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Preliminary Investigation into the Effects of Carbonation on Cement-Solidified Hazardous Wastes

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This paper reports results from a preliminary investigation into the effects of carbonation on a cement-solidified waste material. The waste, which is a commercially blended product, was solidified using different amounts of ordinary Portland cement (OPC) and cured in three different environments: nitrogen, air, and carbon dioxide. After 28 days, the samples were investigated for leachate metals fixation, strength, and microstructural development. Carbonation was found to play an important role in "accelerating" the apparent hydration of binder within the solidified waste forms. Carbonated solidified products were characterized by enhanced calcite contents, higher strength values, and a significant reduction in leachable metals extracted compared to air-cured samples. Samples cured under a nitrogen atmosphere showed significant retardation of hydration, resulting in low strength values but improved fixation of leachable metals.

Introduction

Hazardous wastes are produced by all countries, irrespective of their state of development (1). In the U.K., approximately 4.5 million ton of hazardous wastes is produced per year (2), and it is estimated that over 80% of these are directly sent to landfills without pretreatment (3).

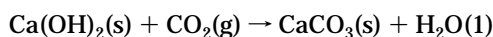
Cement-based solidification is one of the preferred chemical treatment techniques for inorganic hazardous wastes, such as those arising from metal plating and finishing operations (4, 5). This technology has been used to treat a variety of industrial residues and contaminated land for approximately 25 years, and it has the potential for wider application to the treatment of wastes and remediation of contaminated soils (6), particularly outside North America where it is recognized as an established treatment technology. In simple terms, the process of solidification involves reducing the mobility of the encapsulated toxic

waste elements, thereby making the waste more acceptable for land disposal. Solidification is, in general, a simple and economical treatment process involving widely available materials and is applicable to many types of hazardous waste.

In Europe, solidified wastes will soon have to meet standards laid down in EC environmental legislation (7). Hitherto, however, wastes have been required to meet local and national regulation, and there are reports of wastes that appear not to have solidified (8-11). The apparent lack of long-term stability of these materials is of concern as certain potentially mobile waste components present a threat through contamination of groundwater resources.

In order to improve and extend solidification process, research is being carried out by a number of workers to elucidate the mechanisms involved in the fixation of waste species (5, 12-14). In particular, some wastes materials solidified commercially are known to be capable of deleterious interferences with commonly used binding agents. Examination of these materials (15-17) has shown that normal hydraulic and pozzolanic reactions may be significantly retarded or poisoned. Although some of these materials appeared to 'set' and harden in the laboratory, there is mounting evidence to suggest that for some wastes this is a consequence of the effects of exposure to atmospheric CO₂. It has also been reported that carbonation may directly alter the chemical and physical properties of solidified waste forms (18).

Carbonation of concrete and mortars is a well-known phenomenon that may, in certain cases, lead to deleterious effects. Carbonation involves a chemical reaction between calcium hydroxide and carbon dioxide, resulting in the formation of calcium carbonate and water. The principal reactions of hydrated cement with carbon dioxide are



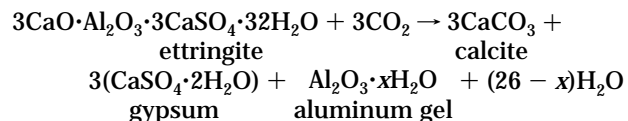
These result from a reduction in pH of pore fluids, volume changes induced by the conversion of portlandite to calcite, the decalcification of CSH gel, and the depassivation of reinforcement, i.e., carbonation can also lead to corrosion of reinforcing steel, which is an electrochemical reaction. Solidified waste forms mixes are unlike concrete mixes. They can contain low cement contents and, in many cases, behave like stabilized soils. Where hydration reactions are compromised by waste-binder interference effects, it is theoretically possible for carbonation to have an effect different from that of a normally hydrated concrete. In such cases, carbonation may be beneficial as may be demonstrated in similar systems such as the carbonation of quick lime stabilized heavy metal soils and residues (19).

There is a wealth of published information related to porosity, strength, permeability, and hydration chemistry of carbonated concrete (20-24). These studies have recently been extended to the influence of carbonation on metal-doped Portland cement paste (25). For example, McWhinney et al. (26) have studied the solidification of metal ion pollutants including Ba, Cr, Pb, Zn, Cd, and Hg in cement and noted high carbonation rates as a feature common to all doped cements. Mollah et al. (20, 26-28)

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have investigated the effects of carbonation on Cd, Cr, and Zn in solidification systems. The results showed that the chemical state of the hydrated silicates were significantly affected and that the fixation of the metals was greatly improved. Nishikawa et al. (29) examined the decomposition of ettringite by carbonation and found that, under dry conditions, gypsum and calcium carbonate are readily identified. Under wet conditions, however, ettringite decomposed to gypsum, calcium carbonate, and aluminum gel as shown below:



These results further suggest that carbonation could have a beneficial effect on certain cement-based systems, mainly through the formation of calcium carbonate, whose presence seems to increase metal binding capacity and improve structural properties.

The present work is a preliminary investigation of these effects using the solidified products of a commercially produced waste that was blended with ordinary Portland cement and cured for 28 days in three different environments. The solidified waste forms were examined for strength, microstructural development, and leachate metal composition.

Experimental Methods

Ordinary Portland cement (OPC) supplied by Blue Circle PLC was used to solidify a commercially produced neutralized waste. The waste employed in this work was obtained from a commercial solidification company located in southern England. The waste originates from blending a variety of individual waste streams to produce a filter cake with 'controlled' properties. It has a solid content of approximately 55% (w/w) and a pH typically within the range of 8–10. The total organic carbon content (TOC) has been found previously to be in the range 2–4%, of which <5 mg/L is aqueous soluble. The particular batch of material examined here had a pH of 8.0, a total dissolved solids content of 9200 mg/L, and an aqueous soluble TOC of 2.0 mg/L. The filter cake was composed predominantly of heavy metal hydroxides originating from sources such as electroplating, galvanizing, and metal finishing operations. It was first oven dried at 105 °C to constant weight and ground using a pestle and mortar to less than 500 µm particle size. The metal contents of the waste were determined in triplicate using a Phillips PV 8050 inductively coupled plasma emission spectrometer (ICP-AES) after acid digestion using a method involving the use of HNO₃ and HCl (30). The results are given in Table 1.

The dried ground waste was mixed with cement and double-distilled water using a planetary mixer employing a fixed mixing regime. Table 2 shows the mix designs used. It should be noted that the variation in W/C ratio was necessary in order to maintain a fixed solid content (typically 55–65%) as used commercially. Cylinders with dimensions of 50 mm × 50 mm were cast in PVC moulds and immediately placed in climate-controlled containers and allowed to mature for 28 days under the following three curing conditions, for comparison: (1) ambient/laboratory conditions (bench), (2) carbon dioxide atmosphere, and (3) nitrogen atmosphere. After 5 days, the cured cylinders

TABLE 1

Metal Content of Waste

	metal content (dry waste) (mg/kg)
CaO (%)	16.6 ± 1.2
Sr	215 ± 3.1
Cr	6638 ± 9.8
Cu	8650 ± 12.7
Mn	3137 ± 4.2
Ni	4825 ± 13.6
Pb	3265 ± 3.5
Sb	1201 ± 9.7
Zn	19475 ± 26.4
Cd	1025 ± 6.8
Ba	575 ± 7.7
As	7464 ± 13.4
Hg	2514 ± 23.4

TABLE 2

Mix Designs OPC/Waste Laboratory Specimens

mixes	waste (%)	OPC (%)	water (%)	solids (%)	W/C ratio
1	0	65	35	65	0.54
2	35	20	45	55	2.25
3	35	30	40	65	1.33
4	35	25	35	60	1.40

were demoulded and returned immediately to their respective containers.

The carbon dioxide environment was maintained at a 50% relative humidity (RH) by passing the gas through a wash bottle containing saturated Mg(NO₃)₂·6H₂O solution to condition the gas to a nominal 50% RH, which is reported to produce the maximum rate of carbonation in hydrated Portland cement (22). The climate container was purged of air and stabilized by passing the CO₂ at 5 mL/min during 10 min. The container was submitted periodically to this regime to avoid carbon dioxide starvation. 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.

At 28 days, unconfined compressive strength (UCS) was determined using an Instron 1195, fitted with a 10 KN load cell and with a cross-head speed of 1.0 mm/min. Three cylinders whose surfaces were prepared by dry grinding when necessary were tested for each strength determination, and the result was reported as a simple mean. The estimated standard deviation was calculated and is indicated as error bars.

Broken cylinders provided samples for leach testing using a modified DIN 38 414 leaching procedure, recommended in the draft on EC Landfill Directive (7). The procedure specified was modified to accommodate reduction in sample size, but the specified solid to eluant ratio was maintained. The samples were prepared in triplicate and turned end over end for 24 h. The leachate was filtered through a Whatman GF/C paper and analyzed by ICP-AES. The results were given as a mean with the respective estimated standard deviation calculated and indicated as error bars.

The mineralogy of the solidified waste forms were also determined using X-ray diffractometry. For this test, separate samples were prepared, in triplicate, by placing freshly mixed material directly in diffraction specimen

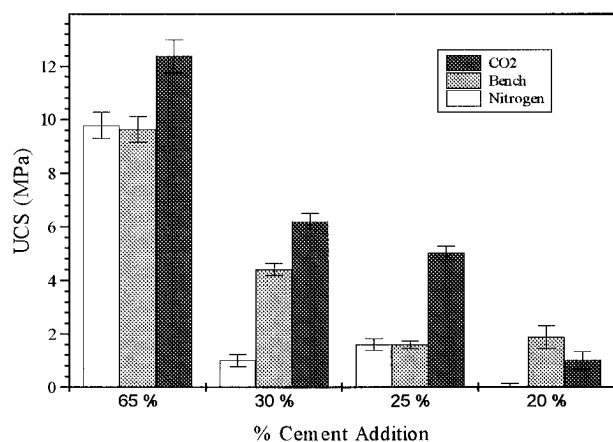


FIGURE 1. Strength development at 28 days.

TABLE 3

Intensity of X-rays (cp/s) Recorded for Solidified Waste Forms^a

phase dev.	atm. exposure			
	65% OPC	30% OPC	25% OPC	20% OPC
calcite				
nitrogen	67	152	118	104
CO ₂	686	261	217	183
bench	144	180	161	146
portlandite				
nitrogen	603	45	60	41
CO ₂	37	31	54	31
bench	42	35	37	65
C ₃ S				
nitrogen	227	83	72	60
CO ₂	59	56	54	22
bench	160	115	103	38
gypsum				
nitrogen	56	295	367	46
CO ₂	58	38	326	106
bench	108	328	348	79
ettringite				
nitrogen	135	140	122	51
CO ₂		42	150	61
bench	60	56	53	50

^a Calcite, 2θ (29.5°); C₃S, 2θ (34.5°); portlandite, 2θ (18.35°); gypsum, 2θ (11.4°); ettringite, 2θ (9.7°).

holders that were then stored in the climate containers for 28 days. Analysis was carried out using a Phillips 2000 Series diffractometer, using Cu K α radiation over the range of 5.0 and 55.0° 2- θ at a scanning rate of 1°/min.

Results

Strength Development. As might be expected, strength increases with the amount of OPC in the mix. Figure 1 shows the strength development of all mixes at 28 days.

The control samples without waste addition (65% OPC w/w) gave the highest strength value of 12.38 MPa for the CO₂-cured sample. The nitrogen- and bench-cured specimens had similar strengths at approximately 10 MPa. However, when waste was included in the mixtures, this relationship changed.

The nitrogen-cured samples gave the lowest strengths for all waste additions. At the lowest OPC content, the strength recorded was well below acceptable limits in that the samples examined were only just self-supporting. The samples cured in CO₂ gave higher strengths for 30 and 25% OPC contents but a lower value at the 20% OPC content.

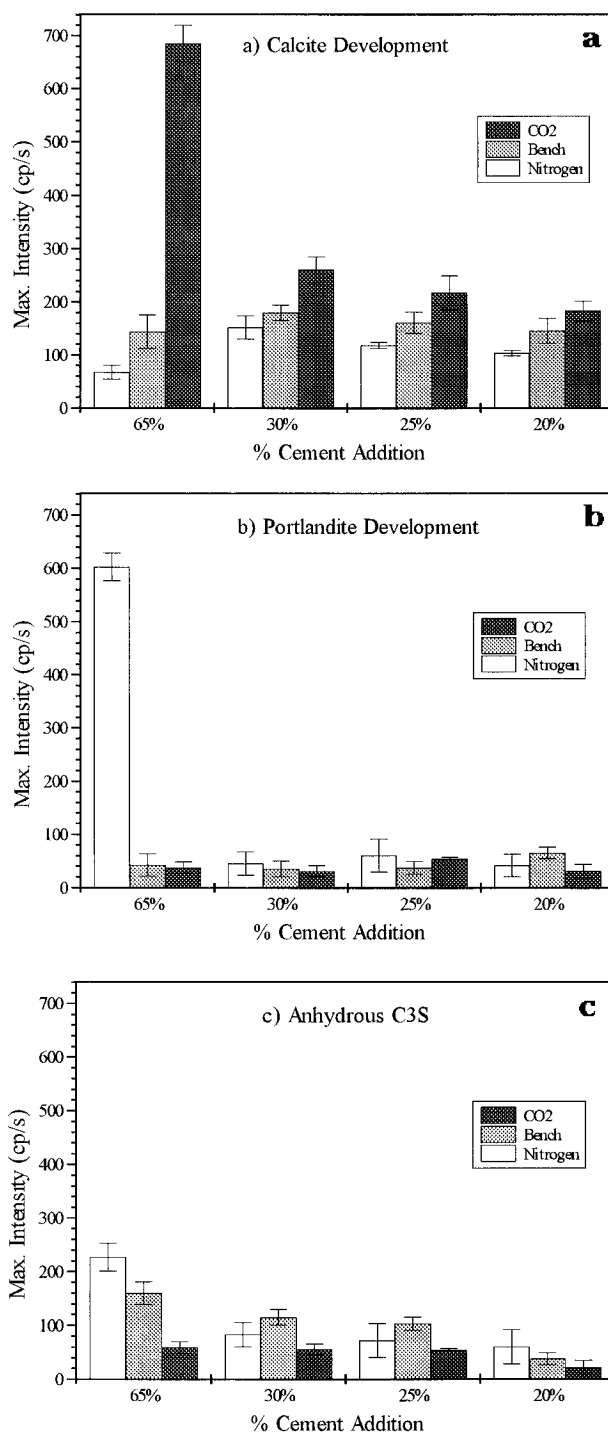


FIGURE 2. (a) Calcite development, (b) portlandite development, and (c) anhydrous C₃S.

Phase Development. Table 3 shows the main crystalline phases identified in the samples at 28 days of age. Phase development, which is estimated by comparing peak intensities of the principal diffraction lines, differs for each set of samples. In the bench-cured samples, portlandite, calcite, and ettringite can be readily distinguished. The nitrogen-cured samples were largely devoid of portlandite but contained larger quantities of ettringite and unhydrated C₃S. In the CO₂-cured samples, calcite, portlandite, and gypsum were important constituents while ettringite was not detected in all samples, including the control. The background intensities recorded were similar for all samples.

The influence of the carbon dioxide curing environment on modifying the hydration of the OPC is demonstrated in

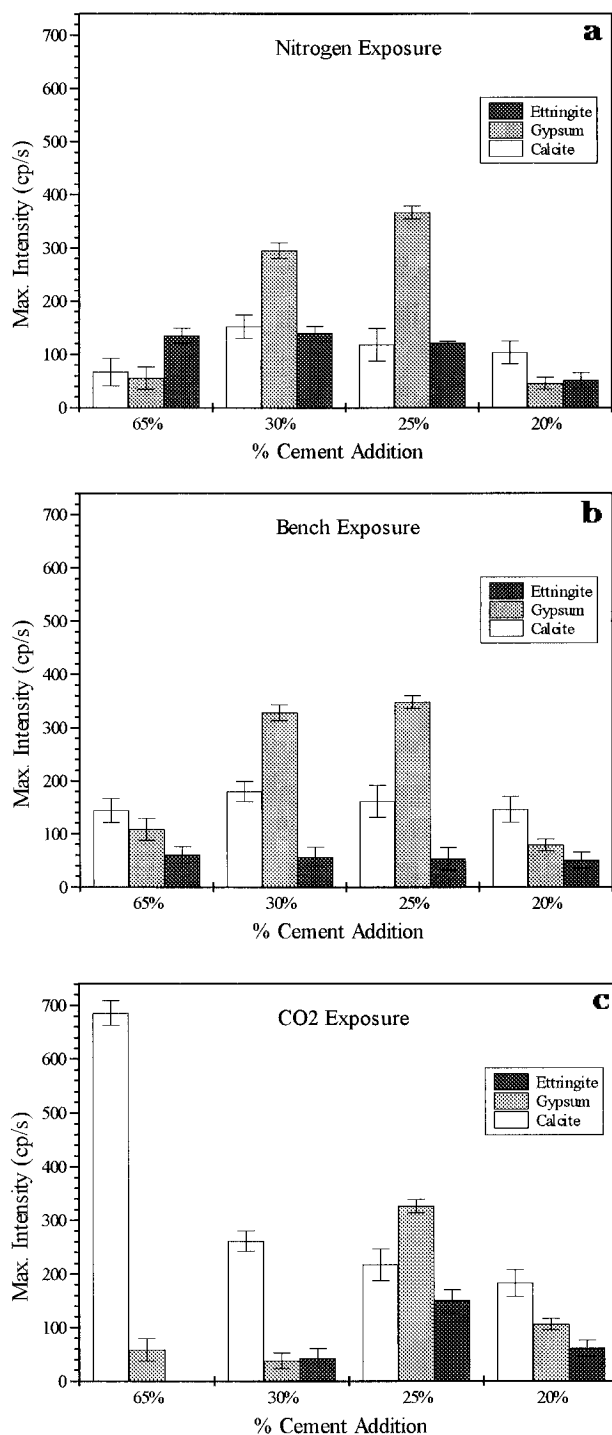


FIGURE 3. Gypsum, ettringite, and calcite development in different curing environments.

Figure 2a–c. Figure 2a shows the gradual increase in the development of calcite in all mixes, according to the following: $\text{CO}_2 > \text{bench} > \text{N}_2$. There also appears to be an inverse relationship between the X-ray intensities of calcite and C_3S , as shown in Figure 2c. Figure 3 shows the intensity of X-rays recorded for gypsum and ettringite and indicates that the latter phase appears to decompose in the presence of CO_2 with a consequent increase in proportion of calcite and gypsum in the product.

Leaching Characteristics. Table 4 gives the metal concentrations in the leachates from the samples cured in the three environments. These results are represented as histograms for the different levels of OPC addition (Figure

TABLE 4

Leachate Metals Concentrations (mg/kg)^a

mix	CaO	Hg	Cr	Cu	Mn	Ni	Pb	Zn	Cd	Ba	As
1N	13.0	2	<1	<1	<1	<1	20	<1	<1	100	120
2N	3.8	7	260	60	<1	20	20	20	<1	60	80
3N	4.6	6	100	20	<1	20	20	20	<1	80	80
4N	6.4	12	200	40	<1	20	20	20	<1	80	80
2C	18.0	3	380	60	<1	60	<1	<1	<1	20	220
3C	4.2	3	233	60	<1	20	<1	<1	<1	40	147
4C	11.0	5	460	60	<1	60	<1	<1	<1	20	160
1B	19.4	1	60	60	<1	<1	40	40	60	120	160
2B	23.8	15	680	140	<1	100	<1	<1	<1	20	220
3B	22.8	23	520	40	<1	80	<1	<1	<1	40	200
4B	22.3	31	500	73	<1	53	<1	<1	<1	47	167

^a CaO in percent. Sample 1C results not available.

4). The bench-cured samples (B) gave the highest readings for a range of metals (Cr, Cu, Zn, Pb, Hg, Ba, and As). The CO_2 -cured samples (C) presented lower values, whereas nitrogen curing (N) provided the lowest leachate metal levels for all levels of OPC addition.

Discussion

The effects of carbonation on solidified waste forms are different from those on structural quality concrete as they may be beneficial and not deleterious. This primarily arises from the increased metal binding capacity and improved structural properties of the solidified waste forms. Work currently in progress is exploring these characteristics through the study of the fixation of toxic species, particularly in precipitated double salts and by sorption into gel hydration products. In addition, there appears to be an important link between certain microstructural features and the mobility of toxic species from solidified waste forms that may be enhanced by natural or accelerated carbonation reactions.

Carbonation has been seen to influence the properties of cement-solidified waste forms in a number of ways. For example, CSH gel products, which are recognized as playing an important role in the fixation of toxic species, are significantly altered. This manifests itself as a change in the ion-exchange capacity of the gel (31, 32) as carbonation proceeds. The gel becomes progressively polymerized as OH and Ca are consumed in the production of CaCO_3 despite the apparent maintenance of morphology (24, 33).

Portlandite, which may be present in abundance within hydrated cement-containing materials, also directly reacts with CO_2 to produce calcite. The volume change accompanying this reaction can help to fill pore space, densify the product, and improve structural integrity. In addition, the direct nature of this particular reaction may lead to the precipitation of calcium metal double carbonates such as calcium zincate when certain toxic species are present in solution (20).

The most obvious effect upon waste forms is on strength. The improvements realized result from the increase in hydration of C_3S driven by the formation of calcium carbonate, which is clearly illustrated in Figure 5 where the amount of anhydrous alite can be seen to be much lower in carbonated samples. Examination of waste forms by XRD (Figure 2 a–c) shows that it is possible to closely observe the relationship between C_3S hydration and the formation of calcite. This relationship suggests that, for the beneficial effects of carbonation to be fully realized, an optimized cement level has to be maintained. However,

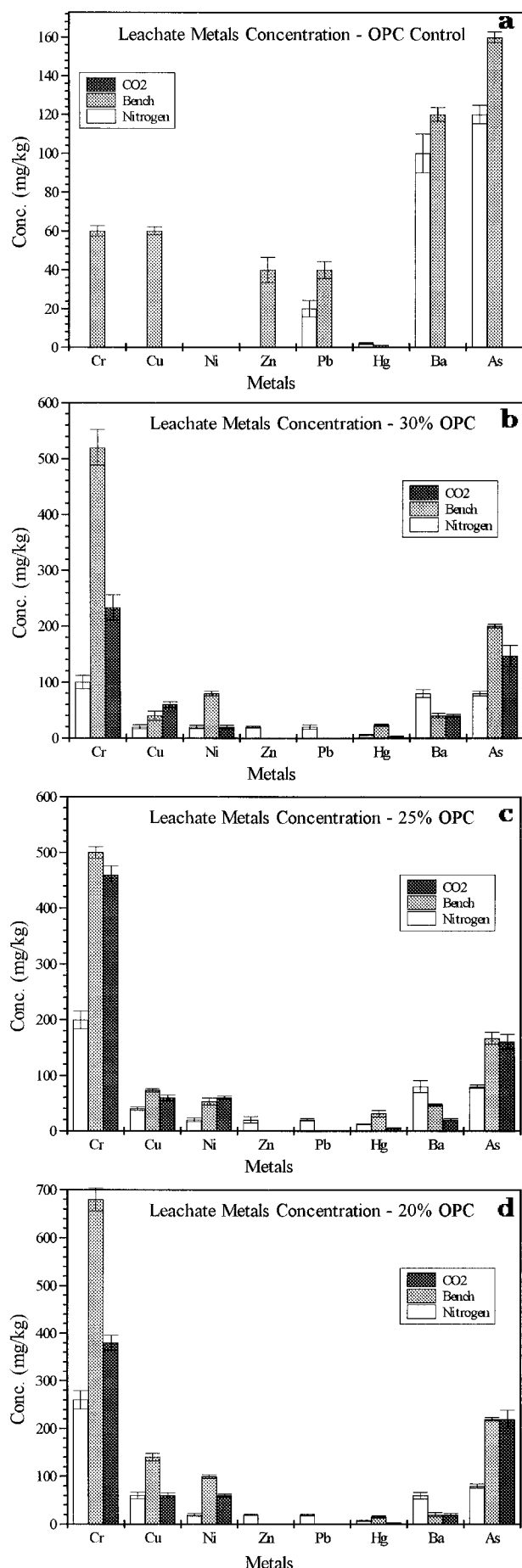


FIGURE 4. Leaching characteristics.

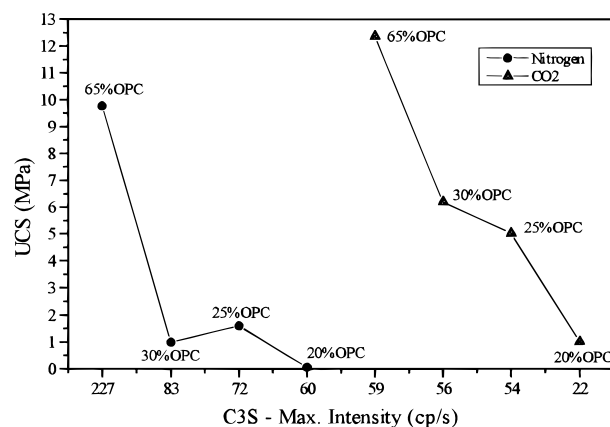


FIGURE 5. Relationship between the amount of anhydrous C_3S and strength development.

this optimum may be cement specific depending on the waste materials to be treated as a result of interference due to waste/binder interactions (15).

The phase development displayed in waste forms can be seen to be dependent upon the curing environment. For example, the nitrogen-cured samples were essentially devoid of hydration-related phases except for a trace amount of CH, which probably formed during mixing. On the other hand, in waste forms where calcite, gypsum, and ettringite were present together, complete carbonation had not taken place. This can be illustrated with reference to eq 1, where ettringite decomposes in the presence of moisture to give calcite and gypsum. Upon completion of the reaction, ettringite, which has been recognized as an important cementing phase in some solidified waste materials, is replaced by these phases and may continue to structurally stabilize the waste form.

The factors that control the production of leachate are complex and interrelated. In this work, however, the effects of carbonation appear to be beneficial, and this is probably a result of several aspects of the carbonation reaction. It is generally recognized that the buffering capacity of waste forms is related to the ability of CSH and CH, for example, to maintain pH. Therefore, it might be expected that those waste forms where normal hydration has proceeded will have improved leaching performance over those where CH, for example, might be absent. This proved not to be the case as was seen when the leaching results from bench-cured samples are compared with CO_2 -cured mixes in spite of the ability of CO_2 to lower local pH conditions by 3 units or more. This in turn suggests that pore modification and perhaps precipitation of salts containing toxic species also had an important effect.

The results from the nitrogen-cured mixes do however clearly illustrate the benefits of stabilizing a waste prior to treatment with OPC. In these samples, hydration did not proceed and the waste maintained the optimum pH conditions of the sludge. This manifested itself with improved leaching results.

The leachate analysis shows an adequate reduction in metal concentration compared to the raw waste. Nevertheless, many questions have arisen, such as the nature of interactions between the hydration and setting of cement paste. The kinetics of accelerated carbonation also need to be studied in some depth, and at the end, the solidified waste specimens may be tested again for strength and subjected to microstructural examination.

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