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Non Portland cements and derived materials

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Abstract

The present paper deals with an overall interpretation of information regarding the behaviour of binders free of Portland cement, containing slag with or without fly ash, activated by sodium and calcium compounds. The information was obtained from experiments regarding the chemically bound water and mechanical strength determination, together with pH measurement, thermal analysis and X-ray diffraction (XRD). The results emphasize the possibility of obtaining alkali-activated binders incorporating slag and with or without fly ash and which have mechanical properties equivalent to normal Portland cement. The binder systems, especially those adequately activated and showing enhanced performance, can incorporate up to 40% fly ash without any major influence upon binder quality.

Quantitative correlations between chemically bound water and mechanical strength of the hardened binder and the decisive factors of influence (e.g. composition and finesses of binders) are reported.

Keywords: Blast-furnace slag; Fly ash; Chemically bound water; Mechanical strength

1. Introduction

In the last few decades particular attention has been paid to activated silicate binders with low or zero Portland cement content [1–8]. The extended usage of these binders is motivated by a number of considerations related to energy savings, economy and ecology. Experimental data and fundamental scientific arguments also clearly support the wide usage of these binders, especially the alkali activated slag cements [3,4,7–22]. At the same time, the direct usage of pozzolans as cement replacement materials has significantly contributed to eco-friendly durable construction materials [23–26].

However, much more research is urgently needed to effect these findings in the production of concrete on an industrial scale. In this respect, strong research effort is needed in order to obtain deeper and more systematic information on the inter-relationship of key variables on material and structural performance, with special attention to the intrinsic factors that control the nature and proportion of the components of the binder system. This is the objective of the current paper, which is based upon results that the authors have reported in the literature in the last few years [13,16,17] and those that are currently being investigated.

2. Experimental work

In the current work, 3 types of blast-furnace slag and 2 types of thermal power plant fly ash (all being Romanian industrial by-products) were used to prepare cementitious-pozzolana mixtures of slag and fly ash. The chemical analysis of the slags and fly ashes used in the studies is presented in Table 1. All the slags were basic. Two slags were equally basic (SG I_a and SG I_b),

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Table 1
Composition of used slags and fly ashes

Oxide composition (%)	Cementitious material or pozzolana				
	Slag SG I_a	Slag SG I_b	Slag SG II	Fly ash ACT I	Fly ash ACT II
SiO_2	34.72	36.88	38.85	52.72	54.86
CaO	44.56	45.02	41.88	9.79	4.52
MgO	4.47	3.26	2.71	2.51	2.62
Al_2O_3	11.00	7.41	12.08	19.00	21.16
Fe_2O_3	0.80	1.07	1.37	8.84	8.22
Na_2O	0.70	0.99	0.18	0.72	0.80
K_2O	0.65	0.97	0.42	2.27	2.54
TiO_2	0.48	0.62	–	0.6	1.19
MnO	0.66	0.84	0.65	–	–
SO_3	0.08	0.26	0.18	1.37	1.62
S_S	0.87	1.49	0.81	0.04	0.04
S_T	1.01	1.09	0.87	0.54	0.61
L.O.I.	–	–	–	1.60	1.82

SG I_a containing more Al_3O_3 than SG I_b but the same amounts of CaO and SiO_2. The third one was less basic (SG II).

The fly ashes differed from each other in their composition, particularly in their CaO content: ACT I had higher CaO content and ACT II lower CaO content, although both can be classified as ASTM—Class F fly ash.

The position of slags within the quaternary system CaO–MgO–Al_2O_3–SiO_2, corresponding to the projection on the section plan with 5% MgO content (Fig. 1), shows that SG I slag belongs to the subsystem mellilite-C_2S–C_3S while SG II belongs to subsystem melilite-CS–C_3S_2. This is in agreement with X-ray diffraction data obtained (Fig. 2), even though the solidification of slags is accomplished in non-equilibrium conditions and in non-equivalent industrial conditions (granulated industrial blast-furnace slags).

The powder mixtures of cementitious material (slag)—pozzolana (fly ash) were prepared for different pozzolana content, ranging between 0% and 60%. The mixtures were ground up to a specific surface of 350–400 m^2/kg; at the same time some selected mixtures were prepared with higher specific surfaces up to 500 m^2/kg in order to emphasize the influence of this parameter on the hardening behaviour of the binder systems.

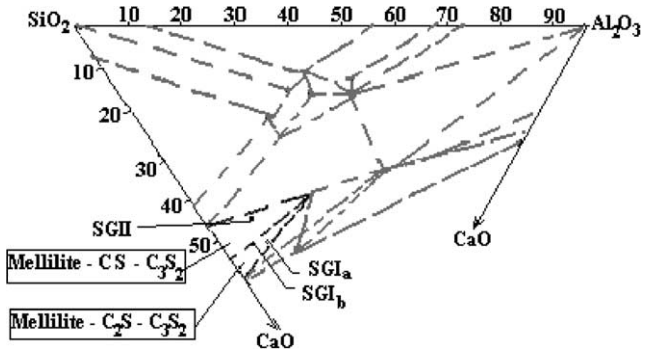

Fig. 1. The domain of slags within the quaternary system SiO_2–Al_2O_3–CaO–MgO (in section plan of 5% MgO content).

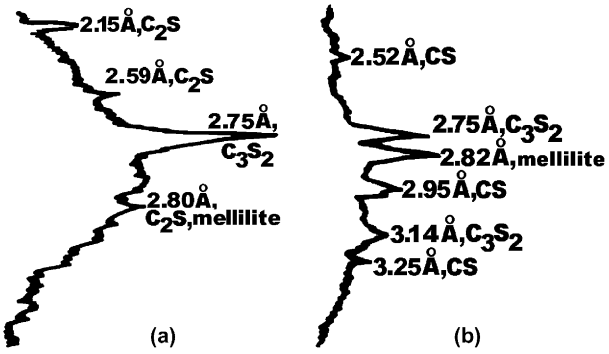

Fig. 2. XRD patterns of slag SG I_a (a) and SG II (b), respectively.

The activators of the cementitious material—pozzolana mixtures were the following: quicklime ($\geqslant$90% active CaO) together with calcium chloride or alkaline salts (Na_2CO_3, Na_2SO_4, $Na_2Al_2O_4$) as well as mixtures of sodium carbonate and sodium sulphate or calcium chloride and sodium sulphate. The quicklime was used in a proportion of 2–6% and calcium and sodium salts in a proportion of 2–7% (by mass of the powder mixture).

The hardening behaviour of the binder systems was monitored both from chemical and mechanical points of view. For this purpose, determinations of chemically bound water and mechanical strength were carried out.

Chemically bound water was determined on cement pastes (water/cement ratio = 0.5). The pastes were cured for 1, 3, 7 and 28 days, at room temperature, in closed space at 100% relative humidity. The cured samples were ground, dried for 2 h at 100 °C up to constant mass. The dried samples were then heat treated at 1000 °C for 2 h, again up to constant mass. It is through that the method of preparation and curing conditions were such that the

contamination of samples with CO_2 is negligible. The proportion of chemically bound water is calculated according to Butt–Taylor method, as:

$$A_1 = \frac{m_1 - m_2}{m_1} \cdot 100$$

where m_1 is the weight of samples after drying and m_2 the weight of the same samples after heat treatment at 1000 °C.

Mechanical strength was determined on mortar microspecimens ($20 \times 20 \times 20$ mm) with binder/sand = 1/3 and water/binder = 0.5 ratios. The microsamples were compacted by vibration and cured, up to the age of testing, in a closed tank with 100% relative humidity. Relative mechanical strength values were determined: $\%R_{rel} = (R_i/R_p) \cdot 100$, where R_i represents the strength of samples cured for several periods of time and R_p the strength of the reference Portland cement CEM I 32.5R according to the European standards UNE-EN 197-1:2002 SR (prepared and hardened for 28 days, in similar conditions).

In order to obtain additional information in certain cases, concerning the evolution of hardening of the binder systems, pH measurements and thermal analysis were carried out. pH measurements were performed with a pH—conductometer JENWAY 3405 Electrochemical Analyser on water suspensions characterized by a water/solid ratio = 10/1. DTA and TG tests were performed on hardened samples (pastes) cured under the same conditions and ages as for the specimens prepared for chemically bound water determinations. A MOM Q-1500 thermal analyser (Hungary) was employed with a heating rate of 10 °C/min.

The information was statistically processed on sets of specimens, with respect to dependence on major influencing factors—compositional and dispersive (including the specific surface). Some selected values obtained for chemically bound water were also correlated with the hardening time. The series of tests carried out made possible the establishment of comparative interrelations of hardening behaviour of cementitious material—pozzolana—activator binder systems, over a significant composition range.

3. Results

3.1. Chemical behaviour of binder systems

Chemical behaviour of cementitious material—pozzolana—activator binder systems has been assessed mainly through the proportion of chemically bound water (A_1) at different ages. The results obtained on pastes prepared from mixtures of slag SG I_a–fly ash ACT II or slag SG I_b–fly ash ACT I with various activating admixtures are shown in Tables 2 and 3, respectively. For comparison purposes, Table 4 presents results on some

Table 2
Chemically bound water for samples prepared with slag SG I_a, fly ash ACT II and activating mixture*

Slag/Fly ash mixture	Age (days)	Chemical bound water (%), for samples activated with												
		5%Na_2SO_4 and (3–6%) lime				5%Na_2SO_4 + 2%$CaCl_2$ and (3–6%) lime				2%$CaCl_2$ and (3–6%) lime				2%$Na_2Al_2O_4$ and 5% lime
		3%	4%	5%	6%	3%	4%	5%	6%	3%	4%	5%	6%	
100/0	1	2.69	2.72	2.77	2.80	3.20	3.43	3.68	3.86	3.57	3.72	4.03	3.97	
	3	4.57	4.69	4.81	4.95	4.95	5.65	5.89	6.21	6.78	6.87	6.93	7.21	
	7	4.82	4.73	4.99	5.64	6.10	6.44	6.82	7.07	8.07	8.10	8.27	8.57	
	14	5.47	5.94	6.12	6.60	n.d.	7.62	7.78	n.d.	8.54	8.59	8.76	9.27	
	28	6.27	6.40	6.85	7.30	8.52	8.59	8.65	8.74	9.20	9.36	9.47	9.52	
90/10	1	2.60	2.64	2.70	2.75	3.17	3.35	3.41	3.51	3.49	3.68	3.82	3.96	
	3	3.82	3.95	4.05	4.48	4.87	5.17	5.42	5.67	6.38	6.45	6.68	7.12	
	7	4.60	4.68	4.81	5.57	5.84	5.98	6.70	7.01	8.02	8.08	8.13	8.50	
	14	5.41	5.81	5.97	6.49	7.34	7.58	7.73	7.80	8.59	8.69	8.87	9.16	
	28	5.93	6.27	6.66	7.08	8.24	8.39	8.43	8.52	9.00	9.18	9.35	9.46	
70/30	1	2.35	2.40	2.46	2.54	3.14	3.19	3.27	3.33	3.45	3.38	3.72	3.95	3.49
	3	n.d.	n.d.	n.d.	n.d.	4.82	5.13	5.38	5.62	6.18	6.29	6.58	6.74	5.81
	7	4.38	4.51	4.81	5.54	5.77	5.89	6.31	6.64	7.73	7.95	8.03	8.39	6.67
	14	4.98	5.67	5.78	6.28	n.d.	7.00	7.42	7.54	8.33	8.33	8.71	8.85	n.d.
	28	5.37	6.13	6.31	6.95	7.65	7.95	8.29	8.49	8.46	8.98	9.29	9.33	8.61
50/50	1	2.33	2.28	2.32	2.39	3.06	3.07	3.10	3.18	3.02	3.30	3.40	3.66	
	3	3.40	3.62	3.83	4.21	4.77	4.92	5.02	5.37	5.84	6.24	6.33	6.45	
	7	4.18	4.42	4.59	5.32	5.58	5.78	6.08	6.51	6.98	7.70	7.86	7.94	
	14	4.95	5.41	5.60	6.34	6.80	6.93	7.12	7.42	n.d.	8.14	8.70	8.80	
	28	5.28	6.00	6.12	6.89	7.64	7.81	7.99	8.12	7.86	8.94	9.00	9.26	

* The slag-fly ash mixture had a Blaine specific surface area of ~400 m^2/kg.

Table 3
Chemically bound water for samples prepared with slag SG I_b, fly ash ACT I and activating mixture

Slag (s)/Fly ash (fa) mixture		Age (days)	Chemical bound water (%), for binding systems			
Weight ratio s/fa	Specific surface (m^2/kg)		un-activated	activated with		
				3%lime + 3%Na_2CO_3	3%lime + 3%Na_2SO_4	3%lime + 1.5%Na_2CO_3 + 1.5%Na_2SO_4
100:0	~350	1	–	4.49	5.60	5.30
		3	–	6.08	7.21	6.80
		7	–	7.22	8.10	7.85
		14	7.10	8.26	9.15	8.75
		28	9.21	10.15	11.60	10.50
60:40	~350	1	–	3.85	5.10	4.00
		3	–	4.30	6.00	5.60
		7	–	5.70	6.80	6.10
		14	–	6.10	8.10	7.00
		28	–	7.25	10.25	9.70

Table 4
Comparative results regarding chemically bound water for samples prepared with slag SG I_a, slag SG II respectively, and fly ash ACT I, activated with a mixture of lime and $Na_2Al_2O_4$

Cementitious material—pozzolana systems	Activating mixture	Chemical bound water (%) after				Observation
		1 day	3 days	7 days	28 days	
70% slag SG I_a + 30% fly ash	2% $Na_2Al_2O_4$ + 5% lime	3.49	5.81	6.67	8.61	The specific surface of cementitious
70% slag SG II + 30% fly ash	2% $Na_2Al_2O_4$ + 5% lime	2.98	3.30	3.59	3.90	material—fly ash mixture
Slag SG I_a	–	0.034	0.785	0.901	6.17	was ~400 m^2/kg
Slag SG II	2% $Na_2Al_2O_4$ + 5% lime	2.27	2.46	2.69	2.90	

samples in which the slag component belongs to different phase equilibrium subsystems—SG I_a and SG II, respectively.

The statistical processing of the results has been performed on sets of samples prepared with the same type of slag, fly ash and activator, with the same specific surface of slag—fly ash mixture and maintaining the proportion of activating salts constant. Polynomial relationships regarding the dependence of chemically bound water (A_1) on the selected influencing factors, were used; high correlation coefficients ($r^2 \geqslant 0.964$) were obtained using the following mathematical relationship:

$$A_1 = \frac{a + bx + cx^2 + dx^3 + ey + fy^2 + gy^3}{1 + hx + ix^2 + jy + ky^2}, \qquad (1)$$

where x is the slag/fly ash weight ratio, y the lime content and a, b,...j, k—regression coefficients.

For the set of samples based on a mixture of slag SG I_a and fly ash ACT II with a specific surface of 400 m^2/kg, activated with lime and Na_2SO_4, Na_2SO_4 and $CaCl_2$, or only $CaCl_2$, the results are shown in Figs. 3–5, respectively.

The results obtained on the sets of samples prepared with slag SG I_b and fly ash ACT I are described by similar mathematical equations (1) using as independent variables the slag/fly ash ratio and hardening time. Thus the kinetics of the chemical process is indicated based upon the compositional parameters of the system. In the case of these sets, Fig. 6 shows the results obtained for two activating mixtures: 3%Na_2CO_3 and (1.5% Na_2CO_3 + 1.5%Na_2SO_4) with the lime proportion kept unchanged at 3%. The specific surface of the cementitious material—pozzolana mixture is 350 m^2/kg.

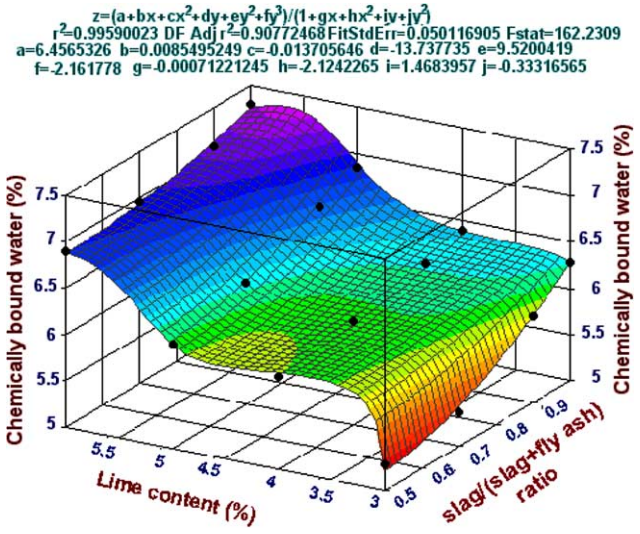

Fig. 3. Statistical processing according to Eq. (1) of the chemical bound water for binding systems prepared with slag SG I_a–fly ash ACT II (~400 m^2/kg) and activating mixture of lime and Na_2SO_4 (5%), after 28 days of curing.

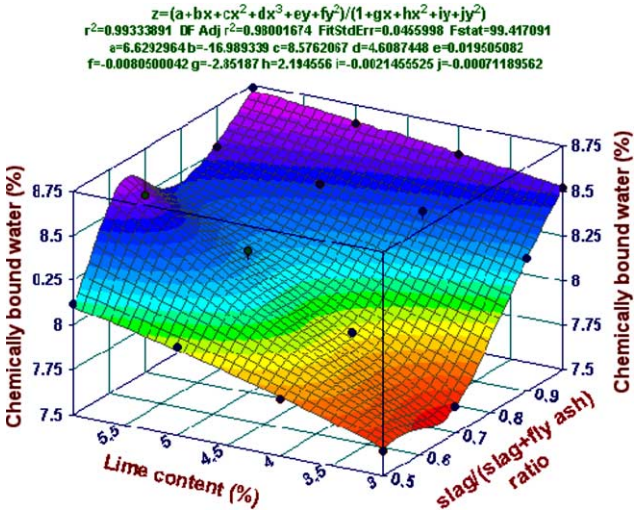

Fig. 4. Statistical processing according to Eq. (1) of the chemical bound water for binding systems prepared with slag SG I_a–fly ash ACT II (~400 m^2/kg) and activating mixture of lime and (5%Na_2SO_4 + 2%$CaCl_2$), after 28 days of curing.

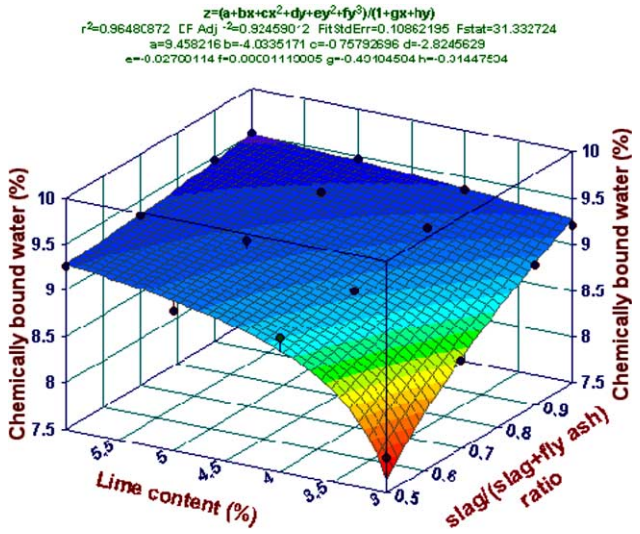

Fig. 5. Statistical processing according to Eq. (1) of the chemical bound water for binding systems prepared with slag SG I_a–fly ash ACT II (~400 m^2/kg) and activating mixture of lime and $CaCl_2$ (2%), after 28 days of curing.

For all sets, the corresponding statistical regression coefficients from Eq. (1) related to the chemically bound water are given in Table 5.

From the experimental data, the significant role of the nature of the cementitious material (slag)—mainly composed of CaO, MgO, Al_2O_3 and SiO_2 is emphasized, as one can see from Tables 2–4 and these are correlated with the information in Figs. 1 and 2. This specific role is determined by the phase composition of the slags, and their position within a certain subsystem of the CaO–MgO–Al_2O_3–SiO_2 system as well as its "thermal history". All these factors are conditioning the nature and the ratio between crystalline and vitreous phases as reported in previous papers [1,2,5,8].

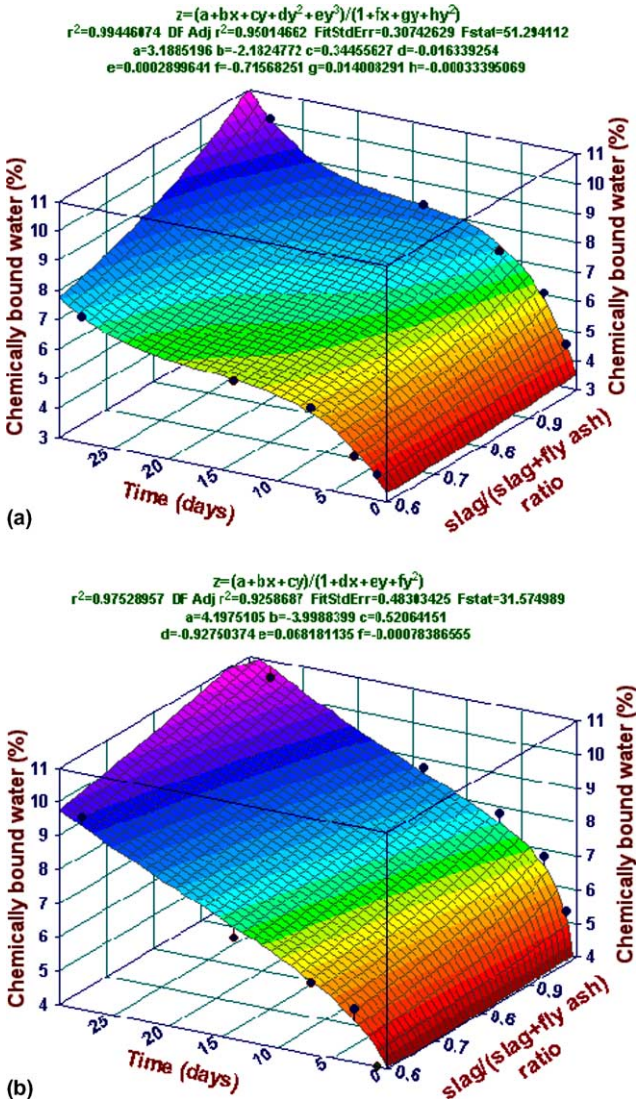

Fig. 6. Statistical processing according to Eq. (1) of the chemical bound water for binding systems prepared with slag SG I_b–fly ash ACT I (~350 m^2/kg) and activating mixture of (a) lime and Na_2CO_3 (3%) and (b) lime and (1,5% Na_2CO_3 + 1,5% Na_2SO_4), after 28 days of curing.

The experimental data obtained when using the same slag to prepare the activated silicate binder also emphasize a scale for the activating effect of activator mixture depending on the nature of alkaline/alkaline earth salts—for a constant CaO content:

$$Na_2CO_3 < (Na_2SO_4 + Na_2CO_3) < Na_2SO_4 \quad \text{(Table 4)}$$
$$Na_2SO_4 < (Na_2SO_4 + CaCl_2) < CaCl_2 \quad \text{(Table 2)}$$

Table 5
The regression coefficients for different binding systems, according to Eq. (1)

Regression coefficients	Values of regression coefficients for binder mixture prepared with				
	Slag SG I_a– fly ash ACT II, with a specific surface of 400 m^2/kg, activated with lime associated with			Slag SG I_b–fly ash ACT II, with a specific surface of 350 m^2/kg, activated with lime associated with	
	5%Na_2SO_5	5%Na_2SO_4 + 2%$CaCl_2$	2%$CaCl_2$	3%Na_2CO_3	1.5%Na_2SO_4 + 1.5%Na_2CO_3
a	6.457	6.629	9.458	3.189	4.198
b	0.009	−16.989	−4.034	−2.182	−3.999
c	−0.014	8.576	−0.758	0	0
d	0	4.609	0	0	0
e	−13.738	0.020	−2.825	0.345	0.521
f	9.520	−0.008	−0.028	−0.016	0.000
g	−2.167	0	0.001	0	0
h	−0.001	−2.852	−0.492	−0.716	−0.928
i	−2.124	2.195	0	0	0
j	1.468	−0.002	−0.314	0.014	0.068
k	−0.333	−0.001	0	0	−0.001

The effects are conditioned by the nature of components—especially the cementitious materials and activating salts but are, also, influenced by the components proportion, including the proportion of pozzolana (fly ash) and activating lime. These dependences are mutually correlated, so they are complex, as suggested by the mathematical relations of type (1)—applied particularly for the chemically bound water, corresponding to each set of samples.

pH measurements of suspensions with slags and mixtures of slag—fly ash—activator, respectively, stress the conclusions drawn from interpretation of the results concerning the proportion of chemically bound water (Table 4). In this way, the decisive role of the nature of slag from cementitious material—pozzolana mixture is confirmed. The pH measurements performed on suspensions with a water:solid ratio = 10:1, when using slags SG I_a and SG II (with or without fly ash ACT II) as given in Table 6, are relevant from this point of view. The role of the activator on modifying the pH condition—even when substituting 30% of slag with fly ash is substantial in the case of binder mixtures prepared with slag SG I_a. The induction period for hydration and pozzolana—type reactions is therefore shortened with more rapid subsequent evolutions.

The thermal analysis performed on mixtures (SG I_a + ACT II) and (SG II + ACT II), activated with 3% $Na_2Al_2O_4$ and 6% lime, also confirms previous conclusions about the role of the slag component. The weight loss, obviously lower in the case of binder with SG II hardened for 28 days, suggests its slower chemical transformation, i.e. a lower content of hardening hydrocompounds. Taking into account the data given in Table 2, it follows that the use of $Na_2Al_2O_4$ and lime as activator leads to almost similar values of the chemically bound water as in the case of $CaCl_2$ with lime. In these conditions, the decrease of the amount of chemically bound water when decreasing the proportion of slag from 90% to 70% in the silicate binder is not greater than 2–3%. Consequently, the weight loss detected in Fig. 7(a) will not be lower than 2–3%. The total weight loss of specimen prepared with SG I_a slag and ACT II fly ash is still some 45% higher than the weight loss determined for specimen prepared with SGII slag and ACTII fly ash (Fig. 7(b)).

So, for the samples prepared with SGI_a slag (Fig. 7(a)) one can see a more important total weight loss accompanied by a different distribution in the temperature range, namely in two major regions, under and above 600 °C. In this case, under 600 °C more important weight losses can be seen (assigned to gelic water together with water resulting from decomposition of $Ca(OH)_2$ and partially from the chemically bound water in hydrosilicates and aluminates. The remaining water is released above 600° when decomposing the formed hydrocompounds (hydrosilicates, particularly), i.e. the endothermic peak is around 720–740 °C.

Table 6
Comparative results of pH measurements

Suspension composition	Activator	pH values for different time (hours)						
		1 h	2 h	3 h	7 h	12 h	24 h	72 h
70% slag SG I_a + 30% fly ash ACT II	2%$Na_2Al_2O_4$ + 5% lime	10.2	–	10.2	–	–	9.2	8.8
70% slag SG II + 30% fly ash ACT II	2%$Na_2Al_2O_4$ + 5% lime	9.3	9.1	8.9	8.8	8.8	8.7	–
Slag SG I_a	–	8.8	–	9.0	–	–	8.8	8.6
Slag SG II	–	8.9	8.7	8.6	8.2	8.2	8.0	–

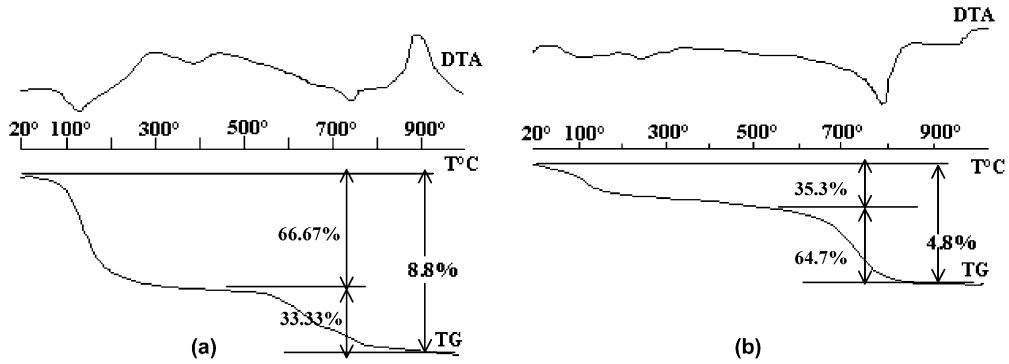

Fig. 7. DTA and TG patterns for samples activated with 3% $Na_2Al_2O_4$ and 6% lime, preserved for 28 days and prepared from: (a) 90% slag SG I_a and 10% fly ash ACT II; (b) 70% slag SG II and 30% fly ash ACT II.

On the contrary, in Fig. 7b a reverse image appears. The endothermic effect from 720–740 °C is obviously larger; in Fig. 7(a) an exothermic effect is noticed at 890 °C, assigned to a crystallisation process that accompanies the decomposition of the low basicity CSH hydrosilicates [8,27–31].

Such behaviour is plausible for the activated silicate binder. The low basicity character of the detected CSH hydrosilicates assumes a high condensation degree of the hardening structures that induces higher mechanical strength. This conclusion is confirmed by the results of the mechanical strength tests that are presented below.

3.2. Mechanical behaviour of hardened binder systems

The mechanical behaviour of the studied binder systems is considered, as already mentioned, through the relative mechanical strength (R_{rel}), as defined earlier. Tables 7 and 8 present the values of the relative mechanical strength for mixtures of cementitious materials (slag)—pozzolana (fly ash) having a Blaine specific surface of 350 m^2/kg when using slag SG I_b and fly ash ACT I, and 400 m^2/kg when using slag SG I_a and fly ash ACT II.

The statistical processing of the results regarding the mechanical strength of the set of hardened samples, prepared as mixtures of SGI_b slag and ACT I fly ash, has

Table 7
Relative mechanical strength of samples prepared with slag SG I_b–fly ash ACT I (with a specific surface of 350 m^2/kg) and activating mixture of lime and (Na_2SO_4 + Na_2CO_3)

Activator-alkaline salt	Slag/fly ash weight ratio	Curing time (days)	Relative mechanical strength (%), for activation with								
			2% lime			3% lime			5% lime		
			and mixed salt activator								
			3%	5%	7%	3%	5%	7%	3%	5%	7%
Na_2CO_3:Na_2SO_4 = 1:1	100/0	3	4.7	7.0	10.8	8.4	11.0	22.6	30.9	41.4	47.2
		7	8.7	n.d.	17.1	20.8	25.5	28.5	51.9	53.5	55.4
		14	22.2	27.1	31.6	33.7	38.5	42.8	57.7	60.8	64.7
		28	33.7	39.7	42.3	40.9	42.3	49.0	68.4	69.9	76.6
	80/20	3	4.4	6.1	10.3	6.6	10.0	18.4	24.5	34.6	41.6
		7	8.6	13.6	17.3	17.1	20.8	23.8	43.9	45.3	51.1
		14	21.2	29.5	29.9	27.4	31.5	36.4	48.4	53.7	57.7
		28	31.0	39.3	41.1	33.6	34.5	43.5	57.0	60.3	62.6
	60/40	3	4.0	5.9	9.1	7.0	10.5	16.1	35.0	35.5	33.2
		7	7.3	14.5	15.7	15.2	17.1	20.8	38.3	42.8	46.8
		14	19.2	24.5	25.9	24.5	27.3	29.7	45.1	48.1	55.2
		28	27.3	35.0	36.7	29.7	31.5	36.7	54.0	55.6	57.3
	40/60	3	3.7	4.8	8.4	5.1	7.9	11.9	18.5	27.3	31.3
		7	7.3	10.0	13.3	12.8	15.7	19.2	33.2	34.6	38.8
		14	15.7	21.5	22.0	20.6	23.6	27.1	37.1	40.9	42.8
		28	23.3	30.6	31.3	25.5	26.2	33.2	43.7	46.3	47.9

Table 8
Relative mechanical strength of samples prepared with slag SG I_a and fly ash ACT II (with specific surface of ~400 m^2/kg), activated with lime and sodium and/or calcium salts

Slag–fly ash weight ratio	Age (days)	Relative mechanical strength (%), for activation with												
		5%Na_2SO_4 and 3–6%lime				5%Na_2SO_4 + 2%$CaCl_2$ and 3–6%lime				2%$CaCl_2$ and 3–6%lime				2%$Na_2Al_2O_4$ and 5%lime
		3%	4%	5%	6%	3%	4%	5%	6%	3%	4%	5%	6%	
100/0	3	n.d.	n.d.	n.d.	24.90	17.40	20.80	22.80	23.80	15.40	21.30	22.80	30.80	
	7	28.20	30.80	32.80	37.95	40.20	40.30	44.10	46.40	54.90	59.00	61.50	67.90	
	14	41.80	45.00	49.00	52.80	60.50	66.20	69.20	75.20	75.10	80.00	83.80	87.40	
	28	45.10	47.95	52.05	57.20	68.20	72.60	75.40	78.70	82.80	85.50	87.40	95.10	
90/10	3	n.d.	n.d.	n.d.	22.80	14.90	20.50	n.d.	24.40	14.10	20.25	24.10	28.20	
	7	25.65	29.50	31.00	35.40	36.20	37.20	41.50	43.60	47.40	52.60	58.50	61.50	
	14	37.20	42.80	44.60	48.50	56.20	60.80	64.20	70.30	74.10	77.95	80.50	85.60	
	28	41.00	44.90	48.20	51.30	63.80	67.40	71.80	74.60	79.70	82.80	84.40	91.80	
70/30	3	n.d.	n.d.	n.d.	n.d.	14.10	n.d.	n.d.	n.d.	n.d.	16.20	n.d.	26.20	n.d.
	7	23.10	28.20	29.50	34.10	32.05	33.30	36.60	38.20	41.00	48.70	51.30	55.10	38.50
	14	33.30	37.95	40.80	45.40	52.05	56.20	61.00	16.90	69.50	75.60	76.90	82.60	67.20
	28	36.90	42.05	44.10	48.50	60.50	63.80	66.20	70.50	75.60	78.70	82.80	86.70	71.80
50/50	3	n.d.	n.d.	n.d.	20.50	n.d.	15.10	18.50	20.50	n.d.	n.d.	20.50	25.10	
	7	22.30	26.90	27.70	30.50	30.50	31.50	33.10	34.60	38.50	44.40	45.40	47.40	
	14	29.50	33.30	35.40	40.00	49.70	51.30	53.80	58.50	65.10	68.50	73.10	78.20	
	28	32.05	35.90	38.70	43.60	56.60	60.00	62.90	67.20	72.10	76.40	78.20	82.80	

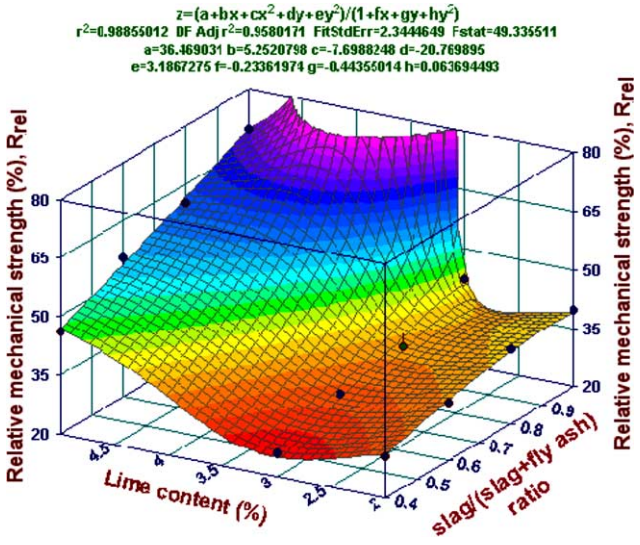

Fig. 8. Statistical processing according to Eq. (2) of the mechanical strength for binding systems prepared with slag SG I_b–fly ash ACT I (~350 m^2/kg) and activating mixture of lime and (2,5% Na_2SO_4 + 2,5% Na_2CO_3), after 28 days of curing.

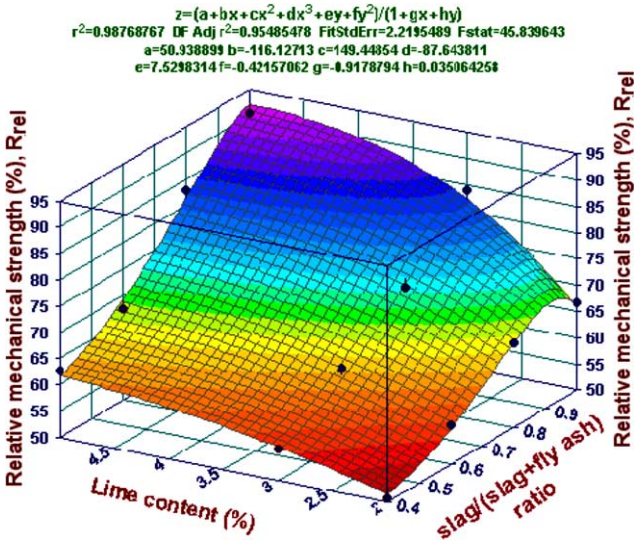

Fig. 9. Statistical processing according to Eq. (2) of the mechanical strength for binding systems prepared with slag SG I_b–fly ash ACT I (~420 m^2/kg) and activating mixture of lime and (2,5% Na_2SO_4 + 2,5% Na_2CO_3), after 28 days of curing.

been done considering different specific surface, e.g. 350 m^2/kg, 420 m^2/kg and 500 m^2 /kg as shown in Figs. 8–10. Also, the results were statistically processed with respect to mechanical strength for the samples prepared with mixtures of slag SG I_a and fly ash ACT II having specific surface ~400 m^2/kg (Figs. 11–13).

The mathematical form adequate from statistical processing of data obeys a similar formula as Eq. (1). The plots in Figs. 8–13, using the same independent variables (i.e. the slag/(slag + fly ash) weight ratio and lime content), and dependent variable (the relative mechanical strength (R_{rel})) were derived by fitting the data to the equation below

$$R_{rel} = \frac{a + bx + cx^2 + dx^3 + ey + fy^2 + gy^3}{1 + hx + ix^2 + jx^3 + ky + ly^2 + my^3}, \quad (2)$$

where the notations of the parameters on the right side of the Eq. (2) are similar to those given in Eq. (1).

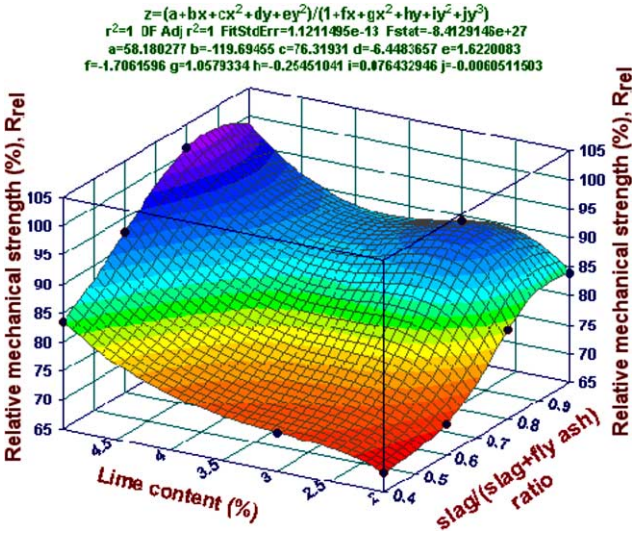

Fig. 10. Statistical processing according to Eq. (2) of the mechanical strength for binding systems prepared with slag SG I_b–fly ash ACT I (~500 m^2/kg) and activating mixture of lime and (2.5% Na_2SO_4 + 2.5% Na_2CO_3), after 28 days of curing.

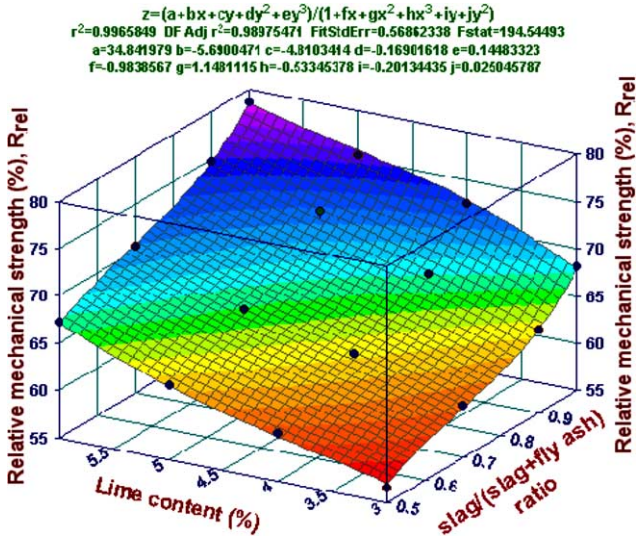

Fig. 12. Statistical processing according to Eq. (2) of the mechanical strength for binding systems prepared with slag SG I_b–fly ash ACT I (~400 m^2/kg) and activating mixture of lime and (5% Na_2SO_4 + 2% $CaCl_2$), after 28 days of curing.

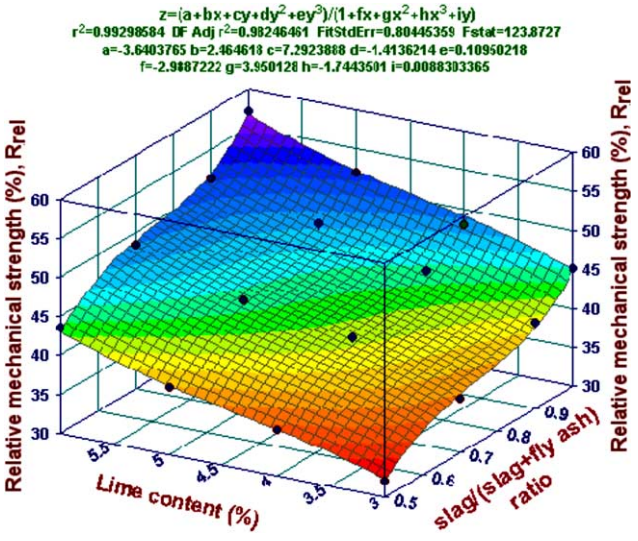

Fig. 11. Statistical processing according to Eq. (2) of the mechanical strength for binding systems prepared with slag SG I_b–fly ash ACT I (~400 m^2/kg) and activating mixture of lime and Na_2SO_4 (5%), after 28 days of curing.

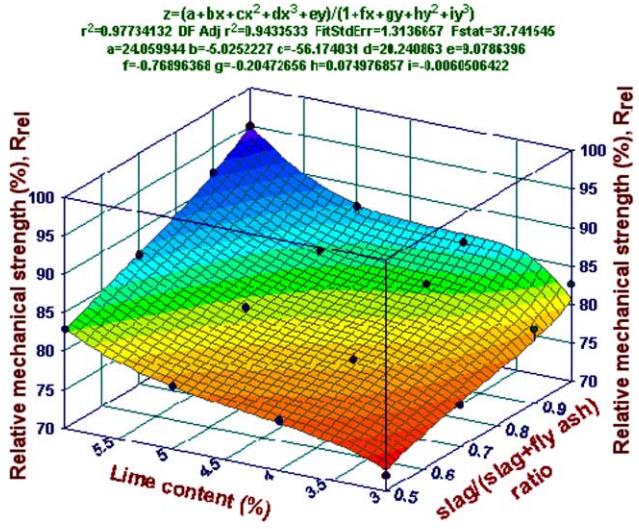

Fig. 13. Statistical processing according to Eq. (2) of the mechanical strength for binding systems prepared with slag SG I_a–fly ash ACT II (~400 m^2/kg) and activating mixture of lime and $CaCl_2$ (2%), after 28 days of curing.

The values of the regression coefficients from Eq. (2), for all sets of samples are given for comparison, in Table 9. The corresponding correlation coefficients have high values within the range $0.977 < r^2 < 1$.

The development of strength during hardening of the binder systems is a consequence of the chemical behaviour of the binder and of the evolution of chemical transformations within these systems. These emphasize similar influence on the development of hardening strength structures, with respect to their intrinsic parameters. In this context, the samples prepared with slag SG II, appear to be less active—as determined from the study of chemical behaviour (A_l and pH associated with thermal analysis—Table 4, 6, and Fig. 7)—and these do not develop significant strength even after 28 days curing, thus suggesting the decisive role of the nature of the slag used upon the hardening behaviour of the activated cementitious material—pozzolana systems.

Table 9
The regression coefficients for different binding systems, according to Eq. (2)

Regression coefficients	Values of regression coefficients for binding mixture prepared with					
	Slag SG I_a–fly ash ACT II, with a specific surface of 400 m^2/kg, activated with lime associated with			Slag SG I_b–fly ash ACT II, with a specific surface of		
				350 m^2/kg	420 m^2/kg	500 m^2/kg
	5%Na_2SO_5	5%Na_2SO_4 + 2%$CaCl_2$	2%$CaCl_2$	Activated lime + (2.5%Na_2SO_4 + 2.5%Na_2CO_3)	Activated lime + (2.5% Na_2SO_4 + 2.5%Na_2CO_3)	Activated lime + (2.5%Na_2SO_4 + 2.5%Na_2CO_3)
a	−3.640	34.842	24.060	36.469	50.939	58.180
b	2.465	−5.690	−5.025	5.252	−116.127	−119.695
c	0	0	−56.174	−7.699	149.449	76.319
d	0	0	20.241	0	−87.644	0
e	7.292	−4.810	9.079	−20.770	7.530	−6.448
f	−1.414	−0.169	0	3.187	−0.422	1.662
g	0.110	0.145	0	0	0	0
h	−2.989	0.984	0.769	−0.234	−0.918	−1.706
i	3.950	1.148	0	0	0	1.058
j	−1.744	−0.533	0	0	0	0
k	0.009	−0.201	−0.205	−0.444	0.035	−0.255
l	0	0.025	−0.075	0.064	0	0.076
m	0	0	−0.006	0	0	−0.006

4. Conclusions

The following conclusion can be drawn from the current study:

- It is possible to produce cementitious binders comprising slag, fly ash and activator, which develop equivalent mechanical strength to that of an ordinary Portland cement.
- The hardening properties of the resultant cements are directly conditioned by the nature and the mass ratio of the components of the binder (i.e. slag—pozzolana—activator).
- The nature of the cementitious phase (slag) and its activation plays a decisive role in the hardening of the studied binder systems. At a significant activation of the cementitious phase (slag), the enhanced hydration-hydrolysis process leads to a basicity of the binder system during hardening that is favourable for pozzolanic reactions; thus, as a result of the cementitious phase hydration and the pozzolanic reaction, the development of strength hardening structures is enhanced.
- The binder systems—especially those finely ground and well activated, can include up to 40% fly ash (as pozzolan), together with slag (as cementitious phase), without affecting the performance of the binder in any significant way.
- Rational polynomial equations are given to quantify the correlation between the chemical behaviour (considered through the chemically bound water) or structural-mechanical properties (considered through the mechanical strength of the hardened system) and compositional factors (slag/fly ash ratio and lime proportion in the activating mixture), specific surface of the silicate mixture (slag and puzzolana) or hardening time.

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