Screening tests for assessing treatability of inorganic industrial wastes by stabilisation/solidification with cement

J.A. Stegemann *, Q. Zhou

Department of Civil, Environmental & Geomatic Engineering, University College London, Chadwick Building, Gower Street, London WC1E 6BT, UK

ABSTRACT

Stabilisation/solidification with cementitious or pozzolanic binders (S/S) is an option for reducing leachability of contaminants from residual, predominantly inorganic, industrial wastes and contaminated soils before disposal or reuse. Treatment by S/S is complicated by the fact that the presence of impurities, such as the contaminants and bulk matrix components present in industrial wastes, can have deleterious effects on cements. Therefore, careful laboratory development and testing of S/S formulations are required prior to full-scale application, to avoid technology failures, including problems with handling and contaminant retention. An understanding of cement chemistry and contaminant immobilisation mechanisms has been used to propose a series of test methods and performance thresholds for use in efficient evaluation of the treatability of industrial wastes by S/S, and optimising S/S formulations: measurement of stabilised/solidified product workability, bleeding and setting time (for flowable mixtures) or Proctor compaction (for compactable mixtures), together with unconfined compressive strength, leachability in a batch extraction with distilled water, and hydraulic conductivity.

1. Introduction

The ideal of the European Landfill Directive [1] is waste minimisation and avoidance of land disposal, but it is not feasible to eliminate or recycle all industrial wastes. Residual wastes may require treatment, and stabilisation/solidification with cementitious or pozzolanic binders (S/S) may be considered the most appropriate treatment for predominantly inorganic wastes and contaminated soils prior to landfilling or utilisation (e.g., [2]). However, treatment by S/S is complicated by the fact that the presence of impurities, such as the contaminants and bulk matrix components present in industrial wastes, can have deleterious effects on cements. Design of stabilised/solidified (s/s) products without due consideration of the potential interactions between cementing components and impurities may result in handling difficulties, failure to set, improper strength development, deterioration over time, and provision of a chemical and/or physical environment in which contaminants are not immobilised.

To enable safe and confident application of S/S technology, full-scale treatment of industrial wastes by S/S should be preceeded by a laboratory development process:

(1) to assess whether the waste under investigation is amenable to treatment by S/S (further referred to as treatability testing), and, if so;
(2) to optimise binder addition for the particular waste and evaluate whether the chemical and physical characteristics of the resulting s/s product are appropriate to the intended disposal or utilisation scenario (further referred to as process optimisation).

In the context of both treatability testing and process optimisation, there is a growing consensus regarding the properties of importance for a scientifically rigorous evaluation of the effectiveness of S/S (e.g., [3–6]), as well as a realisation that these cannot be measured by rapid testing within 2 h of mixing, as has been the typical industrial practice observed by the authors. However, based on an understanding of the underlying chemistry of cement-based systems and contaminant immobilisation mechanisms, it is possible to streamline testing of s/s products for S/S process development. This paper proposes and justifies use of a series of test methods in laboratory development of S/S processes, including treatability testing and the early stages of process optimisation. These tests are intended to complement testing for waste acceptance and classification required by individual regulatory jurisdictions (e.g., UK Environment Agency [7]), and there may be overlap between this proposal and some regulatory approaches. Using these tests can

* Corresponding author. Tel.: +44 20 7679 7370; fax: +44 20 7380 0986.
  E-mail address: j.stegemann@ucl.ac.uk (J.A. Stegemann).

help to employ generic S/S technology to best effect, but can not guarantee that regulatory requirements will be met.
.

2. Key properties of S/S products

The primary intention of S/S is usually to reduce leachability of hazardous or otherwise undesirable contaminants (although improvement of physical characteristics of a waste for handling or geotechnical reasons may be a consideration). The s/s product properties of importance in achieving this goal are discussed in the following; key properties have been shown in italics.

A good understanding of the chemical and physical nature of the waste being treated is necessary to make appropriate decisions regarding treatment, whether or not by S/S. *Contaminant concentrations* in raw waste are easier to measure than in s/s products, and can be used to calculate concentrations in the treated material. Analysis of the *bulk composition* and *solubility* of the raw waste is necessary to understand contaminant speciation and mobility in the waste before treatment, and assess the potential for interferences with hydration of the cement-based binders, such as binder neutralisation as well as acceleration/activation or retardation of setting and/or hardening, false setting, altered water demand and matrix disruption [8]. Waste *physical characteristics* (e.g., moisture content and particle size distribution) will affect processing and handling. The *binder composition* will also affect the nature of the hydration and any interference reactions. Characterisation of the variability of these raw waste and binder characteristics is critical to interpretation of results from testing of treated products and quality control of full-scale processing.

For practical operation of a S/S process, the raw materials (i.e., raw waste and binder) must be blended into a homogeneous mixture, which must then be transferred efficiently to a storage/disposal location, before or after curing under appropriate conditions. Sludges and filtercakes with a high-initial water content are commonly treated to yield a flowable mixture, which is handled by pumping. The ability to process and handle a flowable mixture depends on its *workability*. The *setting time*, which may be severely accelerated or retarded by interference of the waste with binder hydration, provides an important indication of how long this workability is maintained. Accelerated setting will affect processing of the freshly prepared mixture, as the mixture can be mixed and pumped only before it sets. On the other hand, retarded setting may be a problem for landfill operation, e.g., for placement of lifts, or for S/S facilities that cast blocks, which must set and develop sufficient strength before transfer to landfill. Furthermore, strongly retarded or completely inhibited setting indicates failure of the binder to hydrate and start to develop a durable matrix capable of retaining contaminants. Since undesirable contaminants are likely to be present in *bleed water* from s/s products, which can be considered a leachate, it is important to work at a water content that does not result in formation of a significant amount of free water on the product surface.

Relatively dry wastes, such as contaminated soil, or dry finely particulate wastes that have a high water demand due to their high surface area, such as air pollution control residues, may have water added to produce a flowable mixture. Alternatively, they may be treated to produce a relatively dry compactable mixture, which is compacted into place, e.g., with a sheepsfoot roller, using the *optimum moisture content* to achieve a dense monolith upon hardening.

Properly applied, S/S provides the dual advantage of an alkaline chemical environment in which many hazardous contaminants have low solubility, as well as a durable monolithic matrix of low-hydraulic conductivity that provides a physical barrier to control leaching of contaminants into the environment. Both chemical and physical immobilisation depend on *successful hydration of the binders* when mixed with water to form minerals characteristic of cement-based systems (e.g., [9]). By contrast with cement-based construction materials, the *matrix load bearing capacity* is less important, as a s/s product will only need to bear the weight of the overburden and perhaps vehicular traffic. However, the matrix integrity is important for maintaining a low *hydraulic conductivity*, such that the flux of contaminants into the surrounding environment is acceptable; *contaminant mobility by diffusion* is the maximum control of leachability that can be achieved. In this respect, it is important to maintain a low *bulk matrix solubility*, to avoid a rapid failure of the matrix physical integrity caused by its dissolution.

Since contaminants transported from the s/s product into the environment by diffusion or flow must first dissolve in the porewater, reducing *contaminant solubility* is also essential. The solubility of contaminants in s/s products depends on their speciation, which is difficult to characterise. However, regardless of their speciation, the solubility of metals tends to be a function of *matrix pH*. Although different formulations may have different initial porewater pHs, all s/s products will be highly alkaline initially, and this alkalinity will be neutralised over time by acidic influences, which will gradually cause the dissolution of the cement hydration products that compose the matrix, as well as metal contaminants. Thus, measurement of dissolved contaminant concentrations and pH as a function of acid addition (i.e., *acid neutralisation capacity*, ANC [3,4,10]) can help to characterise chemical immobilisation of contaminants (i.e, "availability" of contaminants at different pH values), as well as chemical durability of the s/s matrix.

In addition to these technical requirements, a S/S process must be cost-effective. Whereas materials costs may be reduced by minimising binder addition and using low-cost binders, such as industrial by-products, the mass/volume increase factor of a process and the cost of landfilling must also be taken into consideration.

3. Test methods

While several of the key properties of s/s products can be measured easily and at little expense, a critical assumption in selection of laboratory screening tests for treatability testing is that some easily measured properties of s/s products can act as surrogates for key properties that are more difficult to measure. Hence, the properties of interest for s/s products have been divided into two groups: those that are relatively quick screening tests, in column 1 of Table 1, and extended tests that involve more effort, but are ultimately useful for full evaluation of the longer term environmental stability of a s/s product destined for full-scale application or in process optimisation, in column 1 of Table 2. The properties have been grouped for the raw waste, binder, freshly mixed s/s product, and hardened s/s product. For each of the key properties, a specific measurement and method have been proposed in columns 2 and 3, respectively.

Basic characterisation of raw waste is routinely conducted by both waste generators, and operators of waste management facilities, either for operational reasons or to meet regulatory requirements, such as UK EA Guidance (2006) [7]. Likewise, generators of both manufactured (e.g., Portland cement or lime) and industrial by-product (e.g., ground granulated blast furnace slag, ggbs, or pulverised fuel ash) binders typically characterise their materials on a regular basis. Thus, data about raw waste and binder composition and physical characteristics can be obtained relatively easily. The specific chemical analyses undertaken will depend on the waste type; common examples have been included in column

Table 1
Screening tests for assessment of treatability of industrial wastes by S/S

S/S Product properties of Interest	Proposed measurement	Standard test method	Proposed threshold
Waste			
Contaminant concentrations	Concentrations of heavy metals, anions, toxic organic compounds, etc.	Aqua regia digestion, IC, ICP[a]	Process dependent
Bulk composition	Concentrations of inorganic elements (Al, Na, K), total sulphur, carbon, organic carbon, etc.	XRF, LECO[a]	TOC <1%; others process dependent
Solubility	Distilled water batch extraction with measurement of pH, Eh, TDS and contaminant concentrations	BS EN 12457-2 or 3[a]	Process dependent
Physical characteristics	Moisture content Particle size distribution	Stegemann and Côté [10]	Process/scenario dependent
Binder			
Cost	Trials with different binder dosages	Stegemann and Zhou [22]	Scenario dependent
Composition	Concentrations of inorganic elements, total sulphur, carbon, organic carbon, etc.	XRF, LECO[a]	Process dependent
Freshly mixed S/S product			
Flowable			
Workability	Flow table spread	BS EN 1015-3:1999	Flow table spread > ~175 mm
Setting time	Initial and final setting time by Vicat needle	BS EN 196-3:2005	~2 h < initial setting time < ~8 h Final setting time < ~24 h
Bleeding	Bleed volume measurement	BS EN 480-4:2005	< ~1% of total water after 24 h
Compactable			
Optimum moisture content	Proctor compaction	BS EN 13286-2:2004	Achievement of maximum dry density
Hardened S/S product			
Binder hydration	UCS at 7, 14 and 28 d curing UCS after immersion at 28 d curing Distilled water batch extraction with measurement of pH at 28 d curing	BS EN 196-1:2005 7 d immersion (from 21 d to 28 d) BS EN 12457-2 or 3	$UCS_{28} > UCS_{14} > UCS_7$ $UCS_{after\ immersion} \geq UCS_{before\ immersion}$ pH > ~11.9
Load bearing capacity	UCS at 28 d curing	BS EN 196-1:2005	UCS_{28} > ~1 MPa
Bulk matrix solubility	Distilled water batch extraction with measurement of TDS at 28 d curing	BS EN 12457-2 or 3 and Pr EN 15216:2005	TDS < ~8% (by total dry mass of waste)
Contaminant solubility/matrix pH	Distilled water batch extraction with measurement of pH and Eh at 28 d curing	BS EN 12457-2 or 3	~12.2 > pH > ~11.9
Hydraulic conductivity	Hydraulic conductivity at 28 d curing	ASTM D5084-03	Hydraulic conductivity < ~10^{-9} m/s

ICP = inductively coupled plasma spectroscopy; IC = ion chromatography; XRF = X-ray fluorescence.

[a] A variety of standard methods for chemical analysis exist, e.g., "Methods for the Examination of Waters and Associated Materials", from Her Majesty's Stationery Office.

2 of Table 1, with some common techniques for these analyses in column 3, but this list is not intended to be comprehensive and there are a variety of acceptable standard methods.

Treatability studies normally involve preparation and testing of a series of laboratory batches with different water and binder contents. Workability of all flowable freshly prepared mixtures can be determined by measuring spread on a flow table, for instance, using BS EN 1015-3:1999. Initial and final setting time of flowable mixtures can be measured using a Vicat needle method, such as BS EN 196-3:2005. Bleeding of s/s products containing high water content wastes can be measured after 24 h using BS EN 480-4:2005.

For compactable mixes, flow table spread and Vicat needle penetration cannot be measured; rather a Proctor compaction test, such as BS EN 13286-2:2004 can be used to measure the optimum moisture content. Bleeding is not an issue.

One of the practical drawbacks for S/S treatability testing is that binder hydration and interference reactions take place over time; in some cases, the properties of a s/s product may continue to change over several years. Incorporating a curing period of significant length before measuring the properties of the hardened s/s product in treatability studies is therefore unavoidable. Curing must not be conducted under water, as would be the case

Table 2
Extended tests for evaluation of hardened S/S products

S/S Product Properties of Interest	Proposed measurement	Standard test method	Proposed threshold
Binder hydration	UCS at ≥56 d curing UCS after immersion at ≥56 d curing	BS EN 196-1:2005 before and after 28 d immersion	$UCS_{\geq 56} > UCS_{28} > UCS_{14} > UCS_7$ $UCS_{after\ immersion} \geq UCS_{before\ immersion}$
Contaminant mobility by diffusion	Monolithic leaching test with measurement of pH, Eh, TDS and contaminant concentrations by ICP	EA NEN 7375:2004	Scenario (risk assessment) dependent
Acid neutralisation capacity	Batch extractions with acid addition, measurement of pH, Eh, TDS and contaminant concentrations	DD CEN/TS 15364:2006	Scenario (risk assessment) dependent

for specimens of ordinary cement paste or concrete, as contaminant leaching would then occur during the curing period and affect the results of leaching tests on cured specimens; rather, S/S specimens must be sealed in plastic bags to exclude carbon dioxide, with a moist tissue to provide a humid curing environment. Experience suggests that s/s products that do not achieve satisfactory performance within 56 d are unlikely to do so with longer curing; a curing period of 28 d can be considered sufficient for treatability testing. At 28 d, unconfined compressive strength (UCS) can be measured by applying BS EN 196-1:2005, with and without immersion for 7 d before testing [10]. To minimise the amount of waste generated in testing, the method may be adapted to use a 50 mm cube specimen [3,10]. Measurement of total dissolved solids (TDS; pr EN 15216:2005) and pH of the extract from a distilled water batch test such as BS EN 12457-2 or 3, are proposed, as indicators of matrix solubility and leachability, without measuring concentrations of individual contaminants. Hydraulic conductivity must be measured using a method for specimens of low permeability, e.g., according to ASTM D5084-03.

Since the durability characteristics of a s/s product will stem from the occurrence of cement hydration reactions, it is suggested that measurement of UCS can be used to monitor the progress of hydration prior to 28 d, usually at 7 d and 14 d. This is particularly important for s/s products for which a monolith has been obtained by compaction, where setting time data are not available to indicate whether hydration reactions are taking place. It is good practice to determine specimen mass, dimensions, moisture content and specific gravity when measuring UCS, in order to track changes in volume, porosity and saturation, which may aid interpretation of other data and can be used in modelling, e.g., for management scenario-specific risk assessment.

Thus, seven screening tests, namely, workability, bleeding and setting time (for flowable mixtures) or Proctor compaction (for compactable mixtures), together with UCS, distilled water extraction and hydraulic conductivity, are proposed for evaluation of waste treatability by S/S. Sufficient replicates must be conducted to characterise the variability of these characteristics and ensure that the treatability study is relevant in the context of the variability of the bulk waste that will undergo full-scale S/S. Information on the reproducibility of many of these methods for homogenised wastes is available in Stegemann and Côté [3]. The justification for application of these methods, and appropriate extended testing using the methods in Table 2, are discussed in the context of proposed performance thresholds.

4. Performance thresholds

In treatability testing, measured values of the s/s product properties of interest must be compared to threshold values, in order to determine whether the performance of the S/S process is satisfactory. Performance thresholds originating in the fundamental chemical and physical processes upon which treatment by S/S is based are proposed in the following discussion and summarised in Column 4 of Tables 1 and 2.

4.1. Raw waste characteristics

The premise of S/S treatability testing is that it is necessary because the effects of the waste on the binder are difficult to predict; the treatability procedure itself will establish whether or not waste of a particular composition is amenable to treatment by S/S. Therefore, recommendation of specific threshold values for raw waste composition is not appropriate, but information about composition can be useful to examine the waste for the presence of

substances that could lead to deleterious interactions [8]. Some commonly encountered examples include:

- acid, which will consume costly binders in acid/base reactions;
- heavy metals (particularly zinc), which may cause inhibition of hydration;
- aluminium and sulphate, which may result in delayed formation of expansive ettringite, and ultimately destroy the matrix;
- soluble salts (e.g., TDS, sodium, potassium, chloride and sulphate), which will not be immobilised in cement-based systems, and will cause deterioration of the matrix as they rapidly dissolve;
- organic compounds, which tend to be incompatible with the inorganic cement-based matrix, interfering with hydration; also, hydrophilic organic contaminants leach readily, whereas high concentrations of hydrophobic contaminants may form a problematic separate phase.

Therefore, wastes for S/S should have a neutral to alkaline pH, and binder dosages may need to be increased to cope with high concentrations of metals or other interferences. Low concentrations of hydrophobic organic compounds may be successfully immobilised in cement-based systems, but S/S of wastes with an organic content greater than 1% has been discouraged (e.g., by the United States Environmental Protection Agency [11]), and this limit is shown in Table 1. However, even metals industry wastes often exceed this limit, and the implications of exceeding it have not been sufficiently investigated. One aspect for consideration is that it is often possible to destroy organic contaminants using a variety of technologies, rather than choosing treatment by S/S.

Consideration should also be given to raw waste variability; if practically achievable, homogenisation of waste will reduce treatability testing requirements, simplify quality control, and may improve treatability.

Measurements of contaminant solubility in a distilled water batch extraction can further be used in geochemical modelling to estimate contaminant speciation, e.g., using software packages such as PHREEQCi, MINTEQ, MINEQL, Geochemist's Workbench, or Orchestra. In this way, problematic contaminants that require pretreatment can be identified, e.g., oxyanions such as Cr(VI) or complexed metals, whose solubility will not be reduced in a cement-based matrix.

4.2. Binder characteristics

Treatability testing will usually show that most commercial binders are suitable for use in S/S, though different dosages may be required for different waste/binder systems. Selection of a blended binder system that results in formation of high quality C–S–H with little free lime is advisable; this aspect is further discussed below in relation to hardened s/s product properties. It is also possible to use industrial by-products with cementitious or pozzolanic properties (e.g., metallurgical slags other than ggbs) that are not available commercially for conventional cement and concrete applications, but these must be characterised in as much detail as the wastes undergoing treatment, to allow the presence of any additional contaminants to be taken into account.

As the binder is the most expensive aspect of a S/S process, the primary objective of treatability testing is to determine whether acceptable final product properties can be achieved with an economically feasible binder dosage. The cost threshold for economic feasibility of S/S depends on market forces, including regulatory restrictions, and the availability of alternatives for management of the waste.

4.3. Freshly mixed s/s product characteristics

Aside from the binder content, the other variable in preparation of laboratory batches during treatability testing is the water content. In theory, it is desirable to minimise the water content of s/s products to the amount necessary for hydration of the binder; any excess water creates pores in the hardened matrix, which act as channels for contaminant migration. This objective must be balanced with the fact that the mix consistence must facilitate efficient processing and handling. It is suggested that a minimum workability corresponding to a flow table spread of more than 175 mm be used as a guideline for flowable mixtures. Based on experiments at UCL, this value corresponds to the flow of a CEMI paste with standard consistence according to BS EN196-3:2005. An initial setting time longer than 2 h, but less than a normal working day of 8 h will facilitate handling, whereas the final setting time should be less than 24 h, to allow practical operation of the landfill, such as vehicular traffic, or placement of S/S material in lifts. Based on work by the authors, a bleed volume of <1% of the total mass of water after 24 h is considered to be insignificant, in that it will not lead to generation of an undesirable leachate during product setting at full-scale.

Where placement by compaction is practical, compactable s/s products should achieve the maximum density, using the optimum moisture content, as minimising porosity in this way is likely to optimise the physical matrix properties for contaminant retention.

4.4. Hardened s/s product characteristics

The physical and chemical properties of a cement-based matrix are linked, because they both arise from the fundamental nature of the binder hydration products. For this reason, two of the three screening tests suggested for hardened s/s products are useful in evaluating more than one of the key properties, and are therefore associated with more than one performance threshold.

Measurement of UCS can be used as a surrogate parameter to monitor the progress of hydration reactions because, if hydration of the binder is proceeding satisfactorily, the strength at each successive age (7, 14 and 28 d) should be greater than that at the previous age. Since the specimens are not cured under water, measurement of UCS after immersion has been proposed [4], to ensure that any observed strength development is due to hydration rather than drying, and check for matrix dissolution or deleterious swelling caused by reactions with water, such as delayed formation of ettringite or hydration of silica gel, which can result in matrix disruption. For ordinary cement paste and concrete, the UCS of specimens cured in water is greater than that of specimens cured in a humid chamber, due to the greater availability of water for hydration. Thus, the 28 d UCS after immersion of s/s products must be greater than or equal to that before immersion, as a reduction in strength after immersion is suggestive of a problem with matrix physical integrity. Since swelling reactions in particular can be disastrous for the integrity of the s/s product, measurement of UCS before and after immersion should be repeated after longer curing times. The appropriate timeframe requires further investigation, but UCS measurement at 56 d with a longer immersion period, e.g., 28 d, is suggested for extended testing during process optimisation, or of s/s products destined for full-scale application.

Furthermore, UCS provides an indication of load bearing capacity. Guidance from the USEPA requires an immersed UCS of 350 kPa at 28 d to support overburden and equipment [12], whereas the UK EA requires a minimum UCS of 1 MPa at 28 d [7]. The derivation of these values is uncertain, but recent work on a project to develop process envelopes for S/S processes does suggest that s/s products

with a UCS lower than 1 MPa also tend to exhibit poor performance in other respects [13].

Measurement of matrix solubility in a distilled water extraction is recommended because dissolution of the s/s product matrix results in increased porosity, with consequences of decreased durability, increased hydraulic conductivity, and increased contaminant leaching. For the protection of groundwater quality downstream from landfills, regulatory limits on waste solubility (based on measurement of TDS in BS EN12457-2 or 3, on the basis of quantity dissolved per total dry mass of the waste) in the UK are 0.4% for inert waste landfill, 6% for non-hazardous waste landfill, and 10% for hazardous waste landfill. Recent experiments suggest that s/s products containing air pollution control residues from municipal waste incineration with less than approximately 5% soluble chloride will not exhibit loss of strength upon immersion [14]. On this basis, a provisional solubility limit of 8% (of the total dry mass of the s/s product) is suggested. Further work is necessary to develop a robust s/s product durability-linked performance threshold for this parameter, and quantify effects of matrix dissolution on diffusion-controlled leaching rates and hydraulic conductivity.

Measurement of matrix pH in a distilled water extraction is also useful in assessing hydration of the binders, as well as contaminant solubility, as further discussed in the following.

Reaction of the binder with water produces several hydration products; in contact with water (i.e., porewater of a s/s product, or distilled water in a batch extraction), each of these results in a characteristic pH [15]. The most alkaline hydration product is calcium hydroxide (also known as hydrated lime, or portlandite), which has a pH of approximately 12.3. Portland cement (e.g., CEMI) produces approximately 20% calcium hydroxide upon hydration, as well as 70% calcium-silicate hydrate (C–S–H), which is an alkaline metastable gel phase of variable composition and is responsible for the physical integrity of the matrix. The literature indicates that there are three main types of C–S–H (e.g., [16] and [17]). At a Ca/Si ratio of 2 to 3, such as is found in portland cement, calcium-rich C–S–H with a Ca/Si ratio of approximately 1.7 coexists with calcium hydroxide at a pH of 12.3. When pozzolanic materials are blended with cement, they consume calcium hydroxide by reaction with silica to form additional C–S–H. For Ca/Si ratios from 1.7 to 1.1, the pH falls from 12.3 to 11.9 as the C–S–H composition changes; at a Ca/Si ratio of 1.1/1.0, there are indications of pH control at 11.9 by co-existing calcium-rich and silica-rich C–S–H; then for Ca/Si ratios from 1.0 to 0.65, the pH decreases from 11.9 to 9.9. At pH 9.9, silica-rich C–S–H with Ca/Si ratio of 0.65 coexists with silica gel [18], but a structurally stable matrix cannot exist in this low pH range due to the presence of silica gel, which swells as it takes on water and has a relatively high solubility. Although a pH value greater than 11.9 in a distilled water extraction of a S/S product is no guarantee that useful hydration products have formed, a pH lower than about 11.9 suggest that binder hydration may not have taken place, as physically stable C–S–H is unlikely to be present. However, it should be noted that the above pH regimes have been determined for pure systems, and impurities may well affect the pH regimes that prevail in real cements and s/s products.

The pH of a distilled water extraction is also important because the solubility of the metal contaminants most often treated by S/S is pH dependent, as shown in Fig. 1. While the metals shown are less soluble in the alkaline range, they are amphoteric, and their solubilities increase beyond a minimum in the alkaline as well as acid regions. In fact, Fig. 1 shows that metal solubilities increase by several orders of magnitude for a relatively small increase in pH beyond the point of minimum solubility. Therefore, it is worth trying to minimise the pH of a s/s product matrix within the range possible for a material based on C–S–H. Free calcium hydroxide responsible for a higher pH of 12.3 can be consumed by using a
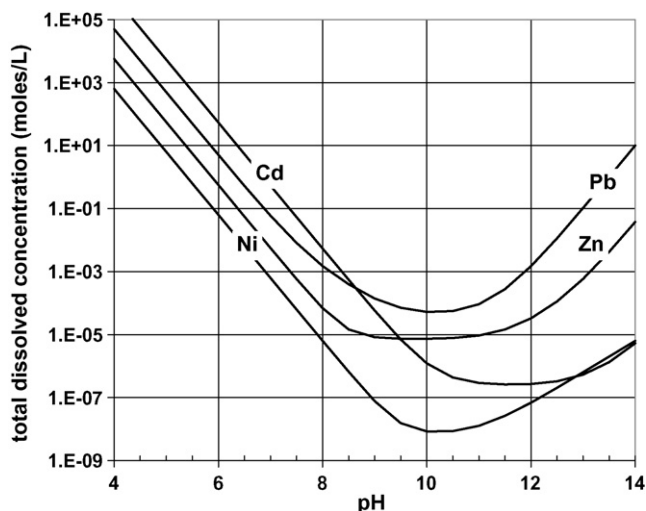
Fig. 1. Cd, Ni, Pb and Zn hydroxide solubility at 25 °C in dilute solution, as a function of pH (based on data in the MINTEQ database [21]).

blended cement binder, containing pozzolanic materials such as ground granulated blast furnace slag or pulverised fuel ash. Pozzolanic reactions are relatively slow, but a pH measurement in a distilled water extraction after 28 d of less than 12.2 indicates that no free lime is present, and the pH will likely continue to drop over time, ultimately approaching the lower limit for C–S–H of 11.9. Free calcium hydroxide is relatively soluble by comparison with C–S–H, so the use of blended binders has the added advantage of creating a denser matrix of lower solubility.

It should be noted that porewater pHs in cement-based products may be higher than the equilibrium pH established by calcium hydroxide, due to the hydrolysis of alkali metal hydroxides (usually Na^+ and K^+) present in the cement or waste. Porewater pHs may often exceed 13 [19] and correspondingly increase porewater concentrations of metal contaminants (Fig. 1). However, high porewater pHs usually result from relatively small quantities of highly soluble salts, which are diluted and/or neutralised in the distilled water extraction and ANC tests, allowing dissolution of the matrix solids to control the pH in treatability testing, as they would likely do in environmental leaching (though the latter has not been well-investigated).

Based on the foregoing justification, and the fact that problem contaminants with unusual behaviour should have been identified in the examination of the raw wastes, screening testing requires determination of only pH and TDS of leachates from distilled water extraction, rather than full chemical analysis. However, it is proposed that individual contaminant solubility be assessed in extended testing, to verify the correctness of the assumptions underlying the proposed screening protocol. The distilled water extraction can be complemented by an ANC test in extended testing, which will investigate the matrix pH response to acid addition, as well as contaminant solubility at different pH values. In the utilisation or disposal environment, acid influences such as carbon dioxide from the air or acidic landfill leachate will neutralise the alkalinity of the s/s product, changing contaminant solubility and gradually resulting in matrix degradation. Thus, the ANC of a s/s product is related to its lifetime in the environment. However, this lifetime will differ depending on the acid supplied by the management scenario.

Transport of contaminants dissolved in s/s product porewater is controlled by the hydraulic conductivity of the matrix, relative to that of the surrounding environment. The rate of leaching can be minimised by ensuring that transport occurs by diffusion, rather than more rapid flow of leachate through the matrix. At hydraulic conductivities less than 10^{-9} m/s, flow through the matrix is sufficiently slow that transport by diffusion dominates over advection [20]. As matrix density can be expected to increase with longer curing, with a consequent reduction in hydraulic conductivity, relaxing the performance threshold to 10^{-8} m/s at 28 d could be considered, but additional work to demonstrate the appropriateness of this approach is required.

An estimate of contaminant release under conditions of diffusion control can be obtained using a dynamic leaching test, i.e., immersion of a monolithic specimen with periodic leachant renewal for chemical analysis (e.g., NEN 7375:2004, prCEN/TS WI 292040:2004). Since contaminant mobility by diffusion is difficult to influence, other than by reducing contaminant solubility and producing a high quality physical matrix, and because a dynamic leaching test is time-consuming and expensive to perform, it is suggested that this test is not appropriate as a screening test, but could be carried out as part of extended testing prior to full-scale application of S/S, if desired.

5. Further remarks

The seven screening tests and corresponding performance thresholds proposed here have been selected to enable full advantage to be taken of the beneficial effects of cementitious and pozzolanic binders in S/S treatability testing. The authors recognise that scenario-specific conditions may require legitimate divergence from the proposed methods, for instance in the case of:

- treatment of high concentrations of organic contaminants, where there is a dearth of treatment alternatives and S/S is shown to be effective;
- unusual operating conditions, where a very rapid or slow setting time can be accommodated;
- relaxation of strength criteria, when maintaining matrix physical integrity (i.e., a monolith) is not essential (though use of hydraulic binders is of questionable benefit in this case);
- disposal scenarios where a risk assessment-based analysis has established that the environment can tolerate the contaminant flux that results when transport occurs by flow rather than diffusion.

Nevertheless, the proposed screening tests are intended to be applicable over a wide range of circumstances.

6. Conclusions

To support confident full-scale application of S/S technology, an understanding of cement chemistry and contaminant immobilisation mechanisms has been used to propose and justify a series of test methods and performance thresholds for use in efficient evaluation of the treatability of industrial wastes and contaminated soils by S/S, and optimising S/S formulations. Measurement of s/s product workability, bleeding and setting time of flowable mixtures, or Proctor compaction of compactable mixtures, together with UCS at 7, 14 and 28 d (with UCS after immersion at 28 d), and pH and TDS of a batch distilled water leaching test and hydraulic conductivity at 28 d, are recommended. Extended testing for optimisation and evaluation of S/S formulations intended for full-scale application, to measure 56 d UCS, diffusion-controlled leaching, and pH and contaminant solubility in an ANC test, helps to verify results from screening and provides information regarding the likely behaviour of the S/S product in the longer term.

Acknowledgements

References

[1] European Commission, Council Directive 1999/31/EC of 26 April 1999 on the Landfill of Waste, 399L0031, Official Journal L182, July 16, 1999, pp. 1–19.

[2] J.R. Conner, Chemical Fixation and Solidification of Hazardous Wastes, Van Nostrand Reinhold, 1989, 692 p.

[3] J.A. Stegemann, P.L. Côté, Summary of an investigation of test methods for solidified waste evaluation, Waste Manage. 10 (1990) 41–52.

[4] J.A. Stegemann, P.L. Côté, A proposed protocol for evaluation of solidified wastes, Sci. Total Environ. 178 (No. 1-3) (1996) 103–110.

[5] L.H. Barnard, B.D. Bone, C.D. Hills, Guidance on the Use of Stabilisation/Solidification for the Treatment of Contaminated Materials, R&D Technical Report P5-064/TR, Environment Agency, Bristol, UK, 2003.

[6] R. Perera, A. Al-Tabbaa, M. Reid, R. Spence, J.A. Stegemann, Chapter 11: testing and performance criteria for stabilized/solidified waste forms, in: R. Spence, C. Shi (Eds.), Stabilization/Solidification of Hazardous, Radioactive and Mixed Wastes, CRC Press, 2004, pp. 281–317.

[7] EA, Guidance for waste destined for disposal in landfills, Interpretation of the Waste Acceptance Requirements of the Landfill (England and Wales) Regulations 2002 (as amended), Version 2, Environment Agency, Bristol, UK, 2006, http://www.environment-agency.gov.uk/commondata/acrobat/wacv2_1006008.pdf.

[8] J.A. Stegemann, Chapter 7: interactions between contaminants and binders, in: R. Spence, C. Shi (Eds.), Stabilization/Solidification of Hazardous, Radioactive and Mixed Wastes, CRC Press, 2004, pp. 151–175.

[9] C. Shi, Chapter 4: hydraulic cement systems for stabilization/solidification, in: R. Spence, C. Shi (Eds.), Stabilization/Solidification of Hazardous, Radioactive and Mixed Wastes, CRC Press, 2004, pp. 49–78.

[10] J.A. Stegemann, P.L. Côté, Investigation of Test Methods for Solidified Waste Evaluation—A Cooperative Program, Environment Canada Report EPS 3/HA/8, Appendix B: Test Methods for Solidified Waste Evaluation, Environment Canada Manuscript Series TS-15, Wastewater Technology Centre, Burlington, Ontario, Canada, 1991.

[11] USEPA, 40 CFR, United States Environmental Protection Agency, Washington, DC, June 1, 1990, p. 22568.

[12] USEPA, Prohibition on the disposal of bulk liquid hazardous waste in landfills—statutory interpretive guidance. Office of Solid Waste and Emergency Response (OSWER) Policy Directive No. 9487.00-2A. EPA/530-SW-86-016, United States Environmental Protection Agency, Washington, DC, 1986.

[13] J.A. Stegemann, Q. Zhou, in: M. Zamorano, V. Popov, A.G. Kungolos, C.A. Brebbia, H. Itoh (Eds.), Development of Process Envelopes for Cement-based Stabilisation/Solidification of Metal Treatment Filtercakes, Waste Management and the Environment IV (Waste Management 2008), WIT Transactions on Ecology and the Environment, vol. 109, WIT Press, 2008.

[14] C. Lampris, J.A. Stegemann, C.R. Cheeseman, Solidification of Air Pollution Control Residues Using Portland Cement: Physical Properties and Chloride Leaching, Waste Management (WM-S-07-0689), submitted for publication.

[15] J.A. Stegemann, R.J. Caldwell, C. Shi, in: J. Goumans, J. Senden, H. van der Sloot (Eds.), Response of various solidification systems to acid addition, Waste Materials in Construction: Putting Theory in Practice, Studies in Environmental Science, vol. 71, Elsevier Science B.V., Amsterdam, 1997, pp. 803–814.

[16] S.A. Greenberg, T.N. Chang, Investigation of the colloidal hydrated calcium silicates. II. Solubility relationships in the calcium oxide-silica water system at 25°, J. Phys. Chem. 69 (1) (1965) 182–188.

[17] A. Nonat, The structure and stoichiometry of C–S–H, Cement Concrete Res. 34 (9) (2004) 1521–1528.

[18] M. Grutzeck, A. Benesi, B. Fanning, Silicon-29 magic angle spinning nuclear magnetic resonance study of calcium silicate hydrates, J. Am. Ceram. Soc. 72 (4) (1989) 665–668.

[19] K. Andersson, B. Allard, M. Bengtsson, B. Magnusson, Chemical composition of cement pore solutions, Cement Concrete Res. 19 (3) (1989) 327–332.

[20] D.E. Daniel, Personal communication by e-mail to J.A. Stegemann, University College London from University of Texas at Dallas, 2006, June 30.

[21] J.D. Allison, D.S. Brown, K.J. Novo-Gradac, MINTEQA2/PRODEFA2—a geochemical assessment model for environmental systems. Version 3. 0 user's manual. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Ga, 1990.

[22] J.A. Stegemann, Q. Zhou, Development of Operating Windows for Cement-based Waste Stabilisation/Solidification Processes, Department of Civil, Environmental & Geomatic Engineering, University College London, in preparation.