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Alkali-activated cementitous materials: Alternative matrices for the immobilisation of hazardous wastes
Part I. Stabilisation of boron

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Abstract

Boron is a nonmetal element that is present in nature in many kinds of minerals and in a lot of industrial products of public use. The importance of this element lies in the fact that boron compounds are present in some water streams from nuclear power plants (Pressure Water Reactor [PWR]) and that the boron-soluble salts modify Portland cement hydration retarding setting and hardening, and negatively affecting its durability characteristics. Thus, the main objective of this research was to study the efficiency against boron of the solidification systems based on alkali-activated fly ashes. Results show that boron does not significantly alter the hardening process of the new matrices. The presence of boron hardly modifies mechanical strengths of activated fly ashes and additionally, boron leaching tests indicate that this stabilisation/solidification system is more effective than traditional ones.

Keywords: Alkali-activated fly ash; Stabilisation/solidification system; Boron; Leaching

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1. Background

The alkaline activation of materials is a chemical process that provides the transformation of determined structures, partial or totally amorphous and/or metastables in compact cemented frameworks. Some aspects of this generic chemical process to be remarked are: kinetics diversity, complexity of chemical reactions, different microstructures developed, etc. Actually, two models of alkaline activation may be distinguished obeying to different starting conditions.

A known example of the first model is the alkaline activation of blast furnace slags in relatively soft alkaline conditions [1–5].

The second model of alkaline activation has been less studied. An example is the case of the activation of metakaolin: process that has been described in terms of a polymeric model at which the products formed are characterised by their high strengths [6–10].

There are some elements establishing a rational parallelism between the process of zeolite formation and the one of the obtention of the cement resultant from alkaline activation of metakaolin, as for instance: The concentration of the reactants present in the reaction; curing temperature; type of alkali; etc. Actually, some authors have concluded that the products from alkaline activation of metakaolin (amorphous to X-ray diffraction [XRD]) are zeolitic precursors [11,12].

This chemical process that might allow transforming glassy structures into very well cemented composites could also be applied to some specific waste materials. For example, fly ashes (a very abundant by-product) are potential materials for being activated.

The specific process of the activation of fly ashes is not so well known, but it may be considered as a set of destruction–condensation reactions (including the destruction of the initial solid substance) that initially leads to a series of unstable structure units and later produces the formation of thixotropic coagulation structures which can

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condense to form the hydrated products. This set of reactions can be divided into three consecutive stages.

◆ The first step may be described on the breaks of Me−O, Si−O−Si, Al−O−Al and Al−O−Si bonds of the initial material. It needs a stimulus, for example, the variation of the ion force of the medium when adding ions with electro-donor properties (alkaline metals).

The result is a redistribution of the electronic density over the silicon atoms that favour the Si−O−Si bond breaks. The hydroxylation degree of silicon may increase above 2 or 3 units forming unstable intermediate complexes that decompose to give place to silicic acid $Si(OH)_4$ and $Si-O^-$ anions.

The presence of cations of alkaline metals balances the negative electrical load of these anions, producing $Si-O-Na^+$ bonds. These alkaline silicates may undergo reactions of ion interchange with divalent ions, forming Si−O−Ca−OH type complexes.

Hydroxyl groups affect in the same manner to Al−O−Si bonds. So, depending on the pH, aluminates in the alkaline solution will be forming complexes of the $Al(OH)_4^-$, $Al(OH)_5^{2-}$ and $Al(OH)_6^{3-}$ type.

◆ In the second step, the accumulation of desegregated products favours their contact, forming a coagulation structure in which polycondensation processes occur.

The easiness of the silicic acid to condense is increased at alkaline pH where it is slightly dissociated or in a molecular state. Thus, at pH >7, the desegregation of the Si−O−Si bond gives place to hydroxylated complexes of the $Si(OH)_4$ type as the most stable components, which may condense to form a new Si−O−Si bond leading to the dimmer. OH^- ion acts as a reaction catalyst.

All the processes, composition and stability of the products formed in this step are essentially affected by the alkali amount in the system. From a determined moment, the development of mechanical strengths of the material is accompanied by a pH decrease in the liquid phase. This is possibly due to the absorption and interaction of the alkali with hydrosilicates and hydroaluminosilicates formed, followed by the appearance of hydrosilicates of the zeolite type. If the alkaline metal acted as a process catalyst in the destruction step, it acts as a structure-forming element in the following steps.

◆ Finally, the presence of particles from the initial solid phase, as well as the appearance of microparticles resulting from the condensed structure, gives place to the precipitation of products.

Table 1
Chemical composition of the cement used

Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	SO_3	MgO	Insol.	L.I.
wt.%	20.12	5.44	63.42	3.56	3.22	1.84	0.9	1.50

L.I. = loss on ignition, Insol. = insoluble residuum.

Table 2
Chemical composition of the ash used

Oxide	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	MgO	Insol.
wt.%	58.6	28.0	6.1	4.2	1.6	1.3	0.2

The qualitative and quantitative composition of the reaction products is determined by the mineralogical and chemical composition of the initial phase, the nature of the alkaline components and the hardening conditions.

2. Introduction

Taking into account this scenario, some authors [13] have thought indeed that systems developed on the base of alkaline activation of fly ashes could appear as an alternative for new design of matrices holding ideal characteristics as for solidification/stabilisation of toxic, hazardous and radioactive wastes. Some properties of the new material (pore size distribution, where the very small pores are the most abundant; low permeability; very high alkalinity; good chemical stability; and a three-dimensional microstructure) suggest that excellent performances could be obtained in the immobilisation of certain chemical species where traditional cementitious systems do not give positive results.

Boron, particularly, is a nonmetal element that is present in nature in many kinds of minerals and in a lot of industrial products of public use. The average content of boron in water is ≤ 1 mg B l^{-1} and sea water is close to 5 mg B l^{-1}. Most standards do not control the boron content in drinking water given that the element, as much as its main salts (borates), are not considered as toxic substances, although some studies indicate that a concentration higher than 10 ppm could be harmful. However, the true importance of this element lies in the fact that boron compounds, and specially boric acid, is present in some water streams from nuclear power plants (Pressure Water Reactor [PWR]), in high concentrations (between 30,000 and 40,000 ppm B); and also that boric acid and all its soluble salts modify Portland cement hydration, retarding setting and hardening, and negatively affecting its durability characteristics [14–16].

Nowadays, what is trying to be done to solve these problems is to transform borate ions into low solubility compounds by adding $Ca(OH)_2$ to the system and forcing the formation of compounds such as $Ca(BO_2)_2$. In this way, Portland cement evolves through a “relatively normal” hydration (3 days minimum hardening time). Another mechanism for boron precipitation consists in substituting sulphates from ettringite in order to precipitate borate-substituted ettringite [17–19].

The goal of this research is to study the efficiency against boron of some solidification systems based on alkali-acti-

Table 3
Composition of studied matrices

M-1	OPC
M-2	OPC + 6% of lime
M-3	OPC + 15,000 ppm of B in the dissolution
M-4	OPC + 15,000 ppm of B + 6% of lime
M-5	FA with NaOH 10 M
M-6	FA with NaOH 10 M + 15,000 ppm of B
M-7	FA with NaOH 10 M + 15,000 ppm of B + 6% of lime

OPC = ordinary Portland cement, FA = fly ash.

vated fly ashes and to compare them with those well-known systems based in Portland cement.

3. Experimental

3.1. Materials

A Type I Portland cement has been used to make test samples. Its chemical composition is shown in Table 1. In the case of activated fly ash, a type F ash (ASTM) was used. Its composition is shown in Table 2.

Other materials used (boric acid, calcium hydroxide and sodium hydroxide) are laboratory products for analyses.

3.2. Method

3.2.1. Elaboration of test samples for mechanical strengths

A first series of prismatic test samples sized 1 × 1 × 6 cm was made with Portland cement paste as reference material (matrix M-1). Water/cement (w/c) ratio was 0.6. All samples were submitted to compression and flexural mechanical tests at 1, 3, 7 and 28 days. The curing of samples was carried out in chamber at 21 °C and 95% relative humidity. A second series of samples was prepared in the same way but having 6% lime. The samples were mixed with the same w/c ratio, cured in the same conditions and broken at the same ages (matrix M-2).

Following and similarly to what had been done with reference samples, another series of ordinary Portland cement (OPC) samples was made (matrix M-3). But in this case a solution of boric acid (15,000 ppm of Boron) was used as substitute of mixing water. An additional series of samples containing 6% lime (matrix M-4) also hydrated with boric acid was prepared. The w/c ratio, the curing conditions and mechanical tests were always kept constant.

Table 4
Leaching test data

Leaching time (days)	Matrix	F_j (cm) × 10^2	D_e (cm^2/s) × 10^8	Li	Li (average)
1	M-4, 28 days of curing	4.7	8.19	7.10	*7.28*
3		5.2	7.46	7.12	
7		6.2	6.12	7.21	
15		6.6	3.68	7.43	
28		6.8	2.79	7.55	
1	M-6, 1 day of curing	1.2	0.54	8.26	*7.73*
3		3.0	2.52	7.59	
7		4.1	2.72	7.56	
15		5.2	2.33	7.63	
28		6.3	2.41	7.61	
1	M-6, 28 days of curing	1.1	0.44	8.36	*7.83*
3		2.7	1.95	7.70	
7		3.8	2.26	7.64	
15		4.2	1.54	7.81	
28		6.3	2.32	7.63	
1	M-7, 1 day of curing	0.15	0.009	10.04	*9.31*
3		0.31	0.027	9.56	
7		0.41	0.027	9.56	
15		1.1	0.17	8.93	
28		2.4	0.32	8.49	

Li (leaching index) is a parameter whose value characterizes the resistance of an element against leaching. The higher this parameter is, the stronger is the resistance to leaching. The established limit is 10 or 6 [23], depending on how the units D_e are expressed ($m^2\ s^{-1} \geq Li = 10$, $cm^2\ s^{-1} \geq Li = 6$). This means that values in this table higher than 6 will indicate that the matrix proposed will be efficient as a stabiliser of the element under study.

Finally, other series of samples were made with alkali-activated fly ash (matrices M-5, M-6 and M-7). Activator used was NaOH 10 M solution; solution/ash ratio was 0.6 and curing conditions were the following: during first 24 h samples were kept in a watertight container within an oven at 85 °C, and the rest of the time until the mechanical test (1, 3, 7 and 28 days) they were kept in a climatic chamber

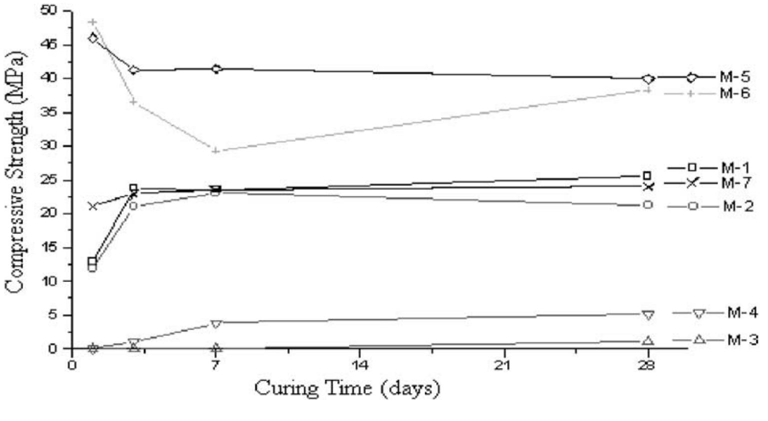

Fig. 1. Evolution of compressive strengths.

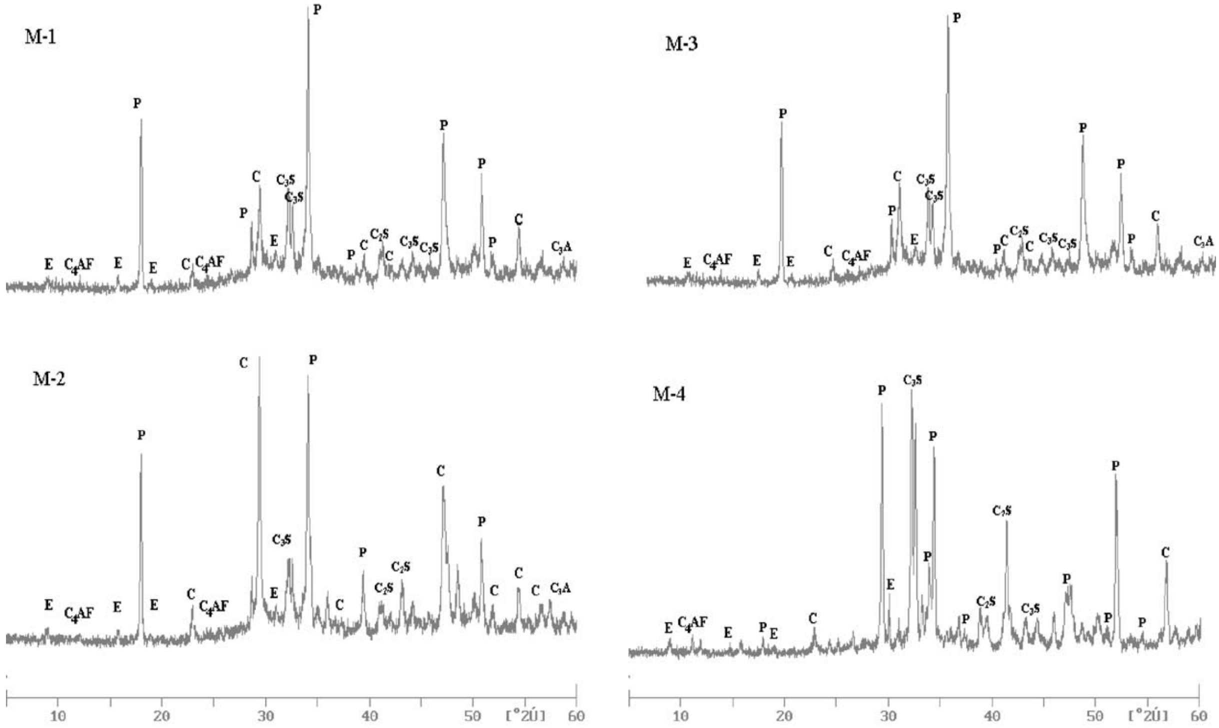

Fig. 2. XRD patterns of matrices M-1, M-2, M-3 and M-4.

at 21 °C and 95% RH. Table 3 shows the composition of each sample.

3.2.2. Preparation of samples for leaching tests

Simultaneously, several series of cylindrical test samples (13 × 6 mm) with matrices M-3, M-4, M-6 and M-7 (all of them containing B) were made with the purpose of carrying out a leaching study. The curing conditions of these cylindrical samples were similar to those established for the prisms submitted to mechanical strength tests, although curing time was established for each particular case: M-3 and M-4 matrices (OPC) were submitted to 28 curing days; M-6 matrix to 1 curing day and 28 curing days; M-7 matrix to 1 single curing day. Leaching method used was the MCC-1 [20] in such a way $V_{\text{leachant}}/S_{\text{sample}}$ ratio = 10 cm. The volume of leachant (deionised water) was 30 ml. This static method is designed to be applied at intervals of 1, 3, 7, 15 and 28 days. Analysis of boron in the leachate was performed by using an UV/Vis Perkin Elmer 330-C spectrophotometer applying the azometine-H method [21].

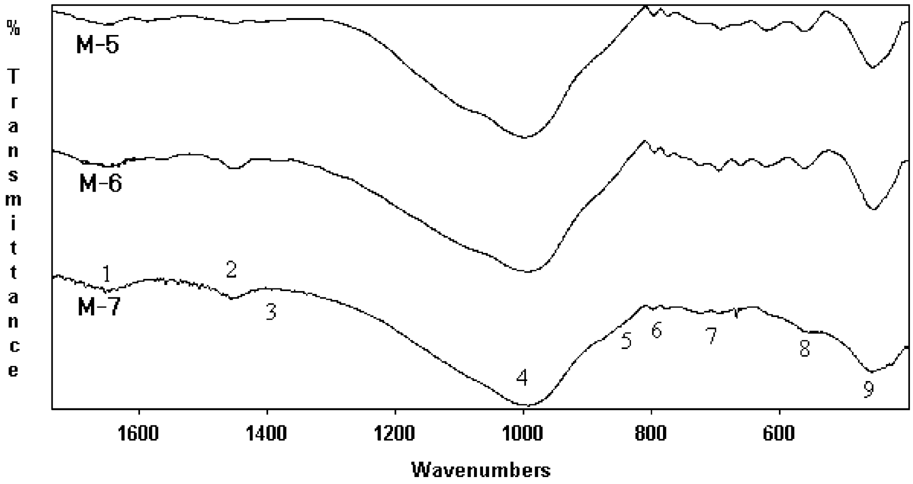

Fig. 3. IR spectra of matrices M-5, M-6 and M-7.

3.2.3. Characterisation of reaction products

XRD was mostly used for the study of Portland cement matrices, but for matrices of activated ashes, the characterisation study was basically performed through FTIR since it gives more and better information (fly ash diffraction pattern shows the presence of a major vitreous phase together with some crystalline quartz, mullite and hematite). After the alkaline activation, the vitreous phase is transformed into the new sodium aluminosilicate network, amorphous to XRD, and the crystalline phases remain unaltered [13].

4. Results

With respect to the mechanical strength experiments, results for every type of matrix are shown in Fig. 1.

With respect to the results obtained from leaching tests, these were transformed into the diffusion parameters described in the Godbee equation [22].

Since boric acid acts as retardant on Portland cement setting and hardening, the study of the solidifying characteristics of matrix M-3 appears to be impossible (this matrix had not enough physical integrity). As for the rest of the matrices, M-4 (28 curing days), M-6 (1 curing day), M-6 (28 curing days) and M-7 (1 curing day), results are shown in Table 4.

Finally, concerning the characterisation of the reaction products, Figs. 2 and 3 show main results.

Fig. 2 displays the diffraction patterns of matrices M-1, M-2, M-3 and M-4. All of them correspond to Portland cement systems after 28 days of hydration. Basically, graphs show the presence of crystalline phases, which are usual in Portland cement hydration, such as CSH gel, ettringite (E) and portlandite (P) and also calcite (C). However, in addition to hydrated phases, diffraction peaks corresponding to phases of anhydrous cement (C_3S, C_2S, C_3A and C_4AF) can be observed, too, since test time has not been long enough to totally hydrate the material. Addition of lime to the system (matrices M-2 and M-4) accounts for a higher intensity of the peaks corresponding to portlandite.

With respect to the cement hydrated with water containing boron (matrices M-3 and M-4), the expected decrease of cement hydration rate occurs [15]. No hydration products are formed; however, phases of the anhydrous OPC are mainly observed. Somehow, addition of a small amount of lime allows the cement to hydrate, although certainly quite slowly.

In Fig. 3, FTIR spectra of matrices M-5, M-6 and M-7 can be observed. Such spectra correspond to the cementing systems based on alkali-activated fly ashes.

Interpretation of spectra is carried out with the help of Table 5 in which wave number values corresponding to the characteristic bands of each sample are shown.

"Typical" bands of B compounds appear around 1450 cm^{-1} and in the 900–1000 cm^{-1} area, which coincide with bands of sodium carbonate and with those typical of the "alkaline polymer" (the reaction product).

Table 5
Interpretation of bands from FTIR spectra

Band number and wavelength	Bands interpretation
1 (1650 cm^{-1})	Band ν_2 (deformation) corresponding to H_2O. Hydration water present in the cavities of the structure.
2 (1451 cm^{-1})	Band ν_3 corresponding to Na_2CO_3.
3 (1411 cm^{-1})	The presence of this band indicates formation of $Na_2CO_3{\cdot}H_2O$.
4 (998 cm^{-1})	Characteristic band of "alkaline polymer" corresponding to T–O tension bond (being T = Si or Al). Original ash (before activation) keeps this band drifting towards higher energy values.
5 (867 cm^{-1})	This band proves the formation of monohydrated sodium carbonate.
6 (796–773 cm^{-1})	At these wave number values, the characteristic "doublet" of the quartz present in starting material appears. Band ν_5 (Si–O–Si)
7 (726–693–661 cm^{-1})	This "triplet" indicates formation of "alkaline polymer," and agrees with a T–O–T (T′) combination band.
8 (621–562 cm^{-1})	Band present in the starting material corresponding to mullite.
9 (456 cm^{-1})	Band corresponding to a deformation of O–Si–O (A_1) bond.

Finally, concerning matrix M-7 (alkali-activated mixture of ash and a small amount of lime), FTIR spectrum is found similar to earlier cases. In this particular case, it is most important to point out that there are no O–H tension bands corresponding to the lime (3600 cm^{-1} region).

5. Discussion

5.1. Mechanical strength

We have already drawn attention on the fact that presence of boron compounds in hydration water of Portland cement retards the setting and hardening process. This slowdown of setting and OPC hardening is basically justified in literature because of two different phenomena: (1) Inhibition of the portlandite nucleation; (2) Formation of a protective coat around the cement grains that prevents their contact with water.

Through the study of matrices prepared for this research by hydrating the OPC in the presence of boron, it certainly becomes obvious that development of such strength is null or almost null after 28 days of curing (Fig. 1). However, incorporation of $Ca(OH)_2$ to the boric acid solution, used to hydrate cement, has a direct influence in the reaction mechanism of OPC hydration, favouring the development of acceptable compressive strength after 7 days of curing (4 MPa). This remarkable increase of mechanical strength is due to the formation of $Ca(BO_2)_2 \cdot 2H_2O$, compound fixing the calcium with lime incorporated to the system. Thus there is no need to extract calcium from the OPC. However, hydration of Portland cement, even in the presence of lime, happens in an “anomalous” way since the mechanical strength it develops is not the same as the one developed when OPC is hydrated with pure water. The explanation to this phenomenon should be looked for in the kinetics of the reactions and not in the stoichiometry since the whole of $Ca(OH)_2$ added to the system is necessary for the complete formation of the calcium metaborate.

Mechanical strengths developed by activated fly ashes are much higher than those reached by Portland cement (Fig. 1). Fly ash activation, as already explained, occurs because the caustic solution interacts with the vitreous silica-aluminates of the starting material. This interaction leads to the formation of a pseudo-zeolitic three-dimensional structure, that is very compact and is able to develop compressive strengths higher than 45 MPa, just 24 h after activation starts. Boric acid seems not to affect significantly the mechanical strength development of the cementing system except for the first 7 days at which strength loose occurs. During this period, boron interferes in the activation mechanism of fly ashes by reacting with some sodium and some hydroxyl groups present in the system. When the whole boron added to the mixture has precipitated in the form of sodium borate, the chemical equilibrium conditions needed for the network structure to condense (to increase the level of polymerization) are re-established. This is a hypothesis and no experimental evidence has been obtained; however, it agrees with the leaching data and with the theory of phases equilibrium.

Finally, let us point out that the addition of a small percentage of lime into the activator solution generates a similar effect to that of the OPC; in other words, precipitation of calcium meta-borate is stimulated and it does not alter the evolution of activation reactions of fly ashes, and therefore, it does not affect the mechanical strength development of the system.

5.2. Leaching

The application of the MCC-1 test [20] and later analysis of data obtained allows asserting that matrix built with activated fly ash in the presence of lime conspicuously optimises results obtained from the OPC matrix with incorporated lime, as for boron leaching values (Fig. 4).

Comparison of matrices made of activated fly ash (M-6, 1 day cured and M-6, 28 days cured) with matrix M-4 of Portland cement (28 days curing) reveals that mean leaching index Li is just alike in the three cases (Table 4). However, matrix made with fly ash activated in the presence of a small amount of lime (M-7, 1 day curing) evidences a stabilisation efficiency higher than the rest of the system (boron leaching is 100 times smaller than the rest of the evaluated cases). In fact, initial leaching in this matrix is practically null, but starts to have significant values at 15 leaching days. Leaching index for this case is 9.31, and the maximum percentage of leachate, at 28 days, is under 20% of boron initially present (Fig. 4).

The factor “curing time” (1 day or 28 curing days), does not seem to have a significant role in the values of average leaching.

As for leaching mechanisms, they can be described using the parameter F_j. Fig. 5 represents F against $t^{1/2}$ for every studied matrix. From this figure it is inferred that in matrix M-6 (1 day curing), leaching is considered to be controlled by diffusion mechanisms from the third day. Initial deviation of the linearity happens because boron is not bearing an instantaneous initial leaching (as it usually occurs with heavy metals), but it does slowly.

In matrix M-6 (28 days curing), linearity of the graph F versus $t^{1/2}$ appears again (same as in previous case) on the third day, but this matrix behaviour cannot be considered totally controlled by diffusion mechanisms since, at 15 days,

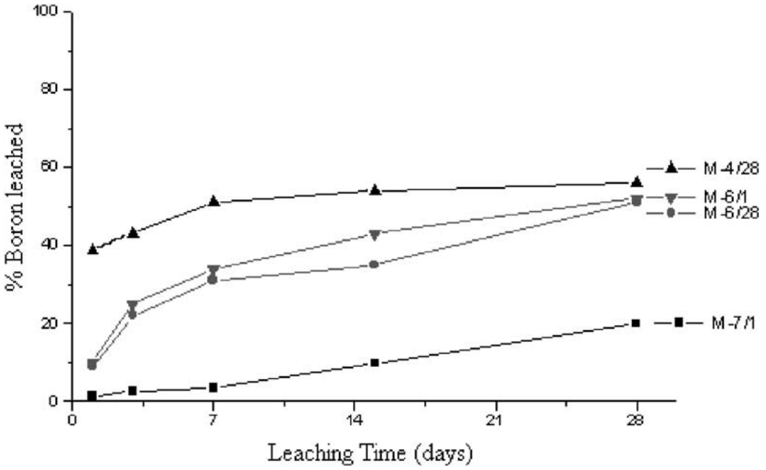

Fig. 4. Representation of the leached boron (wt.%) versus leaching time.

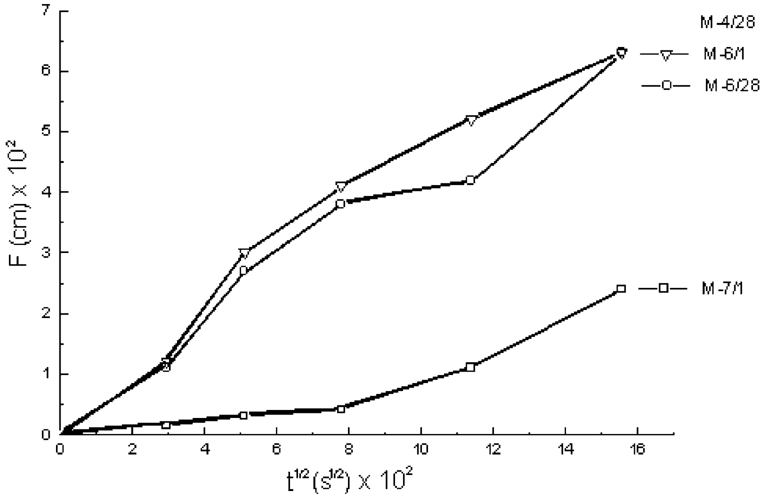

Fig. 5. $F/t^{1/2}$ representations for each studied matrix.

a sudden reduction of leaching occurs that will later on increase until values are comparable to those obtained for M-6 at 1 day curing. In this case, the leaching process is considered under control of other more complex factors.

Comparing the above mentioned data with those of the Portland cement matrix (M-4, 28 days curing), it was observed that the latter has an initial leaching remarkably high at low leaching times (at longer times, leaching mechanism is similar to the cases already discussed: mechanism controlled by diffusion), which agrees with consulted bibliography [23].

Finally, matrix M-7, 1 day curing, bears a leaching mechanism that can also be considered controlled by diffusion, although in this case initial leaching is very low. At medium and longer periods, leaching increases until reaching 20% (after 28 days leaching). Therefore, diffusion controls leaching for the first 7 days; for the 21 remaining days, the leaching process is controlled by other undefined mechanisms.

5.3. Chemical processes

Alkaline activation of fly ash in such work conditions favours the formation of a pseudo-zeolitic amorphous polymer [13]. This compound is identified through XRD following the shift of the characteristic halo of the starting material from $(2\theta)=26°$ until $(2\theta)=30°$. The rest of the crystalline compounds present in the starting material (quartz and mullite) do not react and they remain in the final product. Moreover, it has been proved through FTIR that band corresponding to the deformation of H_2O molecules is found around 1650 cm^{-1}, and that T–O tension band (T, Si or Al) is found between 997 and 1002 cm^{-}; which means a shift toward lower energy values than in the starting material, which is symptomatic of the activation reaction in progress. Alkaline activation of ash not only generates alkaline aluminium-silicate, but also a minor formation of some zeolitic compounds of the type of hydroxisodalite. The Na^+ remaining in excess or not having reacted yet goes through carbonation and forms thermonatrite.

In other respects, in those studied samples of activated ash, no significant differences are observed between matrices containing boron and those that do not (the added amount of boron is small and thus it is hard to detect through XRD the possible formation of any crystalline compound). FTIR spectra (see bands 2 and 4 in Fig. 3) indicate an overlapping of the signals generated by reaction products from ash alkaline activation, and signals of boron compounds of possible formation.

Thus, the following hypothesis can be established.

Concerning matrices M-6 (1 day curing and 28 days curing), when preparing NaOH 10 M activating solution, and adding an amount = 15,000 ppm of B as boric acid, such compound (Lewis acid) will form anions of type $B\ (OH)_4^-$, which means that the activating solution will be formed by Na^+ cations, HO^- anions and the already mentioned $B(OH)_4^-$.

Therefore, B atoms present in the system shall precipitate to form compounds such as $NaB(OH)_4$ or other kinds of sodium borates, which will partially fill the holes, pores, etc. of the whole matrix. The main factor affecting the leaching degree is the solubility of this type of compounds in the usually rather high alkaline conditions of these systems.

In matrix M-4 (28 days curing), addition of lime in the cement hydration water (water containing 15,000 ppm of dissolved boron) favours OPC hydration since calcium meta-borate formed favours the noninteraction of boron and calcium atoms from anhydrous OPC phases, and consequently, portlandite can nucleate. Accordingly, it is reasonable to think that boron atoms pertaining to meta-borate remain encapsulated in the cavities of the porous structure of cement paste, and they would not leach due to the big size of the crystals of the compound formed and its low solubility.

The boron ready for leaching should be found in the form of more soluble compounds. It is improbable (there are no biographical data) that boron replaces Si within the CSH gel structure, which is the main reaction product during cement hydration.

Finally, regarding matrix M-7, the fixation mechanism of boron could be understood as a mixed mechanism of both previously mentioned ones: simultaneous precipitation of calcium and sodium borates, which would justify mechanical behaviour, or behaviour concerning leaching.

6. Conclusions

(a) Activated fly ashes cementing systems are shown to have a higher and faster mechanical strength development than OPC systems.

(b) Boron negatively affects Portland cement hydration (lime addition improves the hydration rate of OPC when boron is present), and consequently, the mechanical strengths gaining. However, boron does not affect the alkaline activation process of fly ashes.

(c) Alkali-activated fly ashes improve the boron leaching rate of Portland cement systems. Leaching indexes and diffusion coefficients calculations indicate that boron diffusion is 100 times less in “activated fly ash–lime” matrices ($D = 4.89 \times 10^{-10}$ cm^2/s) than in “OPC–lime” matrices ($D = 5.2 \times 10^{-8}$ cm^2/s).

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