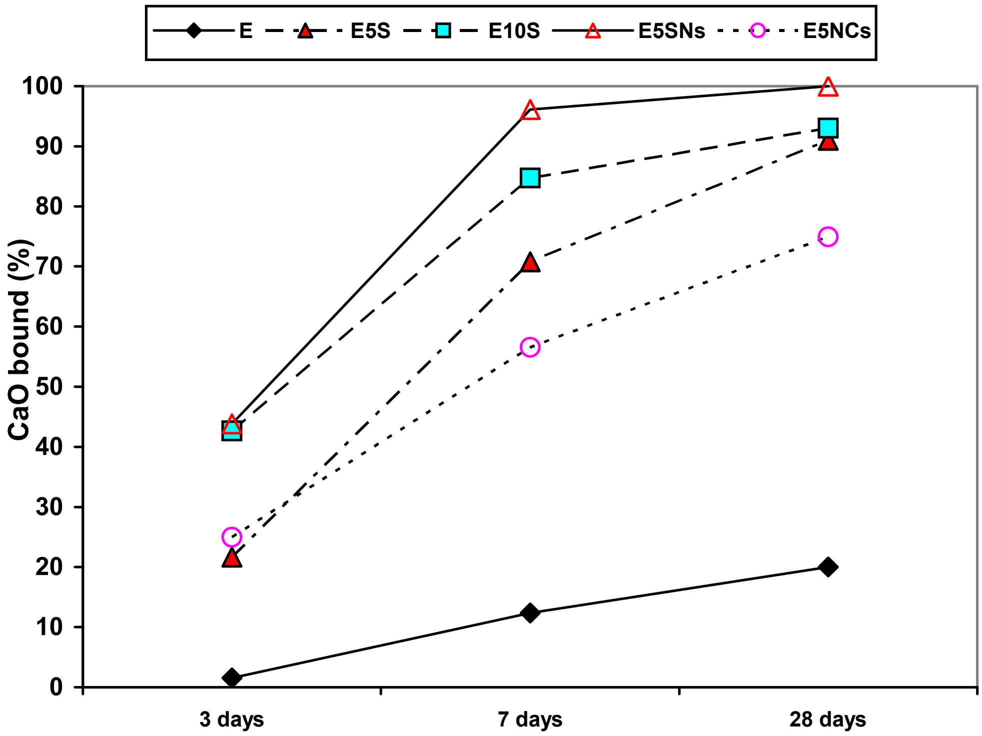

Fig. 3 – CaO bound vs. time.
E – fly ash+ 20% lime; **E5N** - fly ash+ 20% lime + 5%NaOH; **E5S** - fly ash+ 20% lime + 5% sodium silicate; **E10S** - fly ash+ 20% lime + 10% sodium silicate; **E5SNs** - fly ash+ 20% lime + 5% sodium silicate + 4.2% Na_2SO_4.

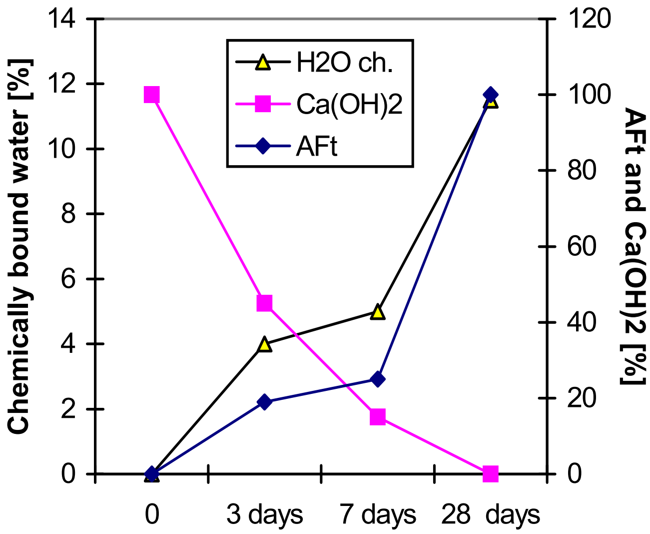

Fig. 4 – Hydrates vs. time for mixture **E5SNs.** Chemically bound water and $Ca(OH)_2$ content was assessed by TG and ettringite (AE_t) content by XRD.

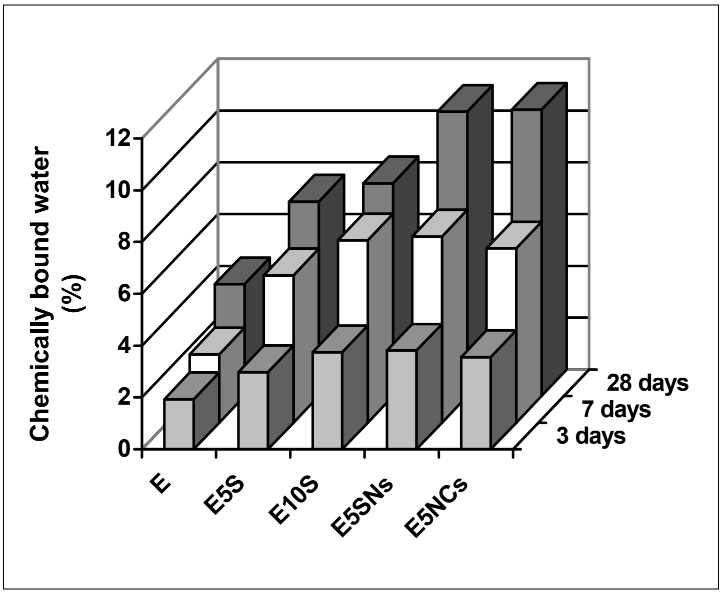

Fig. 5 – Chemically bound water in hydrates for the binders: **E** – fly ash+ 20% lime; **E5S** - fly ash+ 20% lime + 5% sodium silicate; **E10S** - fly ash+ 20% lime + 10% sodium silicate; **E5SNs** - fly ash+ 20% lime + 5% silicat de sodiu + 4.2% Na_2SO_4; **E5NCs** - fly ash+ 20% lime + 5% NaOH and 5% $CaSO_4$.

2. Hardening processes in fly ash-lime-sodium silicates (NaOH, sulfates) – water systems

The compressive strength of the mortar specimens vs. time are presented in figures 6-8.

The binders with sodium silicate (NaOH and sulfate) content develops even after 3 days of hardening measurable compressive strengths opposite to the one containing only fly ash and lime (E), regardless the lime content – figures 6 and 7.

At longer hardening times (28 and 60 days), the binders with sodium silicate content have an important strength increase (up to 100%) as compared with the compressive strength developed by the fly ash – lime binder. The increase of the sodium silicate content (from 5% to 10%) has a positive influence on the early age strength. The increase of the basicity of the system, due to the supplementary NaOH addition, has also a positive effect on the compressive strengths, especially on those developed at longer hardening times (28 and 60 days). The higher compressive strengths were developed by the binders with sodium sulfate (E5SNs) and calcium sulfate (E5NCs) content, probably due to the formation of ettringite as reaction product in these systems. The positive effect of the needle like ettringite crystals upon the mechanical strength of the hardened matrix is well documented.[1,2] The formation of ettringite was also reported by Shi *et.al.*[18] to be decisive for the development of good mechanical strengths in systems containing fly ash and lime activated with Na_2SO_4.

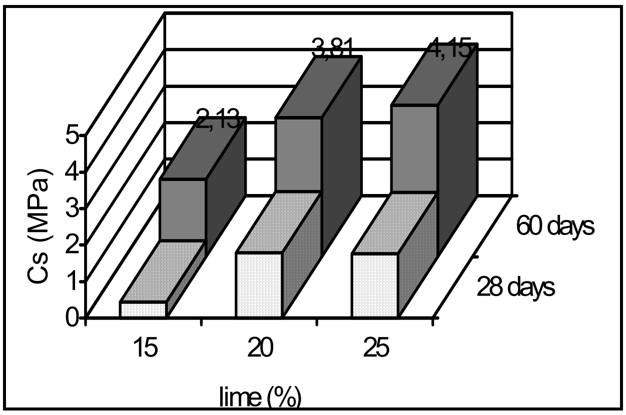

Fig. 6 – The influence of lime content on the compressive strength developed by the binders based on fly ash (water/binder=0.64).

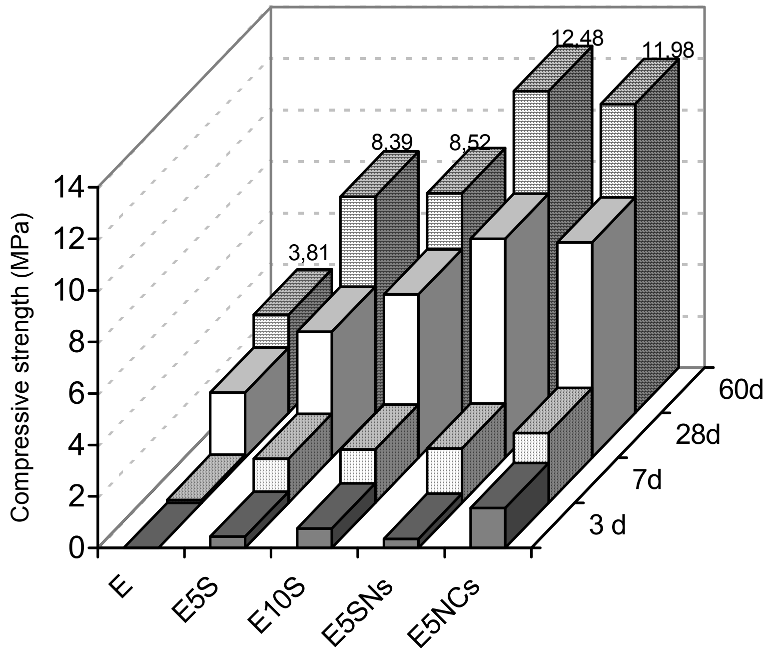

Fig. 7 – Compressive strength for the binders: **E** – fly ash+ 20% lime (w/b=0.64); **E5S** - fly ash+ 20% lime + 5% sodium silicate (w/b=0.77); **E10S** - fly ash+ 20% lime + 10% sodium silicate (w/b=0.84); **E5SNs** - fly ash+ 20% lime + 5% sodium silicate + 4.2% Na_2SO_4 (w/b=0.77); **E5NCs** - fly ash+ 20% lime + 5% NaOH and 5% $CaSO_4$ (w/b=0.5).

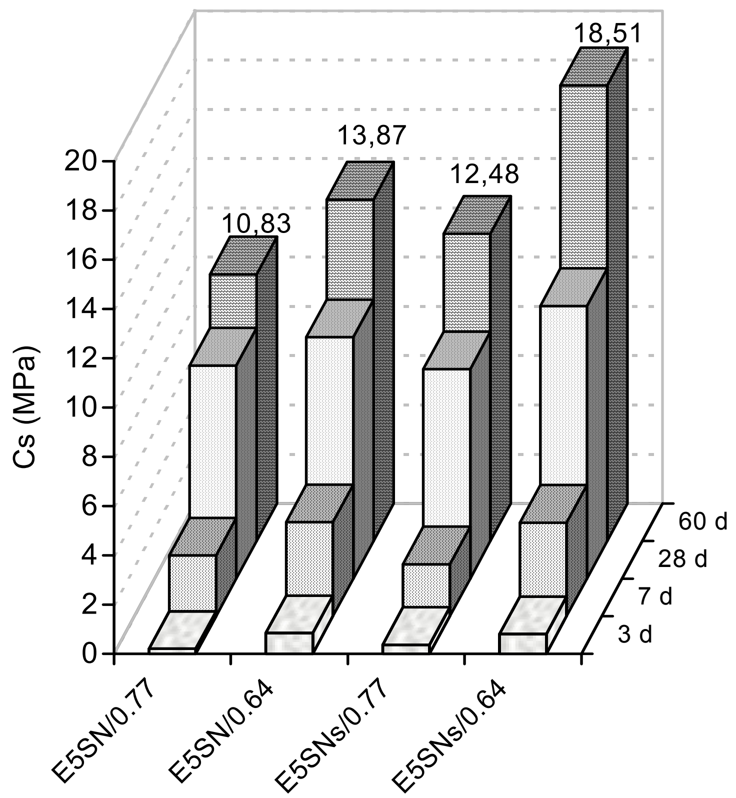

Fig. 8 – Compressive strength for the binders: **E5SN** - fly ash+ 20% lime + 5% sodium silicate +5% NaOH with w/b=0.77 and 0.64 and **E5SNs** - fly ash+ 20% lime + 5% sodium silicate + 4.2% Na_2SO_4 with w/b=0.77 and 0.64.

The increase of the mortars fluidity, noticed for the systems with 5% sodium silicate and NaOH or Na_2SO_4 additions, allowed the reduction of the water to binder ratio for E5S mortar specimens' preparation. The reduction of the water content leads, as expected, to an increase of the compressive strength values - figure 8.

CONCLUSIONS

Sodium silicate act as a catalyst for the dissolution of aluminate and silicate phases present in the fly ash vitreous phase and increases the $Ca(OH)_2$ bounding, through pozzolanic reaction, in calcium silicates hydrates

The increase of the basicity of the system, when 5% NaOH is used as admixture together with sodium silicate, increases the speed of the hardening processes. The increase of the compressive strength when Na_2SO_4 or $CaSO_4$ is added in the system is mainly due to the ettringite formation; the presence of needle like ettringite crystals can reinforce the binding matrix and consequently increases the strength.

Eco-friendly binders based on waste (fly ash) with alkaline activation may be produced at normal curing temperature with positive environmental and economic effects.

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