CHAPTER 18 - SOLIDIFICATION AND STABILISATION

One of the options generally suggested as a means to reduce the solubility of trace metals contained in incinerator residue streams, is solidification. Another related process which modifies the chemical properties of the residues is stabilisation. Although these terms are frequently used interchangeably, for the most part they are distinctly different, since they modify the behaviour of material in different ways. This chapter provides an overview of the various techniques available for use on MSW incinerator residues, and defines a protocol to assess the environmental and engineering suitability of solidified/stabilised residues.

18.1 DEFINITION OF PROCESS

The use of solidification and/or stabilisation techniques is widely considered to be a viable option for the treatment of many types of hazardous wastes. Development of specific formulations for different types of waste began in the late sixties and early seventies (Conner, 1990). The techniques were applied to stabilise either mine backfills, base courses for roads or most notably for the treatment of nuclear waste.

The term Solidification/Stabilisation (S/S) is the generic term used to describe a wide range of techniques which can transform wastes into less environmentally problematic forms. This usually involves physical and/or chemical immobilisation of the waste constituents. US EPA has presented the following definition (Conner, 1990):

> **Solidification** refers to the techniques that encapsulate the waste in a monolithic solid of high structural integrity. The encapsulation may be of fine waste particles (micro-encapsulation) or of a large block or container of wastes (macro-encapsulation). Solidification does not necessarily involve a chemical interaction between the wastes and the solidifying reagents, but may mechanically bind the waste into the monolith. Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching and/or by isolating the wastes within an impervious encapsulate.
>
> **Stabilisation** refers to those techniques that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilisation.

Frequently, both stabilisation and solidification processes are combined, thereby changing both the physical and chemical structure, and ensuring even if the monolith deteriorates that the contaminants will remain in the matrix. Numerous alternatives for accomplishing these changes have been proposed including:

- mixing different waste types together
- adding hydraulic binding agents to the waste
- sequentially washing the waste then adding hydraulic binding agents
- adding organic binding agents

Although many techniques have been proposed, and some are used commercially for treating hazardous industrial waste streams, few are in commercial scale operation for MSW incinerator residues.

18.2 EFFECTS OF SOLIDIFICATION/STABILISATION

18.2.1 Physical Changes

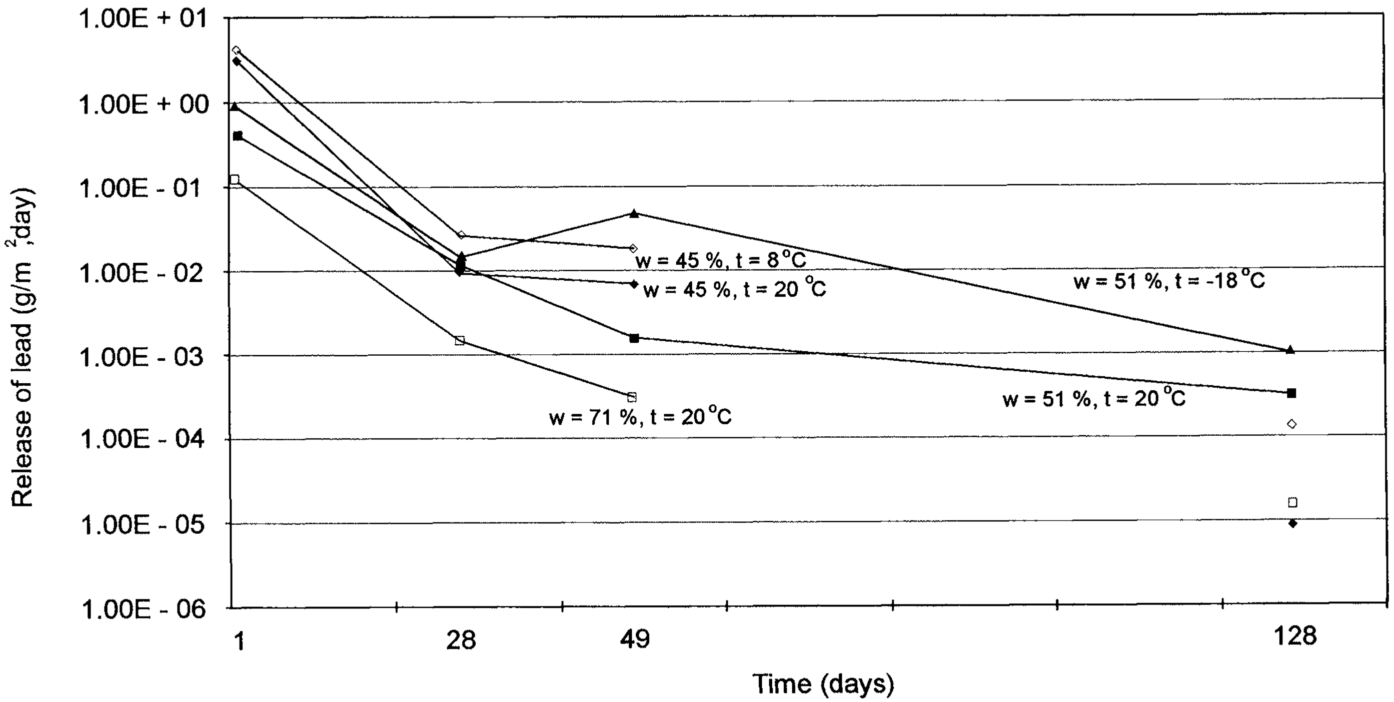
Solidification processes are typically designed to reduce the surface area to volume ratio of a waste, while at the same time decreasing the porosity and increasing the tortuosity of the material to minimise the release of contaminants to the environment. Consequently, the mere act of agglomerating finely divided materials into larger solid particles reduces the exposed surface area and thus potentially reduces the rate of release of contaminants from the mass. In addition, most solidification formulas are designed to generate physically strong and durable materials which maintain the integrity of the solidified matrix over geological time periods.

The effectiveness of such physical changes can be influenced by many factors. For instance, cement- based systems are affected by curing temperatures and moisture content. Typically, it is generally acknowledged that higher temperatures hasten the setting reactions of the solidified material, whereas moisture contents above or below optimal moisture/density content will result in weaker matrix strengths and poorer durability. A Swedish study provides graphical proof of the effect of moisture and temperature on the leachability of lead from an APC residue mixed with water before compaction (Kullberg et al., 1989). The data indicate that although the release of lead normally decreases with time, the release rate of Pb is higher when less than optimal water content and lower curing temperatures were used (Figure 18.1).

Furthermore, many chemical reactions can result in shrinking, swelling or changes in the time required for setting of the solidified materials. For example, the formation of ettringite, alkali-aggregate type reactions, and the oxidation of metals result in swelling of the matrix, which in turn, can reduce strength and durability (e.g., Neville, undated). In addition, the hydration of elemental metals can result in the liberation of gases (H_2, CO, C_2H_2, etc.), especially in the presence of organic compounds (Soundarajan, 1989), which can form small voids within the solid matrix and potentially reduces its overall strength.

Weathering, either due to freeze/thaw, wet/dry cycles or even erosion, can also result in a significant reduction in the physical integrity of the matrix, thereby increasing the exposed surface area and increasing the potential for contaminant release from the

Figure 18.1 Influence of Storage Temperature (t) and Water Content (w) on the Flux of Pb from APC Residue



Adapted from Kullberg et al., 1989

matrix. Another important consideration is the adequacy of the mixing process. The results from two studies have indicated that sufficient mixing time is required to permit some chemical reactions to occur which enhance the overall strength of the solidified material and hasten the setting time of the mixtures (Freidli and Brunner, 1989; Environment Canada, 1993).

18.2.2 Chemical Changes

Solidification processes generally result in chemical changes that incorporate free water into the solid through chemical reactions, and can potentially bind metals into the matrix. These reactions can either reduce, or in some instances increase, the leachability of metals. The chemical binding of metals can include transforming soluble metal salts into insoluble silicates, hydroxides or carbonates, whereas other changes can result in the incorporation of a metal into a crystal adsorption mechanism. Pozzolanic reactions are examples of crystalline adsorption mechanisms offering potential long-term immobilisation of metals. Unlike metals, organic compounds do not readily lend themselves to such techniques since the larger organic molecules are not easily incorporated into a crystal structure. Furthermore, it is more difficult to form insoluble precipitates from organic compounds. However, it should be noted that most organic compounds present in MSW incinerator residues, such as PCDD/PCDF, are relatively insoluble in water, and consequently, applying solidification processes for the sole purpose of immobilising these compounds is unwarranted. Thermal treatment, sorption processes or physical containment are more appropriate processes to treat organic compounds.

It is possible that the combination of certain binders/additives with APC residues can have a negative effect on the chemical and physical stability of a solidified material. For example, a Swedish study (Kullberg et al., 1991) indicated that some additives, such as gypsum, had negative effects. The presence of oils and greases, zinc, phenols and high concentrations of sodium have also been demonstrated to have a detrimental effect on the physical strength of solidified materials (Cullinane et al., 1987).

The chemical stability of solidified/stabilised materials is dependent on the chemistry of both the matrix and the leaching solution. Dissolution and desorption are the most dominant processes which influence the mobilisation of contaminants, whereas immobilising and demobilising processes compete in typical non-equilibrium situations, such as under exposure to the natural environment. Since the rate of dissolution of trace metals is pH dependent, the release can be influenced by a reduction in the pH, either due to the dissolution and loss of calcium oxide from the matrix, or due to the creation of carbonates from the exposure to carbon dioxide.

The physical constraints to the diffusion of ions out (or into) a matrix are dependent on the density of connected pores within the matrix (or the "tortuosity"). Generally, the weaker the product, the more "open" the pore structure (reduced tortuosity), and hence the greater the potential release rate. Some inert species as such as salts can be used to determine the density of the network, since their mobility is generally only restricted by physical constraints. On the other hand, the chemical conditions in the matrix (pH, redox, complexation) dictate to what extent many trace metals can be released. The difference in effective mobility between the salts and the trace metals indicates the degree of chemical retention. These phenomena are discussed in more detail in Chapter 20.

18.3 EVALUATION OF SOLIDIFICATION/STABILISATION PROCESSES

Since the aims of solidification/stabilisation processes include:

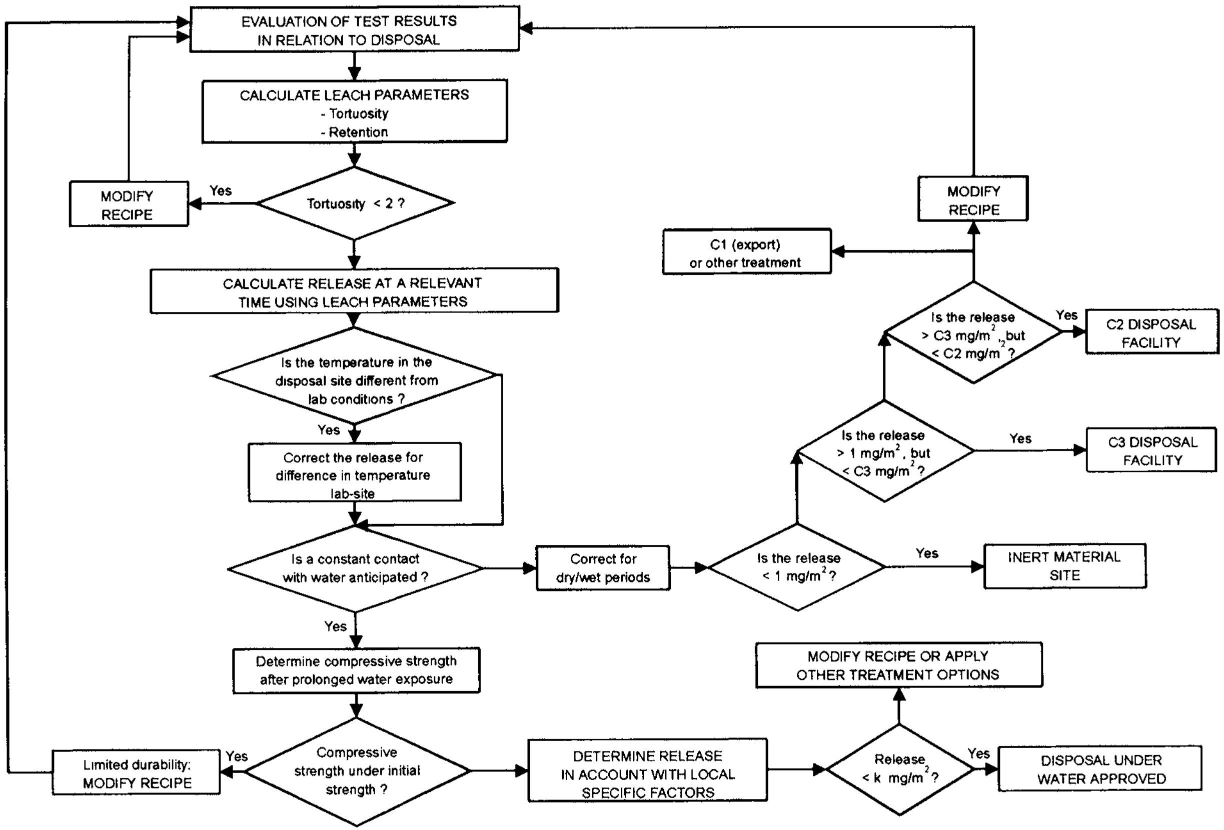
- enhanced physical properties
- increased size of agglomerated particles to reduce interaction with water
- solids with no free liquid
- improved handling characteristics
- reduced contaminant mobility

Evaluating these effects clearly requires a wide range of protocols which address both the physical and chemical transformations. Physical properties such as size, density and strength are common tests used on solidified materials, whereas leaching tests are most common for stabilised materials. A number of protocols incorporating various standard engineering and chemical evaluation tests have been used to assess these solidified residues (e.g., Donnelly and Jons, 1988; Friedli and Brunner, 1989; Sawell et al., 1989; v.d. Sloot, 1990; Environment Canada, 1991). An example of a relatively comprehensive protocol is outlined in Figure 18.2. It is recommended that in addition to chemically and physically characterising the solidified material, leaching procedures should also be used to determine both the potential for contaminant release and the rate of release (see Chapter 20).

Recognising the limitations with extrapolating laboratory data, it is also suggested that field verification studies should be undertaken (e.g., see Figure 18.3).

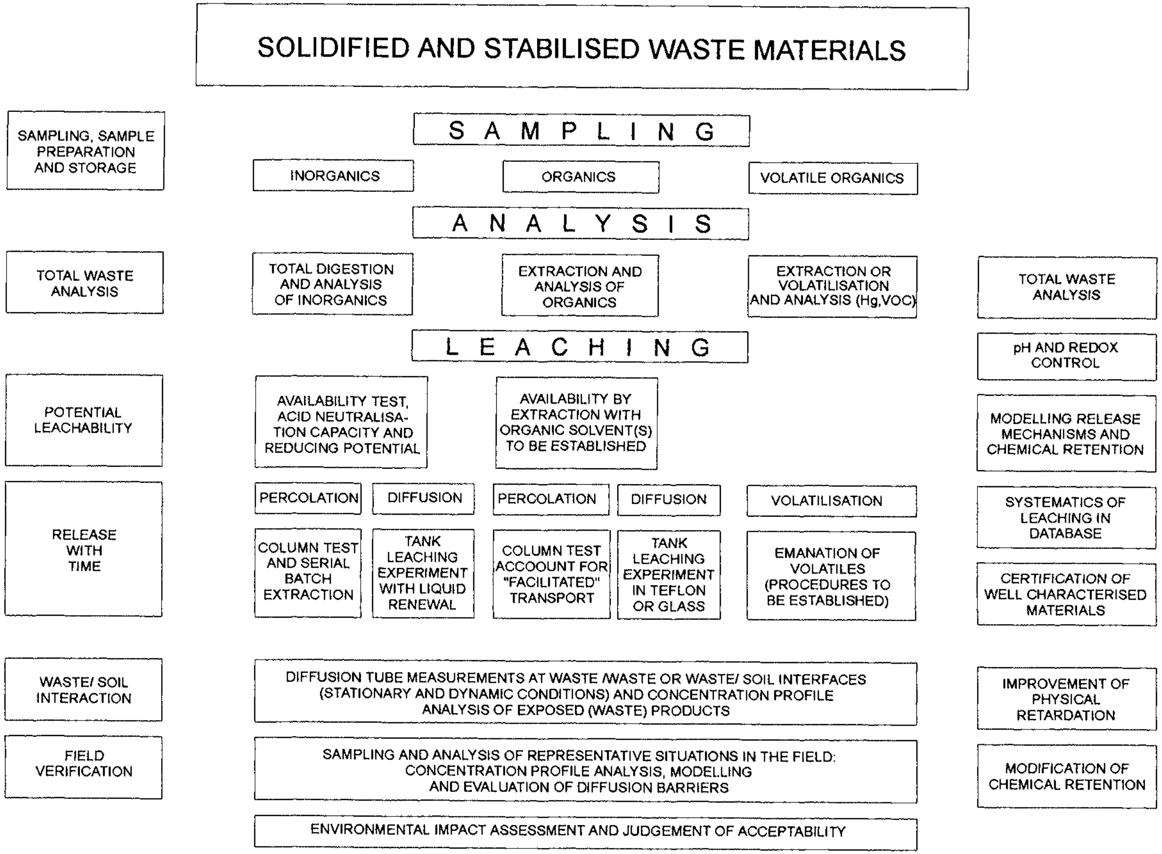
Another protocol suggested specifically for cement-based solidified wastes is a 3 step testing procedure which is outlined in Table 18.1 (Environment Canada, 1991). The first level involves a characterisation of the untreated material with special emphasis placed on identifying species that may adversely affect the cement-based additives. An inert constituent, such as Cl, is generally used to evaluate the tortuosity. The next level of testing assesses the effectiveness of the chemical fixation and the final stage involves evaluating the physical stability of the material.

Figure 18.2 Flow Schematic for Environmental Assessment of S/S Materials in Relation to Disposal



van der Sloot et al., 1993

Figure 18.3 Framework for Assessing the Leachability of S/S Wastes



Adapted from van der Sloot, 1990

Table 18.1
Test Methods to Investigate Cement Stabilised Materials

Level	Performance Indicator	Testing Method	Recommended Method	Minimum Number of Replicates
0	Process description	No testing required	N/A	NA
0	Mass/volume change	Bulk density	WTC Protocol, Method 2	3
0	Porosity/saturation	Moisture content Bulk density Solids specific gravity	WTC Protocol, Method 4 WTC Protocol, Method 2 WTC Protocol, Method 3b	3 3 2
0	Organic content	Total organic content	(WTC, 1985)	3
0	Contaminant concentration	Digestion/extraction and analysis	(U.S. EPA, 1980)	3
1	Initial leachate concentration	Low L/S ratio extraction	WTC Protocol, Method 9	4
1	Amount of contaminant available for leaching	Low pH extraction	Modified TCLP	4
1	Acid neutralisation capacity	Titration with acid	WTC Protocol, Method 11	3
2	Contaminant mobility in the matrix	Dynamic Leaching Test	ANSI/ANS 16.1	1
2	Hydraulic Conductivity	Constant Head Permeability	WTC Protocol, Method 5	4
2	Physical Strength (before/ after immersion)	Compressive Strength	WTC Protocol, Method 6	4
2	Weathering	Freeze/Thaw or Wet/Dry Cycles	ASTM D 4842-89 ASTM D 4843-89	4
2	Biodegradability	Biological Growth	ASTM G 21-70 and G 22-76	3

Environment Canada, 1991

18.3.1 Physical Tests

Since the solidification process changes the physical characteristics of the residues, it is appropriate to test the untreated residues, as well as the solidified materials. These results provide a comparative analysis of the characteristics before and after treatment. However, it should be noted that any test program should be related to the objectives of treatment process and the ultimate disposal scenario. Furthermore, not all of the tests are applicable to the both the untreated and treated residues. Consequently, it is recommended that several of the physical tests listed in Table 18.2 be performed on the untreated and treated materials (where applicable) to quantify physical properties.

Table 18.2
Recommended Physical Tests for Evaluation of S/S Materials

Category	Test	Material	Reference
Indices	Grain Size Distribution	Untreated	ASTM D422/C136, DIN66115
	Moisture Content	Both	ASTM D2216
	Swelling	Treated	ASTM D3877-80
	Carbon Content - LOI	Untreated	ASTM C25-93a, APHA 209E
Density	Bulk	Both	ASTM C29, E1109-86
	Dry	Both	ASTM C29
	Solids Specific Gravity	Both	ASTM D854-92, C127 & 128
Compaction	Modified Proctor	Untreated	ASTM D1557
Strength	Unconfined Compression	Treated	ASTM D1633
	Triaxial	Treated	
Hydraulic Conductivity	Constant Head	Untreated	ASTM D2434-68
	Flexible Wall Permeameter	Treated	ASTM D5084-90
Durability	Freeze/Thaw	Treated	ASTM D4842-90
	Wet/Dry	Treated	ASTM D4843-88
	Immersion	Treated	

The total carbon content of the untreated residue provides an indication of the relative amounts of solidifying agents required, or even the feasibility of the treatment process. Although no specific criteria have been established for this parameter, generally, the greater the carbon content, the greater the quantity of reagents which are required.

The grain size distribution usually indicates the specific surface area which can assist with estimating the quantity of stabilising agent needed. For example, a material containing a narrow band of particle sizes is generally less stable and needs more solidification additives to fill in the voids to promote greater strength. Moisture content determinations on both the untreated and treated materials is necessary to estimate the amount of water required during processing, and to calculate the weight increase factors of the treated material. To predict the optimum water content, a Proctor compaction test should be made on the untreated material. The stabilising reactions generally require access to free water, which is why the water content should be slightly higher than the Proctor compaction test indicates as optimum. The data on swelling provides an indication of the expansion which can be expected after treatment and deposition of the material.

The strength of a treated product indicates to what extent chemical bonding has occurred. However, the bonding may be considered "temporary", since it is due more to capillary forces and salt precipitation than the actual formation of pozzolanic bonds. The unconfined compressive strength test can also be used to estimate the durability of a treated product, however, this should be conducted on samples which have been cured, then immersed in water prior to testing. The compressive strength test involves subjecting a S/S sample of a specified size to increasing pressure until the structural integrity of the solid material fails.

Minimum compressive strengths are required for material deposited in a landfill. It is generally acknowledged that 350 kPa (50 psi) is necessary to withstand the operation of heavy machinery on top of the material in the landfill, however, other strength requirements have been recommended. For example, Austrian standards are based on compressive strengths exceeding 1,000 kPa (Verordnung proposed 1992), whereas Environment Canada (1991) has recommended a strength exceeding 350 kPa (after immersion in water) when placed in a monofill and 3,500 kPa in a sanitary landfill. Carlsson and Tuutti (1992) proposed that a S/S material with a strength exceeding 1,000 kPa should also be relatively durable.

Determining the permeability of a material is as important in evaluating S/S residue as compressive strength. Permeability is generally defined as the rate at which a substance is able to pass through a solid body. In S/S materials, it relates to a factor which limits the interaction of a solvent with the solidified matrix, and thus limits the transport of contaminants out of the solid. The permeability of S/S materials is generally measured as hydraulic conductivity and compared to the hydraulic conductivities of soils. Typically, dense, compacted clays provide a coefficient of conductivity less than 10^{-9} m/s, and it has been recommended that S/S materials have hydraulic conductivities less than 10^{-8} m/s (Environment Canada, 1991), 5×10^{-9} m/s (Austria, Proposed Verordnung, 1992) and 10^{-9} m/s (Kullberg et al., 1989).

Durability tests should be conducted on S/S materials to assess the response of a solidified matrix to the expansion and contraction of the solid matrix due to extremes in climatic conditions. Two tests have been used widely, namely the freeze/thaw and wet/dry weathering tests. These tests expose cubes or cylinders of S/S samples to alternating cycles of freeze/thaw, or wet/dry. Control specimens are generally exposed to alternating cycles of immersion in water and humidification. Consequently, weathering due to climatic extremes is expressed as a corrected weight loss value. This value is calculated by subtracting the cumulative weight loss through hydration only (control) from the cumulative weight loss resulting from the exposure to freeze/thaw or wet/dry conditions (see Figure 18.4). The criterion generally used to assess sample durability is based on a corrected weight loss of less than 10% of their total weight through physical weathering. It is suggested that weathering due to dissolution in water or salt water (erosion) should also be considered as a criterion to provide an indication of whether or not the S/S matrix should be precluded from use in a marine reef or permitted to be deposited below the groundwater table.

Many of these parameters provide valuable data on the physical properties of the material which indicate appropriateness of the treatment process for the eventual disposition of the material. Furthermore, it is recommended that the initial evaluation of a treatment option be conducted over a sufficiently long period of time to develop sufficient data to ensure the objectives of the treatment process are being met. Once this has been accomplished, selected surrogate parameters can be used for quality control. These selected parameters do not necessarily have to be a measure of the most important characteristics, but they should be sensitive enough to indicate changes in the treated product.

18.3.2 Chemical and Leaching Tests

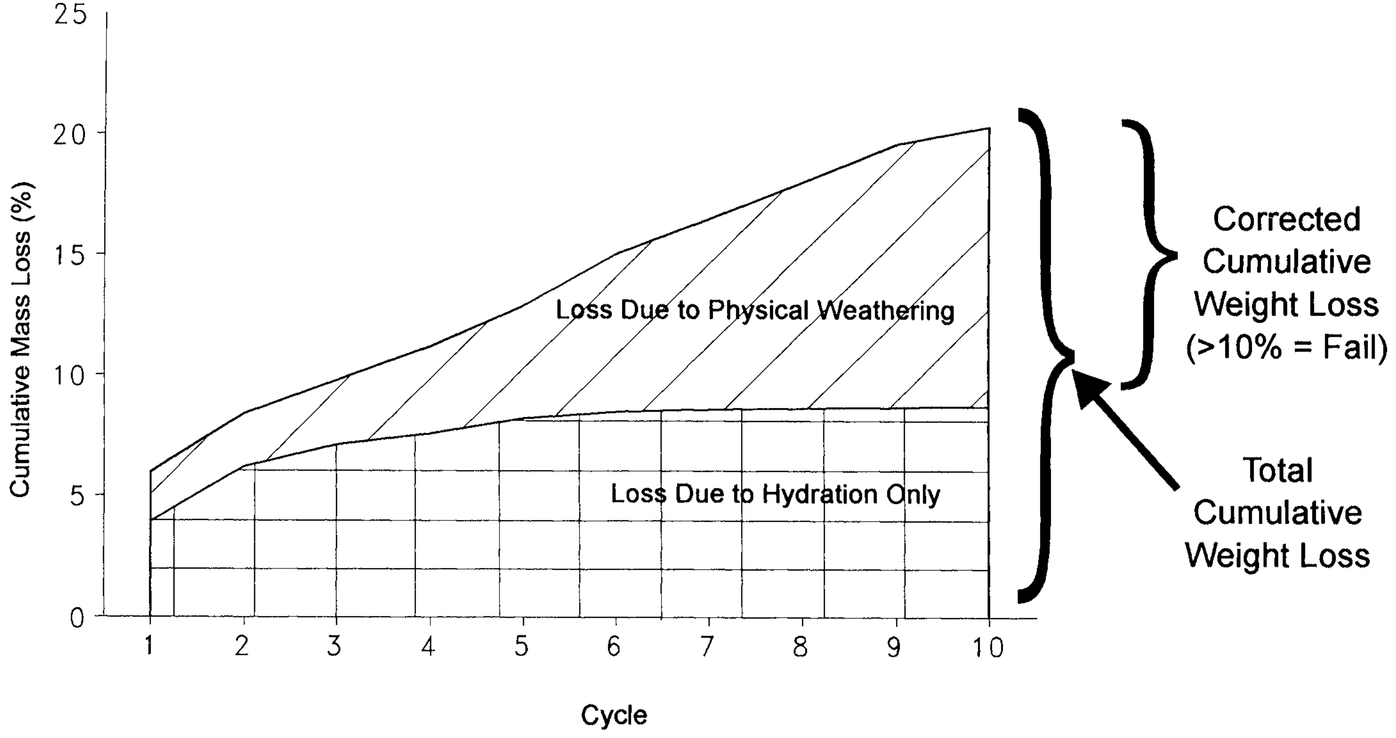
Since stabilisation and sometimes solidification processes are capable of changing the chemical nature of a waste, both the treated and untreated residues should be evaluated using chemical and leaching tests to assess the degree of those changes. A list of recommended tests is given in Table 18.3.

Table 18.3
Recommended Chemical and Leaching Tests for S/S Materials

Test	Material	Reference
Total metal concentration	Both	
Acid Neutralisation Capacity	Both	Environment Canada, 1991
Total Availability	Both	
Tank Leaching Test	Treated	ANS 16.1, TVA or NVN 5432
Water Solubility Test	Both	Environment Canada, 1991

The chemical composition of both the untreated and treated materials should be determined to compare the dilution effects of the S/S agent and to provide a benchmark for further evaluation. In addition to measuring the total concentration of metals, the data from a total availability test can be used in conjunction with data from leaching tests to estimate the potential release of contaminants from the S/S matrix.

Figure 18.4 An Example of Data Analysis from Weathering Tests



Determination of the acid neutralisation capacity can also be useful for estimating the resistance to change in pH after deposition and estimating potential leachability under different disposal scenarios.

Solidified materials are generally formed into monoliths with very low hydraulic conductivities and as such should be evaluated as a solid form as well. The release of contaminants from monoliths is generally governed by diffusion and not by percolation, therefore the ideal testing process should simulate diffusion in the environment. One method is the tank leaching procedure which permits an assessment of contaminant release from a solid monolith, whereas leaching tests conducted on ground samples (such as a total availability test or equilibrium leach test) provide an indication of potential contaminant release from a solid matrix which has disintegrated.

As detailed in Chapters 14 and 20, tank leaching tests are conducted on monolithic cubic or cylindrical shapes. The monolith is submerged in either distilled water or an acidified water for various periods and the resulting change in contaminants in the solution is used to calculate the release. These data are presented either as a flux (mg/m^2.day) or a diffusion coefficient (m^2/s). Typical tank leaching tests are defined by either the ANS 16.1 (United States), TVA (Switzerland) or NVN 5432 (Netherlands) tests. Since the release rates will generally decrease with time, the cumulative amount released over time can be compared to the total amount available for leaching, then placed into context by generating an effective diffusion coefficient which takes into account chemical, as well as physical retention factors (see Chapter 20).

Care must be taken in the interpretation of tank leaching data. The best comparison is the relative leachability between different samples. This comparison allows various formulations to be evaluated on a consistent basis. It should also be noted that if diffusion coefficients are used to estimate environmental impacts, the disposal conditions should be considered in relation to the manner in which the S/S material will be in contact with water. For example, tank leaching tests can be used to closely simulate reef disposal options where monoliths are used to create artificial underwater environments. Since land disposal is generally accomplished above normal groundwater levels, the monoliths are not continually immersed, and hence there is a much lower contact time between the solid and water.

18.3.3 Other Factors

In addition to the factors which influence the effectiveness of S/S material discussed above, other factors such as the mixing and moulding equipment, the system used to transport the material to the disposal site, and the disposal method, can all influence the final properties of the material. Vibration during transportation can cause the constituent materials to separate, thus creating different chemical and physical properties within the separated layers. Continuous mixing prior to deposition is a simple means to avoid this problem.

In general, treated residues have a very low hydraulic conductivity which impedes percolation and promotes surface run off from disposed materials. Salts, especially chlorides, are very difficult to chemically bind within the most solidified matrices. The rate of release of chlorides can be improved by diminishing the total exposed surface area, although it should be noted that leaching of the exposed surface also results in a loss of solids which may increase the hydraulic conductivity. The loss of solids can also occur due to biodegradation of the organic carbon in the solidified matrix from the residues.

Another consideration is the potential long-term influence of some of the additives used during the treatment of residues. For example, TMT#15™ is used to precipitate trace metals from scrubber solutions, however, the long term stability of the heavy metal compounds formed with TMT#15™ is still not known. It has been speculated that if the organic structure degrades due to microbial activity, the associated metals may become available for leaching. In addition, the sulphides may not be stable over the long-term and oxidation may result in formation of metal sulphates which can be available for leaching. Consequently, it is recommended that the effectiveness of any solidification/stabilisation based treatment should be considered not only for the short-term physical benefits, but the potential long-term effects of additives as well.

18.4 REVIEW OF AVAILABLE PROCESSES

18.4.1 Stabilisation Without Additives

Simply by mixing an APC residue with fly ash and water, a stabilisation effect may be achieved if the handling includes compaction at the optimum water content. The time elapsed between slurrying and placement in the disposal site must be minimised, or the permeability generally deteriorates (Kullberg et al., 1989). Although these residues from dry or semi-dry APC systems exhibit "temporary" setting qualities, these are not considered pozzolanic reactions which can bind metals into the matrix. Moreover, although this "freezing" of $CaCl_2$ and other salts provides some strength to the solid matrix, the material is highly susceptible to disintegration due to hydration.

In contrast, many combined residues from wet scrubber systems show self-binding properties. One example of this is the Bamberg model (Reimann, 1990), where the ESP ash (26 kg/t) is mixed with 12 kg neutralising sludge (1 kg TS) from the first washing step in the APC system and 30 kg gypsum sludge (3 kg TS) from the second washing step. The mixed product becomes a paste, which increases in temperature to 65 °C in a few hours. The stabilisation process requires weeks for proper curing. Although it has been found that the chlorides still leach, the metals become less leachable due mostly to their transformation to sulphides.

18.4.2 Solidification/Stabilisation with Binders

Binders, both organic and inorganic, are commonly used as S/S reagents. Table 18.4 outlines typical binders in both categories. Cost plays a major role in the selection of binders because large quantities are normally required.

Table 18.4
Typical Binder Reagents

Wastes	Commercial	Bitumen	Polymeric
Cement kiln dust	Portland cements	Hot emulsion	Epoxy
Blast furnace slag	Lime	Cold emulsion	Polyesters
Lime kiln dust	Limestone		Polyolefins
Coal fly ash	Quicklime		Urea Formaldehyde

Inorganic binders are normally chosen because of their lower cost. Polymers are the most expensive binders (up to $500/tonne of processed waste), and do not react with the waste but rather encapsulate the materials to prevent their release. Combinations of inorganic and organic binders have been proposed, including (1) polystyrene and cement and (2) polymer gels and silicates with lime cement.

Cement-Based Systems

The early development of cement-based fixation techniques was in the area of low level radioactive waste disposal. The development then proceeded into the area of high volume waste disposal, particularly with respect to sludges contaminated with heavy metals and to contaminated soils. Cement has also been used with complex wastes containing PCB, oils and oil sludges, wastes containing vinyl-chloride and ethylene dichloride, resins, asbestos, sulphides and other materials. The adding of cement generally decreases the hydraulic conductivity and porosity of the treated material, and increases the tortuosity, durability, strength and volume. Once the material has cured, the release rate of metal contaminants will usually be low, as long as the physical integrity of the material remains intact.

Cement-based techniques have the following advantages:

- widely available at a reasonable cost
- the technique of mixing and handling is well developed
- the necessary equipment is readily available
- the technique is tolerant to chemical variations in the waste
- the strength and permeability of the final product can be varied by controlling the amount of cement added in the process

The disadvantages of cement-based techniques are:

- cement adds considerably to the weight of the waste
- pretreatment may be necessary for waste containing impurities that affect the setting and curing of cement
- cement/waste mixtures of low strength are often vulnerable to acid leaching solutions
- the matrices do not effectively bind chloride salts

Cement based techniques generally use Portland Cement along with other additives to modify the properties of the cement. These have both positive and negative benefits such as increased shrinkage and reduced strength. The waste materials are mixed with Portland cement and sufficient water to ensure proper hydration reactions for bonding the cement. The waste is incorporated into the cement matrix and in some cases undergoes physical/chemical changes which further reduce contaminant mobility. Typically, metal hydroxides or carbonates can be formed which are less soluble than other ionic species of metals. The final products can vary from a granular, soil like material to a solid monolith, depending upon the amount of reagent added, the type of waste, and the water content.

Metal salts including those of manganese, copper, lead, tin and zinc have been found to cause large variations in setting times and final strength. Sodium salts such as arsenate, borate, phosphate, iodine and sulphide have been found to act as retarders.

Because high sulphur bearing wastes can result in sulphate attack on the cement matrix, special formulations (either Type II or Type V cements) may be preferable. Type II cement, as classified by ASTM C150, has a limited amount of C_3A (tricalcium aluminate) and C_3S (tricalcium silicate) and is used where moderate exposure to sulphate is anticipated. Type V is preferable for exposures where high alkalinity is expected and in structures exposed to seawater. Tricalcium aluminate is the compound most susceptible to sulphate attack and therefore minimum quantities (<5%) are present in Type V cements.

Two major programs were undertaken to evaluate the effect of cement-based solidification processes on incinerator residues, namely the Environment Canada sponsored studies under NITEP (1988 through 1991 and summarised in Environment Canada, 1993), and a US EPA study (Kosson et al., 1993). Only the major conclusions from these studies are included here. More detailed information can be obtained from the referenced reports.

The Environment Canada studies were conducted on APC residues from four different types of incinerator facilities. Portland Type II cement was used as the basis for the all formulations and one of three different types of waste pozzolans including:

- cement kiln dust
- coal fly ash
- blast furnace slag

The study is outlined in greater detail in the next section.

The US EPA study was conducted on bottom ash, APC residue and combined bottom ash/APC residue using 4 different vendor specific technologies which covered a range of processes and a control formulation using Portland cement as the only solidification additive.

The 4 vendor specific formulations included:

- Portland cement, polymeric additives and other proprietary additives
- Portland cement, soluble silicates and dry carbonaceous material
- cement kiln dust and proprietary additives
- soluble phosphate additive (patented WES-Phix process)

Some of the results from the two programs were very similar. First, none of the formulations tested were effective at reducing the potential release of salts from the residues, irrespective of residue type. This was not surprising, since it appears to be a typical result for most cement-based formulations used on wastes containing readily soluble salts. With respect to the physical strength of various formulations, the EPA study observed that the control specimens (cement additive only) resulted in unconfined compressive strengths (UCS) greater than or equal to the other solidification-based formulations with proprietary additives. Furthermore, the study also found that the formulations which resulted in the greatest UCS were also the most resistant to weathering. In addition, it was noted that the physical properties of cement-based formulations for bottom ash and combined ash could be greatly improved "by optimising process design based on results of multiple test criteria" (Kosson et al., 1993).

All of the solidification-based formulations from the EPA study resulted in more physical, rather than chemical changes to the trace metals in the different types of incinerator residues. However, one stabilisation formulation was shown to have reduced the potential release of lead from the residues (see Stabilisation). Conversely, the Environment Canada studies indicated that some of the solidification formulations resulted in both chemical and physical retention of trace metals in APC residues. It should also be noted that both studies concluded that the rate of release of "potentially toxic metals" from S/S treated residues would be very slow. The disparity between the earlier conclusions regarding chemical retention merely emphasises that the effectiveness of individual solidification formulations can vary, and therefore should be evaluated on their own merits based on a battery of physical, chemical and leaching tests.

Examples

There are a number of facilities which make use of some type of cement-based S/S process to treat the different ash streams from MSW incinerators.

"Monofill^{TM}" is a cement-based additive developed by Cementa Sweden. This material is used to stabilise the APC residue at the Hogdalen incinerator in Stockholm. The recipe calls for mixing 1000 kg of residue with 460 kg of the "Monofill^{TM}" additive and 1290 L of water (Sundberg, 1991). Approximately 8,000 tonnes of APC residue are treated annually.

A German process was developed to stabilise residues with cement between 1982-1986 (Wewer & Maurer, 1990). The formulation was based on mixing 65% APC residue together with 35% cement. The water addition was 35% of the total dry weight. Although the technique was deemed feasible, it was decided not to build a full-scale system because less expensive disposal was available in old coal and salt mines. Furthermore, it was found the salts could not be effectively retained in the solidified matrix.

In Germany, 19 incinerator plants are using the "UTR Technology" (UTR, 1992) to stabilise about 150,000 tonnes of ash annually. APC residues are stabilised with cement and proprietary additives prior to disposal in quarries. There is little other information available on the process.

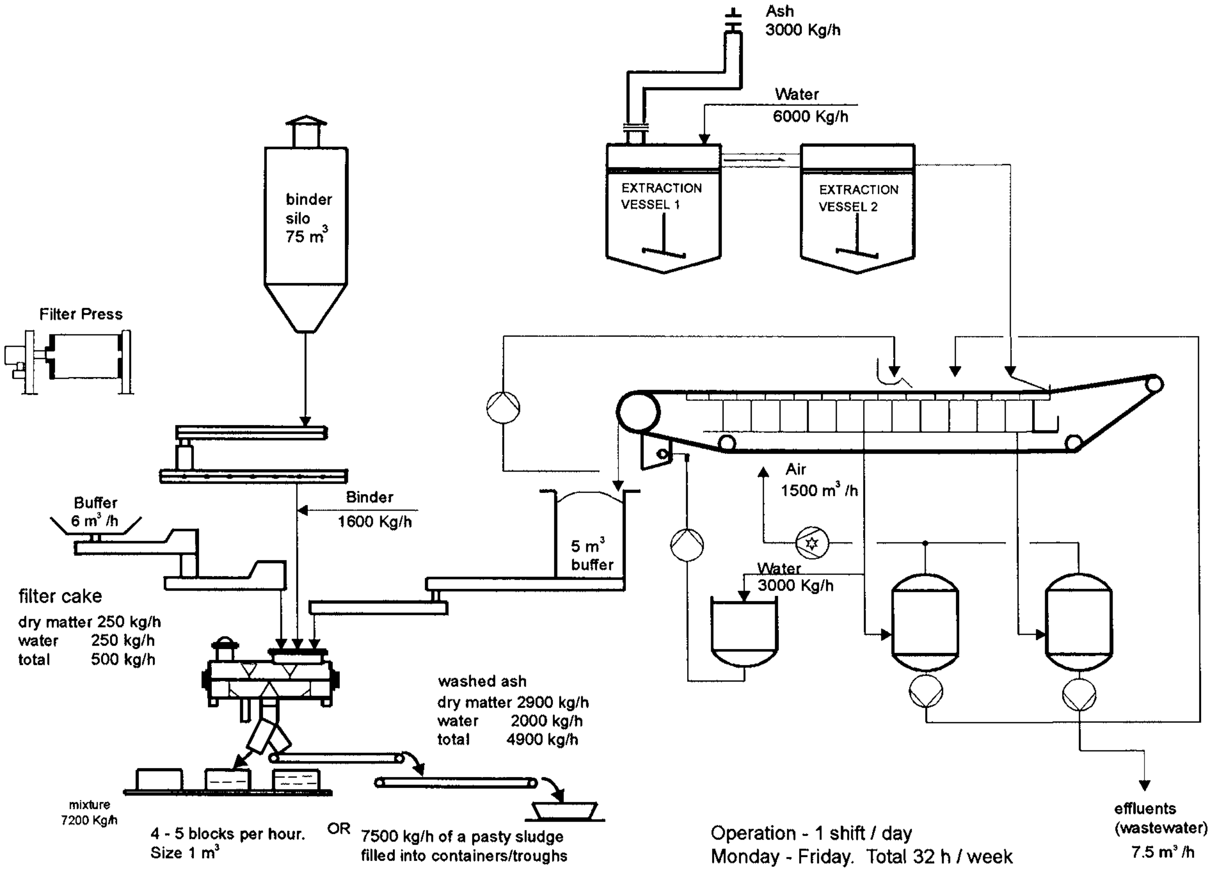
"Alinitcement" is a hydraulic chloride containing a binder which has been used to stabilise APC residues. The theoretical composition is 21 CaO - 6 SiO_2 - Al_2O_3 - $CaCl_2$ (RKW, 1992). "Alinitcement" can be used in mining as a back filling material and as stabilising agent for other wastes. The leachability of salts from this material is reduced by dilution to 50%.

In Vienna, all types of incinerator residues are transported to a central processing facility where the magnetic material is separated and particles over 50 mm in size are removed (Magistratabteilung 48). The remaining material is stabilised with Portland cement and water. The mixture is 1,300 kg bottom ash, 350 kg fly ash, 200 kg cement and 120-150 kg water. The stabilised residue is used to build dikes around a conventional MSW landfill site.

IVR-Techform (Inertiserung von Rauchgasrückständen) is used at a number of incinerator facilities in Switzerland. The APC residue is first washed at L/S of 2:1 before it is stabilised. The sediment from the washing process is mixed with 620 kg cement and additives, and 775 kg of water. A schematic of the system is given in Figure 18.5 which is used to treat 26,000 tonnes of APC residue annually.

In Japan, about 110 facilities use some type of cement-based stabilisation process to treat APC residues (Wakamura and Nakzato, 1992).

Figure 18.5 The Principal Design of the IVR Stabilisation System



Techform ENG AG, 1992

Waste Pozzolanic Systems

Pozzolanic materials are defined as siliceous substances that react with lime in the presence of water. The presence of high concentrations of silicates distinguishes these materials from the Portland cement or lime-based systems. Although they are much less expensive than cements, formulations generally require a higher proportion of these additives, compared to cements, to promote sufficient physical strengths. Waste pozzolans include coal fly ash, fluidised bed combustion material, cement-kiln dust and processed blast furnace slag.

The major advantages with waste pozzolanic-based systems are:

- the binders are inexpensive and are generally widely available
- the processing equipment is widely available and simple to operate
- the chemistry of pozzolanic reactions is relatively well known

However, processes using waste pozzolans can suffer from problems similar to cement-based processes, especially with regard to setting, curing and stabilising organic laden materials. For example, the decomposition of organic material in sludge stabilised waste can result in increased permeability and decreased strength.

The major disadvantages of waste pozzolanic-based systems are:

- the binders add weight to the disposed materials
- formulations can be susceptible to acidification if there is insufficient buffering capacity
- curing and setting problems can occur due to inorganic salts in incinerator residues
- these formulations are temperature sensitive and may set very slowly at lower temperatures

The final products generated from these formulations can vary from a soft fine-grained material to a hard monolithic block.

As indicated previously, solidification formulations using waste pozzolans have been tested by both Environment Canada and the US EPA. Although most of the samples tested by Environment Canada were observed to swell during the curing period, this did not appear to be detrimental to the hydraulic conductivity or the physical strength of the samples. It was also noted that despite the fact that the weight of the total material (including water) increased by about a factor of 2, the density also doubled, resulting in very little, to no volume increase. All of the formulations generated material which had hydraulic conductivities as low as dense compacted clays ($<6 \times 10^{-8}$ m/s). All of the average compressive strength results indicated that the formulations exceeded the suggested criteria for placement in monofills (350 kPa) or landfills (3,500 kPa). Comparatively, the coal fly ash formulations resulted in the lowest strengths, however, the strength of the formulations tended to increase with the experience gleaned from each successive study.

The formulations in the Environment Canada studies were also subjected to freeze/thaw weathering to determine their durability. Formulations for two of the four residues tested generated solidified specimens which were very durable. However, the weight loss observed from all of the samples was due mostly to dissolution, rather than physical weathering. The reason for the lack of durability was the dissolution of salts and lime in the solid matrix, and sulphate attack on the pozzolanic bonds. The observed dissolution of salts is consistent with the findings from the EPA study. However, unlike the EPA study, there was no significant correlation between UCS and durability observed during the Environment Canada study.

There are currently two known facilities using a cement-kiln dust based process designed by Energy Answers Corporation to treat APC residues, namely the SEMASS incinerator facility in Rochester, Massachusetts, and the SWARU incinerator facility in Hamilton, Ontario.

Chemical Stabilisation

Frequently, elements such as cadmium, lead or mercury can be present in incineration residues as mineral phases that are available for leaching. These readily soluble mineral phases are usually metal salts such as $CdCl_2$, $PbCl_2$ or $HgCl_2$. Chemical stabilisation can convert these minerals to less soluble forms that reduce the environmentally available fraction for leaching.

Successful chemical stabilisation requires the use of chemical additives that produce a more thermodynamically favoured solid phase (see Chapter 13). Three additives that have been used successfully at the full-scale level are sulphides, activated carbon and phosphates. Other additives such as ion exchange resins, clays and carbonates have also been used in laboratory studies.

Sulphides are generally used as either a mercury sorbent in APC systems, i.e., either in dry or wet scrubber systems, or as a precipitating agent in treatment of wastewater from wet scrubber systems. The principal forms include inorganic additives (Na_2S) or organic additives such as TMT#15™. The principal immobilisation reaction for the inorganic based system is:

$$Na_2S + HgCl_2 \Rightarrow HgS + 2NaCl \qquad (18.1)$$

The principle immobilisation reaction for the organic based system is:

$$H_2 + HgCl_2 \Rightarrow HgS + 2H^+ + 2Cl^- \qquad (18.2)$$

In the case of HgS (cinnabar), a precipitate forms within the inorganic system, which has an extremely low solubility product of 1×10^{-25} (K^{SP}), indicating that HgS is an extremely insoluble precipitate. In the case of the sulphhydryl complex (TMT#15™), the stability constant (K) is extremely high (1×10^3), indicating the organosulphhydryl mercury complex is a stable complex with both the inorganic and organic additive systems. Caution must be used in interpreting the long-term geotechnical or biogeochemical stability of the precipitate or complex. Although it is possible for HgS to be oxidised and release of the Hg^{2+}, this is probably not a concern under normal disposal conditions. In the case of the organosulphhydryl mercury complex, the organic portion of the complex is susceptible to biodegradation. The sulphhydryl group also shows some susceptibility to oxidation.

Powdered activated carbon has also been used to control mercury in dry scrubber systems. Unlike the sulphur based treatment systems, the activated carbon uses the principal of sorption to sequester mercury. The mercury forms an inner sphere complex with sorption sites on the carbon providing a relatively stable bonding environment. This process is used in a growing number of incinerator facilities around the world.

With respect to residue treatment, the use of orthophosphate has been shown to be effective in controlling metal solubility in bottom ash, APC residue and combined ashes (Eighmy et al., 1989). Wheelabrator Environmental Systems has patented a process involving the addition of soluble orthophosphate to form insoluble metal phosphate minerals, such as lead phosphate ($Pb_3(PO_4)_2$), chloropyromorphite ($Pb_5(PO_4)_3Cl$) and hydroxypyromorphite ($Pb_5(PO_4)_3OH$).

The principal immobilisation reaction to form simple metal (denoted as Me) phosphates is:

$$3Me^{2+} + 2PO_4^{3-} \Rightarrow Me_3(PO_4)_2 \qquad (18.3)$$

The principal immobilisation reaction to form chloropyromorphite is:

$$5Pb^{2+} + 3PO_4^{3-} + Cl^- \Rightarrow Pb_5(PO_4)_3Cl \qquad (18.4)$$

The principal immobilisation reaction to form hydroxypyromorphite is:

$$5Pb^{2+} + 3PO_4^{3-} + OH^- \Rightarrow Pb_5(PO_4)_3OH \qquad (18.5)$$

All of these phosphate minerals have relatively low solubility products (10^{-12} to 10^{-13} for the metal phosphates, 10^{-28} for the pyromorphites) indicating these minerals are very insoluble. Unlike sulphide based minerals, phosphate minerals are geochemically stable (Eighmy et al., 1989). Wheelabrator is utilising this process at three of its mass burn facilities in the United States to treat combined bottom ash and scrubber residue. It is also under license to other incineration facilities.

Other additives have been considered to chemically stabilise metals in ash. One bench-scale study involved the use of the mineral trona ($Na_4(CO_3)_2$) to provide carbonate to promote the formation of metal carbonates such as $CdCO_3$ (otavite). This approach (Thompson, 1988) was found to reduce lead, cadmium and zinc leachability in column leaching tests on modular bottom ash/boiler ash blends.

All of the above-mentioned chemical additive systems require good blending, mixing and moisture control to ensure intimate contact of the additive with the leachable fraction of the metals or elements in the residues. Moisture control can also be critical, particularly if some level of dissolution of the existing phase is required prior to reprecipitation as sulphides, phosphates or carbonates.

18.4.3 Stabilisation With Organic Additives

Stabilisation with organics is a micro-encapsulation process which assumes that the waste material does not react chemically with the encapsulating material. Thermoplastic materials, such as bitumen, paraffin and polyethylene are the most common of the organic additives used to bind waste materials into a solid mass. One to two parts of dried waste can be mixed with one part bitumen at elevated temperatures (>100 °C) using specialised equipment to generate a hydrophobic solid material after cooling. Bitumen techniques are limited to the waste materials which do not contain high concentrations of salts such as nitrates or chlorides since they will react with the bitumen and can cause deterioration. In many cases, the bitumen-waste mixture is placed in a container such as a steel drum. The use of special equipment for heating and mixing restricts the use to small volumes and these processes are therefore relatively expensive.

The encapsulation techniques utilising paraffin and polyethylene are similar to that used for bitumen. The thermoplastic material is mixed with a sludge at elevated temperatures and then allowed to cool. The resulting mixture is often containerised before disposal.

The advantages of the thermoplastic technique include:

- the rate of contaminant release is generally much slower than for other techniques
- the thermoplastic material is relatively impervious to most aqueous solutions
- the thermoplastic material generally adheres well to incorporated materials

The disadvantages are:

- the technique requires expensive equipment and skilled labour

- the process poses a risk of volatilising some contaminants
- most thermoplastic materials are flammable
- wet sludges must be dried before mixing
- the technique is expensive
- it is not suitable for high volume wastes
- it is susceptible to chloride attack and is not recommended for APC residues

At three different plants in Japan (Wakamura and Nakzato, 1992) the fly ash from incineration is stabilised with bitumen. The bitumen and the fly ash are carefully mixed, so all ash particles are covered. A sketch of the technique is shown in Figure 18.6.

18.4.4 Macro-encapsulation

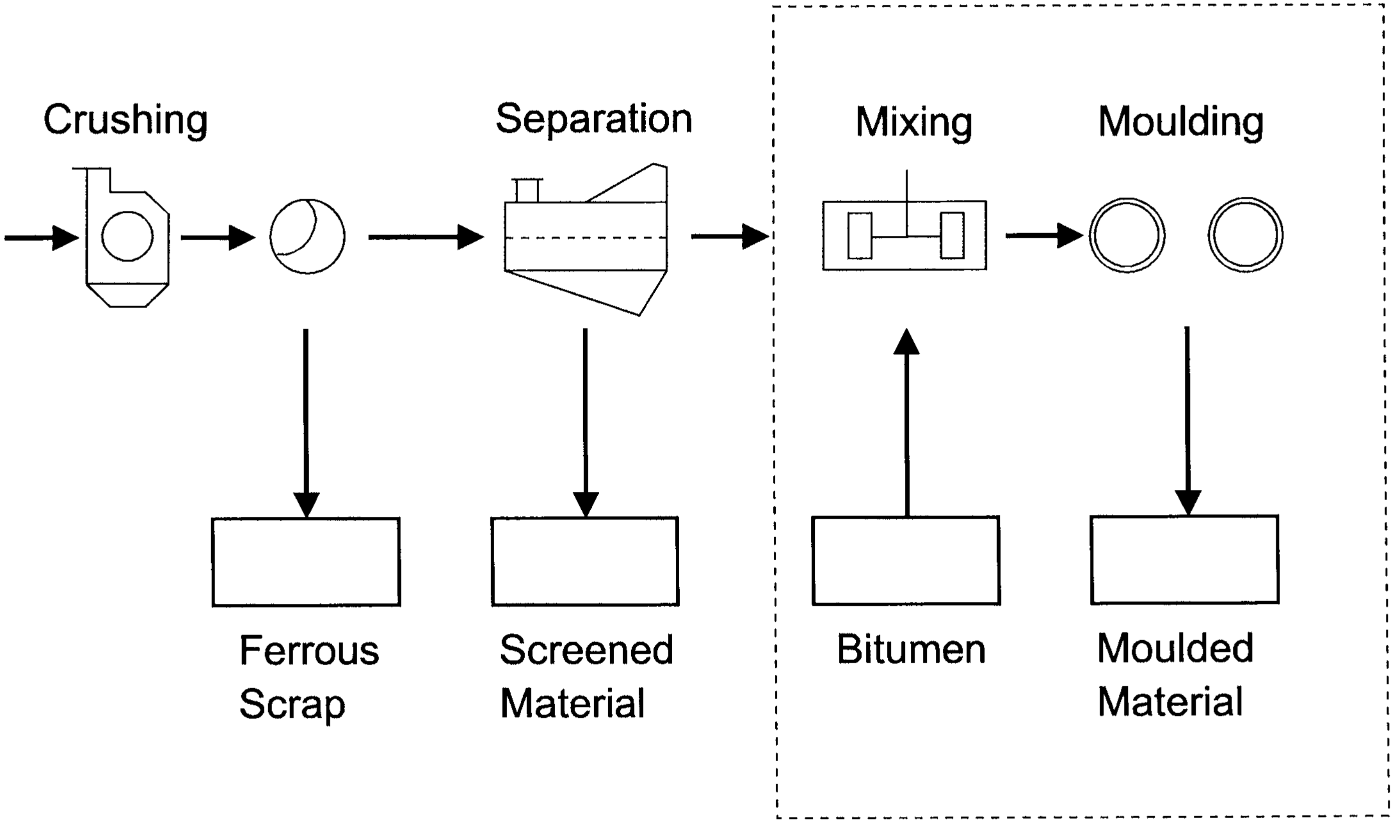
Macro-encapsulation involves enclosing the waste in a coating or jacket of inert material, thus placing an impervious barrier between the contaminant and the environment. Wastes treated in this manner include low radioactive materials, electroplating sludges and coal scrubber sludges. The technique has not been widely used, but its use can be warranted for specialised applications.

Macro-encapsulation is also defined as the protection of disposed waste by a cover with a very low permeability. This cover may be of natural soil, like clay, or by a synthetic liner.

18.4.5 Costs

Costs for any stabilisation/solidification process are site specific and depend upon the type of waste, pretreatment requirements, transportation distances, disposal criteria, regulatory criteria, health and safety requirements, assurance and quality control. In addition, the fluctuations in currency exchange rates makes it difficult to provide specific figures, consequently no costs are given here. It is recommended that the cost of any treatment process be evaluated based on the relative increase in cost it may cause on the tipping fee for the incoming waste.

Figure 18.6 Three Plants in Japan Using Stabilisation with Bitumen



Wakamura and Nakzato, 1992

REFERENCES

Carlsson, B. and K. Tuutti. "Solidifiering Och Deponering Av Specialavfall", Stifelsen Reforsk, FoUnr 66, 1992.

Conner, J. Chemical Fixation And Solidification Of Hazardous Wastes, van Nostrand Reinhold. New York, 1990.

Cullinane, M.J., R.M. Bricka and N.R. Francingues. "An Assessment of Materials That Interfere With Stabilisation/Solidification Processes", Paper prepared for the US EPA Hazardous Waste Engineering Reseach Laboratory by the US Army Engineer Waterways Research Station under Contract DW96930146-01, 1987.

Cullinane, M.J. and L. Jones. "Solidification and Stabilization of Hazardous Wastes. Part 2", Journal of Hazardous Materials Control, p. 24-58, March/April 1989.

Demmich, J. Mechanismen und angewandte Verfahren zur Verfestigung von Rückständen.

Eighmy, T.T., S.F. Bobovski, T.P. Ballestero and M.R. Collins. "Theoretical and Applied Methods for Lead and Cadmium Stabilization in Combined Ash and Scrubber Residue", Proceedings of the Second International Conference on Municipal Solid Waste Combustor Ash Utilization, Resource Recovery Report, 1989.

Environment Canada. Proposed Evaluation Protocol for Cement-based Solidified Wastes, Prepared by J. Stegemann and P. Cote for Waste Management Branch, Report EPS 3/HA/9, 1991.

Environment Canada. The National Incinerator Testing and Evaluation Program: A Summary of the Characterization and Treatment Studies on Residues from Municipal Solid Waste Incineration. Prepared by S.E. Sawell and T.W. Constable for Waste Management Branch, Report EPS 3/UP/8, October 1993.

Friedli, P. and P.H. Brunner. "Solidification of Filter Ashes from Solid Waste Incinerators", Proceedings of the Third International Conference on New Frontiers for Hazardous Waste Management, US EPA, 1989.

Kosson, D.S., T. Kosson and H.A. van der Sloot. US EPA Program for Evaluation of Treatment and Utilization of Municipal Waste Combustor Residues - Phase I, Laboratory Testing of Solidification/stabilization Processes, Report prepared for US EPA Risk Reduction Engineering Laboratory under CR 818178-01-0, Cincinnati, Ohio, 1993.

Kullberg, S. A-M. Fällman and J. Hartlen. Auslagung Unbehandelter und Stabilisierter Restprodukte Ein Modell zur Prognostizierung von Umweltbelastungen durch Deponien. VDI Berichte Nr. 753, 1989.

Kullberg, S. A-M. Fällman and J. Hartlén. Stabilisering och Deponering av Rokgasreningsprodukter fran Sopforbranning. Stifelsen for Varmeteknisk Forskning, Bransleteknik Nr. 370, 1991.

Kullberg, S. and J. Hartlén. Stabilisering/solidifiering och Vitrifiering/forglasning av Avfall - en International Oversikt. Stiftelsen Reforsk, FoU nr. 80, 1993.

Magistratabteilung 48. Stadtreinigung und Fuhrpark 1992. Personal Communication with Dipl.- Ing R. Siebenhandl. Austria, 1992.

Ministry of Housing, Physical Planning and Environment. "General Administrative Order on Building Materials (Soil and Water Protection)". Netherland Government Gazette, No. 121, June 26, 1991.

Neville, A.M. Properties of Concrete, Published by John Wiley and Sons, New York, undated.

NUKEM GmbH. Personal communication with Dipl. Ing. H. Renetzeder, 1992.

Reimann, D.O. "Filteraub-/Sorptionsschlamm - Mischverfahren - Bamberg Modell". Beiheft 29 zu Mull und Abfall (Hrsg. D.O. Reimann/J. Demmich), Erich Schmidt Verlag Berlin, s 65-68, 1990.

Richlinien für die Ablagerung von Abfällen.

Soundararajan, R. "Development of Organophilic Binders With Incinerator Ash for Stabilising Industry Organic Wastes", Proceedings of the Municipal Solid Waste Technology, San Diego, California, Published for US EPA by Technical Resources, Inc., 1989.

Sundberg, J. Stabiliserad rokgasreningsprodukt fran Hogendalenverket, deponering och miljopaverkan, 1991.

Techform Engineering AG. Entsorgung von Rauchgasreinigungs - Rückstanden aus Müllverbrennungsanlagen nach dem IVR Verfahren., 1992.

UTR. Personal Communication with Mr. Poschwatta, Umwelt-Technologie und Recycling, Germany, 1992.

van der Sloot, H.A., G.J.L. Wegen and E. Vega. Evaluate van Testmethoden en Criteria Voor de Beeerdeling van Uitloogggedrag en Duurzaamheid van Immobilisaten, Stichting CUR. 1993.

van der Sloot, H.A. Performance Tests of Solidified and Stabilized Waste Materials for Environmental Assessment and Quality Control. Workshop on Waste Characterization/ Classification, Sigtune, Sept. 23-24, 1992. Swedish Geotechnical Institute, March, 1993

Verordnung des Bundesministers für Land- und Forstwirtschaft über die Begrenzung von Sickerwassermissionen aus Abfalldeponien. Proposal, 24 Febr 1992.

Wakamura, Y. and K. Nakzato. "Technical Approach for Fly Ash Stabilization in Japan. 85th Annual Meeting and Exhibition, Air and Water Management Association, June 22-26 1992, Kansas City, Missouri, 1992.

Wewer, H. and P.G. Maurer. Zementadditiv-Verfahren nach NUKEM. Restoffe aus der Rauschgasreinigung von Abfall - Sonderabfallverbrennungsanlagen sowie von Kohlenkraftwerken. ISBN 3 503 2888 9, 1990