Effect of carbonation on properties of blended and non-blended cement solidified waste forms

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Abstract

Five types of cement and two pozzolans were used to investigate the influence of carbonation on the properties of solidified waste forms. The waste chosen was a commercially blended product which was mixed with cement and then cured in three different environments: nitrogen, air and carbon dioxide for 28 days. Samples were examined for strength development, setting time, microstructural development and leachate metal fixation. Samples cured in a carbon dioxide rich environment showed distinct changes in mechanical properties, microstructure and fixation of metal species. Carbonation was also found to play an important role in the hydration of the binder waste form mix. Carbonated solidified products were characterised by enhanced calcite contents, higher strength values and a significant reduction in leachable metals concentration for all the cement types examined when compared with samples cured in nitrogen. It is also shown that the type of cement or cement–blended system can be optimised to obtain maximum improvement in fixation of waste species in a carbonated product. © 1997 Elsevier Science B.V.

Keywords: Carbonation; Solidified waste forms

1. Introduction

Solidification processes are designed to improve the physical and chemical characteristics of hazardous wastes. The most common methods of solidifying wastes use cement (ordinary Portland cement, OPC), sometimes with pozzolanic additives such as fly ash. The practical application of Portland cement for the solidification of hazardous wastes, containing metals such as Pb, Zn, Cr, Cd, Hg, Cu and As has raised several questions

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regarding the long-term durability and stability of the cations within the solidified cement matrix [1–3]. It has now been established that both individual and synergistic effects of waste species can be involved in deleterious interactions with the cement-based binder systems [4] and these findings demonstrate that the wide-spread application of specific hydraulic systems may be unwise and that wastes should be routinely assessed for their suitability for this type of treatment.
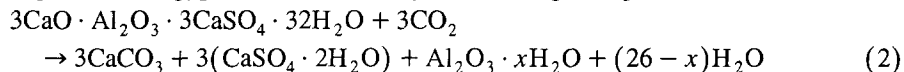
In order to improve and extend solidification processes, research is being carried out by a number of workers to elucidate the mechanisms involved in the fixation of waste species [5–8]. The chemistry of cements and their hydration products, which are also important in this respect, have been thoroughly reviewed [9–11]. OPC [2] type cements are dominated by silicate phases which form some 85% of the anhydrous material. The two most important products formed from the hydration of tricalcium silicate (C_3S) and β-dicalcium silicate (β-C_2S) are calcium silicate hydrate (C–S–H) and calcium hydroxide (CH). C–S–H is amorphous or poorly crystalline gel product produced by the generalised reaction described in Eq. (1) [12].

$$6Ca^{2+}_{(aq)} + 5HSiO^-_{3(aq)} + 7OH^-_{(aq)} \rightarrow 6CaO \cdot 5SiO_2 \cdot 6H_2O \tag{1}$$
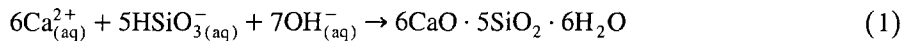
The hydration of OPC is affected by the presence of carbon dioxide. This phenomenon may lead to deleterious effects in structural concrete. These result from a hydration of $CO_{2(aq)}$ leading to the formation of H_2CO_3, HCO^-_3, CO^{2-}_3. This takes place almost instantaneously, lowering the pH locally by 3 or more units [13], leading to eventual depassivation of steel reinforcement.
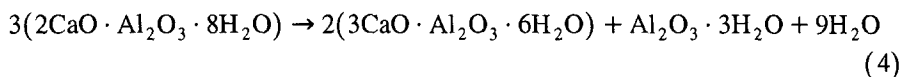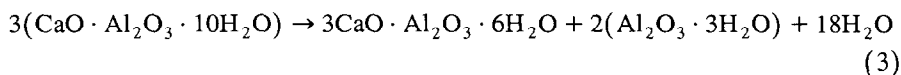
The pore volume of carbonated cement paste changes as a result of the conversion of CH to calcite and decalcification of C–S–H gel. The volume change accompanying this reaction can help to fill pore space, densify the product and improve localised structural integrity. The removal of calcium from C–S–H during carbonation results in a highly polymerised silica gel which is acid stable and maintains the same morphology as the original calcium silicate hydrate. This "stable" silica structure may actually improve chemical bonding of certain metal cations with the components of cement matrix [14].

The amount of aluminate phases present depend on the cement type. C_3A, the main aluminate phase present when hydrated, forms the hydrated aluminate phases known as AFt, and the most important AFt phase is ettringite. Ettringite is sometimes the main phase formed during the solidification of waste forms and promotes an early age strength, but other metal cations may replace the Ca^{2+} or Al^{3+} or both. This substitution may be an advantage as a fixation mechanism for certain solidified waste species as discussed by Hassett and McCarthy [15]. Ettringite also decomposes in the presence of CO_2 to give calcite, gypsum and alumina gel, according to Eq. (2) [16].

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2$$
$$\rightarrow 3CaCO_3 + 3(CaSO_4 \cdot 2H_2O) + Al_2O_3 \cdot xH_2O + (26 - x)H_2O \tag{2}$$

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[2] Nomenclature used in this work: OPC: ordinary Portland cement; RHPC: rapid hardening Portland cement; SRPC: sulphate resistant Portland cement; WOPC: white ordinary Portland cement; CF: calcium aluminate cement (cement fondu); SF: silica fume; PFA: pulverised fuel ash; CA: monocalcium aluminate; C_3A: tricalcium aluminate; CH: calcium hydroxide (portlandite); AH_3: hydrous alumina (gibbsite); CAH_{10}, C_2AH_8, C_3AH_6: calcium aluminate hydrates; AFt: hydrated alumina phases (ettringite).

Calcium aluminate cements are also subject to carbonation. These cements, which are not as popular as OPC for structural concrete, are relatively expensive, but may have certain advantages when used for solidification of waste forms. Calcium aluminate cements introduce rapid strength gain and have a high resistance to chemical attack. However, the chemistry and mechanism of carbonation both differ from OPC. No portlandite (CH) is normally formed during hydration and the phenomenon, known as conversion, which involves the transformation of the meta-stable hydrates CAH_{10} and C_2AH_8 to stable C_3AH_6, as is indicated by Eq. (3) and Eq. (4), may cause "structural" instability when the water:cement ratio is above certain limits.

$$3(CaO \cdot Al_2O_3 \cdot 10H_2O) \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 2(Al_2O_3 \cdot 3H_2O) + 18H_2O$$
$$(3)$$

$$3(2CaO \cdot Al_2O_3 \cdot 8H_2O) \rightarrow 2(3CaO \cdot Al_2O_3 \cdot 6H_2O) + Al_2O_3 \cdot 3H_2O + 9H_2O$$
$$(4)$$

The monocalcium aluminate (CA), is the major anhydrous phase and hydrates at low temperatures ($< 20°C$) to form CAH_{10} and AH_x gel which in the presence of $C_{12}A_7$ leads to the formation of some C_2AH_8 [17]. C_2AH_8 appears as hexagonal plates and on exposure to CO_2, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ is formed. The formation of calcite in this binder can be facilitated by the presence of alkali carbonates, which may be present in a waste according to the Eq. (5) [18]:

$$K_2CO_3 + CaO \cdot Al_2O_{3\,aq} \rightarrow CaCO_3 + K_2O \cdot Al_2O_3 \qquad (5)$$
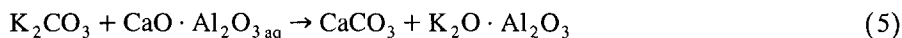
The carbonation of cementitious materials has been widely reported in the literature. Most work to date has concentrated on the effect of changes in porosity, permeability and hydration chemistry of carbonated structural concrete [12,14,19–22]. In the last 5 years, these studies have been extended to include the influence of carbonation on metal doped Portland cement paste [14,23–25]. This work demonstrated the possibility that carbonation could affect the chemical state of the hydrated silicates and, consequently in certain cases, the fixation of the metals could be greatly improved. As an example, Smith and Walton [26] studied the carbonation of solidified low level radioactive waste. They found that some radionuclides that pass through the "carbonated zone" may become incorporated into the carbonate phase through solid solution reactions with calcite. Results such as these suggest that carbonation could have potential beneficial effects on certain cement-based waste systems.

Solidified waste forms generally contain low cement contents and, in many cases, behave much like stabilised soils. Often normal setting processes do not always take place because of waste–binder interference effects and in these solidified waste forms satisfactory strength may never be attained, and microstructure can be significantly altered. These waste forms can also exhibit reduced fixation capacity for certain metal species. Therefore, where hydration reactions are compromised by waste–binder interference effects it is possible for carbonation to have a beneficial effect. Lange et al. [27], examined the effects of carbonation on solidified hazardous wastes, and demonstrated that the use of carbon dioxide can overcome severe retardation effects by "driving"

hydration reaction of C_3S. Indeed, the benefits of carbonation have been realised for treating heavy metal soils and residues elsewhere [28].

The present work, which is part of a wider study, attempts to address some of these issues and examines the effects of carbonation on the mature properties of a blended inorganic waste bound by a variety of blended and non-blended hydraulic binder systems.

2. Experimental methods

2.1. Materials

Five different types of cement and two pozzolans were used in this work. They were: Ordinary Portland Cement (OPC), White Portland Cement (WOPC), Rapid Hardening Portland Cement (RHPC), Sulphate Resisting Portland Cement (SRPC) and Calcium Aluminate Cement (CF). Table 1 gives the suppliers, Bogue and oxide analyses of these cements. The properties of the two pozzolans employed: Pulverised Fuel Ash (PFA) and

Table 1
Analysis of cements used

Cements	OPC	RHPC	WOPC	SRPC	CF
Supplier	Blue Circle	Blue Circle	Blue Circle	Blue Circle	Lafarge
Phase					
C_3S (%)	52	54	64	57	
C_2S (%)	19	18	22	19	
C_3A (%)	7	9	4.4	0	
C_4AF (%)	6	8	1.1	17	
CA (%)					
$C_{12}A_7$ (%)					
C_2A_5 (%)					
Oxide					
SiO_2	20.4	20.5	24.5	21.4	4.9
Al_2O_3 (%)	4.1	5.1	1.9	3.6	51.6
Fe_2O_3 (%)	2.1	2.7	0.35	5.7	1.5
CaO (%)	63.8	64.1	68.7	64	37.2
Free lime	1.5	1.0	2.5	0.6	na [b]
MgO (%)	2.1	1.2	0.55	0.7	na
Alkali Eq. [a]	0.6	0.7	0.2	0.5	na
SO_3 (%)	2.9	3.3	2.0	2.0	na
IR [c]	0.4		< 0.1	0.6	na
LOI [c]	3.2	1.2	1.0	1.5	na

[a] Alkali equivalent = $Na_2O + 0.658\ K_2O$;

[b] na = not available;

[c] IR = insoluble residue (%). LOI = loss on ignition (%).

Obs.: aluminate phases were not determined, however, CA, $C_{12}A_7$ and C_2A_5 were known to be present but not quantified.

Table 2

Analysis for pozzolanic materials

Pozzolans	PFA	SF
Supplier	Ready Mixed Concrete	Ready Mixed Concrete
Oxide		
SiO_2	47.7	89
Al_2O_3	25.7	1.5
Fe_2O_3	11.3	1.2
CaO	2.3	0.6
Free lime	na [b]	na
MgO	1.7	0.6
Alkali Eq. [a]	3.4	0.6
SO_3	1.2	na
TiO_2	1.0	0.2
P_2O_5	na	0.1
C	na	1.4
Mn_2O_3	na	0.3

[a] Alkali equivalent $= Na_2O + 0.658\ K_2O$.

[b] na = not available.

Silica Fume (SF), are described in Table 2. This range of binders was selected to cover as wide a range of chemical and mineralogical compositions as possible, within the most commonly used cementitious binder.

A neutralised waste which is commercially solidified, was obtained as a filter cake of approximately 55% (w/w) solids content composed predominantly of heavy metal hydroxides originating from sources such as electroplating, galvanising and metal finishing operations. The waste was oven dried at 105°C to constant weight and then ground using a pestle and mortar to a particle size of less than 500 μm. The metals content of the waste was determined in triplicate using a Philips PV 8050 Inductively Coupled Plasma Emission Spectrometer, (ICP-AES) after acid digestion in HNO_3 and HCl [29]. The mean of these results are given in Table 3 for selected metals.

2.2. Mix designs

The dried ground waste was mixed with the different cements, pozzolans and double distilled water using a planetary mixer employing a fixed mixing regime. Table 4 shows the mix designs used. Control (waste-free) mixes were also prepared using the same binders. It should be noted, however, that the variation in water:cement ratio was necessary in order to maintain a fixed solid content (55–65%) as is typically used commercially. Cylinders with dimensions of 32 × 32 mm were cast in PVC moulds and immediately placed in atmosphere-controlled containers and allowed to mature for 28 days under the following three curing conditions:

1. Normal atmospheric/laboratory conditions (bench)
2. Carbon dioxide atmosphere
3. Nitrogen atmosphere

Table 3
Metal content of waste

	Metal content (dry waste) (mg kg^{-1})
CaO (%)	16.6
Sr	215
Cr	6638
Cu	8650
Mn	3137
Ni	4825
Pb	3265
Sb	1201
Zn	19475
Cd	1025
Ba	575
As	7464
Hg	2514

After 5 days, the cured cylinders were demoulded and returned immediately to their respective containers.

The carbon dioxide environment was maintained at a 50–60% relative humidity by passing the gas through a wash bottle containing $Mg(NO_3)_2 \cdot 6H_2O$ solution to condition the gas to a nominal 50% rh, which is reported to produce the maximum rate of carbonation in hydrated Portland cement [19]. The temperature was maintained between 20 and 23°C. The nitrogen samples were stored under a dynamic system, where the nitrogen was allowed to flow slowly through a closed container holding the samples under the same temperature conditions. Attempts were made to control the humidity at

Table 4
Mix designs

Mix	Waste (%)	Cement (%)	Pozzolan (%)	Water (%)	W/C
1	30	30 OPC		40	1.3
2	30	30 RHPC		40	1.3
3	30	30 SRPC		40	1.3
4	30	30 WOPC		40	1.3
5	30	30 CF		40	1.3
6	30	28 OPC	2 SF	40	1.4
7	30	20 OPC	11 PFA	40	2.0
8	30	28 RHPC	2 SF	40	1.4
9	30	20 RHPC	11 PFA	40	2.0
10	30	28 SRPC	2 SF	40	1.4
11	30	20 SRPC	11 PFA	40	2.0
12	30	28 WOPC	2 SF	40	1.4
13	30	20 WOPC	10 PFA	40	2.0
14	30	28 CF	2 SF	40	1.2
15	30	20 CF	10 PFA	40	2.0

60% rh to simulate at the ambient conditions, however, the relative humidity was found to vary between 60 and 70%.

2.3. Methods

At 28 days Unconfined Compressive Strength (UCS) was determined using an Instron 1195 compression testing apparatus, fitted with a 10 kN load cell and with a crosshead speed of 1.0 mm min^{-1}. Three cylinders, whose surfaces were prepared by dry grinding as necessary, were tested for each strength determination and the result reported as a simple mean and estimated standard deviation.

Broken cylinders provided samples for leach testing using a modified DIN 38 414 leaching procedure, as recommended in the draft on EC Landfill Directive [30]. The leachant used in this test was deionised water. The procedure specified was modified to accommodate reduction in sample size but the specified liquid to solid ratio (10:1) was maintained. The samples were prepared in triplicate and turned end over end for 24 h. The pH before and after a 24 h extraction procedure was recorded and then, the leachate was filtered through a Whatman GF/C paper and analysed by ICP-AES. The results were given as a mean with estimated standard deviation.

The crystalline phase distribution of the solidified waste forms was determined using X-ray diffractometry. Immediately prior to analysis the samples were ground to less than 150 μm. Analysis were carried out using a Philips 2000 series diffractometer, using Cu K-alpha radiation, over the range of 5.0–55.0 deg 2θ at a scanning rate of 1 deg min^{-1}.

3. Results

3.1. Strength characteristics

The results are given in Fig. 1 for cement pastes only, cement–waste and cement–waste–admixture in three different environments. The estimated standard deviation is indicated as error bars. As might be expected, the cement paste only samples gave the highest recorded strength. CF had a strength recorded at 39.1 MPa in CO_2 atmosphere and was registered as the highest value, while the lowest strength was registered for WOPC at 17.5 MPa. The same trend for the five cements were followed in the presence of the different environments. They are: CF > RHPC > SRPC > OPC > WOPC.

However, when waste was included in the mixtures the described relationship changed. RHPC gave the highest strength for all three environments, and the following trend was observed: RHPC > CF > WOPC > SRPC = OPC.

The addition of SF and PFA in the presence of waste caused some change in strength development of different cements. Silica fume particularly improved the strength of samples in which CF was used (9.04 MPa), followed by SRPC (8.0 MPa). PFA addition was found to cause a decrease in 28 days strength by as much as 50–60% for all cement–waste designs, with two exceptions: the SRPC and WOPC–waste mixes when cured in nitrogen atmosphere.

For all mix designs, nitrogen-cured samples gave the lowest strength. For cement

paste only, a reduction of strength, compared to CO_2 cured samples, of up to 40% was noted. Whereas for cement paste–waste addition and cement paste–waste–SF–PFA a reduction of 70 and 53% respectively were recorded. The results clearly indicate that these differences result from the curing environment employed.

3.2. Phase distribution

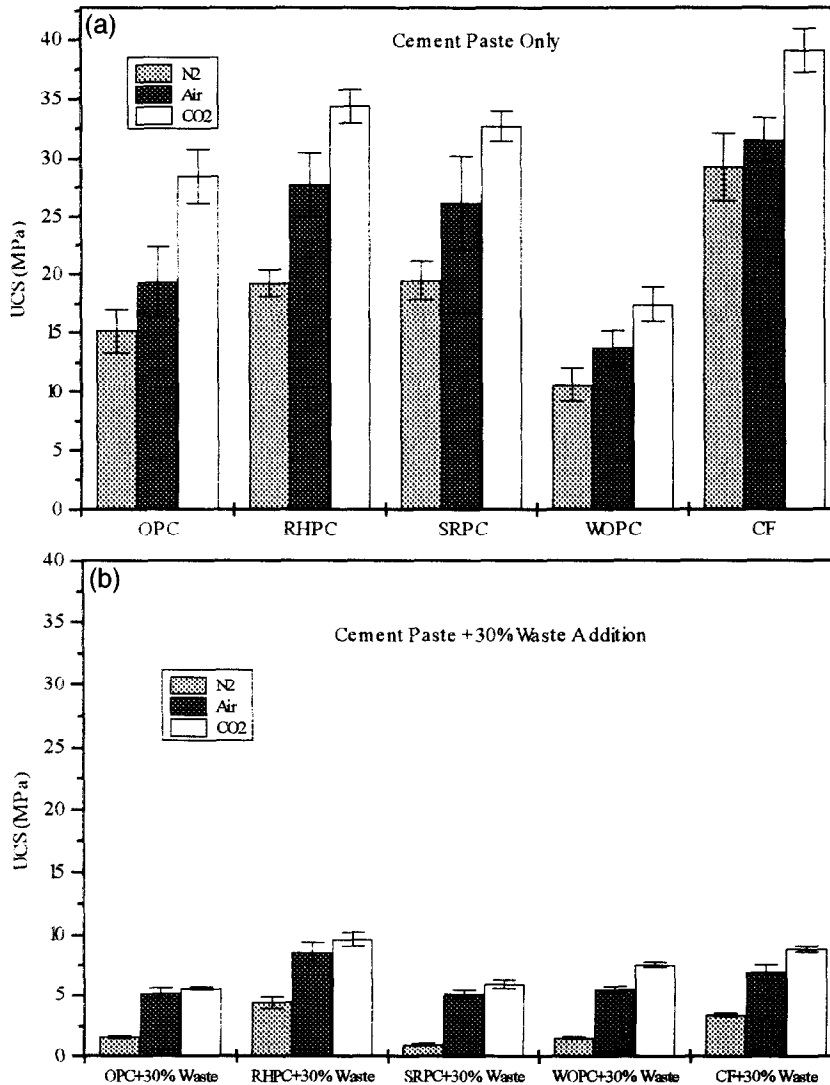The phase development, within the binder–waste samples is characteristic and may be seen by a comparison of the principal diffraction lines for each set of samples. In
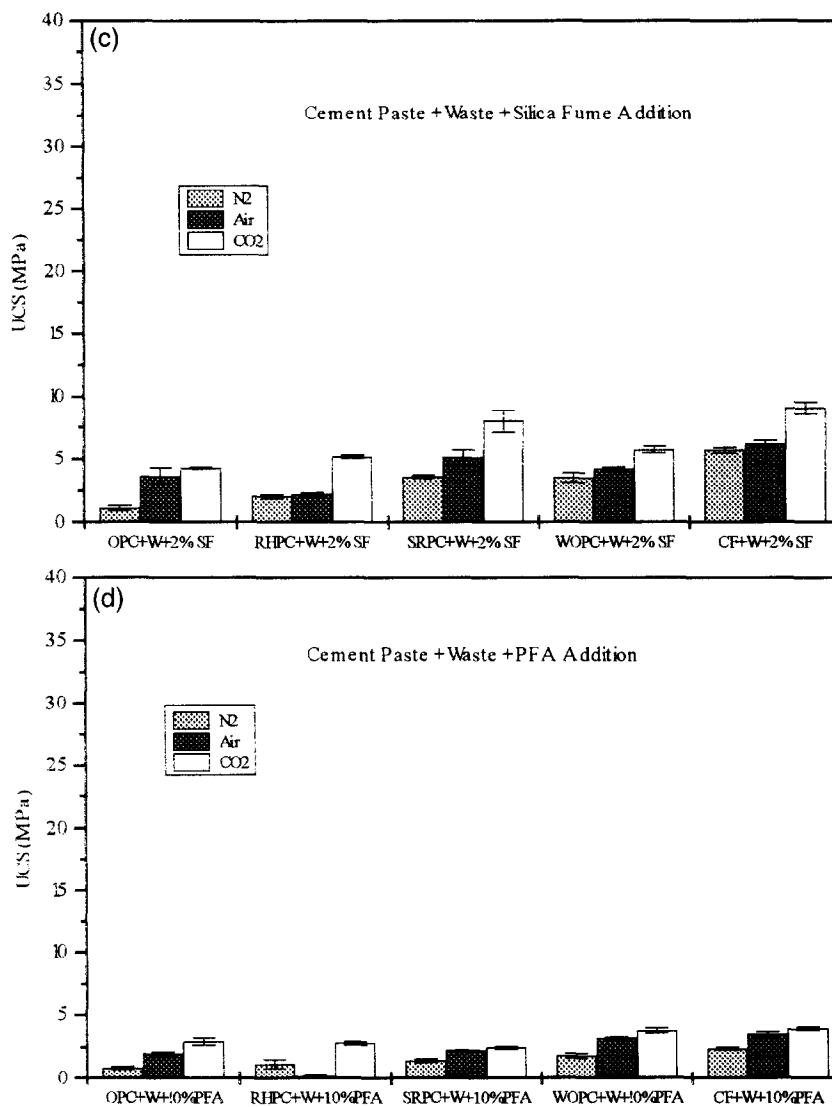

Fig. 1. Strength results after 28 days.

Fig. 1 (continued).

every case, a control chart was obtained using pure cement and the background intensities recorded were similar for all samples. Fig. 2 shows the X-ray diffraction patterns for samples with 30% w/w of waste mixed with the five different cements cured in carbon dioxide and nitrogen atmospheres. The dried raw waste was also analysed and its diffractogram is given in Fig. 2. The waste is largely an amorphous material and the crystalline components are various hydrates of calcium sulphate, calcite and portlandite. Portlandite, which is added during the pre-treatment phase (neutralisation) of the waste, can be seen in Fig. 2, as a peak at 28.6 2θ (d-spacing 3.11 Å).
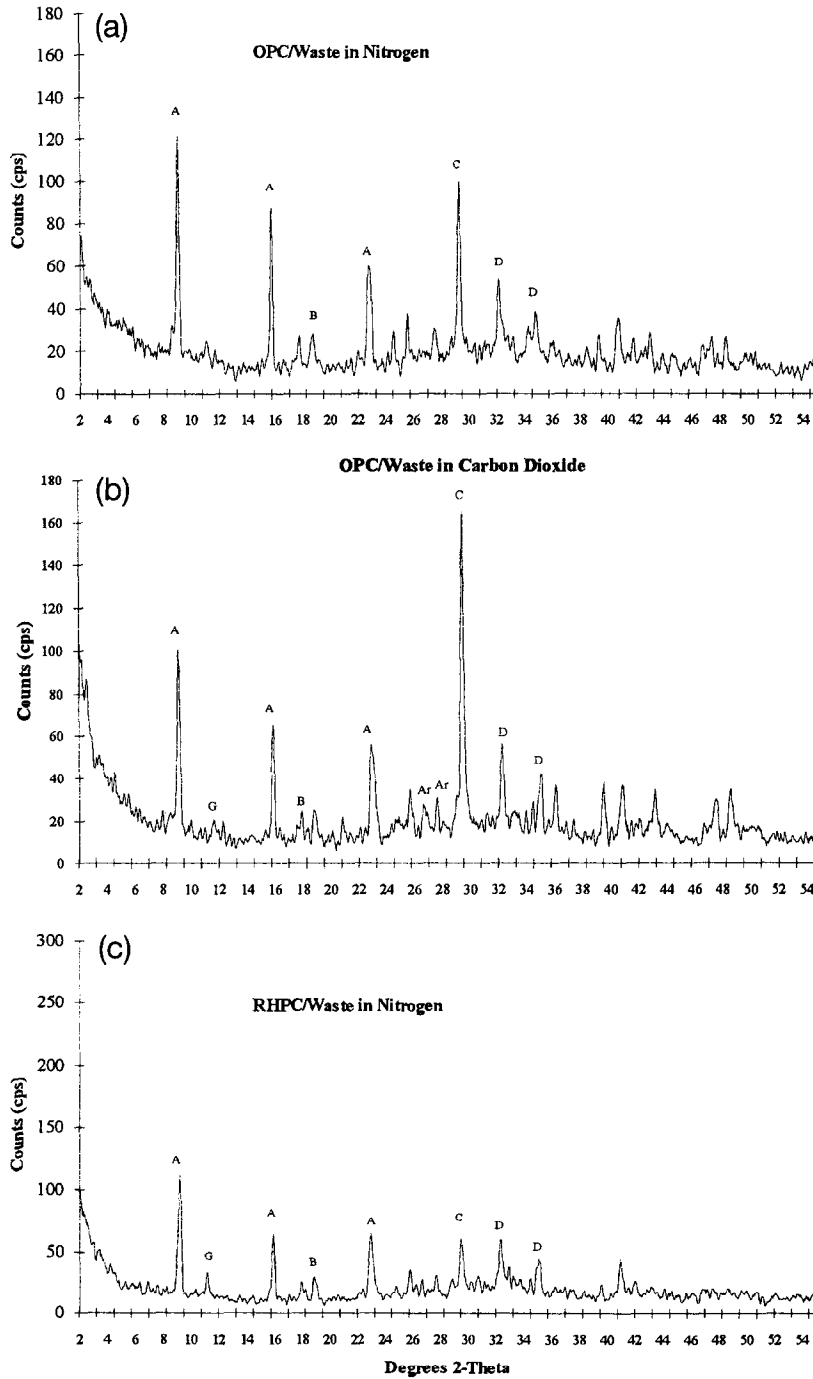
Fig. 2. Qualitative X-ray diffractograms, where A = ettringite, B = portlandite, C = calcite, D = C$_3$S, G gypsum, H = hemihydrate, Ar = aragonite and CA = CAH$_{10}$.
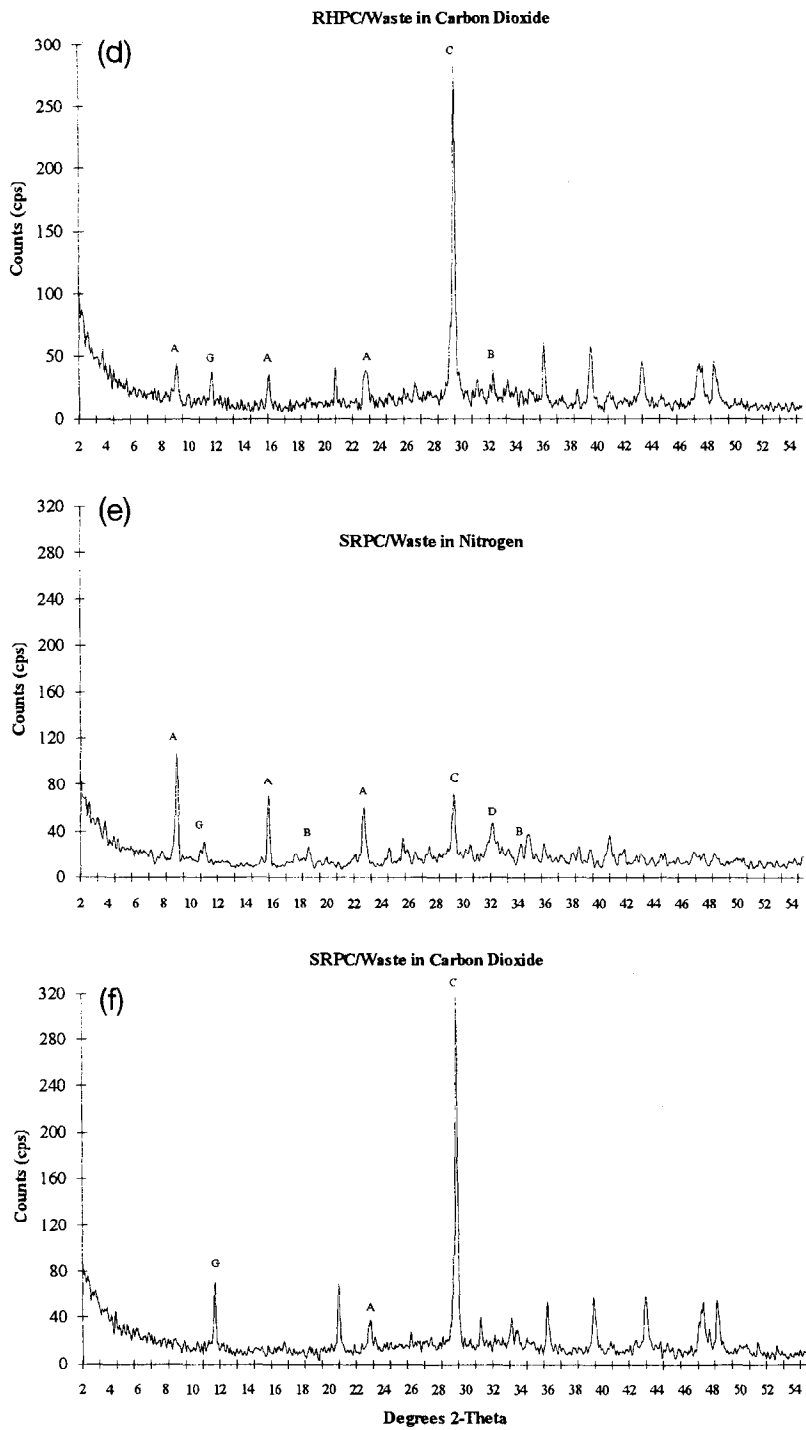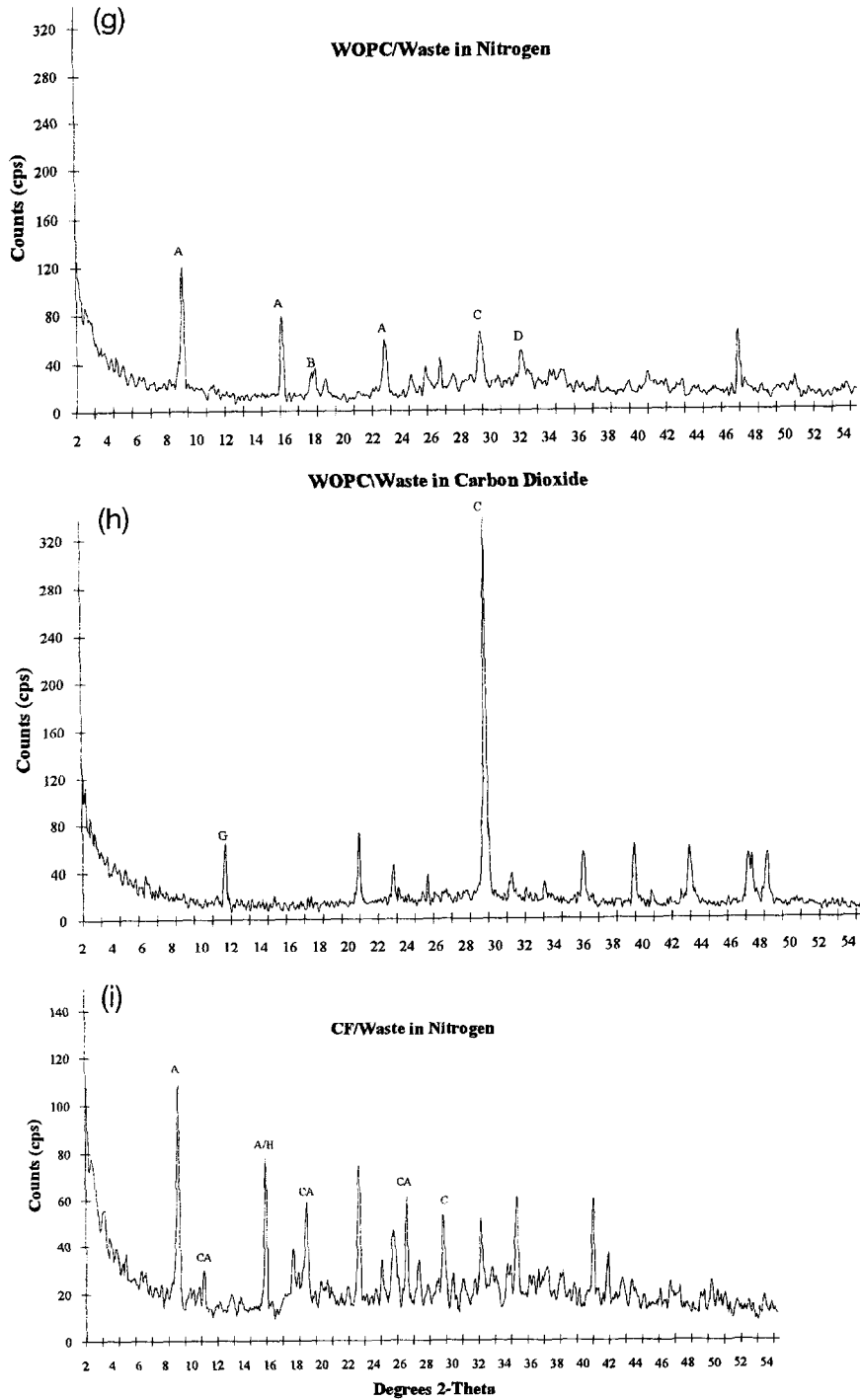
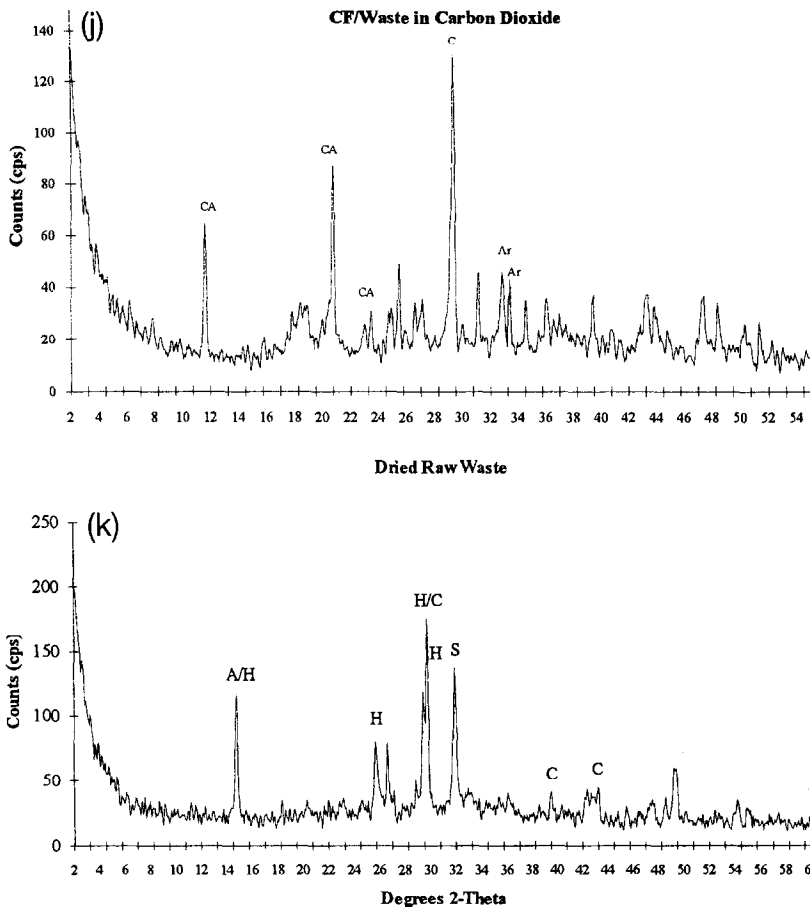Fig. 2 (continued).

Fig. 2 (continued).

Fig. 2 (continued).

The influence of the carbon dioxide curing environment in modifying the hydration of OPC, SRPC, RHPC, WOPC and CF is well demonstrated in Fig. 2. For all samples, the amount of calcite increased in the following sequential order: $CO_2 >$ air $> N_2$. Ettringite appeared to decompose in the presence of carbon dioxide as discussed previously with a consequence increase in proportion of calcite and gypsum in the product. Aragonite was also present in some of the diffractograms as indicated. Vaterite, which is a relatively unstable phase was not detected. Calcite, the most stable polymorph of $CaCO_3$, was the phase commonly detected in this work.

3.3. Leaching characteristics

The concentrations determined in leachates from the different samples for the selected metals Cr, Cu, Zn and As are given as histograms in Fig. 3. The pH values after 24-h extraction procedure are recorded on Table 5. The carbon dioxide-cured samples

presented the lowest values for leachable metal for all mixes. First, the benefits of using a carbon dioxide curing environment by comparison with nitrogen/ambient conditions for solidified waste forms are shown to improve metal fixation. Second, for different metals, a distinct binder–metal interaction appears to occur, demonstrating that it may be advantageous to select cement binders depending on the metal content of the wastes. Also, the pH values of the samples cured in CO_2 indicated that carbonation has occured, lowering the pH by 3 to 4 units in comparison to nitrogen cured samples. Solidified
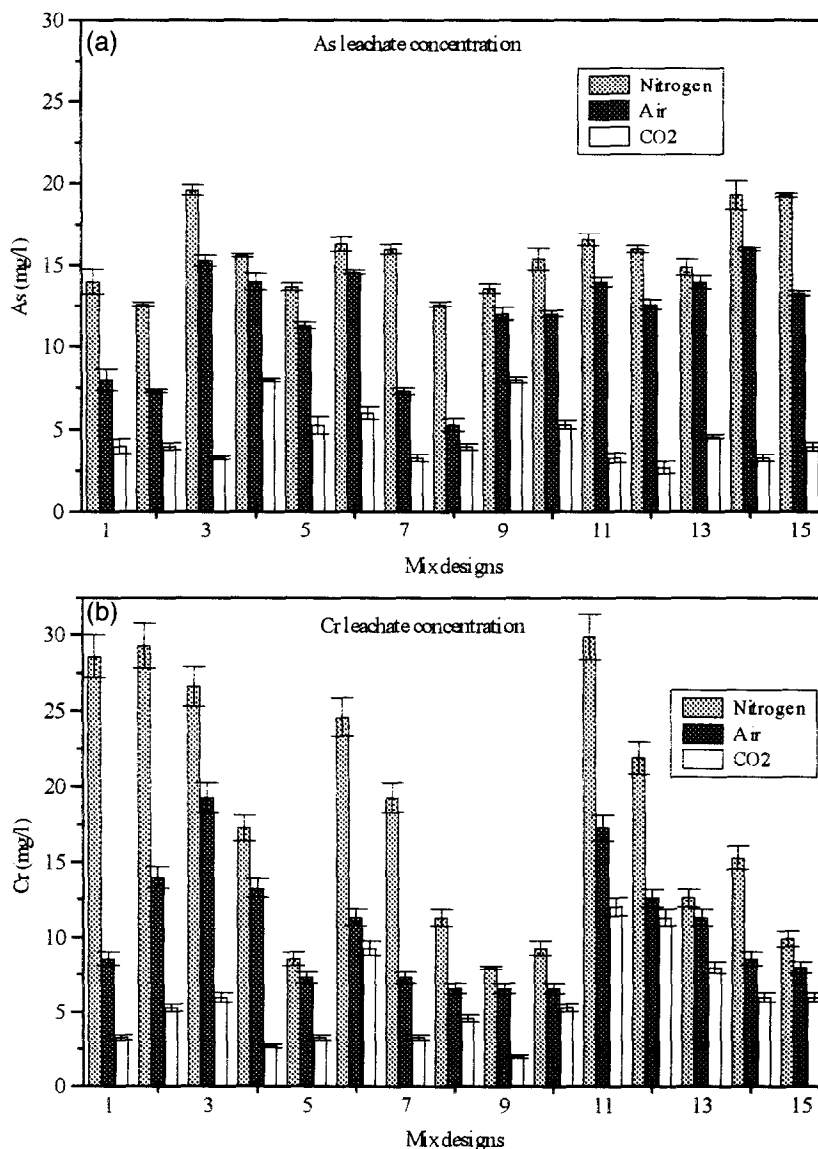

Fig. 3. Leachate metal concentration for As, Cr, Cu and Zn for different mix designs.
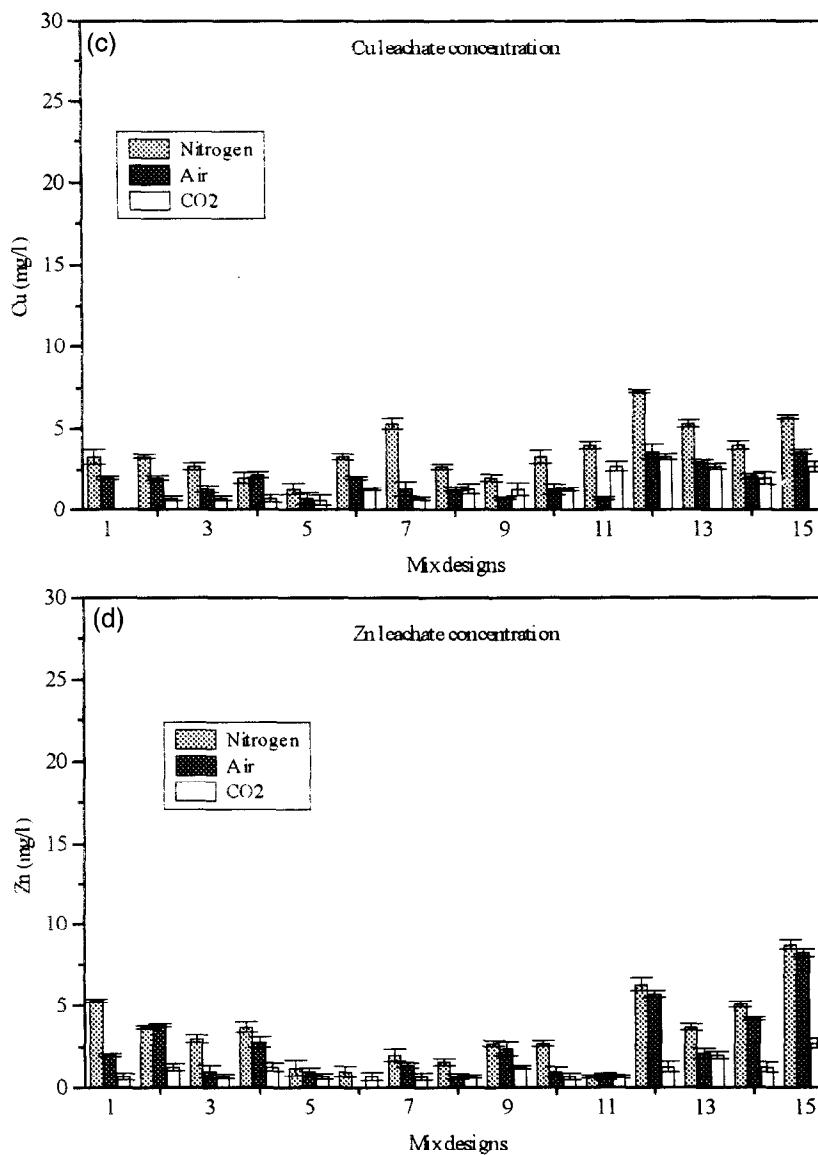
Fig. 3 (continued).

wastes cured in normal (ambient) atmosphere showed a slight drop in pH, possibly as a result of the effects of atmospheric carbonation.

The addition of PFA and SF to sample mixes generally increased leachable metal concentrations for metals such as Cr and Cu by up to 20% when compared to cement–waste mixes. On the other hand, metals such as Zn and As showed much lower leachate concentrations when PFA was added. A reduction by up to 15% of leachable metal concentration for these metals was observed.

Table 5
pH after 24-h leaching test

Mixes	pH after 24 h extraction		
	Carbon dioxide	Nitrogen	Bench
1	10.90	11.43	11.40
2	10.60	11.44	11.40
3	8.74	11.43	11.55
4	8.66	11.44	11.46
5	8.30	11.00	10.57
6	7.92	11.31	11.35
7	7.88	11.30	10.93
8	9.48	11.30	11.35
9	8.22	11.31	10.92
10	10.67	11.41	11.27
11	9.25	11.32	10.80
12	8.13	11.46	11.45
13	7.87	11.35	11.21
14	8.90	10.99	10.37
15	8.10	10.87	10.06

The results outlined above indicate a significant improvement in both the physical and chemical properties of solidified waste forms when carbon dioxide was used as the curing environment. The carbonated solidified products in comparison with samples cured in nitrogen, were characterised by increased calcite contents of between 50 and 70%, increased strength of between 60 and 70% and a significant reduction in the leachable metal concentration by up to 85% for metals such as Zn, Cu, Cr and As.

4. Discussion

The effects of carbonation on the properties of cement bound waste forms are distinct and are generally beneficial rather than deleterious as is the case with structural concrete. The principal advantages result from improved metal binding capacity and mechanical properties.

Carbonation has been seen to play an important role in the hydration and polymerisation of silicates [14] and the fixation of toxic metals appears to be linked at least in part with the formation of calcite; the possible formation of solid solutions with a large number of cations [26] and/or by sorption into gel hydration products [31]. However, the reactions taking place during binder hydration are complex and are probably modified by the addition of wastes-contained species. Consequently, it may be necessary to consider, for example, the influence of antagonistic and synergistic effects of complex mixtures, which can interfere with hydraulic and pozzolanic reactivity when choosing inappropriate binder systems.

The principal effects of carbonation on the properties of blended and non-blended cement solidified waste forms can be summarised under the following headings.

4.1. Portland cements

The most obvious effect of carbonation upon waste forms is related to strength development. All four Portland cement–waste samples showed an increase in strength when cured in carbon dioxide. This may be due to an acceleration of hydration of C_3S driven by the formation of calcium carbonate. Examination of waste forms by X-ray diffraction showed that is possible to observe the relationship between C_3S hydration and the formation of calcite.

RHPC gave the highest strength values of all the Portland cements examined. This high-early-strength cement is more finely ground and has a slightly higher C_3A content. The hydration of C_3A forms ettringite, that may promote higher early strength values in waste forms and which decomposes in the presence of CO_2 to form calcite which may improve continued structural stability.

The phase development in waste forms may, therefore, be primarily dependant upon both the curing environment and binder type. Ettringite, which is discussed above, clearly is decomposed to form gypsum and calcite. Calcite was also found in abundance in C_3S-rich binders, such as RHPC and WOPC.

A significant difference was found to exist between the levels of leachable metals in samples cured under the CO_2 and the N_2 atmospheres. The drop in leachate pH values after 24-h extraction, on samples cured under CO_2 atmosphere, showed that not only carbonation had occured, but also that certain metals such as Cr, Cu and Zn were retained in the waste form.

The minimum solubility of $Cr(OH)_2$ is between pH 8.5 and 9.5, for $Zn(OH)_2$ it is at pH 9.2 and $Cu(OH)_2$ it is at pH 9.0 [5]. On the basis of this it might be expected that a higher amount of Cr, Cu and Zn might be released as pH drops below these values as result of carbonation (typically pH 8.0–8.5). The fact that was observed indicates that physical containment of these metals is enhanced; probably as a result of the formation of calcite, modifying pore structure and the precipitation of double salts containing toxic species. However, direct evidence of the latter was not obtained from an analysis of waste form X-ray diffractograms, although some unidentified peaks were apparent.

The modification of C–S–H, previously discussed [26], where a $C–S–H–CO_2$ reaction can compete and compliment the $CH–CO_2$ reaction leading to a siliceous product characterised by a degree of polymerisation higher than the original C–S–H; and which may capture certain metals may also be important. In the literature [32], there is evidence to suggest that some metals, such as zinc, may enhance carbonate formation through the precipitation of $CaZn_2(OH)_6 \cdot 2H_2O$, which can prevent the formation of a tobermorite structure and "liberate" $Ca(OH)_2$ normally bound between two octahedral silicate sheets. Consequently, $Ca(OH)_2$ will be more accessible to carbon dioxide for carbonate formation.

4.2. Calcium aluminate cement

When CF was used to solidify the waste, strength values up to 35% higher than OPC were obtained because of the continued high reactivity of CA despite the presence of waste.

Examination by X-ray diffraction indicated the presence of calcium carbonate in the solid phase. The formation of calcite indicates the presence of free lime which may not have been anticipated but which was most likely facilitated by the presence of alkali carbonates from the waste and by a reaction with the hydrated calcium aluminates (Eq. (5)). The alkali carbonate thus acts as catalyst in the modification of calcium aluminates to form calcite.

Leachate analysis showed a significant reduction in extractable metal concentration for samples exposed to a carbon dioxide environment. Again, changes in the pore structure due to the presence of calcite and a possible incorporation of some metals by AH_3 gel could explain this phenomenon.

4.3. Pozzolanic additives

Mineral admixtures may significantly affect the size, distribution, and structure of cement paste hydrates. The addition of PFA and SF to cement cause some changes to the composition of hydration products. Less CH was produced and the Ca:Si ratio in C–S–H was reduced [33–35]. SF particles typically fill the void space between cement grains and a pozzolanic reaction takes place with portlandite. For PFA, as a consequence of the breaking down of the alumina–silica glass structure, the content of aluminium, potassium and sodium in C–S–H increases and reaction products tend to precipitate within the small pores [36].

In this study, cement–waste samples blended with PFA showed a lower 28-day strength when compared with samples blended with SF. This is explained as being due to initial retardation by precipitation of reaction products of cement on the PFA particles [35].

The hydration reactions in cement–waste systems incorporating PFA and SF were responsible for changes in microstructure. A decrease in the amount of calcite was observed for samples cured in carbon dioxide when compared to cement only binder. The pozzolans remove CH from the binder, densify and reduce gas permeability making it more difficult for CO_2 to diffuse into the paste.

From the leaching results it was clear that PFA and SF improved the metal fixation for some of binder systems, for example Cr in the WOPC–SF mix cured in carbon dioxide.

5. Conclusions

The work outlined here investigates some properties of selected binder systems mixed with a commercially solidified waste that were cured in carbon dioxide, air and nitrogen atmospheres.

The principal conclusions of this study are summarised as follows:

1. Samples cured in a carbon dioxide environment produced significantly improved mechanical properties and increased toxic metal binding capacity, when compared to samples cured in nitrogen or normal atmospheric conditions. The carbonated solidified products had mean strength values increased by up to 70% and leachable metal concentrations reduced by up to 80%.

2. The type of binder selected appears to play an important role in how effectively waste metals can be immobilised. Thus, the nature of the binder used needs to be taken into account in order to maximise the effective solidification and fixation of the waste material within the carbonated waste form.

The importance of improving the quality of solidified wastes is not only necessary because unstable solidified materials are a potential threat to the environment, but also because of the commercial and economic aspects associated with increasing waste management legislation. In this respect, controlled carbonation could be an important and useful tool. Further work in identifying the carbonation mechanisms and their effect on the nature of bonding of different waste species within hydrated cement-based systems is now in progress and will be reported at a later date.

Acknowledgements

References

[1] C.D. Hills, C.J. Sollars and R. Perry, Cement Concr. Res., 23 (1993) 196.
[2] L.W. Jones, Interference mechanisms in waste stabilization/solidification processes, Literature review. Hazardous Waste Engineering Research Laboratory, Office of Research and Development, US EPA, Cincinnati, OH, USA, 1988.
[3] L.B.B. Peer, Designing OPC/waste mixes using Environment Canada protocols as evaluation criteria, Paper presented at Williamsburg Conference, USA, November 1993.
[4] J.R. Conner, in R.D. Spencer (Ed.), Chemistry and Microstructure of Solidified Waste forms, Lewis, USA, 1993.
[5] J.R. Conner, Chemical Fixation and Solidification of Hazardous Waste, Van Nostrand–Reinhold, New York, 1990.
[6] P.L. Bishop, Haz. Wastes Haz. Mater., 5(2) (1988) 129.
[7] H.J. McWhinney, D.L. Cocke, K. Balke and J.D. Ortego, Cement Concr. Res., 20 (1990) 79–91.
[8] M.S.Y. Bhatty, Fixation of metallic ions in Portland cement, Portland Cement Association, Skokie, II, (cited in Connor, 1990), 1986.
[9] A.R. West, Solid State Chemistry and its Implications, John Wiley, New York, 1987.
[10] H. Taylor, Chem. Ind., 19 (1981) 620.
[11] H.F.W. Taylor, in Proceedings of the 10th International Symposium on Reactivity of Solids, 1985, p. 39.
[12] H.F.W. Taylor, Cement Chemistry, Academic Press, London, 1990.
[13] A. Maries, in Cement and Concrete Science Conference, University of Oxford, UK, 21–22 September 1992.
[14] M. Mollah, T.R. Hess, Y. Tsai and D.L. Cocke, Cement Concr. Res., 23 (1993) 773.
[15] D.J. Hassett and G.J. McCarthy, Fixation of trace elements by ettringite: a screening study final topical report, N. Dakota University, Grand Forks, N. Dakota, October (1990), reported in NTIS Environ. Pollut. Control, 92(21) (1992) 48.
[16] T. Nishikawa, K. Suzuki and S. Ito, Cement Concr. Res., 22 (1992) 6–14.
[17] F.M. Lea, The Chemistry of Cement and Concrete, 3rd edn, Edward Arnold, London, 1970.
[18] R.G.J. Montgomery, S. Rashid, A. Campas and W.B. Woolley, in Concrete 2000: Economic and Durable

Construction through Excellence, Proc. Int. Conf., University of Dundee, Scotland, UK, Vol. 2, 1993, pp. 1857–1879.

[19] J.F. Young, R.L. Berger and J. Breese, J. Am. Ceram. Soc., 57 (1974) 394.

[20] P.A. Slegers and P.G. Rouxhet, Cement Concr. Res., 6 (1976) 381.

[21] K. Suzuki, T. Nishikawa and S. Ito, Cement Concr. Res., 15 (1985) 213–224.

[22] J. Calleja, Durability, in Proc. 7th Int. Symp. Chem. Cement, Paris, Part VII-2, 1980, pp. 1–43.

[23] H. McWhinney, D. Cocke and L. Donaghe, in HMCRI 7th National RCRA—Superfund Conference on Hazardous Waste and Hazardous Waste Material, St. Louis, MO, 2–4 May 1990.

[24] M. Mollah, Y. Tsai and D.L. Cocke, J. Environ. Sci. Hlth, A27(5) (1992) 1213.

[25] M. Mollah, Y. Tsai, T.R. Hess and D.L. Cocke, J. Haz. Mater., 30 (1992) 273.

[26] R.W. Smith and J.C. Walton, in Scientific Basis for Nuclear Waste Management XIV, Vol. 212, 1991, pp. 403–409.

[27] L.C. Lange, C.D. Hills and A.B. Poole, Environ. Sci. Technol, (30): 25 (1996).

[28] DCR Process, Miller Environment technical notes, 1978.

[29] A.I. Vogel, Vogel's Textbook of Quantitative Chemical Analysis, 5th edn, Longman, England, 1989.

[30] Commission of the European Communities, Council Directive Draft on the Landfill of Waste, SYN 335, Brussels, June, 1993.

[31] I.G. Richardson and G.W. Groves, Cement Concr. Res., 23 (1993) 131.

[32] M.Y. Mollah, J.R. Parga and D.L. Cocke, J. Environ. Sci. Hlth, A27(6) (1992) 1503.

[33] M. Atkins, D.E. Macphee and F.P. Glasser, in Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Proc. 3rd Int. Conf. American Concrete Institute, Detroit, 1989.

[34] D.M. Roy, in Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Proc. 3rd Int. Conf. American Concrete Institute, Detroit, 1989.

[35] P.K. Mehta, in Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Proc. 3rd Int. Conf. American Concrete Institute, Detroit, 1989.

[36] A.L.A. Fraay, J.M. Bijen and Y.M. de Haan, Cement Concr. Res., 19 (1989) 235.