

# Chemistry and microstructure of cement pastes admixed with organic liquids

I. Natali Sora<sup>a</sup>, R. Pelosato<sup>a</sup>, D. Botta<sup>b</sup>, G. Dotelli<sup>b,\*</sup>

<sup>a</sup>*INFM and Laboratorio di Chimica Strutturistica, Dip. di Ingegneria Meccanica, Università di Brescia, via Branze 38, 25123 Brescia, Italy*

<sup>b</sup>*Dip. di Chimica Industriale e Ingegneria Chimica, Politecnico di Milano, P.zza L. da Vinci 32, 20133 Milano, Italy*

Received 26 April 2001; accepted 26 September 2001

---

## Abstract

The influence of organic admixtures on hydration process of cement pastes have been investigated to assess the possibility of immobilizing toxic organic wastes in cement-based materials. The model organic waste used is a mixture of water, methanol and 2-chloroaniline: 100/76/4 volume ratios, respectively. Four pastes were obtained admixing this solution with two different cements (ordinary and white Portland), with weight ratios equal to 0.40 and 0.65, respectively; in addition, cement pastes without organic wastes were prepared (water to cement ratio 0.40). The progress of hydration process of these six series of samples was monitored for the first 8 months of ageing by thermogravimetric analysis; moreover, a detailed microstructural investigation on mature pastes was performed by quantitative X-ray diffraction and scanning electron microscopy. Dynamic leach tests were carried out on samples cured for 28 days, according to the international standards. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Cements; Microstructure; Organic waste; Solidification; Stabilisation

---

## 1. Introduction

In recent years the effect of organic admixtures on physical and mechanical properties of cement-based materials has been the subject of extensive research<sup>1</sup> and their use is becoming more and more widespread in the field of building materials.<sup>2</sup>

In the building industry organic admixtures are used to improve the properties of the final products and the amount added with respect to the binder is invariably very low, normally no more than a few weight percentages. On the contrary, a completely different approach must be adopted in a cement-based stabilisation/solidification (S/S) technology,<sup>3</sup> because the larger the amount of waste entrapped, the more effective is the process. Indeed, S/S may be broadly defined as a treatment process aimed to contain a waste by chemical binding or by complexing or simply by physical entrapping and to prevent it from entering the environment. Cement-based S/S technology is currently applied in the treatment of hazardous wastes prior to landfilling and it is particularly effective when dealing with low-level

radioactive wastes<sup>4</sup> and heavy-metal bearing sludge,<sup>5</sup> even if chemical and microstructural changes induced in the hardened cement matrix are incompletely understood.<sup>5,6</sup> However, this process is not currently viewed as applicable in the treatment of liquid organic wastes, because they have been shown to have a generally detrimental effect on the properties of cementitious materials;<sup>7</sup> moreover, they could be released during the mixing or curing process. This serious drawback might be avoided using adsorbents for the organic component of the industrial waste, prior to conventional cement-based solidification. Research on this subject is very active and the organophilic clays seem to be the most promising choice<sup>8</sup> but the properties of products obtained by mixing of organophilic clays containing the organic waste with cement are barely known:<sup>9–11</sup> the effect of specific waste components on the physical and permeability properties of cemented materials has even less well investigated.<sup>12</sup>

The preparation of the cemented waste requires prolonged contact with water (setting period and afterwards), which might cause the release of the organic, even if pre-adsorbed on the organophilic clay. Considering that even low concentrations of organic compounds may interfere with cement set, this problem must be seriously taken into account.

---

\* Corresponding author. Tel.: +39-02-23993232; fax: +39-02-70638173.

*E-mail address:* [giovanni.dotelli@polimi.it](mailto:giovanni.dotelli@polimi.it) (G. Dotelli).

The aim of this work is to investigate the effects of the addition of large amounts of liquid organic streams to a cement paste and particularly the influence of the organics on the hydration process. The model waste here adopted is a solution of 2-chloroaniline, representative of an important class of toxic compounds (aromatic amines), dissolved in water and methanol. The latter is mainly added to make the liquid phase homogeneous; indeed, the 2-chloroaniline has a low solubility in water: 3670 mg/l.<sup>13</sup> Moreover, the presence of the methanol makes the model waste more similar to the industrial streams, which are usually complex mixtures. The progress of hydration was studied by measuring several parameters by thermogravimetric (TGA) analysis; moreover, a detailed microstructural investigation was performed on mature cement pastes (5 months) by quantitative X-ray diffraction (QXRD) and scanning electron microscopy (SEM equipped with EDS); in addition, the degree of immobilisation of 2-chloroaniline was assessed via dynamic leach testing (DLT).

## 2. Experimental

### 2.1. Sample preparation

Two types of Portland cements, as supplied by the producer, were used to prepare the samples: CEM I 42.5 and CEM II/B-L 42.5R, according to UNI ENV 197. Hereafter the two cements will be briefly referred to as CEM 1 and CEM 2, respectively, and the usual abbreviations of the cement chemistry nomenclature will be used: SiO<sub>2</sub> = S, Al<sub>2</sub>O<sub>3</sub> = A, SO<sub>3</sub> = S, MgO = M, CaO = C, Fe<sub>2</sub>O<sub>3</sub> = F, CO<sub>2</sub> = C, H<sub>2</sub>O = H. The first cement is an Ordinary Portland Cement (OPC), while the second is a white cement containing large amounts of calcium carbonate; the raw oxide and Bogue compositions of the OPC and of the white cement clinker are reported in Table 1. Two pastes were prepared from the powders mixed with deionized water only (water to cement, w/c, 0.40); four pastes were obtained by admixing the cement with aqueous organic solutions in two different weight ratios: solution to cement (s/c) 0.40 and 0.65, respectively. The homogenous aqueous solution was obtained by mixing water, methanol and 2-monochloroaniline (2MCA) in the following volume ratios: 100/76/4 (for the solution composition see Table 2). Details of the six samples, together with their short designations are reported in Table 3. The hand mixed pastes were cast into PMMA moulds (18.0×5.0×5.0 cm), partially filled and sealed on top with polyethylene films. The moulds were vibrated for one minute to remove any air bubbles and voids. After 1 or 2 days, depending on samples, the hardened blocks (18.0×5.0×1.0 cm) were demoulded, crushed into smaller pieces, put in the moulds and sealed again. The environmental chamber, where the

Table 1

Raw oxide composition and Bogue calculation for the two cements used in the experiments (all data are in wt.%)<sup>a</sup>

UNI ENV 197	CEM I 42.5 CEM 1	CEM II/B-L 42.5 R CEM 2
CaO	60.94	68.6 <sup>b</sup>
SiO <sub>2</sub>	20.56	23.8 <sup>b</sup>
Al <sub>2</sub> O <sub>3</sub>	4.97	3.95 <sup>b</sup>
Fe <sub>2</sub> O <sub>3</sub>	2.53	0.19 <sup>b</sup>
SO <sub>3</sub>	3.16	–
MgO	2.53	0.98 <sup>b</sup>
K <sub>2</sub> O	1.01	0.14 <sup>b</sup>
Na <sub>2</sub> O	1.25	0.77 <sup>b</sup>
LOI	3.91	0.68 <sup>b</sup>
TOTAL	100.86	99.11 <sup>b</sup>
Insoluble residue	1.47	0.58 <sup>c</sup>
CaO free	0.81	–
LOI	–	10.81 <sup>c</sup>
<i>Bogue calculation</i>		
C <sub>3</sub> S	38.43	50.03
C <sub>2</sub> S	26.99	9.73
C <sub>3</sub> A	7.60	7.06
C <sub>4</sub> AF	7.69	0.40
CS*H <sub>2</sub>	6.79	8.60
Total	87.52	75.81

<sup>a</sup> CEM 2 contains large amounts of a secondary constituent, i.e. limestone, and this explains the high values of cement LOI.

<sup>b</sup> Raw oxide composition and LOI refers to the clinker phase.

<sup>c</sup> Insoluble residue and LOI refers to the cement.

samples were cured was at 23±1 °C and 50% RH. At different curing times crushed samples of each series were extracted from the ageing chamber and dried to constant weight at 85 °C for 8 h, to stop hydration: free liquid (water or water and methanol, depending on the samples) was thereby eliminated. Dried samples were grounded in an agate mortar, sieved to minus 80 mesh and the resulting powders stored in desiccators.

### 2.2. Thermogravimetric analysis (TGA)

TGA analysis was carried out in nitrogen on about 20 mg of powdered dried heating to 900 °C at 10 °C/min rate. Three weight-loss parameters were obtained from the thermogravimetric curve: 100–400 °C, 100–900 °C (loss on ignition, LOI) and the stepwise loss associated with the calcium hydroxide dehydration, occurring between 425 and 550 °C. All values (including free liquid) are reported as grams per gram of ignited residue and are corrected with respect to the thermogravimetric loss of unreacted cement powder.

### 2.3. X-ray diffraction analysis

The X-ray diffraction (XRD) data were collected at room temperature with a Philips PW 1710 diffractometer, using graphite monochromated Cu-K<sub>α</sub>

Table 2  
Composition of the organic solution used and physical properties of the substances<sup>a</sup>

Compound	Volume fractions	Molar fractions	Weight fractions	Molecular weight (g/mol)	Specific gravity (g/cm <sup>3</sup> )
Water	0.56	0.750	0.61	18.01	1.020
Methanol	0.42	0.245	0.36	32.04	0.787
2-Chloroaniline	0.02	0.005	0.03	127.58	1.212

<sup>a</sup> The estimated density of the solution is 0.902 g/cm<sup>3</sup>, while calculated with the following formula:  $\rho = \sum_{i=1}^3 \rho_i w_i$ , results 0.925 g/cm<sup>3</sup>, where  $w_i$  are weight fractions.

Table 3  
Compositions of the six series of pastes prepared; in the four columns abbreviations, type of cement, water to cement ratio and water to organic solution ratio are reported

Sample	Cement	Water/cement ratio	Solution/cement ratio
D5 <sup>a</sup>	CEM I 42.5	0.40	–
D6	CEM I 42.5	0.25	0.40
D7	CEM I 42.5	0.40	0.65
D8 <sup>a</sup>	CEM II/B-L 42.5 R	0.40	–
D9	CEM II/B-L 42.5 R	0.25	0.40
D10	CEM II/B-L 42.5 R	0.40	0.65

<sup>a</sup> These pastes do not contain organic compounds.

radiation. The step scan was 0.02° and the measurement time of 4 s per step. The solidified specimens were ground in an agate mortar. The XRD line profile analysis of heavily overlapping peaks was made using the WINFIT computer program.<sup>14</sup> The fitting parameters were refined by the Levenberg–Marquardt method.<sup>15</sup> The profile shape function used is a split Pearson VII. The refined profiles were used for the determination of peak positions, intensities and areas.

The hydration of the cement pastes was estimated by calculating the amount of calcium hydroxide, which is a crystalline product of the hydration reactions of tricalcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>) and β-dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>). The quantitative X-ray diffraction analysis (QXDA) was applied by using the equation proposed by Copeland and Bragg<sup>16</sup> relating the ratio of the intensities ( $I_0$  and  $I_1$ ) of the XRD lines of two components of a mixture to the ratio of the weight fractions ( $w_0$  and  $w_1$ ) of those components

$$I_1/I_0 = aw_1/w_0 \quad (1)$$

where  $a$  is a proportionality constant.

#### 2.4. Scanning electron microscopy

A scanning electron microscope (SEM) equipped with a Link energy dispersive spectrometer (EDS) was used for the morphological and chemical analysis of the hydrated samples. The polished samples were gold coated to prevent charging effects.

#### 2.5. Leach test

The toxicity characterization leaching procedure (TCLP) was carried out in compliance with the UNI 8798 standard and the dynamic leaching test (DLT) performed. The fresh pastes were cast into cylindrical PVC moulds (3.2 cm height and 22 cm diameter), sealed and cured for 28 days in a room at 23 ± 1 °C and 50% RH. Then the six samples were demoulded, smoothed with emery polishing paper and cleaned with a compressed air jet. Afterwards, each of them was hung in a 500 ml jar, capped with a PTFE-lined screw cap. Deionized MilliQ water was poured until a 250 ml volume, in which the cement cylinder was completely immersed: the samples were maintained at 24 °C, without agitation, for predetermined times. The water was periodically renewed.

#### 2.6. Enrichment and analysis

The aqueous solution (250 ml) was transferred into a conical flask, to which 1 ml of isooctane was added. The mixture was shaken for 5 min and left for 15 min. Then MilliQ water was added through the side arm until to raise the level of the organic layer in the central arm of the liquid microextraction device. Afterwards the extract was collected and transferred into a 1-ml calibrated glass vial to get a measure of recovery. One ml of each sample was injected in a gas chromatograph. The 2-chloroaniline analysis was performed with a Carlo Erba Mega mod.5100 instrument, equipped with an on-column injector, a flame ionization detector and a HP fused silica capillary column, 0.32 mm internal diameter, 50 m length, coated with a 5% phenylmethylsilicone rubber, 0.5 mm thickness. The oven temperature was increased from 70 to 130 °C at 4 °C/min, then at 10 °C/min until 250 °C, with a final isothermal time of 5 min. The 2-chloroaniline concentration was determined by comparison with standard solutions.

### 3. Results and discussion

#### 3.1. Thermogravimetric analysis

In normal cement pastes, i.e. those obtained by mixing water and cement powder, water that did not yet

react with cement has to be removed, usually by drying the paste at 105 °C in an atmosphere of uncontrolled humidity. This water is conventionally defined as “free water”,<sup>17</sup> while the water that has already reacted is called “bound water”. In fact, there are at least two different types of bound water: chemically bound, which has been directly incorporated into the structure of the cement hydration products, and physically bound, which is strongly adsorbed on the surfaces of the cement particles and reaction products. However, in the present case the initial liquid phase is a solution containing about 40% by weight of organic compounds (Table 2) and especially methanol whose boiling point is 64.65 °C; thus free water should be better-defined as free solution, but for simplicity we will stick to the usual definition. It is highly probable that the methanol be almost completely evaporated on first drying, even considering that no new phases were detected by XRD analysis, as pointed out below; on the contrary, the 2-chloroaniline may be supposed to stay in the sample, since its boiling point is 209 °C. Anyway, a more gentle drying procedure have been followed, i.e. prolonged desiccation at 85 °C.

Results obtained from the thermogravimetric analysis are shown in Figs. 1 and 2 for the two triplets D5, D6, D7 and D8, D9, D10, respectively. In detail, the weight-loss between 105 and 400 °C ( $w_{\text{CSH}}$ ) is due to decomposition of hydration products<sup>18</sup> other than calcium hydroxide, which is instead determined by the stepwise loss<sup>19</sup> at around 500 °C ( $w_{\text{CH}}$ ). The LOI, determined by the thermogravimetric loss between 105 and 900 °C ( $w_{\text{LOI}}$ ), is used to calculate the total degree of hydration ( $\alpha$ , reported in Figs. 1a and 2a). In order to have an estimation of the hydration degree of the six pastes, starting with a simplified hydration reaction scheme<sup>20</sup>, it is possible to calculate the water amount needed to completely hydrate the cement ( $w_{\text{T}}$ ), once the Bogue phase calculation has been performed. In the present case it was obtained  $w_{\text{T}}$  equal to 0.267 and 0.211 g of water per gram of ignited residue for CEM1 and CEM2, respectively; then the calculated degree of hydration results  $\alpha = w_{\text{LOI}}/w_{\text{T}}$ .

As expected, addition of the organic mixture to the paste had a remarkable retarding effect on the hydration process of both cements (Figs. 1a and 2a): reaction started after almost 1 week and then accelerated. Indeed, it is well known that alcohols, among which methanol<sup>3</sup> and phenol,<sup>21</sup> not only have a retarding effect on the hydration process, but also contribute to the formation of amorphous portlandite; on the contrary, there is a complete lack of information on the influence of aromatic amines on setting and hardening of cement pastes.

After eight months the samples containing the largest amount of water, i.e. D7 and D10, almost equated the hydration degree of the organic-free pastes D5 and D8; indeed, these four pastes contained equal amounts of water, i.e. 40 g per 100 g of cement powder. The amount

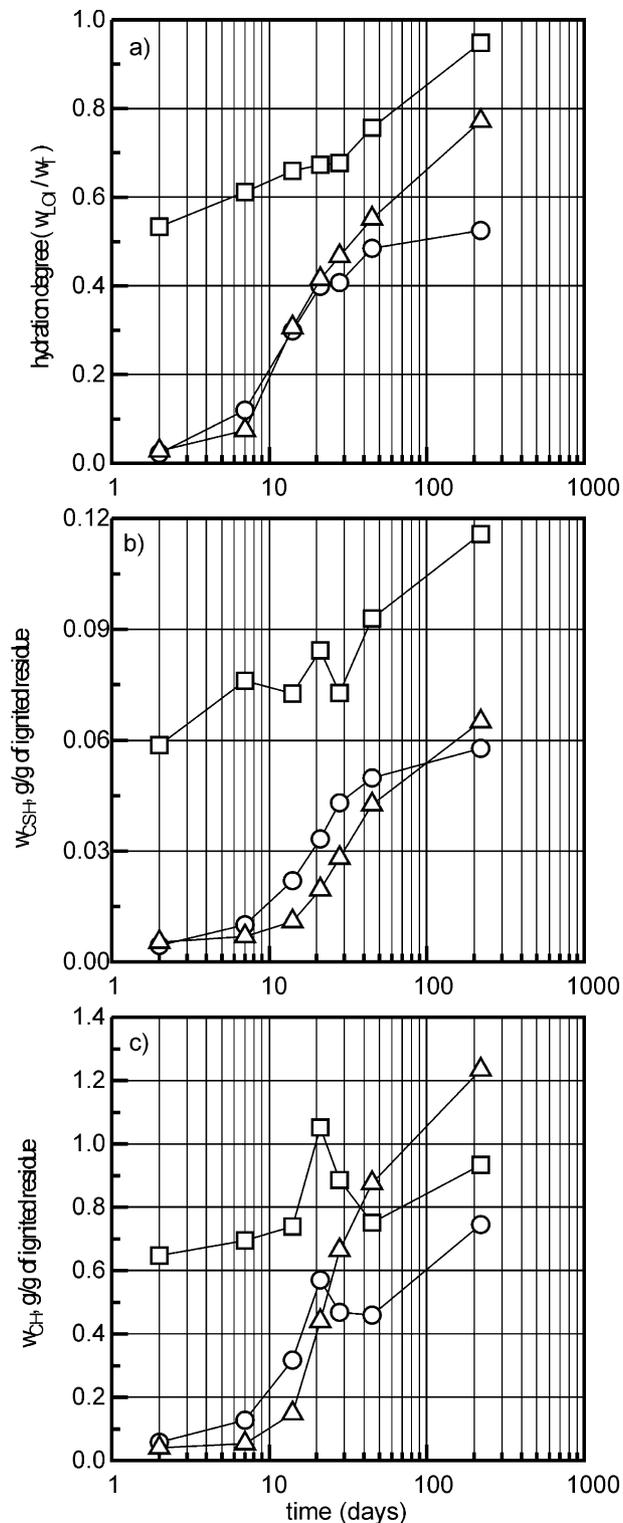


Fig. 1. Thermogravimetric results for samples D5 ( $\square$ ), D6 ( $\circ$ ) and D7 ( $\triangle$ ) at different curing times: (a) hydration degree  $\alpha = w_{\text{LOI}}/w_{\text{T}}$ ; (b) weight loss between 105 and 400 °C,  $w_{\text{CSH}}$ ; (c) calcium hydroxide,  $w_{\text{CH}}$ ; all data are in grams per gram of ignited residue.

of hydration products,  $w_{\text{CSH}}$ , other than portlandite was practically the same in all pastes containing the organic admixture but was substantially lower than in the normal

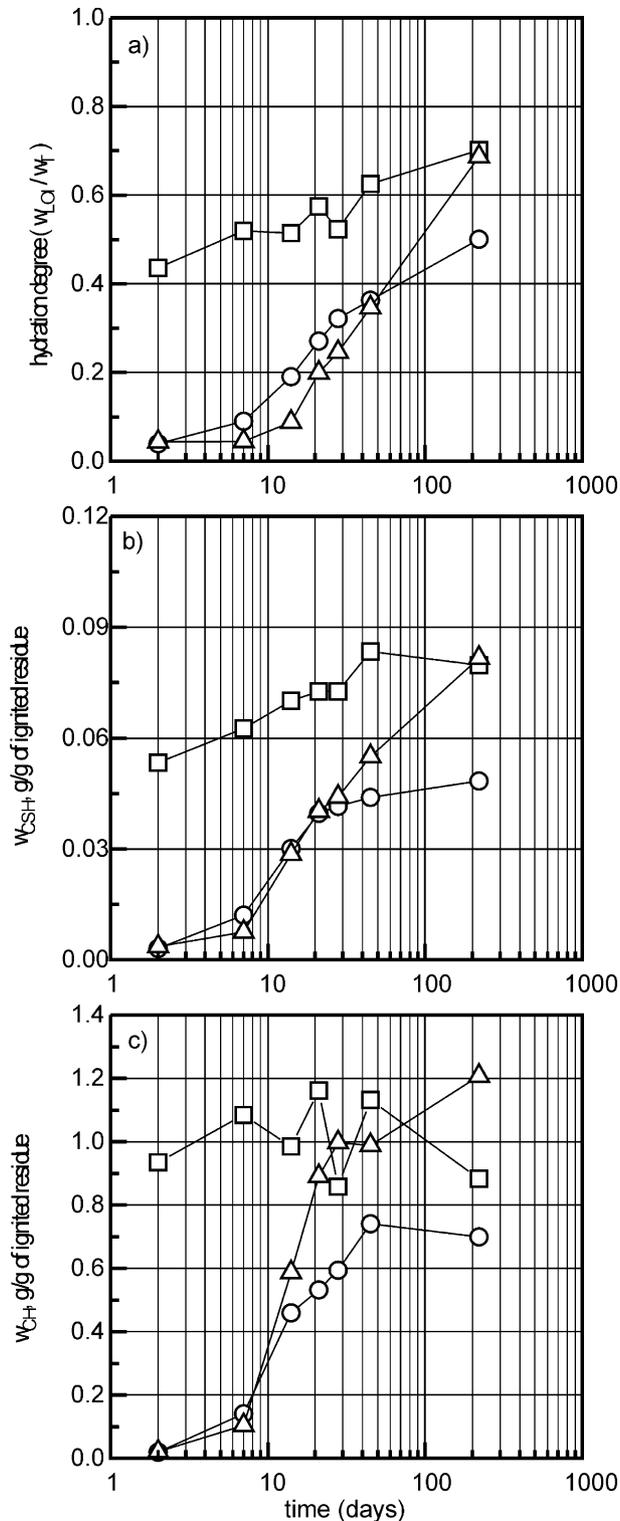


Fig. 2. Thermogravimetric results for samples D8 ( $\square$ ), D9 ( $\circ$ ) and D10 ( $\triangle$ ) at different curing times: (a) hydration degree  $\alpha = w_{LOI}/w_T$ ; (b) weight loss between 105 and 400 °C,  $w_{CSH}$ ; (c) calcium hydroxide,  $w_{CH}$ ; all data are in grams per gram of ignited residue.

pastes (Figs. 1b and 2b), apart from sample D10 whose hydration sped up after the first two months of curing. In all the organic-containing samples, the amount of

calcium hydroxide behaved similarly: it increased much more rapidly than in normal pastes (Figs. 1c and 2c), for instance in samples D7 and D10 exceeded that of normal pastes. Indeed, the portlandite content increased almost continuously with hydration in all the organic-containing samples, although  $w_{CH}$  data for D5 and D8 were scattered and almost constant only on average (Figs. 1c and 2c). This might be explained either by the occurrence of accidental carbonation or by the formation of carbonated compounds. In fact, XRD patterns showed the presence of  $Ca_4Al_2O_6CO_3 \cdot 11H_2O$  only in samples D5 and D8, while there was no other evidence of strong carbonation.

In samples D6 and D9, containing small amounts of water, the hydration process slowed down with curing time and the hydration degree was always lower than in D5 and D8, while in D7 and D10 the opposite is true: after the first week, there was an increase of  $\alpha$ . As a result, the addition of the organic admixture seemed to have a retarding effect on the hydration, without suppressing it; indeed, at late stages of curing the controlling factor is the water/cement (w/c) ratio: samples D6 and D9, i.e.  $w/c = 0.25$ , reached 50% hydration in 8 months, while D7 and D10 reach more than 70% but is still increasing.

### 3.2. Microstructural characterisation

The powder diffraction patterns from 5-month-old hydrated pastes prepared with OPC and white Portland cement are shown in Figs. 3 and 4, respectively: the main clinker phases (alite, belite, aluminate phase and ferrite phase), calcite, magnesium oxide and few products of hydration reactions (calcium hydroxide, ettringite, hydrogarnet,  $Ca_4Al_2O_6CO_3 \cdot 11H_2O$  and amorphous calcium silicate hydrate (C-S-H)) were identified. D5 paste had very small amounts of alite, aluminate phase and ferrite phase, while in patterns of D6 and D7 pastes no evidence of  $Ca_4Al_2O_6CO_3 \cdot 11H_2O$  was found. In patterns of Fig. 4 alite, belite, calcite, magnesium oxide and few products of hydration reactions (calcium hydroxide, ettringite,  $Ca_4Al_2O_6CO_3 \cdot 11H_2O$  (in sample D8) and amorphous calcium silicate hydrate (C-S-H)) were identified.

The hydration of the samples was estimated by using Eq. (1). In order to calculate the proportionality constant  $a$  of Eq. (1) calibration curves were obtained from X-ray intensity measurements on binary mixtures of calcium carbonate,  $CaCO_3$ , and calcium hydroxide,  $Ca(OH)_2$ , for which the ratio of the weight fractions was known. Since the three pastes were prepared simultaneously for both cements, accidental carbonation by reaction of calcium hydroxide with carbon dioxide from the atmosphere occurred to the same extent in each batch. This assumption is corroborated by the fact that the areas under non-overlapping calcite peaks at  $d$ -spacing 2.49, 2.28 and 1.87 Å are similar for all ordinary

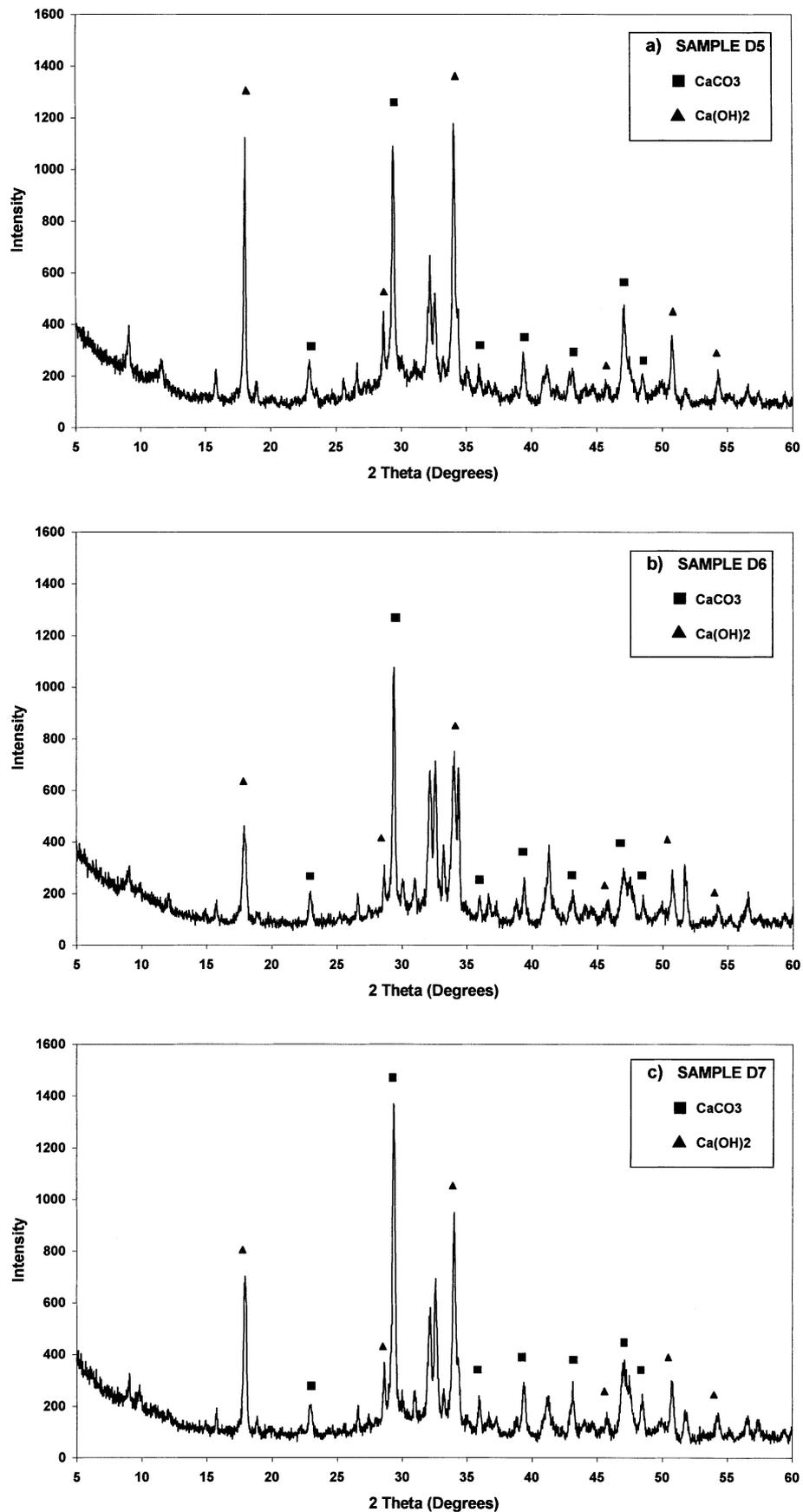


Fig. 3. XRD patterns of 5-month-old cement pastes from CEM 1 (D5, D6, D7).

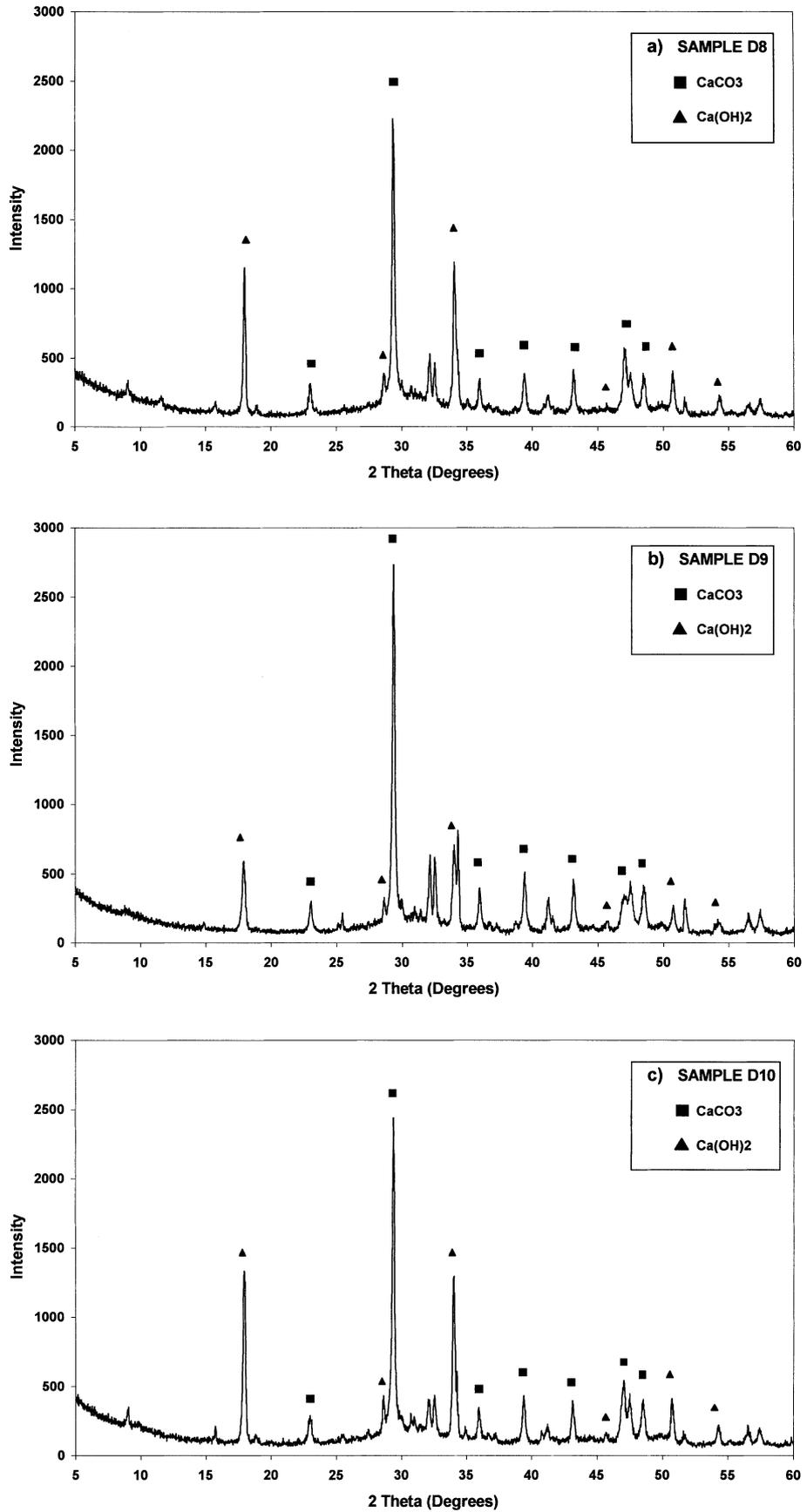


Fig. 4. XRD patterns of 5-month-old cement pastes from CEM 2 (D8, D9, D10).

Portland cement-based (CEM1) pastes. The areas under the corresponding calcite peaks for all pastes based on white Portland cement (CEM2) were about twice of those for ordinary Portland cement based pastes. In view of these considerations, calcite diffraction peaks at  $d$ -spacing = 2.49, 2.28 and 1.87 Å were used as reference standard whereas the  $\text{Ca}(\text{OH})_2$  relative weight fraction  $w^R$  was measured from peaks at  $d=4.89$ , 2.62 and 1.79 Å. The parameters  $w^R$  of samples D6 and D7 are defined as the ratio of their  $\text{Ca}(\text{OH})_2$  absolute weight fraction to that for specimen D5, which was prepared without methanol and 2MCA. The values of  $w^R$  for specimens D6 and D7 are about 0.57 and 0.60, respectively. Correspondingly, the values of  $w^R$  for specimens D9 and D10 are about 0.36 and 1.01 of the absolute weight fraction for D8, respectively. The apparent poor agreement with the results of thermogravimetric analysis is partly due to the formation of amorphous portlandite, as already observed by other researchers;<sup>21</sup> furthermore, it should be remembered that the microstructural characterisation has been performed on 5 month-aged samples, while the last thermogravimetric analyses were on samples 8 months old; in these 3 months a sharp increase in carbonation of some samples has been observed by TGA measurements.

A semi-quantitative analysis was made to determine the degree of reaction of the main clinker phases (alite, belite, aluminate phase and ferrite phase) of the 5-month-old cement pastes. The evaluation was performed by means of the strongest XRD lines of tricalcium aluminate and ferrite phase at  $d=2.70$  Å and at about  $d=2.64$  Å, respectively, taking account of overlapping peaks from the hydration products. In particular, in the range of  $d$ -spacing 2.60–3.10 Å the diffuse peak of amorphous or poorly crystalline calcium silicate hydrate (C-S-H) was subtracted. For alite and belite the analysis is complicated by the fact that every belite diffraction peak sufficiently intense for QXRD is overlapped by an adjacent alite peak; the peaks at  $d=2.97$  Å and  $d=2.75$  Å were used for alite and belite, respectively. Table 4 shows results. In pastes D6 and D9, mixed with an aqueous solution of methanol and 2MCA (weight ratio solution/cement,  $s/c$ , 0.4), the hydration reactions of the main clinker phases were significantly slower than in pastes D5 and D8 prepared

with water and cured under the same conditions. Paste D7 exhibited different behaviour than paste D10. It is worth noting that in white Portland cement pastes the hydration reactions are less retarded in comparison to

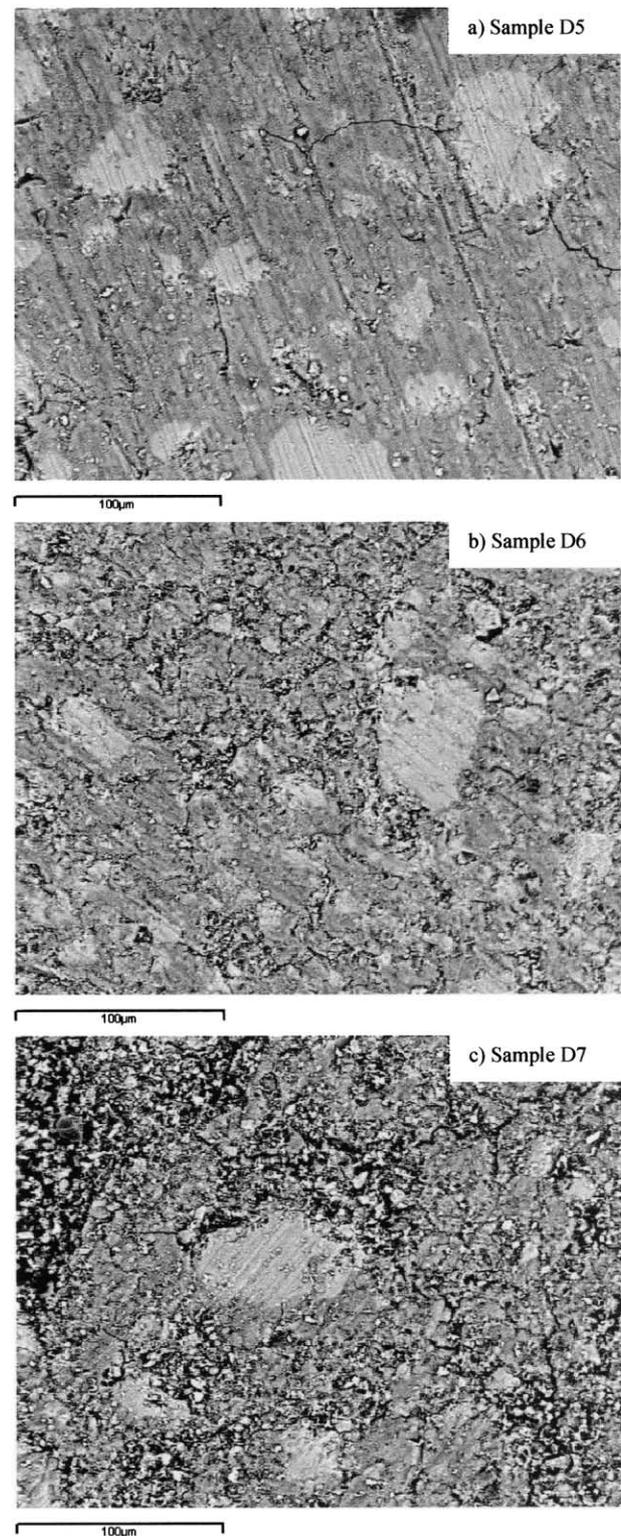


Fig. 5. SEM micrographs of 5-month-old cement pastes from CEM 1 (D5, D6, D7).

Table 4

The results of the semi-quantitative analysis on unreacted alite and belite phases and those from QXDA for  $\text{Ca}(\text{OH})_2$  on 5-month-old samples

Ratio	$w^R$ ( $\text{Ca}_3\text{SiO}_5$ )	$w^R$ ( $\beta\text{-Ca}_2\text{SiO}_4$ )	$w^R$ ( $\text{Ca}(\text{OH})_2$ )
D6/D5	2.1	1.7	0.57
D7/D5	1.9	1.6	0.60
D9/D8	1.8	1.5	0.36
D10/D8	0.9	1.1	1.01

those prepared with ordinary Portland cement of the same s/c ratio. There are conflicting reports on the effects of methanol on hydration reactions of alite and belite in pastes. Some authors found that primary aliphatic

alcohols alter the pore structures of cement pastes and that methanol reacts with calcium hydroxide giving calcium methoxide,<sup>22</sup> but there are contrasting opinions.<sup>23,24</sup> Anyway, in our study no evidence of calcium methoxide was found although effects on the pore structure could not be excluded.

Fig. 5 shows backscattered electron images of polished sections of 5-month-old pastes prepared with ordinary Portland cement. The EDX microanalysis indicated that in light grey areas of specimen D5 the Ca/Si ratio was about 2.0 while in D6 and D7 Ca/Si = 2.3

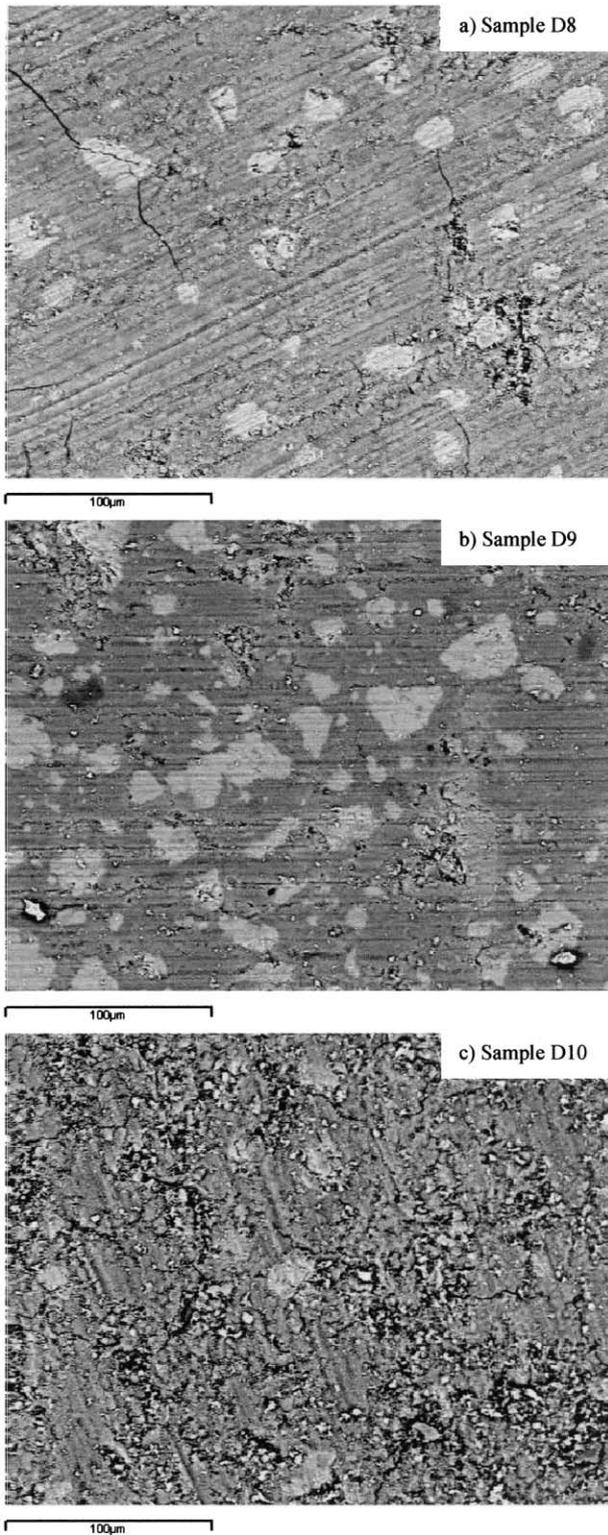


Fig. 6. SEM micrographs of 5-month-old cement pastes from CEM 2 (D8, D9, D10).

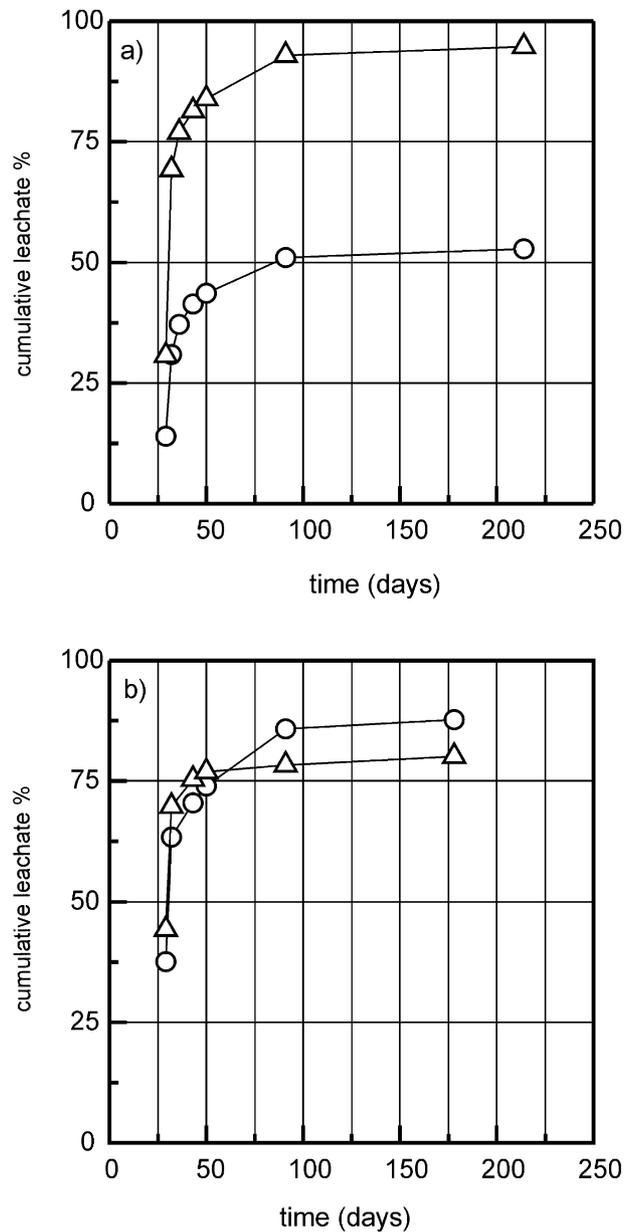


Fig. 7. Cumulative amount of 2-chloroaniline released during the dynamic leach test, started after 28 days of curing in the environmental chamber: (a) samples D6 (○) and D7 (△) and (b) samples D9 (○) and D10 (△). Data are referred to the total amount of 2-chloroaniline originally contained in the sample.

and 2.5, respectively. These results suggest that light grey areas consisted of  $\beta$ - $\text{Ca}_2\text{SiO}_4$  for D5 and of a mix of  $\beta$ - $\text{Ca}_2\text{SiO}_4$  and  $\text{Ca}_3\text{SiO}_5$  for D6 and D7. The dark grey regions formed the matrix in which the unreacted clinker phases were embedded and mainly consisted of hydration products. Small black areas indicating the presence of pores were more frequent in D7 and D6 than in D5.

Fig. 6 shows backscattered electron images of white Portland cement pastes, 5 months old. Three types of areas are visible: light grey regions of unreacted  $\beta$ - $\text{Ca}_2\text{SiO}_4$  and  $\text{Ca}_3\text{SiO}_5$  phases ( $\text{Ca}/\text{Si} = 2.6\text{--}3.0$ ), darker grey regions of hydration products and small black areas of pores. The porosity appeared larger in pastes D10 relative to pastes D8 and D9. As expected, in samples containing larger amounts of liquids,  $s/w = 0.65$ , the porosity was larger than in the other samples.

### 3.3. Leach test

Concentration of 2MCA in TCLP leachates was determined at each leachant renewal, according to the timetable suggested by the UNI standard. The DLT was performed for a total of seven and six progressive extractions for the two series of samples (D6–D7 and D9–D10), respectively: results are reported in Fig. 7 as total amount of 2MCA extracted (%) vs. curing time of monoliths; thus the results started after 28 days.

Fig. 7 clearly shows the inadequacy of cement pastes to immobilise 2MCA; indeed, more than 75% was released in all samples apart from D6, where the amount extracted was about 50% of the total. In all cases direct inclusion of an organic admixture in the paste gave poor results.

## 4. Conclusions

The addition of consistent amounts of water–methanol–2MCA solution to cement pastes retards the setting and hardening by some days and slows down the overall process for many weeks. However, the usual reactions do not seem to be altered, as suggested by the XRD analysis on mature samples. Moreover, it is likely that the methanol, due to its high vapour pressure, evaporates more completely than water leaving behind in the matrix just the 2MCA. Indeed, the DLT test confirms that the amount of 2MCA initially included in the monolith was still there but not firmly bound to the matrix, as it was progressively removed in leachates.

The results of the present investigation confirm the need of using sorbents to capture 2MCA, as they are not firmly immobilised in the cement paste. Moreover, where they moved to the pore water solution, for whatever reason, they would have been extracted with potential dispersion into the environment.

## Acknowledgements

The research have been supported from the Ministero dell'Università e della Ricerca Scientifica through the project COFIN 1999–2000. We also thank Riccardo Biancardi and Alessia Quaglia for their help in the numerical treatment of data.

## References

- Edmeades, R. M. and Hewlett, P. C., Cement admixtures. In *Lea's Chemistry of Cement and Concrete*, IV ed, ed. P. C. Hewlett. Arnold, London, 1998, pp. 837–901.
- Rixom, R. and Mailvaganam, N., *Chemical Admixtures for Concrete*, 3rd edn., E & FN Spon, London, 1999.
- Wiles, C. C., A review of solidification/stabilisation technology. *J. Hazard. Mater.*, 1987, **14**, 5–21.
- Zamorani, E., Deeds and misdeeds of cement composites in waste management. *Cem. Concr. Res.*, 1992, **22**, 359–367.
- Man-Chi Lo, I., Tang, C. I., Li, X.-D. and Poon, C.-S., Leaching and microstructural analysis of cement-based solidified wastes. *Environ. Sci. Technol.*, 2000, **34**, 5038–5042.
- Scheidegger, A. M., Wieland, E., Scheinost, A. C., Dähn, R. and Spieler, P., Spectroscopic evidence for the formation of layered Ni–Al double hydroxides in cement. *Environ. Sci. Technol.*, 2000, **34**, 4545–4548.
- Pollard, S. J. T., Montgomery, D. M., Sollars, C. J. and Perry, R., Organic compounds in the cement-based stabilisation/solidification of hazardous mixed wastes—mechanistic and process considerations. *J. Hazard. Mater.*, 1991, **28**, 313–327.
- Zhu, L., Chen, B. and Shen, X., Sorption of phenol, p-nitrophenol and aniline to dual-cation organobentonites from water. *Environ. Sci. Technol.*, 2000, **34**, 468–475 references therein.
- Montgomery, D. M., Sollars, C. J. and Perry, R., Optimization of cement-based stabilisation/solidification of organic-containing industrial wastes using organophilic clays. *Waste Man. Res.*, 1991, **9**, 21–34.
- Man-Chi Lo, I., Solidification/stabilization of phenolic waste using organic-clay complex. *J. Environ. Eng.*, 1996, 850–855.
- Jun, K.-S., Shin, H.-S. and Paik, B.-C., Microstructural analysis of OPC/silica fume/Na-bentonite interactions in cement based solidification of organic-contaminated hazardous waste. *J. Environ. Sci. Health*, 1997, **A32**, 913–928.
- Montgomery, D. M., Sollars, C. J., Perry, R., Tarling, S. E., Barnes, P. and Henderson, E., Treatment of organic-contaminated industrial wastes using cement-based stabilisation/solidification—I. Microstructural analysis of cement-organic interactions. *Waste Man. Res.*, 1991, **9**, 103–111.
- Yaws, C. L., *Chemical Properties Handbook*. McGraw-Hill, New York, 1999.
- Krumm, S., WINFIT beta Release 1.2.1 June 1997.
- Press, W. H., Teukolsky, S. A., Vetterling, W. T. and Flannery, B. P., *Numerical Recipes in C—the Art of Scientific Computing*, 2nd edn., Cambridge University Press, 1992.
- Copeland, L. E. and Bragg, R. H., Quantitative X-ray diffraction analysis. *Anal. Chem.*, 1958, **30**, 196–201.
- Odler, I., Hydration, setting and hardening of Portland cement. In *Lea's Chemistry of Cement and Concrete*, IV edn., ed. P. C. Hewlett. Arnold, London, 1998, pp. 241–297.
- Englert, G. and Wittmann, F., Water in hardened cement paste. *Mater. Construct.*, 1968, **1**, 535–546.
- Midgley, H. G., The determination of calcium hydroxide in set Portland cements. *Cem. Concr. Res.*, 1979, **9**, 77–82.
- Papadakis, V. G., Vayenas, C. C. and Fardis, M. N., Physical

- and chemical characteristics affecting the durability of concrete. *ACI Mater. J.*, 1991, **8**, 186–196.
21. Hebatpuria, V. M., Arafat, H. A., Rho, H. S., Bishop, P. L., Pinto, N. G. and Buchanan, R. C., Immobilisation of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon: leaching studies. *J. Hazard. Mater.*, 1999, **B70**, 117–138.
  22. Taylor, H. F. W., *Cement Chemistry*. Academic Press, London, 1990.
  23. Beaudoin, J. J., Gu, P., Marchand, J., Tamtsia, B., Myers, R.E. and Liu, Z., Solvent replacement studies of hydrated Portland cement systems: the role of calcium hydroxide. *Advn. Cem. Based Mater.*, 1998, **8**, 56–65.
  24. Hansen, E. W. and Gran, H. C., and Machabée, Y., FLR technique exchange of methanol/fluorescent dye with water in water-saturated cement paste examined by NMR. *Cem. Concr. Res.*, 2000, **30**, 535–541.