

The influence of interference effects on the mechanical, microstructural and fixation characteristics of cement-solidified hazardous waste forms

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Abstract

The hydration behaviour of ordinary Portland cement (OPC) and other hydraulic binder systems in the presence of industrial wastes considered "suitable" for cement-based solidification is not always consistent. Waste-binder interference effects can significantly alter the short and long term mechanical, microstructural and binding characteristics of solidified waste forms containing materials from a wide variety of waste streams. In general, the mechanisms of interference can be explained and this lends support to the need for a critical evaluation of current waste form quality control procedures and the development of additional pre-treatment/alternative treatment methods. Future research studies including the in-situ examination of waste forms together with an in-depth quantitative analysis of the effects of waste species on the short- and long-term properties of solidified products is warranted. © 1997 Elsevier Science B.V.

Keywords: Cement-solidified waste; Waste–binder interference

1. Introduction

1.1. Background

Cement-based stabilisation/solidification (S/S) technology is one of several treatment technologies for industrial residues and contaminated land [1–3] and is widely

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used in North America in this respect [4,5]. Ordinary Portland cement (OPC) is often used as the binding agent on its own, or in combination with cement replacement materials [6], which may be hydraulic (cement kiln dust) or pozzolanic (pulverised fuel ash, slag etc.) in nature. Initially designed for the chemical fixation and encapsulation of electroplating sludges and radionuclide wastes, S/S systems are now being applied to a wide range of wastes that may previously have received disposal without pre-treatment. These include mixed organic/inorganic industrial wastes, soils contaminated with toxic metals and organic constituents, incinerator residues and bulk wastes from the power generation industries [7,8]. In many cases this diversification from the origins of the technology has highlighted the process difficulties associated with specific waste types. A fundamental re-evaluation of the evidence from the research literature [9–12] has on occasions conflicted with the claims of commercial S/S operators.

Central to a rational understanding of the chemistry of S/S processes is the ability to distinguish, at both the microstructural and molecular levels, between the mechanistically distinct processes of stabilisation and solidification, and to place research data in the context of field application [3,11].

1.2. Performance monitoring

The test methods used to assess cement-solidified wastes vary [12] but are generally based upon setting and strength development (solidification) and the application of a leaching test to assess the extent of fixation (or stabilisation) of waste-borne elements. Common test methods have been evaluated and reviewed elsewhere [13,14]. Leach tests are invariably accelerated examinations of waste stability and are usually aggressive in an attempt to compensate for their short duration and thus provide conservative assessments of leaching performance that are protective of environment. Leachants such as distilled, de-ionised water and dilute acids are used for this purpose and the results obtained provide an assessment of the extent of waste stabilisation effected during processing and the capacity of binding agents to “neutralise” aggressive leachants. However, because they are accelerated tests, leach tests rarely relate to actual ground conditions at the intended site of disposal, and should instead be regarded as comparative performance tests under standardised conditions. This is a critical factor for consideration when assessing the long-term stability of waste forms from short term tests [15,16]. Furthermore, these mass balance assessments of stabilised waste forms rarely account for the effect of proton activity (pH) on the speciation of inorganic components, some of which may exhibit wide variations in behaviour between valence states (e.g. As(V) As(III), Cr(VI), Cr(III) or ionised forms (NH_4^+ vs. NH_3 , CN^- vs. HCN), for example [17].

Effective containment of a waste involves an interaction of both physical and chemical mechanisms. Whilst effective physical containment is regarded as an essential pre-requisite of any process, and a significant factor governing leaching and long-term performance also relies heavily on the chemical fixation of encapsulated species. When cement is used, for example, these include, sorption, precipitation and lattice inclusion [16]. Where binders are employed, a direct relationship exists between a binding agent and the immobilisation mechanisms at work and this criteria should govern the choice of

a binder on technical grounds. Factors such as adsorption, absorption etc. are of importance as are the availability and cost of materials and the perceived public acceptability of OPC-type binders, together with the reported ability of OPC to hydrate in the presence of a variety of inorganic waste species. These factors have made hydraulic binder systems based on OPC a popular choice and are reviewed on a scientific basis by Macphee and Glasser [18].

The continuing need to develop economic and improved waste management techniques has increased the potential importance of solidification technology throughout the world. This has been supported by increased research particularly from within the nuclear industry (for example, Wilding [19]). As a result, there is an increasing amount of information available that suggests that there are limitations on the suitability of hydraulic binders for this application (for example [11,20,21]). This appears to result from complex interactions with certain common waste-contained species and to the degree to which these interactions may influence the long-term field performance of solidified wastes.

The often loose relationship between the research literature and field application of the technology has been a perennial problem of the S/S. This is often in strict contrast to other remedial technologies such as bioremediation that appear to have developed effective means of translating research efforts into modifications in the field and vice-versa. In contrast, several authors have reported the inappropriate use of S/S for wastes with high organic contents on the grounds of hydration inhibition, yet oil-soaked sludges, petroleum wastes and organic solvents (see Malone and Lundquist for a review [5]) continue to be solidified with varying degrees of success. Such discrepancies between the laboratory and field work require urgent resolution if credibility for the S/S technology is to be sustained.

2. Process research

Portland cement-bound wastes have been examined in the laboratory by a number of workers. Importantly, few have clearly demonstrated that “normal” hydration reactions are taking place in waste–OPC mixtures. Another approach has been to add single compounds, or simple mixtures to OPC and examine the results. There is the tendency to over extrapolate these results to the solidification of real wastes. There is a major problem with this approach as:

1. Real wastes are invariably complex mixtures of compounds with often contrasting physical and chemical properties that are difficult to characterise;
2. The synergistic or antagonistic effects of multiple component mixtures significantly influence both hydraulic and pozzolanic reactivity, and these effects difficult to predict at the present time.

It is, therefore, inappropriate to assume that a compound will behave similarly on its own as in an admixture with other compounds. When cement-bound waste forms are setting and undergoing strength development, “normal” reaction mechanisms may not be taking place. This is a particularly important factor since “false set” reactions have been shown to be capable of producing rigidity in solidified products. This can be

mistaken for normal binder activity in cement-based systems with and without certain pozzolanic additions [10].

The following work describes selected results from a series of recent laboratory investigations in the use of hydraulic systems to solidify real waste materials using calorimetric, microstructural and mechanical methods of analysis. The objective of these studies has, in each case, been to bridge the divide between single component studies and real wastes and provide robust analyses of the mechanistic control in genuine S/S systems.

2.1. Structural development during solidification

The structural development of cement-based solidified wastes is claimed to result from complex hydration reactions that stiffen and densify the product and impart structural integrity [6]. The hydration reactions of OPC have been widely studied and are described in detail by Taylor [22]. The four main anhydrous phases, namely alite (C_3S) belite (C_2S), tricalcium aluminate (C_3A) and ferrite (C_4AF) hydrate at different rates.¹

The dominant hydration phases under normal conditions are C–S–H, a gel of variable stoichiometry, and calcium hydroxide (CH) which together form some 90% w/w of the solid hydration products of an OPC paste [23] as discrete phases or as an intimate mixture. The remaining solid products are hexacalcium aluminoferrite trisulphate “ettringite” type phases (AFt) and tetracalcium aluminate monosulphate “monosulphate”-(AFm)/ C_4AH_{13} solid solution phase which may be accompanied by C_4AH_{13} or similar phases.

Bonen and Diamond [24] have shown that the composition of C–S–H is distinctive between that derived “in situ” from larger cement grains to that formed by smaller grains which infills porosity as amorphous or skeletal groundmass (mean gross Ca/Si ratios of 2.1, 2.3 and 2.8, respectively). Intimate C–S–H and CH mixtures are characterised by Ca/Si ratios of 1.7 to 1.8 and as both ettringite and monosulphate components may be associated similarly, the composition of this phase may appear to change wildly. This is an important factor for consideration when assessing the interactions of C–S–H with waste contained species.

In practice, the amount of cement used during commercial solidification may vary considerably depending on waste type, success at the pilot scale and cost. For example, cement contents varying from 5% to 20% w/w may be routinely used to solidify. The lower levels of cement addition cannot always be adequate enough to physically coat all the individual waste particles present in the solidifying mixture, but nevertheless, treated products tend to set and develop rigidity. This is generally assumed to be the result of physical changes induced by normal “hydration processes” despite the ability of “false set” mechanisms, such as the precipitation of salts like gypsum, to impart “adequate” strength [10,11]. These mechanisms also appear to be supplemented, in certain cases, by the results of atmospheric carbonation which hitherto has received only limited attention. This enhanced strength, however, must not be interpreted as effective solidification

¹ Nomenclature used in this work: C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, H = H₂O.

Table 1
Strength development for increasing zinc plating waste additions

UCS (kPa)	Waste addition (% w/w as solids)		
	1	2	3
7 day	5196	2788	39
28 day	5837	4417	69

despite the fact that in certain cases, carbonation may prove to be beneficial in nature [25].

The strength requirements for solidified products in the UK, for example, are governed by the issue of a waste management licence by the controlling Waste Regulation Authority (WRA). A 28 day strength of 700 kPa is typical of that considered acceptable but criteria may be as low as 350 kPa depending on the circumstances of testing. For materials that may contain a cement content of 20% w/w, these strength requirements are surprisingly low despite the limiting effects of relatively high water/cement ratios. Even so, it is known that these strengths may not always be achieved and that solidified products sometimes require reprocessing before the required strength is met.

As a considerable number of chemical species are known to interfere with, or even completely disrupt OPC hydration, a reliance upon physical parameters alone to indicate

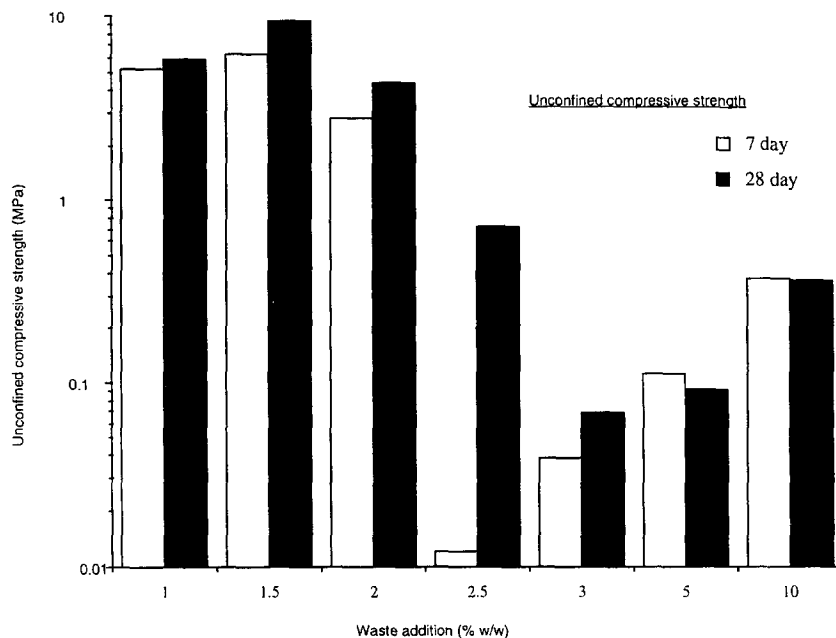


Fig. 1. Strength development for waste additions to OPC.

“normal” binder activity should be treated with suspicion. Indeed, as solidified products are expected to harden over a 2–5 day period [6] waste/binder interference and retardation effects must be a commonly accepted phenomenon.

A simple way of examining the effects of waste is by adding progressive quantities to OPC. Apart from the strength loss gained by dilution effects, the influence of waste on the development of physical and other parameters can be established. As seen during previous work [10], a severe strength loss could be observed at very low additions. For example, Table 1 shows 28-day strength development of Portland cement paste with increasing additions of a zinc-containing metal plating waste. At 3% addition (w/w total solids) a reduction in strength of approximately 99% of the OPC paste control was observed. Fig. 1 shows the general effect of increasing waste additions, as typified by a zinc/chromium plating residue on unconfined compressive strength (UCS). Fig. 2 shows the effects on setting, as defined by cone penetrometry, of waste forms containing increasing proportions of a commercially blended inorganic waste product produced from a variety of waste streams.

Nevertheless, the development of “short term” structural stability must also not be considered as a guarantee of long-term waste form properties. The potential for diverse and adverse chemical interactions between waste components and matrix may cause dimensional instability [26] resulting from the encapsulation of reactive metals, ion-exchange resins or potential expansive phases.

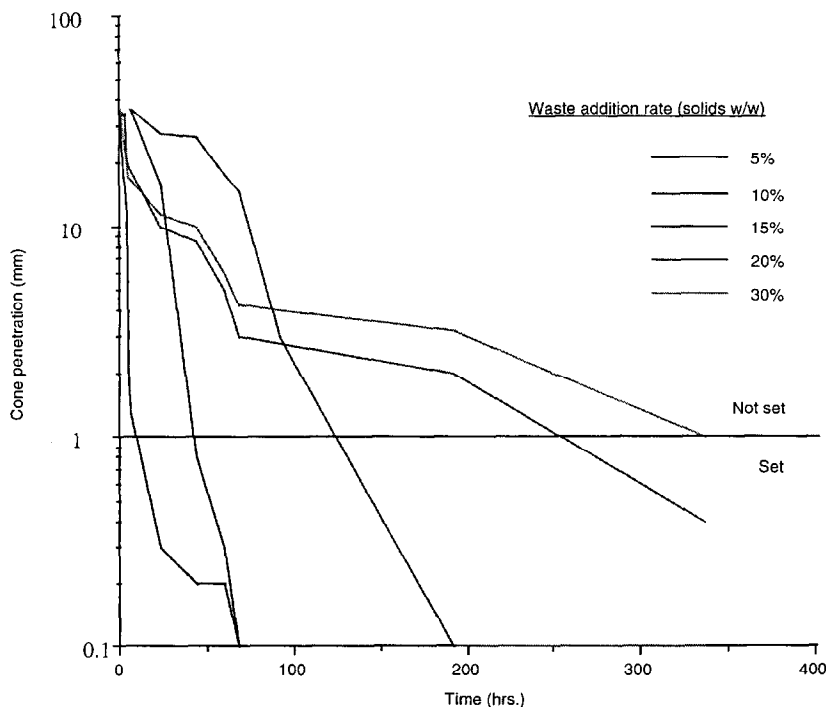


Fig. 2. Setting curves for waste addition to OPC.

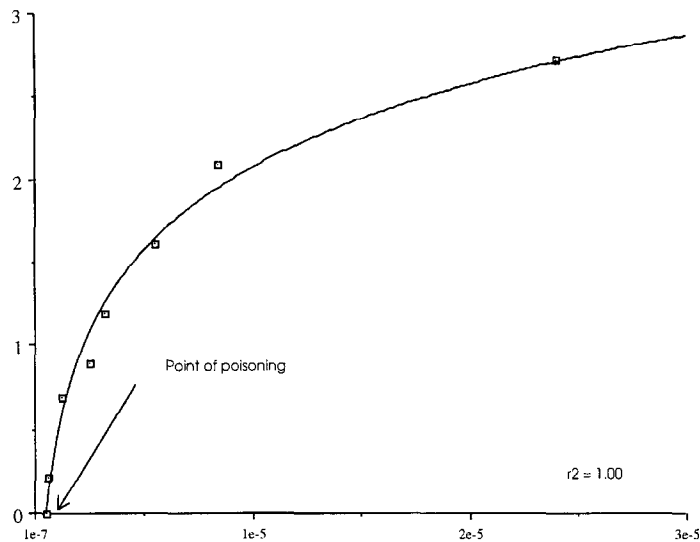


Fig. 3. Poisoning of hydration by waste additions.

2.2. Hydration of hydraulic binder systems

The hydration of OPC is exothermic and can be examined by isothermal conduction calorimetry. As hydration proceeds, a characteristic rate of heat is produced that is a function of composition, hydration efficiency of the system, temperature and other effects [27,28]. In general, however, the heat of hydration curve for OPC closely resembles that produced by C_3S and can be correlated to the amount of CH evolved [22].

Waste/OPC mixes tend to produce heat of hydration curves that are dissimilar to the pure hydraulic or blended binder systems. Often, as the waste content of a system increases, the main exotherm becomes less pronounced and broadens. At waste/binder ratios typically used during commercial operations, the main hydration exotherm may be absent and normal hydration is therefore indefinitely retarded. Fig. 3 illustrates these poisoning effects for a commercially blended waste stream containing materials derived from, for example, metal plating and finishing operations and laboratory residues containing a range of heavy metals. Here, the maximum rate of heat evolved, as defined by the gradient of the hydration curve, for incremental additions up to 30% w/w (solids) are plotted against time (in reciprocal seconds) taken for the maximum amount of heat to be evolved. Table 2 gives typical total heats recorded for a zinc and chromium

Table 2
Total heat of evolved at 120 h for increasing zinc plating waste additions

Waste addition (% solids w/w)	0	0.25	0.5	1.0	1.5	2.0	2.5
Total heat evolved (kJ kg^{-1} solids)	291	302	285 ^a	280 ^a	182	144	20

^a Extrapolated values.

containing plating waste during calorimetric analysis up to 120 h after mixing. The point of poisoning, where the main period of heat evolution is absent and indefinitely retarded, is also given in Fig. 3. This point, which corresponds to a particular waste addition, provides a convenient reference point to measure and compare the total heat produced by different waste products.

It appears normal to find that despite the drastic reduction in the total heat of hydration produced by poisoned solidified products a small, but measurable, rate of heat ($0.02\text{--}0.04\text{ W kg}^{-1}$ solids) can often be recorded indicating that limited reactions which are probably diffusion controlled may continue. A comparison between the total heats given in Table 2 for the 2 and 2.5% w/w waste additions can be used as an illustration. For OPC, for example, a typical heat of hydration of approximately 400 kJ kg^{-1} can be realised at 28 days age where values of $< 70\text{ kJ kg}^{-1}$ are typical for poisoned binder systems. It is worth noting here that the heat of hydration characteristics of poisoned systems can be largely reproduced in the laboratory by employing simple mixtures of, for example, heavy metal hydroxides [29].

2.3. Microstructural development of solidified waste forms

The microstructural development of solidified products results directly from the hydration of the binders used. Hydration processes cause densification, a reduction in permeability and can improve the ability of the product to combat aggressive conditions after disposal. On examination, cement-solidified wastes should ideally be expected to clearly display the products of hydration, but results may vary considerably contingent on the waste and binder used.

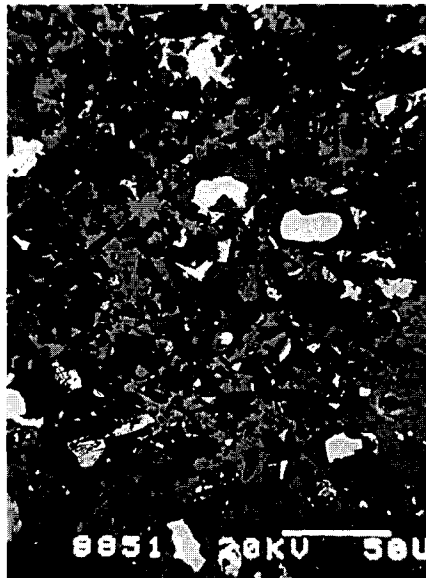


Fig. 4. Micrograph of solidified waste form (BSE image).

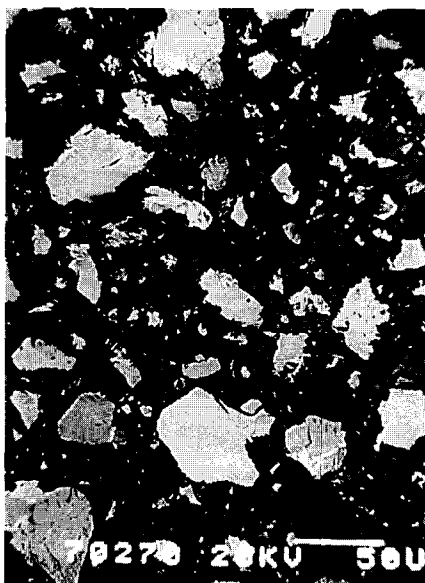


Fig. 5. Micrograph of waste form with hydration interference (BSE image).

The solid phase of hydrated cement paste is dominated by C–S–H gel which can be difficult to characterise by electron microscopic techniques. Other phases such as CH, AFt and CS are more crystalline. When present in solidified products, they are often found associated with voids owing to the relatively higher water contents of these materials.

By way of illustration, Fig. 4 shows a backscattered electron (BSI) micrograph of an OPC-solidified product containing a small quantity (0.25% w/w total solids) of a chromium plating waste. Porosity appears black, CH, infilling porosity as light grey, amorphous and skeletal C–S–H as dark grey and larger cement phenograins display characteristic white coloured unhydrated cores enveloped by a ‘shell of hydration product’ [30]. In this instance, the product is characterised by an intimate mixture of waste enveloped by hydration products. Fig. 5, however, also shows a BSI image of a waste form containing a zinc/chromium plating filter cake and OPC from the same batch of cement at 56 days of age. Here, in the authors opinion, the overall degree of hydration, as defined by the average depth of hydration shells on larger phenograins was less as a result of interference effects. In addition, the degree of porosity occupied by C–S–H groundmass was also reduced, although some growth of AFt (not evident in this micrograph), owing to limited reactivity of the aluminate/ferrite cement phases, was observed [31].

It should be noted that in the study undertaken by Diamond and Bonen [30] the relative degree of hydration of adjacent cement grains in concrete at normal water/cement ratios was found to vary wildly. Nevertheless, solidified wastes which are affected by retardation and interference effects can display phenograins with an overall lower degree of hydration typified by reduced hydration shell thickness and a more open

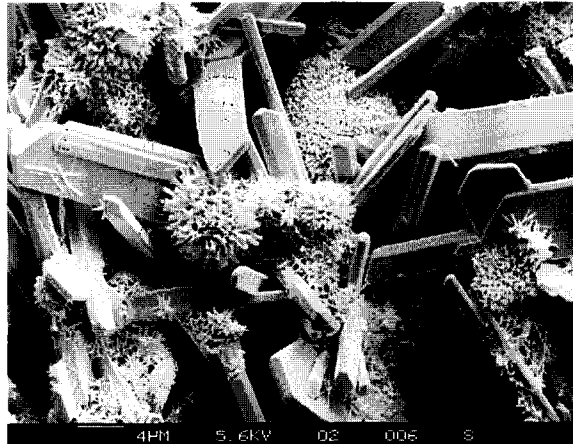


Fig. 6. Solidified FGD waste showing ettringite and euhedral gypsum development.

microstructure characterised by sparse and discontinuous skeletal and amorphous C–S–H gel distribution. These waste forms also have a lower than expected compressive strength, extended setting times and reduced total heats of hydration.

An additional example of waste specific effects is shown in Fig. 6. Here we illustrate the hydration products observed in stabilised (synthetic) flue gas desulphurisation (FGD) waste augmented with OPC [11]. Products of OPC hydration such as CH and C–S–H, as described above, are clearly absent and instead we see small ettringite and euhedral gypsum crystals surrounding PFA and forming an interlocking matrix. Here then, alternative enhanced ettringite development appears to play a key role in strength development consistent with ettringite crystallisation which occurs when sulphate from the FGD waste remains available in the solution phase.

X-ray diffraction techniques can be used to chart the progress of hydration of waste/binder mixes. CH, AFt, monosulphate and the original cement clinker phases can all be readily detected, although sometimes crystalline components of the waste may significantly complicate the diffraction patterns obtained. For example, during increasing addition to OPC of a mixed metal plating waste (zinc and chromium) known to poison hydration, the intensity of portlandite reflections obtained (d -spacing at 4.90 Å) decreased until resolution was no longer possible. At the same time, the intensity of peaks obtained for AFt decreased dramatically whereas the intensity of the reflections for C_2S (2.80 Å) and C_3S (2.76 Å) increased markedly indicating that the relative proportion of the anhydrous cement phases increased, as hydration became retarded, despite dilution effects. Fig. 7 illustrates this effect with reference to a solidified product containing material from the blended, commercially solidified, waste stream previously described. Fig. 8, however, further illustrates this effect in a plot of comparative X-ray intensities recorded for portlandite (CH) against 7 day UCS for a number of waste forms containing incremental additions of this waste material.

The mineralogy of laboratory-produced, OPC-based waste forms in which hydration has been indefinitely retarded is often characterised by the presence of AFt/AFm

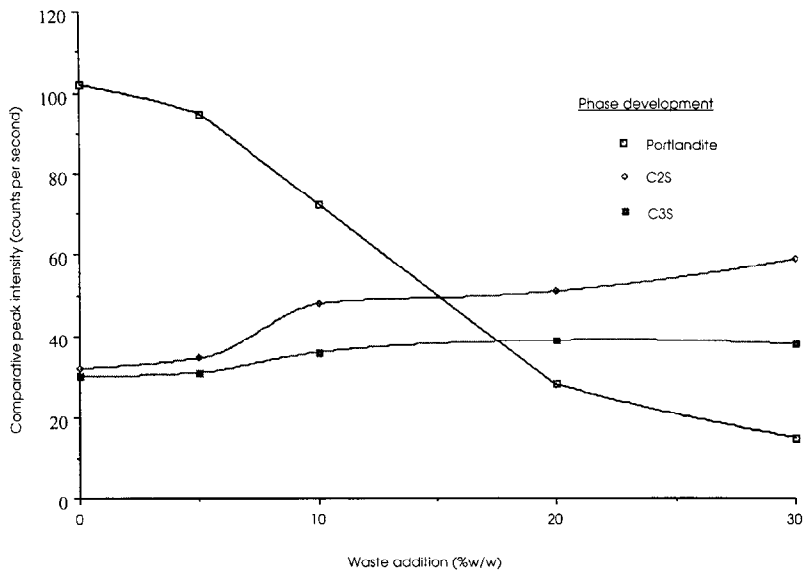


Fig. 7. Effect of blended waste additions on X-ray intensity for portlandite, C₂S and C₃S.

phases. In the absence of other phases, early age development ettringite “type” mineralogy may be largely responsible for the waste form properties at this age. At later ages, however, other phases of importance may result from diffusion-controlled reactions discussed above.

Therefore, inhibition of hydration by waste specific effects is of primary concern as it

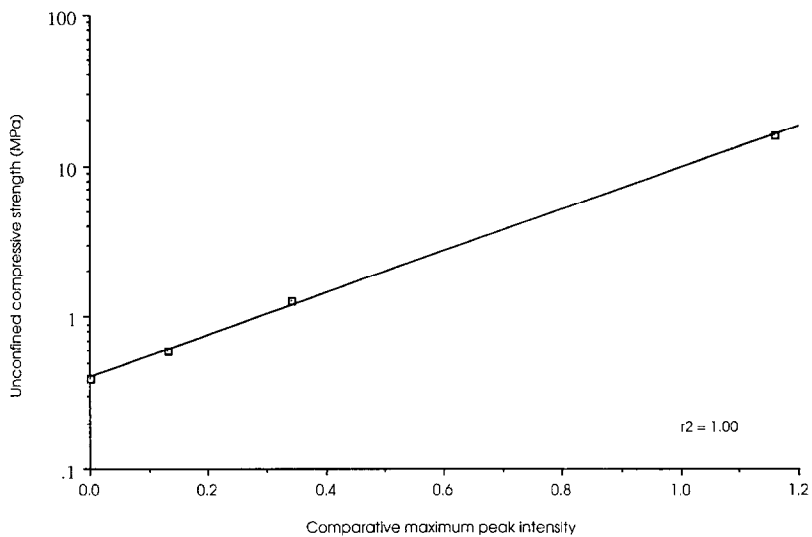


Fig. 8. Relationship between portlandite X-ray intensity and 7-day UCS.

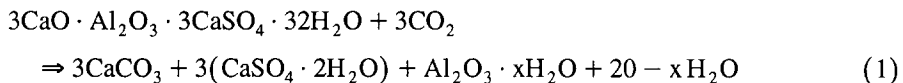
can result in significantly impaired physical and leaching performance (e.g. such as that reported with copper and chromium sludges by Shin et al. [32]). It should also be noted that waste-dependent time effects have also been identified elsewhere [33] and that longer term changes in the microstructure and fixation capability in waste forms do occur; thereby reinforcing the view that current testing protocols cannot be used to reliably predict the longer-term properties and performance of waste forms.

2.4. Effect of carbonation of solidified waste forms

The influence of carbonation on the properties of solidified wastes has hitherto been largely neglected. Carbonation is capable of inducing setting and strength development in waste forms where hydration is significantly retarded. In addition, susceptibility of waste forms to carbonate may explain why, for example, some wastes may be more easily processed during summer months when warm temperatures and drying winds can facilitate carbonation. A similar effect may also explain why, in the authors experience, samples of cement-bound wastes sealed in plastic bags often appear not to set whereas companion samples exposed to laboratory conditions develop strength within a few days. Analysis by X-ray diffraction can be used to examine the enhanced development of carbonation but it should be pointed out, however, that alternative reasons for this phenomenon may also apply.

The process by which carbonation proceeds may also be different for different wastes and also dependent upon the severity of retardation of hydration. In general, the carbonation reaction may be expected to involve AFt/AFm, C–S–H gel and CH. The carbonation reaction undertaken by ettringite may be represented in Eq. (1) [34], whereas Eq. (2) shows that for CH. In Eq. (1), aluminium is not shown as transforming to gibbsite as might be expected. This probably represents the authors uncertainty as to whether the pure phase was formed. The carbonation of C–S–H may be expected to result in the production of silica gel and CaCO₃, which for the latter, could form in the sequence: vaterite, aragonite and calcite particularly if the degree of cement hydration is low [35].

Carbonation reactions for ettringite



Carbonation of portlandite



The changes induced by carbonation can be expected to affect both microstructure and fixation characteristics of disposed waste forms. The pH and redox conditions within a waste form can be expected to be significantly altered as carbonation proceeds. This could result in phase changes within the waste/binder system and in the extreme, changes in the fixation characteristics of the waste form which may result in the selective release of specific waste components [36]. Carbonation can also be expected to be a factor for consideration in waste forms disposed in open or partially buried environments, although



Fig. 9. Alite (C_3S) "rich" OPC displaying "gel" dominated microstructure.

the latter much less so. The influence of seasonal variations in groundwater levels and the possibility of CO_2 gas generation from both organic (e.g. from an adjacent sanitary landfill) and inorganic processes (waste/binder interactions) augmented by the effects of acidic ground conditions may yet prove to be important factors for consideration.

2.5. Binder chemistry and waste form properties

One cannot assume the mere presence of a hydraulic cement within a process formulation will provide adequate strength and fixation. Different cement and pozzolan systems may exhibit a wide variety of chemistries and even relatively minor changes in the anhydrous nature of binder systems can have significant effects upon the microstructural development of waste forms. For example, the alite content of Portland cement falls within the general range 50–70% w/w (Bogue analysis), aluminate and ferrite between 10 and 30% w/w with belite making up the balance. The micrographs, Figs. 9 and 10, show waste forms bound by "modified" OPC. Here, the aluminate and ferrite compositions were fixed and the alite and belite components were "adjusted" to vary between 24 and 50% w/w and 70 and 10% w/w, respectively. The micrographs clearly show major differences in the microstructure observed for the end members of the series at the same waste loading of 40% w/w.

Fig. 11 shows how cement type can influence early age properties of waste forms. Here contrasting shaped curves have been produced from plotting strength development against setting time for blended OPC and high alumina cement (HAC) for a range of waste additions (0–40% w/w) of a commercially blended waste stream. The products were produced with a fixed solids content of 55% w/w and examined for mechanical, microstructural and leaching properties. With the OPC-based binder, an increasing waste/binder ratio resulted in extended setting times and lowered strength. For HAC, however, as strength decreased with increasing waste additions, setting times which were defined by cone penetrometry were found to decrease markedly.

Shin et al. [32] have shown that the leaching properties of waste forms containing

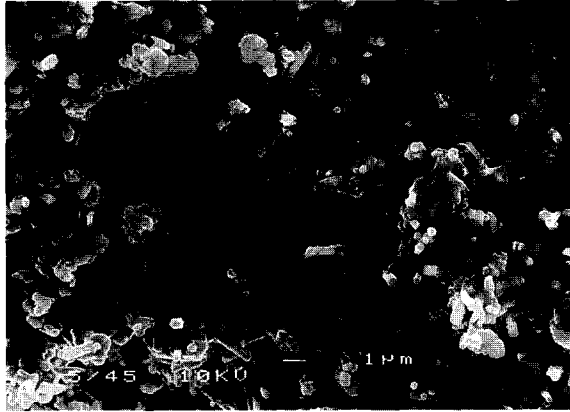


Fig. 10. Belite (C_2S) "rich" OPC displaying crystalline microstructure with gypsum.

heavy metals can be significantly influenced by binder choice. Fig. 12 illustrates the effect of binder choice on the amount of leachable chromium determined on waste forms containing commercially blended inorganic wastes at a fixed waste/binder ratio. The five binders shown consisted of a 1:10 blend of metakaolin with OPC, rapid hardening Portland cement, sulphate-resisting Portland cement, white Portland cement and a calcium aluminate cement. The waste forms, which were treated similarly, were subject to a single leaching test procedure. The estimated standard deviation indicated on the

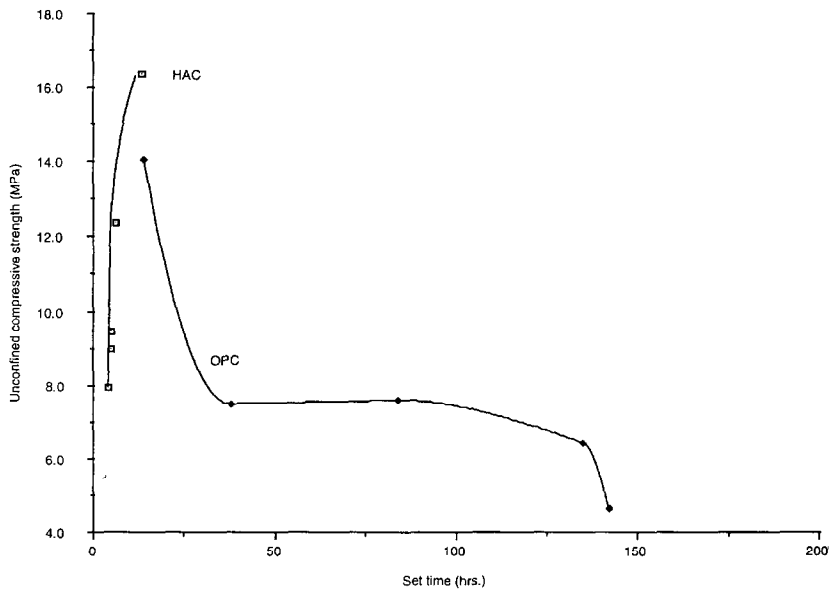
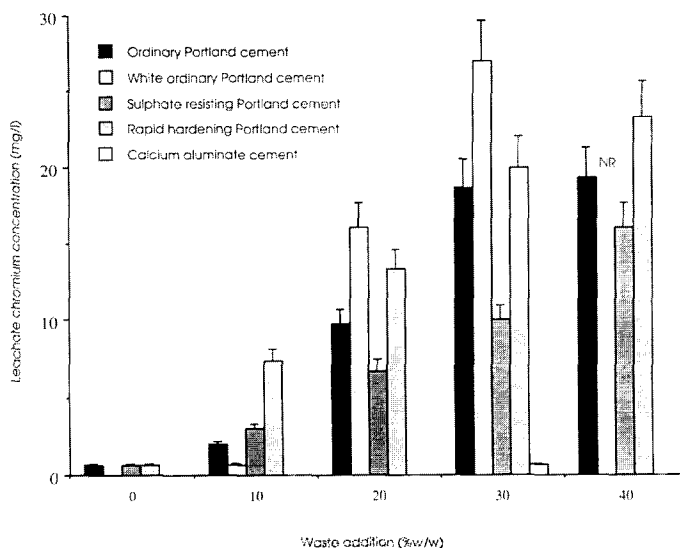


Fig. 11. Influence of binder type on waste form setting and strength characteristics.



NR = no result available.

Error bars = estimated standard deviation.

Fig. 12. Leachate chromium concentration from metakaoline–cement blended binders. (NR = no result available. Error bars = estimated standard deviation.)

figure as error bars was calculated from control samples of known composition. The results clearly indicate that, in this instance, the differences in the leaching performance resulted from the binder systems employed. Nevertheless, the careful selection and proportioning of hydraulic binders can be augmented by pre-treatment steps to minimise the effects of variability within waste [26].

In addition to phase composition, kinetic factors are of significance to the potential stability of solidified waste forms. For a series of pozzolan solidified flue gas desulphurisation wastes examined at 28 days and 84 days respectively, dissolution of gypsum and renewed growth of ettringite was demonstrated by microstructural analysis. Continued formation of significant quantities of ettringite in these matrices over time and subsequent to product hardening could potentially be expansive in both OPC and PFA-FGD systems and cause loss of strength, disruption of microstructure as implied by the strength data obtained in this study [11].

3. Implications for field application

The process of solidification is entirely contingent upon the formation of stable hydration products that bind waste components and provide a solidified product with strength and dimensional stability. A number of intimately linked components are responsible for the properties of the hardened cementitious system [16] and can be described as: crystalline, amorphous phases, aqueous phase; and porosity.

Table 3

Classification of interference effects for waste additions to OPC leading to indefinite retardation (poisoning) of hydration

Reaction	Waste type (process)	Initial phase (prior to poisoning)	Final phase (after poisoning)	Total heat (evolved to P^a)
Initial	Zn Ni, Zn, Cr	e.g. C_3AH_6	AFt	Low (40 kJ kg^{-1} ^b) > 50% > 24 h
Initial	Zn Ni, Cr, Cu	AFt	AFt	Moderate (50 kJ kg^{-1}) < 50% < 24 h
Initial/ intermediate	Numerous (blended) ^c	AFt	AFt	High (70 kJ kg^{-1}) < 60% < 120h

^a P denotes the point of poisoning (the waste addition at which indefinite retardation occurs).

^b Total heat of hydration for OPC is taken as 400 kJ kg^{-1} for comparison purposes.

^c Commercially neutralised, blended and solidified product.

If any of these components is compromised, then others will be adversely affected [16]. For example, where OPC is concerned, C–S–H dominates the solid phase of the hydrated product and contains most of the gel pores. These pores have a high surface area and largely control the sorption potential of the cement. In addition the relationship between C–S–H and CH [37] significantly influences microstructural development and the buffering capacity of a cementitious product. Interference from a waste with either of these phases, for example, will have an important effect and properties such as durability performance may be adversely affected.

3.1. Classification of hydration interference

The disruption of hydration processes can be clearly seen reflected in the calorimetric, mechanical and microstructural properties of solidified products [30]. In spite of significant interference with hydration, a variety of metal plating and finishing wastes produced waste forms where the early age, < 120 h reactivity of alumina-containing phases, was of importance (Table 2). In this case, phase development could be related to the heat of hydration. From this work, which involved an examination of solidified products containing increasing waste additions, a tentative classification system of interference effects was produced, and is summarised in Table 3. The resultant waste specific nature of hydration curves obtained from waste OPC mixtures of differing proportions, as shown in this work may place a requirement on calorimetry to be incorporated in future performance assessment criteria.

3.2. Mechanisms of interference

Solidified waste forms are very different from laboratory-prepared cement pastes in which many observations concerning hydration behaviour have been recorded. Nevertheless, it is logical to consider that hydration must proceed in manner that is predictable to a certain degree even though the field hydration environment may be hostile. In the author's opinion, the very fact that a limited but measurable degree of heat of hydration

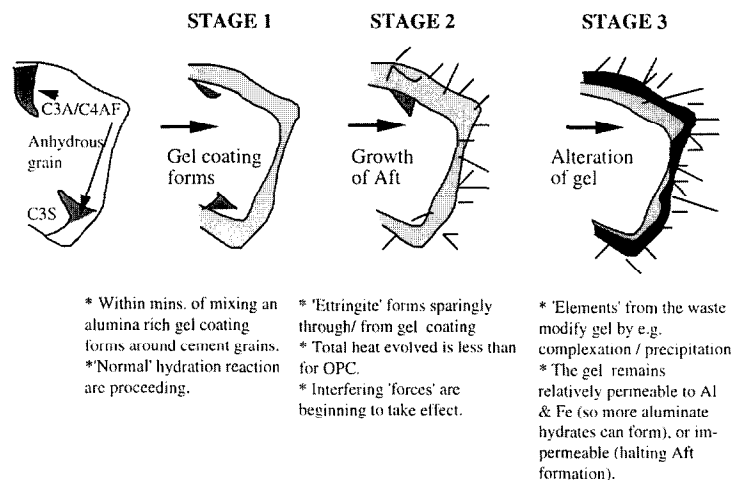


Fig. 13. Generalised mechanism for interference with hydration of OPC.

occurs in affected waste forms suggests that "normal" hydration reactions are likely to be stifled by the interference effects from waste-borne agents.

From hydration studies on OPC [38], it is known that the aluminate phases are capable of producing AFt within < 10 min of mixing cement with water. Within a short time, a gelatinous layer can be observed to form and, at the end of the induction period, further products of hydration "burst" through. The formation of the gel coating around cement particles is an important reaction rate determining step and when modified by waste contained species, as observed for admixtures [39,40], it could easily explain interference with normal hydraulic activity and the consequent low heats of hydration recorded [31].

Modification of the gel coating described may be achieved through complexation or precipitation effects rendering it essentially impermeable, e.g. complexation and removal of calcium at the surface of hydrating cement grains by anionic or cationic agents will limit the production of both CH and C-S-H and, where appropriate, alter the chemistry of these phases (e.g. gel Ca/Si ratio during progressive hydration) by, for example, the removal of calcium through precipitation effects. Subtle but selective differences in the interference mechanisms operating on a gel coating may also explain why some products show minor AFt development whereas others do not. By way of illustration, Fig. 13 gives a schematic representation of the effects of interference on the progress of hydration of a cement grain. It should be noted, however, that other mechanisms may also be in operation during poisoning of hydration. Fig. 14 shows a micrograph of a waste particle partially enveloped by AFt. This particular waste form contained an OPC-based solidified zinc metal plating residue derived from a cyanide-based process and was largely devoid of this phase with the exception shown. This clearly illustrates that selective mechanisms were in operation, were influenced by localised physico-chemical effects and that the spatial distribution and microstructure of phases important to the fixation of toxic species may be discontinuous within a solidified waste form.

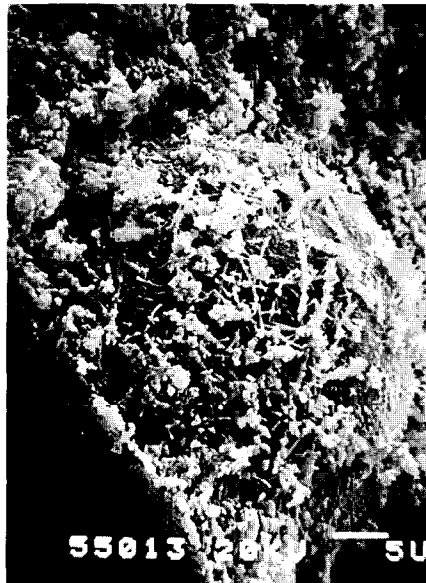


Fig. 14. Aft enveloping metal plating waste particle as a result of selective physico-chemical effects.

In general, it can be concluded that the evidence available from microstructural, calorimetric and other techniques suggests that the hydration of OPC and tricalcium silicate are essentially similar [22]. The main difference appears to surround the nucleation and growth of C-S-H during hydration. It should be of no surprise, therefore, that a correlation exists between the results from studies employing these techniques in respect of the effects of waste/binder interference effects and this is of fundamental importance.

The addition of complex chemical admixtures, such as waste, to cement-based and pozzolanic systems significantly influences the way in which the cement subsequently behaves. The effects at work may be the result of opposing accelerating and retarding forces which are controlled by soluble species present within the admixture. Subtle variations in the way in which interference takes place implies that the balance of forces in action can be changed, whether intentional or not. Macphee and Glasser [18] discussed the immobilisation science behind cement-based systems and concluded that the interactions of a certain metallic species were controlled by various mechanisms including pH-driven precipitation and transient forces. It may, therefore, be possible at some future time to use admixtures in a controlled way to prevent destructive interference of hydration. However, this would depend on the development of a detailed understanding of the complex chemical and physical processes that take place during solidification and, in this respect, there is a considerable quantity of work still to be done.

The fact that wastes routinely interfere with hydration processes during solidification appears to have had little influence on the widespread use of this management technique at the present time, particularly as solidified wastes clearly pass current, though often

incomplete, quality acceptance criteria that render them “suitable” for disposal. There is, however, a fundamental lack of field data relating to the performance of solidified products thereafter. This is now being recognised [18,20,41,42] as a major problem because the satisfactory field service of these materials is of the utmost importance to operators and land owners alike, and should be clearly demonstrable. If field data highlights significant differences between the performance of those products that contain hydrated binding agents as against those that do not, then the situation may change. Already this may be happening as reports of failed solidified wastes within the UK [43,44] are available and they suggest that in fact “unsuitable” inorganic materials have been widely processed with little regard to longer term properties and field performance.

4. Summary and conclusions

The above studies using a combination of systems and genuine waste additions show that the mechanical, microstructural and calorimetric properties developed by solidified wastes are largely controlled by the nature of the waste being treated. These effects are particularly evident and of acute significance at the binder levels used commercially.

If hydration reactions are being commonly compromised, as this work suggests, then the basis for using OPC to solidify wastes is undermined because the reactions claimed responsible for physical and chemical encapsulation of waste species are not always present. Even when strength criteria are being met, it is possible that false set reactions involving not only the rapid, limited, development of ettringite and precipitation of salts are responsible. This means that normal hydration reactions may appear to be present when they actually are not.

For cement-based solidification processes to be optimised the hydration behaviour of binders should be monitored and should be used in the assessment of solidified product quality. Those wastes found capable of poisoning hydraulic and pozzolanic binder hydration should be considered for additional pre-treatments or treated by other means to ensure optimum disposal is achieved.

The time dependent nature of ageing processes that may occur in or at the interface of S/S deposits and ground water are complicated by waste form chemistry, local geology and hydrology and the potential mechanisms of degradation of both organic constituents and inorganic toxic species. These interactions, which cannot be evaluated at this time, may be predicted by future techniques incorporating novel modelling systems and advanced materials testing protocols. Nevertheless, certain changes to the way solidified wastes are currently assessed are technically possible and could lead to improvements in solidified product quality.

Notwithstanding the outcome of our work there is a considerable amount of information available to suggest that stabilisation/solidification technology is suitable for inorganic and organic waste materials and this illustrates the gap between academic research and industrial experience. The potential of this form of waste management is in part, reliant upon these differences being reconciled by detailed research work, and studies are urgently required that establish the physico-chemical reasons for field “successes” as well as failures. In this respect, the research community now looks to

the technology operators to relay the successes back to the laboratory for mechanistic interrogation. Future studies should therefore embrace both parties in combined processes and product testing programmes that allow the in-situ examination of waste forms together with an in-depth quantitative analysis of the effects of waste species on the short- and long-term properties of solidified wastes.

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