Journal of Hazardous Materials, 24 (1990) 103-109
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

AN OVERVIEW OF THE HISTORY, PRESENT STATUS, AND FUTURE DIRECTION OF SOLIDIFICATION/STABILIZATION TECHNOLOGIES FOR HAZARDOUS WASTE TREATMENT*

EDWIN F. BARTH

Stabilization Section, Risk Reduction Engineering Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH 45268 (U.S.A.)

Summary

Solidification/stabilization (S/S) technology processes are currently being utilized in the United States to treat inorganic and organic hazardous waste and radioactive waste. These wastes are generated from operating industry or have resulted from the uncontrolled management of hazardous waste. This paper will overview the development to date of this technology and its future direction which is strongly influenced by industry needs and/or government regulations. Key areas where knowledge is limited and factors impacting future utilization will be identified.

Introduction

The difference between the terms solidification and stabilization must first be addressed. In general, solidification can be simply defined as the conversion of a liquid material into a non-liquid material. The definition needs to be broadened when solids are treated to connote that available surface area is reduced. Solidification processes may not necessarily decrease leachability. Stabilization generally refers to a purposeful chemical reaction that has occurred to make waste constituents less leachable. The difference in these terms is important since existing metal waste treatment process may involve both phenomena but organic waste treatment may only involve the former. Emerging S/S technologies are focusing on stabilization of organics, with the formation of strong bonds between the contaminant and binder.

History of process development

Solidification/stabilization (S/S) binding processes have developed from man's attempt to better navigation or transportation. In ancient times (3,000 B.C.) the Chinese Dschou dynasty had customs for road construction [1]. The Roman port of Cosa (2nd century B.C.) utilized mortar called pozzolana for harbor protection. It is of interest that these harbor structures of Cosa still

*Paper presented at the GCHSRC Second Annual Symposium: Mechanisms and Applications of Solidification/Stabilization, Lamar University, Beaumont, TX, U.S.A., February 15-16, 1990.

exist, indicating long-term durability. Pozzolana was volcanic tuff obtained from the neighborhood of Pozzol. Roman roads (Appian Way) were "stabilized" with lime for better properties. Concretes today are based on an 1824 patent covering limestone and clay for mortar [2].

In the United States, road construction methods were refined to include stabilization with lime. Early research and development work on road stabilization and durability was performed by the U.S. Army Corps of Engineers.

Waste treatment by S/S processes can be traced back to the disposal of low level radioactive waste in the 1950s. The goal of these processes was limited to solidifying the liquid waste to a form more suitable for transportation and disposal. These processes were optimized. Urea formaldehyde and asphalt systems were then evaluated to provide more consistency, lower weight, and better space efficiency [3]. Guidance for S/S treatment processes involving low-level radioactive treatment appeared in the later 1970s and 1983 [4].

Although hazardous waste management practices were generally not mandated before the 1970s, solidification additives such as sodium silicate or lime/fly-ash were being evaluated for industrial waste streams, for convenience. Municipal sludges were treated with solidification processes to produce a more solid material and reduce pathogens.

Present status

In the 1980s, amendments to the Solid Waste Disposal Act (SWDA), Resource Conservation and Recovery Act (RCRA), and the Hazardous and Solid Waste Amendments (HSWA) provided guidance for S/S systems. There were prohibitions on liquid disposal in landfills, with a strength requirement (4 kg/cm^2 or 50 lb/in^2) for solidification processes and no free liquid passing through the paint filter test [5]. RCRA/HSWA regulations began to focus on leaching characteristics of treated waste.

Land ban restrictions resulted in treatment standards for listed hazardous waste streams. These standards were based on Best Demonstrated Available Technology (BDAT), which specified a treatment level (leach test value) that must be met before disposal. Several of these waste codes considered S/S processes (see Table 1).

Also, a delisting process for converting a waste to a non-hazardous level was formulated. Several delisting petitions were approved, one involving the treatment of 80 million gallons (3×10^8 l) of petroleum waste by CHEMFIX at the Amoco Wood River facility. Three existing Guidance documents for S/S processes have been published by the U.S. EPA [6–8].

Superfund remedial actions cover the remediation of uncontrolled hazardous waste sites. Over 20 percent of the decisions for these sites in fiscal year 1988 included S/S at last as part of the treatment process. Many of these decisions involve sites contaminated with inorganic and organic constituents.

TABLE 1

Example of U.S. EPA RCRA hazardous wastes for which S/S is being evaluated as a treatment technology

Waste code	Description of waste	Pollutant of concern for S/S
K048-52	Dissolved air flotation (DAF) float from the petroleum refining industry	chromium, lead
K061	Emission control dust/sludge from the primary production of steel in electric furnaces	chromium, lead, cadmium
K046	Wastewater treatment sludges from manufacturing formulation and loading of lead-based initiating compounds	lead
F006	Metal finishing sludges	cadmium, chromium, lead, nickel, silver
F012, F019	Metal finishing sludges	cadmium, chromium, lead, nickel, silver
K022	Distillation tar (treated)	chromium, nickel
K001	Wood preserving sludges (treated)	lead

Remedial actions involving S/S processes have already been completed at the Bioecology site in Texas, the Pepper Stele site in Florida, and the McKin site in Maine. Solidification/stabilization processes have been recognized to be of enough importance to be evaluated in the U.S. EPA's SITE program and Department of Defense HAZWRAP program.

The Nuclear Regulatory Commission (NRC) and EPA guidances and regulations have opened up business for a variety of fixed plant and mobile (vendor) S/S businesses. Several vendors exist, most with (a) proprietary reagent(s) for optimal performance. The author will not attempt to identify these vendors individually, but estimates a number greater than 30. Since these reagents are not normally readily identifiable, the chemical stabilization reaction they represent may be discussed in the next section on future direction of processes.

Future direction of processes

With the assumption that current state-of-the-art processes involve inorganic/pozzolanic binders for metallic waste streams, the following discussions will focus on the direction of binder type utilization for stabilizing organics or non-traditional methods for stabilization of metals.

Natural modified clays. Several natural clays, such as bentonites and attapulgites, have chemical properties which may favor stabilization reactions. The incorporation of a quaternary ammonium compound between the layers of clay structures shows promise for sorption or chemisorption reactions [9,10].

Slags. The incorporation of slag in a binding mixture may allow favorable oxidation/reduction reactions of metal species to less mobile forms [11,12].

Zeolites. Zeolites have shown promise as a soil amendment to sorb metals [13].

Fly-ashes/activated carbon. Besides offering properties to decrease porosity, fly ashes and activated carbon may have chemical properties for sorption.

Humic, fulvic, and other organic acids. Humic and fulvic acids can complex with metals [14]. Low molecular weight organic acids and bases (non-humic) can also form complexes with metals [15].

Xanthates. Chemical leaching tests have shown xanthate sludges to reduce the leachability of metals compared to hydroxide sludges [16].

Substituted ettringite formation. Research has been performed to substitute the hazardous metal for natural metals in the mineral ettringite [17].

Pre-roast. The stabilization of arsenic compounds has been evaluated with the use of a pre-roasting step [18].

Thermoplastic. Thermoplastic and thermosetting processes such as asphaltization, or jacketing a waste with polyethelene, have been evaluated for their usefulness for their stabilizing hazardous and radioactive waste.

Slurry wall formulations. Slurry wall formulations can be modified with binders to help minimize the release of contained contaminants.

Improved cementacious product. Research has been performed to enhance the durability of concretes by utilizing fibers, water soluble polymers, silica fume, etc. [19].

Dechlorination. The U.S. EPA is aware of Agency data that infers dechlorination of polychlorinated biphenyls after S/S treatment. However, this phenomenon has not been supported by chemical theory, nor have by-product formations been isolated.

Vitrification. Vitrification processes are sometimes categorized under S/S processes. This high-temperature process can volatilize and/or stabilize metals and also volatilize/destroy (by pyrolysis) organics. Lower energy input systems need to be developed for these systems to lower energy costs.

Technical research needs

Before any S/S technical research need is discussed, academia must focus on reuse, recycling, or pre-concentration techniques. Alternate uses of waste products need to be evaluated and proven environmentally acceptable. The use of fly-ashes for binders or for road beds, and the formation of bricks from sewage sludge are examples.

Once recovery techniques are exhausted, stabilization pre-treatment unit processes involving soil washing and volatile stripping need to be optimized. Alternatively, S/S systems could be mechanically modified to partition the volatile contaminant from the contaminated solid into the gaseous phase, then captured.

Research is needed to fundamentally understand the bond formation between contaminant and binder. Bonding strength evaluation techniques need to be applied to stabilization evaluations.

Research on stabilization processes for waste streams that are contaminated with multiple metals that are amphoteric (such as wood treating waste) needs to be optimized. Mass balances on the volatilization pathway and byproduct formation need to be performed.

Research is needed to focus on the long-term integrity and leaching phenomenon of the treated materials. No verifiable, peer reviewed leaching test procedures exist for site specific disposal applications. Existing leaching or extraction procedures are often mis-applied or too severe. The incorporation of leaching data into groundwater models needs to be evaluated.

Irradiation and biological degradation pathways need to be understood. Safety of proprietary reagents needs to be addressed. Colloidal transport of metals that may be disguised by being filtered [20] needs to be evaluated for the safety of S/S application. Oil and grease extraction techniques need to be evaluated for the same reason.

Cement reactions and natural factors that impact permeability need to be better understood. More durable concretes need to be developed. Mixing techniques, especially with viscous waste or waste clays need to be improved.

Other factors impacting S/S utilization

Five other factors must be presented that will impact S/S utilization in the future.

Economics. Currently, many S/S processes are being implemented because process costs are lower than several other technologies, especially if performed *in situ*. However, should severe leaching procedure techniques and disposal and treatment facility regulations require more binder specialization, the costs may approach those of technologies such as vitrification.

Regulations. Existing and developing disposal regulations on recycling, reuse, volume reduction, destruction, and mobility reduction. Mobility reduction standards may be based on more stringent leaching methodologies.

Research and development. Research and development activities strongly follow regulations. Waste minimization, destruction technologies, and non-destructive techniques preceded by pre-treatment, are primary research areas.

Quality control. Currently, real time construction quality control procedures for leachability do not exist. Therefore, some systems may be at risk if proper evaluation procedures were not followed. The effectiveness of mixing systems needs to be evaluated.

Public acceptance. There is a public concern with S/S processes since waste is not destroyed after treatment. However, destructive technologies that may include potential air emissions are also treated with concern by the public.

Future outlook

Solidification/stabilization processes have roots in the betterment of transportation and navigation systems. Solidification/stabilization processes are viable for many metallic waste streams, but only emerging for organic waste. Several vendors exist for the current need of treatment systems. Future utilization will depend on stabilization process enhancement versus the ability of destruction processes to lower treatment costs.

References

1 Soil Improvement Manual, American Society of Civil Engineers, New York, NY, 1978.
2 S. Popovics, Concrete Marketing Materials, McGraw-Hill, New York, NY, 1981.
3 J. Conner, Chemical Fixation and Solidification of Hazardous Waste, Van Nostrand Reinhold, Princeton, NJ, 1990.
4 Technical Position on Waste Form, 10 CFR 61, Nuclear Regulatory Commission, 1983.
5 U.S. EPA, Guidance for the Prohibition on the Placement of Bulk Liquid Hazardous Waste in Landfills, OSWER Policy Directive No. 9487.00-2A EPA 530-SW-86-016, Washington, DC, 1986.
6 U.S. EPA, Guide to the Disposal of Chemically Stabilized and Solidified Waste SW-872, Cincinnati, OH, 1982.
7 U.S. EPA, Handbook for Stabilization/Solidification of Hazardous Waste, No. 540/2-86/001, Cincinnati, OH, 1986.
8 U.S. EPA, Stabilization/Solidification of CERCLA and RCRA Waste, No. 625/6-89/022, Cincinnati, OH, 1989.

9 S. Boyd, M. Mortland and C. Chou, Sorption of organic compounds on hexadecyltrimethyl ammonium smectite, J. Am. Soil Sci. Soc., 52 (1988).
10 R. Soundararajan and E. Barth, The evaluation of an organophilic clay for chemically stabilizing a waste containing organic compounds, Hazard. Mater. Control J., 3(1) (1990) 42–45.
11 M. Gilliam, et al., Performance testing of blast furnace slag for immobilization of technetium in grout, Proc., Spectrum, Pasco, WA, 1988.
12 C. Langton, Slag based material for toxic metal and radioactive waste stabilization, Proc. of Trondheim Conference, 1989.
13 R. Hoye, J. Herrmann and W. Grube, Testing of natural zeolites for use in remediating at Superfund site, Proc. 3rd Int. Conf. on New Frontiers for Hazardous Waste Management, Pittsburgh, PA, EPA 600/9-89-072, Cincinnati, OH, 1989.
14 J. Pahlman and S. Khalafalla, Use of Lignochemicals and Humic Acids to Remove Heavy Metals from Process Waste Streams, U.S. Bureau of Mines Report of Investigations No. 9200, Washington, DC, 1988.
15 Soils for Management of Organic Wastes and Waste Waters, Soil Science Society of America, 1975.
16 M. Bricka, Investigation and Evaluation of the Performance of Solidified Cellulose and Starch Xanthate Heavy Metal Sludges, Technical Report EL-88-5, U.S. Army Engineer Waterways Experimental Station, 1988.
17 D. Hassett, et al., Ettringite as an Agent for the Fixation of Hazardous Oxyanions, University of North Dakota, Energy and Mineral Research Center (unpublished report), Grand Forks, ND, 1990.
18 J. Trepanowski, et al., Investigation of Stabilizing Arsenic Bearing Soils and Wastes Using Cement Casting and Clay Pelletizing/Sintering Technologies, Proc. 3rd Int. Conf. New Frontiers for Hazardous Waste Management, Pittsburgh. PA, 1989.
19 S. Weisbud, Hard Science, Sci. News, 134 (1988).
20 R. Puls and M. Barcelona, Ground Water Sampling for Metals Analysis, U.S. EPA 540/4-89/001, 1989.