Implementation of solidification/stabilization process to reduce hazardous impurities and stabilize soil matrices

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Abstract. A wide variety of technologies is available for the treatment of contaminated soil in both the vadose zone (originating above the water table) and saturated zone (originating below the water table). Several processes involve immobilizing soil contaminants by physically, chemically or biologically. Among them, a wide range of wastes, both solids and liquids, are being treated by "solidification / stabilization" (S/S). In solidification, by adding binding reagents, physical state of the waste being changed by encapsulating a waste to form a solid material from liquid as well as to restrict contaminant migration to leaching by decreasing the exposed surface area. Whereas stabilization through chemical reactions immobilizes the hazardous materials by reducing them to less soluble or toxic form. Characteristics of different types of reagents/additives of S/S technology both from inorganic and organic origin are presented in this paper. In-situ and ex-situ application of S/S technology and their advantages-disadvantages are discussed with basic approaches. Finally, introducing with internal and external factors influencing the long-term durability of S/S treated materials as well as monitoring & treatment management of it after processing are briefly presented.

1. Introduction

Since world war II, rapid industrialization has been causing extensive contamination of soil and groundwater resources. Thus, it is imperative to limit the contamination of environment including soil, groundwater, air not only due to ecological concern rather than minimizing the expenditure of cleaning technique. In between all of these, accumulation of toxic metals into the soil causes serious risks to human health, plants, animals and surrounding ecosystems. Different sources responsible for accumulating and dissipating of toxic metals in soils are illustrated in table 1.

Table 1. Various sources related to mass balance of toxic metals into soil [1, 2].

Accumulation sources	Dissipation sources
Parent material	Crop removal
Atmospheric deposition	Loss by leaching
Fertilizer sources	Loss by volatilization
Agricultural sources	
Organic waste sources	

Solidification/Stabilization (S/S) technology has been widely used to immobilize metals leaching either by solidifying liquids, sludge and other physically non-stable hazardous wastes into stable solids or making it more stable by chemical alteration of the contaminant with respect to further dissolution. The ultimate focus of Solidification/Stabilization process is on the transformation of toxic metal contaminated soil into a less toxic form.

2. Uses of effective remediation technologies

The sweeping experience by remediation experts and engineers with different remediation technologies over the last thirty-five years has resulted in greater acceptance for soil and groundwater cleanup. However, most of remediation engineers have preferred technologies related to time dependent testing even when some of these technologies produced minimum amount of restoration of contaminated sites. Over the past few decades, U.S. Environmental Protection Agency (U.S.EPA) has issued several Superfund programs to facilitate field tests of a variety of new technology aiming to site clean-up and remediation in such a manner, that residual risk is reduced to an acceptable level.

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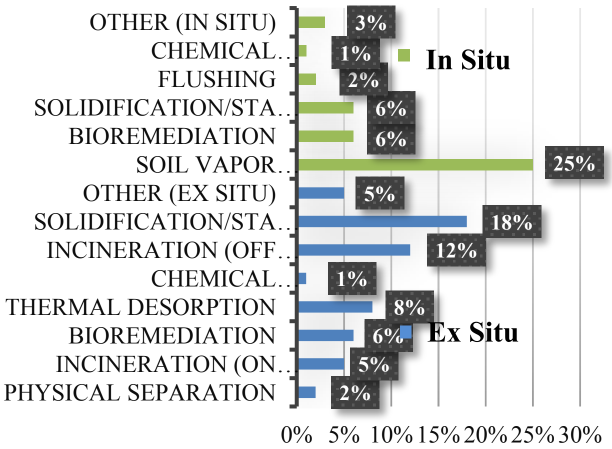

Figure 1. Source Control Treatment projects (FY 1982-2002) [3-11].

According to U.S.EPA., Report on 2003, treatment technologies selected for each fiscal year from 1982 thru 2002 is shown in ***figure1*** which displays the most used source of treatment technologies over this twenty-year period [3-11]. Figure 1 shows S/S as the second most frequently selected technology at 18% for ex-situ remediation technology whereas only 6% for in-situ remediation which is far behind from mostly popular soil vapor extraction (25%). But considering the next ten fiscal years [11-14], for in-situ technologies (FY 1982-2012, after EPA-542-R-13-016) S/S is the second most frequently selected technology at 22%, slightly behind soil vapor extraction at 24%.

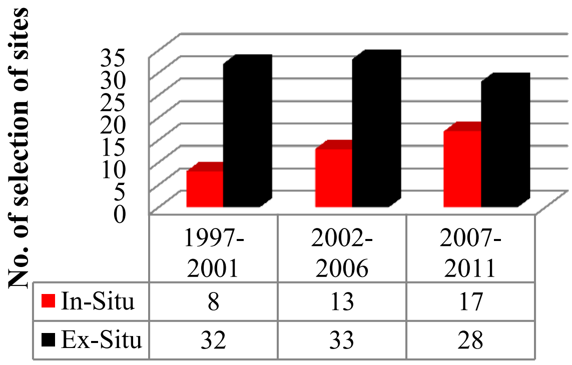

Figure 2. Relative increase in selection of in-situ vs ex-situ S/S (USEPA 542-R-13-016).

Historically solidification/stabilization technology has been employed far more in ex-situ than in-situ but recently the scenario is changing. From ***figure 2*** it is found that in ten years period from 2002-2011, the rate of number of selection for in-situ remediation is increasing over ex-situ remediation which all are based upon USEPA Superfund remedy program, (EPA, 2013) [14].The successful decontamination of contaminated soils and groundwater depends on several factors including soil properties (physical and/or chemical), nature of contaminants, local climatic conditions, interactions between soils and contaminants and type of technology used for site-restoration.

Table 1. Generalized contamination found at sites for which S/S was selected under the Superfund Program. (EPA-542-R-00-010), [11].

Waste Type	Percentage
Organics only	6%
Metals Only	56%
Metals and Organics	31%
All other	7%

It seems to be increasing acceptance that for contaminated soil with metals (such as As, Zn, Cd, Cr, Sb, Hg) S/S technology can effectively treat however it was seldom used in organic contaminated field. As per EPA reported table 1, S/S method was used approximately 6% in total for the cases involved to organic site treated. Now increased depth of treatment is possible with powerful in-situ augers as this trend is spreading.

3. Characterization of the Contaminated Mass

As S/S treatment is mainly focused to produce a less toxic and less mobile form of the metals in the waste materials, it can also be applied to other inorganic compounds as well as most organic compounds. But during the early development of S/S, this method was used to remove metals from solution as the chemistry was already established and practiced for water treatment. From table 2, it displays main mechanisms responsible for distribution of metals in soils and sediments.

Table 2. Chief mechanisms responsible for metals in soils [15].

Mechanisms	Processes
Adsorption	To surface of clay minerals, oxides/hydroxides (Mn, Fe, Al) and organic matter
Precipitation-coprecipitation	With secondary minerals (carbonates, oxides/hydroxides, fluoride, sulfides)
Complexation	With organic matter
Penetration	Heavy metals into crystalline structure of primary minerals

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3.1. Physical characteristics of contaminated soil

Particle size, moisture content, temperatures are typical soil properties that are required to be measured before S/S application [16]. To determine pre-treatment and requirements for materials handling, it is essential to investigate the gradation of contaminated soil. And moisture content indicates reagent/additives formulations needed for contaminated sites. Moreover, reagent/additives have an insignificant effect on reducing water content in contaminated soils. Impact on process performance and curing time can be resulted from temperature considerations.

3.2. Chemical characteristics of contaminated soil

Contaminants (concentration, type, variability), pH, leaching behavior are important factors of chemical characteristics of contaminated soil [16]. Environmental impacts through emissions, formulation of reagents are determined considering contaminants chemical behavior. Leaching characteristics help to judge immobilization percentage of contaminants which is greatly affected by binder type and curing time. And soil pH helps to predict the conditions of reaction and it has impact on leaching characteristics.

4. Reagents and/or additives for solidification/stabilization

Binder refers to reagent and/or additives used for the S/S treatment of contaminated soil. Inorganic and organic binder systems categorize the whole binder system used for S/S treatment. By the addition of solidification agents (such as cement, fly ash, blast furnace slag, pozzolanic material, silicates, lime), physical process of transformation of liquid substances into solid substances is implied. On the other hand, to make metals insoluble chemical agents (such as polymers) cause precipitation of this metals through stabilization technologies involving chemical reactions. Characteristics of some common types of binder are listed in ***table 3.***

Asphalt/bitumen is the most common type of organic binder used in the S/S process [19]. Bitumen has viscous property in a great extent which enables itself to physical encapsulate with contaminants in the waste during S/S application. Rather than bitumen, sulfur polymer and polyethylene are other common types of organic binders which are used for S/S treatment [8].

In chemical stabilization of contaminated soils, a new binder named SPC (composes of single superphosphate and calcium oxide) is an efficient material for the remediation of metal contaminated soil. From the laboratory experiment of Xia et al., 2017 [20] on untreated soil sample, they found Pd, Zn and Cd concentration of untreated soil samples are 22.41, 326.71 and 9.11 mg/L respectively [20].

Table 3. Characteristics of inorganic binder of S/S process.

Binder category	Types of binder[a]	Characteristics of binder
Inorganic binder system	Portland cement (PC)	Most commonly used for S/S technology [16]. Employed as solidifying agent as it permits complete immobilization of several metals. Depending on the nature of contaminant, solidification process is executed through mixing Portland cement (PC) and contaminated mass with or without water. Portland cement has impact on health issues such as skin contact, eye contact, or inhalation. Though risk of injury mainly depends on duration and level of exposure and individual sensitivity.
	Fly ash	In the solidification/stabilization of heavy metal sludge, fly ash [17]is used since it has cement-like characteristics. To chemically immobilize metals from contaminated soil, fly ash relies on both pH control (CaO is provided in the fly ash to control pH) and chemical reactions. As fly ash is fine in nature, it is very dusty and may be reacted with water to reduce its dusting.
	Blast furnace slag	By product of pig iron manufacturing process which contains alumina, silica and lime as its ingredients. Utilized as partial replacement of Portland cement (PC) in S/S technology [18]. Where minimum amount of cost involved with the remediation project, blast furnace slag is preferred as replacement of PC.

[a] Bentonite, calcium oxide, calcium hydroxide, cement kiln dust, lime kiln dust, magnesium oxide are other types of suitable binders for S/S process.

But with the increase of SPC content and curing time, leached concentration of these metals after stabilization decreases at a significant rate which indicates that SPC chemically immobilize the metal contamination which decreases toxicity as well as leach ability.

A careful observation from ***figure 3*** is that with the highest percentage of SPC (10%) in 14 days and 28 days Pd, Zn and Cd concentration is below the toxicity limit specified by the Resource Conservation and Recovery Act (RCRA) (US EPA 2017) [21]. The variation of soil pH and unconfined compressive strength (UCS) with SPC content at different curing times is also discussed in the literature [20]. To evaluate the strength parameters and leachability of contaminated soils- pH, contaminant concentration, UCS test are usually performed utilizing SPC content as a binder to solidify with different curing time.

evaluation of S/S treated soil is possible as it can be obtained during processing. ***Figure 4*** is example of typical ex-situ S/S treatment-systems.

Depending on the site, in-situ S/S treatment below the water table is possible without dewatering which is one of the major advantages of this technology [23]. Moreover, no need of logistics to transport treated material prior to treatment, and if final treated material is positioning off-site in that cases transport is considerable. Where excavation for treatment close to

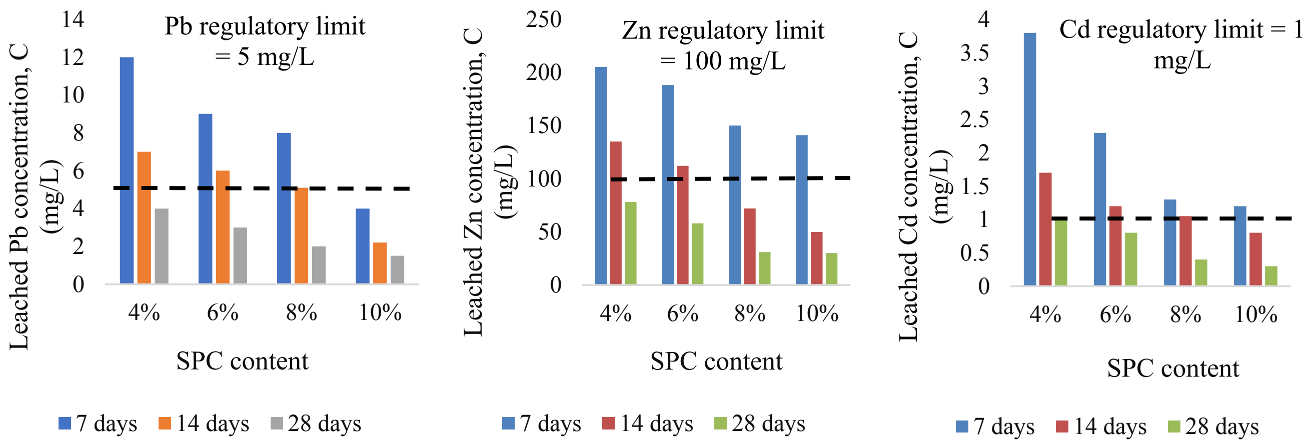

Figure 3. Metals concentration with increasing SPC (chemical agent) in different curing time

5. Ex-situ and in-situ application of S/S

In ex-situ method, contaminated media (such as soil, sludge, sediment) involved with excavation which is later transferred either on-site or off-site for subsequent mixing depending on the technical considerations. However, in in-situ treatment, S/S technology is applied into the contaminated soil where it is found and no need to transfer treated soil to another location. Table 4 shows processing schemes available both for ex-situ and in-situ S/S treatment technology.

Table 4. Basic approaches associated with S/S treatment.

Ex-situ S/S processing [22]	In-situ S/S processing [12]
In-drum	Vertical auger mixing
In-plant	Shallow in-place mixing
Direct-mixing	Injection grouting

Ex-situ treatment is suitable for shallow soils where water table is below the contaminated soil and this eases quality control compared to in-situ treatment [23]. Selective materials can be removed through this technology and more importantly it is a cost-effective treatment option. An additional advantage is that rapid

existing structure, as it may cause harm, in-situ is the most suitable treatment process for that condition. On the other hand, it is necessary to develop enough bearing capacity of treated material/ground to support the equipment as in-situ treatment progresses. ***Figure 5*** displays in-situ S/S equipment operating on previously treated material [17].

Figure 4. Typical ex-situ S/S equipment, including plant processing, reagent tank, water tank, stacker and haulage

Figure 5. In-situ S/S mixing equipment operating on top of previously treated material.

6. Monitoring & treatment management of S/S material after processing

It is necessary to monitor treated S/S mass in a long-term basis as this technology involving with the immobilization of contaminants rather than fully removal. The impacts of some possible factors on the durability of S/S treated mass are enlisted in ***table 5*** [24].

Table 5. Responsible factors for S/S treated mass degradation.

Factors responsible for S/S treated mass degradation	Influenced parameters
Internal chemical reactions	pH, Liquid to solid ratio, redox potential, sorption.
Geochemical and/or biological impacts of the surroundings	Hydrogeological conditions, leachability.
Physical mechanisms	Cracking, settling, erosion, particle size, pore structure.

A graphical illustration in ***figure 6*** displays internal and external aspects associated with long-term durability of S/S treated mass. There are some physical tests available (such as bound water, chloride permeability, density (bulk), density (dry), setting time (initial), setting time (final), modulus of elasticity, moisture content (% wet weight), permeability, oxygen permeability, slump, soundness, tensile strength, specific gravity, unconfined compressive strength, water absorption at 80°C (%), shrinkage/expansion (%) etc.) of treated S/S materials for monitoring purposes [18, 24].Nevertheless regarding future land use and post remediation maintenance, long-term monitoring plan and treatment management should be established. However, to check any changes in leachate characteristics various monitoring piezometers are installed over several years for tracing the effectiveness of considered S/S remediation process on a long-term basis.

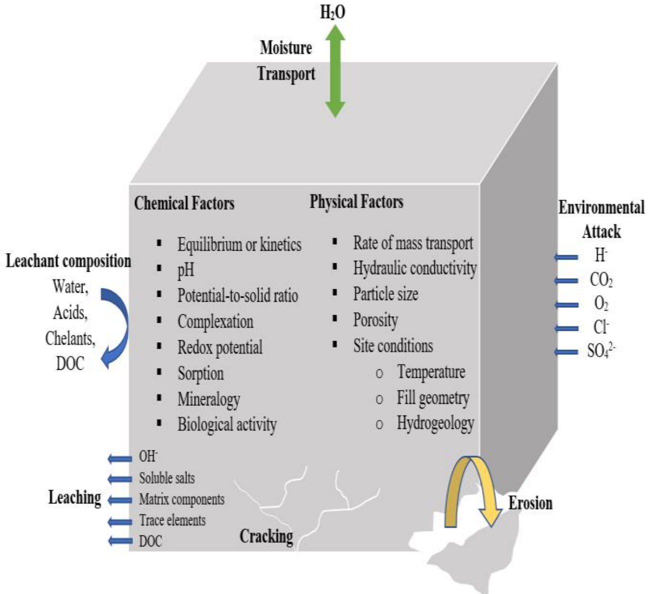

Figure 6. Internal and external factors influencing the long-term durability of S/S treated materials[25].

7. Conclusion

A summary of the fundamental factors associated with solidification/stabilization technologies, remedy of inorganic and organic contaminants using solidifying and stabilizing agents are discussed. In-situ S/S technology is getting more frequent nowadays compared to ex-situ which is based upon USEPA Superfund remedy program. Physical and chemical characteristics of contaminated soil play a vital role in predicting the conditions of reaction and have impact on process performance. Inorganic binders like Portland Cement (PC), fly ash, blast furnace slag are commonly used as solidifying agents to immobilize the contaminants via physical encapsulation. Standard tests for verification method of treated materials such as leachability, pH is considered in this paper. Finally, it is essential to monitor treated S/S mass in a long-term basis as this technology involved with the immobilization of contaminants rather than fully removal.

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References

1. Alloway BJ *Heavy metals in soils* Blackie, London (1995)
2. Lombi E and Gerzabek MH Determination of mobile heavy metal fraction in soil: results of a pot experiment with sewage sludge *Commun Soil Sci Plant Anal***29**2545–56 (1998)
3. US EPA *Guide to the disposal of chemically stabilized and solidified waste* SW-872(United States Environmental Protection Agency, Cincinnati) (1982)
4. US EPA *Prohibition on the placement of bulk liquid hazardous waste in landfills-statutory interpretive guidance* OSWER policy directive no. 9487.00-2A EPA **530**-SW-86-016(United States Environmental Protection Agency, Washington, DC) (1986a)
5. US EPA Handbook for stabilization/solidification of hazardous waste (EPA 540/2-861/001 (United States Environmental Protection Agency, Cincinnati) (1986b)
6. US EPA Stabilization/solidification of CERCLA and RCRA waste EPA 625/6-89/022 (United States Environmental Protection Agency, Cincinnati) (1989)
7. US EPA Clean water act (Sec. 503, Vol.58, No. 32) (United States Environmental Protection Agency, Washington, DC) (1993)
8. USEPA Innovative site remediation design and application4 Stabilization/solidification EPA 542-B-97-007 (United States Environmental Protection Agency, Washington, DC) (1997)
9. US EPA Solidification/stabilization resource guide EPA 542-B-99-002 (United States Environmental Protection Agency, Washington, DC) (1999)
10. US EPA Solidification/stabilization use at superfund sites EPA 542-R-00-010 (United States Environmental Protection Agency, Washington, DC) (2000)
11. US EPA Cleaning up the nation's waste sites: markets and technology trends 4th edition, EPA542-R-04-015 (United States Environmental Protection Agency, Washington, DC) (2004)
12. US EPA In situ treatment technologies for contaminated soil EPA 542/F-06/013 (United States Environmental Protection Agency, Washington, DC) (2006)
13. US EPA Toxicity characteristic leaching procedure Method 1311Test methods for evaluating solid waste, physical/chemical methods SW-846 (United States Environmental Protection Agency, Washington, DC) (2007)
14. US EPA The clean water act Priority pollutants: Appendix A to 40 CFR Part 423(United States Environmental Protection Agency, Washington, DC) (2012)
15. Cloutier RG and Dube JS An evaluation of fresh water sediments contamination: The Lachine canal sediment case, Montreal, Canada Water, Air and Soil Pollution102 259-79 (1998)
16. Harris MR, Herbert SM and Smith MA Remedial treatment for contaminated land VII (Construction Industry Research and Information Association (CIRIA), London) (1995)
17. Bates E and Hills C *Stabilization and Solidification of Contaminated Soil and Waste: A Manual of Practice*602 (2015)
18. Al-Tabbaa A and Perera ASR UK stabilization/solidification treatment and remediation – Part I: binders, technologies, testing and research *Land Contamination Reclamation***14**703 (2006)
19. Bone BD, Barnard LH, Boardman DI, Carey PJ, Hills CD, Jones HM, MacLeod CL and Tyrer M Review of scientific literature on the use of stabilization/solidification for the treatment of contaminated soil, solid waste and sludge (SC980003/SR2) The Environment Agency, Bristol (2004)
20. Xia WY, Feng YS, Jin F, Zhang LM and Du YJ Stabilization and solidification of a heavy metal contaminated site soil using a hydroxyl apatite-based binder 2017; **156**:199–207 (2017)
21. US EPA Resource Conservation and Recovery Act (RCRA) Laws and Regulations (2017)
22. Wiles CC *A review of solidification/stabilization technology***14**5–21 (1987)
23. Rahman IMM, Begum ZA and Sawai H Solidification/Stabilization: A Remedial Option for Metal-Contaminated Soils *Environmental Remediation Technologies for Metal-Contaminated Soils* Chapter 6 145-46 (2015)
24. ITRC *Development of performance specifications for solidification/stabilization Interstate* Technology & Regulatory Council, Washington, DC (2011)
25. Garrabrants AC and Kosson DS Leaching processes and evaluation tests for inorganic constituent release from cement-based matrices *Stabilization and solidification of hazardous, radioactive, and mixed wastes* (CRC Press, Boca Raton)229–79 (2005)