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Technology Transfer

EPA

Stabilization/ Solidification of CERCLA and RCRA Wastes

Physical Tests, Chemical Testing Procedures, Technology Screening, and Field Activities

Table 3-1. Solidification case studies.

Site/ contractor	Contaminant (concentration)	Treatment volume	Physical form	Chemical pretreat-ment Y/N	Binder	Percentage binder(s) added	Treatment (batch/ continuous in situ)	Disposal (onsite/ offsite)	Volume increase, %	Scale of operation
Independent, Nail, SC, Region IV	Zn, Cr, Cd, Ni	6,600 yd^3	Solid/soils	N	Portlant cement	20%	Batch plant	Onsite	>Small	Full scale (de-listing in progress
Midwest, U.S. Plating Company, Envirite	Cu, Cr, Ni	16,000 yd^3	Sludge	N	Portland cement	20%	In situ	Onsite	>0	Full scale
Unnamed, ENRECO	Pb/soil 2-100 ppm	7,000 yrd^3	Solid/soils	N	Portland cement and proprietary	Cement (15-20%) proprietary (5%)	In situ	Landfill	Mass >20% (volume >30-35%)	Full scale
Marathon Steel, Phoenix, AZ Silicat, Tech.	Pb, Cd	150,000 yd^3	Dry - landfill	N	Portland cement and silicates (Toxsorb)™	Varied 7-15% (cement)	Concrete batch plant	Landfill	NA	Full scale
Alaska Refinery HAZCON	Oil/oil sludges	2,300 yd^3	Sludges, variable	Y	Portland cement and proprietary	Varied 50+	Concrete batch plant	Onsite	>35%	Full scale
Unnamed, Kentucky, ENRECO	Vinyl chloride Ethylene dichloride	180,000 yd^3	Sludges, variable	Y	Portland cement and proprietary	Varied 25 +	In situ	Onsite (2 secure cells built on site)	>7-9%	Full scale
N.E. Refinery ENRECO	Oil sludges, Pb, Cr, As	100,000 yd^3	Sludges, variable	N	Kiln dust (high CaO content)	Varied, 15-30%	In situ	Onsite	>Varied, ~20% average	Full scale
Velsicol Chemical Memphis Env. Centre	Pesticides and organics (resins, etc.) up to 45% organic	20,000,000 gallons	Sludges, variable	N	Portland cement and kiln dust, proprietary	Varied (cement 5-15%)	In situ	Onsite	>Varied ~10% or less	Full scale
Amoco Wood River Chemfix	Oil/solids Cd, Cr, Pb	90,000,000 gallons	Sludges	Y	Chemfix proprietary	NA, proprietary	Continuous flow (pro-prietary process)	Onsite	Average 15%	Full scale (site delisted 1985)

(continued)

Table 3-1. (continued)

Site/ contractor	Contaminant (concentration)	Treatment volume	Physical form	Chemical pretreat-ment Y/N	Binder	Percentage binder(s) added	Treatment (batch/ continuous in situ)	Disposal (onsite/ offsite)	Volume increase, %	Scale of operation
Pepper Steel & Alloy, Miami, FL VFL Technology Corporation	Oil sat: soil Pb - 1000 ppm PCB's - 200 ppm As - 1-200 ppm	62,000 yd^3 (plus 5000 tons of surface debris)	Soils	Y	Pozzolanic and proprietary	~30%	Continuous feed (mixer proprietary) design	Onsite	~1%	Full scale
Vickery, Ohio Chemical Waste Management	Waste acid PCB's (<500 ppm), dioxins	~235,000 yd^3	Sludges (viscous)	Y	Lime and kiln dust	~15% CaO ~5% kiln dust	In situ	Onsite (TSCA cells)	>~9%+	Full scale
Wood Treating, Savannah, GA Geo-Con, Inc.	Creosote wastes	12,000 yd3	Sludges	Y	Kiln dust	20%	In situ	Onsite lined cells	>~14%	Full scale
Wyandotte, MI Treatment Plant Chem Met	Various/combined	20 million gal/yr	Various	N	Lime		Continuous	Offsite (secure landfill)		In-plant process
Chem Refinery, TX HAZCON	Combined metals, sulfur, oil sludges, etc.	90,000 gal. (445 yd^3)	Sludges (synthetic oil sludges)	N	Portland cement and proprietary	NA	Continuous flow	Onsite (secure landfill)	>Estimated 10%	Full scale
Chicago Waste Hauling, American Colloid	Metals: Cr, Pb, Ba, Hg, Ag	55 gallon/ batch (bench study)	Various		Proprietary	10-40%	Batch mix (pug mill)	NA	>Variable	Bench scale
API sep. sludge, Puerto Rico, HAZCON	API separator sludges	100 yd3	Sludges	N	Portland cement and proprietary	50% cement ~4% pro-prietary	Concrete batch plant	Offsite secure landfill	>~4-5%	Fluff scale
Metalplating, WI, Geo-Con, Inc.	Al - 9500 ppm Ni - 750 ppm Cr - 220 ppm Cu - 2000 ppm	3000 yd3	Sludges	N	Lime	10-25%	In situ	Onsite landfill	>4-10%	Full scale
James River Site Virginia	Kepone contaminated sediments		Wet soil sludges	N	Cement-base, thermoplastic, polymer	Various	Various		NA	Bench scale only

(continued)

Table 3-1. (continued)

Site/ contractor	Contaminant (concentration)	Treatment volume	Physical form	Chemical pretreat-ment Y/N	Binder	Percentage binder(s) added	Treatment (batch/ continuous in situ)	Disposal (onsite/ offsite)	Volume increase, %	Scale of operation
Massachusetts, American Reclamation Corporation	Oil/gasoline contaminated soils	Variable	Wet soil	Y	Bitumen	Variable	Batch	Used as road patch/ paving mate-rials	NA	Bench (pilot in process)
Saco Tannery Waste Pits, Maine/VFL Tech. Corporation	Cr (>50,000 ppm Pb (>1000 ppm) and organics	Varied	Sludge		Fly ash, quicklime	30% fly ash 10% quick lime	In-situ	Onsite	>15%	Pilot scale
Sand Springs Petro-chemial, Complex, OK/Arco	Sulfuric acid, and organics		Sludge		Fly ash, quicklime	Varied	Batch	Onsite		
John's Sludge Pit, KS/Terracon Consultants, Inc.	Pb, Cr, acid		Sludge		Cement kiln dust and fly ash	Varied	Batch		>Variable	Bench scale
Gold Coast, FL	VOC's and metals	1500[a] yd^3	Soil					Onsite		
Gurley Pit, AR	PCB's and organics	432,470[a] yd^3	Soil					Onsite		
Liquid Disposal Landfill, MI	PCB's, VOC's, heavy metals		Soil					Onsite		
Northern Engraving, WI	VOC's, organic, and inorganics	4400[a] yd^3	Sludge					Onsite		
Mid South, AR	PAH's, organics, and inorganics	45,750[a] yd^3	Soil					Onsite		
Hialea, FL Geo-Con, Inc.	PCB's 0.800 ppm	300 yd^3 (7,000 yd^3 total)	Wet soil	N	HWT-20™ (cement based)	15%	In situ	Onsite	>Small	Pilot scale

(continued)

Table 3-1. (continued)

Site/ contractor	Contaminant (concentration)	Treatment volume	Physical form	Chemical pretreatment Y/N	Binder	Percentage binder(s) added	Treatment (batch/ continuous in situ)	Disposal (onsite/ offsite)	Volume increase, %	Scale of operation
Douglassville, PA HAZCON	Zn, 30-50 ppb Pb, 24,000 ppm PCB's, 50-80 ppm Phenol, 100 µg/liter Oil and grease	250,000 yd^{3a}	Various soil/ sludges	N	Portland cement and proprietary	NA	Batch	NA	NA	Pilot scale
Portable Equipment, Clackamas, OR CHEMFIX	Pb, Cu, PCB's	40 yd^3	Soil	N	Cement, silicate	NA	Batch	NA	NA	Pilot scale
Imperial Oil Morganville, NJ Soliditech	PCB's	50 yd^3	Soil	N	Cement, proprietary	NA	Batch	NA	NA	Pilot scale

NA - Data not available
[a] Total volume onsite.

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Stabilization and Solidification of Contaminated Soils and Sludges Using Cementitious Systems: Selected Case Histories

MICHAEL MACKAY AND JOHN EMERY

Practical stabilization and solidification of soils and sludges exhibiting contamination from heavy metals or organic compounds can be accomplished using readily available, conventional, or byproduct cementitious (hydraulic or pozzolanic) materials, such as portland cement, slag cement, cement kiln dust, lime kiln dust, hydrated lime, and fly ash. Case histories are presented documenting the use of various combinations of cements, fly ash, and byproduct kiln dusts, since the mid-1970s to stabilize and solidify a wide range of contaminated materials. Such materials include PCB-contaminated granular road base, steel industry sludges, contaminated lake-bottom sediments, rotary kiln slag from a secondary lead smelter (acid battery reclaimer), and a very wet former fly ash fill site. Stabilization processes developed have enabled treated materials to satisfy environmental and engineering requirements. Field testing, laboratory stabilization process development, and process implementation (pilot and full-scale) are discussed.

Contaminated land is the legacy of the industrial prosperity and urban development of the past century. People, particularly those in industry, are acutely aware that many waste-handling and management practices followed previously and considered appropriate at the time were not adequate. Soil and groundwater in urban areas worldwide are contaminated with a variety of undesirable compounds that result from industrial processes and disposal of municipal refuse: hydrocarbon products; heavy metals; organic compounds; byproducts such as municipal incinerator ash, fly ash, and bottom ash from coal-fired thermal power generation; industrial and sewage sludges; and other more hazardous materials. As public and scientific awareness of the contamination problem increases, and as economic pressures in urbanized areas push up the value of even severely contaminated real estate, site remediation has become a major technical interest. Although there is a wide variety of remediation options available, only two are currently considered established technologies by the United States Environmental Protection Agency (EPA): high-temperature incineration, and stabilization and solidification. The EPA considers all other technologies for site remediation innovative (1).

REVIEW OF STABILIZATION AND SOLIDIFICATION TREATMENT TECHNOLOGY

Stabilization of contaminated materials generally involves two distinct components, stabilization, whereby the mobile contaminants are complexed to prevent them from dissolving in the groundwater, and solidification, whereby the stabilized materials are encapsulated to limit exposure and form a monolithic mass protecting them from long-term deterioration in the soil or groundwater in which they are placed. Many concepts involved in stabilization are similar to those involved in the cement and concrete industry, and positive stabilization results can usually be achieved using common cementitious (portland cement, slag cement, hydrated lime), pozzolanic (fly ash, silica fume), or byproduct (cement kiln dust, lime kiln dust) materials.

Methods involved in the stabilization of soils exhibiting high metal concentrations must consider several items to ensure satisfactory stabilization and permanent solidification. Leachable metals must be stabilized by complexing them in their least soluble form. For many common metals, stabilization requires that the pH of the material be limited to a level of minimum solubility for the metals of concern. Most metals are polyvalent, and therefore, amphoteric, which means that the hydroxide compounds formed can act as either acids or bases. At pH levels outside of a relatively narrow band (7 to 11), some hydroxide compounds can break down; the liberated metals become mobile and can enter subsoil or groundwater. Therefore, in stabilizing such a material, it is necessary to provide an environment within a pH band that minimizes solubility of metal hydroxides. The final pH of the stabilized material must remain within this limited pH band also, and the physical characteristics of the stabilized material must resist changes in surface and groundwater conditions and contact water pH to have long-term durability.

In conjunction with the formation of meta-stable metal hydroxide compounds, it may be necessary to complex the metals in more stable forms. For example, metal silicate compounds can be formed that are nearly insoluble across a wide pH range. Several proprietary chemical fixation systems for metals and metal hydroxide wastes involve adding soluble sodium silicates and silicate setting agents to assist the stabilization process (Chemfix, Hazcon, K20/LSC, Sorbond, Petrifix, and Soliditech are some examples). However, portland cement, fly ash, and other supplementary cementitious materials also contain varying amounts of silica; they react with metals and each other to form stable metal silicate compounds. Their interaction is considered in selecting a suitable additive for stabilization. The EPA Superfund Innovative Technology Evaluation program currently is evaluating several stabilization and solidification processes that involve proprietary (silicate-based) additives. Early indications are that the proprietary additives do not significantly improve the effectiveness of stabilization over that of encapsulation (solidification) using cementitious stabilizing agents (2).

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After stabilization of metal-contaminated soils and sludges, solidification or fixation of the material often is necessary to facilitate materials handling and minimize contact between the stabilized material and surrounding environment after landfilling. Relatively loose, dry contaminated material may be difficult to safely handle (because of blowing and dusting problems) and require the addition of water. Water itself may leach heavy metals from material and represents another potential waste stream to be considered. Solidification allows the waste and associated moisture to be treated together. Note that it is often necessary to add additional moisture to adjust pH and assist cementitious reactions (hydration). Resulting material then can be landfilled, forming a large impermeable monolithic mass. By this, it is implied that the contact area of the stabilized material with the surrounding soil and surface groundwater is minimized, which greatly reduces the leaching potential of the contaminated material. Updates from the North Atlantic Treaty Organization Committee on Challenges of Modern Society pilot study indicate that reduced leachability of contaminants after stabilization and solidification treatment is largely the result of entrapment (encapsulation) of contaminants within the cementitious matrix, rather than chemical binding to the matrix (*2*). Encapsulation also can serve to contain organic compounds that may be present in the contaminated soil, although that is a technically controversial issue, particularly with respect to controlling air emissions (volatilization) during treatment, and the lack of standard methods for evaluating the extent to which organics actually have been treated.

Treatment alternatives available for heavy metals contamination are extremely limited. Whereas some reduction of heavy metals using bioremediation and soil washing/metals chelation techniques has been reported, stabilization and solidification methods still represent the best available technology for contamination involving heavy metals.

Various cementitious and byproduct materials are available that have been used successfully in the stabilization of hazardous wastes and contaminated soils. Use of them involves a number of combinations and proportions of contaminated materials, plus stabilizing additives depending on the physical characteristics of the contaminated material (consistency, moisture content, or gradation) and the toxic constituents (solubility potential or concentration). Selecting the process and associated stabilizing agents for a particular material contaminated with heavy metals is largely based on the ability of the fixative to control pH, both in the short-term (for several years) and long-term (for several decades), and thereby minimize solubility of ionic forms of heavy metals and metal hydroxides. Portland cement, slag cement, fly ash, hydrated lime, byproduct kiln dusts, silica fume, and steel slag fines can all be used as stabilizing agents, individually or in combination with other stabilizing agents or chemical fixatives (usually proprietary). The most appropriate stabilizer is selected on the basis of physical and chemical characteristics of the waste and overall treatment economics. The Environment Canada Wastewater Technology Centre, with the support of the EPA and the Ontario Ministry of the Environment, published a proposed evaluation protocol for cement-based solidified wastes (*3*) that represents the most thorough laboratory assessment of the physical and chemical integrity of stabilized and solidified materials, short- and long-term.

CASE HISTORIES

Since the mid-1970s, a number of projects have documented successful use of conventional or byproduct cementitious (hydraulic or pozzolanic) materials for stabilization and solidification of a wide variety of wastes and contaminated materials. Several projects were selected to represent a range of wastes and contaminated materials and to demonstrate the effective use of cementitious systems for stabilization of heavy metals and organic contaminants and the subsequent solidification of a variety of soil and sludge types and moisture conditions (dry to near fluid). Case histories are presented documenting the use of various combinations of cements, fly ash, and byproduct kiln dusts to stabilize and solidify PCB-contaminated road base, steel industry sludges, contaminated lake-bottom sediments, rotary kiln slag from a secondary lead smelter (acid battery reclaimer), and a very wet former fly ash fill site.

PCB-Contaminated Road Base, Lake Clear, Ontario

In 1981 and 1982, investigations of unusually high concentrations of PCB in fish in Lake Clear led to the discovery that PCB-laden waste oil had been used for dust control on several gravel roads adjacent to the lake. Relatively high levels, in the range of 50 to 700 μg/g, were identified in the upper levels of the granular roadbase, shoulders, and ditch of two sections of road, the total length of which is about 8 km. The high PCB concentrations at the surface decreased to about 1 μg/g at a depth of about 0.5 m. The total volume of contaminated material involved was estimated to be about 6 260 m^3 (*4*).

The remediation approach accepted by the Ontario Ministry of the Environment was to subexcavate the contaminated material and incorporate it into a very low permeability monolithic mass and place it in a suitably designed site. The following criteria were established for the remediation:

- Contaminated soil was to be stabilized into a solid mass having a permeability of less than 1×10^{-7} cm/sec;
- Any off-site migration was to be within acceptable limits (PCB concentration in groundwater less than Ontario Drinking Water Quality Objective of 3 μg/1); and
- If considered appropriate after technical evaluation, the disposal site was to be on an identified parcel of crown land about 600 m from the lake.

To meet the disposal criteria for the estimated 6 260 m^3 of contaminated material, a laboratory mix design and bench scale testing program was completed by the authors, with the overall objectives of (*a*) encapsulating the PCB-contaminated soil into a monolithic, durable mass to prevent the loss of free particles and (*b*) reducing the permeability of the mass to less than 1×10^{-7} cm/sec. A series of test specimens was prepared using normal Type 10 portland cement, bentonite, and cement-bentonite as prospective stabilizing and solidification agents. Small samples were mixed by hand in the laboratory and compacted (tamped) into 100-mm high by 100-mm diameter tobacco tins, sealed with a twist lid, placed in double plastic bags to maintain moisture conditions, and allowed to cure. Unconfined compressive strength development at 20°C was monitored using a pocket penetrometer. After a curing period, samples were submitted to an environmental laboratory for distilled water leach and Ontario Regulation 309 (acid) leachate extraction analyses.

On the basis of laboratory tests, it was concluded that satisfactory stabilization and solidification (acceptable reduction of leachable compounds and adequate solidification of the mixture) was achieved using 10 percent of portland cement by mass of dry soil. The mixture, when compacted to at least 95 percent Standard Proctor Maximum Dry Density, exhibited the desired very low permeability and sufficient compressive strength to give good resistance to weathering and erosion. An alternative mix consisting of 12 percent cement kiln dust and 3 percent portland cement was also developed and confirmed to meet the basic design criteria after minor adjustments to the mix proportions.

Following the positive evaluation of the laboratory mix design and bench scale testing, a full-scale remedial work program was implemented. The subexcavation of the contaminated soils and road reconstruction were completed under one contract, and the mixing and disposal of the stabilized material were conducted under a separate contract. Tendering for the mixing and disposal of the contaminated material allowed the bidder to select the stabilization and solidification mixture, and the alternative 12 percent cement kiln dust to 3 percent portland cement mix was used. Contaminated soil was mixed with the stabilizing agents in advance using a central plant, then the mixture was transported, placed, and compacted at the disposal site using conventional soil-cement procedures. Before the contaminated soil was processed in the plant, any oversized rocks and boulders were removed by screening. The screened rocks and grubbing material were placed in layers in the middle of the compacted monofill. Contaminated materials and the stabilization and solidification mixture were monitored continuously using a field laboratory, measuring moisture content, compressive strength development (pocket penetrometer), and field compaction. The 4:1 cement kiln dust to portland cement ratio was maintained throughout, and the total amount of cement kiln dust and portland cement adjusted (increased) to ensure that a satisfactory moisture content was maintained for proper compaction (95 percent Standard Proctor Maximum Dry Density minimum).

The final volume of the stabilized and solidified monofill was measured to be 8 100 m^3, with the increase in volume of 1 840 m^3 (about 29 percent) attributed to the stabilizing agents and some native material picked up when cleaning up the work area. Of the 8 100 m^3, approximately 4260 m^3 was contaminated material processed through the mixing plant, and the remaining 3 840 m^3 was oversized rocks, boulders, and grubbing material.

The average PCB concentration of the contaminated soil after screening was determined to be about 21.5 µ/g. The monofill was situated at least 2m above the groundwater table in the unsaturated soil zone and, as such, was not in direct contact with the groundwater system. The monofill design promoted surface runoff and minimized infiltration by mounding and construction of a conventional soil-cement cap; solidification prevented the migration of PCB by subsurface movement of fines. The low permeability of the monofill further limits infiltration and hence minimizes the potential for leaching of PCB in the long term.

Theoretical computations were made to estimate the amount of PCB that could move off site under actual site conditions. Based on a PCB solubility of 0.4 µg/l for the average concentrations of contaminated soil representative of the monofill mass, it was calculated that the probable concentration of PCB in the groundwater following beneath the monofill was between 0.01 and 0.05 µg/l, which is well below the Ontario drinking water objective, 3 µg/l. Cost of remediation was about $850,000, using established technology and readily available equipment and procedures. The Ontario Ministry of the Environment considered the remediation an acceptable solution to containing PCB residues in Lake Clear.

Steel Industry Sludges and Contaminated Lake-Bottom Sediments

Expansion of a steel plant in Hamilton, Ontario, required the removal of a large quantity of a very soft, water-laden sludge and sediment mixture from an old harbor area and slip and its replacement with suitable fill to provide a construction site (5). Some treatment of the sludge sediment to meet landfill disposal requirements was required, and various stabilization methods were evaluated in the laboratory and small field trials before one was adopted. It was determined that the sludge sediment could be satisfactorily stabilized to meet both environmental (solubility of potential toxic constituents in accordance with Ontario Regulation 309) and engineering (bearing capacity) requirements for industrial fill applications. Thus, the reclamation process adopted for the old harbor area involved removing the sludge sediment by stone fill displacement below the water surface, dredging, stabilization, and either disposal to landfill or return to the site for fill above the water table. Other applications of the process also were developed, for use in stabilizing very soft sediments, basic oxygen furnace clarifier sludge, dust high in trace elements, or contaminated dredge spoils, for example.

Geotechnical studies indicated that the sludge sediment was fairly consistent in appearance along the harbor and slip; it was very loose, oily, black, organic, metallic (mainly from iron oxide) waste mixed with lake-bottom sediment, and its moisture content was highly variable (29 to 75 percent mass of water to total mass), as was its bulk density (1300 to 1650 kg/m^3) and loss on ignition (7 to 31 percent). Although most of the site's contaminants were of industrial origin (rolling mills), at early stages the slip received municipal sewage. The result was a rather unpleasant and variable industrial sludge and sediment mixture.

To give various strengths and rates of strength gain to the highly variable sludge and sediment, stabilization involved a number of possible combinations and proportions of sludges and sediments and stabilizing agents, such as fly ash, byproduct kiln dusts, steel slag fines, portland cement, and slag cement. Byproduct materials were used when possible, and either little or no portland cement was added, to minimize costs. Because the project involved nearly 300,000 m^3 of sludge and sediment, a wide range of byproducts was evaluated to ensure supply continuity.

Construction soil stabilization (soil-cement) concepts were adopted, which involve initial drying of the very wet sludges and sediments using high surface area materials (fly ash, kiln dusts), and then pozzolanic or hydraulic reactions as required. For disposal to landfill, just some drying and fairly low strengths (shear strength $\approx$ 0.01 to 0.02 MPa, equivalent to soft clay) were desirable, whereas for fill, initial handling strength and then high strength development (shear strength $>$ 0.1 MPa, equivalent to a very stiff clay) were required.

A simple laboratory program, similar to that described for the Lake Clear remediation, was developed so that a wide range of stabilizing agents and addition rates could be considered for field trials and costing. The approach is considered more representative of conditions in a large mass of solidifying material than open curing, for which significant strength development may result from simple drying instead of cementitious reactions. Supplemental tests monitored pH, moisture content, temperature and bulk relative density. Typical laboratory stabilization trials for a 46 percent moisture content sludge and sediment are summarized in Table 1.

The laboratory stabilization trial results meeting the strength requirements for landfill or fill indicate that, whereas high organic content was not stopping pozzolanic and hydraulic reactions, it was probably inhibiting them. Quick (unslaked) lime kiln dust is much more efficient in this respect than is ordinary calcitic or dolomitic lime kiln dust, and slag cements require a fair degree of alkaline activation. The 1980 additive costs were $2.00 to $4.00 per tonne of final stabilized material.

TABLE 1 Laboratory Stabilization Trials

Wt. % Sediment (wet)	Mass % Additives	Penetrometer Strength, MPa 1 Day	7 Day	14 Day	21 Day
80	15 lime kiln dust (quick) 5 portland cement	0.29	0.43	>0.43	>0.43
80	15 lime kiln dust (quick) 5 slag cement	0.25	0.31	0.41	0.43
80	15 cement kiln dust (bypass) 5 portland cement	0.04	0.42	0.43	>0.43
80	15 lime kiln dust 5 portland cement	0.12	0.20	0.22	0.24
80	15 fly ash (- 8% carbon) 5 lime kiln dust (quick)	0.07	0.12	0.17	0.18
75	15 lime kiln dust 10 fly ash (- 8% carbon)	0.16	0.27	0.30	0.34
75	20 cement kiln dust 5 portland cement	0.02	0.20	0.43	>0.43
75	15 fly ash (- 8% carbon) 5 lime kiln dust 5 portland cement	0.12	0.24	0.43	>0.43
75	15 fly ash (- 8% carbon) 5 lime kiln dust 5 slag cement	0.04	0.12	0.15	0.32

Larger bench scale testing was completed; it involved preparation of several large 90-kg samples and various stabilizing agents using an Eirich R-7 mixer that, using only drum rotation, simulated a large stabilization plant pugmill. Sealed curing and curing under a 0.8-m head of water were completed at a 7°C to 13°C temperature range to simulate cooler field conditions. The results supported the smaller-scale test methodology adopted.

Solubility of toxic constituents in the industrial sludge and contaminated sediment was evaluated using a very severe, modified Organization for Economic Cooperation and Development solubility test procedure (*6*) that determines the dissolution rate for each constituent of interest. The procedure involves leaching 1 g of sludge and sediment per 0.05 l of distilled water during five 24-hr cycles of vigorous (3 Hz) shaking, with the supernatant drawn off and filtered between cycles and submitted for chemical analysis.

Solubility test results indicated that stabilization reduced trace element constituent levels in all cases except Cu and Pb, but these were still well below the maximum allowable despite the very severe nature of the test, and the stabilized material was fully acceptable from an environmental viewpoint.

Pilot-scale and full-scale field implementations resulted in a final stabilization and solidification process consisting of (a) a chute that allowed excavated material to be fed into a standard ready-mix truck; (b) central additive storage silos for storing and adding the stabilization agents, with the most reactive agent added last to allow for visual control of initial stiffening; and (c) mixing and transporting for discharge at a designated location where strength monitoring was completed on the stabilized material. The ready-mix truck operation proved so efficient during pilot-scale testing that it was adopted in place of a large base stabilization plant for full scale implementation.

At its peak, six 14-yd^3 ready-mix trucks were used with about 1,000 t of sludge and sediment stabilized in an 8-hr shift. Optimum stabilizing agents (based on economics and availability, after first confirming strength development and stabilization capabilities) were determined to be 8 to 12 percent highly reactive byproduct quick (unslaked) lime kiln dust, and 3 to 5 percent slag cement (replacing portland cement). After successful stabilization of the harbor and slip materials, the process was used to stabilize very soft sediments from another area of the plant, and a similar fixed plant process was developed to stabilize basic oxygen furnace clarifier sludge on a continuous basis. In each case, the stabilized product was approved by the Ontario Ministry of the Environment for fill applications or landfilling, on the basis of a former unsaturated column leachate method (since replaced by the Ontario Regulation 309 Leachate Extraction Procedure). It was estimated that the cost of stabilization and solidification (in 1980 dollars) was about $8.00/t using byproduct stabilizing agents.

Rotary Kiln Slag from Secondary Lead Smelter (Acid Battery Reclaimer)

An acid battery reclaiming plant uses a long rotary kiln and soda ash lead-reduction approach to recover lead from spent batteries. The secondary lead smelting operation has a very low environmental impact; its SO_2 emissions are carefully controlled. Feed materials—primarily lead sulphate, lead oxide, and lead sulphide resulting from crushing of 3.5 million spent lead storage batteries per annum, with soda ash and iron added to capture sulphur in the rotary kiln slag plus coke as a reducing agent/energy source—are fed gravimetrically into the long rotary kiln operating at a temperature of about 1100°C. Resulting molten salt lead is tapped out into 60-tonne holding kettles, with the slag overflowing at the hot end of the kiln and into slag pots to cool. About 31 to 32 percent slag is produced per unit of bullion on average, or about 45 tonnes of rotary kiln slag per day ($\approx$16,500 t/year).

Rotary kiln slag differs from conventional iron silicate lead slag produced by other primary and secondary smelters: it is low in silicates and iron, high in sulphur and sodium, and quite soft and friable. Shortly after being turned out of the slag pot, rotary kiln slag cools to a hard state in large chunks. The fresh slag reacts immediately on contact with air, oxidizing from the surface inward (expending heat). After several weeks of exposure to air and precipitation, rotary kiln slag breaks down to a consistency similar to very moist cohesive soil. The somewhat alkaline rotary kiln slag does not meet Quebec Ministry of the Environment landfill disposal requirements for solid waste (*7*), being slightly high in leachate test lead, and it is physically unstable until fully broken down, that is, after several weeks to months of exposure to air and precipitation. Rotary kiln slag is completely dry when turned out, but it retains about 60 percent moisture when fully broken down in an outdoor stockpile.

A bench scale testing program was developed to stabilize and solidify rotary kiln slag. A series of laboratory trials was completed for the aged, stored slag and the relatively unoxidized fresh slag to determine the optimum stabilization and solidification processes necessary to fully oxidize the slag, reduce the leaching of heavy metals, and durably solidify the material to meet Quebec Ministry of the Environment's requirements.

A series of laboratory trials was completed using several stabilizing agents and solidifiers, including portland cement (Type 10 and Type 50), fly ash, and hydrated lime, in various combinations and proportions. Initially, small samples were prepared in the same fashion as described for the Lake Clear and industrial sludge and contaminated sediment projects. Because lead, and lead hydroxide solubility is particularly sensitive to changes in pH, as indicated in Figure 1 (8), the pH of the stabilized material must be maintained within a narrow range of about 9 to 11. Stabilization trials for the stored slag and fresh slag were completed separately, recognizing that the relatively unoxidized fresh slag had to be pretreated (aged) before stabilization and solidification.

The stored slag was variable in moisture content (approximately 35 to 60 percent by dry mass) and in physical characteristics, suggesting that the degree of aging throughout the stockpiled material was inconsistent. Forty stabilization trials were conducted to develop an optimum stabilization recipe based on pH, unconfined compressive strength development, appearance (density, porosity, permeability), and durability.

As a result of the trials, stabilization and solidification mixes incorporating fly ash were eliminated. (pH was too high and it had inadequate strength development. Larger 2-kg samples were prepared by mechanical mixing, using mixtures incorporating Type 10 portland cement with and without hydrated lime. For these trials, the moisture content of the stored slag was increased to 60 percent by mass to control pH and provide additional moisture to assist in oxidizing any unreacted slag pieces that were still present in the stored slag.

Throughout the testing program, samples were subjected to environmental analysis in accordance with Quebec Ministry of the Environment's leachate extraction test procedures. It is an agitated acid leachate extraction procedure similar to the USEPA EPTox procedure and the Ontario Regulation 309 Leachate Extraction Procedure. Test results indicated that stabilization and solidification using 10 percent Type 10 portland cement by wet mass of stored slag resulted in a material satisfying the Quebec ministry's requirements for solid waste.

Fresh slag presented a separate set of challenges. The presence of unreacted pieces in the fresh slag required that a prestabilization and solidification step be introduced into the process to rapidly age the slag before treatment, otherwise the material would not be stable, and subsequent slag expansion destroyed the cementitious matrix. Laboratory testing indicated that the fresh slag could be quickly broken down by adding water in stages (a maximum of about 90 percent by dry mass), in conjunction with regular mixing of the wetted slag to expose it to air. After about one week, the condition of the fresh slag was similar to that of the stored slag, allowing the fresh slag to be stabilized and solidified in the same way as the stored slag, using 10 percent Type 10 portland cement.

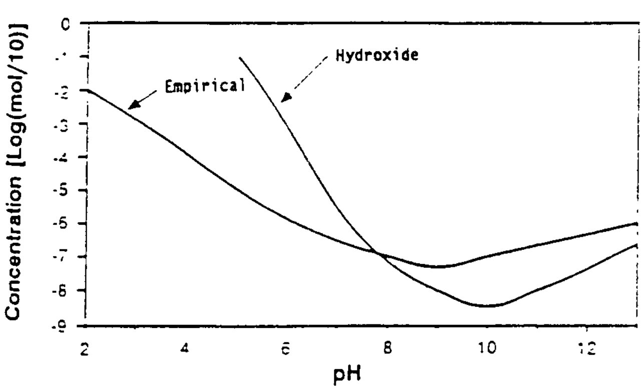

FIGURE 1 Solubility of lead versus pH in a cement/fly ash stabilization and solidification system (8).

The laboratory bench scale testing program was completed in June 1991. Pilot-scale field testing was completed at the plant in the fall of 1991, with similarly positive results for the stabilization and solidification. Results of the pilot-scale field testing indicated that the process for aging fresh slag needed refinement.

Former Fly Ash Fill Site

In 1967 or thereabouts, approximately 100,000 m^3 of Type C (low CaO) fly ash from Ontario Hydro's coal-fired thermal generating station was placed in a former sand and gravel pit situated in the northeast corner of metropolitan Toronto. The fly ash was innocuous from an environmental point of view (almost inert fill, with the exception of slightly elevated arsenic and boron levels). However, under Ontario Regulation 309 and its nonregistrable, nonhazardous limits, the fly ash is very loose and wet; as such, it is not suitable for the proposed construction of a large and prestigious commercial/industrial development. Reconditioning the fly ash fill is necessary if the material is to be used as engineered fill below road and parking lot areas.

Testing of the fly ash confirmed that its in situ moisture content was about 45 to 50 percent, and its consistency ranged from dry to near fluid.

Because of its relatively low CaO content, the fly ash fill material, although pozzolanic, does not possess significant hydraulic properties. Laboratory trials were conducted in spring 1991 to determine a reconditioning process for the material so that it could be used economically for engineered fill applications at the site.

Laboratory trials were conducted on large, bulk samples of the fly ash obtained from the site with a large backhoe. Field samples were double bagged to preserve their moisture condition, then carefully split into smaller representative subsamples for laboratory trials. A series of small-scale trials was completed using portland cement, hydrated lime, and lime kiln dust initially identified as potential stabilizing and solidifying agents. The test method used was similar to that previously described using 100-mm high × 100-mm diameter cans, with strength development (rate and unconfined compressive strength using a pocket penetrometer) of interest for engineered fill use, and pH measured for environmental reasons. Note that the fly ash fill area was already alkaline, and a significant increase in pH was not desirable.

Test observations indicated that portland cement and hydrated lime were not suitable stabilizing and solidifying agents. At even low addition levels (<5 percent), the fly ash mixtures set very rapidly (within hours) to strengths greater than 0.4 MPa. For engineered fill applications at this site, it was desirable to have a mixture that remained workable until it could be placed and compacted using conventional construction equipment with a final, unconfined compressive strength similar to stiff clay, so it could be excavated later if future construction was necessary.

Byproduct dolomitic lime kiln dust proved most effective. Additional trials were completed to refine the addition levels, and it was determined that 8 percent lime kiln dust (by wet mass) resulted in a satisfactory engineered fill mixture that could be readily handled (placed and compacted using conventional equipment), which possessed adequate strength (approximately 0.3 MPa after about 2 days and 0.4 MPa after four weeks). The reconditioned fly-ash mix, although possessing relatively high unconfined compressive strength, could be broken up by hand, indicating that it could be re-excavated easily using conventional construction equipment.

A sample of the reconditioned fly ash was subjected to environmental analysis (Ontario Regulation 309 Leachate Extraction Procedure) for comparison with Ontario requirements for drinking water and wastes. Although the boron level was slightly elevated, fluoride and selenium, the leachate from the stabilized and solidified reconditioned fly ash, satisfied Ontario drinking water standards and was well within the nonregistrable, nonhazardous designation for wastes.

On the basis of the reconditioning results and leachate analyses, the fly ash was classified as a special waste and accepted by the Ontario Ministry of the Environment for use as engineered fill at the site. The reconditioned fly ash may be used beneath parking lot and roadway areas outside the building footprint. It is anticipated that pilot-scale and full-scale reconditioning of the fly ash will proceed on-site in 1992, as the site is developed.

CLOSING COMMENTS

Results of more than 15 years of experience confirm that cementitious systems—portland cement, fly ash, hydrated lime and byproduct materials, such as cement and lime kiln dusts, silica fume and slag cement—can be used to durably stabilize and solidify a wide variety of soils, sludges, sediments, and other wastes containing unacceptable levels of organic and inorganic toxic constituents. Such systems can be designed using relatively simple laboratory procedures, based on a thorough understanding of the cementitious components involved and their reactions with the waste materials and toxic constituents. The systems also can be practically implemented using conventional, readily available materials and equipment. New protocols for evaluating cement-based solidified wastes will greatly assist in the assessment of the longevity of stabilization and solidification remediation (particularly with respect to contaminated materials containing organic compounds); such protocols are expected to further support EPA current position that stabilization and solidification is an accepted technology for the treatment of contaminated materials.

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Remediation of Oil Refinery Sludge Basin

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Abstract

Work was completed in early 1992 to clean up a 5.5 acre (2.2 ha) stormwater sludge basin for an oil refinery company. The basin, which had served as a stormwater collection and settling pond for over 40 years, contained oily sludges with high concentrations of certain metals and volatile organic compounds. The closure plan included a combination cement-bentonite slurry wall and jet grouting along the perimeter of the basin. The sludge and contaminated soil beneath the basin were solidified in place using a specially developed soil mixing technique.

Keywords

Cement-bentonite slurry wall, jet grouting, Shallow Soil Mixing, slurry wall, soilcrete, solidification, stabilization.

Introduction

Located along the southern shore of Lake Michigan is one of the oldest refineries in North America. For more than 40 years a 5.5 acre (2.2 ha) stormwater sludge basin had served as the plant's stormwater collection and settling pond. Oil sludges and other contaminants including certain hazardous metals and organic compounds would be carried with the

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stormwater and deposited in the basin. A series of baffles and weirs within the basin helped direct the flow and regulate storage. Surface skimmers were used to remove oil and the basin was periodically cleaned with backhoe and clamshell equipment to remove settled contaminants.

The 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) of 1976 established strict standards for the handling, storage and disposal of hazardous wastes. As part of the regulations, all surface impounds which treat or store hazardous wastes must either be double lined or taken out of service. In addition hazardous materials within surface impoundments and contaminated soil beneath the impoundments must be removed and disposed of in secure landfills or treated and properly disposed of on-site.

The remediation method chosen for this project consisted of in place stabilization of the sludge and contaminated underlying soil. To prevent the migration of any contaminants into the groundwater, a seepage barrier was installed along the perimeter of the basin and keyed into the underlying clay layer. A geomembrane and clay soil cap were placed over the entire basin.

Site Evaluation

A site investigation was conducted to determine the chemical composition of sludges within the basin and depth of contaminated soil below. The program consisted of proportioning the basin into five zones. Soil borings were taken to determine the depth of the sludge and contaminated soil. A total of five sludge cores were taken from each zone using a grid system and radom number selection process. The samples from each zone were mixed together to form a composite sample representing the particular zone. Testing protocol was performed in accordance with EPA-SW-846[1] procedures. The average wet weight of the sludge was about 72 pcf (1153 kg/m^3). Table 1 gives the results of the chemical analysis of the sludges in zones 1 and 5. From the sampling program it was determined the depth of the contaminated soil extended approximately three feet below the bottom of the unlined basin.

Closure Plan

Following the site investigation program an evaluation was made on the most suitable method of disposal. Closure plans involving in-place remediation as well as contaminant removed and off-site disposal were studied. Costs were compared between on-site versus off-site disposal. It was estimated off-site disposal and site cleanup, including backfill and groundwater treatment, would cost approximately $40 million. An in-place closure was estimated to be about $8 million. In addition, in-place closure provided the owner complete control over the remediation method and long-term performance of the closure.

The principal component of the closure plan was in-place treatment of the sludge and contaminated underlying soil. Also included in the overall remediation was the use of jet grouting and a cement-bentonite slurry wall along the perimeter of the basin shown in Figure 1. A final cap consisting of clay and geomembrane liner was used to cover the basin. Figure 2 provides a schematic cross sectional view of the final cover design.

Preconstruction Testing Programs

The critical natural of the project and regulatory performance specifications made it imperative that preconstruction testing programs be completed for each specialty geotechnical construction technique. The objective of the testing programs was two-fold; 1) demonstrate the feasibility of the selected materials to achieve performance specifications, and 2) provide material usage estimates for pricing the construction. Representative samples of the site soils, sludges, and groundwater were obtained and local sources sampled for evaluation as construction materials. The most critical items tested were the slurry wall, jet grout curtain, and sludge solidification.

Slurry Wall

The most important properties of slurry walls are low permeability and compatibility with the contaminated groundwater. Initially, both soil-bentonite (SB) and cement-bentonite (CB) slurry mixtures were tested. The testing program included index testing of local material sources, in particular mixing water, borrow soils for the SB slurry method, and cement for the CB slurry, workability tests, permeability tests, and unconfined compressive strength (UCS) tests of the CB slurry mixtures. Critical to the success of slurry walls is the compatibility of the CB and SB slurry with the contaminated groundwater. Index tests demonstrated that both SB and CB materials were compatible. Figure 3 compares the UCS of the CB slurry mixtures with published data.[2] Permeability tests were performed on both SB and CB trial mixtures using contaminated groundwater as the leachate. In general, a CB slurry with a bentonite to water (b/w) ratio of .06 and a cement to water (c/w) ratio of 0.18 produced an initial permeability of 1×10^{-6} cm/sec which gradually decreased as the CB continued to cure (Fig. 4). Soil-bentonite trial mixtures generally produced permeabilities in the range of 1×10^{-7} cm/sec which held steady for the three pore volume duration of the test.

From a performance viewpoint, both CB and SB slurry wall methods were acceptable based on their demonstrated permeability and compatibility. From a technical viewpoint, a SB slurry wall was somewhat less permeable; however, the downward trend of the CB slurry mixture held the promise of similar results. Further investigation of the compatibility of the CB slurry mixture with commercial petroleum products (diesel fuel) showed a surface tension effect could actually seal off the surface of a CB slurry wall from any permeation.

The on-site soils at the project site, consisted mostly of clean sand with less than 7% fines (material passing a No. 200 (0.074 mm) sieve). Studies[4,5] have indicated the backfill material for SB slurry walls should contain a minimum of 15 to 20% fines to prevent the bentonite particles from being washed out of the soil matrix by piping. To accommodate a SB slurry wall at this site, a significant quantity of fines or a massive bentonite addition (approximately 10%) would be required.

In addition to the cost of importing extra material to the site a SB slurry wall required considerably more material handling, mixing and cleanup than a CB slurry wall. Since all excess material had to be solidified, the cost of a SB slurry wall was significantly increased. A CB slurry wall had a higher material cost but a simpler construction process. Furthermore, all spoil was cement coated making cleanup less costly. Another advantage of a CB wall was the flexibility in construction sequence to accommodate site conditions. After evaluating all the above factors, a CB slurry wall was selected as the best solution for this project.

Jet Grout

Jet grouting or "soilcrete" as it is commonly referred to is a soil improvement technique which has been used in Japan and Europe for over 15 years. The technique involves the intimate mixture of native soil and cement slurry through the use of high pressure injection. A single, double or in some cases triple stem jet pipe is lowered to the required depth. Cement slurry is then pumped through the hollow stem of the pipe and released into the soil through jet ports located along the side of the pipe near the base. Typical pressures range from 4000 to 6000 psi (28 to 41 MPa). While the slurry is being injected, the pipe is rotated and slowly withdrawn from the hole at a typical rate of about 1 ft/min (0.3 m/min). The rotating, high pressure jetting action fractures soil formations several inches (centimeters) from the pipe and intimately and uniformly mixes the native soil with cement-slurry. The result is a cylindrical column of treated soil 2 to 6 ft (0.6 to 1.8 m) in diameter.

Jet grout testing was similar to cement-bentonite slurry wall testing except that native soils were incorporated into the mixture. Compatibility tests were also essentially the same as for slurry wall testing. However, with jet grouting, the cement addition rate is more critical and must be developed to achieve the target permeability of 10^{-6} cm/sec. With jet grouting, laboratory procedures suffer from an inability to model the hydraulic shearing and mixing as performed in the field.

In addition to the problem of modeling the jet grouting technique, modeling the soil profile was especially difficult. Previous remediation efforts had resulted in an overlying layer of bentonite and pea gravel on top of the native soils between the double sheet pile wall. The bottom up mixing of jet grouting could be expected to better distribute the pea gravel and bentonite throughout most of the jet grout columns.

The limitations of laboratory testing made a field demonstration of the technique imperative. Therefore, both neat grout and grout with soil formulations were made in the laboratory using conventional mechanical mixers and tested for strength and permeability.

A number of nontraditional materials were tested in the jet grout testing program including blast furnace slag, fly ash, gypsum, and attapulgite. Although none of the mixtures were able to meet the 1×10^{-6} cm/sec criteria, a mixture consisting of approximately 450 pcy (267 kg/m^3) of cement and 90 pcy (53 kg/m^3) of bentonite was ultimately selected for field testing.

Sludge Solidification

Developing a representative testing program for the sludge solidification phase of the project proved as challenging as the jet grouting program. Samples were taken at various depths and locations within the sludge basin. Sampling of the various sludge layers and pockets were complicated by the presence of 2 to 10 ft (0.6 to 3.0 m) of overlying water.

Because the project design relied upon the slurry wall and jet grout curtain for containment, solidification specifications focused on homogenous mixing to reduce liquids using strength as an indicator of stabilization. Solidification testing relied upon finding an additive ratio which produced a minimum 28-day unconfined compressive strength of 35 psi (242 kPa) at the least cost.

Based on its long and successful history in waste stabilization/solidification, portland cement was identified as the principal binding reagent. Samples were prepared at 12, 15, 18 and 21 percent cement content, based on the total weight of sludge. Samples were molded in 3x6 in. (7.5x15 cm) and 6x12 in. (15x30 cm) cylinders and 2x2x2 in. (5x5x5 cm) cubes and tested for compressive strength at 7, 14 and 28 days.

Consideration was also given to using cement with fly ash to reduce project costs. The optimum cement/fly ash mixture consisted of 17% cement and 4% fly ash which provided a 28-day UCS of 64 to 75 psi (441 to 517 kPa). Although a cement/fly ash mixture provided higher strengths then cement only mixtures, the costs and controls required in handling, storing and mixing two reagents versus one out-weighed the potential savings in material costs alone. It was decided, therefore, to use cement only for the sludge solidification.

Field Testing and Construction

The laboratory testing programs provided the basic guidance for planning the project but full scale field tests were also performed on the slurry wall, clay liner, jet grout curtain and the sludge solidification to confirm the laboratory results, fine tune construction procedures, and to verify the methods and materials selected for the work. These tests involved actually performing the work with production scale equipment on areas of the project which latter became part of the final work.

Slurry Wall

The first phase of the testing program began with the installation of the CB slurry wall. From the initial site investigation it was determined the soil beneath the sludge basin consisted of fine to medium sand underlain by a relatively impervious silty clay at a depth of approximately 40 ft (12 m). The slurry wall was designed to key into the silty clay layer. The slurry wall extends along the perimeter of the sludge basin and ties into the double row of sheet piling.

The CB slurry wall field test consisted of constructing a 3-ft (0.9 m) wide, and 42-ft (13 m) deep panel using a standard backhoe. The CB slurry was produced by initially mixing bentonite and water in one of the two 5 yd^3 (3.8 m^3) high-shear, recirculating colloidal mixers as shown in Figure 5. A 10,000 gallon (37800 L) tank was used to provide additional mixing and storage. Although earlier laboratory studies pretreated the site water with soda ash to enhance bentonite hydration, a source of mixing water on-site was found which did not need pretreatment.

The hydrated bentonite slurry was then pumped from storage to a second mixer where cement was added. A variable-speed, volumetric screw feeder was used to accurately meter the cement into the slurry. In addition to the high-shearing action of the colloidal mixer, the CB slurry mixer was equipped with three layers of multiple mixing blades along a vertical shaft located in the center of the tank.

After mixing, the slurry was pumped through a 6-in. (15 cm) diameter hose to the slurry trench. All excavated trench spoil was wasted in the sludge basin. This material which contained a considerable quantity of cement-bentonite slurry, hardened sufficiently and required little or no additional cement during the solidification phase.

Field testing consisted of strength and permeability tests of CB slurry samples obtained at the mixing plant and slurry wall. Samples of fluid CB slurry were taken at various depths within the trench prior to hardening. All samples were cured from 7 to 45 days prior to testing.

The test results indicated the strength of the hardened CB slurry was about 25% greater then that obtained in the preconstruction laboratory testing program. The permeability of the cured CB slurry was quite similar to the preconstruction laboratory results with values averaging about 5×10^{-7} cm/sec after 28 days. Work on the slurry wall continued uninterrupted and was completed in about five weeks.

Jet Grout

Field testing and evaluation of the jet grout method was expected to be very interesting, since the preconstruction laboratory testing program had only produced marginal results. The full scale jet grout field test consisted of grouting between the two sheet pile walls for a distance of 100-ft (30.5 m) to a depth of 45-ft (13.7 m). The jet grouting method select was the triple stem method which uses an air and water jet to cut and displace the soil while the grout is tremied into place. Initial grouting parameters included grout pressures of 5800 psi (40,000 kPa) with an injection rate of 150 L/min using a grout with a c/w = .25 and a b/w = .05.

The presence of the sheet piling and previously placed bentonite mixture created unanticipated problems. The sheet piling confined the slurry and the bentonite reacted with the cement releasing bond water from the bentonite. These two conditions along with the use of water as a shearing agent prior to grouting significantly diluted the slurry mixture resulting in undesirable strength and permeability values. To correct the situation the cement content of the grout was doubled to 900 pcy (534 kg/m^3) and the grouting pressure was reduced. A second test section was constructed using the new mixture and procedures.

Field testing and sampling consisted of strength and permeability tests on both fluid samples and cored samples obtained after the grout curtain had cured approximately 60 days. The specified minimum unconfined compressive strength of 50 psi (345 kPa) was easily obtained. Samples of the soilcrete generally gave UCS of 80 to 600 psi (0.55 to 4.1 MPa) in 14 to 28 days.

Permeability results tended to vary with the test method. Coring the soilcrete was difficult and prone to producing poor samples due to the presence of the pea gravel throughout the soilcrete. Cored samples which were obtained typically resulted in permeability values in the range of 1×10^{-5} cm/sec. Fluid samples of the soilcrete obtained from within the grout curtain during construction and molded into samples gave much better results and eliminated the problems of coring. These samples gave more consistant results which approached 5×10^{-7} cm/sec after about 60 days of curing. Rising and falling head bore hole permeability tests[6] installed in the jet grout wall produced the lowest permeabilities. Piezometers were installed about every 50-ft (15 m) and monitored for up to 50 days. The results from these tests gave results in the range of 2×10^{-7}cm/sec.

The results indicated the permeability values from the field piezometers and fluid samples met the project's maximum permeability requirements of 1×10^{-6}cm/sec. The core samples gave permeability results 10 to 100 times greater than either the field piezometers or fluid samples. Due to the problems encountered in obtaining and testing core samples, it was decided to accept the jet grout wall based on the field piezometer and fluid sample test results.

Sludge Solidification

Treatment of the sludge was principally accomplished by a method referred to as Shallow Soil Mixing (SSM). SSM utilizes a crane mounted mixing system to uniformly mix-in-place the waste with the solidifying reagent. The single mixing auger, 12 ft (3.7 m) in diameter is driven by a high-torque turntable. The mixing auger is enclosed in a specially designed cylindrical hood, as shown in Figure 6, which allows for the capture of organic vapors and dusts emanating from the mixing operation. The solidifying reagent is pneumatically conveyed to the hood as the mixing auger proceeds downward through the waste. Once the auger reaches the specified depth it is raised and often reinserted to provide the necessary blending.

The construction method normally consists of creating alternating primary columns which are allowed to set. Secondary columns are then installed which overlap the primary columns resulting in a continuous treatment of the waste impoundment. Figure 7 shows the overlapping pattern used for this project.

The field test for the SSM system required the treatment of 10,000 ft^2 (930 m^2) of sludge in zone 1 to a depth of 20 ft (6 m). The 100x100 ft (30.5x30.5 m) area was divided equally to test four cement contents — 12, 15, 18, 21 percent by weight. Each section included 40 treated columns or a total of 160 columns for the entire field test.

Samples were collected immediately after mixing for 14 and 28 day unconfined compressive strength (UCS) tests. Figure 10 shows the results of UCS tests for the field test program. The completed columns were also tested using standard penetration tests (SPT) and cone penetrometer tests (CPT). Based on the results of the testing program, a 21 percent cement content was recommended to achieve the minimum required 28-day UCS of 35 psi (242 kPa).

Following the test program full scale production began using a presurveyed grid system to mark the exact location of each insertion point. As the solidification progressed a bulldozer was used to grade the solidified sludge to the required level. Approximately 110,000 yd^3 (84,000) of sludge was solidified. It was estimated that the total volume of treated sludge increased only about three percent over the volume of untreated sludge in the basin prior to treatment.

In addition to the SSM system, the backhoe mixing method was used initially along the center dike in zone 1 to allow access for the SSM equipment. The backhoe method was also used in confined areas such as underneath the catwalks and along the sheet pile wall where the SSM system could not reach. The cement content for the backhoe method was increased from 2 up to 10 percent to allow for variations in mixing and sludge composition.

Quality control testing consisted of depth measurements, cone penetrometer and unconfined compressive strength tests. Depth measurements were recorded for each treated column. Cone penetrometer and unconfined compressive strength tests were performed a minimum of one per 1000 yd^3 (765 m^3) of treated sludge. Results indicated the solidified sludge satisfied the minimum UCS requirement of 35 psi.

The final steps in the remediation was placement of the cover which is shown schematically in Figure 2 and installation of a dewatering system within the solidified sludge. The dewatering system isolates the sludge basin by maintaining a phreatic surface below the natural groundwater level resulting in a positive flow into the treated area. Water withdrawn from the treated area is processed through the plant's on-site wastewater treatment facility. Eventually the site will accommodate several above ground storage tanks.

Conclusions

1. Use of on-site remediation using insitu solidification, underground seepage cutoff walls and an impermeable cover was approximately one-fifth the cost of off-site disposal and site cleanup.

2. Both the soil-bentonite and cement-bentonite slurry wall methods exhibited a low permeability and acceptable compatibility with the sludge. However, the CB slurry wall was the preferred method due to the need to import borrow material and the extra material handling, mixing and cleanup associated with the SB slurry method.

3. It was difficult to evaluate the jet grout method based on sampling techniques used. Strength and permeability values from fluid samples differed greatly from core samples. Also the use of water as a shearing agent significantly diluted the slurry mixture causing a doubling of the cement content in order to satisfy the permeability requirements.

4. The Shallow Soil Mixing method worked well. The total volume of treated sludge increased only about three percent over the volume of untreated sludge in the basin prior to treatment.

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Table 1—Chemical Analysis of Stormwater Basin Sludges

	Concentration (mg/L)	
METALS:	Zone 1	Zone 5
Arsenic	6.6	7
Barium	110	98
Cadmium	1	0.78
Chromium	1000	1200
Copper	110	130
Lead	540	630
Manganese	230	170
Mercury	.0038	.0026
Nickel	37	27
Vanadium	530	520
Zinc	6	6.8
VOLATILES:		
Benzene	76	78
Ethylbenzene	170	120
Methyl Ethyl Ketone	250	ND
Xylenes (total)	500	120
SEMI-VOLITILES:		
1-Methylnapthalene	480	440
Naphthalene	330	300
Phenanthpene	140	170

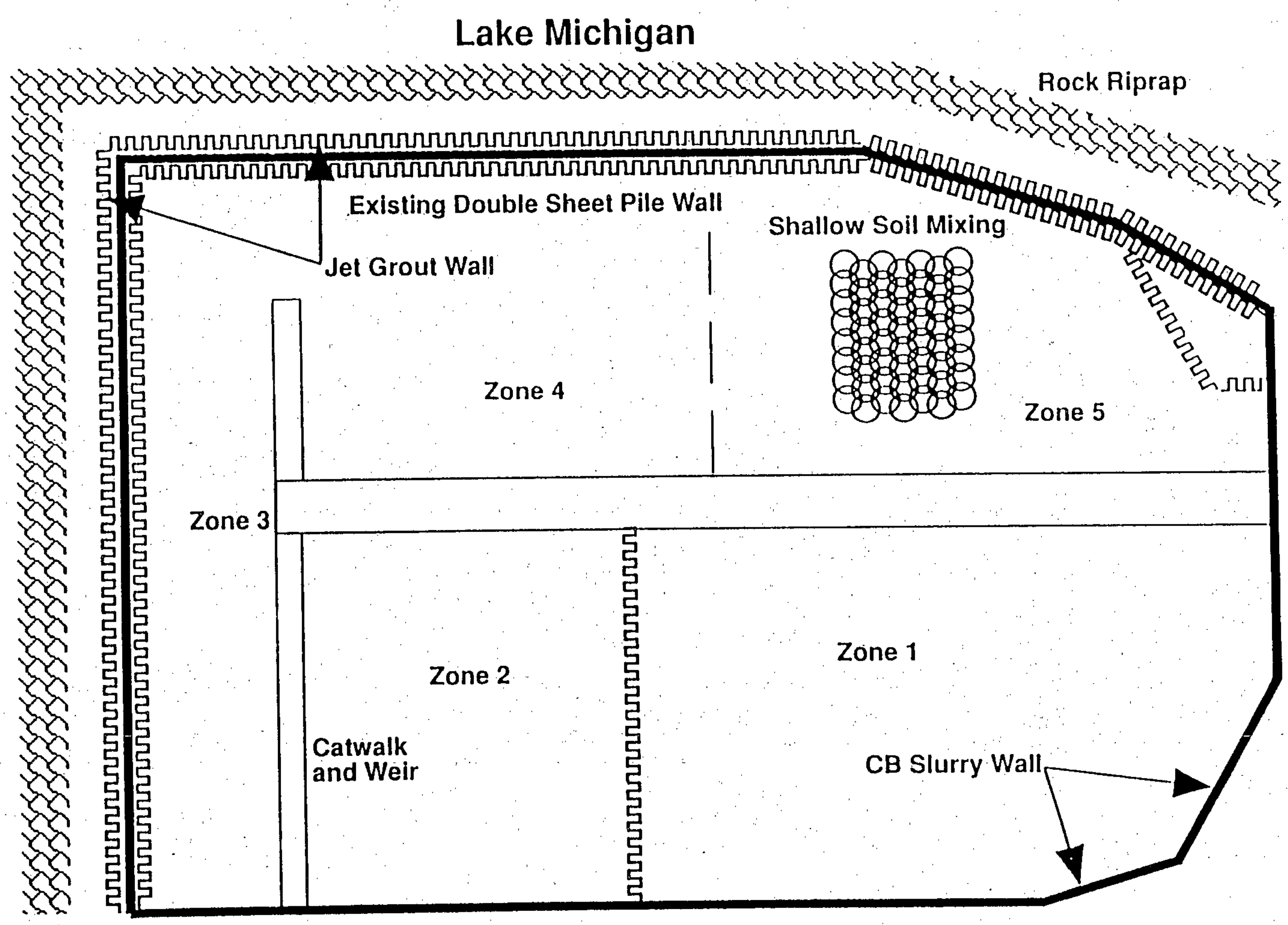


Figure 1. Stormwater sludge basin remediation plan.

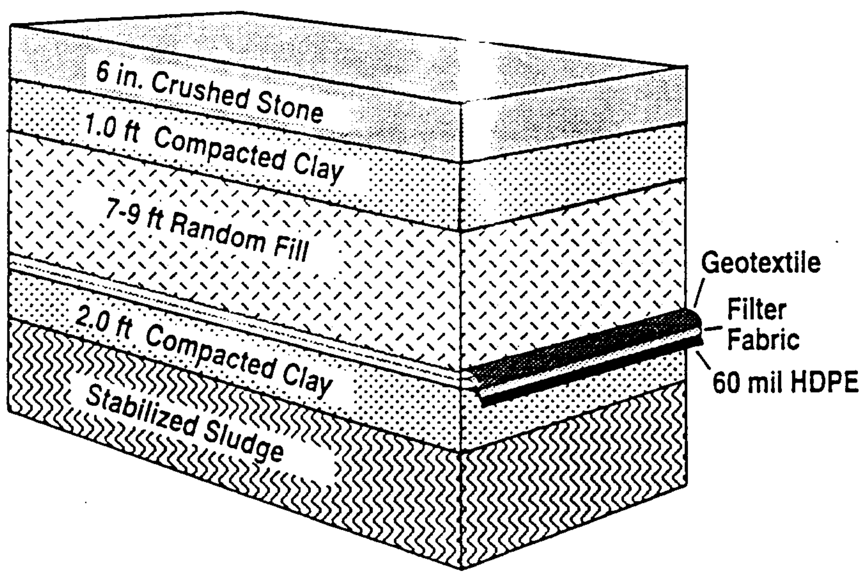


Figure 2. Schematic of final cover.

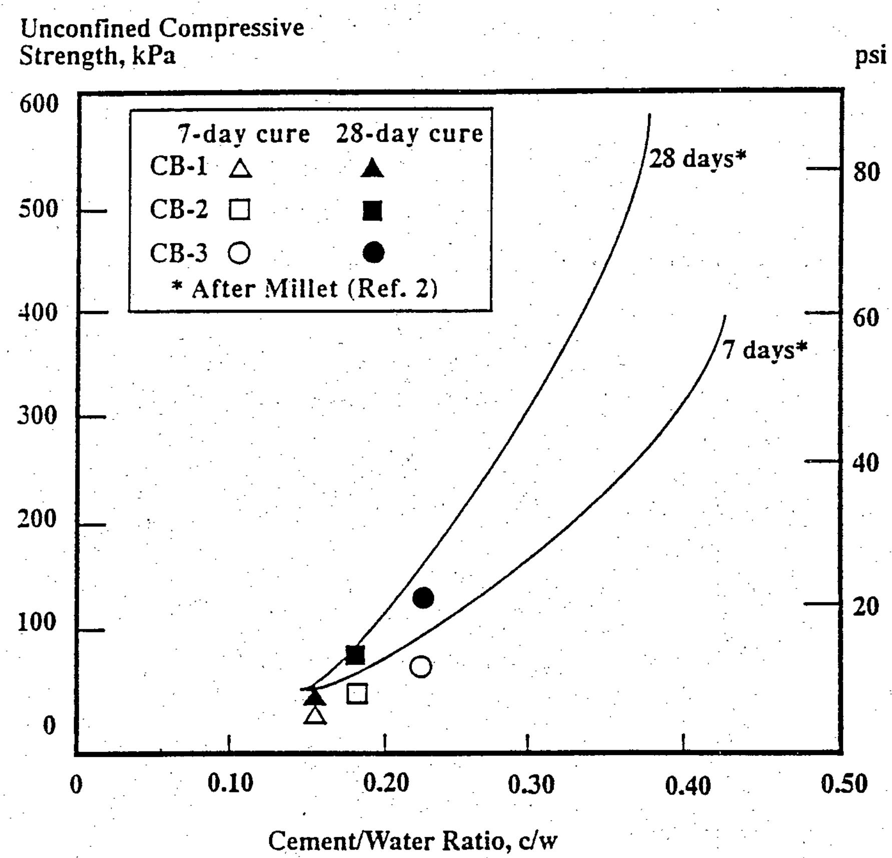


Figure 3. UCS of cement-bentonite mixtures.

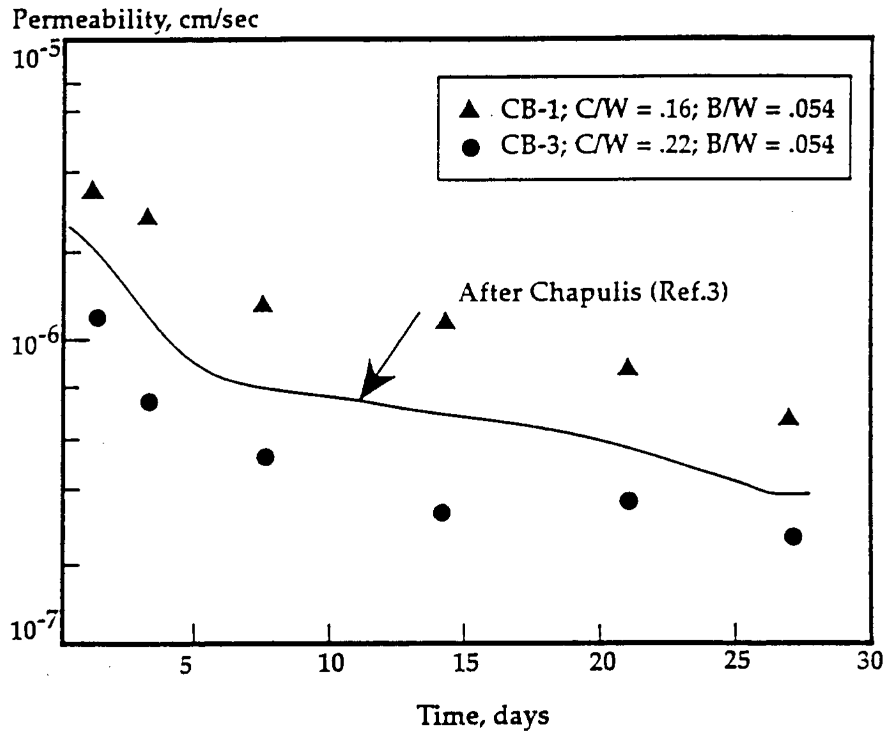


Figure 4. Permeability of cement-bentonite mixtures.

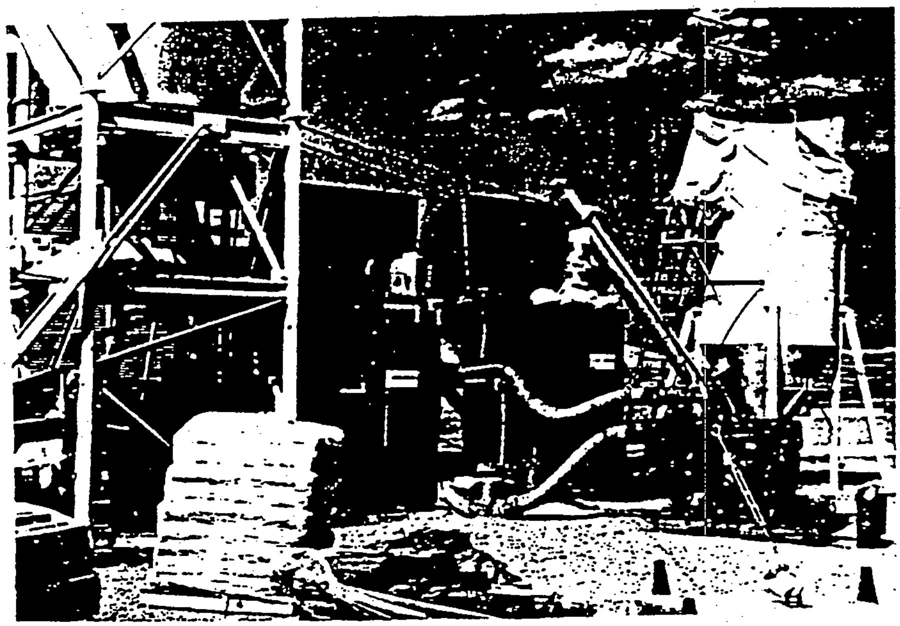


Figure 5. Two high-shear colloidal mixers with cement and bentonite storage silos along side each.

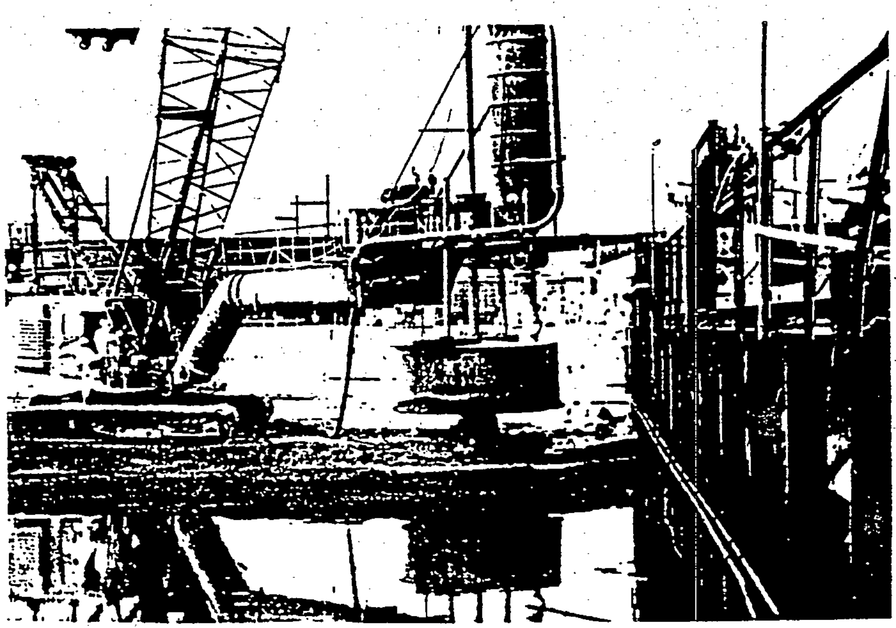


Figure 6. Insitu treatment of sludge using Shallow Soil Mixing System. Note hood over auger to contain organic vapors and dust.

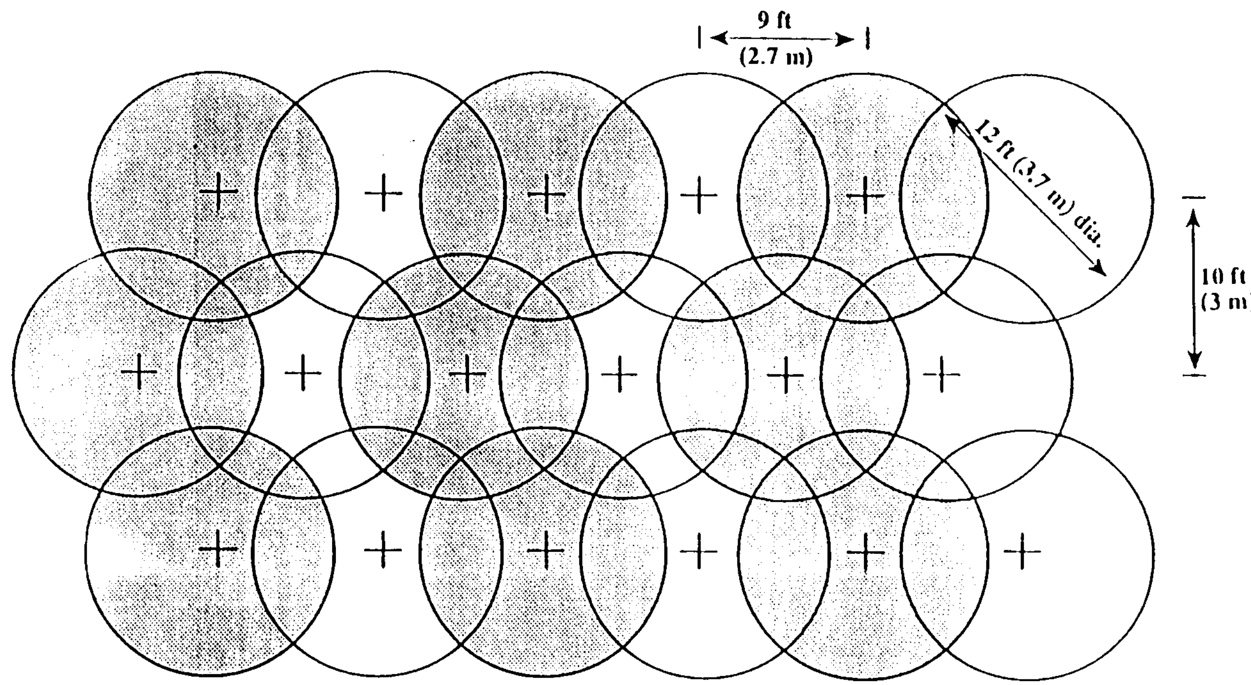


Figure 7. Overlapping pattern of SSM columns with primary columns indicated by shaded area.

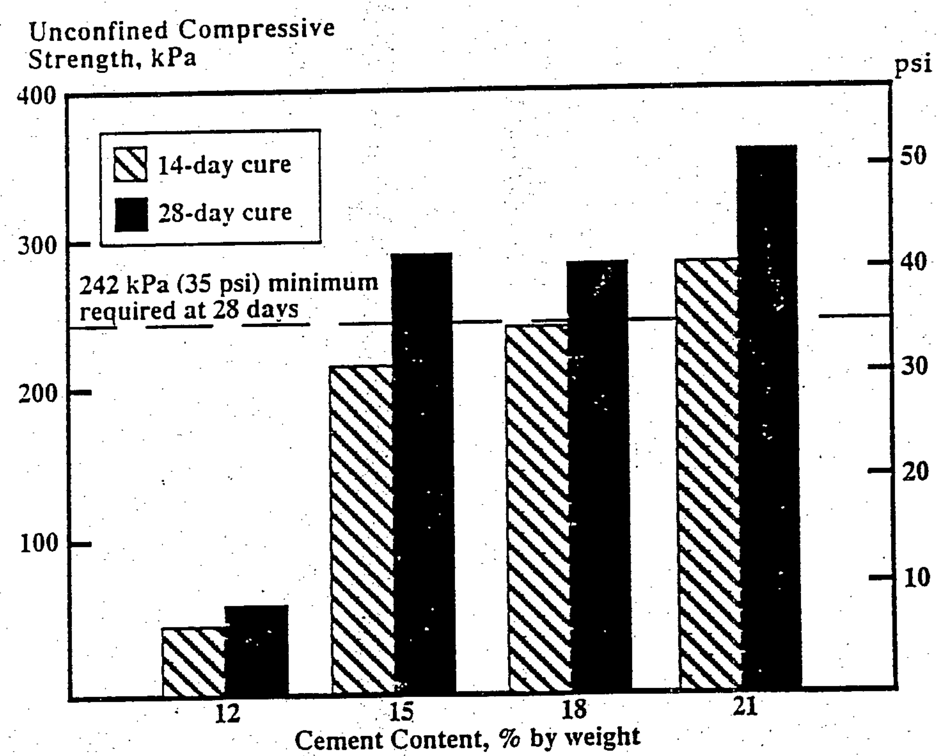
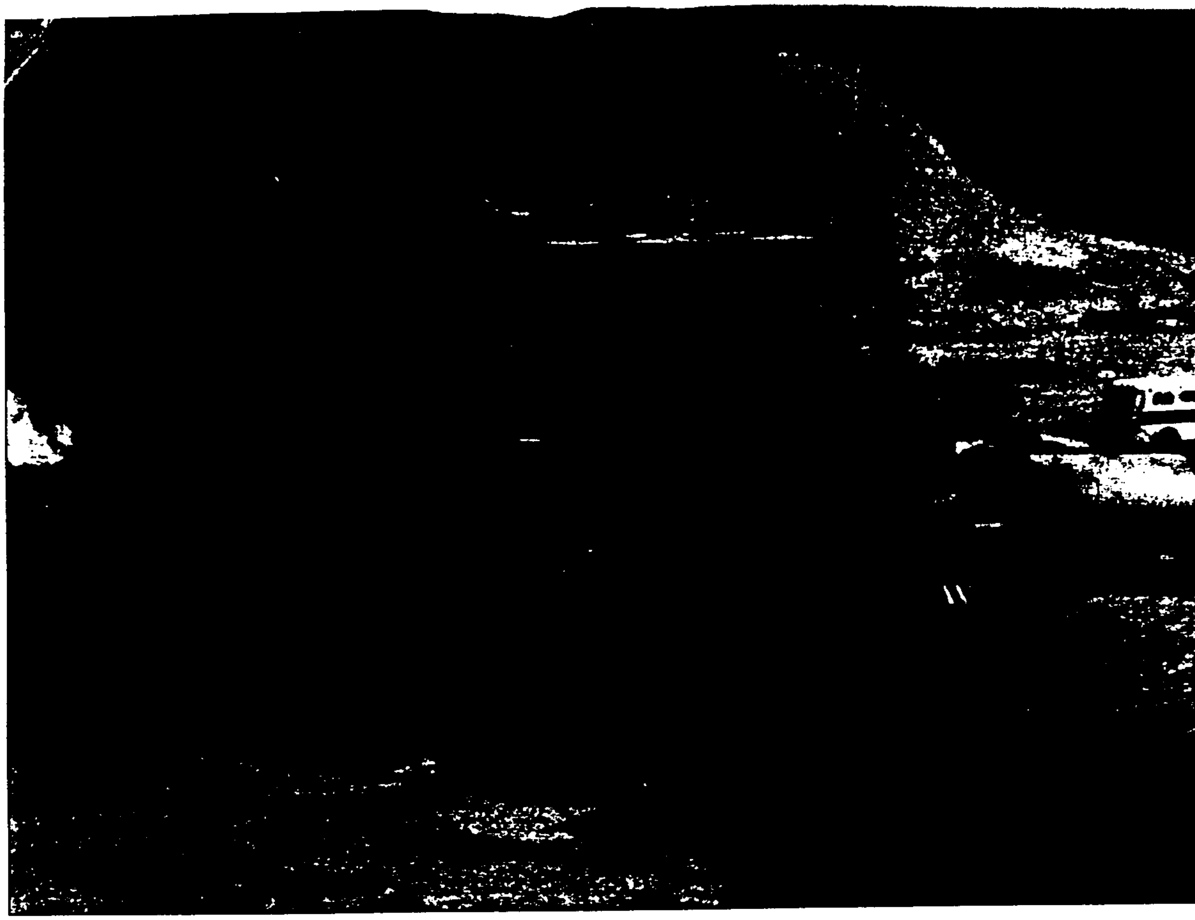


Figure 8. UCS results from SSM field test program.



OILCRETE

Facing tighter hazardous-waste legislation, oil companies search for ways to detoxify oil-waste pits.

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Simply add cement or fly ash. That's the appeal of cementitious stabilization, which turns hazardous materials into stationary and inert "wastecrete." The same technique can now be used to produce "oilcrete."

This method was developed primarily to deal with the most dangerous types of hazardous waste, such as the radioactive variety. Now, several states are working on legislation to redefine oil-field wastes as hazardous. Potential government cleanup orders are causing oil companies to look for inexpensive methods of cleaning up their drilling by-products. The job will be a big one; in Wyoming alone, there are at least 20,000 oil reserve pits.

Cleaning up oil wastes involves mixing cementitious materials into the waste. This limits the solubility of the hazardous constituents in the waste, decreases the waste surface area exposed to the environment and improves its handling characteristics and physical properties.

Although the terms *stabilization* and *solidification* are sometimes used interchangeably, they are actually two separate processes. The primary benefit of stabilization is that of limiting the solubility or mobility of the hazardous contaminants, while solidification produces a strong, durable solid-waste block. Mixing cementitious materials into the oil waste, creating a solid mass of oilcrete, achieves the benefits of both stabilization and solidification.

Cement and fly ash maintain the waste at a high pH in the range of 9–11, immobilizing most multivalent cations (toxic heavy metals) as insoluble hydroxides. The hydrated cementitious products formed will also chemically and physically bind metal ions. The organics present in oil can interfere with hydration (the reaction between cementitious materials and water that creates the hardened mass). Certain salts (zinc, copper and lead) may also prevent or retard hardening of the wastecrete. Mixes that do not solidify allow leaching of the waste.

Wastes with high concentrations of particular cations can be pretreated with additives specifically chosen to immobilize those contaminants. Anions, although less

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oxic than cations, are also much [illegible] soluble product.

Class C fly ash, unlike class F, has a high lime content that can form cementitious products. Most wastecrete mixes using class F fly ash contain cement; some mixes with class C don't need cement or other additives. However, fly ash from different plants may have very different characteristics, even within a particular classification. Since the fly ash varies in its effectiveness in solidifying wastes, trial mixes are necessary.

With some exceptions, 1 ton of cementitious material will solidify at least 1 cu yd of oil waste, achieving a minimum compressive strength of 20 psi in five days. It is also possible to mix the cementitious material with a cheap absorbent, soil, to obtain 20 psi strength while saving money. However, this usually results in an 80–90% volume increase.

MOST IN SITU OIL-SLUDGE TREATMENT PROJECTS WILL COST BETWEEN $12 AND $25 PER CUBIC YARD OF SLUDGE.

In situ mixing is the simplest and most economical disposal plan for wastes. This process, performed in holding ponds, makes use of common construction machinery. Contractors use front-end loaders or backhoes for lagoons under 40 ft wide, and clamshells or draglines for larger ones. Before mixing, large volumes of cement and fly ash can be easily incorporated into the ponds, either by pneumatic or mechanical methods.

Pneumatic equipment can be used to distribute the cementitious materials over the pond or to inject the cement and fly ash directly into the waste. Pneumatic injector tubes can add material and mix it into the waste at the same time. After thorough mixing, the material is allowed to set for 1–3 days to harden. The stabilized/solidified wastecrete is either capped with soil or removed to a disposal facility.

Although in situ mixing is typically the most economical alternative, uniform addition of the cementitious materials and consistent mixing requires careful control. Without uniform hardening, leaching tests will not be relevant to the entire mix. The addition of the cementitious material per unit area must be specified and the construction equipment must be able to reach both the center and bottom of the pond.

The ideal cementitious stabilization/solidification treatment renders the waste chemically nonreactive and gives it physical properties that allow the land over the disposal site to be used for building sites or crops. However, wastes with high concentrations of toxic metals, organics or salts are generally not suitable for agricultural use even after cementitious stabilization treatment.

CASPER CASE HISTORY

An oil-sludge pit (see photo) near Casper, Wyo. was stabilized and solidified in fewer than two weeks, at a cost of $13 per cubic yard of oil sludge. The pit contained 7,000 cu yd of a water-based drilling fluid, used to cool the drill bit and clean the hole. The pit had been leaking before the stabilization process, which required 820 tons of class C fly ash. The contractor mixed the fly ash and soil into the waste; in 24 hours the mix could support a person's weight. Adding soil absorbed the excess water and reduced the amount of fly ash required by approximately 25%. Five-day strength was 31.2 psi.

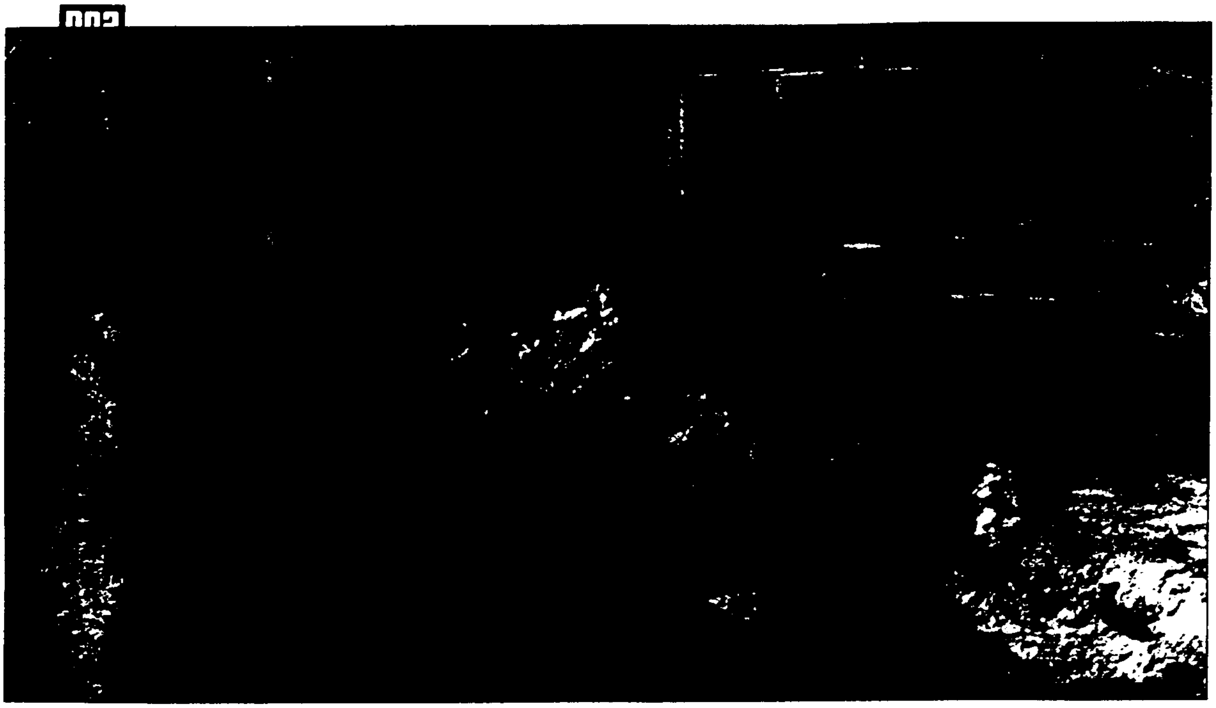
After the mix hardened, the contractor used construction equipment to remove the wastecrete and evaluate the effectiveness of the treatment. Although the original size of the pit was 150 ft long by 50 ft wide by 25 ft deep, the contractor dug beyond these boundaries. This field inspection indicated that the oil waste at the pit bottom had solidified and that the underlying soil was uncontaminated. After the addition of soil, the contractor refilled the pit in layers, spreading and compacting each layer of pulverized oilcrete. Overburden was added and landscaped, returning the site to its original terrain and vegetation.

Western Ash Co., Denver, tested numerous trial mixes to determine the type and amount of locally available cementitious material necessary to produce the oilcrete. The oil wastes considered were oil-based drilling fluid (greater than 10% oil), water-based drilling fluid (less than 10% oil) and a refinery sludge. These preliminary tests compared the type and amount of cementitious additive with the resulting compressive strength and volume increase. A minimum compressive strength of 20 psi, enough to support approximately 30 ft of overburden, was considered to be a successful mix design.

CONSIDERATIONS

Specifications for stabilized/solidified wastes should consider:

- Leachability. Leaching tests evaluate the maximum concentration of contaminants that ground water can remove from the hardened waste. The EPA Toxicity Contaminant Leachate Procedure (TCLP) involves grinding the waste to ensure maximum surface contact area with an acidic extraction fluid. The ratio of waste to extraction fluid is set to achieve a saturated solution. The contaminant concentration level is analyzed and evaluated against the toxicity characteristics set by the EPA.
- Free-liquid content. The dead weight of the soil can cause water to be forced out of buried waste. EPA regulations currently allow no free water in the waste.
- Physical stability under buried conditions. The waste may not be able to support construction equipment if it is too compressible. The contractor must be able to compact it adequately, and it should be reasonably impermeable (typical permeability ranges from 2×10^{-4} to 2×10^{-8} in./sec). Excessive permeability increases leaching of contaminants.
- Reactivity and ignitability. Most stabilized and solidified waste is nonreactive and nonignitable. However, it may be necessary to determine whether the waste is in danger of reacting with other wastes, synthetic or clay liners, or absorbents.
- Biodegradation. Biological activity is undesirable since it can produce acids that interfere with the cementitious solidification process,



About 820 tons of fly ash stabilized 7,000 cu yd of water-based drilling fluid in a Casper, Wyo. pit.

dissolving and leaching metals from the waste. Tests such as ASTM G21 and G22 are used to determine the ability of the wastes to support biological attack.

• Strength and durability. Depending on the waste's final use, strength may be of vital importance. Unconfined compressive strengths (ASTM C39) of cementitious stabilized/solidified wastes range from 1 to 4,000 psi. Usually, only 20 psi is required for burial, as this will support 30 ft of overburden. If the solid waste is to be used for other purposes such as backfill, foundation support or roadbed support, greater strength may be required. A very conservative minimum would be 150 psi, the same as required by the Nuclear Regulatory Commission for radioactive waste.

Durability is important when the waste is exposed to freeze-thaw and wet-dry cycles. Wastecretes generally have low to moderate durability. Since they are usually buried, only minor effects of temperature and moisture are expected. Oilcrete that is exposed to the environment needs to be tested for freeze-thaw durability using ASTM D560 and wet-dry durability using ASTM D559).

TRIAL-MIX DESIGNS

Trial-mix designs for wastes are similar to those for concrete. The cementitious waste mix is evaluated for volume increase, setting times, compressive strength and durability.

As a rule, cement is more expensive than fly ash. In the Rocky Mountain region, portland cements are sold for approximately $60 per ton and the other cementitious materials range from $5 to $15 per ton depending on location.

The final mix is generally the one with the smallest proportion of cement that will produce acceptable wastecrete. The mix may be all class C fly ash or cement, or a combination of cement and class F or C fly ash. This allows the design of an economical blend that meets specifications for strength and durability. Typically, ratios of cementitious materials to wastes range from 30% to 100% by weight. When cement is used, the ratio of cement to total additives varies from 20% to 80%.

Other additives may be necessary to accelerate set times, improve strength and durability, bind specific cations and anions, minimize interfering organic compounds or simply absorb water. The trial-mix designs are used to evaluate the effect of various proportions of these additives on the properties of the oilcrete.

Even if the trial-mix design provides the necessary physical properties, the wastecrete must also undergo a leaching test to determine if the toxic chemical concentrations in the leachate are within the EPA standards. The leaching test is only performed after the trial-mix designs have established the cementitious content and cement/fly-ash ratio necessary for the oilcrete to achieve the required physical properties.

A laboratory-mix design may still not provide the final information necessary to establish project specifications. Small-scale field tests can help evaluate safety problems in handling waste, the construction equipment necessary to achieve uniform and consistent mixing and pumping, appropriate batch sequencing and mixing times, volume increase, and high temperatures that may drive organics off into the atmosphere.

Cementitious stabilization is an inexpensive method of waste cleanup that does not necessarily require a remote dump site. Depending on owner's requirements and job-site conditions, most in situ oil-sludge treatment projects will cost between $12 and $25 per cubic yard of sludge. C

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