

FACTORS FOR SELECTING APPROPRIATE SOLIDIFICATION/ STABILIZATION METHODS*

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Summary

The solidification/stabilization (S/S) of a waste can be compared with the production of concrete. To make concrete (whether cement based or asphaltic) aggregate is mixed with binder to form a mass that sets up into a rock-like material. In the case of S/S, a waste containing material such as water, dissolved inorganic metal salts, or organic compounds is mixed with some form of binder to form a stable material with reduced leachability of the contaminants. This paper presents information that can be used to select the S/S method for treating a given waste.

Introduction

Before starting on the discussion, it is necessary to define two key terms, solidification and stabilization. They are often used interchangeably but mean different things. Solidification is the act of tying up free water in a waste to improve its handling characteristics or to make it acceptable for landfill disposal — “landban restrictions.” The term stabilization refers to the treatment of a waste which results in the decrease of the mobility of contaminants in a landfill environment. The treatment of aqueous wastes requires that it be solidified as well as stabilized, but even solid materials may require stabilization prior to disposal in a landfill.

Contaminant mobility is normally thought of as only its rate of leaching into an aqueous phase, but one should also consider its mobility to the air via vaporization, not just to ground or surface water. Therefore, the stabilization of a hazardous waste requires that the product have reduced levels of both.

Having defined terms, we will now consider the types of S/S processes available: S/S can be broken into the following six major categories:

- (1) Cements based binders
 - portland cement
 - cement klin dust

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- fly-ash mixtures
- (2) Lime based binders
 - lime
 - lime kiln dust
 - mixtures of fly-ash and lime
- (3) Absorbents
 - hydro and organophilic clays
 - wood chips, sawdust, rice hulls
- (4) Thermoplastic materials
 - asphalt bitumen
 - thermoplastic polymer
- (5) Thermosetting polymers
- (6) Vitrification.

This paper will discuss only the first two categories of S/S with a brief mention of the others.

Solidification/stabilization methods

Absorbents (such as sawdust or expanded clay) are generally not considered to be an acceptable method of solidifying liquids. While certain metals and even, possibly, some organics may have their leachability diminished by absorption on solids, this has generally been discarded in favor of other S/S practices. Clearly, absorption will have little impact on the stabilization of solid materials, such as contaminated soil.

Thermosetting materials such as asphalt or polyethylene have been used to encapsulate radioactive wastes; however, their use for the treatment of hazardous wastes has been limited and little data exist to support their use at this time. Thermosetting polymers have also been used to encapsulate solidified radioactive wastes. They have been suggested as a possible binder for hazardous waste; however, except for the treatment of off-specification monomers by reacting them to form polymers, this method of stabilization has not, to the author's knowledge, been used beyond the experimental stage. Basically, both thermosetting and thermoplastic materials can be used to coat or encapsulate wastes that are solids or have been solidified by other means.

Vitrification is a relatively new means of stabilizing wastes containing large amounts of solid materials. Vitrification is a process by which the waste is melted into a solid, rocklike material. This has been done *in situ*, by Geosafe Corporation of Kirkland, WA, and is a commonly used means of treating ash from a rotary kiln incinerator. In the former application, electrodes are inserted into the ground around the contaminated site and an electric current is passed between them. The current melts the soil and organic compounds evaporate. The area being processed is shrouded with a hood which captures released organics and particulate air emissions for capture or further treatment.

In the latter application, an incinerator is operated at a temperature high enough to melt the ash. The molten ash is quenched, forming a rocklike slag which (if the process is appropriately used and operated) immobilizes metals in the waste. In both cases, the organic constituents are removed from the waste and burned or otherwise treated.

This brings us to the cement and lime based S/S procedures. They are used commercially and have been successful in reducing the leachability of metals for many types of wastes. In order to understand how these processes work, it is necessary to state the objectives of a successful S/S process. They are:

- (1) Chemically react with the free water in the waste to form a dry solid.
- (2) Make the contaminants as immobile as possible.

The cement and lime based processes achieve the first objective by incorporating the water into the solid matrix as discussed below. They achieve the second objective by first making the contaminants as insoluble as possible and then further restricting their mobility by encapsulating them in the resultant matrix. As will be shown below, this encapsulation can result in significant reductions in the leachability of RCRA listed metals.

Portland cement

With portland cement and lime based materials S/S is analogous to the manufacture of cement-based concrete. Concrete consists of the following four major components: coarse and fine aggregate, water, portland cement, and additives. When these are mixed, the portland cement chemically reacts with the water and binds to the aggregate and within as little as one hour to as long as a day or two, the mass sets up into a monolith. The material continues to age over years changing with time. Concrete that is decades old does not have the same properties as the material that is a week or two old. The strength, set time, porosity, and other physical properties of the concrete are established by appropriate choice of ingredients and additives.

Portland cement is a mixture of a number of minerals, the most important being calcium silicates, calcium aluminates, and iron oxide. Table 1 lists the ratios of these found in the four most common grades of portland cement. Mixing the cement with water triggers numerous chemical reactions. Table 2 shows the four major ones. As can be seen, basically the di- and tri-calcium silicates form hydrates releasing calcium hydroxide. The calcium hydroxide and water react with the tri- and tetra-calcium aluminates forming hydrates of these compounds. The hydrates then react with additional water in the mix to form the crystalline hydrate structure which constitutes the solid matrix.

Figure 1 illustrates how the setting up of the cement as part of a concrete or solidified waste matrix ties up water. First, the water reacts to form the hydrates. This clearly satisfies the criterion of chemical reaction. As the cement hardens, the crystal structure further incorporates water into it. This is generally still considered to be chemically bound water, although the binding is

TABLE 1

Common types of portland cement^a

Compound	(wt.%)			
	I	II	III	IV
Tricalcium silicate	53	47	58	25
Dicalcium silicate	24	32	16	54
Tricalcium aluminate	8	3	8	2
Tetracalcium aluminate	8	12	8	12
Total	93	94	90	93

^aSource: Portland Cement Association.

TABLE 2

Fundamental chemical reactions of portland cement^a

2 (3Ca·SiO ₂) Tricalcium silicate	+ 6 H ₂ O Water	→	3 CaO·2SiO ₂ ·3H ₂ O Tobermorite gel	+ 3 Ca(OH) ₂ Calcium hydroxide
2 (2CaO·SiO ₂) Dicalcium silicate	+ 4 H ₂ O Water	→	3 CaO·2SiO ₂ ·3H ₂ O Tobermorite gel	+ Ca(OH) ₂ Calcium hydroxide
4 CaO·Al ₂ O ₃ ·Fe ₂ O ₃ Tetracalcium aluminate	+ 10 H ₂ O Water	+ 2 Ca(OH) ₂ Calcium hydroxide	→	6 CaO·Al ₂ O ₃ ·12 H ₂ O Calcium aluminate ferrite
3 CaO·Al ₂ O ₃ Tricalcium aluminate	+ 12 H ₂ O Water	+ Ca(OH) ₂ Calcium hydroxide	→	3 CaO·Al ₂ O ₃ ·Ca(OH) ₂ ·12 H ₂ O Tetracalcium aluminate hydrate

^aSource: Portland Cement Association.

generally not as strong as in the first case. Finally water remains on the surface and in the capillaries or pores of the cement. This water is clearly not chemically bound; however, a certain amount can be present and the resulting product would still appear to be dry and will pass the paint filter test.

Lime

Lime-based processes behave in a similar manner to cement-based ones. Pure lime, Ca(OH)₂, does not form a solid matrix when mixed with water. It will, however, tend to precipitate many of the metals that are regulated under RCRA from a solution. If the lime (or lime/metal hydroxide mix) remains in contact with air, it will slowly absorb CO₂ forming limestone (calcium carbonate). It can similarly absorb sulfur oxides to form gypsum. The same can happen if the lime slurry remains in contact with waters containing dissolved carbon dioxide or sulfur oxides. These reactions require that the carbon dioxide

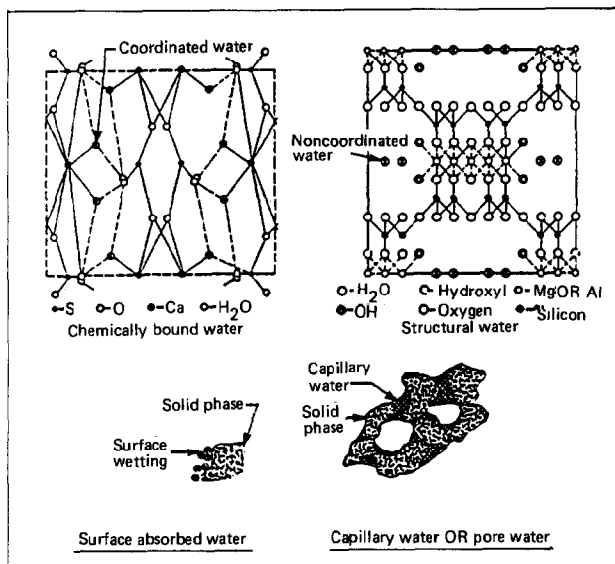


Fig. 1. Mechanisms for retaining water in cement.

migrate from the air or aqueous phase into a solid, so that they occur over years. They are one of the principal reasons why wastes treated by lime-based S/S processes continue to gain strength for very long periods of time.

While the carbonate formation is important for the long-term stability of S/S wastes, lime is often mixed with other materials to produce a binder which sets up more quickly. If the lime is mixed with iron and aluminum bearing minerals, it will form a crude form of cement. Many types of coal power plant fly-ash contain at least some amounts of iron and aluminum. If these are mixed with the lime, then the mixture can react with the wastes in a manner analogous to portland cement. A few types of coal fly-ash contain the appropriate minerals in proportions that allow them to set up on their own or to contribute to the setting up of cement. These are used commercially as cement additives for concrete. Lime and lime/fly-ash mixtures tend to be less expensive than cement or cement kiln dust. They, however, tend to set up more slowly than the cement products and generally form a physically weaker solid. In fact, tests conducted by the author have shown that they are still hardening after 30 days.

Lime-based binders (or lime addition when cement-based binders are used) can be preferable for the treatment of acidic wastes. There are two reasons for this. First, acidic wastes have to be neutralized prior to S/S treatment. Lime based materials are cheaper neutralizing agents than cement-based materials. Secondly, the metals that one is typically trying to immobilize are less soluble in basic media. The lime-based materials have a relatively high acid buffering

capacity. As a result, the pH of the S/S product will remain high for a longer period of time minimizing the mobility of the metals.

Site-specific considerations in selecting S/S scheme

Let us examine how one goes about selecting an appropriate S/S scheme. First one must ascertain whether the waste is located at a remediation site where it will remain after fixation, or whether it will be sent to a landfill. Then one must look at the physical consistency of the waste and its toxic constituents to determine whether the waste must be solidified and/or stabilized. Finally, one must determine whether it is possible to stabilize the toxic constituents.

If the waste is going to a landfill, then the economics of a process dictates that it be solidified and stabilized as rapidly as possible, so that operating time can be minimized. This is true regardless the S/S occurs at a remediation site (i.e., a Superfund site) or at a treatment facility. Under these circumstances, the cost of materials is, generally, less of a factor in the treatment process. The economics favor rapid throughput.

Many times when S/S is used for an on-site remediation, the treated waste will remain on-site. A special lined and capped bunker or landfill may be constructed to store the waste. If the S/S process reduces the mobility of the hazardous constituents adequately, then the waste may be left on-site with a minimum of site preparation. If not, then it will be stored in an on-site bunker. The time that it takes the waste to set up and for its leachability to be reduced is less critical if the mass can cure in an on-site bunker. As a result, lime/fly-ash types of binders may be adequate. They are less expensive than the cement based materials and can reduce the leachability of many metals.

If the waste's final resting place will be an unlined or open area at a site, then the trade-off between speed and environmental impact becomes more difficult. The laboratory testing procedures must be set up to determine how, for example, a sudden rainstorm while the waste is curing could impact the process.

Having addressed the site-specific considerations, consider now the physical consistency of the waste. Again, this involves a trade-off. If the waste contains large amounts of water, then solidifying it will require large amounts of binder. Cement or cement kiln dust is usually more expensive than fly-ash with lime, limestone, or lime/kiln-dust addition. However, the latter may not produce an acceptable product. Site conditions may dictate that the material be suitable for leachability testing within 24 hours, for example. Or the leachability of the lime-based product may be too high. Cement may be needed to achieve this. One may, however, add lime to the mix to increase its buffering capacity and partially reduce the amount of cement required when treating a highly aqueous or acidic waste.

Results and discussion

Finally one comes to the main issue, the waste, the toxic constituents. Work we have conducted [1-4] has shown that cement and lime/fly-ash types of binders do not stabilize organic compounds very well. In fact, the act of mixing the waste will release a significant percentage of the organics present to the air. The addition of binders that increase the waste's temperature during mixing further increase the emissions. In addition, the U.S. Environmental Protection Agency (EPA) is presently in the process of proposing regulations that will require control of organic emissions from S/S processes if the wastes contain more than a small amount of volatile organics [5]. Figure 2 summarizes the results of a series of tests we conducted which attempted to S/S organic compounds in a soil matrix. As can be seen, large portions of the organic constituents were volatilized during the mixing. Not shown here is that significant portions of the remaining organic constituents continued to volatilize over time from the solidified waste matrix [6,7].

Organics

While one set of tests is a tenuous base on which to make generalizations, they raise the question of whether there is any theoretical mechanism for the immobilization of most common organics by an S/S process. However, the results are highly tentative. With the exception of a few weak reactions, such as phenol forming a phenoxide, the author does not know of any mechanism that could do more than physically encapsulate organic constituents. Even the few cases where some form of chemical reaction might occur, the chemical bonds are very weak and readily reversed in aqueous solution. Until some clear evidence of such chemically binding of organic constituents is obtained, the use of S/S for them should be considered tentative.

Recent tests have given some indication of successful stabilization of relatively low levels of PCBs [8,9]. These results are encouraging and indicate that it is possible to reduce the mobility of these compounds when they are present in low levels; however, it is the author's belief that these results are most likely due to physical entrapment of the material in the solidified solids. The compounds are highly hydrophobic and migrate very slowly through soil and water.

This does not mean that wastes containing organics and metals are not potential candidates for S/S. Firstly, heavy, non-volatile, organics, like PCB will not volatilize from the waste and pose little air emission problems. They are generally not very mobile in the environment, so that the physical act of encapsulating them in the binder matrix will reduce their leachability even further. Their presence in higher concentrations could impede the ability of the binder to set up, but this problem is minimal if the organics are present in low

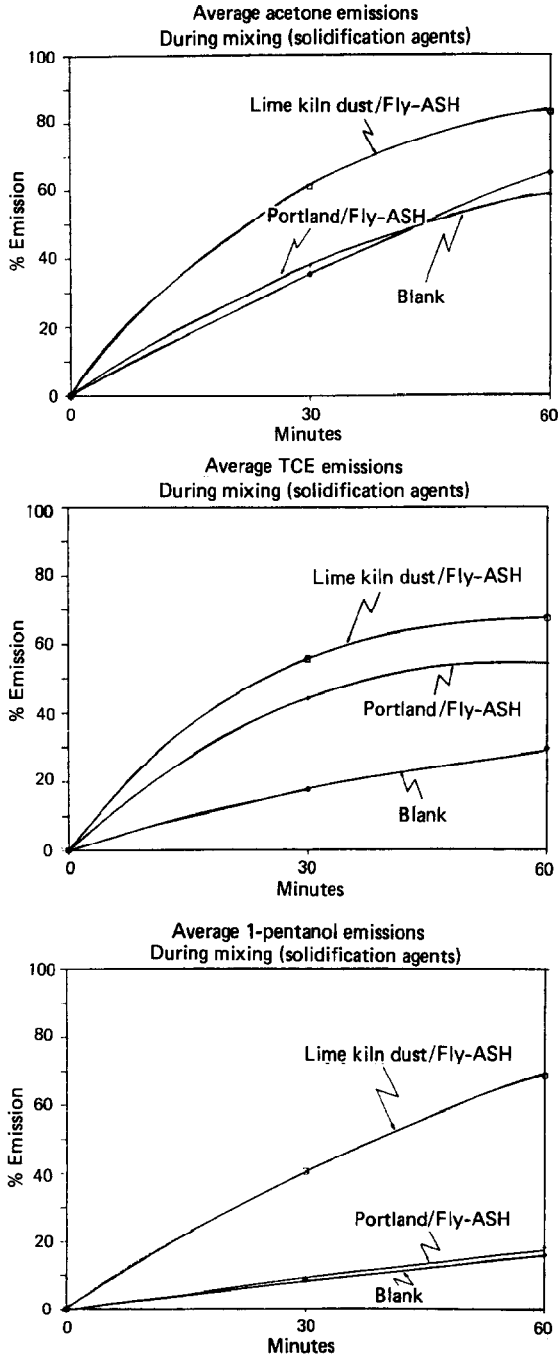


Fig. 2. Cumulative organic emissions during mixing.

concentrations. If their concentrations are higher, it may be possible to minimize their impact on setup by the use of additives [8].

The ability of S/S to reduce the mobility of organic compounds has not been shown. Wastes containing these, along with metals, may still be treated by first removing the volatile and semi-volatile organics by some form of stripping prior to treatment and then stabilizing the residue. Air stripping has been used to remove volatile organics; steam stripping can remove semi-volatile compounds. It may even prove possible to take advantage of the heat of hydration of certain binders, especially those containing quick-lime, to strip organics out of the waste during the mixing process [1,2]. This technique will require that the mixer include a vapor capture and control system, but pending regulations will make this necessary regardless of what happens to the organics. Further research to take advantage of this phenomenon appears warranted.

Inorganics

Unlike organic constituents, inorganic compounds can be stabilized by S/S [2,4], although, of course, one needs to match the process to the waste for this to succeed. Table 3 summarizes the results of a study we conducted on a synthetic soil that was developed by EPA as a surrogate for soils found at Superfund sites. Very high reductions in metals leachability were achieved by treatment with both cement and lime/fly-ash based binders. Although not shown here, the study also showed that volatile organic compounds continued to be emitted from the S/S material. Table 3 gives the results of TCLP¹ extractions on each of four different types of soil (identified as "RAW") and then shows the TCLP results for the soils treated with portland cement (PC), cement kiln dust (KD), or a 1:1 mixture of lime and fly-ash (LF). The results are given as the ppm observed in the leachate, column (a), and a percentage reduction over the original material, column (b). The percentage reduction included a correction for sample dilution by addition of the reagents.

All of the metals except for chromium showed an excellent reduction in leachability, as measured by the TCLP. The increase of chromium, while small, was consistent. Several possible reasons were postulated for this. In our opinion the most likely is that in the original matrix, the soil bound the chromium very well by itself. This is evident by the very low TCLP results on the original soils. Three of the four were non-detectable. The addition of the binder changed the soil's pH dramatically. The binders are all highly alkaline. It is possible that this may have actually increased the chromium's mobility.

Other possible, but in our opinion less likely, explanations are that there were trace amounts of chromium in the binder and that because all of the results were so close to the detection limit, the higher chromium values for the treated materials are simply an artifact of the dilution correction. The first

¹TCLP stands for Toxicity Characteristic Leaching Procedure.

TABLE 3

TCLP Summary for metals, SARM tests

Sample no. (SARM)	Binder (day)	Arsenic		Cadmium		Chromium		Copper		Lead		Nickel		Zinc	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b
<i>I</i>	RAW	ND		0.53		ND		0.61		0.49		0.27		9.2	
1	PC(14)	ND	-	ND	100	0.06	+	0.07	81	0.15	75	0.04	70	0.23	96
14	KD(14)	ND	-	ND	100	0.06	+	0.04	81	ND	100	ND	100	0.27	94
27	LF(14)	ND	-	ND	100	0.02	+	0.03	98	ND	100	ND	100	0.14	94
1	PC(28)	ND	-	ND	100	0.06	+	0.06	83	0.15	75	0.04	73	0.49	91
15	KD(28)	ND	-	ND	100	0.09	+	0.03	80	ND	100	ND	100	0.62	73
27	LF(28)	ND	-	ND	100	0.02	+	0.03	98	ND	100	ND	100	ND	100
<i>II</i>	RAW	ND		0.73		ND		0.89		0.7		0.4		14.6	
4	PC(14)	ND	-	ND	100	0.03	+	0.04	92	0.15	82	0.04	83	0.09	99
16	KD(14)	ND	-	ND	100	0.08	+	0.07	79	0.44	+	ND	100	0.25	97
30	LF(14)	ND	-	ND	100	ND	-	ND	100	ND	100	ND	100	0.22	99
4	PC(28)	ND	-	ND	100	0.03	+	0.06	89	0.15	83	0.04	83	0.54	94
16	KD(28)	ND	-	ND	100	0.05	+	0.09	89	0.37	+	ND	100	0.78	89
29	LF(28)	ND		ND	100	ND	-	0.03	90	ND	100	ND	100	0.02	100
<i>III</i>	RAW	6.39		33.1		ND		80.7		19.9		17.5		359	
7	PC(14)	ND	100	ND		0.07	+	0.15	100	0.63	95	ND	100	0.58	100
21	KD(14)	ND	100	ND	100	0.22	+	1.02	96	13.3	+	ND	100	4.38	95
33	LF(14)	0.81	52	0.02	100	0.03	+	2.96	87	51	+	ND	100	3.81	96
7	PC(28)	ND	100	ND	100	0.07	+	0.09	100	ND	100	ND	100	0.69	100
21	KD(28)	0.21	98	ND	100	0.12	+	0.85	96	18.3	+	ND	100	4.07	95
33	LF(28)	0.79	51	0.02	100	0.07	+	2.59	87	51	+	0.03	99	3.97	96
<i>IV</i>	RAW	9.58		35.3		0.06		10		70.4		26.8		396	
10	PC(14)	ND	100	ND	100	0.06	+	0.14	100	0.39	99	ND	100	0.39	100
23	KD(14)	0.16	95	ND	100	0.11	+	1.88	97	12.4	43	ND	100	4.57	97
	LF(14)	1.61	50	ND	100	0.07	+	1.92	96	91.8	+	ND	100	3.22	96
10	PC(28)	ND	100	ND	100	0.06	+	0.17	100	0.37	99	ND	100	0.74	100
23	KD(28)	0.27	92	ND	100	0.12	+	1.67	97	21.4	9	ND	100	3.72	97
	LF(28)	0.98	59	0.02	100	0.07	+	2.18	95	65	+	ND	100	3.64	96
Detection limit		0.15		0.01		0.01		0.02		0.15		0.04		0.01	

(a) TCLP results in ppm.

(b) percent reduction, corrected for dilution.

ND - below detection limit.

+ - increase over raw SARM.

explanation is possible, but unlikely since the three binders came from different sources but showed similar increases for chromium. The second is also conceivable, but since chromium was identified in all of the samples, albeit in trace quantities, this source of error would only cast the actual value in doubt, not the presence of the chromium in three wastes where it was not detected prior to S/S.

Treatability

The final step in evaluating a waste's suitability for treatment by S/S and identifying the optimum amounts and types of binder, additive, and water, is to conduct a series of treatability studies. These studies can get very expensive, involving the production of a large number of samples. We have found it best to perform them in two stages. First screen all binders and additives at a minimum of three levels to see which ones will result in the product setting up in a reasonable length of time. It is relatively easy to mix batches of waste, binder, and additives at different concentrations, mold them in an expensive mold (paper or plastic disposable cups often work well), and check them after one or two days to see if they have hardened. A device like a cone penetrometer can help in identifying which samples hardened the best.

The products which hardened best as determined by the initial screening study can then be subjected to a more comprehensive, formal screening designed on a statistical basis. For example, if only a few parameters at a few levels need to be tested, then a factorial design may be practical. If the number of samples that such an experimental program generates is prohibitive, then the protocol could utilize a modification of a full factorial design. At this point, large number of samples can be molded. It is recommended that all samples with a given composition be mixed in one batch. Then one or more portions of the batch should be placed into a glass sample jar with an inert lining on the lid. The balance should be molded into cubes or cylinders for unconfined compression strength (UCS) testing.

There is no actual correlation between UCS and leachability; however, because of the relative high cost of the TCLP and other chemical tests, the results of the compression testing should be used to eliminate those samples which produce physically unacceptable products. If, for example, a certain binder/waste/additive combination continuously resulted in structurally weak samples, then one would tend to not subject this mix to further, more expensive, testing with the TCLP.

Unfortunately, this option is not possible for those types of binders which do not form monolithic solids. Some binder waste combinations form dry granular materials which satisfy all leaching requirements. Leaching performance is the major concern and should override the structural tests. The cost of testing such binders will tend to be higher since one cannot use the structural test to rule out obviously unsuitable combinations.

Conclusions

In summary, S/S can be used to reduce the leachability and improve the stability of many wastes. In fact, there are few practical alternatives available at present for wastes that contain heavy metals. S/S is generally not suitable

for the stabilization of organics, although it can be used in combination with other treatment schemes which remove the organics from the waste.

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