# Factors affecting hazardous waste solidification/stabilization: A review

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## Abstract

Solidification/stabilization is accepted as a well-established disposal technique for hazardous waste. As a result many different types of hazardous wastes are treated with different binders. The S/S products have different property from waste and binders individually. The effectiveness of S/S process is studied by physical, chemical and microstructural methods.

This paper summarizes the effect of different waste stream such as heavy metals bearing sludge, filter cake, fly ash, and slag on the properties of cement and other binders. The factors affecting strength development is studied using mix designs, including metal bearing waste alters the hydration and setting time of binders. Pore structure depends on relative quantity of the constituents, cement hydration products and their reaction products with admixtures. Carbonation and additives can lead to strength improvement in waste–binder matrix.
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*Keywords:* Stabilization/solidification; Hydration; Unconfined compressive strength; Pore structure; Carbonation

## 1. Introduction

Stabilization is a pre-landfill waste treatment process, which has been used for different types of industrial wastes, but is particularly suited to those containing heavy metals [1,2]. The solidification/stabilization (S/S) process utilizes chemically reactive formulations that, together with the water and other components in sludges and other aqueous hazardous wastes, form stable solids. The material used for solidification/stabilization (S/S) not only solidifies the hazardous waste by chemical means but also insolublizes, immobilizes, encapsulates, destroys, sorbs, or otherwise interacts with selected waste components. The result of these interactions are solids that are non-hazardous or less hazardous than the original waste. The degree of effectiveness of these S/S products is defined basically by two parameters strength and the leach resistance. The continuing need to develop economical and improved waste management techniques has increased the potential importance of solidification technology through out the world, in a process defined as best demonstrated available technology (BDAT) [1,2].

Methods used for studying effectiveness of S/S process are physical, chemical and microstructural. Hills and Pollard [3] used setting and strength development as indicators of solidification and leach test to assess the extent of fixation.

Researches has investigated range of wastes for which the proportions of cement, wastes, and fillers which consistently produce satisfactory product. Solidification may vary considerably with waste type, upon scaling up, and in cost. S/S of wastes has been examined in the laboratory by a number of workers. Often, pure chemical components of one contaminants of concern increasingly or simple mixtures are added to OPC and other stabilizing agents (ashes of different origin, lime, clay, silicates, etc.) to stabilize the contaminant of concern [4,5]. Than the results are extrapolated to solidification of waste.

This review is a discussion of the published data relating to the ways in which the inclusion of hazardous wastes bearing heavy metals such as sludges, filter cakes, fly ash and slags affects the properties of cement and other binders. Emphasis is given on the mix design effect on unconfined compressive strength (UCS), hydration, effect of carbonation, pore structure, pore volume, and environmental factors affecting S/S. While remaining consistent with a critical overview of the subject, emphasis has been

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*Abbreviations:* S/S, solidification/stabilization; BDAT, best demonstrated available technology; UCS, unconfined compressive strength; PFA, pulverized fuel ash; GGBS, granulated blast furnace slag; SEA, sulphur extended asphalt; CSH, calcium silicate hydrate; $C_3A$, tricalcium aluminate; CH, calcium hydrate; AFt, hexacalcium aluminoferrite trisulphate; AFm, tetra calcium aluminate monosulphate; SRPC, sulphate resistance Portland cement; WOPC, white ordinary Portland cement; ABFC, activated blast furnace slag; ANC, acid neutralizing capacity

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Table 1
Physico-chemical quality criteria for solidified/stabilized waste

| Physical properties | |
|---|---|
| Setting time | 5–72 h |
| Compressive strength | $\geq$0.35 MPa |
| Chemical properties | |
| Metal concentration in TCLP leachates (mg/l) | |
| Cd | 0.5 |
| Cr | 5 |
| Pb | 5 |
| Zn | 300 |
| Eco toxicity to *Daphnia magna* | $\leq$750 mg/l |



Fig. 1. Unconfined compressive strength development after different curing days. Source: adapted from Malviya and Chaudhary [39].

placed in this article on recently published material. To evaluate the degree of fulfillment of the S/S objectives specific criteria are given in Table 1 [6,7].

Cement is most frequently used and widely studied binder. Solidification with cement is widely understood and simple, is easily available and results in a stable product [8]. In general other binders (sulphate resistant Portland cement (SRPC), white cement, kiln dust, lime, fly ash, pulverized fuel ash (PFA), silicates, etc.) partially replace OPC, which can have a positive or negative effect on strength, setting time and hydration.

## 2. Unconfined compressive strength (UCS)

Strength test data often are used to provide a baseline comparison between unstabilized and stabilized wastes. Unstabilized waste materials generally do not exhibit good shear strength, however, if the waste is stabilized into a cement like form, the strength characteristics can be expected to increase significantly [9,2]. Minimum required unconfined compressive strength for a stabilized/solidified material should be evaluated on the basis of the design loads.

EPA considers a S/S material with a strength of 0.35 MPa to have a satisfactory unconfined compressive strength. This minimum guideline has been suggested to provide a stable foundation for materials placed upon it in a landfill. In UK acceptable 28-day strength is 0.7 MPa but as low as 0.35 MPa is also considered depending on test specimen [3]. A study by Stegemann et al. [10,11] reported unconfined compressive strength values for 69 stabilized/solidified wastes ranging from 0.06 to 19.99 MPa.

UCS test are performed at different time intervals of 1, 3, 7, 14, 28, 90, etc. days to monitor the effect of the changes in the mineralogical composition of waste, with increasing time, and environmental exposure. Fig. 1 reveals that the UCS increases with an increase in curing time, strength of waste binder matrix is less than pure binder matrix [12,13].

### 2.1. Strength of the S/S product

Cement contents varying from 5% to 20% are routinely used to solidify waste. Low cement content does not adequately coat individual waste particles, but still tends to result in set and rigidity of the waste form. This is assumed to be the result of physical changes induced by n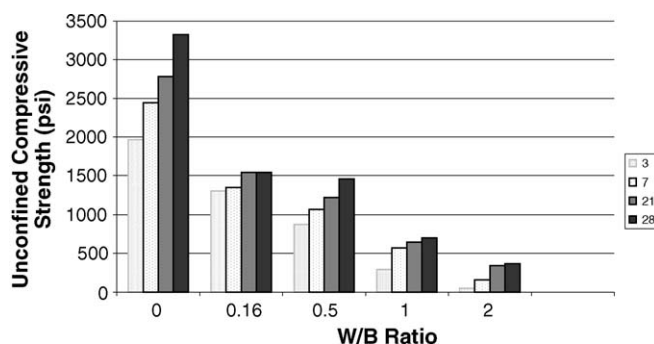ormal "hydration process" despite the "false set" mechanism (that is, precipitation of salts such as gypsum that impart adequate strength) [14,15].

Solidified materials are weak (strengths typically <1 MPa), and contain significantly less cementitious materials and more water, than, for example, concrete. It is known that compressive strength is dependent on the quality of pore structure of the cement-based materials. This quality is moreover dependent on the kind and quantity of the constituents forming the pore structure, that is cement hydration products and their reaction products with admixtures [16].

Precipitation of waste elements as cations or carbonate result in an increased demand for $Ca^{2+}$ ions in the waste matrix affecting strength development. The unhydrated cement fractions satisfies the increased demand of $Ca^{2+}$ ions and accelerates hydration of $C_3S$. In addition, residual cement grains are generally decalcified and silicate structures are subjected to increased polymerization of the cement [3,17].

Due to waste addition CSH hydration is poisoned. In these situation ettringite plays an important role. The main product of hydration giving the early strength and stability is ettringite, which is provided primarily by the self-cementing ability of ashes. This is supported by the fact that gypsum has been previously reported [18] to be main binding agent in some solidified products, and that addition of up to 5% gypsum is known to enhance both setting and strength development of pozzolanic/OPC mixes [19]. This is further supported by the experimental proof by Hills and Pollard [3], the importance of the strength contribution of gypsum formation can be gauged by reference to PFA/CaOH mixes, where the highest waste loading gave the highest strength, initial stiffening and shortest setting time, in contrast to OPC and PFA/OPC [20].

### 2.2. Interferences of waste in strength development

Solidified products are expected to harden over 2–5-day period. The effect of waste is studied by adding progressive quantities to OPC. A severe strength loss could be observed at low waste additions for example introduction of Zn, Pb, Cd at 1% by weight do not effect strength development [21]. A 3% (w/w total solids) addition of zinc containing metal plating waste resulted in a 99% reduction in the 28-day strength [3].

For the waste stream of electroplating, galvanizing, metal finishing operations and zinc plating waste UCS of 2.1, 15 and 1.0 MPa resulted from OPC combined with ground granulated blast furnace slag (GGBFS). OPC combined with PFA and OPC alone, respectively [22]. Yang and Chen [23], stabilized incinerator ash with OPC and GGBFS. With replacement of OPC by slag resulting in better compressive strength. They also tried Polymer SP (a water reducing agent), with no effect on UCS. Lombardi et al. [13] reported UCS reduction of about 80%, but more than sufficient for disposal in landfill. Lin et al. [24] S/S lead bearing waste with sulphur, sulphur extended asphalt (SEA), OPC type I. The 7-day UCS increased with sulphur, after the particles and contaminants were wetted. Sulphur binder increased the binding force with particles. UCS decreases with increasing SEA (up to 25%), because SEA is a viscous material at room temperature. The use of higher binder content than optimum increased the film thickness of binder, which coated the aggregate and resulted in loss of UCS. On spiking waste with oil + sulphur, the strength loss was about 25–30%, because oil can reduce the viscosity of asphalt and thus affect the strength and stability of asphalt/soil mixture. On incorporation of oil fuel ash in cement mortars [25], the strength of oil fuel ash mortars was significantly less in comparison to control mortar samples.

The UCS decreased by 56% when the alkali content in OPC increased from 0.15 to 2.8 wt.%. Addition of 2 wt.% sodium sulphate to OPC/electroplating sludge had little impact, although the strength of OPC reportedly decreases with increasing sodium sulphate concentration. For sludge containing Ni, Cr, Cd, and Hg metals OPC + Class F fly ash (OPC to fly ash to sludge, 0.2 to 0.6 to 1) and Class C fly ash and Lime (Lime to fly ash to sludge, 0.3 to 0.5 to 1) impart better strength than OPC (OPC to sludge, 0 .3 to 1) [26].

According to the study by Macsik and Jacobson [27], slag and quick lime cannot contribute to an increase of the undrained shear strength. Slag must be combined with standard Portland cement. The combination of 87 wt.% sulphide soil, 6.5 wt.% slag, and 6.5 wt.% OPC gave the required strength.

Adding H$_3$BO$_3$ (0.5 and 10 wt.%) decreased UCS at 3 days, but the UCS approached control values after 28 days [28]. Specimens lose strength after leach testing. From an initial strength of 19.85 to 0.46 and 0.05 MPa after 7 and 14 extractions. The leaching of matrix resulted in dissolution of Calcium from CSH gel, which resulted in decrease of strength as the left out skeleton rich in Si with no physical strength [13].

Many additives have been tried, including silica fume and blast furnace slag [29], silica fume is a pozzolanic material. The glassy silica fume reacts with lime byproduct made by hydrating cement to produce more CSH and less calcium hydroxide in the cement paste [30]. Slag lime combinations were advocated to result in rapid setting characteristics and production of a dense durable matrix. SEM investigations reflect less porosity. This porosity reduction makes the paste less vulnerable to the mechanism of deterioration [29]. Concrete incorporating blast furnace slag results in improved resistance to chloride ingress [31].

Gypsum induces the structural densification by formation of AFt and AFm phases. Therefore, the value of compressive strength increases and leaching of metals like Pb decreases. By using gypsum and fly ash, compressive strength increased via active generation and substitution of aluminate hydrates [7]. Roy et al. [26] reported that the effect of sodium sulphate on cementious binder, similar to sulphate attack on concrete. A 2 wt.% solution of sodium sulphate can lead to severe deterioration. The failure of OPC during sulphate attack is usually attributed to the large increase in volume due to ettringite formation.

### 2.3. Factors affecting strength development

#### 2.3.1. Waste/binder and water/binder ratio

UCS decreases as water increases in most solidification recipes. Chlor-alkali plant sludge was stabilized by a commercial solidification agent. It was found that the smaller the sludge to binder ratio, the better the physical and chemical properties of the solidified monoliths. This conclusion resulted from durability, unconfined compressive and TCLP testing [32]. The reasons for reduction in UCS as reported by Todorvic et al. [33] is due to variable pore structure and visible holes (if mixtures are too wet). When OPC is blended with fly ash [13] with the increases in the fly ash to OPC ratio, the water demand of the mix increase and a decrease in the strength was observed. Similar results are reported for the study conducted on steel finishing unit sludge and OPC [26]. Lower strength resulted from the lower Portland cement and much higher water contents. Generally, a waste/binder ratio of 0.4–0.5 is used with a water/solid ratio of 0.4–0.6. Super plasticizers (20 ml/kg of cementious material) are added to improve fluidity and to reduce water/binder ratio [34].

Cement content and curing were reported as the most important factor, with the water-to-solids ratio being less important for the ranges investigated [35]. The influence of water/cement ratio was reported to be secondary compared to the constituents of matrix [30]. Similar comment is given by Zivica [16]. Compressive strength depends on the quality of pore structure of the cement-based materials. This quality is moreover dependent on the kind and quantity of the constituent forming pore structure (cement hydration products and their reaction with admixtures). Wang and Vipulanandan [36] reported that the strength of metal laden cement mortar is affected by the water/binder ratio at 1, 3 and 14 curing days.

Water content of cement–fly ash–soil mixture decreases as curing time and cement content increases. The influence of cement content was more pronounced than that of curing time [37]. Effect of humidity was studied on the compressive strength of atmospheric fluidized bed combustion ash and pulverized fly ash. Relative humidites of 65% and 90% were maintained in climate cells and the high relative humidity in the stabilized material led to higher ultimate compressive strength. However, this may induce the formation of more ettringite, principally increasing the chances of carbonation [12].

The effect of variable particle size on strength of OPC–fly ash mortars was studied by Erdogdu and Turker [38] concluded that different size fractions fill the pores in the original ash–mortar mixes, results in higher strength values than expected.

### 2.3.2. Bulk density

The increases in the binder content (OPC, OPC + sulphur, OPC + SEA) increases the bulk densities because the binders filled the void space of solidified specimen [14,39]. Knoll and Andres [40] compared unit weight of the fresh samples to the bulk density of the cured samples and assessed volume changes during the S/S process. A 28 day cured unit weight is larger than that of the freshly mixed sample. This increase in unit weight with curing time results from hydration of the pozzolan filling void spaces with CSH.

## 3. Initial setting time and hydration

The calcined product of the cement consists mainly of four mineral phases: alite ($C_3S$), belite ($C_2S$), aluminate ($C_3A$), and ferrite ($C_4AF$). Other phases are free lime (CaO) and gypsum ($CaSO_4 \cdot 2H_2O$). Alite and belite hydrate to CSH and portlandite. When lime and gypsum are present, aluminate hydrates into calcium aluminate hydrate ($C_4AH_{13}$) [41]. UCS decreases with increasing crystalline phases [26,42].

Hydration of OPC is exothermic and is studied by isothermal conduction calorimetery. 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 [43,44]. A pure OPC hydration curve closely resembles that produced by $C_3A$ and can be corrected to the amount of calcium hydroxide evolved [45]. Waste/OPC mixes tend to produce heat of hydration curves that are dissimilar to a pure hydraulic or blended binder system. Hydration of OPC in stabilized/solidified product depend on the nature and relative quantity of waste. The maximum rate of heat evolved is defined as the gradient of hydration curve. Hills et al. [46] established that cement hydration is poisoned by industrial hydroxide sludge, when the waste:cement ratio is above a certain limit. This threshold depends on the nature of the waste. The mixing of metal hydroxide sludge of Cr (0.06–7%), Zn (0.5–10%), and Fe (1–2.25%), resulted in hin-
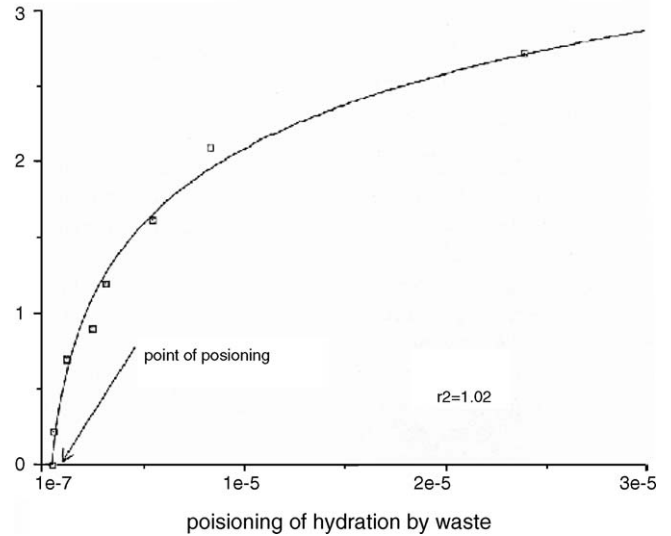


Fig. 2. Poisoning of hydration due to waste addition. Source: adapted from Hills and Pollard [3].

drance of the hydration process, characterized by an initial peak followed by lack of an exothermic reaction. The initial peak is due to precipitation of a solid phase, which hinders hydration. Increasing waste quantity increases size of the initial peak (indicating more precipitation) followed by hindrance (Fig. 2). At low concentration hydration is continued but it is disturbed [47–49]. Cioffi et al. [50] found that waste content as high as 60 wt.% did not alter the hydration products. However, the extent to which hydration takes place is reduced when the waste content is greater than 20 wt.%.

Hills et al. [14] discussed the mechanism of hydration interference (Fig. 3). From the hydration studies on OPC, it is known that the aluminate phases are capable of producing AFt within <10 min of mixing with water. Within a short period time, a gelatinous layer can be observed to form and, at the end of an induction period, further products of hydration "burst" through.
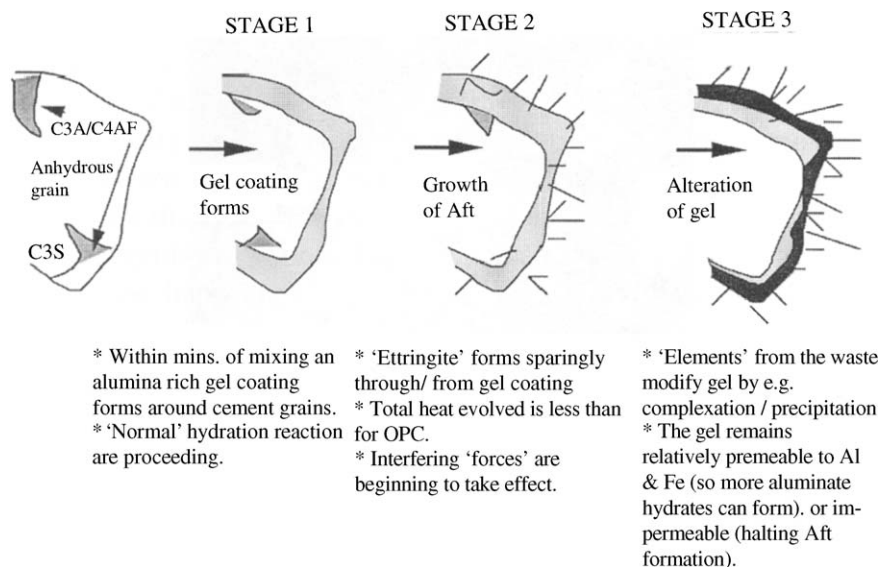


Fig. 3. Generalized mechanism of hydration poisoning. Source: adapted from Hills and Pollard [3].

The formation of the gel coating around cement particles is an important reaction rate determining step, when waste is introduced this step is modified. Modification may be complexation or precipitation effects rendering the gel layer 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. Another modification may be altering the chemistry of these phases (e.g. gel Ca/Si ratio during progressive hydration), for example by removal of calcium through precipitation. Subtle but selective differences in the interference mechanism operating on a gel coating may also explain why some products show minor AFt development whereas others do not [31].

The standard initial and final setting time reported for OPC should not be less than 45 min and more than 10 h, respectively [49]. The variations for initial and final setting time after the addition of PbO to cement pastes at admixture percentage of 0, 1, and 4 varies from 3 to 5 h 40 min, and 7 to 27 h 15 min, respectively [16]. With the increase in waste content the main exotherm becomes less pronounced and broadens. At commercial operations of 20 wt.% binder, the main hydration exotherm may be absent and normal hydration is indefinitely retarded. With the waste addition rate of 5, 15, 20, 30 wt.%. The increase in time with respect to zero waste/cement system was 80, 180, and 350 h and no set for 30% waste, respectively [9]. Similar, results are reported by Vall and Vazquez [51], but they experimented with additives like $CaCl_2$, that accelerates set.

Adding waste ameliorates this acceleration. The increase in setting speed caused by a set accelerator was inversely proportional to the percentage of waste. Bobrowski et al. [21] reported, that the presence of $Cd^{2+}$ distinctly reduces initial setting time, lead ions prolongs the initial and final setting time and reduce the strength of OPC mortars by 30%. Zinc in OPC pastes induces the occurrence of "flash setting" in which mortars set immediately and after stirring they regain plasticity. Chromium did not affect the setting time. Similar observations are reported on the setting time of alkali activated slag cement [52]. Tamas et al. [53] reported rapid setting, with a rapid rise in temperature and lump formation in a system with 0.6 mol/kg of nickel with adsorbent silica fume, fly ash and activated carbon.

The rate of hydration was reported to be insensitive to temperature over a range of 0–40 °C. Janusa et al. [54] reported that the lower curing temperatures of a lead bearing waste/cement matrix decreases the solubility of lead salts formed in the cement, resulting in an increase in gelatinous coatings on grains. This increase of coating at lower curing temperatures, causes less contact between cement grains and water, retarding the hydration process and the solidifying/stabilizing power of cement. By varying the curing temperature, the solubility of waste salts directly influences the heat of hydration and ultimately the holding capacity of cement for added waste.

A reduction in setting time is produced due to the presence of oil fly ash (OFA) in cement paste and high percentages of OFA result in flash set. The use of setting retarders is also reported in the literature [25]. A correlation was given between setting times an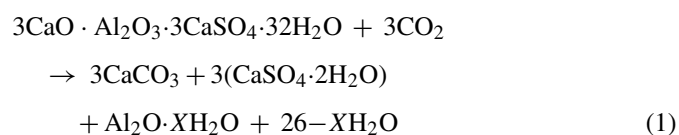d immediate leaching. Retardant elements such as $Pb^{2+}$ increase the rate of leaching while accelerant elements like $Cr^{3+}$ reduce leaching [30].

Fly ash washing pretreatment improved the setting behavior of fly ash–cement mixtures. This could not be ascribed only to the partial removal of alkali chlorides and sulphates from the fly ash, but was related primarily to the interaction of fly ash with water, that leads to a rapid formation of hydrate phases such as syngenite, gypsum ($CaSO_4 \cdot 2H_2O$), ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), calcium hydroxyzincate ($CaZn_2(OH)_6 \cdot 2H_2O$) and laurionite (Pb(OH)Cl) [55,56]. The transformation of heavy metal compounds such as zinc oxide into less reactive forms, coupled with the formation of protective layers of hydrate phases over the grains of fly ash, may explain why the washing step was capable of converting fly ash into a material that adversely affected cement hydration to a much lower extent than unwashed fly ash [57,55]. One draw back of washing process is that adding the washing water to the mix increases the final water/solid (w/s) ratio for 35%, 50%, 75%, 90% FA + OPC (unwashed w/s = 0.35, 0.37, 0.41, 0.46, washed w/s = 0.5, 0.585, 0.71, 0.80). Higher w/s reduces the compressive strength of solidified products, enhances the risk of heavy metals leaching from solid and increases the final volume of solidified/stabilized product [58–63].
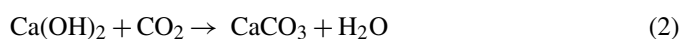
## 4. Carbonation

Carbonation is capable of inducing setting and strength development in the waste forms where hydration is significantly retarded. Carbonated S/S product develops higher strength in comparison to non-carbonated products [9,64].

Carbonation has influenced the properties of cement 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 [65] 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 [66,67]. Carbonation involves reaction with phases like AFt/AFm, CSH gel and CH. Carbonation of CSH produces silica gel and $CaCO_3$. Carbonation of ettringite is presented in Eq. (1):

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2$$
$$\rightarrow 3CaCO_3 + 3(CaSO_4 \cdot 2H_2O)$$
$$+ Al_2O \cdot XH_2O + 26 - XH_2O \tag{1}$$

Ettringite may be present in abundance within hydrated cement-containing materials and directly reacts with $CO_2$ to produce calcite. The volume change accompanying this reaction can help to fill pore spaces, 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 [68,69].

Eq. (2) represents the carbonation of portlandite:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{2}$$

Waste containing heavy metals has increased susceptibility to carbonation. Incorporating waste species into a carbonate phase by a mechanism involving solid solution reactions with calcite also improves metal fixation [70]. Carbonation appeared to overcome severe retardation effects through acceleration of the $C_3S$ hydration and resulted in improved mechanical and chemical properties of the blended material [71]. When accelerated carbonation was used for cement mortars significant strength could be generated within minutes for different w/c ratios and compaction molding [72,73]. The presence of metal waste in the cement product influence the gas permeability [74] consequently causing both a degree of decalcification of the anhydrous calcium silicate phases and an acceleration of hydration leading to the widespread formation of $CaCO_3$.

The strength of metal waste solidified/stabilized with OPC, OPC + blast furnace slag and OPC + pulverized fuel ash, improved because of carbonation [75]. For almost all waste containing mixes, $CO_2$ uptake was reported 3–6 wt% higher than for the control mixes. Pulverized fly ash reduced the rate of carbonation. Rate of carbonation was not reported to be proportional to the maximum $CO_2$ consumed [13]. The order of susceptibility for carbonation was studied by Lange et al. [75], OPC > SRPC > WOPC, with 60 wt.% loading of multi-metal bearing waste. The conclusion drawn on the basis of this observation was that, the cement phases like ferrite plays an important role, as ferrite is significantly less in WOPC. In a similar study, all these cement were utilized with PFA, ABFC, and GGBS, carbonation resulted in decreased UCS for ABFC and PFA system. PFA had a little effect on carbonation of OPC, SRPC, and WOPC. Granulated blast furnace slag (GGBS) resulted in the highest $CO_2$ uptake above waste/binder ratio 0.5 for all cement/waste systems. Mechanism suggested is that the $CO_2$ enhances the microporosity inside the reaction product [48]. GGBS/cement phases contain less calcium hydroxide than Portland cement, resulting in pronounced reaction between CSH and $CO_2$.

The consumption of $CO_2$ was less in multiple metal bearing solidified waste than the single metal (zinc) bearing waste. It was concluded that the concentration of specific metals or other waste species within a waste might be important in governing the rate of carbonation reaction. The presence of other elements, organics and anions also influence carbonation by reacting with cement paste and influencing the $CO_2$ effective diffusion coefficient [75].

Carbonation is also affected by the moisture content. Water is necessary for reaction with $CO_2$ but too much water severely limits the rate of reaction, as the pores are filled with water, the penetration of $CO_2$ is reduced, decreasing the rate of $CO_2$ diffusion. If the pores are completely dry, the reaction of $CO_2$ is absent. This implies solvation of $CO_2$ is critical for effective carbonation. Different water contents are required for different cements. As water content increases, induction time increases [75].

Carbonation of OPC and OPC + 50,000 ppm of Cd for 30 days resulted a decrease to neutral pH of pore fluid but no change in the concentration of Cd. Thus carbonation had no adverse effect on cadmium immobilization [52]. Carbonation increases the leachability of $SO_4^{2-}$ and heavy metals such as Zn and Cr [76].

Carbonating waste prior to solidification results in more complete carbonation. The addition of $Ca(OH)_2$ to the recipe was with the intention of promoting $CaCO_3$ formation. However contrasting results were found as strength was improved but metal retention was decreased. $Ca(OH)_2$ would increase $CaCO_3$ formation both through providing nucleation sites for precipitation and as a consequence of undergoing carbonation itself [77].

## 5. Pore volume

Hardened cement is a porous material with a trimodal pore distribution. The system formed by the smallest pores, gel pores, are approximately 0.01 $\mu$m in diameter. These are likely associated with inner layer spacing. The next layer pores averaging about 0.1 $\mu$m in diameter are due to the original water filled space in porous cement gel and are called capillary pores. The volume of these pores is directly proportional to the water/cement ratio. The largest pores are formed by air voids. The pore system has continuity as demonstrated by Darcy's permeability.

The addition of metal results in significant physical changes. Lead in Portland cement causes disappearance of 1 $\mu$m pores with increased numbers of 0.1 $\mu$m pores. Chromium addition causes a wide variety of pore diameters to appear with the small 0.01 $\mu$m diameter pores dominating indicating involvement of this metal in silicate formation. Lead addition changes the relative amount of pores in the structure, while the Cr addition affects the pore formation mechanism [78]. Mercury addition has no effect on pore volume. Micropores dominate in a Zn doped matrix with the volume of mesopores being only 31% volume [79].

The addition of metal nitrate result in reduction in cement hydration by greater than 50% and at the same time reduce the total porosity [20]. Powers [80] related strength to the cement gel/porosity ratio in the cement microstructure and thus to hydration degree and the w/c ratio. Higher hydration degrees correspond to higher amounts of cement gel and lower amounts of remaining porosity and thus to higher strength. Pressing cement solidified waste pastes decreases porosity and results in UCS improvement [81].

The role of pore structure of solidified materials during leaching was evaluated by Bishop et al. [82]. It was found that pore structure varied depending upon the wastes used and solidification mix formulation tested. The pore structure of samples changed remarkably during leaching, total pore volumes and pore size increases. The percentage of larger pores (diameter greater than 6000 nm) increased from 5 vol.% for before leaching samples to above 23 vol.% after leaching. Changes in pore structure were primarily due to leaching of calcium hydroxide. Higher the alkalinity in a sample, the greater the change of pore structure due to leaching [82].

## 6. Pore solution

Pore solution is the solution that is contained within solid cement but is not combined into solid hydration product. Pore water is extracted using high compression devices. Pore solution of cement has a high concentration of alkali metal cations, which

are balanced by OH ions. The OH-anions are responsible for high alkalinity. Other anions like aluminate and silicates are insoluble.

Chromium has limited solubility in pore fluid. The chromium concentration increases in the pore fluid with time. On spiking cement with 89,000 ppm Cr (III) the Cr content of the resulting pore solution increased from 0 to 0.24 to 2.2 ppm, at 0, 34 and 250 days, respectively. Increasing the Cr(III) content of the system does not increase its pore fluid concentration. On spiking with Cr (VI), the dissolved Cr remains high, up to 200 ppm even after 250 days and the dissolved Cr valence state remains Cr(VI) [83].

pH of pore solution depend both on the presence of adsorbent/fillers and heavy metals. Presence of Ni and Cd decreased the pH value due to formation of metal hydroxide. Both metals were not found in pore solution (concentration < 1 ppm) and the concentrations were comparable to that of original cement pastes made using fresh water. These results imply that the Cd and Ni was quantitatively bonded into the cement matrix [84]. Similar results are reported by Diez et al. [52] with a similar pH and charge balance of pore solution for a similar composition. Using a cadmium spike of 5000, 15,000, 30,000 and 50,000 ppm, the concentration in the pore solution was around 0.1 ppm after 28 days similar to the control samples. They suggested the formation of compounds like $Cd(OH)_2$ as a strong possibility and some matrix incorporation is also expected like $Ca \, Cd(OH)_2$. For silica fumes + OPC combination the pH of the pore solution was lower due to reaction between calcium hydroxide and $SiO_2$. Fly ash, activated carbon does not alter the pH. This study contradicts observations made by Byfors et al. [85]. Lead increased the dissolved calcium and silicon concentration in the pore fluid during initial hydration of cement and cement fly ash mixtures [36].

## 7. Effect of environment on S/S product

Exposure to the environment has significant effects on the properties of the S/S wastes, particularly in the near surface region. The combination of wet/dry, freeze/thaw cycling carbonation, alkali-aggregate reaction, sulfate attack and other environmentally induced stresses has caused extensive structural degradation to a significant depth. The vulnerability of the treated wastes to chemical and physical attack depends to a large extent on factors such as permeability, chemical and mineralogical composition, and microstructure of the cement paste, as well as the cement and waste aggregates [86]. An unexpected feature of the exposed S/S waste was the precipitation of massive plates of $Ca(OH)_2$ crystals that were found just below the surface. The formation of these relatively large crystals was attributed to the high concentrations of $Ca^{2+}$ and $OH^-$ and other ions leached into the pore water when the structurally degraded S/S material becomes saturated. As the surface region dries, moisture movement combined with evaporation increases pore water ion concentration, resulting in the plate like $Ca(OH)_2$ crystals. This leaching and reprecipitation of readily soluble alkaline metal and associated anions causes redistribution of the acid neutralization capacity to the exposed top of the S/S waste. Above the

plates the S/S waste is extensively carbonated as a result the acid neutralization capacity was significantly reduced. $Ca(OH)_2$ has a high ANC, but redistribution close to the surface makes this $Ca(OH)_2$ more accessible to $CO_2$ and carbonation, which partially neutralizes this ANC. The laboratory testing was based on the assumption that the material tested is representative of S/S waste after disposal. The results from the study by Fitch and Cheeseman [87] show that this assumption is not necessarily correct. The waste material after 10 years of environmental exposure was very different from that present after 28 day curing in the laboratory. The leaching properties of material tested after 28 days also seem to be very different from leaching of environmentally exposed S/S waste. This raises the issue of how representative data is obtained for samples from 28 day curing compared to long term S/S waste performance [88,89].

The microbial degradation/corrosion by bacteria like *T. thioxidans* is reported by many workers, because of microbial activity, the land filling of cement-based solidified wastes together with organic waste is not recommended [89].

Hockley and Van der Sloot [90] studied the effect of 8-year exposure to a marine environment on cement–lime solidified coal ash. Using XRD and concentration profiles dissolution of calcium hydroxide, calcium sulphite and ettringite began at the block surface and proceeded as a moving boundary toward the interior. Minor elements like As, Sb and B also exhibited moving boundary effects, perhaps through association with the mineral phases. The diffusion-dominated release was restricted because of precipitation of small crystals in the pores near the block's surface. The researcher advocated stabilizing the energy waste and subsequent disposal in the marine environment. In another similar study, analyses of leached composites identified a 40–60 $\mu$m calcite layer that was absent in control specimen. This suggested that a reaction between the composites and the seawater resulted in the precipitation of calcite onto the block surface, encapsulating the composites and protecting them from seawater attack and dissolution [91].

Freezing–thawing, wetting–drying durability tests were performed by Yang [32]. A solidified electroplating waste monolith with 20 wt.% of the OPC replaced by blast furnace slag were reported to be capable of passing both these physical durability tests. However, solidified monoliths with 40% replacement failed in the freezing and thawing test. Yang assessed the effect of these physical durability conditions on compressive strength. Freezing–thawing affected strength more adversely than wetting thawing.

## 8. Volume of stabilization product

From the economic aspect, a point not to be neglected when depositing waste in landfill is the volume of stabilized waste, in other words, increased waste volume due to stabilization. Construction of a landfill requires a capital investment; therefore, efficient utilization of landfill volume capacity brings financial savings.

Vondruska et.al. [92,93] showed a net volume decrease, explained by the large difference between apparent and absolute density of ash, which were measured and found to be

0.920 and 2.98 g/cm$^3$. That is, wetting and consolidating the ash into cement eliminated a larger volume of air voids than the volume of water and stabilizing materials added. The solidified/stabilized products can be put to practical use, such as, in road embankments and/or river dikes with cover soil, depending on the compressive strength and leaching characteristics [94]. The results by Shieh and Roethel [95] and Bednarik et al. [96] showed that sewage sludge can be stabilized into block form by using fly ash, lime, gypsum, and cement. The blocks were classified as non-hazardous and a reuse option was proposed for artificial reef construction.

## 9. Conclusions

The fact that wastes routinely interfere with hydration processes during solidification appears to have a little influence on the widespread use of this technique at the present time, particularly as solidified wastes clearly pass, current quality acceptance criteria that render them "suitable" for disposal. However, there is a fundamental lack of field data relating to performance of solidified products thereafter. This is now being recognized as a major problem because the satisfactory field service of these materials is of utmost importance. This situation is changing as the reports of failed solidified wastes are available and they suggest that 'unsuitable' inorganic materials have been widely processes with little regard to long-term properties and field performance.

Factors important for performance of solidification process:

1. An in depth analysis of all testing process parameters and conditions are necessary to ensure achieving of S/S objectives.
2. The design of the S/S equipment and infrastructure depend on the expected waste content or loading of the final waste form.
3. Important parameters to assess solidification are strength, setting time and extent of hydration. Mixing waste with cement can have either a positive and negative effects on the cement matrix properties. Binders other than cement are generally used as partial replacement of cement. Compressive strength is dependent on the quality of the pore structure of the cementitious matrix. In turn, this quality depends on the kind and quantity of the constituents forming the pore structure, that is cement hydration products and their reaction products with admixtures. The pH of pore solution is depends on the presence of waste species.
4. Metal bearing waste can have either a positive or a negative effect on the strength development. Different waste metals have different effects individually and in combination (with other typical metals) with binders in a solidified/stabilized matrix. In OPC with a metal-doped system, including up to 1 wt.% waste metal is safe. However including up to 3 wt.% of metals like Zn, Ni, Pb can result in strength reduction of 99%.
5. Factors affecting strength development in order of importance are cement content and curing time, followed by water to solid ratio. For attaining the desired strength, a waste/binder ratio of 0.4–0.5 and a water/solid ratio of 0.4–0.6 are generally used, with the exact value with in this range depends upon the type of waste being solidified. Extended curing and high humidity generally increase strength. Upon solidification, the bulk density of waste increases, a positive economic result for final disposal purposes.
6. Species like sulphate and borate adversely affect strength development. Sulphates may form ettringite after set resulting in distinctive expansion. Addition of 2 wt.% sulphate has an adverse effect.
7. Hydration can be retarded in the solidified/stabilized product, the extent depending upon the quantity and type of waste species. The gel-formation step of OPC hydration is altered upon inclusion of waste. The addition of up to 60 wt.% waste may not alter the nature of hydration products, but the waste content greater than 20 wt.% reduce the extent to which hydration take place.
8. Setting time changes with waste addition. Different waste species have different effects with no effect on setting upon Cr inclusion, ranging from flash set for Zn and Ni, to prolonged setting for Pb. Setting speed is inversely proportional to percentage of waste.
9. Aging and weathering affect chemical, physical, and microstructural properties of waste material. The calcium content is affected most. Freezing–thawing affects products most adversely.
10. Performance of solidified/stabilized product can be improved by: additives like silica fume, sulphur polymer, $CaCl_2$, $Ca(OH)_2$, $Na_2SO_4$, and $K_2SO_4$. Pretreatment of waste, like sulphate washing of fly ash and sludges, results in performance improvement.
11. Carbonation affects waste by improving mechanical and chemical properties. Concentration of specific metal or other species within a waste might be important in governing rate of carbonation.
12. Despite interferences and some negative effects on cement matrices solidified waste clearly passes current quality acceptance criteria for disposal in most cases. Criteria revision is required for ensuring long-term environmental safety.

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