

Review

Organic compounds in the cement-based stabilisation/solidification of hazardous mixed wastes—Mechanistic and process considerations

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(Received November 26, 1990; accepted in revised form May 15, 1991)

Abstract

The pretreatment of hazardous wastes by cement-based stabilisation/solidification is of increasing importance as an alternative to the direct landfill of toxic materials. Inorganic and organic compounds are known to have a range of beneficial or harmful effects on cement hydration and their presence within construction materials has been strictly controlled. This paper reviews cement and pozzolanic hydration and the use of organic admixtures as a prerequisite to a discussion of the effects of organic wastes in cement. The pre-adsorption of organic contaminants is reviewed and presented as a potential extension of existing solidification processes for the successful treatment of mixed organic/inorganic wastes.

Introduction

Cement-based stabilisation/solidification (S/S) is a chemical treatment process which aims to either bind or complex the components of a hazardous waste stream into a stable insoluble form (stabilisation) or to entrap the waste within a solid cementitious matrix (solidification [1]). Hazardous industrial wastes, however, often contain constituents which may interfere with the hydration reactions of cement or pozzolanic materials, and certain organic compounds are among the known inhibitors of cement set [2, 3]. Whilst chemical stabilisation/solidification of hazardous wastes prior to disposal is of increasing importance, only a limited research effort has been directed towards elucidating the effects of specific waste components on the containment and physical properties of the final waste–cement product.

Within the construction industry, a wide range of organic materials has been employed to improve the performance and workability of cement blends [4, 5]. Such admixtures are routinely introduced in order to retard set during transport, lower heat production, increase water resistance and develop ulti-

mate cement strength. Consequently, experience with a variety of organic additives has resulted in the identification of organics as either inhibitors or accelerators of cement set [6], and care has been taken accordingly to ensure that aggregates or other components do not contain deleterious materials.

The complexity of hydration reactions, variations in processing parameters and differences in waste-cement formulations have precluded an accurate prediction of the effects of organics in S/S processes. The results of single-component organic additions to the cement mix are, in general, poorly understood. Consequently, forecasting the outcome of complex and variable compositions, such as those found in many mixed organic/inorganic waste streams, is extremely difficult. Further fundamental research on the behaviour of organic compounds in cement-based S/S is therefore clearly essential. From a processing perspective, however, several researchers have attempted to counteract the problems of set inhibition by using adsorbents to isolate the organic fraction of these wastes prior to cement fixation [7–9]. Whilst the majority of these studies to date have been performed at the laboratory or pilot scale, the results have indicated that this could form the basis of a successful approach to the solidification of organically contaminated wastes.

Cementitious reactions

Hydration of cement

The ultimate properties of cement-based S/S products depend largely on the characteristic behaviour of the cement additives and how they react with the wastes. An extensive literature exists on the chemical and physical processes occurring during the hydration of ordinary portland cement [10, 11] and this information provides a sound foundation for an understanding of cement hydration in the presence of organics.

Ordinary portland cement (OPC) is an hydraulic cement; it sets, hardens and does not disintegrate in water [12]. Anhydrous OPC consists of angular particles ($\sim 20 \mu\text{m}$ in diameter) and is typically comprised of the following major constituents [13]:

tricalcium silicate	(C ₃ S)	54% (w/w)
dicalcium silicate	(C ₂ S)	17
tricalcium aluminate	(C ₃ A)	11
alumino-ferrite	(C ₄ AF)	9
gypsum	(CSH ₂)	4

where C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, \bar{S} = SO₃ and H = H₂O in cement chemists nomenclature. The hydration of C₃S is the dominant mechanism in the overall hydration and hardening process of OPC. The general hydration reaction can be written as:

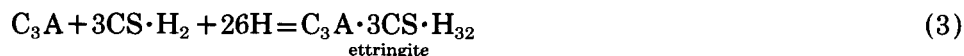


where $\text{C}_{1.7}\text{SH}_x$ is calcium silicate hydrate and CH is calcium hydroxide (portlandite [13]). Calcium silicate hydrate (CSH) is an ill-defined, poorly crystalline solid, which in hardened cement pastes accounts for $\sim 70\%$ of the hydrated material [14] and is principally responsible for strength development.

Several distinct stages in the hydration of C_3S have been identified [15–17]. Initially, when OPC is dispersed in water (Stage I, Fig. 1), calcium ions are rapidly leached from the solids to form a solution of mainly CH [15], leaving behind silica-rich cement grains. The aqueous CH is thought to react with silicic acids on the surface of the cement to form a gelatinous semi-permeable membrane of CSH around the cement particles [18–20]. This semi-permeable membrane causes a dormant phase in the hydration process as the osmotic pressure within steadily increases. This pressure eventually causes the membrane to rupture (Stage II, Fig. 1) with the development of new CSH radiating out from the anhydrous grain. Breaching of the gelatinous membrane is now believed to occur by a scaling (exfoliation) process [10] whereas previously, rupture was thought to occur via an “osmotic pumping” mechanism [14] which formed radial tubules of CSH. These “tubules” have subsequently been associated with the hydration of C_3A and C_4AF in the presence of gypsum [21]. Stage III of the hydration process is also characterised by initial CH crystallisation [22] and the transformation of CSH gel which exposes additional surface area of the anhydrous particles. The hydration of C_3A , whilst not critical to initial strength development, is essential in determining setting times and the characteristics of early hydration stages [23]. In the absence of sulphate, the hydration of C_3A can be represented as:



Most OPCs contain small quantities of sulphate in the form of gypsum (calcium sulphate) to prevent flash setting of the cement due to the reaction of C_3A (eq. 2). This modifies the hydration of C_3A to:



The formation of ettringite (Eq. 3) slows the hydration of C_3A by precipitation onto its surface. Ettringite forms both long prismatic crystals with hexagonal cross-sections, and amorphous layers. Its formation brings a volume increase, which, if ettringite is formed after initial set, disrupts the structure causing an increase in permeability and a concomitant loss in strength [24]. In time, the ettringite may react with dicalcium aluminate (Eq. 4) and produce monosul-

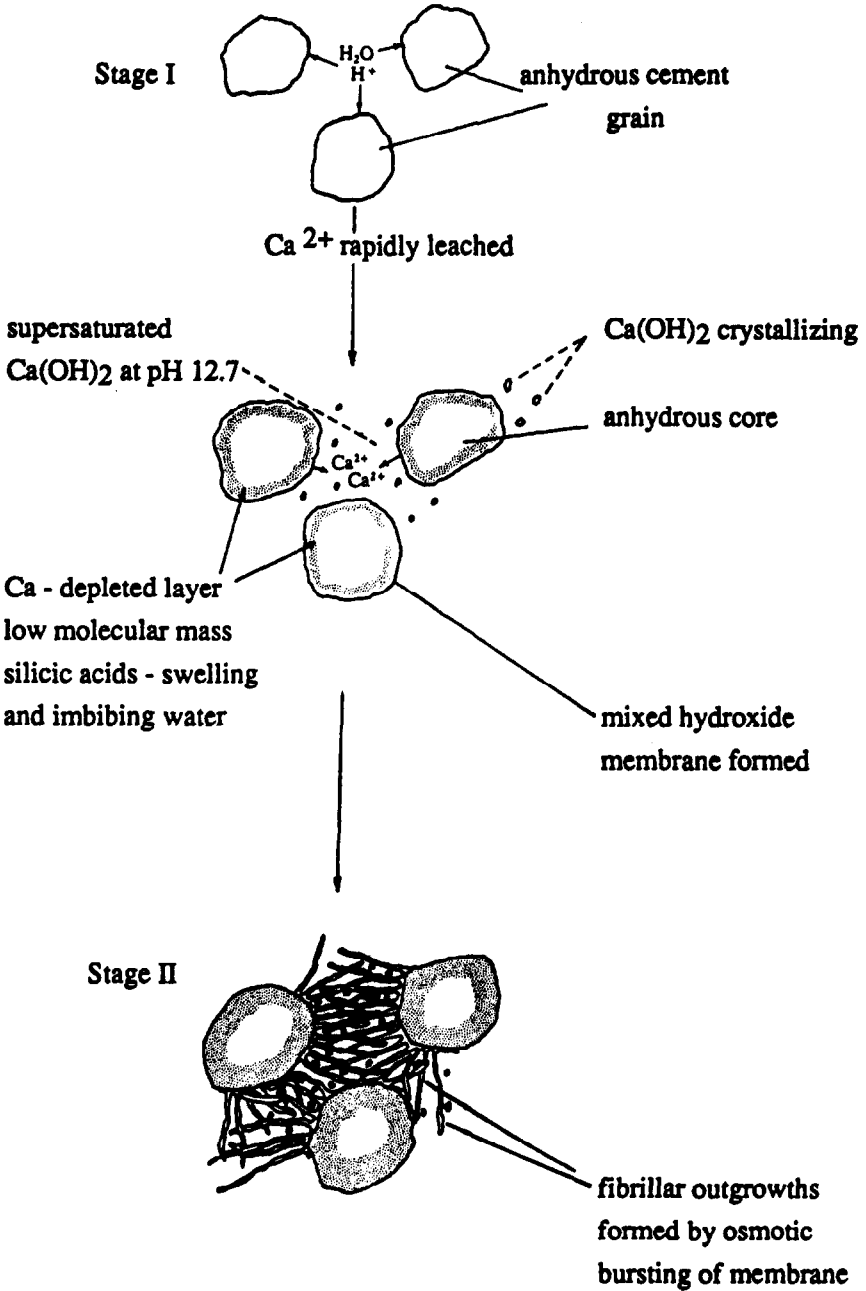


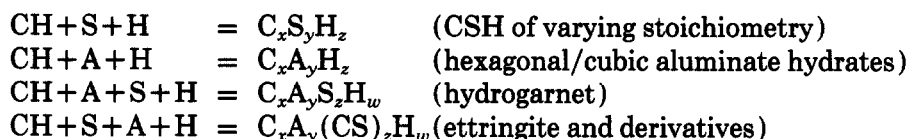
Fig. 1. Schematic model for the hydration and setting of portland cement [15].

phoaluminate. Monosulphoaluminate provides 15–20 % (v/v) of hydrated OPC and is the primary constituent vulnerable to sulphate attack.

Hydration of pozzolanic materials

The term “pozzolana” is used to describe a range of materials which react with lime, set and develop strength in the presence of water [13, 25]. Pozzolana principally consist of reactive (amorphous) silica and alumina and these include materials such as volcanic glass, calcined clays, fly ash and metallurgical slags. The use of blended portland–pozzolana cements generally brings about improved durability, sulphate resistance and obvious economic benefits. At present, the main pozzolanas in commercial use are pulverised fuel (fly) ash (PFA) and ground, granulated blast furnace slag (GGBFS [26]). Both materials have received extensive attention in the cement literature and PFA in particular has been used for many years in cement-based S/S processes [1].

The reaction products of pozzolan hydration are similar to those of OPC, the major difference being that in contrast to cements, pozzolans consume lime rather than produce it. This is an important factor in sulphate corrosion resistance and is also relevant to differences between the two systems with regards buffering capacities and the effect of additives. Hydraulic blast furnace slags, for example, react with lime and water to produce identical hydrates to OPC i.e. CSH and hydrated aluminates [27]. Similarly, a study of eight U.S. fly ashes and their reactions with hydrated lime over periods of up to 32 weeks [28] led to the following set of proposed reactions and resultant products:



Pozzolanic reactions, therefore, are similar to the hydration reactions of portland cement although generally they take place more slowly, with times to final set being measured in days rather than hours. In both cases, the strength of the final product results essentially from the formation of hydrated calcium silicates (CSH) and thus organic compounds which inhibit this process can be expected to affect cement and pozzolanic systems alike.

Organic compounds as additives in cement products

The properties of concrete in both fresh and hardened states can be modified by the addition of specific compounds, many of which are organic in nature [2]. The use of such admixtures in the concrete industry has been regularly reviewed [28–31]. An understanding of the role played by organic admixtures during cement hydration can provide a basis for assessing the possible effects

of organic waste constituents in cement-based S/S. Admixtures have been broadly sub-divided into three categories depending on their interaction or function within the cement–water system [2]:

- (a) *Surfactants* affect the cement–water system immediately upon addition by influencing the surface tension of the water and by adsorbing onto cement grain surfaces.
- (b) *Set-controlling* materials are capable of dissociation in water, ionise and affect the chemical reactions between the cement and surrounding hydration water after a time lapse of between several minutes or even hours.
- (c) Finely-ground, *mineral additives* affect the rheology of the fresh concrete formulation, but their chemical effects are generally less important and manifest themselves only after several days or even months.

The major function of organic-based admixtures is for water reduction and as plasticisers. By reducing the interparticulate attraction between cement grains, surfactants prevent the agglomeration of particles and facilitate better dispersion, thus reducing the amount of hydration water for a required workability [32]. Water-reducers can also be used to increase slump, hence improving ease of placement [33] and to obtain higher strengths by the use of lower water/cement ratios. They include organic compounds such as lignosulphonic acids (and their salts), citric acid and gluconic acid. Detailed studies on the effect of superplasticisers on the different stages of cement hydration have also been performed. Recognised superplasticisers, which have a far greater effect than conventional plasticisers, include naphthalene compounds, melamine and sulphonated hydrocarbons. Such compounds have been shown to retard set without affecting the total heat of hydration [34] and superplasticisers derived from gluconate and lignosulphonate have been observed to stabilise the formation of ettringite by inhibiting its subsequent conversion to monosulphate in the presence of lime [35].

Air-entrainment admixtures are used in cement blends to increase entrapped air, enhance durability and reduce the potential frost damage of concretes [36]. Typically, these are organic surfactants which possess a non-polar hydrocarbon “tail” with an anionic polar group attached at one end of the molecule. The surfactant molecules are capable of coating the surface of small air bubbles and preventing them from coalescing or separating from the mixture during blending. In addition, they may also neutralise the charged surface of cement grains causing them to become hydrophobic, thus resulting in a lower rate of hydration and a subsequently delayed set [2].

The third major use of organic admixtures is to intentionally retard set in order to allow prolonged workability and thus facilitate transport of the liquid concrete [37]. Superplasticisers can be used as retarders due to their ability to delay bond formation between hydration products and so delay crystallisation [38, 39]. More commonly used retarding admixtures, however, contain carboxylic acids. These are thought to interfere with hydration by strongly ad-

sorbing on to the cement particle surface in their ionised carboxylate forms [40]. Citric acid has been found to be particularly effective [41] at high concentrations whilst acting as an accelerator at low levels of addition [42]. Sugars are well established set retarders with the retarding action again being described in terms of the adsorption onto and the poisoning of hydrating surfaces. Sucrose and raffinose in particular have been attributed with the ability to solubilise cement constituents giving rise to dramatic increases in the amount of silica present in solution [43].

Cement–organic interactions

The variables associated with the use of admixtures in concrete production are numerous and increase accordingly when a hazardous mixed waste is being considered for cement-based stabilisation/solidification.

An example of the complexity surrounding the interactions of organics with cement matrices is the effect of phenol and its substituted analogues on hydrating cement paste [44]. In one such study [44], several phenols with varying substituent groups were solidified with types I and III portland cement. The solidified products were examined intermittently at selected cure times using water and solvent extraction (leach testing), optical and electron microscopy, X-ray diffraction and NMR spectroscopy. Whilst in each case the phenol substrate was readily leached from the cement matrix, significant differences in physical characteristics (e.g. setting times and compressive strengths), matrix morphology and phase composition were observed. The authors thus concluded that even subtle alterations in the chemical structure of the interfering organic may result in major differences in the nature of the cement–organic interaction.

The effects of low concentrations of some organic compounds on cement strength and hydration are well documented [28, 45–48]. In an attempt to elucidate the mechanisms of chemical interference by waste components during cement-based fixation, much research is now being directed towards investigating interactions between single organic components and OPC. Phenol, for example, has been found to have an adverse effect on long-term strength development at concentrations as low as 0.2% (v/v) [49] and 3-chlorophenol was observed to inhibit cement hydration by stabilising ettringite formation, retarding its conversion to monosulphate [50]. Trichlorobenzene was shown to reduce the mean pore diameter of cement pastes in which it was incorporated [51] but without leaching significantly from the hardened product. An examination of the effect of three common organic wastes on the microstructure of the cement matrix [52] demonstrated that whilst methanol and phenol inhibited ettringite formation, trichloroethylene appeared to stimulate it.

A significant contribution to data on the microstructural behaviour of cement in the presence of organics has come from workers at Louisiana State

University, Baton Rouge, LA [53–59] who examined the effects of ethylene glycol, *p*-bromophenol and *p*-chlorophenol on cement hydration using a wide range of microstructural, and some macrostructural techniques. Ethylene glycol was shown to have a retarding effect upon cement and occupied three distinct sites in the hydrated cement matrix. The microstructure was also altered, producing grainy nodular surfaces which lacked crystallinity. It was postulated [59] that ethylene glycol was small enough to substitute for water molecules during hydration and thus cause product deformation. Parabromophenol was observed to react with CSH gel which then underwent phase separation forming a concentrated crystalline phase. Although *p*-bromophenol had no overall effect on the hydration products, the chlorinated analogue was found to cause morphological changes in the hydration products and shown to be both closely associated with the CSH gel as well as homogeneously distributed within it.

Conduction calorimetry is being used increasingly to classify the effect of organic compounds on the hydration of cement paste. Initial studies performed by Taplin [60] identified hydrocarboxylic groups as particularly effective retarders of cement set. Recent developments in the technique have facilitated its use on a quantitative basis for surveying a wide range of organic admixtures [61], the retarding efficiency of which have been generally found to increase with molecular weight. In a further study, the most effective retarders were also found to inhibit the precipitation of CH from aqueous solution and this has led to the derivation of a “retardation index” for inhibiting organics [62].

Close examination of the functional groups responsible for retardation of cement set has led to a variety of conceptual models being proposed to explain the interference mechanisms of organics on cement and pozzolan hydration. These mechanisms include adsorption, nucleation, complexation and precipitation [28,39] and have recently been thoroughly reviewed by Jones [2].

Stabilisation/solidification of organic wastes

Conventional cement-based S/S processes are designed to bind or complex soluble metal ions present in an inorganic waste stream by firstly neutralising the waste to precipitate them as insoluble metal hydroxides. Addition of OPC follows to produce a solid cementitious matrix. Structural integrity of the resultant solidified mix is provided by the cementitious and pozzolanic reactions of OPC, PFA, kiln dust or other pozzolans added with water during the process. These conventional processes are generally unsuitable for the treatment of wastes containing organic compounds [63] due to the interfering effects of contaminating organics on the various hydration reactions. Consequently, the treatment of mixed organic/inorganic waste by such processes has often been problematic in the past. In an attempt to overcome this problem, several authors have adapted or extended existing S/S processes using proprietary binders and/or industrial adsorbents to isolate the organic content of these wastes prior to solidification.

Pre-adsorption of organics in cement-based S/S processes

A range of commercial industrial adsorbents including activated carbon, quaternary ammonium exchanged clays and zeolites have been evaluated for the adsorption of retarding organics in mixed waste streams prior to cement-based solidification. A survey of adsorbents intended for use in the cement-based S/S of oily wastes, for example, showed that each of the materials examined was capable of adsorbing up to 30% (w/w) of the oily waste prior to successful solidification with OPC [64]. In an extension of the Soliroc[®] process [7], acidic organic wastes arising from the manufacture of fine chemicals were treated with and without the inclusion of powdered activated carbon. In the latter case, the wastes were mixed with reactive silicates to form silicic acids, neutralised to precipitate the silica gel polymer and then, following the addition of activated carbon (1–10% w/w), final cementation was achieved by the addition of hydraulic cement.

Claimed reductions in the COD (chemical oxygen demand) of leach test filtrates were in the order of 70–90% (w/w) compared to 20–50% (w/w) for the process without the inclusion of carbon. Kyles et al. [65] screened a range of conventional and novel processes for the S/S of four wastes including an electroplating filter cake contaminated with chlorinated solvents, an acidic tar residue from petroleum refining, a mixed waste containing an array of dyes and pigments and an oil filter cake, again from petroleum refining. The study compared S/S with kiln dust, PFA, calcium oxide and activated carbon and found that whilst most of the techniques examined produced solid products, carbon adsorption prior to fixation proved the only effective means of immobilising the organic constituents such that they were less vulnerable to leaching. In a third study [8], decolourising charcoal and quaternary ammonium exchanged clay were utilised for the cement-based fixation of aqueous phenol, 3-chlorophenol and 2,3-dichlorophenol solutions (100–2000 ppm). The charcoal (1–2% by weight) displayed rapid adsorption of the phenolics and effective stabilisation of organics in the solidified products. In addition, charcoal was observed to aid cement hydration and increase compressive strength.

Exchanged clays have also received considerable attention as potential adsorbents for the S/S of organically contaminated wastes. In such a system, the organophilic nature of the quaternary ammonium salt (QAS) exchanged clay enhances the clay's capacity to adsorb organic compounds from aqueous media [66]. In two similar studies [8, 67] tetra-alkylammonium substituted bentonite clays were employed as pre-stabilisation adsorbents for phenol, 3-chlorophenol and 2,3-dichlorophenol before being incorporated into a range of cementitious matrices. Both studies reported a clear trend between the degree of polarity for the substituted phenols and their ability to be adsorbed by the QAS-clays. Leachability and physical strength measurements performed on the solidified phenol solutions confirmed pre-adsorption as a potential pre-treatment requirement of mixed waste solidification. Patent adsorbents con-

taining sodium magnesium fluorolithosilicate and QAS-exchanged sodium bentonite have been used in a similar fashion to immobilise and successfully solidify a wide range of organic containing wastes [68].

Unexchanged and thermally treated clays have also been utilised for the pre-adsorption of organics in mixed waste streams. Escher and Newton [69] used an OPC/bentonite clay mix to solidify three wastes contaminated with cyanide and phenol. In a novel development, spent clay from the edible oil industry was converted to a low-cost clay-carbon adsorbent by the chemical activation of residual oil on the mineral surface. Activated spent bleaching earth was then evaluated for the cement-based S/S of an organically contaminated pickling acid waste and its performance compared with a typical water treatment carbon [9]. The effects of adding activated spent clay at 10% (w/w) to the mix reflected the bifunctional properties of the clay-carbon material. Reductions in leachable TOC (total organic carbon) of up to 37% (w/w) were observed as a consequence of the adsorptive nature of the carbon char, whilst the fired clay support imparted 240–300% increases in compressive strength as a result of its pozzolanic activity.

Proprietary and pozzolanic systems for the treatment of organic wastes

In recent years a number of bench scale and pilot studies have been reported on wastes containing significant concentrations of organic compounds. In addition to utilising a range of industrial adsorbents, some of these studies have presented the use of proprietary trade name products, the contents and structures of which, unfortunately, are not reported. Two such studies examined the treatment of a mixed, liquid organic waste and a contaminated soil using an identical commercial process with varying degrees of success [70, 71]. Whilst the liquid waste produced a hardened solidified form, the authors were still able to leach >87% (w/w) of the organic contaminants from the product, using distilled-deionized water. In contrast, the PCB contaminated soil was successfully solidified with negligible volatile and leachable TOC in leach test filtrates. Cement only and proprietary cement-based processes have also been used to treat PCB contaminated dredge material [72]. Three S/S processes were evaluated in this study and the OPC treatment found to be the most effective for the containment of PCBs.

The detailed effects of organic waste components in pozzolanic S/S systems have not been widely investigated [2]. A number of workers have proposed that unpyrolysed organics are capable of adsorbing onto the reactive sites of fly ash and preventing cementation reactions between certain constituents [73–76]. Pozzolans have been shown to solidify clay soil with an organic content of 11.4% (w/w) [76] and the addition of 5% (w/w) lignite fly ash in this case was demonstrated to increase compressive strength by 40%. The organics in this study were added up to 8.5% (w/w) of dry reagents and ranged in chemical structure from simple alcohols to substituted aromatics and in aqueous

solubility from highly soluble to virtually insoluble. From investigations of cement strength it was inferred that aliphatic and dicarboxylic acids neutralised lime and therefore interfered with pozzolanic hydration. Methanol, xylene and benzene acted initially as set retarders without, however, affecting ultimate strength. Examinations of hardened pastes using scanning electron microscopy (SEM) indicated that the presence of interfering organics altered the morphological structure of the pozzolanic hydration products at concentration levels as low as 6.1% (w/w).

In conclusion, it is generally recognised [1, 2, 77] that a significant correlation exists between cementitious and pozzolanic hydration reactions, and therefore, under this hypothesis, the mechanistic details of chemical interference by a range of organics should be applicable to both systems.

Conclusions

Although cement-based S/S processes are attracting increasing attention for the treatment of hazardous wastes prior to landfill, a number of research studies have shown that the organic constituents of mixed waste streams can have a detrimental effect on the hydration of cementitious and pozzolanic materials. Whilst the inhibiting effect of organics on cement set have been utilised to advantage in the construction materials industry for many years, the distinct mechanisms of cement/organic interaction are still poorly understood despite the postulation of several interference models. It is evident, however, that even at low concentrations, organics can produce significant micro- and macrostructural changes to the properties of hydrating cement and that chemical functionality plays an important role in determining the relative extent of inhibition.

Research on pure organic/cement pastes has shown that, in general, non-polar organics do not hinder strength development in cementitious or pozzolanic systems. Further study of chlorinated hydrocarbons, however, which comprise a large section of these compounds and are prolific in mixed waste streams, is still required. Organic waste constituents containing hydroxy (sugars, alcohols), carboxylate (acids) and possibly amine functionalities can be expected to inhibit or even prevent cement/pozzolanic hydration altogether. These functionalities are commonly found in biological sludges, paint residues and many solvent wastes [1].

On the basis of research on organic/cement interactions to date, it is dear that conventional cement-based S/S processes must be applied with strict caution to the treatment of inorganic wastes which may contain additional organic contaminants. Industrial adsorbents such as activated carbon and organophilic clays have shown promise as pre-solidification agents for organic waste components but their use beyond the pilot scale has yet to be validated, as have the long term effects of weathering on the final waste forms. Adsorbents have,

nevertheless, been used commercially in the US but documentation is poor and the composition of many such materials is subject to commercial confidentiality thus hindering a rigorous assessment of their mode of action. They are, in addition, often expensive and their use would undoubtedly incur a cost penalty to the S/S process, although this may become of limited importance in an era of rising costs for all waste disposal options. The search for low-cost alternatives is therefore an area requiring further investigation.

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