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Alkali-activated cementitious materials: Alternative matrices for the immobilisation of hazardous wastes

Part II. Stabilisation of chromium and lead

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Abstract

This research focuses on the study of the stabilisation/solidification capacity of a cementing matrix, which has been made using alkali activation of fly ash, in the presence of toxic elements chromium and lead. Such capacity has been compared with that of Portland cement. Leaching tests carried out proved that this new matrix is able to stabilise and solidify lead in a very efficient way (analysed lead concentrations from leaching are in parts per billion). However, it does not present itself as efficient concerning chromium fixation since this element strongly disturbs the alkali-activation mechanism of the ash.

Keywords: Activated fly ash; Chromium; Lead; Leaching

1. Introduction

Chromium is a chemical element that is included in the transition metals. It is one of the most widespread metal and holds the fourth position among the 29 biologically most important metals on the earth's crust. At low levels, it is an essential element for animal metabolism, but at levels close to 0.1 mg g^{-1} of the body weight, it can be lethal.

In nature, chromium can be found either as Cr^{6+} or as Cr^{3+}. Cr^{+6} is an oxidant form, which makes it very toxic for biological systems. *Trivalent* chromium (III) is relatively nonreactive and less toxic.

Many authors have studied chromium solidification using Portland cement as confinement matrix. Otomoso et al. [1] studied the stabilisation/solidification mechanism of chromium in tricalcium silicate. They concluded that addition of chromium as Cr(III) accelerates the C_3S hydration while the Cr(IV) does not have any remarkable effect except for the shortening of the C-S-H gel fibres formed at early ages and the increase of the matrix porosity.

Bishop [2] examined the kinetics and solidification mechanisms of chromium in a type II Portland cement and concluded that chromium fixation presumably occurs in silicates.

On the other hand, Wang and Vipulanandan [3] added K_2CrO_4 (ranging from 0.5% to 5% of the cement weight) to a Portland cement matrix (type I). They observed that addition of chromium lengthened the initial and final setting time and that when the Cr(VI) content was increased in cement, the compressive strength decreased [3]. However, Zamorani et al. [4] found that low chromium levels in the system accelerated the setting time.

Finally, Wang and Vipulanandan [3] performed leaching tests on cement matrices where chromium has been added and concluded that leaching of Cr(VI) by applying the TCLP process depends on the initial chromium concentration and on the leaching time. They also concluded that K_2CrO_4/cement ratio should not be higher than 0.2% in order not to exceed the chromium concentration of 5 ppm established by the TCLP method.

Unlike other minerals that are necessary for living individuals, even in small amounts, lead does not have any known beneficial organic function for the human being. On the contrary, its presence can create health problems.

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Table 1
Chemical composition of the cement used

Oxide (wt.%)						Insol.	LOI
SiO_2	Al_2O_3	CaO	Fe_2O_3	SO_3	MgO		
20.12	5.44	63.42	3.56	3.22	1.84	0.9	1.50

LOI = loss on ignition; Insol. = insoluble residuum.

Cartledge and Butler [5] investigated the different lead salts' behaviour when solidified in a Portland cement matrix. These authors proved that lead/cement system involved mixed salts of hydroxide, sulphate and nitrates, which retard cement hydration due to the formation of an impervious layer around the clinker grains. As the pH of the aqueous phase in the cement porous system undergoes fluctuations during the hydration process, lead nitrates undergo successive solubility and precipitations on the surface of the cement matrix. Alford and Rahman [6] reached the same conclusions and proved that mixed lead salts precipitate and form a gel, and that due to the formation of this gel, the system could expand causing microcracking and reducing both its stability and its mechanical properties.

Thevenin and Pera [7] studied the interactions between lead nitrate and ordinary Portland cement (OPC), and also with a Portland cement plus blast furnace slag. These authors concluded that lead stabilisation in hydraulic binders occurs by means of a combination of the following mechanisms:

addition: $\text{C-S-H} + \text{Pb} \rightarrow \text{Pb-C-S-H}$,
substitution: $\text{C-S-H} + \text{Pb} \rightarrow \text{Pb-S-H} + \text{calcium}$,
precipitation of new compounds: $\text{Pb} + \text{OH} + \text{Ca} + SO_4 \rightarrow \text{mixed salts}$.

Chatelet et al. [8] confirmed that lead solidification in hydrated calcium silicate (C-S-H) happens as soon as the C_3S starts hydrating. The "Pb-C-S-H" formed is a C-S-H gel of a regular stoichiometry where lead substitutes calcium.

The main objective of this research is to study of the use of alkali-activated fly ash as confinement matrix for chromium and lead elements. Again, it has to be remarked how scarce the available bibliography is regarding the use of this kind of materials (alkaline cements) as matrices for solidification of toxic and hazardous elements. Possibly, Van Jaarsveld et al.'s works [9,10] are the closest to our research. Particularly, these authors studied the solidification of lead in systems prepared through the activation of mixtures of fly ash and kaolin or metakaolin, finding that lead leaching kinetics correspond to a mechanism of diffusion or even a combination of mechanisms (diffusion plus other more complex ones). Moreover, they got the conclusion that lead solidification within this system is a combination of physical encapsulation and chemical bond.

2. Experimental

2.1. Materials

The same base materials used in the first part of this research (Portland cement and fly ash) have also been used in this second part.

A type I Portland cement was used to make reference samples (the chemical composition is shown in Table 1). A type F fly ash was used for preparing the new cementitious system (chemical composition of fly ash shown in Table 2).

Other materials used (sodium hydroxide, chromium oxide and lead nitrate) were laboratory products for analyses.

2.2. Method

2.2.1. Reference test samples for control of mechanical strength and for chemical and mineralogical characterisation

Prismatic test samples (1 × 1 × 6 cm) made with Portland cement paste were prepared using a water/cement ratio = 0.3. Paste was mixed until complete homogenisation and was poured and compacted into metallic moulds. Later, samples were cured at 21 °C and 95% relative humidity and submitted to compressive and flexural failure at ages 1, 3, 7 and 28 days.

In addition, some series of prismatic test samples (1 × 1 × 6 cm) of alkali-activated fly ash were prepared. This time, an 8-M NaOH solution was used for mixing with the fly ash. Activating solution/fly ash ratio was 0.3. The resulting paste was poured into metallic moulds, which were later put in a stove at 85 °C for 24 h. Once finished, they were drawn out of the stove and test samples were demoulded and put into a curing chamber (21 °C and 95% RH). The test samples were then submitted to mechanical tests at curing ages of 1, 3, 7 and 28 days.

2.2.2. Chromium and lead addition to the conglomerating systems

For the purpose of studying the effect of chromium and lead on the matrices mentioned above, other series of test samples were made with the same materials but known amounts of chromium (2.6% of Cr^{6+}) in the form of CrO_3 and lead (3.125% of Pb^{2+}) in form of $Pb(NO_3)_2$ were added.

CrO_3 was added to the mixing water of the Portland cement. Hydration reactions in this particular case are so

Table 2
Chemical composition of the ash used

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

Table 3
Compressive strengths (MPa)

	Curing time (days)			
	1	3	7	28
OPC	37.64	43.98	45.15	51.18
OPC + 2.60% Cr	16.18	32.77	53.14	52.62
OPC + 3.125% Pb	–	–	–	–
Fly ash + 8 M NaOH	35.59	32.53	35.09	33.77
Fly ash + 8 M NaOH + 2.60% Cr	–	–	–	–
Fly ash + 8 M NaOH + 3.125% Pb	30.51	21.01	23.43	25.05

exothermic that a part of the water of the system evaporated resulting in a very dry paste (very difficult to handle).

In the case of fly ash, the presence of 2.6% chromium (VI) lead to insufficient hardening during its activation and consequently it does not develop mechanical strength.

Lead, as mentioned above, was added in the form of Pb $(NO_3)_2$, which is a very soluble salt in water. The immediate effect of this element on Portland cement is an alteration of its normal hydration, the reason why no data on mechanical strength of this material have been collected.

As for the fly ash specimen, it has to be pointed out that Pb $(NO_3)_2$ is insoluble within an NaOH-activating solution, which makes it necessary in the paste preparation to perform first the homogenisation of the ash and the lead nitrate before mixing with the alkali solution.

Mechanical strengths of prisms were measured in accordance with the equipment specified in standard "UNE 80-101-91" [11], and the reaction products were characterised mostly through X-ray diffraction (XRD) and Fourier-transformed infrared (FTIR).

2.2.3. Leaching tests on matrices of activated slag according to MCC-1P method

This leaching test was explained in the first part of this research [12]. It was applied exclusively to the case of Pb-doped ash since ashes in the presence of chromium did not harden (data related to Cr and Pb leaching in Portland cement matrices are found in bibliography) [3,5]. Therefore, cylindrical activated fly ash samples having Pb (13 × 6 mm) were made and kept for curing for 24 h at 85 °C.

Once the curing time was completed, test samples were measured, accurately weighed, and then put into plastic containers that had been added with 30 ml deionised water (leachant). The leachant volume/matrix surface ratio (constant) is equal to 10 mm.

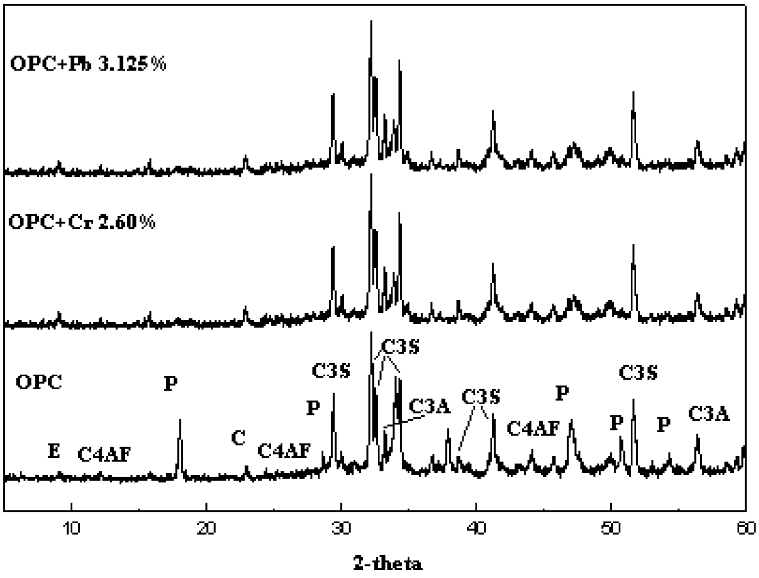
Plastic containers were kept in watertight containers full of water, which were stored in a curing chamber, thus assuring maximum possible humidity.

When leaching time was over at 1, 3, 7, 28, 56 and 90 days, leachates were extracted from the plastic containers and put in refrigerator to avoid evaporation. Lead content was measured through induction-coupled plasma emission spectrometry (ICP).

As for the solid matrices, they were kept in the dryer for 24 h and weighed afterwards. Finally, they were stored for further study.

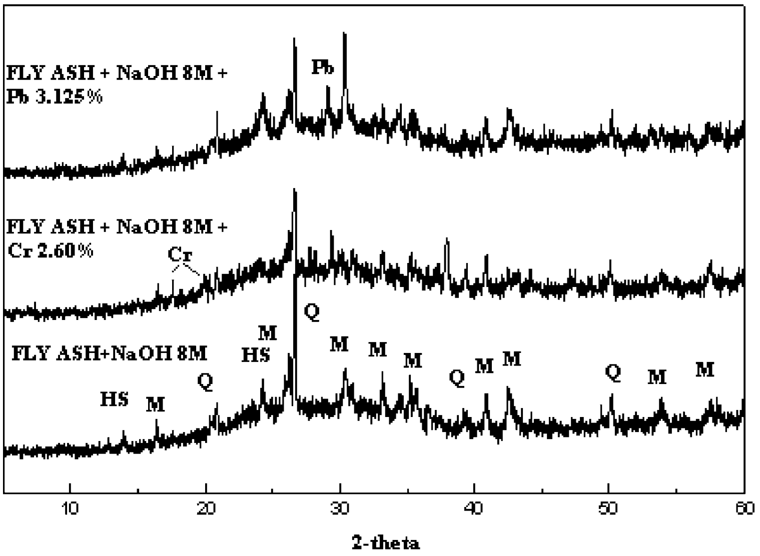
3. Results

Table 3 shows the results obtained from mechanical failure tests. Figs. 1 and 2 show the XRD patterns of matrices prepared with and without addition of Cr and Pb.



E- ETTRINGITE, P- PORTLANDITE

Fig. 1. XRD patterns of OPC, OPC + 2.60% Cr and OPC + 3.125% Pb.



M- MULLITE; Q- QUARTZ; HS- HIDROXIDALITE; H- HERSCHELITE;
Cr- $Na_2CrO_4 \cdot 4H_2O$; Pb-Pb_3SiO_5

Fig. 2. XRD patterns of fly ash, fly ash + 2.60% Cr and fly ash + 3.125% Pb.

As for the OPC used as reference material, peaks corresponding to crystalline phases of an anhydrous Portland cement and an amorphous halo around $2\theta = 29°$, which correspond to the C-S-H-gel formed during hydration, can be seen through XRD (Fig. 1).

In the case of cement samples bearing chromium, a radical decrease of the portlandite peaks is observed and it finally disappeared (Fig. 1). However, no formation of any chromium crystalline compound is observed.

Something similar occurred in samples containing lead (see Fig. 1). Signals corresponding to portlandite diminished and finally almost completely disappeared. No formation of chromium crystalline compound is detected in this case.

As for the matrix of activated fly ash, the addition of 2.60% chromium encouraged the formation of $Na_2CrO_4{\cdot}4H_2O$, as observed through XRD (see Fig. 2). This fact is ascertained through FTIR (see Fig. 3). In addition, the formation of zeolites of the hydroxisodalite

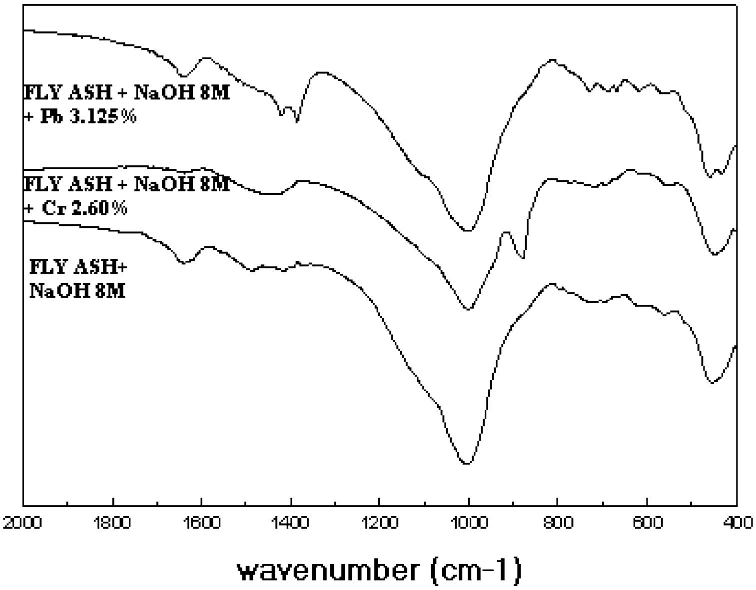


Fig. 3. IR spectra of activated fly ash samples with and without chromium and lead.

Table 4
Amount of lead in the leaching water

Leaching time (h)	Lead weight at the beginning (mg)	Leached lead (mg)	Leached lead (°/l)
24	18.8562	0.0030	0.0002
72	18.2281	0.0063	0.0003
168	18.6781	0.0099	0.0005
336	18.7343	0.0162	0.0009
672	18.9375	0.0150	0.0008
1344	18.0031	0.0240	0.0013
2160	17.7781	0.0255	0.0014

type ($Na_6Al_6Si_6O_{24} \cdot 8H_2O$) is discerned through these techniques.

In the case of samples containing lead, formation of Pb_3SiO_5 can be observed through XRD (see Fig. 2). In this case, the formation of zeolites of the herschelite type is also observed.

Finally, the results related to the leaching tests are as follows.

Regarding activated fly ash matrices that contained chromium, no data could be drawn since they were not sound enough and they broke when they were pulled out of the mould.

However, in similar ash matrices containing lead the situation was very different. Table 4 shows the amount of leached lead for every tested age (lead was measured through ICP).

As performed in the first part of this research [12], taking as a base the consideration that leaching occurs through diffusion mechanisms and applying the equations by Godbee et al. [13], the coefficient of effective diffusion (D_e), F parameter and the leaching rate (L_i) were determined (see Table 5).

This leaching rate (L_i) characterises the resistance against leaching of the element confined within the activated fly ash matrix, in such a way that the higher its value, the more strength this element opposes leaching. When the value of this parameter is more than 6, the matrix becomes efficient for confining the element.

Table 5
Results of the leaching tests of fly ash + 8 M NaOH + 3.125% Pb: F_j (cm), D_e ($cm^2\ s^{-1}$) and L_i

Leaching time (h)	F_j (cm) × 10^4	D_e ($cm^2\ s^{-1}$) × 10^{-13}	L_i
24	0.58	1.94	12.71
72	1.26	1.46	12.84
168	1.93	1.73	12.76
336	3.16	2.81	12.55
672	2.89	1.11	12.95
1344	4.87	1.46	12.83
2160	5.24	1.06	12.97

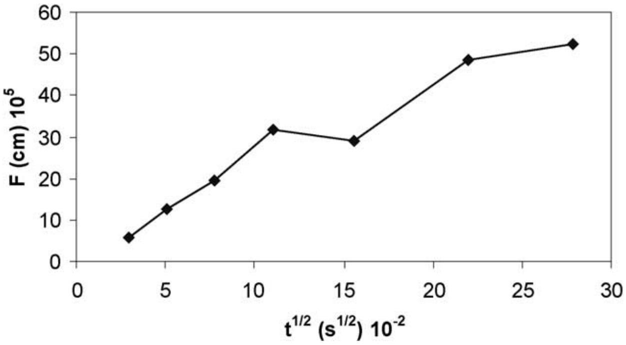


Fig. 4. F vs. $t^{1/2}$ for the activated fly ash matrix with 3.125% of lead.

Representation of F (cm) vs. t (s) and F (cm) vs. $t^{1/2}$ ($s^{1/2}$) shall indicate the mechanism through which leaching occurs in the studied matrix (see Fig. 4).

4. Discussion

The purpose of this research was, indeed, to prove the stabilisation/solidification capacity of a novel cementing matrix of activated fly ash when facing elements of acknowledged toxicity such as chromium and lead and to compare such capacity to that of Portland cement (confinement matrix of a rather broad use).

It is well known that alkali-activated fly ash encourages the formation of a pseudo-zeolitic amorphous polymer [14]. This compound has been characterised mostly through FTIR [15], NMR [16] and other analytical techniques [17]. Because of alkali activation, minor zeolitic compounds of the hydroxisodalite and/or herschelite type also appear. Na^+, which is in excess or which has not reacted yet, goes through carbonate and forms thermonatrite. On the other hand, quartz and mullite, which are usually present in fly ash, do not react during the activation process. Therefore, they are found in the phases of the final product.

4.1. Effect of chromium on alkali activation of fly ash

Activated fly ash samples that contained chromium were studied through XRD and FTIR techniques, which detected the presence of $Na_2CrO_4 \cdot 4OH_2O$. In the infrared spectrum, a band corresponding to chromate (CrO_4^{2-}) appeared at 885 cm^{-1} and XRD reveals the formation of $Na_2CrO_4 \cdot 4H_2O$ because of the peaks appearing at 2θ values of 19.86°, 17.53° and 27.72°.

In Ref. [18], no solubility value of this chromate has been found. Nevertheless, Ref. [18] just mentioned that it is a yellow compound, monoclinic, deliquescent and with a fusion temperature of 19.92 °C. The solubility value of Na_2CrO_4, which could be considered very close to that of chromate, is found in Ref. [18]. On the surface of some specimens, it could be observed that sodium chromate precipitated, which formed yellow crystals. This crystallisation was thought to be due to an environment with lesser relative humidity than the equilibrium humidity of the saturated solution of that salt, which justifies the precipitation of this chromate.

On the other hand, as explained before [12], fly ash activation occurs as a consequence of the interaction of NaOH present in mixing water, with vitreous silico-aluminates from the starting material. This interaction is responsible for the formation of a very compact, three-dimensional, pseudo-zeolitic structure that is capable of developing high mechanical strength just after the 24-h activation has started.

From mechanical strength values reported in Table 3, it is observed that chromium greatly affects the activation process of fly ash, even causing the neutralisation of strength development. The interpretation of these mechanical strength results is coherent with data obtained from mineralogical characterisation since most of the needed sodium for fly ash activation goes towards the formation of the $Na_2CrO_4 \cdot 4H_2O$ and not to formation of alkali–silica–aluminates. Moreover, it is possible that small amounts of Cr (smaller than 2.6% used in this work) affect, but in a lesser proportion, the mechanical evolution of this kind of matrix; however, due to the high solubility of this compound, an almost null fixation of chromium within the system is also expected and, on the contrary, a high leaching rate.

4.2. Effect of lead in matrices of alkali-activated fly ash

In this case, and according to the results obtained, it is confirmed that the new suggested system is capable of solidifying and stabilising lead to a great extent since concentrations of such element found in leaching after performing the MCC-1P test are in the range of parts per billion (leaching rate values, L_i, higher than 10 cm^2 s^{-1} have been obtained, which proves that the matrix recommended is efficient as lead solidification system).

Fly ash samples containing lead, studied through FTIR, did not show any band that could be assigned to any compound of this element. However, XRD detected the formation of Pb_3SiO_5 in the mentioned matrices (the presence of peaks appearing at values of 2θ of 29.10° and 33.20° proves it).

The solubility value of this lead silicate formed in the matrix made with alkali-activated fly ash has not been found in Ref. [18], but it has been found that other lead silicates, such as Pb_5SiO_7 or $PbSiO_3$, show a very low solubility, which would account for the very low lead concentrations detected in the fluid after carrying out the different leaching tests.

In the cementing system of this study, a decrease of mechanical strength resulting from the presence of the toxic element is observed (see Table 3). In spite of this fact, acceptable mechanical strength is obtained.

As for mechanisms through which leaching of lead occurs, they can be studied by means of parameter F_j. It is inferred, in accordance with Fig. 4, that the mechanism controlling lead leaching is diffusion.

4.3. Effect of chromium and lead on Portland cement matrices

No data on mechanical strength have been obtained from cement samples with lead since they do not get hydrated and they break before pulling them out from the mould. This inhibition of the cement hydration can be due to the formation of a lead sulphate as suggested by Ortego et al. [19] or even to the formation of a layer of metallic ions around the C_3S, which prevents the access of water to the cement grains, as proposed by Tashiro [20].

However, the effect of chromium on the mechanical strength of Portland cement has to be pointed out. When adding 2.60% of such element, a decrease of initial strength occurs at one curing day (see Table 3), although at 28 curing days, the strength values obtained are equal to those of the reference test sample.

5. Conclusions

Here are the main conclusion drawn out from this research:

(a) The matrix of alkali-activated fly ash is not only unable of solidifying and stabilising chromium but also can gets null in the presence of 2.60% of such element.

(b) Chromium affects the activation mechanism of fly ash and, consequently, its hardening process, since $Na_2CrO_4 \cdot 4H_2O$ is formed. This compound holds a high solubility.

(c) In Portland cement systems, chromium is found in the form of Ca_2CrO_4, which induces a rise in the mechanical strength, compared to samples that does not contain such element.

(d) It appears reasonable to state that the proposed cementing system of alkali-activated fly ash is able of solidify and stabilise lead since the analysed concentrations of this element from leaching are in the range of parts per billion. The mechanism that controls lead leaching in those matrices is diffusion.

(e) It has been proven through FTIR and XRD that the lead compound formed in the matrix made of fly ash is Pb_3SiO_5, a very insoluble compound that assert the results of the leaching tests.

(f) Lead inhibits hydration of Portland cement in such a way that test samples break before they are removed from the moulds.

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References

[1] O.E. Otomoso, D.G. Ivey, R. Mikula, Electron microscopic and ^{29}Si-nuclear magnetic resonance spectroscopic studies of chromium doped tricalcium silicate, in: J.P. Hager, B. Mishra, C.F. Davidson, J.L. Litz (Eds.), Treatment and Minimisation of Heavy Metal-Containing Wastes, 1995, pp. 129–141.

[2] P.L. Bishop, Leaching of inorganic hazardous constituents from stabilized/solidified hazardous wastes, Hazard. Waste Hazard. Mater. 5 (1988) 129–143.

[3] S. Wang, C. Vipulanandan, Solidification/stabilization of Cr (VI) with cement. Leachability and XRD analyses, Cem. Concr. Res. 30 (2000) 385–389.

[4] E. Zamorani, I.A. Sheikh, M. Della Rosa, G. Serrini, Physical properties and leachability of MLW stream containing Cr, Ni and Cd inmobilised in a cement matrix, in: W. Lutze, R.C. Ewing (Eds.), Mater. Res. Soc. Symp. Proc. 127, 1989, pp. 489–494.

[5] F.K. Cartledge, L.G. Butler, D. Chalasani, H.C. Eaton, Immobilization mechanisms in solidification/stabilization of Cd and Pb salts using Portland cement fixing agents, Environ. Sci. Technol. 24 (1990) 867–873.

[6] N.M. Alford, A.A. Rahman, The effect of lead nitrate on the physical properties of cement pastes, Cem. Concr. Res. 11 (2) (1981) 235–245.

[7] G. Thevenin, J. Pera, Interactions between lead and different binders, Cem. Concr. Res. 29 (1999) 1605–1610.

[8] L. Chatelet, J. Yvon, J.Y. Bottero, A. Bouchelanhem, in: N.J.M. Cases, F. Thomas (Eds.), Statut des sels de plomb et de zinc dans les matrices à base de ciment, 1er congrès international, Sur les P.S.S., F. Thomas, Grenoble, France, 1995, pp. 199–206.

[9] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, L. Lorenzen, Factors affecting the immobilization of metals in geopolymerized fly ash, Metall. Mater. Trans., B, Proc. Metall. Mater. Proc. Sci. 29B (1998) 283–291.

[10] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, L. Lorenzen, The potential use of geopolymeric materials to immobilise toxic metals: Part I. Theory and applications, Miner. Eng. 10 (7) (1997) 659–669.

[11] UNE-EN 196-1, Métodos de ensayos de cementos: Parte 1. Determinación de resistencias mecánicas, 1996, pp. 461–491.

[12] A. Palomo, J.I. Lopez de la Fuente, Alkali activated cementitious materials: Alternative matrices for the immobilisation of hazardous wastes: Part I. Stabilisation of boron, Cem. Concr. Res. (this volume).

[13] H. Godbee, et al., Application of mass transport theory to the leaching of radionuclides from solid state waste, Nucl. Chem. Waste Manag., (1980) 29 (Section 1).

[14] A. Palomo, M.T. Blanco-Varela, M.W. Grutzeck, Alkali-activated fly ashes. A cement for the future, Cem. Concr. Res. 29 (8) (1999) 1323–1329.

[15] A. Palomo, F.P. Glasser, Chemically-bonded cementitious materials based on metakaolin, Br. Ceram. Trans. J. 91 (1992) 107–112.

[16] A. Palomo, S. Alonso, Alkaline activation of fly ashes. A NMR study of the reaction products, Cem. Concr. Res. (submitted for publication).

[17] M.L. Granizo, S. Alonso, M.T. Blanco-Varela, A. Palomo, Alkaline activation of metakaolin. Effect of calcium hydroxide in the products of reaction, J. Am. Ceram. Soc. 85 (1) (2002) 225–231.

[18] R.C. Weast (Ed.), Handbook of Chemistry and Physics, 49th ed., 1968–1969, pp. B211–B246.

[19] D.J. Ortego, S. Jackson, G.S. Yu, H. McWhinney, D.L. Cocke, Solidification of hazardous substances: A TGA and FTIR study of Portland cement containing metal nitrates, J. Environ. Sci. Health A24 (6) (1989) 589–602.

[20] C. Tashiro, The effects of several heavy metal oxides on the hydration and the microstructure of hardened mortar of C_3S, 7ème Congr. Int. Chim. Cim. (Paris) II (1980) 37–42.