Lecture 5

Stabilization and Solidification of Hazardous Wastes

1. Introduction

- Widely applied in management of HW with objectives of:
  - Reduction of the waste toxicity and mobility
  - Improvement in engineering properties of stabilized material
- S/S technologies are applied to the treatment of;
  - industrial wastes,
  - wastes prior to secure landfill disposal,
  - contaminated land where large quantities of soil containing contaminants are encountered.

1. Introduction

- *Stabilization* is a process where additives are mixed with waste to minimize the rate of contaminant migration from waste and reduce the toxicity of waste.
- Contaminants are fully or partially bound by the addition of supporting media, binders or other modifiers.
- *Solidification* is a process employing additives by which the physical nature of the waste (strength, permeability and/or compressibility) is altered during the process.

Definitions

- *Fixation* is often used synonymously with stabilization.
- Stabilization is accomplished through the addition of reagents that:
  - Improve the handling and physical characteristics of waste.
  - Decrease the surface area across which transfer of contaminants can occur.
  - Limit the solubility of any pollutants contained in waste.
  - Reduce the toxicity of the contaminants.

Definitions

- *Leaching* is the process by which contaminants are transferred from a stabilized matrix to a liquid medium such as water.
- Stabilization must be considered as a waste treatment process that reduces, to an acceptable or geologically slow rate, movement of contaminants into environment.
- $Zn_3(PO_4)_2$ ores provide the source of Zn for metallurgical processes, and a stabilization technique that precipitates Zn as $Zn_3(PO_4)_2$ is likely to be the optimum technique in terms of environmental effectiveness

Applications

- The three major areas of application for stabilization technologies are:
  - Land disposal – the stabilization of waste prior to secure landfill disposal
  - Site remediation – the remediation of contaminated sites
  - Solidification of industrial wastes – the solidification of nonhazardous, unstable wastes, such as sludges

Land disposal

- Land disposal of liquid waste increases the likelihood of contaminant migration. Liquid waste (wet sludges) must be stabilized prior to landfilling.
- To effectively stabilize liquids, the stabilization agents cannot be absorbents such as sawdust.
- Liquids absorbed by agents could be easily desorbed in landfill when compressed under additional loads.
- Liquids must be chemically/physically bound by reagents so that they are not expelled by consolidation stresses or leached out by downward percolation of precipitation.

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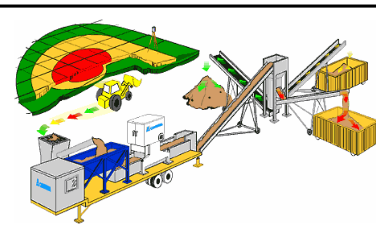
Site remediation



- Remediation of contaminated sites having organic wastes, inorganic wastes, and/or contaminated soils may be accomplished by employing stabilization technology.
- For site remediation, stabilization is used to;
  - improve the handling and physical characteristics of wastes
  - decrease the rate of contaminant migration by decreasing the surface area across which the transfer of pollutants can occur and by limiting the solubility of pollutants
  - reduce the toxicity of certain contaminants

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Solidification of industrial waste

- Many of the nonhazardous industrial waste may not enganger the public health or the environment.
- However, these wastes are frequently structurally unstable, aesthetically unsuitable, and their condition precludes other uses of the site area.
- Primary goal is to improve the structural integrity of waste
- Effectiveness of the process can often be evaluated by measuring of material's strength.
- Addition of cement kiln dust to an oily sludge to neutralize and stabilize it.

2. Mechanisms

- An understanding of the fundamental physical/chemical mechanisms that control effectiveness of stabilization reagents is essential to the correct implementation of stabilization as a HW management technology.
- Successful stabilization employs one or more of the following mechanisms: macroencapsulation, micro-encapsulation, absorption, adsorption, precipitation and detoxification.

Macroencapsulation

Cross-section of macroencapsulated heterogeneous debris in phosphate ceramics.

- The mechanism by which HW constituents are physically entrapped in a larger structural matrix; that is, the HW constituents are held in discontinuous pores within the stabilizing materials.
- Integrity of the mass must be maintained to avoid leaks.
- The stabilized mass may break down over time because of imposed environmental stresses such as cycles of freezing and thawing, wetting and drying, introduction of percolating fluids and physical loading stresses.

Microencapsulation

- HW constituents are entrapped within the crystalline structure of the solidified matrix at a microscopic level.
- As with macroencapsulation, because the waste is not chemically altered or bound, the release of contaminant from the matrix is a possibility with lesser risk.

Absorption

- It is the process by which contaminants are taken into the sorbent in the same way that a sponge takes in water.
- Primarily used to remove free liquid to improve waste-handling characteristics, that is, to solidify the waste.
- Liquids are free to squeeze out of the material if the mass is subjected to consolidating stresses.
- Use of absorption is considered a temporary measure
- The most common absorbents are: soil, fly ash, cement kiln dust, lime kiln dust, clay minerals (bentonite, kaolinite, vermiculite, zeolite), saw dust, hay and straw

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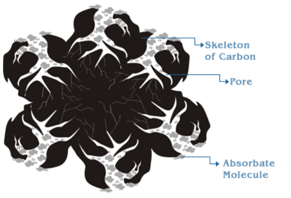
Adsorption



- Phenomenon by which contaminants are electro-chemically bonded to stabilizing agents within the matrix.
- These are typically considered surface phenomena and the nature of bonding may be through van der Waal's or hydrogen bonding.
- Unlike macro- and microencapsulation, additional physicochemical stress is necessary to desorb the material from their adsorbing surfaces.
- As a result, adsorption is considered more permenant.

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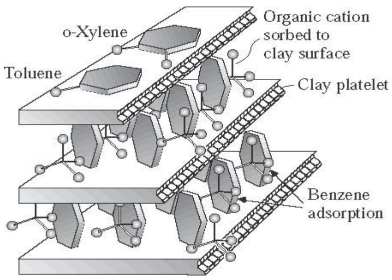
Adsorption

- Modified clays are altered by replacing exchangeable inorganic cations adsorbed on the clay surfaces with long chain cations making them organophilic.
- Organic waste molecules are then adsorbed to clay.
- Adsorption bond strength must be overcome if the organic waste molecules are to be released to migrate into environment.



Organic waste adsorped to an organophilic clay

Precipitation

- Certain processes precipitate contaminants from waste, resulting in a more stable form of the waste constituents.
- Precipitates such as sulfides, silicates, carbonates and phosphates are then contained within the stabilized mass
- This phenomenon is applicable to the stabilization of inorganic wastes such as metal hydroxide sludges.
- Metal carbonates are less soluble than metal hydroxides.
  $Me(OH)_2 + H_2CO_3 \rightarrow MeCO_3(s) + 2H_2O$
- Under strongly acidic conditions, the metal may be redissolved and be free to migrate into the environment.

Detoxification

Cr^{6+}
Cr^{3+}

- Certain chemical reactions taking place during the stabilization may result in a waste with reduced toxicity.
- Detoxification is any mechanism that changes a chemical constituent that is either less toxic or nontoxic.
- As example is the reduction of Cr(VI) to Cr(III) during stabilization with cement-based materials.
- Cr(III) has a lower solubility and toxicity than Cr(VI).
- Leaching of the reduced Cr(III) poses a lesser threat to the environment than the leaching of the original Cr(VI).

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3. Technology

- A detailed description of stabilization technology can best be categorrized by a discussion of the various types of additives (reagents) employed.
- Binder is used to denote a reagent that contributes to the strength gain associated with stabilization.
- Sorbent is used to denote a reagent that contributes to retaining contaminants in the stabilized matrix.
- There is an extensive range of sorbents and binders available in the worldwide marketplace.

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Cement

- Used as principal reagent in the stabilization of HWs.
- Most common cement is portland cement, which is made by firing a mixture of limestone and clay (or other silicate) in a kiln at high temperatures.
- Kiln produces a clinker, which is ground to a powder that is a mixture of calcium, silicate, aluminum & iron oxides.
- Main constituents are tri- and dicalcium silicates.
- For cement based stabilization, HWs are mixed with cement followed by addition of water for hydration, if necessary because the HW does not have enough water.

Cement

- Hydration of the cement forms a crystalline structure, consisting of calcium aluminosilicate.
- This results in a rock-like monolithic, hardened mass.
- Concrete, is a particulate composite consisting of hydrated cement and aggregate.
- Reactions of tri- and dicalcium silicates:

  $2(3CaO.SiO_2) + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$

  $2(2CaO.SiO_2) + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2$
- The most rapid reaction in portland cement is:

  $2CaO.\ Al_2O_3 + 6H_2O \rightarrow 3CaO.\ Al_2O_3.6H_2O + heat$

Cement

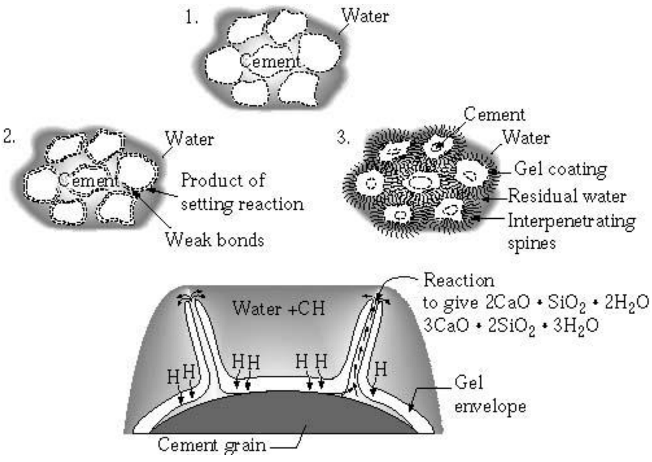

Figure 11.6 Schematic representation of cement hydration (Lagrega et al., 2001)

Cement

- Best suited for inorganic wastes containing heavy metals.
- As a result of high pH, metals are retained in the form of OH^- or CO_3^{-2} salts within the hardened structure.
- Pb, Cu, Zn, Sn and Cd are bound in the matrix by chemical fixation, forming insoluble compounds
- Hg is predominantly held by physical microencapsulation.
- Organic contaminants interfere with hydration process, reduce the final strength and are not easily stabilized.
- Other additives (modified or natural clays) may be added to avoid the interference and enhance stabilization.

Cement

- Advantages:
  - Well known, including handling, mixing, setting & hardening
  - Widely employed in construction field, thus material costs are relatively low, equipment & personnel readily available.
  - Dewatering of wet sludges and wastes is not necessary, as water is required for cement hydration.
  - The alkalinity of cement can neutralize the acidic wastes.
- Disadvantages:
  - Sensitivity of cement to certain contaminants that could retard or prohibit proper hydration & hardening of material.

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Pozzolans

- A material that can react with lime in the presence of water to produce a cementitious material.
- The reaction of aluminosilicious material, lime and water results in the formation of a concrete-like product termed pozzolanic concrete.
- Pozzolanic materials include fly ash, ground blast furnace slag and cement kiln dust.
- Like cement-based stabilization, most stabilization applications involving the use of pozzolans are for inorganic materials.

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Pozzolans

- The high pH environment is well suited for waste contaminated with heavy metals.
- Elevated levels of Cd, Cr, Cu, Fe, Pb, Mg, Mn, Se, Ag and Zn in sludge is stabilized after treatment with fly ash and lime reagents.
- Stabilization significantly slows leaching of metals.
- Unburned carbon in fly ash adsorbs organics from HW.
- As a result, a pozzolan such as fly ash may have beneficial effects in the stabilization of both organic and inorganic species.

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Lime

- Stabilization of sludges is frequently accomplished through the addition of $Ca(OH)_2$ (=hydrated lime).
- Resulting reaction with waste materials may result in hydrates of calcium-silicate,-alumina or -aluminosilicate.
- Additional stabilization can be accomplished through the use of other ingredients in smaller quantities.
- Lime may also be added to raise the pH of acidic sludges with fly ash that provide the main stabilization reactions.
- Lime-based stabilization is best suited for inorganic contaninants & has been widely used for metal sludges.

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Organically modified clays

- Produced when organophobic natural clays are organically modified to become organophilic.
- Modification is accomplished through the replacement of inorganic cations within the clay with organic cations.
- After the replacement, organic molecules are adsorbed within the crystalline structure of the clay.
- Organophilic clays typically are added to the waste first and allowed to interact with the organic components.
- Additional agents are added to provide shear strength and solidify the material into a monolithic mass.

Modified lime

- Specifically developed for stabilization of organic wastes.
- Quicklime (CaO) has been modified to form a technology for S/S of oily sludges, oil-contaminated soils, acidic oil sludges and heavy metals.
- This dispersion by chemical reaction process has been found to be successful in stabilizing liquid contaminants and heavy metals in contaminated soils.

Thermosetting organic polymers

- A monomer such as urea-formaldehyde that acts as a catalyst is mixed with HW to form a polymeric material.
- A sponge-like mass is thereby formed, trapping solid particles of HW within matrix (microencapsulation).
- Liquid wastes are generally left untrapped.
- Therefore, the final waste product would need to be dried and containerized prior to ultimate disposal.
- Principal advantage is that it generally results in a low density material relative to other fixation techniques.
- Not applicable to site remediation because of its cost, fire hazard and volatilization of organics.

Thermoplastic materials

- HW may be stabilized by blending molten thermoplastic materials with wastes at high temperatures.
- Molten thermoplastic materials include asphalt, paraffin, bitumen, polyethylene, polypropylene and sulfur.
- When cooled, the solidified material is characterized as a thermoplastically coated waste & typically containerized for ultimate disposal.
- This technique has been predominantly employed for radioactive waste applications because of its cost.

Thermoplastic materials

- Organics are volatilized at the operating temperatures, requiring control of air emissions during the process.
- Primary limitations;
  - Presence of materials that could deteriorate the TM.
  - Presence of organic chemicals that act as solvents to the stabilizing TMs.
- Thus, a potential for long-term degradation exists.
- However, thermoplastically stabilized waste is quite resistant to leaching and biodegradation.

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Vitrification

- A stabilization technique without addition of reagents.
- Glassmaking or vitrification involves melting and fusion of materials at temperatures above 1600°C followed by rapid cooling into a noncrystalline, amorphous form.
- Applied both in situ and in-plant.
- Considered as a S/S process, because it renders the waste more structurally stable with a reduced potential for contaminant migration into the environment.

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In situ vitrification

- High temperatures needed to melt the soil into a molten mass are achieved by applying electric current.
- As current flows, heat builds up, causing the soil to melt.
- Soils become more conductive & molten mass becomes a heat transfer medium, allowing molten mass to grow.
- Typically, electrodes spaced a maximum of 26 feet apart in a rectangular pattern are employed.
- Once initiated, electronically conductive molten mass grows downward & outward to desired treatment depth.

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In situ vitrification

- As temperature increases, organic materials first vaporize and then pyrolyze into elemental components.
- Gases move slowly through the molten mass (which is quite viscous) toward the surface, and those gases that are combustible burn in presence of O_2 on offgassing.
- A hood is constructed over the area to collect all gases.
- Gasses are treated to ensure that air standards are met.
- Because of high temperature (1600 - 2000°C), residual contamination remains in the residue (the glass).

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In situ vitrification

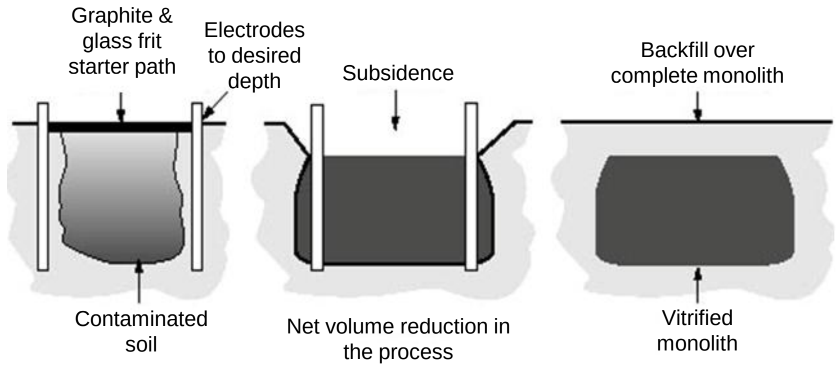

Figure 11.12 *In situ* vitrification(Lagrega et al., 2001)

In situ vitrification

A hood is employed to capture gases. Captured gases require treatment. Offgas treatment system depends on site contaminants

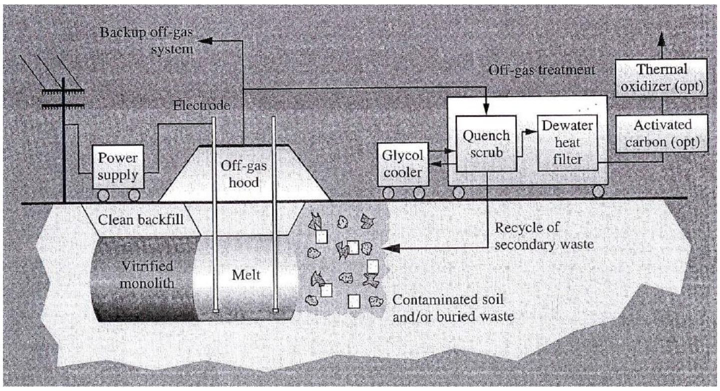

Figure 11.13 GeoMelt/SV system schematic (Lagrega et al., 2001)

In-plant vitrification

- Has potential to treat HW (contaminated soil) & produce a product that may be usable (e.g., as a road aggregate).
- A starter mix of recycled glass, fly ash and limestone is used to initiate the process.
- Contaminated soil is then introduced into the furnace for the melting and fusion stages that last a min. of 5 hrs.
- Air emissions can be captured and treated by traditional air treatment technologies.
- Leaching tests have shown the glass to be inert.

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TABLE 11-2
Reagent applicability for waste stabilization[30]

Waste component	Cement-based	Pozzolan-based	Thermoplastic	Organic polymer
Nonpolar organics as: oil and grease, aromatic hydrocarbons, halogenated hydrocarbons, PCBs	May impede setting. Decreases durability over a long time period. Volatiles may escape on mixing. Demonstrated effectiveness under certain conditions.	May impede setting. Decreases durability over a long time period. Volatiles may escape on mixing. Demonstrated effectiveness under certain conditions.	Organics may vaporize on heating. Demonstrated effectiveness under certain conditions.	May impede setting. Demonstrated effectiveness under certain conditions.
Polar organics as: alcohols, phenols, organic acids, glycols	Phenol will significantly retard setting and will decrease durability in the short run. Decreases durability over a long time period.	Phenol will significantly retard setting and will decrease durability in the short run. Alcohols may retard setting. Decreases durability over a long time period.	Organics may vaporize on heating.	No significant effect on setting.
Acids as: hydrochloric acid, hydrofluoric acid	No significant effect on setting. Cement will neutralize acids. Types II and IV portland cement demonstrate better durability characteristics than Type I. Demonstrated effectiveness.	No significant effect on setting. Compatible, will neutralize acids. Demonstrated effectiveness.	Can be neutralized before incorporation.	Can be neutralized before incorporation. Ureaformaldehyde demonstrated to be effective.
Oxidizers as: sodium hypochlorate, potassium permanganate, nitric acid, potassium dichromate	Compatible.	Compatible.	May cause matrix breakdown, fire.	May cause matrix breakdown, fire.
Salts as: sulfates, halides, nitrates, cyanides	Increases setting times. Decreases durability. Sulfates may retard setting and cause spalling unless special cement is used. Sulfates accelerate other reactions.	Halides are easily leached and retard setting. Halides may retard setting, most are easily leached. Sulfates can retard or accelerate reactions.	Sulfates and halides may dehydrate and rehydrate, causing splitting.	Compatible.
Heavy metals as: lead, chromium, cadmium, arsenic, mercury	Compatible. Can increase set time. Demonstrated effectiveness under certain conditions.	Compatible. Demonstrated effectiveness on certain species (lead, cadmium, chromium).	Compatible. Demonstrated effectiveness on certain species (copper, arsenic, chromium).	Compatible. Demonstrated effectiveness with arsenic.
Radioactive materials	Compatible.	Compatible.	Compatible.	Compatible.

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4. Testing

- What does a stabilized HW mean?
- How can the effectiveness of S/S be measured?
- How strong does the solidified material need to be?
- How fast can contaminants leach from stabilized HW?
- Assessment of effectiveness of stabilization requires the measurement of physical, engineering and chemical properties of the stabilized material.
- A large number of laboratory tests are utilized to evaluate the effectiveness of stabilization.

Extraction and leaching tests

- Reduction in the rate at which contaminants can migrate into the environment is the first and foremost reason for selecting S/S as a HW management technique.
- Extraction and leaching are used interchangeably and are the process by which contaminants are transferred from a solid or stabilized matrix to the leachate.
- Finally, the overall ability of a stabilized material to leach contaminants is termed leachability.

Leaching test methods

- Paint filter test
- Liquids release test
- Extraction procedure toxicity test (EPTox)
- Synthetic precipitation leaching procedure (SPLP)
- Toxicity characteristic leaching procedure (TCLP)
- Modified uniform leach procedure
- Equilibrium leach test
- Dynamic leach test
- Sequential leach test
- Multiple extraction procedure

Leaching test methods

- Variables that affect the contaminant conc. in leachate.
  - Leachant-to-waste ratio
  - Surface area of the waste (grinding the stabilized mass)
  - Type of leachant (d$H_2$0, acetic acid, simulated acid rain)
  - pH of the leachant
  - Contact time
  - Extent of agitation
  - Number of replacements of fresh leachant
  - Extraction vessel
  - Temperature

Paint filter test

- Evaluates the absence or presence of free liquids in bulk and containerized HWs.
- Rapid, economical, easy to conduct & easy to evaluate.
- Wastes are placed in a standard paint filter; if liquid is drained by gravity within 5 min, the HW is considered to contain free liquids & must be treated prior to landfilling.
- May also be used after stabilization to determine if the stabilization process has been effective in eliminating free liquids from the HW.

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Toxicity characteristic leaching procedure (TCLP)

- Performed to determine if a particular waste meets the applicable treatment standards to be land-disposed.
- Used to evaluate the effectiveness of stabilization and for classification of materials as hazardous or nonhazardous
- Stabilized material is crushed to a particle size smaller than 9.5mm and mixed with a weak acetic acid extraction liquid in a liquid-to-solid weight ratio of 20:1.
- Agitated in a rotary extractor for a period of 18 hrs at 30 rpm and 22^{o}C.

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Toxicity characteristic leaching procedure (TCLP)

- After 18 hours, the sample is filtered through a 0.6-0.8 μm glass fiber filter and the filtrate is defined as the TCLP extract.
- This TCLP extract is analyzed for a wide variety of HW constituents including volatile and semivolatile organics, metals and pesticides.
- Results of the extract analysis are compared to the national regulatory level to determine the nonhazardous classification.

Chemical test methods

- Total waste analysis
  - Metals by ICP or AAS
  - Organics by GC and GCMS
- Total organic carbon (TOC)
- Loss on ignition (volatile solids)
- pH
- Fourier transform infrared spectra (FTIR)
- Differential scanning calorimetry and thermal gravimetric analysis

Physical and engineering property tests

- Moisture content: used to determine the amount of water (or liquid) in a given quantity of material
- Wet and dry bulk density: Bulking (increase in volume) associated with stabilization is evaluated by using bulk unit weights that provide information for weight-volume relationships and for calculating density and void volume.
- Specific gravity: Density of solids divided by density of water is specific gravity. Specific gravity is numerically equal to the density of solids as water has a density of 1.0 g/cm^3.

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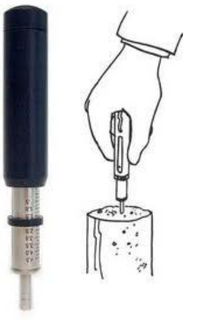
Physical and engineering property tests

- Particle size distribution: To determine the particle size distribution, sieves are employed for coarse fractions. Gravitational methods employing a hydrometer are used to separate the fine fraction particles.
- Pocket penetrometer provides information on strength of material being tested. It is a standardized cylinder that is pushed into material to measure penetration resistance, estimating unconfined compressive strength in tons/m^2.



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Physical and engineering property tests

- Microstructural examination: Stabilized mass can be examined by X-ray diffractometry, optical microscopy, SEM and energy dispersive microscopy to better understand the nature of stabilization processes at work.
- Supernatant formation during curing and rate of setting: These test methods characterize the performance of treated wastes in the first few hours after mixing. They are particularly suitable for concrete-like (high-slump) materials and not suited for soil-like materials. These tests give early information regarding suitability of mix.

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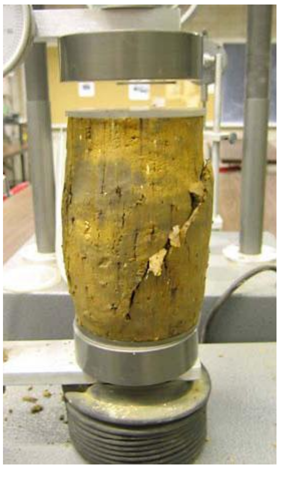
Physical and engineering property tests

- Unconfined compressive strength test is conducted to determine the strength of cohesive materials (ranging from soft clays to concrete).
- A cylindrical specimen is axially loaded to failure.
- Axial load and corresponding deformation are measured.



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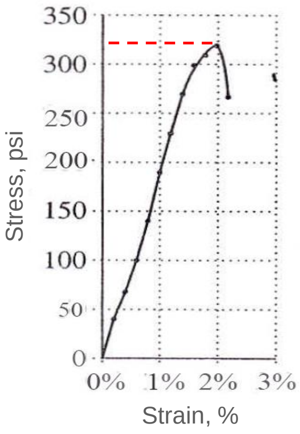
Physical and engineering property tests

- From these measurements, the applied stress and resulting strain can be calculated and the stress-strain relationship is plotted
- The unconfined compressiye strength is then the maximum applied stress in the test.



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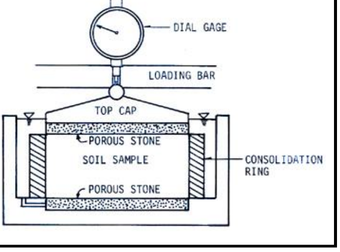
Physical and engineering property tests

- Some form of consolidation test may be well suited for the evaluation of the settlement of stabilized waste.
- Consolidation test measures the time rate of one-dimensional compression as well as the relationship between applied vertical stress and total deformation.
- During a consolidation test, an axial load is applied to the material, which is restrained from lateral deformation.



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Physical and engineering property tests

- Hydraulic conductivity (permeability) is the ability of a material to conduct or discharge water in response to an applied hydraulic gradient.
- It is used to estimate the flow rate of fluid through a porous material.
- As a result, hydraulic conductivity is used to calculate information regarding the rate at which chemicals in the treated waste may migrate into the environment.

Physical and engineering property tests

- Durability test methods are needed to assess the long-term performance of the stabilized mass.
- Durability testing is used to evaluate the ability of a material to resist repeated cycles of weathering.
- A successfully solidified waste material will remain intact throughout these tests, so that the area of the waste directly exposed to leaching is not greatly increased.
- Experience has shown that most specimens that withstand freeze/thaw cycles also withstand wet/dry cycles, but the reverse is not necessarily true.