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ENGINEERING AND DEVELOPMENT SUPPORT OF GENERAL DECON TECHNOLOGY FOR THE DARCOM INSTALLATION RESTORATION PROGRAM

Task 4. General Technology Literature Searches (II)
Solidification Techniques for Lagoon Waters

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Judith F. Kitchens

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December 1980

Submitted to:

Commander
U.S. Army Hazardous Materials Agency
Aberdeen Proving Ground (Edgewood Area), Maryland 21010

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Project Officer

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This report presents a review and evaluation of the available information on techniques for solidification of lagoon water containing hazardous wastes. The processes which were evaluated were cement-based techniques, lime-based techniques and organic polymeric techniques. The applicability of these techniques to solidification of Basin F at Rocky Mountain Arsenal is discussed.

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SUMMARY

The purpose of this study was to evaluate processes for solidification of lagoon water and sediments. The solidification methods evaluated in this study included:

- Cement-based techniques
- Lime-based techniques
- Organic polymer techniques

Most methods require the processing of the lagoon water by pumping it to the processing site and then disposing of the solidified waste. Before any solidification can be accomplished, the lagoon water must be solidified on lab scale to determine the proper mix of solidification chemicals for that particular waste. Solidification technology is very dependent upon the nature of the waste to be solidified. In addition to the major solidification chemicals, small amounts of various other chemicals are also utilized to insure rapid, set and good curing characteristics for the solidified material. To determine the type and quantity of these chemicals needed, the lab tests are essential. The material after solidification in the laboratory undergoes tests to determine the leachability of the wastes from the solid and the compressive strength and friability of the material.

Generally, the solidification methods depend on decreased permeability for fixation properties. The permeabilities for most of the methods range from 10^{-6} to 10^{-8} cm/sec, which is lower than the permeability of normal soil. The solidification methods also depend upon chemical bonding to the wastes and physical entrapment of waste particles for their fixation properties. When physical entrapment is important, the compressive strength of the fixation method and the friability of the solidified product becomes important. Compressive strength is a direct function of process cost. The compressive strengths for cement processes range from .4 to 5.5 N/mm^2. As an example of the increase in costs for higher compressive strengths, Stablex Corporation offers a compressive strength range of 1.4 to 5.5 N/mm^2 with a corresponding cost range of \$5.00 to \$350.00 per metric ton of waste solidified. The lime methods have final compressive strengths that are comparable to the cement methods. Data on compressive strengths for organic polymer solidified materials are sketchy.

Generally, the waste to be solidified contains between 40 and 60% solids. If the sludge as produced does not contain at east 40% solids, the sludge is dewatered prior to solidification. Solidification of material that contains less than 40% solids is cost prohibitive because of the high requirement for processing chemicals.

The material that is to be solidified must be homogeneous prior to being mixed with chemicals. Most processes require a mixing chamber prior to passage to the mixer where chemicals are added. Homogeneity is necessary because the chemicals which are added to solidify the waste are custom designed to each waste problem. Different components in the waste can drastically alter the setting or curing of the solidified mass. For example, organic materials can cause the spalling of cement products, therefore, wastes containing high levels of organics may require pretreatment prior to solidification with cement or lime-based processes. Organic polymer methods are affected by components which may act as poisons to the initiator or promoter reactions required for the formation of the polymers. Factors such as these must be taken into account prior to planning a solidification program. Homogeneity of wastes prevents the formation of a solidified waste with different final properties depending upon what materials were present in the original liquid waste.

The methods surveyed generally did not recommend solidification *in situ*. One of the cement processors (Sludgemaster, Inc.) had equipment and a procedure to do *in situ* solidification, but it was not his recommended method for large scale solidifications. The DCM Method (Takanaka Komuten, Ltd.) can also be used for *in situ* solidification.

Costs for the various processes vary greatly depending upon the nature of the material to be solidified and the desired final characteristics of the materials. Cost estimates range from $5.00 to $350.00 per metric ton of wastes treated. Cement and lime-based processes are generally cheaper than organic polymer processes. However, cement and lime processes result in an increase in waste volume and mass since generally solidification materials are mixed with the waste on a one to one ratio.

Solidification may be a viable alternative to the Basin F problem at Rocky Mountain Arsenal. However, it is not known if this material can be satisfactorily solidified. Laboratory tests must be performed on the actual material before the technical feasibility and reliable cost data can be obtained. Estimates of costs for solidification of Basin F range from $14.3 to $42.9 million for solidification of 600 x 10^6 liters of sludge containing 29% solids If Basin A sediment is combined with Basin F wastes, 750 x 10^6 liters of sludge containing 38% solids will have to be processed at costs between $26.42 and $61.3 million. Thus, solidification of the Basin F wastes will be an expensive undertaking. It is recommended that other alternatives for disposal of these wastes be considered. If solidification then still appears to be a viable alternative, extensive laboratory testing with 5 different solidification processes is recommended.

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I. INTRODUCTION

A. Objective

The purpose of this report is to provide the U.S. Army Toxic and Hazardous Material Agency (USATHAMA) with current state-of-the-art technology for the solidification of liquid wastes such as those found in lagoons. The types of wastes found in lagoons can range from pesticides and other organic wastes to heavy metals and simple inorganic cations and anions. The nature of the material to be solidified is important and will help to determine the solidification agent best suited for the treatment of that particular waste. Included in the report is information concerning:

- applicability of solidification methods to specific wastes
- leachability of wastes from solidified masses
- costs for different solidification processes
- range of treatable contaminant concentration (if available)
- interferences for solidification processes

B. Background

The Army and the chemical industry have routinely stored hazardous wastes in lined and unlined lagoons, due to lack of technology for the safer storage or disposal of these wastes. These wastes contain a wide variety of hazardous materials such as pesticides, organo-phosphates, sulfur containing materials, inorganic salts and heavy metals. In many cases, hazardous wastes have been added to existing lagoons without concern for the type of wastes already present in the lagoon.

Lagoons can only be considered a short term solution to the disposal of toxic liquid wastes because lagoons run the risk of leaching the wastes to ground waters and subsequently contaminating lakes, streams, and other potable water sources. Lined lagoons are safer than unlined lagoons but lined lagoons are subject to liner damage through mechanical means or chemical disintegration by the toxic wastes. Lagoons also occupy vast quantities of land and are physically unattractive.

A relatively new alternative to storage of toxic wastes in lagoons is the solidification of the liquid waste into an inert material with low leachability. The solidified waste is much easier to handle or transport and may even be a usable product, e.g., a landfill or paving material. Solidification is a long term solution to toxic waste disposal. The solidified product provides a repository for heavy metals, salts and other inorganic materials which resembles the type of geological formations the inorganic materials are found in naturally. Organic materials present a more difficult problem. Most solidification processes do not work well with high levels of organic materials. Commonly, organic materials which can not be burned-off are treated by encapsulation so that they are not a surface problem during the solidification process.

A good solidification agent must be able to contain the toxic materials so that they are chemically unreactive and immobile. This goal can be achieved by the incorporation of the toxic materials in the crystal lattice of the solid materials or by their inclusion in an encapsulated form of the solid material. Maintenance of alkaline pH will immobilize many of the multivalent cations as insoluble hydroxides. The ideal waste treatment should produce a product that is usable. A soil-like product capable of supporting plant life or a monolithic mass with good structural stability, low permeability and resistance to weathering effects or biological attack is a good product of a solidification process. Because of the types of wastes incorporated in the solid product, a soil-like product will be unsuitable for agricultural land. However, it could be utilized for wooded or grass land. The rock like solid product could be used as landfill or foundation material for buildings or roadways.

The most attractive fixation process should be economical and not require large amounts of energy. If economically feasible, materials which are scarce in the earth's crust (e.g. manganese, chromium and nickel) should be reclaimed before the water is solidified.

No stabilization process developed to date can be used with every type of waste. Each process must be tailored to the waste it is to stabilize. Since different components in the sludge can either weaken or strengthen the final product, the only way to determine the optimum method for stabilization of a particlar sludge is to subject a sample of the sludge to lab scale processes first. The solidified lab sample is then tested for stability, leachability, friability, etc.

This report includes the description of current commercially available methods for the solidification of waste materials. Information on possible new processes, not now commercially available but which have future potental, is also presented. A short descriptive summary of each major type of solidification process, including the advantages and disadvantages of each process, is presented in Section II. This summary is followed by a description of different commercial solidification processes including:

- the name of the processor
- specific details of the process (when available)
- what types of wastes are treatable by this process and wastes that that are excluded
- leachability data
- the approximate costs of solidification
- any past history for the application of the method.

Of particular interest to the Army is the solidification of Basin F at Rocky Mountain Arsenal. This basin contains a variety of organics and inorganics which are slowly leaching into the ground water. One potential method to halt or slow down this leaching is to solidify the water and sludge in the basin. The applicability of the various solidification techniques to basin F are discussed in Section III of this report.

II. SOLIDIFICATION PROCESSES - DESCRIPTION AND APPLICATION

The goals desired when solidifying liquid wastes include:

- improvement of handling and physical characteristics of the waste
- reduction of surface area available for a leaching interface
- immobilization of toxic wastes by decreasing solubility

No one method of solidification addresses all the stated goals. Each solidification problem must be handled individually and the process chosen for each problem would be the process which best handles each of the above goals for that waste.

The solidification process categories discussed in this report include:

- Cement-based
- Lime-based
- Organic polymer

There are other solidification processes which are not included in this study because they are not applicable to the solidification of lagoon water. These processes are self-cementing processes, glassification, thermoplastic and encapsulation. Glassification is an extremely expensive method of toxic waste disposal used only with highly radioactive materials. Encapsulation requires the solidified toxic waste be placed in an impermeable jacket. This method is both very expensive and not applicable to large volumes of waste. Self-cementing processes require the waste to be a cementing agent when it is mixed with another waste such as slag. Thermoplastic processes require the waste to be dried before or after encapsulation. This type of process is not applicable to solidification of lagoon water.

The processes discussed in this report differ widely in their costs, applicability and the amount of pretreatment required. In choosing the process for a particular waste, consideration must be taken of the type of pollutants in the waste, the ultimate disposal site for the waste, the availability of raw materials, the cost of processing, the increase in bulk of the final product and the design and location of the landfill site, if the solid product is to be used as landfill. Many of the techniques were not developed for waste lagoons. Most of the processes were originally used with radioactive materials. The developed processes were then applied to other types of wastes.

A. Cement-Based Techniques

1. General Description

The most common component in cement-based techniques is Portland cement. Portland cement has long been used for the solidification of radioactive liquid waste. Portland cement is inexpensive, sets rapidly and has high structural strength when solidified. These properties make it an attractive candidate for solidification processes.

Portland cement is a fine powder which consists of 50% tricalcium and 25% dicalcium silicate, 10% tricalcium aluminate and 10% calcium aluminoferrite. When water is added to this mixture, a colloidal calcium-silicate-hydrate gel is produced. During the hardening process, thin, densely packed silicate fibrils form. These fibrils form an interlacing network which solidifies into a solid monolithic mass. The cement surrounds added materials (such as wastes) and encapsulates them within the matrix. Some additives are actually incorporated within the chemical bonds of the cement matrix. Different additives can affect the hardening process by increasing the rate of solidification, increasing the strength of the final product, decreasing the rate of solidification, or weakening the final structural strength of the product (Bogue, 1955).

Portland cements can be divided into five categories (Bogue, 1955):

- Type I is the common cement normally used in construction
- Type II is used with moderate sulfate concentrations (150-1500 mg/kg)
- Type III develops a high early strength and is used in large mass concrete work
- Type IV develops a low heat of hydration and is used in large mass concrete work
- Type V is used with high sulfate concentrations (greater than 1500 mg/kg)

Most solidification of toxic waste is accomplished using Type I (Environmental Laboratories, WES, 1979; Thompson et al., 1979). Types II and V are used inspecial applications when the sulfate concentrations of the waste warrants their use.

Most hazardous wastes do not require pretreatment before being mixed with Portland cement. The wastes can be mixed directly with the cement and the suspended solids will be aggregated in the cement matrix. Cementation is particularly useful for toxic metals because cement is naturally alkaline and the resulting metal hydroxides and carbonates are generally insoluble. Metals may also be incorporated in the cement crystal structure. The strength and stability of the resultant cement can be enhanced by the presence of sulfides, asbestos, latex or solid plastic in the sludge. Organic materials, silt, clay, coal, or lignite can delay or prevent the setting and curing of the concrete. Very fine insoluble material can also weaken cement, because it can coat larger particulate material and prevent the formation of strong bonds between cement and the particles. Other impurities which can delay the setting of cement are salts of zinc, copper, lead, manganese and tin; sodium salts of arsenate, borate, phosphate, iodate, and sulfide; and sulfate salts. Sulfate salts form calcium sulfoaluminate hydrates which cause swelling and spalling of the solidified waste concrete. Special low alumina cements (Type V) were developed to prevent this problem. High levels of organics also cause the spalling of the concrete (Thompson *et al.*, 1979; Environmental Laboratories, WES, 1979).

Most retarding and swelling problems can be prevented by using additives in the mixing of the waste-cement mixtures or by altering the cementation process. Additives are also used to restrict the leaching and migration of toxic wastes from the set and cured concrete. Many of the additives are proprietary, therefore information on them is limited. Among the additives used to improve the cementation processes are clay or bentonite, silicates, vermiculites, lime and lime-flyash. A schematic drawing of a basic cement-silicate solidification process is presented in Figure 1.

Advantages of cement based solidification processes are (Enviromental Laboratory, WES, 1979):

- Inexpensive and plentiful raw materials
- Well-developed and well-known technology
- Common equipment and non-specialized labor
- Drying or dewatering of the sludge not required for typical solids levels of 25-60%
- System tolerates chemical variation in sludge
- Pretreatment required only when the waste contains impurities that prevent setting or curing of cement.
- Variation of the amount of cement added in the process controls the final strength and permeability of the product.

Disadvantages of the cement based solidification processes are (Environmental Laboratory, WES, 1979):

- Large amounts of cement are required for fixation. The weight and bulk of the final product can be double that for other processes

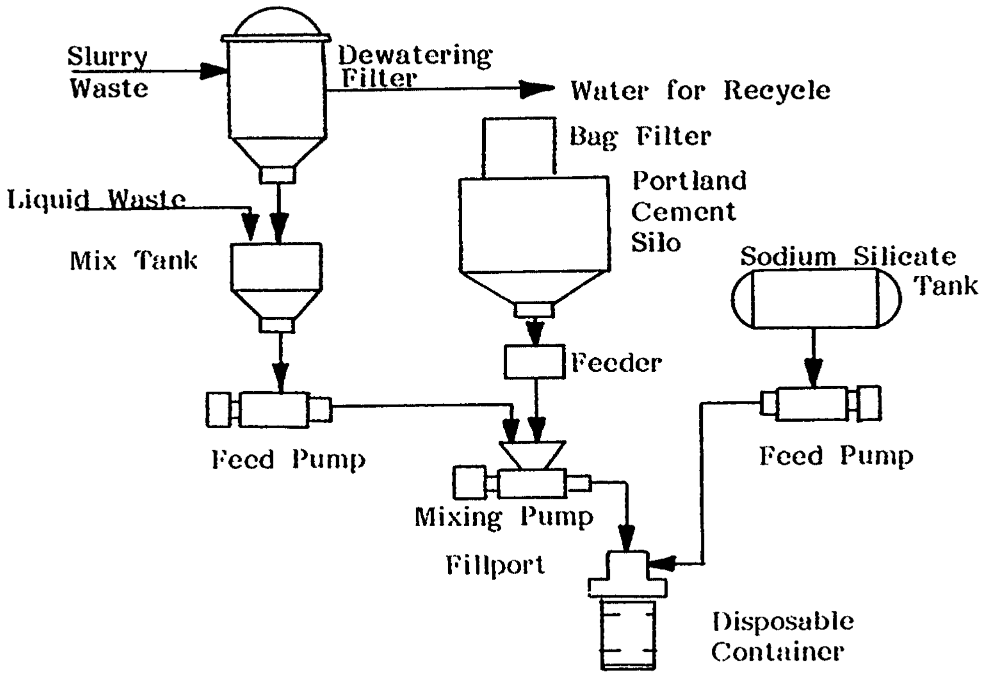


Figure 1. In-Line Cement-Silicate Solidification System (Subramanian and Mahalingam, 1979b)

- Acidic materials can leach toxic wastes from the solidified product

- When waste contains considerable levels of setting retarders, pretreatment is required.

2. ETC Solidification Process

U.S. Vendor: Environmental Technology Corporation
1517 Woodruff Street
Pittsburgh, Pennsylvania 15220
(412) 381-5011

a. Process Description

The ETC solidification process is a patented process (Kupiec and Escher, 1979) which uses a mixture of bentonite clay and Portland cement to solidify aqueous hazardous materials. Bentonite acts as a good ion exchanger, capable of absorbing both inorganic and organic materials. Bentonite has a large surface area with a spongy structure and exhibits a strong negative polarity. The addition of bentonite to the sludge-cement mixture enhances the strength of the cement.

ETC claims that the mixture results in enhanced ability to entrap and bind contained waste materials (Kupiec and Escher, 1979). It is further claimed by ETC that the combination of bentonite, cement and industrial wastes at alkaline pH causes the conversion of organic acids and salts to their sodium salts and the entrapment of the organic materials as insoluble compounds in the concrete matrix.

The consistency of the final product can be varied from that of a soft clay to that of a hard rock by varying the ratio of bentonite to Portland cement in the concrete. ETC uses 10% or less by weight of fixation agent to liquid waste (Kupiec, 1980). The time required for a solidification varies from 30 minutes to five hours. The material after treatment is fluid and is pumped to a holding site for solidification and then removed after it has completely set.

b. Types of Wastes Treated

ETC has treated waste materials from pickling steel (Kupiec and Escher, 1979). The sludge was neutralized using lime and then treated with bentonite-cement. The resultant clay-like product absorbed all the sludge liquid and chemically bound and encapsulated the wastes in the sludge. The amount of leachate removable from the solidified product was said to be minimal and the clay-like product was used to grow grasses. ETC claimed the resultant clay-like product was impermeable to water.

Other wastes treated by this method were sludges from flyash and sulfur dioxide, sludge from acid mine drainings, sludges from oil tank bottoms, and sludge from paint manufacture. The commercial experience of ETC lies mostly with the solidification of metal hydroxide sludges from pickling processes.

c. Leachability of Treated Wastes

The permeability of the clay is on the order of 10^{-6} cm/sec or less and the strength of the solidified product is 1.38 N/mm^2 (200 psi) (Michael Baker Jr., Inc., 1978). Chemical stability increases with time and, apparently, atmospheric CO_2 reacts with the matrix to produce insoluble metal bicarbonates (Michael Baker, Jr., Inc., 1978). The decreased permeabilities of the solidified product is responsible for a reduction in leachability. ETC claims that solubility and leachable components decrease with time and the solidified compounds are relatively insoluble. The expected range of leachate from flue gas desulfurization (FGD) sludges are: TDS, 1000 ppm; SO_4, 400 ppm and minimal Na, K, and Ca. Heavy metals are not expected to exceed safe levels for potable water. The method is reputed to be very good for trace metal retention with heavy metals being better retained than the lighter metals (Michael Baker, Jr., Inc., 1978).

Leaching tests were performed on ETC solidified wastes. These wastes were placed in open lined trenches containing perforated plastic pipe which collected the leachate in collection buckets. After one month, the leachate from various sludges had 1000-5000 mg/l TDS, 500-800 mg/l SO_4, and 150-600 mg/l Cl. Heavy metals were analyzed at less than 0.01 mg/l Ni, Zn, Fe, Cr and Mn. Cu was found at 0.03 - 0.04 mg/l (Environmental Laboratory, WES, 1979).

d. Process Limitations and Advantages

The ETC process is usable at any temperature above freezing although better results are obtained at temperatures above 35°F (1.7°C). At temperatures below 35°F, the curing rate is decreased, however, the physical strength is enhanced. Curing stops at temperatures below freezing, but the process resumes when the temperature increases. Addition of lime to adjust pH of raw sludge will also decrease curing time. The material, after drying, shows a tendency to absorb atmospheric water. Moisture does not seem to affect the cured material, but the liquid sludge, cement, bentonite mixture will not set under water (Michael Baker, Jr., Inc., 1978).

ETC claims the ability to solidify organics when they are present at less than 5% of the total concentration (Kupiec, 1980). Their process can be applied to "once only" operations with the use of mobile equipment. If on-line solidification is desired, a permanent processor can be installed.

e. Economics of ETC Process

The process costs for solidification by the ETC process are typically 0.7 to 2.64 cents/liter (Kupiec, 1980). On a dry sludge basis, the cost of solidification of one metric ton of dry sludge solids ranges from $5.51 to $26.46 depending on the desired strength of the final product. For $5.51 per metric ton with four weeks of curing, 3.1 N/mm^2 (450 psi) develops and for $14.33 per metric ton, 4.8 N/mm^2 (700 psi) will develop with the same curing time. These figures are estimated from figures given and adjusted to 1980 costs using the CE plant cost index (Chemical Engineering, 1980; Michael Baker, Jr., Inc., 1978).

3. Chemfix®

U.S. Vendor: Chemfix, Inc.
P.O. Box 1572
Kenner, LA 70063
(504) 729-4561

a. Process Description

The Chemfix® process is a two part inorganic chemical system which reacts with polyvalent metal iors and other waste materials to form a chemically and structurally stable solid. It is a patented process that makes use of soluble silicates and silicate setting agents which react to form the solid matrix. The matrix itself is described as a pseudo-mineral. The base of this material is tetrahedrally coordinated silicon atoms alternating with oxygen atoms in a linear chain. The oxygenations are charged and react with polyvalent metals to form strong ionic bonds between adjacent chains. These bonds give rise to a three-dimensional cross-linked polymer which resembles natural minerals. The polymer has a high stability, high melting point, and a rigid, friable structure similar to soil (Salas, 1979).

The chemistry which takes place in this process is complex and can be divided into three clases (Michael Baker, Jr., Inc., 1978):

- Very rapid reactions take place between soluble silicates and polyvalent metal ions which produce very insoluble metal silicates. These insoluble compounds are non-toxic and can not be re-solubilized. They resemble natural minerals from which the metals were originally extracted. Environmentally they are very stable.

- The soluble silicate and the reactive compounds of the setting agent react to form a gel structure which acts as a sponge and absorbs large quantities of water while retaining a solid structure. The gel reaction occurs rapidly so that solids in the wastes are held in place by a variety of chemical and physical bonding mechanisms much like an ion exchange resin. Wastes such as oils are also trapped in the structure and immobilized.

- The setting agent and the wastes undergo a variety of hydrolysis, hydration and neutralization reactions.

These reactions take place with relatively small amounts of silicate and setting agents. The volume of chemicals added to the wastes is typically 10% or less of the volume of the wastes.

The physical and chemical properties of the solidified product depend on the amount of solidification agent added to the waste sludge. Typical permeability for stabilized sludges is 10^{-5} to 10^{-6} cm/sec. Permeability appears to remain constant. The compression strength of the final product is approximately 0.43 N/mm^2 (4.5 tons per square foot) (Michael Baker, Jr., Inc., 1978). If the solidified product is cured in place, it will undergo little settling; however, if the material is excavated, the amount of settling increases. It is hypothesized that if the material is cast in place and remains untouched, the amount of leaching from the solidified product will be less than the values reported from laboratory leaching tests.

The solidified product can be used for landfill material, covered with soil and used as grass land. The material can support light construction. Since it is a pseudo-mineral, it behaves like geological rock and sand, and is therefore subject to erosion.

b. Chemfix® Standard Leaching tests

Chemfix®, Inc. has developed a standard leaching test method for determining the leachability of wastes from their solidified products and the ability of their products to stop or slow down the leaching of contaminated water. This test method is as follows (Salas, 1979):

- 100 g of the material to be leached is placed in a chromatography column containing a 2.5 cm cotton or glass wool plug.
- the material is compacted in the column
- the column is filled with distilled water and/or leachate is allowed to seep through the material at the rate of 1 cm^3/min.
- The leachate is collected in 100 ml portions. Eight portions represent 0.64m groundwater passing through the material in a field.
- The leachate is analyzed by atomic absorption, spectrographic, colorimetric or wet methods (as appropriate) to determine the concentration of any constituents that were leached from the material. Results are reported in ppm.

When a leachate is passed through a material, normally a curve similar to that shown in Figure 2 is obtained. The concentration of the leachate residues falls off rapidly in the initial 0.64 m and then slowly declines with depth.

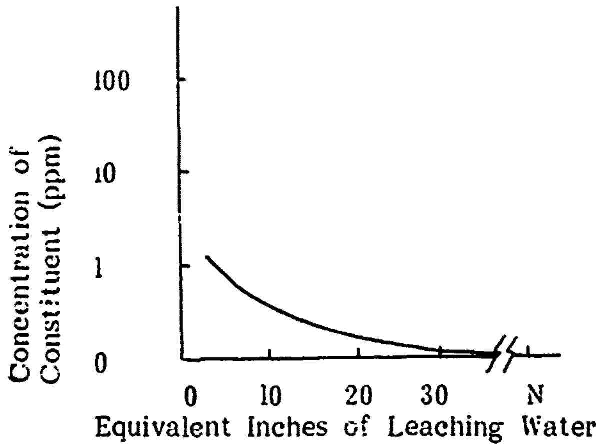


Figure 2. Typical Plot Derived from Chemfix® Leaching Test (Salas, 1979)

An example of the type of data obtained with this test is presented in Table I. In this table, the sanitary landfill leachate was passed through two materials which had previously been stabilized by the Chemfix® process. As can be observed from the table, there is a dramatic reduction in the amount of contaminant passing the first 64 cm (25 inches). Further reduction in most contaminants is observed afer 254 cm (100 inches).

c. Leachability of Wastes Treated with Chemfix®

The Chemfix® process has been in commercial use for over seven years with over 380 million liters of wastes treated. The products can and have been used in clean fill material and land reclamation and cover material. The types of materials and amounts processed are shown in Table II. Leaching tests of several on these solidified wastes are presented in Tables III and IV. The Chemfix® solidified wastes leaching data are compared to the dewatered wastes before treatment (where data was available) and the USPHS drinking water standard and EPA metal finish industry and Japans effluent standards in Table III. As can be observed from the table, the leachates from the Chemfix® solids were well below the effluent standards and below the USPHS drinking water standards in most instances. Chemfix® solids from an automotive assembly plant wastes were subjected to a variety of leaching tests. These tests included leaching with distilled water, sulfuric acid (pH 1-6), hydrochloric acid (pH 1-6), nitric acid (pH 3-6). acetic acid (pH 3-6) and hyroxybenzoic acid (pH 3-5). The results of the distilled water leaching tests are shown in Table IV. All the metals, cyanide and phenol were below 0.10 mg/l after

Table I. Comparison of EPA Sanitary Landfill Leachate Before and After Passing Through Chemfix® Processed Industrial Wastes (Chemfix®, Inc., 1980)

Analysis of Leachates (ppm)

Constituent	Raw Leachate	Material #1 64 cm of Leachate	Material #1 254 cm of Leachate	Material #1 % Reduction of Constituent	Material #2 64 cm of Leachate	Material #2 254 cm of Leachate	% of Reduction of Constituent
Iron	720 ppm	3.0	< 0.10	99.99	1.9	1.2	99.8
Manganese	3.2	1.5	< 0.50	84.0	2.4	1.0	69.0
Nickel	87	2.1	< 0.10	99.9	< 0.10	< 0.10	99.9
Zinc	42	0.80	< 0.10	99.8	1.1	< 0.50	99.0
Copper	1,200	1.1	< 0.10	99.99	2.0	< 0.10	99.99
Total Chromium	3.8	< 0.50	< 0.25	93.0	< 0.10	< 0.10	99.7
Cyanide	2.1	< 0.50	< 0.10	99.5	1.0	0.70	67.0
N, as NH_3	375	110	110	71.0	140	100	73.0
N, as NO_3	2.4	12	< 0.25	90.0	2.1	< 0.10	96.0
COD	~ 38,000	~ 1,800	~ 1,000	97.0	~ 9,500	~ 1,700	96.0

~ = Approximately

< = Less Than

All results are expressed in ppm.

Table II. Solidification Projects Conducted by Chemfix®, Inc. (Michael Baker, Jr., Inc., 1978)

Location	Type of Waste	Quantity of Wastes, liters
Bearing Manufacturing Plant Michigan	Metal Finishing	3,400,000
Inorganic Chemical Plant	Arsenic Containing	1,515,000
Chemical Plant Ontario, Canada	Hg, NaOH, Cl, brine sludge	1,325,000
Electronic Manufacturing Plant Pennsylvania	Electronics Fabrication	53,000,000
Organic Chemical Plant Texas	Mixed organic-inorganic Wastes	19,000,000
Oil Refining Pennsylvania	Sewage Sludge	4,500,000
Automative Assembly Plant Ohio	Metal Finishing Wastes	19,000,000

Table III. Leaching Tests with Chemfix® Solidified Wastes (Salas, 1979)

Treatment	Solid of Waste	pH	Dissolved Solids	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	COD	Phenol
USPHS Drinking Water Standards		5.8-8.5	500	.01	.05	1.0	.3	.05	2.0	.05	5.0		.001
EPA Effluent Guideline-Metal Finishing Industry		6-8.5		0.1	.05	0.2	0.5	1.0	1.0	.05	0.5		
Japan Effluent Standard		5.8-8.0		0.1	0.5	3.0	10.0	10.0		1.0	5.0	160	5.0
Chemfixed	Metal Finishing Sludge	8.0	300		< .05	< .10	< .02		.10	< .02			
Chemfixed	Chemical Waste			< .10	< .05	< .05	< .02	.10	.10	< .10	< .02		
Chemfixed	Oil Refinery Waste				<.05	< .10	< .10		< .10	< .10	< .10		
None	Mixed Metal Etching Fluid	1.9	30,000		210	2700	8400		160				
Chemfixed	Mixed Metal Etching Fluid	8.0	300		<.05	.029	0.15		0.20				
None	Sanitary Landfill Leachate				0.25	.075	4.0		1.75		1.4	1,250	3.6
Chemfixed	Sanitary Landfill Leachate				< .05	< .05	< 0.10		0.25				0.25

Table IV. Chemfix® Processed Automotive Assembly Waste Leaching Study Lab Leachate of 6/71 Field Material Generated by Chemfix® Process (Chemfix®, Inc., 1980)

Constituent	Raw Sludge	Inches of Leachate Water°			
		0-64 cm	64-128 cm	128-191 cm	191-254 cm
Total Chromium (Cr)	103	<0.25	<0.25	<0.10	<0.10
Iron (Fe)	10,800	<0.25	<0.25	<0.10	<0.10
Manganese (Mn)	122	<0.10	<0.10	<0.10	<0.10
Nickel (Ni)	212	<0.25	<0.25	<0.10	<0.10
Phenol	*	<0.10	<0.10	<0.10	<0.10
Cyanide (CN⁻)	*	<0.10	<0.10	<0.10	<0.10
Zinc (Zn)	2,200	<0.25	<0.10	<0.10	<0.10
Copper (Cu)	121	<0.25	<0.25	<0.10	<0.10

All results in ppm

° = Each 64 cm Leachate represents approximately 800cc of Distilled Water.

< = Less Than

* = Not Analyzed

127-191 cm (50-75 inches) of water leachate. None of the acid leachates showed concentrations of any components above 0.10 mg/l after 254 cm (100 inches) of leachate (Chemfix® Inc., 1980). Thus, the metals are strongly bound to the silicates and leaching is prevented even under acidic conditions.

d. Process Limitations and Advantages

The Chemfix® technique requires the ability to pump the sludge waste, therefore, dewatering to 20-40% solids content results in the best process chemistry. If the raw wastes contain 55-60% solids, they are difficult to handle (Michael Baker, Jr., Inc., 1978). The best pH for the solidification is 5-7, however, pH values of 4-11 can be handled under less rigid operating conditions. If needed, lime can be added to adjust pH. Depending on the solids concentration, additive requirements can be up to 10% (by volume) of the wastes (Environmental Laboraotry, WES, 1979).

The process does not work well with wastes containing high levels of chlorides, since the solid product does not retain the chloride. Other problem contaminants are sulfate, sodium, monovalent cations, colloidal materials, and organic materials (Environmental Laboratories, WES, 1979). In some cases, pretreatment of wastes can remove some of these problems. The leaching of these materials is retarded even though they are not fixed. The Chemfix® process is not affected much by varying climates. Extreme cold can retard the curing process but the retardation is only 5-10% slower than at normal temperatures (Michael Baker, Jr., Inc., 1978).

The material to be solidified has been pumped as much as one mile to the solidification equipment. However, the solidification reactions occur rapidly and to prevent obstruction of lines, it is best to have the disposal site near the equipment (Michael Baker, Jr., Inc., 1978). Chemfix® has a mobile plant capable of solidifying 380,000 liters/10 hour day (Environmental Laboratory, WES, 1979).

e. Economics of the Chemfix® Process

The cost of fixing any wastes varies with the content of the waste. The only information available is a range of costs. The real costs can only be determined after laboratory tests on the waste to determine the optimum solidification mixture for that particular waste. Costs only vary with the solid content of the waste. The costs of solidification processing and disposal are $8.00 to $12.70 per metric ton of dry solids for a 50% solids cake including 0.8 to 1 cent per liter of $6.00 to $10.50 per metric ton dry basis for reagent chemicals (Michael Baker, Jr., Inc., 1978). These costs are adjusted to 1980 costs using the CE index (Chemical Engineering, 1980). A comparison of costs for solidification of various concentrations of sludge wastes are presented in Figure 3. Generally, Chemfix® is used for dewatered sludges with solid concentrtions of 50-55% weight percent solids. The costs given in the figure are 1975 costs and include (Michael Baker, Jr., Inc., 1978):

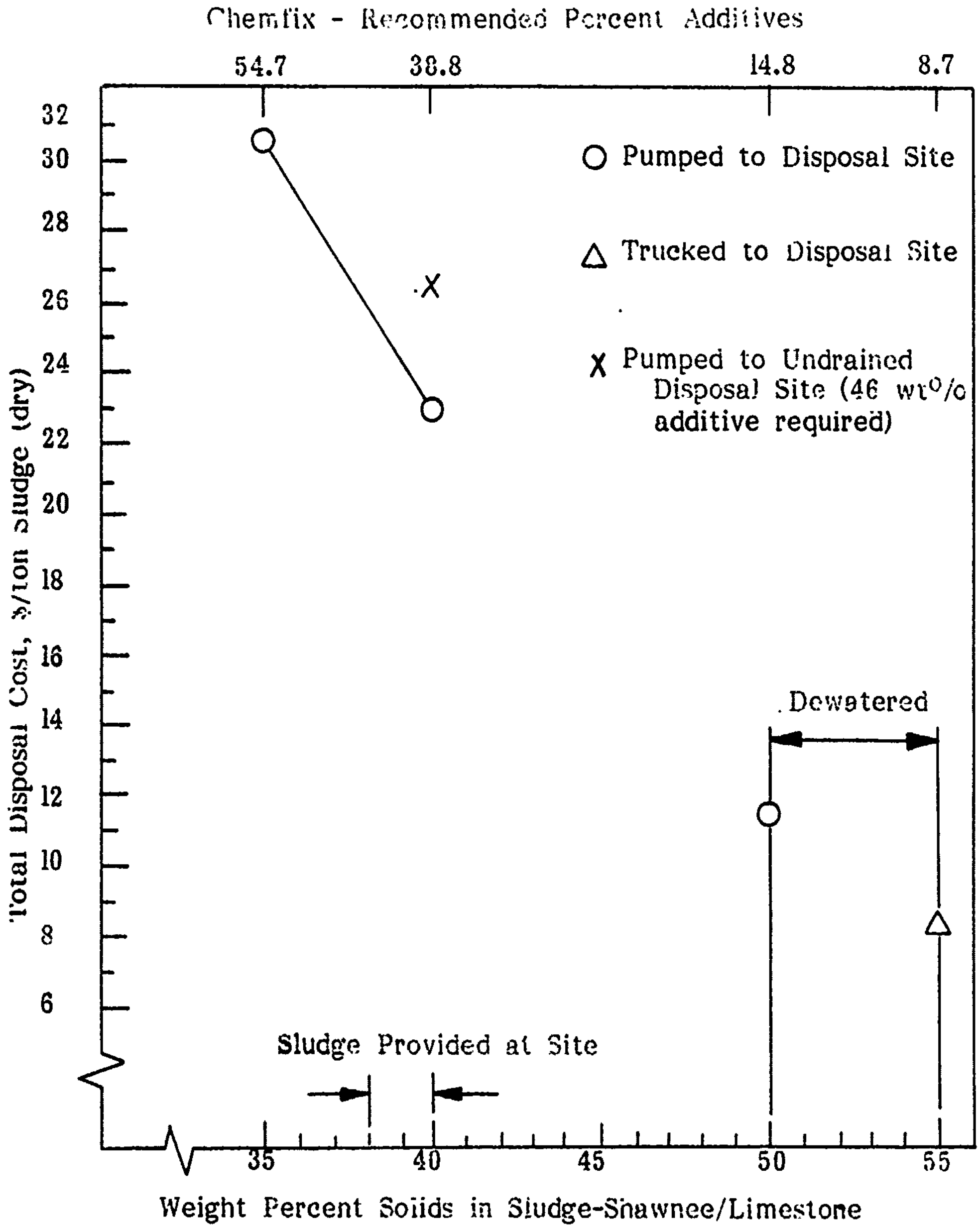


Figure 3. Estimates of Disposal Costs for Chemfix® Process as a Function of Solids Content (Michael Baker, Jr., Inc., 1978)

- additive costs
- labor
- maintenance costs
- power costs
- pumping and/or hauling
- placement and compaction as necessary
- equipment, dewatering
- disposal site land costs (puchase and/or development)

4. Terra-Tite® Process

U.S. Vendor: Stabatrol Corporation
1000 Conshohoeken Road
P.O. Box 578
Norristown, Pennsylvania 19404
(215) 825-2675

Stabatrol Corporation has a proprietary process called the Terra-Tite® method to solidify waste sludge. The process utilizes both chemical reactions and the physical character of the resultant product to fix the toxic waste. The method can be used to solidify a continuous flow of waste sludge. Alternatively the sludge can be first impounded in a lagoon until the solid waste has settled, the sludge is then solidified when the lagoon requires emptying. The sludge processing should take place at an approved landfill due to the rapid solidification of the material. The Terra-Tite® processing equipment can handle either lagooned or mechanically dewatered sludge and dispose of it onsite. This process is also applicable for dry or nearly dry industrial waste. Since Terra-Tite® is a proprietary process, little technical information is available (Smith, 1979).

The process has been used to solidify the following wastes (Smith, 1979):

- Heavy metal and cyanide sludge
- Arsenic salt cake residues
- Mercury brine sludge
- Ore and salt cake residues
- Tungsten ore residue

- Contaminated pot bottoms from aluminum industry
- Calcium fluoride sludge
- Neutralized pickling sludge
- Pigment sludge
- Most inorganic and many organic wastes including sewage sludge

The process is not suitable for: sludges containing less than 12% solids, grease, oils or solvents (except for those which do not contain substantial amounts of grease or oils).

The Terra-Tite® treated material exhibits low permeability, high strength, and low leachability. Permeabilities of 10^{-7} cm/sec are common with unconfined compressive strengths of 0.48 N/mm^2 (5 $tons/ft^2$). Typical values for compressive strength and permeability of treated wastes are presented in Table V. Leachability data are presented in Tables VI through X.

Terra-Tite® process has the capabilities of solidifying 1800 metric tons of material in an eight-hour day (Scornavacchi, 1980). Cost data was not received from the company when they were contacted.

5. Terra-Crete® Process

U.S. Vendor: Sludge Fixation Technology
227 Thorn Avenue
P.O. Box 32
Orchard Park, New York 14127
(716) 662-1005

a. Process Description

The Sludge Fixation Technology (SFT) Terra-Crete® process is used to stabilize flue gas desulfurization (FGD) sludges. SFT has developed a method to use calcium sulfite and gypsum to solidify the sludge. Both these materials are available from the sludge. The processing techniques for this method are patented. The basis for the process is that calcium sulfite hemihydrate acquires cementatious properties upon being heated to its dehydration temperature. Calcium sulfate dihydrate (gypsum) is also cementitious when it is calcined to the hemihydrate. Since FGD sludges supply both of these components, the Terra-Crete® process is well suited to the solidification of FGD sludges (Valiga, 1979).

A schematic diagram of the Terra-Crete® process is shown in Figure 4. The FGD sludge is dewatered by thickening and vacuum filtration. The filter cake is divided into the calciner and the mixer. The portion that is calcined is then stored in a silo for future use. The calcined material is mixed with

Table V. Physical Properties of Terra-Tite® Products (Smith, 1979)

Industrial Facility	Unconfined Compressive Strength		Permeability (cm/sec)
	ton/ft2	N/mm2	
SLUDGES			
1. Electronics Plant (PA)	8.9	.85	6.0×10^{-7}
2. Electronics Plant (NY)	6.0	.57	5.3×10^{-7}
3. Metal Plating Plant (PA)	7.1	.68	2.7×10^{-7}
4. Electrical Components Plant (NY)	8.0	.77	1.1×10^{-8}
5. Chlorine Production Plant (Mid-Atlantic)	31.7	3.03	2.2×10^{-7}
6. Paint Manufacturing Plant (NJ)	7.9	.75	7.2×10^{-7}
7. Electrical Components Plant (PA)	4.1	.39	8.2×10^{-7}
8. Electroplating Plant (NY)	3.2	.31	2.7×10^{-7}
9. Electronics Plant, PCB By-Product (NY)	8.0	.77	1.1×10^{-8}
10. Electrochemical Plant (PA)	6.0	.57	7.8×10^{-8}
11. Electronics Plant (MA)	5.5	.53	2.7×10^{-7}
RESIDUES			
12. Chemical Production (MD)	20.2	1.93	1.1×10^{-7}
13. Arsenic By-Product Waste (Northeast)	51.1	4.88	-
14. Aluminum Production (Northeast)	4.9	.47	9.1×10^{-7}
15. Electrochemical Plant (PA)	22.6	2.16	-

Table VI. Leaching Tests on Electronic Manufacturing Sludge Treated with Terra-Tite® (Smith, 1979)

Constituent		Raw Sludge (ppm)	1 Month	2 Months	8 Months
Cadmium	(Cd)	3.4	<0.002	<0.002	<0.002
Total Chromium	(Cr)	2.8	<0.02	<0.02	<0.02
Copper	(Cu)	60	0.09	0.07	<0.02
Iron	(Fe)	27	<0.05	<0.05	<0.02
Lead	(Pb)	<0.1	<0.01	<0.01	<0.01
Nickel	(Ni)	220	<0.023	<0.02	<0.02
Zinc	(Zn)	63	<0.01	<0.01	<0.01
Cyanide	(Cn)	<0.1	0.02	<0.02	<0.02
Chloride	(Cl)	10,000+	5.0	3.0	2.0
Fluoride	(F)	300	3.2	1.6	1.5
Phosphate	(PO_4)	90	0.13	0.08	0.07
Sulfate	(SO_4)	1500	18.0	10.0	6.0

Table VII. Leaching Tests on Chlorine Production Plant Sludge Treated with Tera-Tite® (Smith, 1979)

Constituent		Raw Sludge (ppm)	Terra-Tite® Leachate Analysis (1 Month)
Mercury	(Hg)	61	0.0016
Sulfate	(SO_4)	1,200	660
Chloride	(Cl)	15,000	1730

Table VIII. Leaching Tests on Metal Finishing Plant Sludge Treated with Tera-Tite® (Smith, 1979)

Constituent		Raw Sludge (ppm)	Terra-Tite® Leachate Analysis (1 Month)
Total Chromium	(Cr)	86	1.01
Nickel	(Ni)	73	0.05

Table IX. Leaching Tests on Metal Plating and Manufacturing Sludge Treated with Terra-Tite® (Smith, 1979)

Constituent		Raw Sludge (ppm)	Terra-Tite® Leachate Analysis (1 Month)
Total Chromium	(Cr)	24	<0.02
Copper	(Cu)	106	<0.02
Iron	(Fe)	2000	<0.02
Lead	(Pb)	102	<0.02
Nickel	(Ni)	118	<0.02
Zinc	(Zn)	8	<0.02
Phosphate	(PO_4)	255	<0.02
Tin	(Sn)	100	<0.02
Cobalt	(Co)	1.	<0.02

Table X. Leaching Tests on Electronics Manufacturing Plant Sludge Treated with Terra-Tite® (Smith, 1979)

Constituent		Raw Sludge (ppm)	Terra-Tite® Leachate Analysis (1 Month)
Cadmium	(Cd)	0.15	<0.002
Total Chromium	(Cr)	470	0.3
Copper	(Cu)	1700	0.1
Tin	(Sn)	7.3	<0.02
Lead	(Pb)	9	<0.01
Nickel	(Ni)	40	<0.02
Zinc	(Zn)	9	0.03
Aluminum	(Al)	62	0.25
Magnesium	(Mg)	410	1
Mercury	(Hg)	0.006	0.005
Manganese	(Mn)	48	0.01

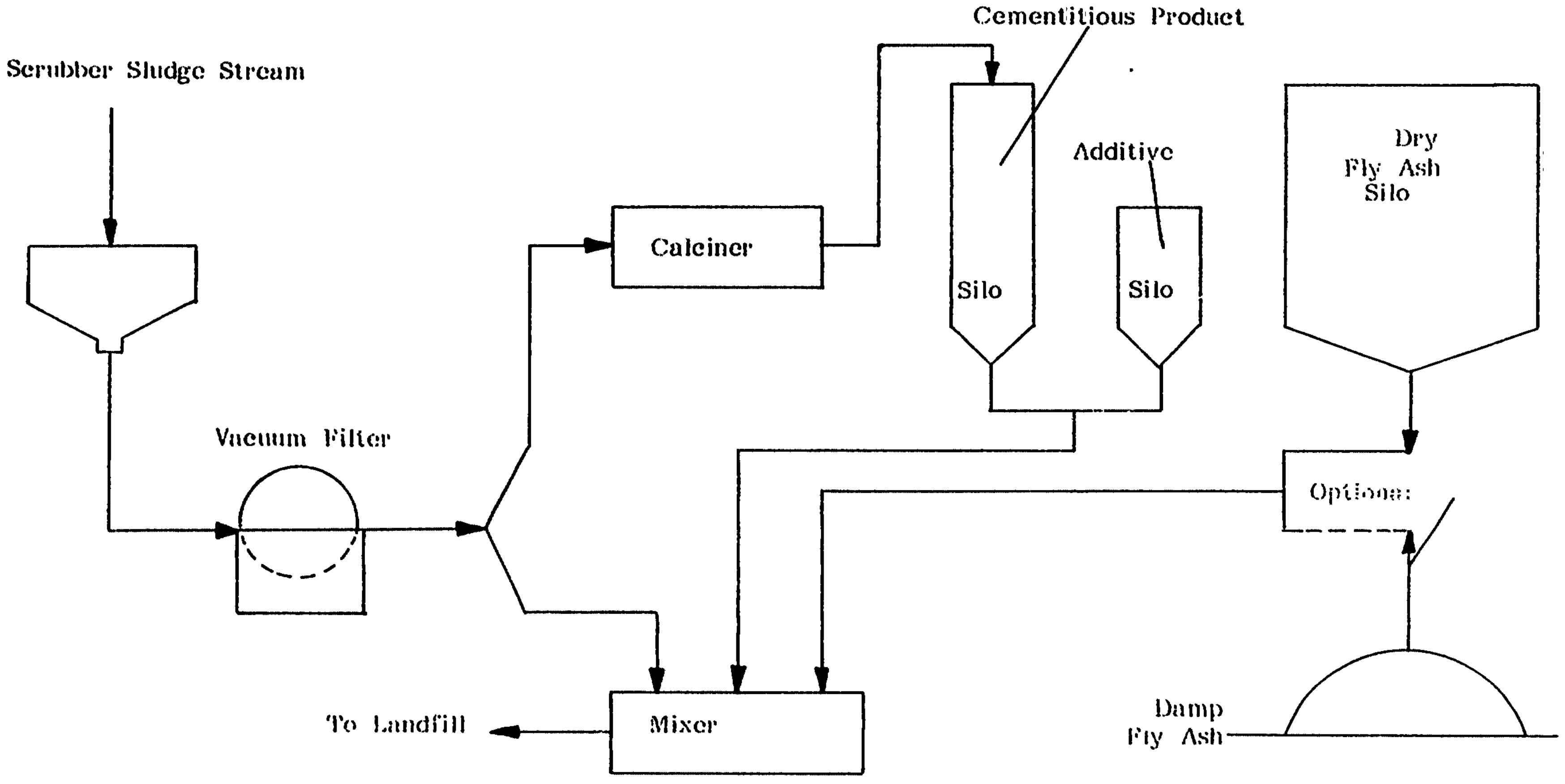


Figure 4. Process Flow Diagram for Terra-Crete® Process for FGD Sludge Fixation (Valiga, 1977)

proprietary additives and then mixed with the rest of the filter cake to solidify the material prior to transportation to landfill. Flyash can also be used in the process to aid the solidification. The solidified product must be compacted prior to disposal because compaction helps to decrease permeability and leachability and increase density (Valiga, 1979). The Terra-Crete® process produces solids of high compressive strength due to the speed which cementation occurs. Within the first few days of placement, the unconfined compresive strength rises dramtically (Figure 5). Early strength is important for good environmental quality control. The final unconfined compressive strength is 2.0 N/mm^2. The permeability of the solid product lies in the 10^{-7} cm/sec range (Valiga, 1979).

b. Leachability of Treated Wastes

Leachate studies were conducted on wastes from both an electric utility and a lead smelter (Valiga, 1979). The wastes were stabilized with Terra-Crete® and cured for 28 days prior to leaching. The cured waste was pulverized before attempting to extract the wastes to simulate a sample that had undergone extremely severe conditions. The pulverized wastes were agitated with water (4 parts water and 1 part solids) for 48 hours and then chemically analyzed. The results are given in Tables XI and XII. The untreated lead smelter sludge was reported to contain 12,000 to 20,000 mg/l lead. As shown in Table XI, less than .01 mg/l was present in the stabilized sludge leachate. However, sulfates tend to leach from the material.

c. Economics of the Terra-Crete® Process

The Terra-Crete® process is attractive for FGD sludges because it utilized FGD waste for solidification process resulting in low costs for solidification chemicals. The costs for Terra-Crete® are estimated to be $2.30 to $3.20/metric ton of wet sludge (Valiga, 1979). These costs include the full Terra-Crete® processing plant, including accessory equipment, mixer, calciner, and placement. The costs are adjusted to 1980 costs using the CE index (Chemical Engineering, 1980).

6. Petrifix® Process

Vendor: PEC-Engineering
Paris, France

The Pec-Engineering process is known as the Petrifix® process. The process uses a mixture of calcium silicates and a proprietary activator to obtain a material composed of hydrated silicates and silico-aluminates in a particular composition and configuration. The reaction is pozzalanic and the chemicals are dosed in a way to keep porosity and shrinkage low. Solidification is not immediate but strength improves with time. The chemicals are relatively inexpensive and do not require special handling or storage.

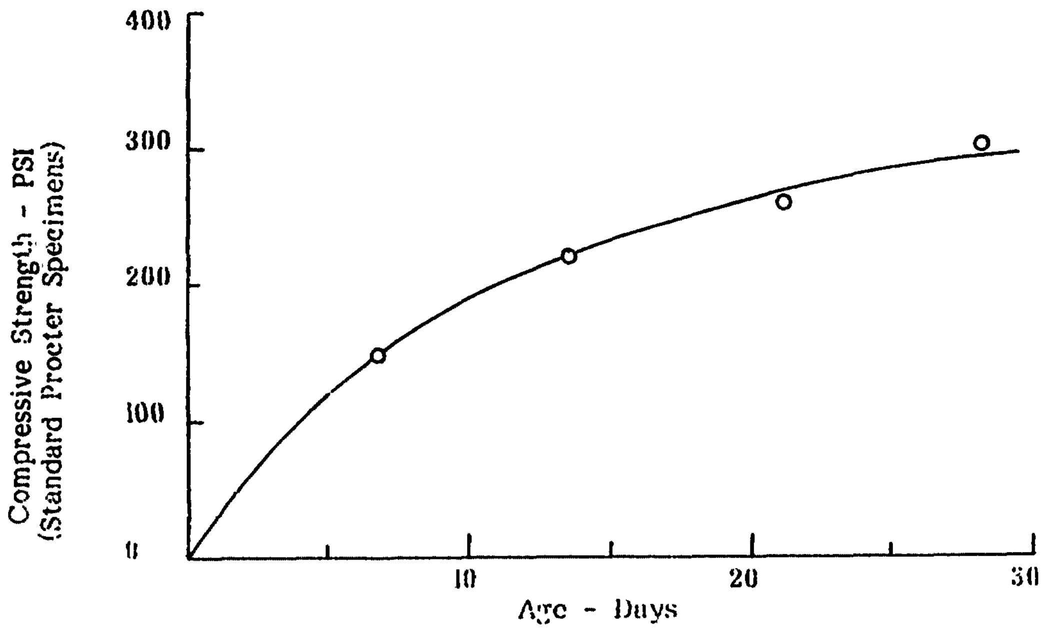


Figure 5. Terra-Crete® Compressive Strength Characteristics (Valiga, 1979)

Table XI. Leachate Analysis of Stabilized Lime FGD Sludge From a Lead Smelter Utilizing the Terra-Crete® Process (Valiga, 1979)

		mg/l
pH	7.9	
Methyl Orange Alkalinity as $CaCO_3$		30.0
Dissolved Solids		1851.0
Antimony		<0.05
Lead		<0.01
Sulfate as SO_4		990.0

Table XII. Leachate Analysis of Stabilized Limestone FGD Electric Utility Sludge Utilizing the Terra-Crete® Process (Valiga, 1979)

		mg/l
pH	7.9	
Phenolphthalein Alkalinity as $CaCo_3$		10.0
Methyl Orange Alkalinity as $CaCO_3$		58.0
Hardness as $CaCO_3$		1610.0
Sulfite as SO_3		9.0
Sulfate as SO_4		1247.0
Total Dissolved Solids		2600.0
Calcium		538.0
Cadmium		0.002
Chloride		8.0
Chromium		0.06
Copper		0.03
Iron		0.27
Lead		0.08
Manganese		0.18
Potassium		40.8
Sodium		70.1
Zinc		0.01

The process includes the following steps (Pichat *et al.*, 1979):

- neutralization
- precipitation (silicates, borates, arsenates, phosphates, plumbates, tungstates)
- absorption (Pb, Zr, V, Mo, Se, Te, U, Pt)
- Chelation (chloride, bromide, iodide, nitrate, nitrite chromate, carbonate)
- solidification
- disinfection

The Petrifix® process has been used with a wide variety of materials (Table XIII). It has a record of good solidification with low leachability. Values for leachability for a typical sludge are given in Table XIV. The process is available in France and England. It is not currently licensed in the United States. No cost data are available in the Petrifix® process.

7. Stablex® Process

U.S. Vendor: Stablex Corporation
Suite 110, Two Radnor Corporation center
Radnor, Pennsylvania 19087
(215) 688-3131

a. Process Description

The Stablex process, developed in the United Kingond, utilizes two silicate based products to form a slurry with the liquid waste. Up to 10 proprietary additives are also used to aid in the solidification. What components are added to the waste and the ratios in which they are added are dependent on the nature of the waste. The process involves the following steps (Schofield, 1979):

- Reception - the process will handle solids, liquids so the types of receptors and mixing facilities can be quite diversified.
- Disintegration - The disintegrators dissolve and disperse the wastes into forms suitable for polymerization. The output of the disintegrators is a stable dispersion or solution of solids and liquids.

Table XIII. Types of Wastes that Can be Treated by the Petrifix® Process (Pichat *et al.*, 1979)

Origin	Type of Waste	Main Pollutants
Electroplating and Metal Finishing	Schlams	Chromates, cyanides, heavy metals, acids (Cr, Zn, Hg...)
Chemical Industry	By-products of effluent treatment	Heavy metals, organometallics, low polymers
Mechanical	Effluent treatment plant	Dusts, oils
Electronics and Electric Industry	Tank bottoms, effluent treatment sludges	Cyanides, copper, zinc, nickel, cadmium
Oil and Petrochemical Industry	Digested sludge catalyst A.P.I. separator sludge	Heavy metals, dusts
Municipal Treatment Plant	Digested sludge	Organics, heavy metals
Agrobusiness	Sewage sludges, organic sludges	Protides, lipides, glucides organometallics

Table XIV. Leaching Tests on Petrifix® Processed Sludge (Pichat *et al.*, 1979)

	Raw Sludge (ppm)	Petrifix (ppm)
Cd	0.6	0.002
Cr^{6+}	1.2	0.003
Cr^{3+}	1.4	0.001
Fe	39.4	0.04
Mn	0.5	0.01
Cu	1.6	0.007
Ni	0.7	0.005
Pb	1.4	0.02
Zn	1.05	0.06
Ca	139.2	17
P	2.0	0.3

— Pretreatment - Some wastes such as arsenic, chromium, cyanide require conversion to chemical forms suitable for polymerization. These wastes are pretreated chemically during disintegration. Materials with a tendency to retard or accelerate polymerization must also be neutralized at this time.

— Polymerization - The dispersed water is transported to a polymerization unit where the proper chemicals are added and the polymerization takes place.

— Product Diposal - The product from the polymerization step is a slurry which can be trucked or pumped to the disposal site. The material begins to set in 24 hours and will be hard in three days. Final strength is achieved in six months.

Details on the process chemistry are not available. The information available claims that the Stablex® product is a synthetic rock formed by the "crystal capture" mechanism. The "crystal capture" mechanism is a combination of two inter-dependent reaction mechanisms. The initial reactions are between the pollutants in the waste and the process chemicals. These are ionic reactions and form strong chemical bonds. The second is the capture of the insoluble pollutants in the crystal lattice formed by the first set of reactions. To release the pollutants complete destruction of the polymer must take place which occurs only at high temperatures or in the presence of strong acids (Schofield, 1979).

Stablex® exhibits low permeability and leachability and high strength. The permeability is on the order of 10^{-7} cm/sec and the strength is on the order of 1.41-5.5 N/mm^2 after twenty-eight days. The compressive strength of the solid product increases with time and obtains maximum strength after six months (Schofield, 1979).

b. Leachability of Stablex® Solids

The leachability data for Stablex® solidified metal wastes are presented in Table XV. The leachabilities were determined by pulverizing the Stablex® product and immersing it in 10 times its weight of distilled water (pH 5.0-5.5) and stirring the material for one hour before analysis of leachate (Schofield, 1979). A dynamic leachate test was also performed where the above mixture was stirred for one hour intervals and repeated extractions were performed. Leachability did not increase with time. In-place leachability studies were performed on sites where the Stablex® products were used as landfill. The analysis of rainwater from a land reclamation site is shown in Table XVI. Core sampes taken at the reclamation site were also subjected to leaching tests. The results of these tests are shown in Table XVII. As can be seen from the table, only low metal levels are detected even after 21 days of leaching. Typical results of 28 days of extracting a powdered Stablex® sample with sulfuric acid at pH 2 are shown in Table XVIII. With the exception of lead, concentrations of metals after 28 days are below USPHS drinking Water Standards.

Table XV. Equilibrium Leaching Tests of Stablex Solidified Product (Schofield, 1979)

Pollutant	Concentration of Pollutant in Waste (ppm)	Concentration of Pollutant in Waste (ppm)	% Leached
Chromium	25,000		
(Hexavalent)	25,000	0.2	0.03
Copper	25,000	0.26	0.03
Nickel	55,000	0.50	0.055
Zinc	101,150	0.15	0.009
Lead	78,090	0.5	0.016
Cadmium	45,590	0.1	0.042
Manganese	14,660	0.08	0.057
Sulfide	9,740	0.1	0.05
Tin	12,500	0.1	0.03
Arsenic		0.16	0.03

Table XVI. Analysis of Rain Water Collecting in Land Reclamation Site (Schofield, 1979)

	Concentration in Leachate, mg/l		
P.V.4 hr	1.8	-	-
BOD	1.6	3.0	1.8
Suspended Solids	63	133	85
Ammoniacal Nitrogen	0.7	0.5	0.1
Nitrite Nitrogen	0.1	0.1	nil
Nitrate Nitrogen	3.3	4.1	2.4
Chloride	99	170	51
Cadmium	nil	nil	nil
Chromium	0.04	0.02	0.02
Copper	0.05	0.05	0.02
Nickel	0.02	0.01	0.12
Zinc	0.08	0.02	0.06
Arsenic	0.26	0.01	0.00
Mercury	0.02	0.01	0.03

Table XVII. Leachate Tests on Core Samples from Reclamation Site (Schofield, 1979)

Concentration in Leachate, mg/l	After 7 Days	After 14 Days	After 21 Days
Ammoniacal Nitrogen	0.02	0.12	0.70
Total Oxygen Demand	107	111	140
Cyanide	<0.01	0.03	0.10
Thiocyanate	<0.01	0.09	0.10
Phenols	0.3	0.3	0.3
Cadmium	< 0.001	<0.001	<0.001
Chromium	0.06	<0.02	0.15
Copper	0.10	0.34	0.14
Lead	<0.01	<0.01	0.40
Mercury	<0.001	-	-
Nickel	0.06	0.25	0.02
Zinc	0.02	1.85	0.02

Table XVIII. Typical Leaching Results of Stablex® Solids with Sulfuric Acid at pH 2 (Schofield, 1979)

Concentration, mg/l	Waste Sample	24 Hours	7 Days	28 Days
Total Cyanide	60 ppm	ND	ND	ND
PCB	1	ND	ND	ND
Cd	10 ppm	0.01 ppm	0.01 ppm	0.01 ppm
Pb	740 ppm	0.22 ppm	0.33 ppm	0.33 ppm
Ni	1160 ppm	0.16 ppm	0.20 ppm	0.23 ppm
Zn	1540 ppm	0.20 ppm	0.22 ppm	0.23 ppm
Cu	300 ppm	ND	0.01 ppm	0.03 ppm
Cr	580 ppm	ND	0.01 ppm	0.01 ppm
Hg	2 ppm	ND	ND	ND
As	163 ppm	0.09 ppm	0.09 ppm	0.11 ppm

ND = Not Detected

c. Process Limitations and Advantages

The Stablex® process is suitable for all inorganic wastes; organic wastes which can be homogeneously incorporated in an aqueous phase by dissolution, suspension or absorption, solid materials such as contaminated filter cartridges, clothing, rubber boots, etc. and heavy metals, such as arsenic, or mercury; asbestos, fluoride, chloride, etc. The process can not be used for oils, solvents and greases which are not miscible with water or very large amounts of water with low levels of wastes (Schofield, 1979).

d. Economics of the Stablex® Process

Costs for this process range from $5.00 to $350.00 per metric ton (materials, labor, equipment included) depending on the type of sludge and the complexity of the waste. As can be seen by the wide range in price, the costs are just rough estimates. In order to determine costs more reliably, the type of waste must be analyzed. Generally, each ton of liquid sludge results in 1.15 to 1.4 tons of solid product, Stablex®. The volume increase for this weight increase is 5 to 10% (Environmental Laboratory, WES, 1979). This process is not currently available in the U.S. However, Stablex® is building a plant in Michigan which is to be operational in 1981.

8. Potential Solidification Processes Not Commercially Available

The Japanese patent literature contains a large number of patents on solidification of wastes. Due to cost and time restriction only a few of what appeared to be the more applicable process patents were translated.

a. Method for Treating Waste Water

Vendor Name: Mitsuboshi Kagaku Goshi Co., Ltd.
Japanese Patent #53-97252
by Yoshiro Wakimura (1978)

The method treats wastewater with Portland cement, an alkaline metal silicate, lime and one or more of the following: aluminum sulfite, aluminum chloride, basic aluminum sulfite, basic aluminum chloride, aluminum phosphate, iron chloride, magnesium chloride, or calcium chloride. Generally, the cement, the alkaline metal silicate, usually sodium or potassium silicate, and lime are added to the wastewater and mixed well. If the silicate is in powdered form, the three materials are mixed prior to addition to the waste. The quantity of each material used is dependent on the nature of the waste to be solidified and the ratios are adjusted to control the strength of the solid product and the settling and curing time. The more cement used the stronger the product; the more silicate and lime used, the shorter the setting time. The fourth component, which may be one or more of the compounds listed above, is added as a hardening agent to the mixture of sludge and solidifying agents. The hardening agent aids in the gelatinization of the silicic acid. The best hardening agent aid appears to be aluminum sulfate because of its excellent hardening properties. With a large amount of hardening agent, the waste mixture hardens rapidly to give a solid mass which is impermeable to water and has a high strength.

The examples given in the patent used 500 g Portland cement, 200 g lime, 40 g silicate and 300 g aluminum sulfate to solidify one liter pulp wastewater which had a total suspended solids concentration of 130 ppm. Solidification occurred within 5 minutes. Other examples used different proportions of the four solidification agents. Typically 1000 g or better or solidification agents are required to solidify 1000 ml of liquid waste.

b. Solidification of Waste Oil

Fudo Kensetsu Co., Ltd.
Japanese Patent #51-96789
by Maksakuni Nakamaura *et al.* (1976)

This process solidifies oil waste which is organic oil-emulsion in water. The components in the solidification mixture are Portland cement, lime and one of the following: sodium silicate, sodium hydroxide, sodium carbonate, sodium aluminate or calcium chloride. The alkaline additives help to disperse the oil and improve the mixability of the cement and lime.

The product has a high compression strength and the solid mass shows no sign of friability after being submerged in water for a month. Normal cements formed from oily sludge and cement, sand and lime showed signs of wear after a month.

The advantages of this method include no pollution of air from burning of the oil wastes and no pollution of water when the wastes are solidified and placed in water.

c. Solidification of Liquid Industrial Waste

Ogasawars, Tetsunori
Japanese Patent #52-103177
by Tetsuro Maeda (1979)

This process solidifies the liquid industrial waste by addition of aluminum silicate and Portland cement. The wastes treated can contain aluminum, boron, cadmium, chromium, copper, iron manganese, nickel, arsenic, zinc, mercury, vanadium, fluorine, sulfite, phosphate, nitrate, thiosulfite, sulfate, cyanide, thiocyanide. The waste can be acid, alkaline, protein, carbohydrates, fat detergent, mineral oil, tar or grease. Treatments of sludges that vary to such an extent cannot be treated easily with a simple solidification procedure. The procedures described by this patent consists of the addition of 50-150 parts by weight alumina silicate and 30-100 parts Portland cement to 100 parts raw material. The resultant material is slurried. Also, an aqueous binder such as PVA, polyacrylic soda, ethylene/acetic vinyl copolymer emulsion, styrene butadiene, or latex is added. These additives help to disperse the cement grains in the slurry. The solid mass contains both a continuous polymer film and the normal concrete matrix. The crystallization of the solid mass is therefore reinforced. The permeability of the solid mass is less than 10^{-4} cm/sec and the compression strength is 10-100 kg/cm^2 after 28 days curing time.

Leachabilities of heavy metals after 28 days curing were as follows: Ni, 77 ppm; V, 0.02 ppm; Fe, 1.2 ppm; Co, 0.2 ppm; Mo, 0.3 ppm; CN, .005 ppm; Sn, Cd, Mn, Cr less than 0.1 ppm and Zn, Cr less than 0.05 ppm.

d. Method for Treating an Industrial Waste and Its Device and Solidifying Agent

Japanese Patent #51-21274
by Takashi Yamada

The solidifying process claimed in this patent is applicable to solidification of industrial waste without dewatering. The process employs an alkali metal silicate (1:1.8-3.75 ratio of SiO_2 to alkali metal oxide), sodium silicate, calcinated plaster ($CaSO_4 \cdot 1/2\ H_2O$) and a pH adjusting agent. The amount of solidifying agents needed depend on the water content of the waste. The solidification process is very rapid. The solidified product has good unconfined compressive strength and "water resisting properties" (permeability). The process can be used with a variety of materials including: 1) metal sludges, 2) water based paint sludges, 3) phosphoric acid and organic phosphate sludges, 4) waste oils, 5) river sludges, 6) animal wastes, 7) pulp wastes and 8) sea water containing sludge. The solidified material can be used for a variety of industrial materials.

B. Lime Based Techniques

1. General Description

Pozzolanic materials such as flyash, ground blast furnace slag and cement kiln dust can react with lime to form a cementation material. Since the pozzolanic materials named are themselves waste products of industrial processes, the use of these materials in waste fixation results in the consolidation of waste.

Flyash has a chemical composition of 30-50% silicon dioxide, 14-30% aluminum oxide, 1.5-4.5% calcium oxide, and 10-30% iron oxide. It is formed in the molten state in boilers and solidifies to a glass when cooled. The composition of the glass is $3\ Al_2O_3 \cdot 3SiO_2$. When mixed with lime and water, the glass is attacked by the alkali to form hydrated calcium oxide silicates and hydrated calcium oxide aluminates. This mixture has the stoichemetry of Portland cement and it behaves like Portland cement when it is mixed with liquid sludge. The cement product requires a longer setting time and is structurally not as strong as cement made with Portland cement (Michael Baker, Jr., Inc., 1978).

Blast furnace slag is the material that rises to the top of blast furnaces during the production of pig iron. Its composition includes the clay material inherent to iron ore, and limestone which is added as a fluxing agent. The slag is molten and has a uniform composition of blended lime, silica, and alumina. The composition ranges are 28-38% silicon oxide, 8-18% aluminum oxide and 35-45% calcium oxide. When the slag is cooled rapidly, it forms a glass, which if ground acts as a cement. The salt is a slow setting cement but the addition of activators such as lime, soda ash, gypsum, potash, or Portland cement accelerate the setting time to a useful range. If lime is added as the activating agent, the pH of the resultant mixture is made alkaline which increases the sequestering of the toxic metals. The blast furnace slag cement hydrates more slowly than Portland cement but the structural strength of the final product is about the same. Stoichiometrically, the composition of the blast furnace slag is the same as Portland cement (Michael Baker, Jr., Inc., 1978).

The advantages of lime based techniques are as follows (Environmental Laboratories, WES, 1979):

- the materials are low cost and readily available
- common equipment is needed for the processing since lime is a common additive to neutralize waste
- the chemistry of lime-pozzolanic reactions is well known
- extensive dewatering is not required since water is a necessary ingredient.

Disadvantages of lime based techniques are as follows:

- lime and other additives add to the weight and bulk of the waste to be disposed
- uncoated lime fixed materials may require specially designed landfills to insure that the material does not lose potential pollutants by leaching
- the techniques may not be suitable for wastes containing high levels of organics.

2. Calcilox® Solidification

Vendor:
Dravo Lime Company
650 Smithfield Street
Pittsburgh, Pennsylvania 15222
(412) 566-4433

a. Process Description

Calcilox® is the proprietary solidification additive of the Dravo Lime Company. This additive is a finely ground, hydraulically active, dry, free-flowing powder of inorganic composition derived from blast furnace slag (Michael Baker, Jr., Inc., 1978). The Calcilox® stabilization technique was developed to treat the thixotropic sludge from flue gas desulfurization process (FGD). In the Dravo processes, dry Calcilox® is added to the FGD sludge based on the dry solids content of the sludge. Dosages of Calcilox® are 5-10% of dry weight of mechanically dewatered slurries (55-70% solids) and 10-15% of dry weight of lower solids slurries (Environmental Laboratory, WES, 1979). The pH may also require adjusting to pH 11 with lime (Michael Baker, Jr., Inc., 1978). The sludge and additives are thoroughly mixed. The mixture is then placed in an impoundment for curing. During curing, the solid particles in the sludge are cemented together by the Calcilox®. As the interparticle bonds form, the void spaces are at least partially blocked, thus, reducing the permeability of the stabilized sludge (Michael Baker, Jr., Inc., 1978).

The Dravo Calcilox® additive process is in commercial application at several power plants located throughout the U.S. It is also been evaluated for coal wastes and uranium mine tailing (Environmental Laboratories, WES, 1979).

b. Properties of the Treated Sludge

The Calcilox® stabilized FGD sludges have a permeabilities in the 10^{-5} to 10^{-7} cm/sec range. Leaching data are very sketchy for the Calcilox® processed sludges. Data indicate that the leaching rates are one to two orders of magnitude below that of the raw wastes (Environmental Laboratory, WES, 1979).

The compressive strength is controlled by the amount of Calcilox® added to the sludge, the solids content of the sludge, and the cure time of the temperature (Labovitz and Hoffman, 1979). Typically, this product has a consistency similar to compacted clayish soil (Environmental Laboratory, WES, 1979).

Dravo has conducted a study comparing the solidifiction properties of Portland cement, lime and Calcilox®. All three materials possess solidification properties and are competively priced. The stabilization tests were conducted over the range of 25-35% solids in the waste slurries and 70-90% solids in the filter cakes. The different materials were compared on the basis of their unconfined compressive strength after 40 days curing time. The results from this study are shown in Table XIX. As can be seen, Calcilox® is the best stabilizer for the treatment of materials in the 25-35% solids range. Calcilox® is generally also superior to Portland cement and lime in the treatment of filter cakes (Hoffman, 1978).

c. Process Limitations and Advantages

The Calcilox® additive can be used to treat inorganic mineral process tailings that contain large amounts of silica and alumina (Environmental Laboratory, WES, 1979). It can not be used with organic or sewage sludges (Environmental Laboratory, WES, 1979). Generally, the solids content of the sludge must be between 10 and 60%. With low solids content, additional Calcilox® agent and longer cure times are necessary to achieve suitable compressive strength (Michael Baker, Jr., Inc., 1978). The pH must be adjusted to approximately 11 as low pH retards setting. The curing is not particular to conditions at the disposal site. Curing will occur in dry conditions or under water. Subfreezing temperatures will retard curing but curing will resume when temperatures rise above freezing (Michael Baker, Jr., Inc.. 1978).

Table XIX. 40-Day Unconfined Compression Strength of Treated and Untreated Fine Coal Refuse (Hoffman, 1978)

Treatment		Sample Number								
Additive	Mixed Solids	1104	1105	1106	1107	1110	1111	1112	1113	1114
		72°(1)	72°	72°	72°	72°	72°	72°	72°	72°
Untreated	25%	*(2)	*	*	*	*	*	*	*	*
	35	*	*	*	*	*	*	*	*	*
	FC(3)	*	6.6	*	*	*	*	5.1	*	*
5% Portland Type I	35	*	*	*	*	*	*	*	*	*
	FC	95.9	85.0	73.9	123.2	18.7	67.6	50.5	60.4	67.1
5% Lime	35	*	*	*	*	*	*	*	*	*
	FC	37.2	23.1	20.0	23.2	7.6	*	8.5	9.6	15.6
5% Calcilox A	35	*	8.8	8.5	10.0	0.8	1.6	4.8	1.4	2.0
	FC	78.6	124.9	80.3	218.2	81.3	50.7	98.5	106.9	89.1
5% Calcilox B	35	*	7.2	4.9	7.5	1.4	2.6	10.2	1.5	2.0
10% Portland Type I	25	*	*	*	*	*	*	*	*	*
	35	1.6	0.8	2.8	*	*	*	*	*	*
	FC	141.3	165.3	141.0	76.1	115.5	141.5	159.4	160.9	145.4
10% Lime	25	*	*	*	*	*	*	*	*	*
	35	*	*	*	*	*	*	*	*	*
	FC	39.8	12.6	22.2	15.2	16.4	13.6	13.3	14.6	16.1
10% Calcilox A	25	6.1	39.4	19.7	20.6	5.4	9.0	7.7	3.7	4.7
	35	15.1	27.0	33.9	38.9	10.8	14.1	4.5	8.4	4.4
	FC	368.6	188.5	494.4	233.7	120.0	116.6	69.9	231.2	224.5
10% Calcilox B	35	10.3	37.5	36.1	32.8	19.5	12.2	33.7	16.4	6.8
15% Portland Type I	25	*	*	*	*	*	*	*	*	*
	35	4.5	2.2	3.6	*	1.9	*	*	*	*
15% Lime	25	*	*	*	*	*	*	*	*	*
	35	*	*	*	*	*	*	*	*	*
15% Calcilox A	25	15.4	31.0	80.6	47.7	12.1	15.5	6.6	10.3	11.6
	35	24.4	30.2	59.4	35.7	17.1	21.0	13.3	24.2	15.0
15% Calcilox B	35	35.9	86.1	80.3	87.9	34.4	26.4	39.3	39.5	24.0

(1) Curing temperature measured in degrees Fahrenheit.

(2) * Indicates specimen did not have a measurable strength at 40 days.

(3) FC - Filter cake solids level - 70% 82% Solids

The stabilized sludge will not reliquify in the presence of excess water, however, reliquification can occur if the material is subjected to severe reworking (Michael Baker, Jr., Inc., 1978).

d. Economics of Calcilox® Stabilization

Costs for the Calcilox® additive are $7.30-9.10 per wet metric ton of sludge or $9.10-18.20 per dry metric ton (Hoffman, 1980). Normally, the weight percent of Calcilox® added to the waste is 5-15% of the dry solids weight (Environmental Laboratory, WES, 1979).

3. Poz-O-Tec®

Vendor: IU Conversion Systems, Inc.
115 Gibraltar Road
Horsham, Pennsylvania 19044
(215) 441-5900

a. Process Description

The Poz-O-Tec® process is a process to chemically stabilize sulfur dioxide scrubber sludges using lime, flyash, and other additives. FGD sludge is dewatered by drum vacuum filtration. The filter cake is mixed with dry flyash and lime in a mixer. The proportions for the system range from .5 to 1 part or more flyash to 1 part sludge (dry weight basis). Up to 4% of dry weight lime is added to the mixure (Michael Baker, Jr., Inc., 1978).

The Poz-O-Tec® process includes three basic steps (Michael Baker, Jr., Inc., 1978):

- reduction of moisture by mechanical dewatering and addition of flyash
- compaction of the mixture to reduce permeability and increase strength
- addition of lime to form cementitious compounds with water and flyash and sludge, thereby increasing strength, and decreasing permeability and moisture content.

The formation of cementitious materials improves the leaching characteristics of the cured product because some contaminants are included in the cementitous bonds. Thus, the permeability of the material is decreased so that there is less liklihood of leaching.

The chemistry of Poz-O-Tec® process involves an initial rapid reaction between the soluble salts in the flyash, the lime and the alumina in the flyash glass. A slower pozzolanic reaction between the silica in the flyash occurs over a period of months (Environmental Laboratory, WES. 1979).

The Poz-O-Tec® process was initially developed for solidification of FGD sludges. Over 4 million tons of the FGD sludge are treated by this process in a single year (Environmental Laboratory, WES, 1979). The process has also been applied to stabilization of wastes containing salts and heavy metal, e.g. electroplating, steel mill and chemical processes wastes (Environmental Laboratory, WES, 1979).

b. Properties of Poz-O-Tec® Solids

Typical Poz-O-Tec® solids have permeability coefficients of 10^{-6} to 10^{-8} cm/sec (Environmental Laboratory, WES, 1979). Permeabilities of 10^{-6} cm/sec are usual with freshly placed Poz-O-Tec® mixtures. The permeability is reduced to 10^{-7} to 10^{-8} cm/sec after curing (Michael Baker, Jr., Inc., 1978). The cured material has the properties similar to low strength concrete (Michael Baker, Jr., Inc., 1978). Unconfined compressive strength of the material is several thousand pounds per square foot (Michael Baker, Jr., Inc., 1978).

Leaching tests on Poz-O-Tec® solids have been performed by IU Conversions Systems Inc. (IUC). The results for Poz-O-Tec® solids immediately after stabilization and after 14 days of curring are presented in Table XX. These results were obtained by surface runoff test and not a forced leaching tests which IUC claims is not applicable to Poz-O-Tec® solids (Michael Baker, Jr.. Inc., 1978). As can be observed from the table, curing improves leachate quality considerably. The leachate composition from Poz-O-Tec® material cured for 3 1/2 months and then extracted using a shaking method is shown in Table XXI. These results are useful for comparison of the Poz-O-Tec® method with other methods of solidification because most solidification methods are tested for leachability using shaking methods.

c. Process Limitations and Advantages

The Poz-O-Tec® process is applicable to all types of calcium-based scrubbing systems wastes. It does not successfully stabilize organic wastes (Environmental Laboratory, WES, 1979). The process is not sensitive to sulfite/sulfate ratios in the sludge. The sludge may range from 30 to 90% solids. Up to 70% of these solids may be metal hydroxides or alkaline sulfates. Flyash composition can range from 10-99% (Michael Baker, Jr., Inc.. 1978). Optimum pH for stabilization is 6.5-9.0 (Michael Baker Jr., Inc., 1978).

The Poz-O-Tec® process is not particularly affected by the environmental conditions of its curing site. The chemical reactions for the cementitious process require temperatures greater than 40°F but the reactions resume when temperature rise. Wet weather does not affect the Poz-O-Tec®. As long as rainfall is not ponded on the landfill area, there should be no effect from rain.

Table XX. Results of Runoff Tests on Two Poz-O-Tec® Stabilized Sludge Samples
(Michael Baker, Jr., Inc., 1979)

Volume Equivalent to Two Inch Rainfall in 60 Minutes
(all results except pH in ppm)

	Immediate		14 Days	
	Sample A	Sample B	Sample A	Sample B
pH	8.6	9.8	7.4	7.6
p'thn. Alkalinity	10.	10.	0.	0.
MO Alkalinity (total)	230.	150.	30.	20.
Hardness	260.	250.	120.	20.
SO_3	10.	30.	5.	5.
SO_4	117.	196.	27.	16.
Cl	276.	10.	66.	6.
Total Dissolved Solids (Meter)	420.	330.	220.	60.
Al	.2	3.	—	< .1
As	< .002	.035	—	< .002
Ca	100.	100.	44.	8.5
Cd	< .01	.005	< .01	< .01
Cr	< .05	<.05	—	< .05
Cu	.03	<.02	—	.07
Fe	<.1	<.1	< .1	< .1
Hg	—	—	—	—
K	3.1	.20	3.8	.74
Mg	.05	.08	.06	.04
Mn	< .02	<.02	—	< .02
Na	7.2	1.00	3.7	.63
Pb	< .05	< .05	< .05	< .05
Sn	<1.	<1.	—	< 1.
Ti	< 1.	<1.	—	< 1.
Zn	< .05	< .02	—	< .05
Total Solids	440.	400.	200.	110.

Source: IU Conversion Systems Laboratory Data

Table XXI. TVA Shawnee Demonstration Pond C Poz-O-Tec® Core
(Samanta, 1977)

(All results except pH in mg/l)

pH	8.4
P'thn. Alkalinity as $CaCO_3$	30.
MO Alkalinity (Total) as $CaCO_3$	70.
Hardness as $CaCO_3$	460.
Sulfite as SO_3	20.
Sulfate as SO_4	172.
Chloride as Cl	316.
Total Dissolved Solids (gravimetric)	750.
Aluminum as Al	4.3
Arsenic as As	.008
Calcium as Ca	150.
Cadmium as Cd	.01
Chromium as Cr	.05
Copper as Cu	.02
Iron as Fe	.1
Mercury as Hg	.006
Potassium as K	160
Magnesium as Mg	.13
Manganese as Mn	.02
Sodium as Na	22.
Lead as Pb	.05
Tin as Sn	1.
Titanium as Ti	1.
Zinc as Zn	.02
Total Suspended Solids	1432.

d. Economics of Poz-O-Tec® Solidification

Costs for this process range from $5.50-$13.60 wet metric ton and $7.30 to $21.80 for dry metric ton. The parameters that affect the range of costs include amount of wastes to be processed, water content, and waste toxicity (Michael Baker, Jr., Inc., 1978). Costs were adjusted to 1980 costs using the CE index (Chemical Engineering, 1980).

4. Silicate Solidification Process

Vendor: Ontario Liquid Waste Disposal, Ltd.
Canadian Waste Technology, Inc.
160 Torbay Road
Markham, Ontario, Canada
(416) 495-9502

a. Process Description

The silicate process utilized by Ontario Liquid Waste Disposal Ltd., is a patented process (Canadian patent #1,009,775; British patent #1,535.024) which involves the following steps (Krofchak, 1977, 1978):

- adjustment of pH to 2-3 using sulfuric acid and ferrous sulfate
- adjust pH with lime to approximately pH 8.5
- react mixture with sodium silicate (or similar silicate) to solidify the mass

In addition to the above steps, different types of wastes may require different types of pre or post treatment. For instance, the process is not suitable for oil type wastes, therefore, an oily waste must be pretreated to remove the oil before the rest of the sludge is solidified. The role of the ferrous sulfate is to reduce various salts to form that will readily react with the lime to form an insoluble prec. An example of this is the reduction of hexavalent chromium to chromic acid or potassium dichromate to trivalent chromium. Trivalent chromium reacts readily with alkali to form a precipitate, but hexavalent chromium does not. The pH for the reduction must be low because ferric sulfate is not very soluble at higher pH. The lime is then added to the mixture to floc out metal precipitates. The final step is to react the mixture with a silicate salt which forms a solid monolithic material with the treated sludge and then fixes the sludge and its toxic materials (Krofchak, 1979). The silicate product formed is analogous to naatural geologic materials (Environmental Laboratory, WES, 1979).

The method has been used to solidify toxic wastes from waste pickle liquor, plating wastes, mine tailing waste, and sewage sludges containing less than 20% organics. The method must be evaluated for each prospective waste on a case to case basis (Environmental Laboratory, WES, 1979).

b. Properties of the Solid Product

The resultant solidified product exhibits permeability on the order of 10^{-5} cm/sec which is comparable to normal soil. The compressive strength of the product can be as high as 20.7 N/mm^2 but for reason of costs, the compressive strength is normally much lower. Leachability tests have been conducted on the solidified product. Column and shaking flask test leachate concentrations from a field sample are presented in Table XXII. The solid appeared to hold and stabilize the heavy metals.

c. Process Limitations and Advantages

The Ontario Liquid Waste Disposal, Ltd. solidification process is applicable to solidification of a wide variety of inorganic wastes including metals, chlorides, sulfates, phosphorus, etc. It is reported to be able to solidify up to 20% organics in inorganic wastes (Environmental Laboratory, WES, 1979). The process is not effective for volatile materials, oils, phenols, or decaying matter when these are present in large amounts (Kropchak, 1979). The volume of waste is not increased by this solidification process (Environmental Laboratory, WES, 1979).

d. Economics of Ontario Liquid Waste Process

Costs for this method are on the order of 2.6 to 8 cents per liter liquid waste. This corresponds to \$20.00 to \$78.50 per cubic meter sludge depending on the nature of the sludge (Krofchak, 1980).

5. Sludgemaster Process

Vendor:
Sludgemaster
P.O. Box 30737
Santa Barbara, California 93105
(805) 969-4260

The sludgemaster process is a method to solidify oil sumps and waste sludges using lime in the form of CaO. The calcium oxide reacts exothermically with the water in the sludge. Steam is given off, and hydrolysis and saponification of the sludge occur (Manchak, 1977, 1978). The patented process (Manchak, 1977) is for the idea and equipment to do *in situ* solidifications of the oil sumps. The dried and cured solid material is suitable for landfill and Sludgemaster claims that if the material is neutralized it is suitable for agricultural purposes.

Sludgemaster has other processes as well (Manchak, 1978). Details on the processes were not readily available from the owner, Frank Manchak. However, in personal communication (Manchak, 1980), he stated that it is possible to use his process for *in situ* stabilization of lagoons. The material is to be stabilized must be rendered homogeneous prior to addition of solidification chemicals. He has equipment which can mix and homogenize the sludge prior to treatment. Whether this is possible, depends upon the nature of the material to be solidified. Leachability and permeability data available are sketchy. A letter from an independent test laboratory states that:

Table XXII. Leachate Results on Waste Solidified by Ontario Liquid Waste Disposal, Ltd. Process (Krofchak, 1979)

Time, days Sample, ml pH	Solidified Product 3SP	3CL2 0-5 150 8.4	3CL2 5-7 78 10.2	3CL4 7-9 31 10.2	3CL7 12-13 36 10.5	3CL10 15-16 35	3CL 100 9 10.5	Tap Water 7.3
Assay, ppm	27,400							
1. Aluminum (Al)	27,400	0.3	0.6	0.2	0.2	0.2	0.1	0.04
2. Arsenic (As)	-----	—	—	—	—	—	—	—
3. Barium (Ba)	170	0.3	0.1	<0.08	<0.08	<0.08	0.08	<0.02
4. Boron (B)	-----	1.0	0.8	0.4	0.3	0.2	0.14	0.95
5. Cadmium (Cd)	118	< 0.1	<0.1	0.1	0.1	<0.1	<0.1	<0.1
6. Calcium (Ca)	165,000	900	580	570	630	630	880	0.56
7. Chromium (Cr)	880	0.22	0.09	0.05	0.01	<0.01	<0.01	<0.01
8. Cobalt (Co)	26	< 0.02	0.02	0.02	0.02	0.02	0.02	0.16
9. Copper (Cu0	61	0.33	0.14	0.11	0.05	0.05	0.27	0.03
10. Iron (Fe)	52,600	0.02	0.08	0.02	0.04	0.01	< 0.005	< 0.005
11. Lead (Pb)	-----	< 0.5	<0.5	<0.5	<0.5	< 0.5	0.3	—
12. Magnesium (Mg)	8,400	0.47	0.34	0.36	0.05	0.02	0.9	3.4
13. Manganese (Mn)	750	<0.001	<0.001	<0.09	<0.04	< 0.08	< 0.001	0.07
14. Mercury (Hg)	-----	—	—	—	—	—	—	—
15. Molydenum (Me)	-----	1.60	0.78	0.59	0.05	0.02	0.96	0.13
16. Nickel (Ni)	144	<0.1	< 0.1	<0.1	< 0.1	<0.1	< 0.1	<0.02
17. Phosphorus (P)	1,120	<0.5	0.5	0.8	0.8	0.9	< 0.1	<0.1
18. Potassium (K)	-----	4	3	2	2	2	—	2
19. Sodium (Na)	7,600	1280	68	41	25	22	1140	22
20. Silicon (SI)	183,000	4.5	4.5	2.8	1.8	1.6	0.91	0.56
21. Strontium (Sr)	190	1.2	0.87	0.73	0.87	0.90	1.4	0.19
22. Titanium (Ti)	1,810	0.001	0.001	0.004	0.006	0.005	< 0.001	0.002
23. Vanadium (V)	52	<0.01	<0.01	<0.01	<0.01	<0.01	< 0.1	0.02
24. Zinc (Zn)	42,800	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

> "The reacted sludge from the Manchak process does not leach with dionized water to any degree. Heavy metal reductions from 86% to 99.9% have been obtained during certified testing. Very low concentrations of various organic pesticides and chemicals have been found in the leachate from reacted sludge reportedly containing much higher concentrations" (BTC Laboratories, 1978).

The estimated costs for the solidification of lagoon type waters range from 1.3 to 2.4 cents per liter liquid sludge. These costs include process equipment, chemicals and operational labor. The final product would have a volume of approximately one tenth the starting waste material.

C. Organic Polymeric Techniques

Organic polymeric techniques were originally developed for and applied to solidification of radioactive wastes so that they could be legally transported. The solidification process is normally carried out in batches and involves mixing of the organic polymer with the wastes to form a homogeneous material. The polymerization catalyst is then added and dispersed uniformly throughout the material. Mixing is stopped prior to polymerization and the material is poured into a drum or other container (Environmental Laboratory, WES, 1979; Holcomb, 1979). The polymers generally do not react with or absorb the wastes. The solidification is accomplished by trapping the waste material in the voids formed when the polymer is cross-linked (Environmental Laboratory, WES, 1979; Holcomb, 1979).

The organic polymeric solidification techniques are still very much in the developmental stages. Urea-formaldehyde resins were the first polymers used for solidification and continue to be the only polymeric solidification method commerically available (Holcomb, 1979). However, the reported biodegradability of this polymer makes it impractical for solidification of toxic wastes. Several commercial companies and researchers have developed promising organic polymeric solidification techniques. These techniques will be discussed in the following sections.

The major advantages of polymer resin solidification include (Environmental Laboratory, WES, 1979):

- less fixative is required for the same amount of liquid wastes
- the waste material is usually dewatered prior to solidification thus reducing volume
- organic resins are not as dense as concrete thus reducing transportation costs
- solidified resins are not flammable and high temperature are not required for the formation of the polymer

The disadvantages of organic polymers are:

- the wastes are not chemically bound to the resin, they are only enclosed in the resin matrix. If the resin matrix is destroyed (such as by biodegradation) the toxic wastes are released
- some of the catalysts used are highly acidic which can increase the solubility of the toxic wastes. Catalyst such as peroxides are highly explosive and caution must be taken in handling them
- uncombined water may be associated with the solidified polymers. This water must be evaporated to form the fully cured polymer and the water may contain toxic waste
- some of the cured polymers are biodegradable
- the reactions which form polymeric resins often releasing harmful fumes
- Commonly the product of the polymer waste reaction is stored in drums which increase transportation and storage costs.

1. Dow Process

. U.S. Developer: Dow Chemical Corporation
2020 Dow Center
Midland, Michigan 48640

The Dow process has been used mainly for solidification of radioactive wastes. The Dow polymer is a commercially available modified vinyl ester resin which forms a stable emulsion with the waste. The polymerization is initiated with the addition of a catalyst and a promoter. The wastes to be solidified may have pH range of 2.5-11.0 with good results in the solidification. The product is placed in either 55 gallon drums or 50 cubic foot containers prior to being mixed with the catalyst and promoter and it is cured in the container (Filter and Roberson, 1977).

The final solid product is a uniform liquid free material which immobilizes wastes homogeneously. There is a minimum of leaching of radioisotopes to the environment and the product is resistant to both high temperatures and radiation. The compressive strength of the final product is on the order of 8.3 to 33.0 N/mm^2 (Filter and Roberson, 1977). The leachability of lithium and cobalt from the Dow polymer system is compared to the leachability of these materials from cement in Figure 6. As can be seen from the figure, the Dow system is comparable to cement.

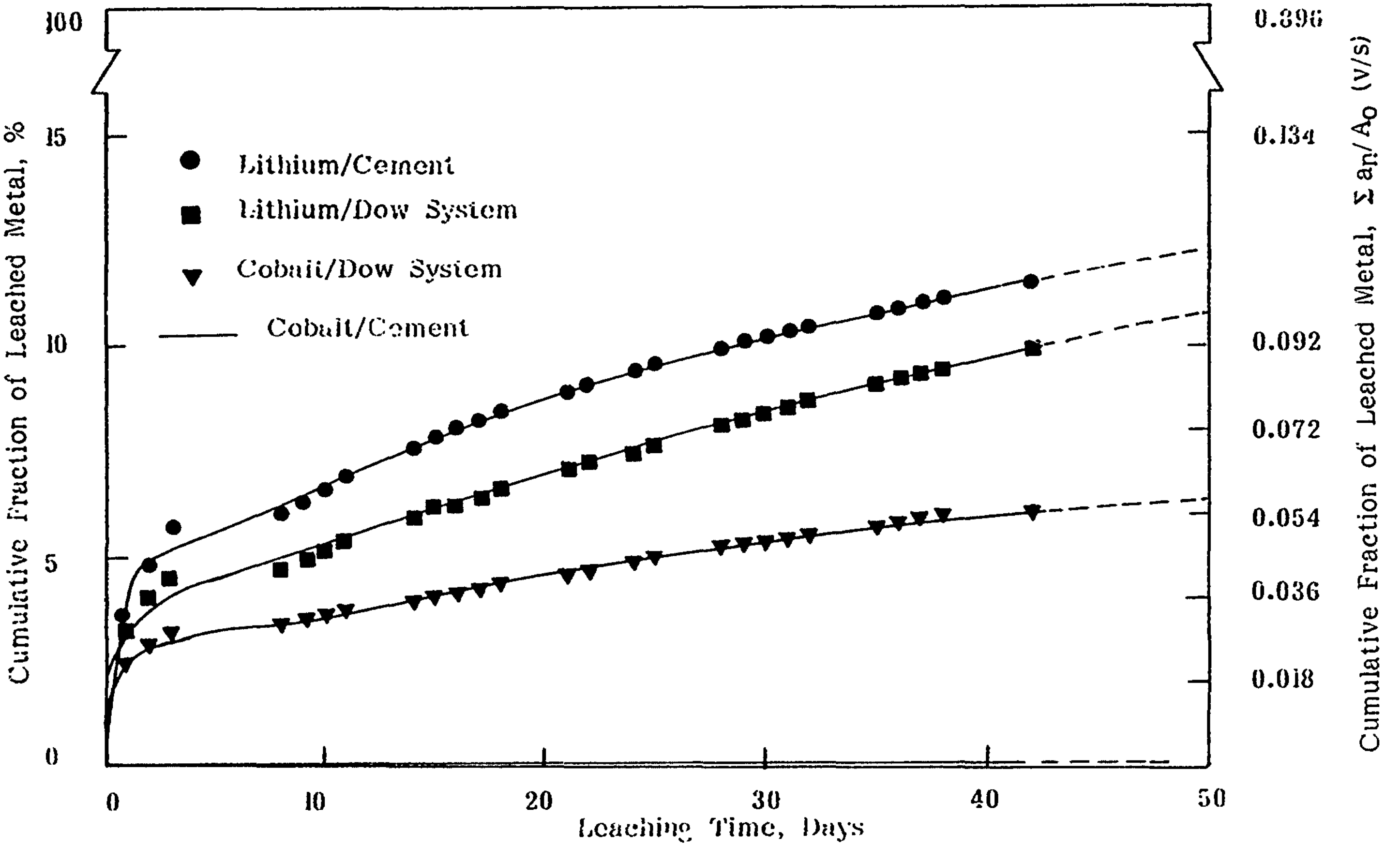


Figure 6. Leach Tests for Cobalt and Lithium With 1.25/1.0 Simulated Waste/Solidification Material (Filter and Roberson, 1977)

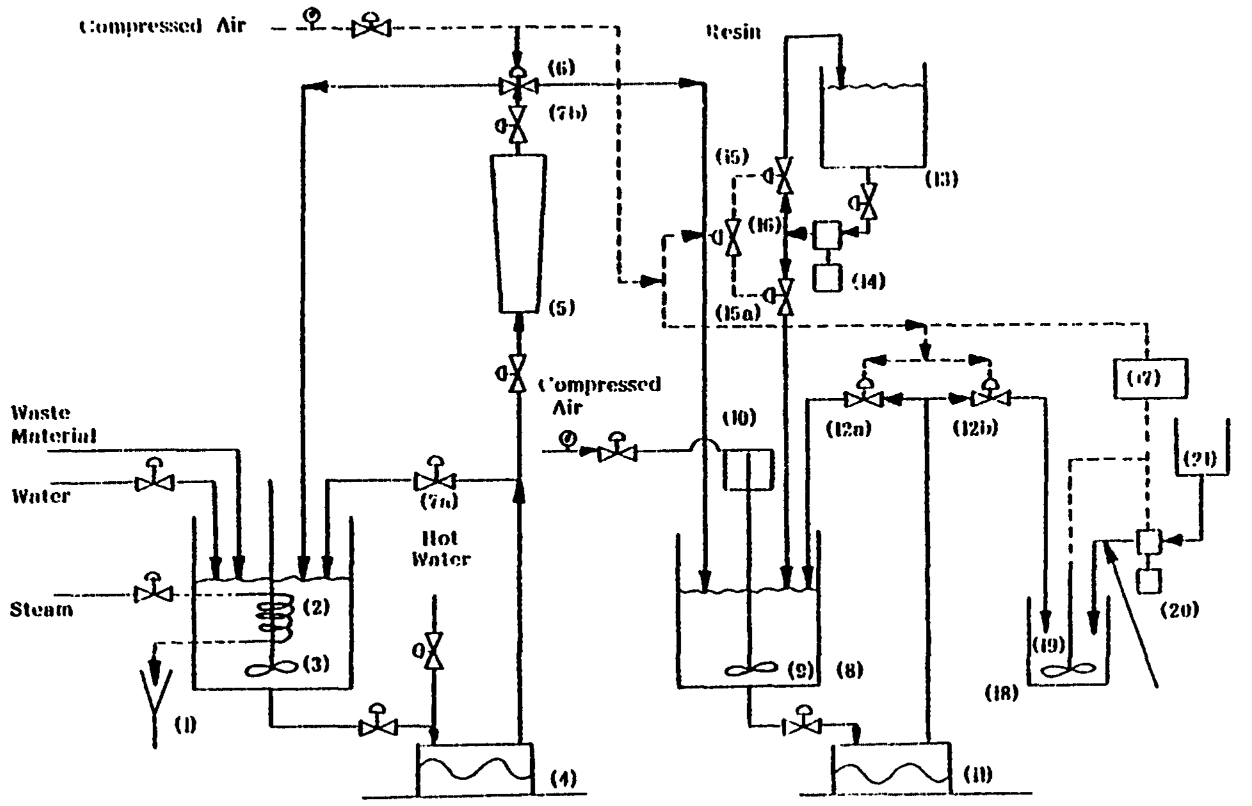
The chemical costs for the Dow process are higher ($1.25/lb) than the chemical costs of some of the other procedures (Donovan, 1980). Since the Dow process has not been used on waste toxic materials such as sludge, cost data for the solidification of sludges is not readily available.

2. Washington State University

Developmental work with polymer solidification performed by Subamanian and Mahalingan (Washington State University, 1979) appears very promising. The process uses water-extended polyesters which are unsaturated polyesters. These esters contain carbon-carbon double bonds in the backbone of the polymer chain. The polymer backbones are composed of unsaturated acids. saturated acids and glycols. The saturated acids provide the spacing for the unsaturated acids and the glycols react with the dibasic acids forming the polyester. The unsaturated acids provide sites for cross linking of the polymeric chains. Important characteristics of the polymer, such as chemical composition, physical properties and water compatability can be determined by the choice of dibasic acids and glycols used to form the polymer. The unsaturated polyester is often dissolved in a polymerizable monomer such as styrene to form a low viscosity liquid which can be emulsified with water. The resultant material is treated with a catalyst which initiates the free radical mechanism of styrene polymerization. The free radical reactions proceed to form polyester chains joined by polystyrene chains. The resultant material contains three dimensional polymer rings of various sizes which encapsulate the waste (Subramanian and Mahalingam. 1979a,b).

A pilot plant was built and operated using this procedure for solidification (Subramanian and Mahalingam (1979b). The plant operation, shown in Figure 7, can be divided into three different functions: 1) the waste solution is preparrd in an aqueous slurry, 2) the waste and the polymer resin are dispersed with each other in a predetermined ratio, 3) the emulsion/dispersion from step two are transferred to containers and the initiator for the solidification is added.

The Washington State University (WSU) procedure has been used primarily with radioactive wastes, however, some test work was performed with sludges. Some of the materials tested by WSU with their solidification method are listed in Table XXIII. As can be seen in the table, most of the materials tested were hard set by the polymerization. Problems arose with wastes such as hexavalent chromium because the chromium is capable of poisoning the polymerization reactions by entering into redox reactions with the promoters and the initiators. Some organic liquids are not toally compatable with the polyester (for example see paint pigment sludge C4) and separation of the emulsion occurs. This separation can be controlled to some extent by decreasing the amount of waste mixed with the polyester. A point apparent with the work performed at WSU, which is also true for all the solidification procedures, is that every waste must be tested on its own merits and the resultant solidification procedure must custom designed to the individual wastes (Subramanian and Mahalingam, 1979b).



1. Waste Preparation Tank
2. Steam Coil
3. Variable-Speed Paddle Mixer
4. Variable-Speed Screw Pump
5. Rotameter
6. 3-Way Ball Valve with Pneumatic Actuator
7. a,b Flow Control Valves
8. Emulsification Tank
9. Variable-Speed Turbon Mixer
10. Air Motor
11. Variable-Speed Screw Pump
12. a,b Ball Valves with Pneumatic Actuators
13. Resin Tank
14. Resin Metering Pump
15. a,b Diaphragm Valves
16. 4-Way Solenoid Valve
17. Timer
18. Solidification Can
19. Variable-Speed Helicone Mixer
20. Initiator Metering Pump
21. Initiator Tank

Figure 7. Pilot Plant Flowsheet - Polyester Process for Encapsulation of Hazardous Wastes (Subramanian and Mahalingam, 1979b)

Table XXIII. Results of Polyester Encapsulation of Hazardous Wastes (Subramanian and Mahalingam, 1979b)

	Waste Type	Dispersion Method[a]	wt% Waste	Initiator and %[b]	Curing Temp (°C)	Time to Peak Exotherm	Solidification Behavior
A1	24% Sodium Sulfate Solution, 30°C	A	75	SR, 1% SR, 1% SR, 1%	25 25 50	120 min 45 min 40 min	Hard set w/o free liquid Hard set w/o free liquid Hard set w/o free liquid
A1a	50% Sodium Sulfate Slurry, 40°C	A	75	LD	RT		Hard set w/o free liquid
A1b	Dry Sodium Sulfate	B	resin 22.2 water 33.3 waste 44.4	LD, 2%	50	120 min	Hard set with loose Structure
A2	12% Boric Acid pH 8, RT	A	72	SR, 1%	25	30 min	Hard set w/o free liquid
A3	20% Boric Acid pH 8.4, 50°C	A	71	LD, 4%	40	100 min	Hard set w/o free liquid; time reduced by further addition of dimethyl aniline
A7	VR Sodium Sulfate Sulfate	B	resin 25 water 37.5 waste 37.5	LD, 2%	RT	45 min	Hard set w/o free liquid
A7a	VR Sodium Sulfate	C	75	LD, 0.5%	RT	10 min	Hard set
A8	Dehydrated Sodium Borate	B	resin 25 water 37.5 waste 37.5	LD, 1%	50	120 min	Retarded solidification reaction; hard set
A8	VR Sodium Borate	C	70	LD, 2%	RT	60 min	Retarded solidification reaction; hard set
A9	VR Sodium Borate	C	70	LD, 2%	50	60 min	Retarded solidification reaction; hard set
C1	Heavy Metals Mixed Organic Waste	A	40	SR, 2%	RT	120 min	Hard set w/o free liquid
C2	Organic Chloride Waste	A	64	SR, 2%	RT	60 min	Highly viscous emulsion, hard set w/o free liquid
C3	Organic Waste	A	75	SR, 2%	RT	30 min	Hard set; thin layer of organic liquid on surface

Table XXIII. (cont.)

	Waste Type	Dispersion Method[a]	wt% Waste	Initiator and %[b]	Curing Temp (°C)	Time to Peak Exotherm	Solidification Behavior
C4	Pigment Sludge	A	69	SR, 2%	RT	30 min	Hard set; thin layer of organic liquid on surface
C5	5% $HgCl_2$	A	60	LD, 4%	RT	-	Phase separation
C6	Chloride Reagent Waste	A	60	LD, 2%	RT	-	Phase separation
C6a	Chloride Reagent Neutralized with NaOH pH 5-12	A	72	LD, 2%	RT	90 min	Hard set w/o phase separation
C7	Process Slurry	A	60	LD, 2%	RT	90 min	Solidified with sticky surface
C8	Cyanide Solution	A	40	LD-X, 4%	RT	60 min	Hard set w/o free liquid
C9	Cyanide Sludge	A	64	LD-X, 4%	RT	16 min	Hard set w/o free liquid
C10	Kepone Sludge	A	50	LD, 2%	50	120 min	Hard set, rubbery solid
C11	PCB	C	50	LD, 2%	RT	11 min	Flexible solid (plasticized)
C12	Arsenic Trioxide	C	70	LD, 1%	RT	15 min	Hard set
C13	Arsenic	C	70	LD, 2%	50	30 min	Hard set
C14	Arsenate Solution	A	60	LD, 2%	RT	100 min	Hard set

[a] Disperson methods are designated as:
A: emulsification of liquid waste (or slurry) in polyester resin;
B: dispersion of solid waste in preformed water/resin emulsion;
C: dispersion of solid into neat polyester resin

[b] Initiator concentration based on resin:
SR: Superox 38
LD. Lupersol Delta
AP: Aposet.

The resultant hard set solids made by this process had compressive strengths which ranged from 11.6 N/mm^2 to 14.9 N/mm^2 depending upon the vigor with which the waste is mixed with the polymer. The compressive strngth also decreased with increasing amounts of waste materials (see Figure 8) (Subramanian and Mahalingam, 1979b).

The leachability of polyester encapsulated sodium sulfate waste was compared with strontium waste ecapsulated in a cement matrix. The cumulative percent metal ions leached in 1000 years from the encapsulated wastes were calculated from the relationship:

$$L = a \bullet T^b$$

where L = cumulative leachability
T = time
a,b = constant determined from experimental data

These comparisons are shown in Table XXIV. The percentage of metal ion leached from the polyester matrix is significantly lower than that observed for cement.

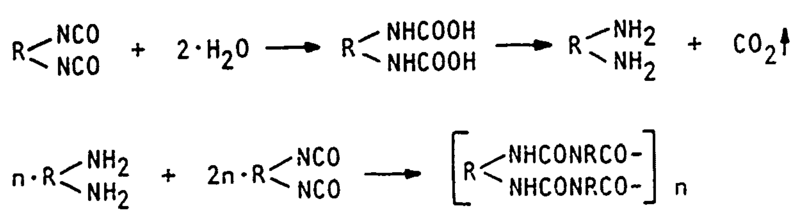
The cost for polyester polymeric solidification using the WSU pilot plant is \$290/m^3 of waste (Subamanian and Mahalinganm, 1979b).

3. Deep Chemical Mixing

U.S. Vendor: TJK, Inc. representative for
Takenaka Komuten Co., Ltd.
7407 Fulton Avenue
North Hollywood, CA 91605
(213) 875-0410

TJK, Inc. is licensed to perform services referred to as Deep Chemical Mixing (DCM) and Takenaka Sludge Treatment (TST). Both of these procedures can use either cement or an organic polymer as the solidification agent. Cement type solidification agents were detailed in earlier sections of this report and no novel information about cementitious agents was available from TJK.

The organic polymer solidification agent is a urea polymer gel produced when an organo-cyanate reacts with water according to the following reactions:



$$R\begin{array}{l}\diagup NCO\\ \diagdown NCO\end{array} + 2\cdot H_2O \longrightarrow R\begin{array}{l}\diagup NHCOOH\\ \diagdown NHCOOH\end{array} \longrightarrow R\begin{array}{l}\diagup NH_2\\ \diagdown NH_2\end{array} + CO_2\uparrow$$

$$n\cdot R\begin{array}{l}\diagup NH_2\\ \diagdown NH_2\end{array} + 2n\cdot R\begin{array}{l}\diagup NCO\\ \diagdown NCO\end{array} \longrightarrow \left[R\begin{array}{l}\diagup NHCONRCO-\\ \diagdown NHCONRCO-\end{array}\right]_n$$

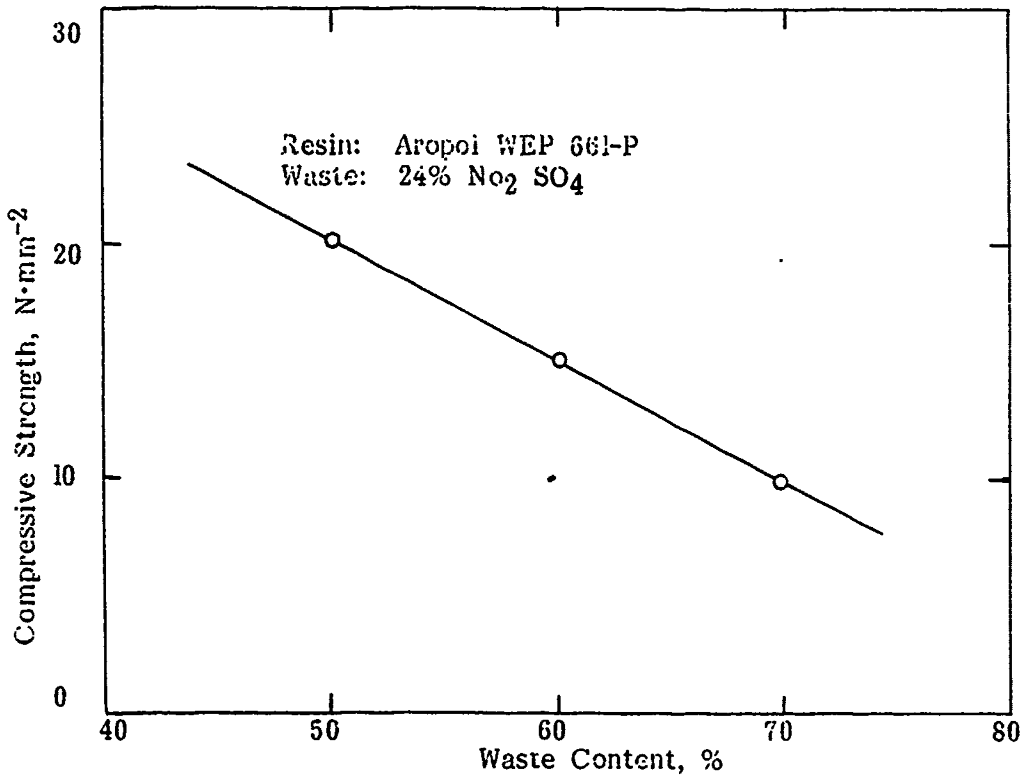


Figure 8. Compressive Strength of Polyester-Encapsulated Sodium Sulfate Waste Composite (Subramanian and Mahalingam, 1979b)

Table XXIV. Comparison of the Efficiencies of the Polyester Matrix and Cement in Immobilizing Metal Ions

Sample	Net Waste (%)	% Metal Ion Leached in 1,000 Years[a] (%)
Polyester Matrix[a,b]		
i-1	14.4	0.048
i-2	14.4	0.44
i-3	14.4	0.051
i-4	14.4	0.053
D-3	14.4	0.053
D-4	12.0	0.066
H-1	14.4	0.174
H-2	14.4	0.084
H-3	14.4	0.189
H-4	14.4	0.280
Cement Matrix[c]		
A-1	6.52	(100% leached out in 172 years)
A-2	6.52	21.6
A-3	6.52	8.62

The polymer has a three dimensional structure which binds solid particles and results in a solid of high structural integrity. Numerical data on uncompressed strength was not available. The water content of the material to be solidified varies form 60-80%.

The TST process requires the pumping of the sludge to the treatment center. The DCM process can take place *in situ.* The mixer used for DCM is shown in Figure 9. DCM has been used primarily as as stabilizer for underwater silt and soft ground. It is used to make these sites stable for construction. The solidification agent is pumped through the shaft of the mixer. The mixer blades mix the solidifying agent with the sludge.

Firm cost data were not available from TJK, Inc., since this process has not been used to solidify lagoon water. An estimate for the amount of polymer required to solidify sludge is 100 liters of polymer to 900 Kg sludge (Christensen and Wakamiya, 1980). The cost for the polymer is approximately $6.00 per liter (TJK, Inc., 1980), so the cost to solidify a Kg of sludge is approximately $.67 per Kg or $670.00 per metric ton for chemicals alone.

4. Method for Treating a Waste Solution

Mitsubishi Rayon
Japanese Patent #49-106965
Takashi Sunamori *et al.* (1974)

This patented process used a mixture of hydrophilic vinyl and divinyl or polyvinyl compounds to solidify liquid wastes containing organic and inorganic substances. A three dimensional gel is formed in which the waste is incorporated. Gellation is rapid. Types of vinyl compounds which can be used include N-metholacrylic amide, N-methylmethacrylic amide, 2-hydroxyethyl acrylate, etc. Divinyl or polyvinyl components which are usable in the invention include N,N'-methylene bisacrylic amide, N,N'-methylbismethacrylic amides, etc. Polymerization initiaters include ammonium or potassium persulfate and a reducing agent such as dimethylaminoproprionitrile.

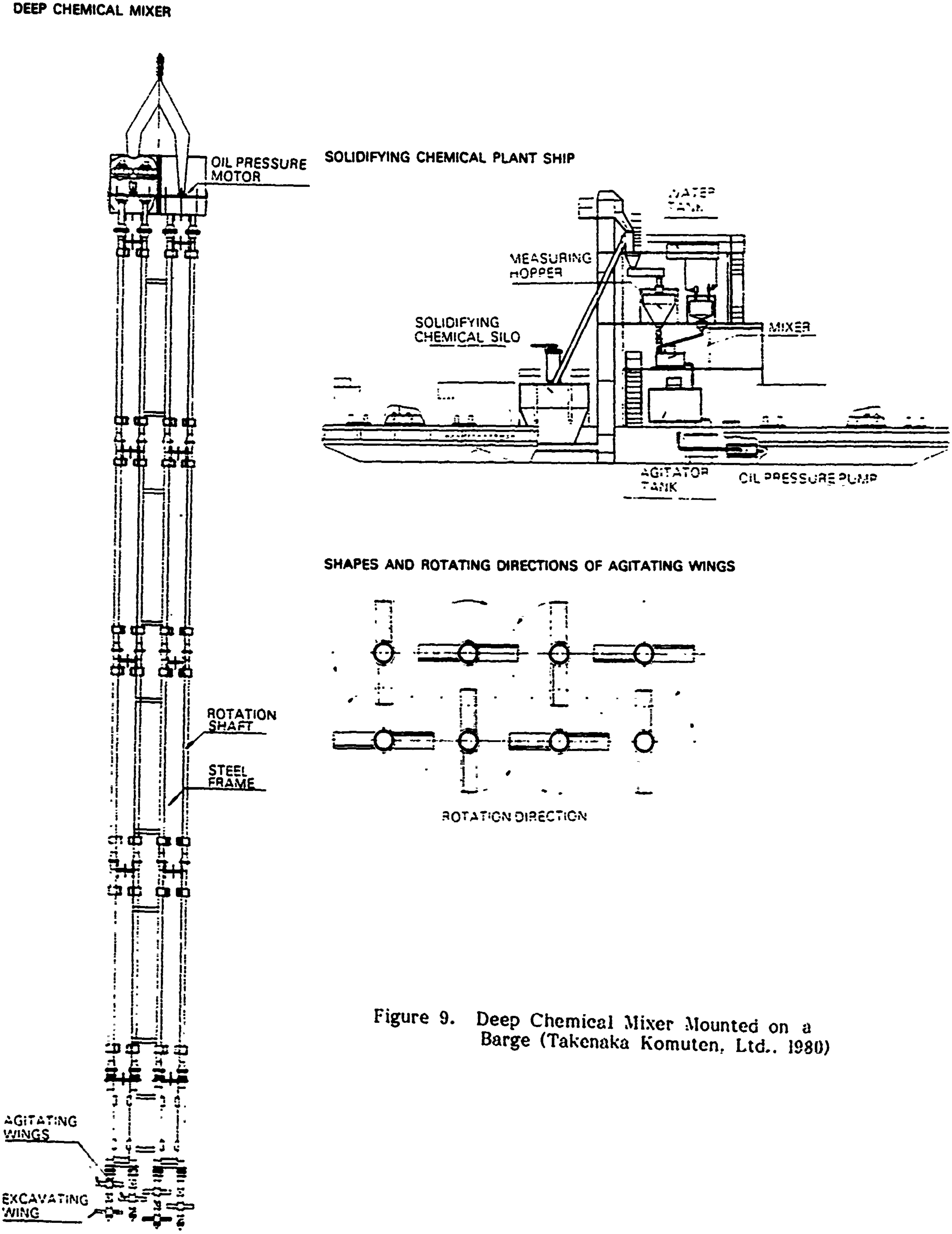


Figure 9. Deep Chemical Mixer Mounted on a Barge (Takenaka Komuten, Ltd., 1980)

III. APPLICATION OF SOLIDIFICATION TECHNIQUES TO SOLIDIFYING THE WASTES IN BASIN F AT ROCKY MOUNTAIN ARSENAL

A. Summary of Techniques

The pertinent features of the various solidification processes discussed in this report are summarized in Table XXV. For the most part, the solidification methods depend on decreased permeability for their fixation properties. The permeabilities for most of the solids range from 10^{-6} to 10^{-8} cm/sec which is slightly less than the permeability of normal soil. The solidification methods also depend upon chemical bonding to the wastes and physical entrapment of waste particles for their fixation properties. When physical entrapment is important, the compressive strength of the fixation method and the friability of the solidified product becomes important. Compressive strength is a direct function of process cost. The compressive strengths for cement processes range from .4 to 5.5 N/mm^2. As an example of the increase in costs for higher compressive strengths, Stablex Corporation offers materials with compressive strengths of 1.4 to 5.5 N/mm^2 with a corresponding cost range of $5.00 to $350.00 per metric ton of waste solidified. The lime methods have final compressive strengths that are comparable to the cement methods. Data on compressive strengths for organic polymer methods were not available.

Generally, the waste to be solidified contains between 40 and 60% solids. If the sludge as produced does not contain at least 40% solids, the sludge is dewatered prior to solidification. Solidifying material that contains less than 40% solids is cost prohibitive because of the high requirement for processing chemicals. The material that is to be solidified must be homogeneous prior to being mixed with chemicals. Most processes require a mixing chamber prior to passage to the mixer where chemicals are added. Homogenity of the waste is required because the chemicals which are added to fixate the waste are custom designed to each waste problem. Different components in the waste can drastically alter the setting or curing of the solidified mass. For example, organic materials can cause the spalling of cement products, therefore, wastes containing high levels of organics may require pretreatment prior to solidification with cement or lime based processes. Organic polymer methods are affected by components which may act as poisons to the initiator or promoter reactions required for the formation of the polymers. Factors such as these must be taken into account prior to planning a solidification program.

The methods surveyed generally did not recommend solidification *in situ*. One of the cement processors (Sludgemaster, Inc.) has equipment and a procedure to do *in situ* solidification, but it was not their recommended method for large scale solidifications. The DCM method (Takanaka Komuten, Ltd.) also could be used for *in situ* solidifications. The DCM method is advertised for solidification of soft ground and river bottoms. Details on the capabilities of DCM for solidifying liquid wastes are not available.

Table XXV. Summary of Solidification Techniques, Their Applicability and Associated Costs

Process	Additive Materials	Types of Wastes Solidified	Types of Wastes Excluded	% of Agent	Solidification Costs‡ (metric ton dry weight sludge)
LTC*	bentonite clay-Portland cement	Heavy metals; inorganics; organics up to 5% of wastes	Organics >5% of wastes	10% (weight)	$5.51-26.46 (does not include equipment costs)
Chemfix™	Soluble silicates and silicate setting agent	Heavy metals	Chlorides, sulfates, monovalent cations, organics	10% (volume)	$6.00-10.50
Terra-Tite™	No data available	Most inorganic and organic wastes	Sludges with 12% solids grease, oils or solvents	No data available	Not available
Terra-Crete™	Calcium sulfite and calcinated gypsium	Flue gas desulfurization sludge	No data available	NA	$2.30-3.20
Petrifix™	Calcium silicates, proprietary activators	Most inorganic and organic wastes	No data available	No data available	Not available
Stablex™	Two silicates	Most inorganic and organic wastes	Oils, solvents, greases	No data available	$5.00-350.00
Calcilox™	Calcilox™	FGD sludges	Organic or sewage sludges	5-15%	$9.10-18.20
Poz-O-Tec™	Lime, flyash, and other additives	FGD sludges, salts and heavy metal wastes	organic sludges	0.5-1 part flyash to 1 part sludges, up to 4% lime	$7.30-21.80
Silicate Solidification	Sulfuric acid/ferrous sulfate, lime and sodium silicate	Inorganic sludges and sewage sludges containing less than 20% organics	High concentration organic sludges, volatile materials, phenols	Data not available	$20.00-78.50/m^3 sludge
Sludgemaster	Calcium oxide	Oily wastes	Data not available	Data not available	1.3-2.4¢/gal. sludge
Dow Process	Vinylester resin	Radioactivated wastes	Data not available	Data not available	$1.75/lb of chemical
Washington State	Unsaturated Polyesters	Radioactive Wastes	Some organics, chromium compounds	Variable	$290/m^3 of waste.
Lakenala	Organo cyanate	Soils	Data not available	Data not available	$670 (chemicals only)

Costs for the various processes vary greatly depending upon the nature of the material to be solidified and the desired final characteristics of the materials. Cement and lime based processes are generally cheaper than organic polymer processes.

B. Specific Applications to Solidification of Basin F

Basin F is a 90-acre waste lagoon located at the Army's Rocky Mountain Arsenal. This lagoon currently contains approximately 378,500,00 liters of water contaminated with organics, heavy metals and anions. The analysis of the water is presented in Table XXVI. The analysis of the Basin F sediment is also shown in Table XXVI. This sediment is heavily contaminated with organics and heavy metals. The solids content of the Basin F water is about 16% (Buhts *et al.*,. 1978). For solidification, it is desirable to have a waste with a solids content of approximately 40%. This solids concentration can be achieved by dewatering the Basin F water or combining the sediment with the aqueous waste.

To determine the solids content of a sediment/lagoon waste mixture, the following parameters were assumed:

- approximately 0.61 m of the lagoon sediment is contaminated
- the sediment contains 50% solids

Thus, for a 90-acre lagoon, 221,000 m^3 of sediment must be treated. If this sediment is combined with the aqueous waste, 600 x 10^6 liters of wastes containing 29% solids will have to be treated. This solids content is still below ideal. However, it could be treated. Alternatively, it could be dewatered or the sediment from Basin A could be combined with it. Basin A is approximately 60 acres. If 0.61 m of sediment in this basin were removed and combined with the Basin F wastes, approximately 750 x 10^6 liters of waste containing 38% solids would have to be treated (assuming Basin A sediment is 75% solids). The resulting mixture should contain less than 4% organics.

Based on the data available on the Basin F and the solidification techniques, only seven techniques appear to be applicable to solidification of the basin:

- ETC
- Terra-Tite®
- Stablex®
- Silicate Solidification (Ontario Liquid Waste Disposal, Ltd.)
- Sludgemaster
- Washington State University
- Takenaka

Table XVI. Basin F Analysis (Buhts *et al.*,.1978)

Chemical	Water Analysis	Sediment Analysis
pH	6.9-7.3	16-10,700 ppm
Aldrin	20-480 ppb	16-10,700 ppm
Isodrin	<1-17 ppb	2-870 ppm
Dieldrin	5-110 ppb	4-3600 ppm
Endrin	3-42 ppb	2-1100 ppm
DDT	-	<2-198 ppm
Dithiane	<20-123 ppb	-
DIMP	6-33 ppm	1-10 ppm
DMMP	320-3750 ppm	<1-82 ppm
Sulfoxide	4-10 ppm	-
Sulfone	19-76 ppm	14-290 ppm
Chloride	47,500-57,500 ppm	-
Sulfate	20,500-32,500 ppm	-
Copper	709-758 ppm	230-21,000 ppm
Iron	5-13 ppm	190-11,000 ppm
Nitrogen	112-147 ppm	-
ortho-Phosphate	99-131 ppm	-
Total Phosphate	2060-2170 ppm	<1-34,300 ppm
Hardness	2090-2858 ppm	-
Fluoride	110-117 ppm	-

The Washington State University Process is not developed to the scale where it can handle large volumes of wastes. Little is known about the Terra-Tite process. The Takenaka processes could be done *in situ* with their DCM, however, this mixer is not currently available in the U.S. Sludgemaster also has an *in situ* process. The Stablex® and Ontario Liquid Waste Disposal, Ltd. processes are also not currently available in the U.S. Solidification of Basin F will require the construction of a permanent solidification unit on site or a mobile unit. Of the companies with potentially applicable solidification techniques for Basin F, only Sludgemaster has a mobile unit.

Reliable costs for solidification of Basin F are impossible to determine without solidification and leaching tests. Depending on the amount and type of chemicals necessary for the solidification, the cost for the solidification alone could range from \$5.00-\$350.00 per metric ton of dry sludge. The \$5-\$50/ton range would be for sludges that have high solids content and use small amounts of chemical. For those sludges approximately 40% solids, cost of \$50-\$150/ton could be expected. For low solids sludges, costs from \$150-\$350/ton are expected. Thus, to solidify 600 x 10^6 liters at 29% solids will cost approximately \$14.3 to 42.9 million; for 750 x 10^6 liters at 38% solids, costs will be \$26.2-61.3 milliion. Processing time for the wastes will be about 16 months (Manchak, 1980).

It must be emphasized that these costs are very rough estimates. The ability of any of the solidification processes to treat the Basin F wastes is unknown. The only way to determine which processes, if any, are viable for the Basin F wastes is to subject the wastes to several of the various solidification procedures and perform leaching tests on the final products.

Solidifiction may be a viable solution to the Basin F problems at Rocky Mountain Arsenal. *In situ* solidification would be the most appealing alternatives, however, it is probably not viable given current U.S. technology. For most processes, the wastes will have to be dredged from the lagoon. The dredging process will add to the cost of the solidification and present toxic exposure problems for workers. The solidified waste will have to be disposed of. The ideal spot for disposal would be the basin. Redisposal in the basin could be achieved if it were diked off in sections.

In general, it appears that solidification of Basin F will be an expensive undertaking, however, more accurate costs can not be established until laboratory testing is performed. If after consideration of other alternatives, further evaluation of solidification is desirable, the following approach is suggested:

- Five processes be evaluated with 3 variables each: ETC, Terra-Tite®, Stablex®, Ontario Liquid Waste Disposal, Ltd., Sludgemaster
- The solidification procedure should be witnessed and verified by an independent observer

- The leaching tests should be conducted by an independant laboratory (all the leaching tests should be conducted by the same independent laboratory)
- The optimum solidification process should be chosen on process costs, leachability and economics.

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