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Grout and Glass Performance Maximizing the Loading of ORNL Tank Sludges

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DEPARTMENT OF ENERGY

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ORNL/TM-13712

CHEMICAL TECHNOLOGY DIVISION

GROUT AND GLASS PERFORMANCE MAXIMIZING THE LOADING OF ORNL TANK SLUDGES

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EXECUTIVE SUMMARY

Grouting and vitrification are currently two likely stabilization and solidification alternatives for radioactive and hazardous mixed wastes stored at Department of Energy (DOE) facilities. Grouting has been used to stabilize and solidify hazardous and low-level radioactive waste for decades. Vitrification has been developed as a high-level radioactive alternative for decades and has been under development recently as a mixed-waste alternative disposal technology.

Wastewater at the Oak Ridge National Laboratory (ORNL) is collected, evaporated, and stored in the Melton Valley Storage Tanks (MVST) and Bethel Valley Evaporator Storage Tanks (BVEST), pending treatment for disposal. In addition, some sludges and supernatants also requiring treatment remain in two inactive tank systems: the gunite and associated tanks (GAAT) and the old hydrofracture facility (OHF) tanks. The sludges contain a high amount of radioactivity, and some are classified as transuranic (TRU) sludges. Some Resource Conservation and Recovery Act (RCRA) metal concentrations are high enough to be defined as RCRA hazardous; therefore, these sludges are presumed to be mixed TRU waste.

The primary objective in the current laboratory work was to maximize the loading and minimize the volume increase in grouting these sludges for final disposal with no requirement for strength, while still maintaining leach resistance. A secondary objective was to test both grout and glass formulations with samples of the actual sludges. These objectives were met and are documented in this report. Sludge loadings of around 90 wt % are possible with minimal volume increases of <10 vol %. In general, the formulation consisted of 90, 8, and 2 wt % wet sludge, dry blend, and hydrogel, respectively. The dry blend of 84, 8, 8 wt % slag, cement, and illitic clay stabilized the hazardous metals and radioisotopes. Hydrogels, a three-dimensional polymeric structure incorporating up to 90% water, allow such high loadings without any bleed water during short-term processing. The grouted waste, however, does not form a strong monolithic waste form at such high loadings, that is, the grout can support the overburden but is weak. It may be best to judge in the field the potential of a treated waste to generate bleed water before adding a hydrogel. If the treated waste is already fairly stiff, adding hydrogel can result in a fairly dry, crumbly waste form that may not be desirable. Toxicity Characteristic Leach Procedure (TCLP) performance proved to be the limiting factor in sludge loading. Developing the formulation to maximize the loading while still passing TCLP tailored the grout fairly specifically for the sludge being tested. Although the surrogates served adequately for predicting actual sludge performance at more robust loadings, pushing the performance too close to Universal Treatment Standard (UTS) limits is risky because the differences between the surrogate and actual sludge could lead to field performance failure. Stabilizing the dichromates in the surrogates established the loading limits for the surrogates. The chromium appeared less leachable in the actual sludges, implying a different species, and conservatively making the surrogates more challenging to stabilize, as intended. However, other RCRA metals were limiting for the actual sludges (silver for GAAT W4 and lead for BVEST W23 and OHF T3) and apparently were less leachable from the surrogates than from the actual sludges at sludge loadings around 90 wt %. Further tailoring of the grout formulations with the actual sludges at 90 wt % loadings was required in order to meet the UTS limits. The MVST-BVEST surrogate was a conservative predictor of MVST W25 sludge performance at the more robust loading of 55 wt % in prior testing.

In summary, performance of the grout decreases as the waste loading increases, becoming weaker and more leachable. Apparently, simple addition of a hydrogel will eliminate free water, a typical waste acceptance criterion. Meeting TCLP limits is not a criterion for deep geological disposal [e.g., Waste Isolation Pilot Plant (WIPP)], but it is for shallow land disposals. Sludge loadings up to about 85 wt % appear to form leach-resistant monolithic waste forms with fair strength. Above 85 wt %, the grouts continue to become less consolidated and more like soil.

Grout and vitrification treatments are inherently different. Grouting adds stabilizing agents directly to the wet sludge, inevitably increasing the volume unless evaporation or other pretreatment reduces the sludge volume. For vitrification, the sludge is inevitably dried and calcined into its refractory oxides, with the accompanying mass and volume decrease, and then its composition adjusted to make a suitable glass melt. The mass loss and densification accompanying vitrification usually result in net volume decreases. The difference in volume between grouting and vitrifying these tank sludges is a key factor in storage and disposal costs, the dominant cost in the economic analysis conducted in a separate report. The key to maximizing the waste-oxide loading for vitrification and more volume decrease is the amount of glass formers-modifiers present in the waste. The key glass ingredients must be within a bounded region to make a "good" glass melt. If the waste doesn't contain the proper composition, then the major constituents must be added to adjust the composition. In addition to the major glass constituents, components that act as nucleation sites and/or have low solubility in the glass melt must be identified in the waste characterization and accounted for in the glass formulation development. In general, these two groups—the major glass-forming components and the minor troublesome components—dictate what waste-oxide loading is achievable. A small fraction of wastes can be vitrified directly into glass without any additional ingredients. Typically, a large fraction of glass components must be added to the waste to achieve the desired composition. Theoretically, a low-waste-oxide loading could be required if the waste contains little or no glass constituents and has a large fraction of a troublesome nucleating agent or low solubility material. However, most wastewater treatment sludges and ashes appear to be acceptable candidates for vitrification with the possibility of achieving reasonably good reduction in volume. The ORNL tank sludges contain high percentages of sodium and calcium; thus, primarily silica needed to be added for making a soda-lime glass waste form. The glass melt solubility of the thorium and uranium present in these sludges were accounted for in the glasses developed by the Savannah River Technology Center (SRTC), with 40 to 45 wt % waste-oxide loadings at less than half the volume of the original wet sludges. Vitrification converted the actual tank sludge samples into dense, leach-resistant final waste forms. Off-gas treatment must be addressed in any field vitrification, but it was not addressed in these laboratory hot tests.

ABSTRACT

The sludge loading limits was explored for the dry blends that had performed more or less robustly at sludge loadings of 50 to 60 wt %. The surrogate sludges had experienced free water problems at higher sludge loadings. Pretreating the sludge to remove water can effectively solve this problem, but hydrogels were found to be effective at preventing free water generation during cure as the stabilizing agents hydrated and consolidated the sludge. As expected, the waste form strength decreased with increasing sludge loading. At the higher loadings of 90 wt % or greater, the treated sludge was like soil in strength, not cement. To meet TCLP criteria, the final waste form required 5 to10 wt % of the stabilizing agents, based on surrogate testing, effectively limiting the sludge loading to about 90 wt %. Subsequent hot testing with actual sludges proved that the surrogate testing had been misleading at these high sludge loadings and may force loadings below 90 wt %. The driver for the surrogate tests was shown to be the sodium dichromate used in the surrogate sludges, but lead proved to be the problem for two actual sludges and silver for the other.

1. INTRODUCTION

Grouting and vitrification are currently two likely stabilization and solidification alternatives for radioactive and hazardous mixed wastes stored at Department of Energy (DOE) facilities. Grouting has been used to stabilize and solidify hazardous and low-level radioactive waste for decades. Vitrification has been developed as a high-level radioactive alternative for decades and has been under development recently as a mixed-waste alternative disposal technology.

Wastewater at the Oak Ridge National Laboratory (ORNL) is collected, evaporated, and stored in the Melton Valley Storage Tanks (MVST) and Bethel Valley Evaporator Storage Tanks (BVEST) pending treatment for disposal. In addition, some sludges and supernatants also requiring treatment remain in two inactive tank systems: the gunite and associated tanks (GAAT) and the old hydrofracture facility (OHF) tanks. The sludges contain a high amount of radioactivity, and some are classified as transuranic (TRU) sludges. Some Resource Conservation and Recovery Act (RCRA) metal concentrations are high enough to be defined as RCRA hazardous; therefore, these sludges are presumed to be mixed TRU waste.

This report culminates the laboratory comparison of grout and glass formulations to stabilize these tank sludges. Two companion reports preceding this report documented the efforts to develop grout and glass formulations capable of stabilizing sludges either from individual tank sets or a mixture of all tank sets, plus the hot testing of the formulations with an actual sludge sample from MVST W25.[1,2] The grout sludge loading was restricted in this prior development work by the inclusion of strength criteria and free water generation. Efforts this fiscal year (FY) focused on maximizing the sludge loading of each tank farm set and minimizing the volume increase, without imposing any strength criteria. The glass surrogate development was performed at the Savannah River Technology Center (SRTC). The grout surrogate development and the hot testing of both grout and glass with samples of actual sludge from individual tank sets were performed at ORNL. This report documents the surrogate grout development and the results of the grout and glass hot tests.

2. OBJECTIVE

The primary objective of this project is to maximize the grout sludge loading of each tank farm set (GAAT, BVEST, and OHF) and to minimize the resulting volume increase, without imposing any strength criteria, while still meeting the leach resistance requirements for a nonhazardous waste. Consequently, the criteria that established the maximum sludge loading follow:

1. *Free water*—the waste acceptance criteria (WAC) for most disposal facilities sets a limit of <0.5 vol % free water on any wastes accepted for disposal.
2. *Land disposal*—the land disposal restrictions (LDR) for the disposal of hazardous wastes must be met, since the tank sludges were presumed to be mixed wastes. This objective implied meeting the Universal Treatment Limits (UTS) for the Toxicity Characteristic Leach Procedure (TCLP).

This objective was met by laboratory testing of surrogate sludges. A secondary objective was the hot testing of actual tank sludges from each individual tank set with both the grout and glass formulations developed for the surrogates.

3. SURROGATES

Surrogate sludge compositions were developed during the prior studies for each tank set—MVST-BVEST, GAAT, and OHF—plus an overall weighted average surrogate sludge to simulate mixing of the sludge presently in inventory.[1, 2] Samples of sludge were obtained from tanks GAAT W4, BVEST 23, and OHF T3 for hot testing. These sludge samples were characterized, and adjustments were made in the surrogate sludge compositions previously reported to more closely represent the actual sludge sample compositions being tested. Then, a grout formulation was developed for each surrogate to maximize the sludge loading. The standard surrogate modified to represent the actual sludge sample was also used in the sensitivity testing of variations in the grout composition. For the maximum water sludge in sensitivity testing, the relative composition of the solids was kept the same and the maximum water content from the prior efforts was used. For the minimum water and maximum "bad actors," the surrogate compositions for each tank set listed in these previous reports were used. These compositions varied significantly from the actual sludge sample compositions. These variations in surrogate sludge composition were representative of the range previously measured in prior tank sludge characterizations.[3-7] These compositions varied significantly from that measured for the actual sludge samples. Ironically, the water content measured in the actual OHF T3 sludge sample exceeded the maximum water content reported in these references for the OHF tank set. It is possible that the actual T3 sludge sample was contaminated with supernatant water. In any case, the apparent contradictory lower water content for the surrogate "maximum water" OHF T3 sludge results from basing this composition on the earlier tank sludge characterization data rather than the composition of the actual sludge sample.

Table 1 lists the composition measured for the GAAT W4 sludge sample and compares this measured composition to the surrogate GAAT sludge composition reported in ref. 2. It was decided to use the prior surrogate composition with only a minor modification (e.g., silver oxide was added). Also, the halides in the surrogate appeared to affect the surrogate TCLP silver performance and were dropped from the surrogate after a few initial tests. Table 2 lists the composition of the surrogate OHF T3 sludges used during the studies documented in this report: standard with and without halides, maximum water, and minimum water-maximum "bad actors." As stated above, the minimum water-maximum "bad actors" surrogates were developed and reported previously.[1,2] In general, "bad actors" were defined as the RCRA metals, sulfate, phosphate, carbonate (or total inorganic carbon, TIC), and total organic carbon (TOC). A photograph of the surrogate GAAT W4 sludge is presented in Fig. 1.

Table 3 lists the measured composition of the BVEST W23 sludge sample and compares this composition with that of the surrogate MVST-BVEST from ref. 1 and the surrogate BVEST W23 sludge used in this study. Table 4 lists the composition of the surrogate BVEST W23 sludges used during the studies documented in this report: standard, maximum water, and minimum water-maximum "bad actors." A photograph of the surrogate BVEST W23 sludge is presented in Fig. 1.

Table 5 lists the measured composition of the OHF T3 sludge sample and compares this composition with that of the surrogate OHF from ref. 2 and the surrogate OHF T3 sludge used in this study. Table 6 lists the composition of the surrogate OHF T3 sludges used during the studies documented in this report: standard, maximum water, and minimum water-maximum "bad actors." As stated previously, these latter two surrogates were based on prior work. The water content for the "maximum water" actually is less than that for the standard surrogate, which was based on the measured composition of the T3 sludge sample. A photograph of the surrogate OHF T3 sludge is presented in Fig. 1.

4. SELECTION OF THE DRY BLEND ADDITIVES FOR FURTHER EVALUATION

The historical inorganic additives used for stabilization and solidification are Portland cement, fly ash, lime, and clay, but also include blast furnace slag, cement kiln dust, high-alumina cements, natural pozzolans, masonry cements, special cements, and cement admixtures.[8, 9] Conner cites the following reasons for the widespread use of these materials in treating wastes.[8]

- Relatively low cost
- Good long-term stability, both physically and chemically
- Documented use on a variety of industrial wastes over a period of at least 10 years
- Widespread availability of the chemical ingredients
- Nontoxicity of the chemical ingredients
- Ease of use in processing (processing normally operated at ambient temperature and pressure and without unique or very special equipment)
- Wide range of volume increase
- Inertness to ultraviolet radiation
- High resistance to biodegradation
- Low water solubility
- Relatively low water permeability
- Good mechanical and structural characteristics

The International Atomic Energy Agency (IAEA) lists the following advantages and disadvantages of cement for the solidification of radioactive wastes:[9]

Advantages

- Material and technology well known;
- Compatible with many types of waste;
- Most aqueous wastes chemically bound to matrix;
- Low cost of cement;
- Good self-shielding;
- No vapor problems;
- Long shelf life of cement powder;
- Good impact and compressive strengths;
- Low leachability for some radionuclides;
- No free water if properly formulated;
- Rapid, controllable setting, without settling or segregation during curing.

Disadvantages

- Some wastes affect setting or otherwise produce poor waste forms.
- the pH adjustment of waste may be necessary.
- Swelling and cracking occur with some products when they are exposed to water.
- Volume increase and high density may develop.
- Excessive heat may develop during setting with certain combinations of cement and waste.
- Dust problems may occur with some systems.
- Equipment for powder feeding is difficult to maintain.
- Potential maintenance problems may result from premature cement setting, especially in the case of in-line mixers.

Portland cement, fly ash, Indian Red Pottery Clay (IRPC), ground granulated blast furnace slag, and water-sorptive agents were selected for use in this study. A brief history and the reason for selection are presented in the following subsections for each material.

4.1 PORTLAND CEMENT

Portland cement, its composition and its chemistry are discussed in great detail in several references and will not be discussed in detail in this report.[8-14] The main points of interest for cement stabilization/solidification are the (1) normal high pH of cement matrices, (2) production of calcium hydroxide in normal cement hydration, and (3) strong binding matrix, resistant to advective water flow and leaching that interacts with and encapsulates the waste. Wastes are generally physically encapsulated heterogeneously in the calcium-silicate-hydrate (CSH) matrix, with the level of dispersion and homogeneity usually dependent on the energy and effort put into physically mixing waste and cement. Despite the inherent composite nature of cement waste forms, the wastes strongly interact with the cement, stabilizing contaminants as desired and sometimes interfering with cement hydration (which is not desired). Although there is evidence that some contaminants are incorporated into the CSH matrix, the main stabilizing mechanism of cement waste forms is the high pH matrix, similar to the lime precipitation of metals in waste water treatment.

This high pH precipitation captures the majority of the RCRA metals and radionuclides. For example, the low solubility at high pH of copper, nickel, iron, cadmium, zinc, silver, and lead are illustrated in the published solubility curves with pH.[8, 15] In general, these solubility curves pass through a minimum as the pH increases, meaning these metals actually start becoming more soluble with pH past a certain point, with the generation of complex hydroxide ions. The minimum solubility for these metals occurs in a pH range from about 9 to slightly more than 11. The normal production of calcium hydroxide during cement hydration and the presence of alkalis in the cement can produce a pore solution pH in the range of 12 to13, well above the minimum solubility for most of these metals.[8] This combination (high matrix pH and increasing metal solubility at this pH level) can actually increase the leachability of some wastes after treatment.

This is one reason neat cement pastes (i.e., pastes consisting only of mixtures of cement and water) are a poor choice for stabilizing wastes and why cement-fly ash combinations are almost always used. Fly ash consumes the calcium hydroxide produced during cement hydration by (1) moderating the matrix pH and (2) eliminating the large soluble portlandite crystals (these crystals dissolve upon immersion, leaving large accessible pores in the matrix, increasing porosity and leachability) found in neat cement pastes. Cementitious waste forms (typically, cement and fly ash) reportedly have a pH of about 11, much better suited for minimizing metal solubility.[16] The solubility behavior of the RCRA metals in cement waste forms mimics these solubility curves to a certain degree, but differ enough to illustrate that "... factors other than hydroxide precipitation are in operation...."[8, 17]

Cements are produced and sold in many forms, any of which may be suitable for stabilizing wastes. Portland cements are the most commonly available cements, typically locally available and cheap. The American Society for Testing and Materials (ASTM) standards specify five standard Portland cements with optional properties available within each type (ASTM C 150 - 89): [18, 8]

ASTM Type Portland Cement	Description
I	General-purpose Portland cement and usually the least expensive
II	Moderate sulfate resistance and moderate heat of hydration; Type II-fly ash is typical substitute when job size can't justify Type IV production
III	High early strength and cold weather use
IV	Low heat of hydration; used in massive structures (e.g., dams), where temperature rise can approach adiabatic; generally not available; mass produced for specific jobs
V	Sulfate resistant

ASTM Type I Portland cement is most commonly used for waste stabilization because of its wider availability and lower cost and can work in most cases with proper tailoring. The way the ASTM specifications are written, ASTM Type II Portland cement can be considered a subset of ASTM Type I Portland cement and quite often cement is marketed as Type I-II Portland cement. If Type II Portland cement is locally available, it may be better to specify Type II because of its better sulfate resistance and lower heat of hydration (many wastes contain sulfate, and the heat of hydration can be a concern for some waste-form applications). In addition, specifying the options of low alkali (LA) and low alumina (if available) may be desirable to make the final waste form more resistant to later destructive expansion from minerals, such as alkali silicates, ettringite, or calcium chloroaluminate.

In summary, the best a priori cement selection may be ASTM Type II Portland cement-LA-low alumina-moderate heat of hydration. However, any of the cement types may be satisfactory for a given application, and such selections should be made on a case-by-case basis, depending on waste composition, cement availability, technical performance, and costs. In the present study, the main function of the cement selected was to ensure activation of the ground-granulated blast furnace slag; hence, it was not necessary to specify the cement listed above since it would not provide the basic waste form matrix. Type I, Type II, or Type I-II would be equally appropriate for this task, although Type II or I-II would still be preferred, if readily available, because of better sulfate resistance.

4.2 FLY ASH

Fly ash is an active pozzolan source that reacts with the caustic alkalis and alkalines, consuming hydroxide and producing alkali silicates and more CSH. Fly ash is only one of several possible pozzolans that can be used with cement or lime to produce cementitious waste forms. Other pozzolan candidates include volcanic glasses, volcanic tuffs, calcined clays and shales, diatomites, rice husk ash, volatilized silica (silica fume), blast furnace slag, and other slags.[9] The key to the reactivity of the fly ash (and many of the other pozzolans) is its glassy structure. Only the amorphous glassy form provides a soluble silica source for reacting with the lime (and other caustics). The crystalline forms, like mullite, are too insoluble, stable, and inert. Fly ash was used in construction concrete decades prior to its use in waste disposal.[8, 9, 19-23]

Using fly ash in concrete has many advantages in certain usages, the most important being cost, as it replaces 25 to 35 wt % of the Portland cement normally used.[8] Incorporating fly ash into cement lowers the heat of hydration, reducing curing temperature, an advantage in producing massive monoliths.[9, 21-23] Fly ash acts as both a pozzolan and a bulking agent, helping prevent settling in relatively low-solids wastes and saving costs by substituting for cement.[8] However, such bulking does result in larger volume and weight increase than for Portland cement alone, "... usually only justified where low handling, transportation, and disposal costs are encountered."[8] However, the relatively higher volume from fly ash is acceptable in its use as a pozzolan. Hydrating cement produces lime as a by-product that forms large soluble crystals in the cured neat cement paste matrix. These crystals dissolve upon immersion, leading to increased accessible porosity and leachability. Pozzolans react with this lime to produce more CSH to fill the available porosity, decreasing accessible porosity and leachability. In other words, fly ash "... helps to bind additional water, decrease the pore pH, and act as an adsorbent for metal ions."[8]

Since strontium behaves similarly to calcium, cement-pozzolans will also tend to tie up ^{90}Sr better than cement alone. Cement-fly ash has traditionally been the stabilizer of choice for ^{90}Sr, although cement alone does stabilize ^{90}Sr quite well.[19, 24-27]

The ASTM standards specify two fly ashes and one natural or calcined pozzolan for use in Portland cement concrete (ASTM C 618 - 91)[8, 28]

ASTM Mineral Admixture Class	Description
N	Raw or calcined natural pozzolans
F	Fly ash, normally produced from anthracite or bituminous coal, has pozzolanic properties
C	Fly ash, normally produced from lignite or subbituminous

coal, has pozzolanic and cementitious properties and may contain lime >10 %

In general, a commercial industry has evolved to supply fly ash cheaply and with adequate quality control to routinely meet ASTM standards, making a valuable by-product out of the large amounts of waste produced daily in the coal-fired power plants across the country. Although both can be and have been used, ASTM Class F fly ash is generally preferred for waste treatment, because of the possibility of "flash set" in the equipment with ASTM Class C fly ash. This difference in reactivity is indirectly related to the higher minimum specified content of silica, alumina, and iron oxide for Class F (≥70 wt %) compared with Class C (≥50 wt %). Although the lime content is not specified in the standard, a large fraction of the remaining composition is "free lime," which can lead to hydraulic cementitious reactions within the fly ash. Typically, the low-lime content of Class F fly ash is quickly consumed, leaving the bulk of the fly ash relatively inert until caustically activated (e.g., by mixing with cement and the subsequent production of lime from hydration). Class C fly ash can contain lime concentrations as high as 30 wt % or higher, a highly reactive mix that can set into a cementitious product in a matter of minutes upon mixing with water ("flash set"). Since the lime content is not specified by the standard, lime content of the fly ash varies from source to source and can vary from batch to batch. For these reasons, ASTM Class F fly ash was selected for this study.

4.3 INDIAN RED POTTERY CLAY

Over the years, illite (Indian Red Pottery Clay), $(OH)_4K_x(Al_4Fe_4Mg_4Mg_6)(Si_{8-x}Al)O_{20}$, has become a proven standard additive in grout formulation development at ORNL for making cementitious waste forms more resistant to the leaching of ^{137}Cs.[25, 26, 29–31] Illite has been known as an effective selective sorbent for ^{137}Cs for decades.[32–34] The gap between illite layers is apparently ideal to allow cesium ions to diffuse between the clay layers and essentially irreversibly trap these ions. Although there are other illitic sources (e.g., conasauga shale), Indian Red Pottery Clay (IRPC) is the most readily available commercial source. The standard recipe evolved into 8 wt % of IRPC in the dry blend of cementitious materials used to stabilize and solidify the waste liquids, solids, or sludges. The 8 wt % in the dry blend was far in excess of the stoichiometric amount needed to load the typical ^{137}Cs contamination found in the wastes into the clay, because even a waste with high gamma activity from ^{137}Cs has a quite low concentration of ^{137}Cs on a molar basis. The main reason for 8 wt % IRPC in the dry blend was to distribute enough IRPC throughout the waste form so that all of the ^{137}Cs had access to the IRPC and mass transport distances were minimized. This strategy has served well for many years as witnessed by the high ANSI/ANS-16.1 leachability indexes reported for ^{137}Cs over the years for grouts containing IRPC.

4.4 GROUND GRANULATED BLAST FURNACE SLAG

Blast furnace slag is a normal by-product of the iron and steel industry. In general, the slag is cooled in two ways: (1) air cooling and (2) water quenching (granulation). Air cooling produces inert crystalline slag useful as an inert fill material, but useless as a cement substitute. The essential components of slag are the same oxides as are present in Portland cement, but "... for use as a cement, rapid cooling is necessary to quench the material to form a reactive glass and to prevent the crystallization of unreacted chemical compounds."[9] Granulated slag hydrates slowly on contact with water, but is activated by caustics (e.g., calcium hydroxide or sodium hydroxide), calcium sulfate, sodium carbonate, and sodium sulfate.[9] The granulated slag is finely ground and marketed as a substitute for cement. The ground granulated blast furnace slags (slags) "... have physical properties similar to those of ordinary Portland cements. The distribution of particle size and the surface area of blast-furnace slags depend on the method of manufacture, but in general their fineness is similar to that of Portland cements."[9, 35]

Slags have been substituted for cement for decades.[36] Slags hydrate slowly to form CSH, the same product formed by cements, but slag alters the morphology and properties of the final product, sometimes in subtle ways, but beneficially in general: [9, 36-43]

- early strength development is slower,
- heats of hydration are lower,
- sulfate resistance is improved,
- lower permeability despite increased total porosity,

- improved frost resistance,
- lower ionic diffusion rates,
- increased salt stability,
- reduced setting rate,
- extended working time,
- pore water contains sulfur species in addition to hydroxide anions,
- high pH and low oxygen potential,
- reduced solubility of most contaminants,
- reduced rate of corrosion of steel containers, and
- other physical and mechanical properties similar to portland cements (e.g., density and compressive strength).

A slag:cement combination of 75:25 virtually eliminates calcium hydroxide as a hydration product (i.e., the presence of excess slag prevents build up of this cement hydration product.[9] This implies that the proper proportion of slag-cement can replace cement-fly ash to stabilize ^{90}Sr. In addition, a combination of 85:15 or higher slag produces a strong reducing environment within the matrix, suitable for reducing pertechnetates or chromates.[44, 45] Thus, slags have been used in grouts developed for radioactive and mixed wastes for a long time.[44-54]

The ASTM standards specifies three strength grades of ground granulated blast furnace slag for use in concrete and mortars based on the slag activity index:[55]

ASTM Slag Grade	Minimum Average Slag Activity Index, %	
	7 d	28 d
80	. . .	75
100	75	95
120	95	115

These slag grades are important for construction purposes, but not necessarily for waste treatment, where strength requirements are usually minimal. The chemical properties normally present in commercially available slag are their most important property for waste treatment and are generally not specified in the ASTM standard. Perhaps the most important property (Re: waste treatment) measured in the standard is the air permeability or Blaine fineness, although no limits are specified.[56] Finer slag usually means a lower permeability, not only in the dry slag, but also in the resulting cementitious matrix. A lower permeability implies "... improved resistance to frost, lower diffusion rates of ions through the hardened cement and improved stability in the presence of salts, such as chloride and sulphate."[9, 42] Typically, Portland cement has a Blaine fineness of 3000 to 4000 cm^2/g and slag, of 4000 to 5000 cm^2/g, but slag >5000 cm^2/g, or even >6000 cm^2/g, can sometimes be acquired. In general, the finer, the better, although it is unlikely that special requests for finer grinding are worth the additional costs. Any commercially available slag suitable as a cement substitute generally improves the matrix properties and imparts the desired properties to the final waste form. Ground granulated blast furnace slag with a Blaine fineness of >4000 cm^2/g was selected for this study.

4.5 WATER-SORPTIVE AGENTS

When a grout is poured and allowed to remain static, the binding and pozzolanic agents (cement, fly ash, slag) tend to settle under gravity and buoyancy, displacing a drainable liquid to the grout surface (phase separation, bleed water, free-standing liquid, or free water).[57-59] Traditionally, two methods have been used to control this free-water generation: (1) increasing the solids-to-liquid mix ratio (or inversely decreasing the liquid, or water, to solids ratio W/S) and (2) adding gel clays. Gel clays disperse in water and form a thick, stable colloidal gel when mixing stops. This prevents suspended particles, such as fly ash, cement, or slag, from settling while minimizing the dry blend added for treatment and the subsequent volume increase. The gel clays from oil field drilling fluids (muds) were adapted for this purpose in waste treatment grouts.

Water-sorptive clays have been used in geotechnical applications [e.g., construction (slurry walls and clay caps) and drilling (drilling muds and cement mixes)] for decades to resist solids segregation (suspension aid), prevent bleed water, and act as an engineered hydraulic barrier to water penetration (into a construction zone, waste disposal site, etc.)]. The most commonly used clay for these purposes is bentonite, sodium montmorillonite, "... a colloidal clay mined in Wyoming and South Dakota. It imparts viscosity and thixotropic properties to fresh water by swelling to about 10 times its original volume. Bentonite (or gel) was one of the earliest additives in oil well cements to decrease slurry weight and to increase slurry volume."[60, 61] The individual clay particles of bentonite are plate-shaped. The particle faces are positively charged; the edges are negatively charged. When mixed with water, the platelets separate and disperse throughout the fluid. When mixing ceases, the clay particles form a multilayered colloidal gel structure due to the attraction of opposite charges. However, the electrostatic double-layer forces are lessened with increasing ionic strength.[59,62] Consequently, high-salt solutions (notably chloride, sulfate, and phosphate salts, as well as acids and bases) collapse these gels, lessening their dispersive effectiveness and releasing the large volume of water collected around the clay particles (i.e., free water can form if salt solutions are grouted).[59, 63]

This susceptibility compromised the use of bentonite in off-shore oil drilling in salty waters. For this reason, attapulgite was adapted as the gel clay used in such salty applications, because attapulgite clay particles carry no charge and are not affected by high-salt content.[59] The individual attapulgite particles resemble needles, rather than platelets. When mixed with water, these needles are dispersed throughout the fluid and become aligned along shear planes. When mixing ceases, a gel structure is formed by the random entanglement of these particles, referred to as a "brush-heap effect." Attapulgite is commercially available only from northern Florida and southern Georgia.[59] Thus, attapulgite has been adopted as the gel clay of choice for salty wastes. Note that although several forms of attapulgite have been tested for DOE salty wastes, only attapulgite 150 (Attagel 150) proved effective.[59, 64] The American Petroleum Institute (API) has issued specifications for both bentonite and attapulgite.[65, 66]

In general, the hazardous waste industry adopted a different strategy for treatment of low-solids wastes (i.e., wastewaters and watery sludges), although clays were not eschewed. Practically any water-sorptive agent was considered a candidate, but sodium silicate may have been the most popular, resulting in numerous patents.[8] Sodium silicate forms a hydrogel, a three-dimensional polymeric structure incorporating up to 90% water (i.e., a small amount of sodium silicate can accommodate a large amount of water). Adding sodium silicate to the grout can be quite effective at controlling free water generation and generally results in a grout with a smooth surface sheen appearance, as opposed to the usual rough wet paste appearance. Sodium silicate does thicken immediately upon mixing with cement. For this reason, it may be added as the last step in mixing to prevent any mixing problems. More recently very effective organic polymer hydrogels have been developed and used as solution grouts, similar to sodium silicate solution grouts. These organic hydrogels have one notable advantage over sodium silicate hydrogels: reversible dessication. Because they are about 90% water, hydrogels are subject to collapse upon dessication. This collapse is irreversible with sodium silicate hydrogels, but reversible with organic hydrogels, as they will swell to their original volume upon re-exposure to water. Two commercial products, marketed for gelling radioactive wastewater or controlling water release from waste spills, are Stergo™ (polyacrylamide) and Water Works SP-400™ (polyacrylic); they were selected as likely candidates for controlling bleed water. Hydrogels are also subject to frost or freeze-thaw damage, not unexpectedly with such a large water content. Care should be exercised in using hydrogels if the waste form will be stored above ground (or above the frost line) and exposed to freezing conditions.

Two other cheap, water-sorptive bulking agents are rice hull ash (mentioned as a pozzolan in the section on fly ash) and perlite. "Perlite is a volcanic material that is mined, crushed, screened, and expanded by heat to form cellular product of extremely low bulk weight." [60] Water is absorbed by capillary action within the large volume of pore structure within this light, porous product. "Rice husks, also called rice hulls, are the shells remaining from the dehusking of paddy rice."[8] Uncontrolled combustion results in ash consisting mainly of crystalline silica minerals such as cristobalite or tridymite, but "... the ash produced at low temperature in a process developed by Mehta and Pitt contains silica in a cellular, high-surface area and noncrystalline form (50 to 60 m^2/g), and is therefore highly pozzolanic." [9, 67] In addition to the pozzolanic reactivity, this high-surface-area material also absorbs water by capillary action.

Perlite was the water-sorptive agent of choice for the grout formulations with sludge loadings <60 wt %. To achieve maximum sludge loadings with minimum volume increase, the water-to-solids ratio (W/S) of this perlite formulation must be controlled by adjusting the sludge water content to avoid bleed water formation in the surrogate grouts. The hydrogels were tested in the laboratory for their ability to control bleed water formation without the need for a unit operation to adjust the grout W/S to a specified level. In summary, the water-sorptive agents selected for testing were sodium silicate, Stergo™, and Water Works SP-400™.

4.6 SELECTING GROUT COMPOSITION FOR EVALUATION

The initial basis for a dry blend that was developed in FY 1996 was the cement-fly ash dry blends historically used for treatment of radioactive wastes:[1]

	Wt %	
	Hydrofracture [29][a]	Hanford [58][b]
Type I Portland cement	42	38
Class F fly ash	34	39
Attapulgite 150 drilling clay	16	15
IRPC	8	8

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[a] Hydrofracture refers to a waste disposal strategy developed for and applied to ORNL tank sludges during the 1960s, 1970s, and early 1980s. Basically, the technique consisted of drilling a deep well into local impervious shale, horizontally hydrofracturing the shale locally at depth, and injecting a "pancake" of grouted sludge into the fractured space.

[b] Hanford refers to the Hanford Grout Program whose strategy was to mix the low-level supernate wastes stored in the Hanford tanks into a grout that was pumped into large concrete vaults. This Hanford Grout Program was canceled.

Typically, a mix ratio of 0.84 and 0.72 kg dry blend/L waste (7-and 6-lb dry blend/gal waste) was tested for these two applications.[29, 58] Assuming a waste specific gravity of about 1.2 (10 lb/gal), these mix ratios give waste loadings of about 60 wt %. Thus, strong monoliths can be expected at waste loadings up to 60 wt %, although some problems with bleed water may be experienced, depending on the water content of the waste and the steps taken to control bleed water. Note that approximately equal proportions of cement-fly ash were used with 8 wt % IRPC. These two grouts were developed for low-solids wastes, and the need for a large fraction of water-sorptive agent in the dry blend was uncertain a priori for the present tank sludge application. (The goal was to develop a grout for the sludge interstitial water content as it rests in the tanks, ignoring retrieval or pretreatment requirements.) Hence, the water-sorptive content was varied, dropping to zero, but increased as needed, depending on the agent and performance. In addition, slag replaced cement as the binder of choice. Cement was included to activate the slag, but a slag:cement ratio of about 90:10 by weight was maintained to enhance the reducing capability of the matrix. In general, IRPC was fixed at 8 wt % in the dry blend for ^{137}Cs stabilization. The fly ash was kept as a proven pozzolan for ^{90}Sr stabilization. (The main mobile radionuclides of interest in these tank sludges are ^{137}Cs and ^{90}Sr.) The fly-ash content was allowed to float to compensate for the varying content of water-sorptive agent.

Thus, the dry-blend formula used to initiate experimental work in FY 1996 follow:[1]

	Wt %
Slag-Type I-II Portland cement (90:10)	40–50
Class F fly ash	25–50
Water sorptive agent	0–20
IRPC	8

A robust dry blend was developed in FY 1996 for the surrogate MVST/BVEST sludge and was used as the basis for the FY 1997 work.[2] The composition of this dry blend follows:[1,2]

	Wt %
Ground granulated blast furnace slag	33
Type I-II Portland cement	20
Class F fly ash	19
Perlite	20
IRPC	8

The intent for the work documented in this report (FY 1998) was to maximize the sludge loading, sacrificing physical strength of the matrix. In FY 1997, the dry blend listed above was limited to a sludge loading of about 60 wt % to make a monolithic waste form with a reasonable compressive strength without bleed water.[2] Controlling the W/S ratio allowed using this dry blend at higher sludge loadings without bleed water, but the strength decreased as the sludge increased.[2] Since perlite was not effective at higher sludge loadings, the work initiated in FY 1998 dropped perlite from the dry blend to investigate other water-sorptive agents. The slag, cement, fly ash, and IRPC were retained for their contaminant stabilization potential.

5. SURROGATE LABORATORY STUDIES

5.1 EXPERIMENTAL

5.1.1 Surrogate Preparation

The surrogate wet sludges were prepared from reagent-grade chemicals according to the compositions listed in Tables 2, 4 and 6. The chemicals were allowed to hydrolyze by mixing with the recipe water at least 20 min. Some additives, such as sodium chloride, were mixed into the sludge prior to mixing with the dry blend.

5.1.2 Blending

The dry blends, which were mixed with the surrogate wet sludge to make grouts, consisted of blends of two or more of the following dry powders: (1) ground granulated blast furnace slag (slag) with a Blaine fineness of 5900 cm^2/g from the Holnam Minerals Co., (2) Type II Portland cement (cement) with a Blaine fineness of 3480 cm^2/g from the South Down Co., (3) Class F fly ash (fly ash) from the Bell Concrete Co., (4) Indian Red Pottery Clay (IRPC) from the American Art Clay Co., and (5) reagent grade sodium silicate powder from the Fisher Scientific Co. The dry blends were blended for 2 h in an 8-qt twin-shell blender (or V-blender) from the Patterson-Kelley Co. Typically, the water-sorptive agents, sodium silicate solution (40% sodium silicate solution from VWR Scientific Co.), Stergo™, and Water Works SP-400™, were not blended into the dry blend, but added last after mixing the dry blend with the sludge because these agents tended to thicken the grout, making mixing more difficult.

5.1.3. Mixing

The grouts were mixed in a Model N-50 Hobart mixer using a flat blade. The surrogate wet sludge was added to the Hobart bowl first, then the dry blend was added to the sludge while mixing on low speed (30 to 60 s). The grout was then mixed on low speed for 2 min and medium speed for 2 min, cast into containers or molds for performance testing, and cured. The procedure for spiking with radionuclides for making leach samples consisted of adding the spike to the wet sludge in the Hobart bowl, mixing on low speed for 20 min, then adding the dry blend using the above procedure.

5.1.4. Curing

The freshly made grout was cured under humid conditions (either sealed with small headspace or stored with a pool of water or wet towel/sponge) at room temperature. A standard cure time of 7 d was adopted for both scope and sensitivity testing, since the 28-d strength development was not a criterion. Some testing was conducted beyond 7 d, since hydration reactions affecting properties continue for months and years.

5.1.5 Performance Testing

The performance tests consisted of measuring the density of the freshly mixed grout, the penetration resistance and bleed water during the cure, and TCLP performance after only 7 d.

The bleed water was measured by casting the grout into a graduated cylinder and measuring the initial volume of grout and the volume of bleed water standing over the solid grout at any given time (modified ANS-55.1 test). This property is reported as vol %, calculated by dividing the observed bleed water volume in mL by the initial grout volume in mL and multiplying by 100. The density of the freshly mixed grout was obtained by measuring the net mass in g of grout in the bleed water test and dividing by initial grout volume in mL to obtain the density in units of g/mL.

For penetration resistance, the force (lb_f) required to push a flat rod with a known cross-sectional area (tips of 1/40 and 1 in.^{2} were used) a preset distance into the partially cured grout was measured (modified ASTM C 1117). This force was divided by the cross-sectional area and reported as penetration resistance (psi). The pressure gauge on the penetrometer reads a maximum pressure of 200 lb_f, limiting measurements on penetration resistance (8000 and 200 psi, respectively, for the two tips used). The penetration resistance can be measured at any time after mixing.

A modified TCLP test was performed for this study. The modified procedure extracts a 10-g sample with 200 mL of extractant, rather than the standard 200-g sample with 2 L of extractant. The TCLP test uses one of two extractants: (1) an acetic acid solution with sodium hydroxide added (TCLP Extraction Fluid No. 1, pH of about 4.9) or (2) the straight acetic acid solution (TCLP Extraction Fluid No. 2, pH of about 2.9). The standard procedure dictates which extractant to use based on the buffering capability of the sample when mixed with a hydrochloric acid solution, but the more demanding TCLP Fluid No. 2 was specified for all surrogate testing. After extracting 18 h, the undissolved solids are filtered from the extract and the extract is digested using a microwave digester. The concentration of the inorganic RCRA metals, except mercury, in the extract were then measured using a Thermo Jarrel Ash (TJA) Inductively Coupled Argon Plasma 61E Trace Analyzer (ICP). Although selenium and arsenic analyses by ICP are not routinely accepted, EPA accepts the higher sensitivity of the 61E. The concentration of mercury in the TCLP extract was measured using a Leeman Labs PS 200 cold-vapor atomic absorption (CVAA) mercury analyzer.

5.2 SURROGATE GAAT W4 SLUDGE RESULTS

The experimental work consisted of two phases: scope testing and sensitivity testing. The scope testing explored the waste form behavior for a limited set of performance tests over a range of compositions to establish an envelope of acceptable waste-form compositions. After establishing this envelope, an acceptable formulation was selected for testing the sensitivity of the formulation to variations in the formulation and surrogate composition.

5.2.1 Scoping Tests

Table 7 lists the compositions tested during the scoping tests with the surrogate GAAT W4 sludge. Table 8 lists the grout density, the grout:sludge volume ratio (calculated from the sludge loading, sludge density, and grout density), and the water:solids ratio. Table 9 lists the bleed water, Table 10 lists the penetration resistance results for these grouts, and Table 11 lists the TCLP results.

Grouts GAAT SG 1-6 in Table 7 confirmed that high cement blends did have trouble stabilizing the dichromate in the surrogate, even as low as 50 wt % sludge loading. This dry blend with sodium silicate solution generated no bleed water at 50 wt % sludge loading, but did generate bleed water at 90 wt % sludge loading. Based on these results and prior experience, the dry blend was switched to high-slag blends for the remainder of the studies. The next series of tests concentrated on establishing the bleed water control strategy for high-sludge loadings.

Grouts GAAT SG 7-15 tested the bleed-water control potential of sodium silicate solution, sodium silicate powder, Stergo™, and Water Works SP-400™ at a fixed sludge loading of 90 wt %. Grout 7 established the bleed-water baseline without any water-sorptive agent at 23 vol %. Sodium silicate solution at 1.1 wt % reduced the bleed water down to 8 vol %, but the bleed water increased back to 25 vol % when the sodium silicate solution was increased to 2.0 wt %. These results imply that controlling the bleed water is more complex than simply increasing the amounts of the water-sorptive agent. The dry blend also interacts with the sludge water, and by holding the sludge loading content constant, increasing the amount of water-sorptive agent means decreasing the amount of dry blend. Apparently the dry blend and sodium silicate solution worked together to better control bleed water in Grout 8, but failed in Grout 9. The sodium silicate powder did not appear to work at all (grouts 10 and 11). The reproducibility of these results was not tested because sodium silicate was dropped as a candidate after these initial series of tests, so these results may be somewhat misleading about the true performance of sodium silicate in such grouts.

Stergo™ and Water Works SP-400™ are commercial products for gelling wastewater or controlling wastewater spills. The instructions for Stergo™ implied a loading of 3.5 wt % of this product for 90 wt % loading of this surrogate sludge. Thus, Stergo™ was tested at 1.0, 2.0 and 3.5 wt % with a fixed sludge loading of 90 wt % (Grouts 12 to 14). This product proved effective at controlling bleed water at these high-sludge loadings, with only the 1 wt % Stergo™ exhibiting a small amount of bleed water (0.4 vol %), despite a water:solids ratio of about 2 (see Table 8). A 2 wt % loading of this hydrogel was adopted as the standard, with no further attempts to optimize. One test of the Water Works SP-400™ hydrogel demonstrated it to be equally effective at 2 wt % in controlling bleed water for a 90 wt % loading of this surrogate sludge. As expected, these grouts developed no appreciable strength at a sludge loading of about 90 wt % (see Table 10).

Reviewing the TCLP results for Grouts 1–15 (Table 11), chromium stabilization appeared to be the factor that would limit sludge loading for this surrogate sludge. Grouts 16–23 attempted to improve stabilization performance at this high loading by caustic activation (adding sodium hydroxide) and sodium sulfide addition. The TCLP performance was worse with either of these two additives, and the key appeared to be the slag content of the grout. Consequently, Grouts 24–30 systematically tested a cement-slag dry blend, varying the sludge loading from 84 to 96 wt %. Grout 31 tested a 90 wt % sludge loading, adding fly ash and IRPC back to the dry blend. Since slag appears to be the key to the sludge loading for this surrogate, Grout 32 maximized the slag in the dry blend by dropping the fly ash. Grout 32 also tested beryllium TCLP performance by adding beryllium bromide to the surrogate at a level representative of the beryllium measured in the W4 sludge sample (this was the only surrogate tested containing beryllium).

Figure 2 illustrates the dependence of the TCLP chromium performance for the surrogate GAAT W4 grouts on the grout slag content. A correlation is apparent for most of the scoping test and sensitivity test results. Most of the exceptions to the obvious trend are those grouts with either caustic activation or sodium sulfide addition. The only other exception is the Grout Sensitivity Test No. 7, which tests the standard grout in the sensitivity test with the minimum water-maximum bad actors surrogate GAAT sludge from ref. 2. (i.e., this surrogate is representative of the worst compositions previously measured in all the GAAT tanks, but not of the W4 sludge sample). Figure 3 illustrates that a semilog plot linearizes the surrogate W4 data (excluding caustic activation, sodium sulfide addition, and the minimum water-maximum bad actors). Rearranging the regression equation given in Fig. 3 results in the following empirical equation for surrogate W4 TCLP performance:

$$\% \text{ Cr extracted} = 56.3\ e^{-0.457\ (\text{wt \% slag})} . \qquad (1)$$

Using the chromium UTS limit (0.86 mg/L) as the quantity extracted and solving for the grout chromium concentration from the % extracted, results in the following equation for the maximum grout chromium concentration as a function of the grout slag content:

$$\text{mg/kg of Cr} = 20\ (0.86)\ (100)/(56.3\ e^{-0.457\ (\text{wt \% slag})}) . \qquad (2)$$

Figure 4 illustrates a plot of Eq. (2). Note that Eqs. (1) and (2) result from an empirical regression of the surrogate W4 data, and it is risky to extrapolate these results beyond the testing range or to other sludges. Significant differences were observed in changing the sludge composition to that representative of GAAT sludge minimum water-maximum bad actors and hot testing the actual W4 sludge sample (see the surrogate sensitivity results and the hot test results). Rather these results indicate the general trends that can be expected and a general idea of the values.

Lead also proved to be troublesome. Lead was expected to be sensitive to pH, not the slag content. Although the correlation is not as apparent as for the chromium-slag interaction, Fig. 5 illustrates that the TCLP lead extract concentration may be dependent on the final extract pH.

5.2.2 Sensitivity Testing

The scoping tests were used to test candidate grout formulations and select one as a potential candidate for grouting the tank sludge. Sensitivity testing is the evaluation of the sensitivity of this selected formulation to changes in waste composition and changes in the concentration of the grout ingredients. The dry blend selected for sensitivity testing consisted of: 84, 8, and 8 wt % of slag, cement, and IRPC, respectively. About 8 wt % of this dry blend in the grout was used to stabilize the contaminants, plus another 0.1 wt % of sodium chloride was added to assist in stabilizing the silver. Bleed water was controlled with 1.9 wt % of Stergo™, leaving 90 wt % for the surrogate sludge. The standard grout composition resulting from this formulation is listed as Grout No. 1 in Table 12. A ±10% variation in formulation was chosen as the basis for the sensitivity testing. A subset of four variations in formulation, among all the possible variations, were selected for this sensitivity test. Table 12 also lists these four grouts selected for sensitivity testing. The sensitivity testing also consisted of testing the variation in sludge composition possible in the tank sludges. To test any possible effects of variation in sludge composition, the standard grout formulation was also tested with surrogate sludge at the maximum water content (from previous characterization data) and with surrogate sludge at the minimum water content and the maximum concentration of bad actors (from previous characterization data). (The bad actors were defined as the RCRA metals, sulfate, halides, carbonate, phosphate, and tributylphosphate.) Table 2 lists the three surrogate sludge compositions used in the sensitivity testing of the surrogate GAAT W4.

Tables 13 through 15 list the following results for the sensitivity testing of the overall grouts: grout density, grout:sludge volume ratio, water:solids ratio, bleed water, penetration resistance, and TCLP performance.

The standard grout (Grout No. 1) had a density of 1.25 g/mL, a volume increase of 9 vol %, no free water, a 7-d penetration resistance of 20 psi, and an acceptable TCLP performance. The variation in grout and surrogate composition made the density vary from 1.12 to 1.41 g/mL and the volume increase vary from 7 to 11 vol %. None of the GAAT sensitivity grouts exhibited bleed water. The composition variations significantly affected the 7-d penetration resistance, ranging from 0 to 46 psi, but the grouts never developed much strength. The dry blend composition variations with standard surrogate sludge significantly affected the TCLP performance with the TCLP extract concentration exceeding UTS limits for chromium and lead with Grout No. 2 and for lead with Grout No. 4. The surrogate sludge with the minimum water content and maximum bad actor concentrations resulted in a chromium extract concentration well above the UTS limit. Obviously, a 90 wt % sludge loading pushes the limitations of grouting, making the resulting grout sensitive to variations in composition. Although all the surrogate sensitivity grouts met the UTS limit for silver, it was silver, not chromium or lead, that caused problems in the hot test of the W4 sludge sample, described in Sect. 6.

5.3 SURROGATE BVEST W23 SLUDGE RESULTS

The experimental work consisted of two phases: scope testing and sensitivity testing. The scope testing explored the waste-form behavior for a limited set of performance tests over a range of compositions to establish an envelope of acceptable waste form compositions. After establishing this envelope, an acceptable formulation was selected for testing the sensitivity of the formulation to variations in the formulation and surrogate composition.

5.3.1 Scoping Tests

Table 16 lists the grout compositions tested during the scoping tests using the W23 surrogate sludge. Table 17 lists the grout density, the grout:sludge volume ratio (calculated from the sludge loading, sludge density, and grout density), and the water:solids ratio. Table 18 lists the bleed water and penetration resistance results for these grouts, and Table 19 lists the TCLP results for these grouts.

The dry blend, without sodium chloride, developed for the surrogate W4 sludge was tested with the surrogate W23 sludge over a range of high-sludge loadings. Performance was satisfactory, and no further refinements of the dry blend were attempted. Once again, the chromium TCLP performance proved to be the limiting factor in determining maximum sludge loading.

Figure 6 illustrates how the grout density, grout:sludge volume ratio, and penetration resistance varied with sludge loading. Figure 7 illustrates the % chromium extracted during TCLP with grout slag content for the surrogate W23. More values were below the quantitation limits and more scatter was found in this data set. Nevertheless, Fig. 8 illustrates the semilog plot of the % chromium extracted with grout slag content, including the regression line and equation. Rearranging this equation results in the following equation:

$$\% \text{ Cr extracted} = 305\ e^{-0.931\ (\text{wt \% slag})}\ . \tag{3}$$

5.3.2 Sensitivity Testing

The scoping tests were used to test candidate grout formulations and to select one as a potential candidate for grouting the tank sludge. Sensitivity testing is the evaluation of the sensitivity of this selected formulation to changes in waste composition and changes in concentration of the grout ingredients. The dry blend selected for sensitivity testing consisted of 84, 8, and 8 wt % of slag, cement, and IRPC, respectively. About 8 wt % of this dry blend in the grout was used to stabilize the contaminants. Bleed water was controlled with 2 wt % of Stergo™, leaving 90 wt % for the surrogate sludge. The standard grout composition resulting from this formulation is listed as Grout No. 1 in Table 20. A ±10% variation in formulation was chosen as the basis for the sensitivity testing. A subset of four variations in formulation, among all the possible variations, was selected for this sensitivity test. In addition, Table 20 lists these four grouts selected for sensitivity testing. The sensitivity testing also consisted of testing the variation in sludge composition possible in the tank sludges. To test any possible effects of variation in sludge composition, the standard grout formulation was also tested with surrogate sludge at the maximum water content (from previous characterization data) and with surrogate sludge at the minimum water content and the maximum concentration of bad actors (from previous characterization data). (The bad actors were defined as the RCRA metals, sulfate, halides, carbonate, phosphate, and tributylphosphate.) Table 4 lists the three surrogate sludge compositions used in the sensitivity testing of the surrogate BVEST W23.

Tables 21–23 list the following results for the sensitivity testing of the BVEST W23 grouts: grout density, grout:sludge volume ratio, water:solids ratio, bleed water, penetration resistance, and TCLP performance.

The standard grout (Grout No. 1) had a density of 1.44 g/mL, a volume increase of 7 vol %, no free water, a 7-d penetration resistance of 106 psi, and acceptable TCLP performance. The variation in grout and surrogate composition made the density vary from 1.33 to 1.53 g/mL and the volume increase vary from 6 to 9 vol %. None of the GAAT sensitivity grouts exhibited bleed water, except the grout made with minimum water-maximum bad actors surrogate (0.8 vol % bleed water). The composition variations significantly affected the penetration resistance, ranging from 0 to 120 psi, but none of the grouts developed any appreciable strength. The dry- blend composition variations with standard surrogate sludge had little effect on the TCLP performance, and all extract concentrations were below the limiting values for UTS. On the other hand, varying the waste composition did significantly affect the TCLP performance and the TCLP extract concentrations for selenium, and thallium exceeded the UTS limits for the minimum water-maximum bad actors surrogate.

5.4 SURROGATE OHF T3 SLUDGE RESULTS

The experimental work consisted of two phases: scope testing and sensitivity testing. The scope testing explored the waste-form behavior for a limited set of performance tests over a range of compositions to establish an envelope of acceptable waste-form compositions. After establishing this envelope, an acceptable formulation was selected for testing the sensitivity of the formulation to variations in the formulation and surrogate composition.

5.4.1 Scoping Tests

Table 24 lists the grout compositions for the surrogate OHF T3 sludge. Table 25 lists the grout density, the grout:sludge volume ratio (calculated from the sludge loading, sludge density, and grout density), and the water:solids ratio. Tables 26 and 27 list the bleed water and penetration resistance test results and the TCLP test results for these grouts.

OHF SG 1–7 tested the same dry blend used for surrogates W4 and W23 at different loadings of surrogate OHF T3 sludge, with no additional additives. The TCLP extract concentrations for chromium and lead exceeded the UTS limits at sludge loadings above 86 to 88 wt % (see Table 27). For this reason, the same series of grouts were prepared using caustic activation in Grouts 8–14. Caustic activation improved the TCLP performance, passing UTS at nominal sludge loadings up to 90 wt % (addition of the sodium hydroxide solution diluted the nominal 90 wt % sludge loading down to 88.4 wt %).

Further improvements were attempted in Grouts 15–17 using other additives. The large tributylphosphate (TBP) content of the surrogate OHF sludge was suspected of causing interference with the hydration and stabilizing reactions. A powerful oxidant, potassium permanganate, was added to the sludge prior to mixing with the dry blend in an attempt to destroy the TBP before adding the dry blend in Grout 15. The key to stabilizing chromate is reduction to the cation, so adding a powerful oxidant was a gamble. Only the stoichiometric amount of permanganate was added for complete oxidation of the TBP. It was hoped that the TBP and permanganate would destroy each other to a low enough concentration such that they would not affect the stabilization potential of the dry blend. Obviously, this gamble did not pay off, as witnessed by the high TCLP extract concentrations of chromium and mercury. Apparently, the powerful oxidant compromised the chromium and mercury stabilizing potential of the dry blend.

Adding iron chloride and aluminum sulfate are two common treatments for phosphate precipitation (both sodium phosphate and TBP were present in the surrogate) in wastewater.[68] One of each was added in Grouts 16 and 17, respectively, in combination with caustic activation to find out if, potentially, phosphate precipitation would improve TCLP performance with surrogate T3. No significant difference was apparent between phosphate precipitation with caustic activation and caustic activation alone, so caustic activation of the dry blend was adopted for sensitivity testing.

Tributylphosphate (TBP) is suspected of causing some of the poor performances observed for the surrogate OHF. Grouts 18 and 19 were made without adding TBP to the surrogate to test this surmise. The composition of these two grouts is most directly comparable to Grout 8 in Table 24, which was made with TBP in the surrogate. Grout 8 had a hint of more bleed water and being slightly firmer than Grouts 18 and 19 (see Table 26), but these observed differences were judged insignificant. At least for chromium, the TCLP performance improved by an order of magnitude without TBP, 0.585 mg/L for Grout 8 compared with 0.05 to 0.063 mg/L for Grouts 18 and 19. Chromium was the problem RCRA metal during surrogate OHF testing in FY 1997 and during the current study with surrogate T3. Even though not definitive, these TCLP results support the contention of interference by the high TBP content in the OHF surrogate.

Figure 9 illustrates the dependence of the TCLP chromium performance on the grout slag content for the surrogate OHF T3 grouts. Figures 10 and 11 illustrate the correlations in the linearized semilog plots for the scoping test standard dry blend and caustic activation results.The regression equations are given on the plots, resulting in the following two equations for the surrogate T3:

Standard Dry Blend

$$\%\ \mathrm{Cr\ extracted} = 68\ e^{-0.135\ (\mathrm{wt\,\%\ slag})} \tag{4}$$

With Caustic Activation

$$\%\ \mathrm{Cr\ extracted} = 98\ e^{-0.38\ (\mathrm{wt\,\%\ slag})} \tag{5}$$

All regression equations differ significantly from each other, but are fairly consistent in predicting improved chromium retention with increasing slag content.

5.4.2 Sensitivity Testing. The scoping tests were used to test candidate grout formulations and select one as a potential candidate for grouting the tank sludge. Sensitivity testing is the evaluation of the sensitivity of this selected formulation to changes in waste composition and changes in concentration of the grout ingredients. The dry blend selected for sensitivity testing consisted of: 84, 8, and 8 wt % of slag, cement, and IRPC, respectively. About 8 wt % of this dry blend in the grout was used to stabilize the contaminants. Caustic activation of this grout by addition of sodium hydroxide to adjust the pH of the surrogate sludge (from 11 to 13) was required for contaminant stabilization during the 7-d cure. Adding sodium hydroxide diluted the dry blend and sludge loadings in the final grout composition. Bleed water was controlled with 2 wt % of Stergo™. The standard grout composition resulting from this formulation is listed as Grout No. 1 in Table 28. A ±10% variation in formulation was chosen as the basis for the sensitivity testing. A subset of four variations in formulation, among all the possible variations, was selected for this sensitivity test. Table 28 lists these four grouts selected for sensitivity testing, which also consisted of testing the variations in sludge composition possible in the tank sludges. To test any possible effects of variation in sludge composition, the standard grout formulation was also tested with surrogate sludge at the maximum water content (from previous characterization data) and with surrogate sludge at the minimum water content and the maximum concentration of bad actors (from previous characterization data). (The bad actors were defined as the RCRA metals, sulfate, halides, carbonate, phosphate, and tributylphosphate.) Table 6 lists the three surrogate sludge compositions used in the sensitivity testing of the surrogate BVEST W23.

Tables 29–31 list the following results for the sensitivity testing of the OHF T3 grouts: grout density, grout:sludge volume ratio, water:solids ratio, bleed water, penetration resistance, and TCLP performance.

The standard grout (Grout No. 1) had a density of 1.17 g/mL, a volume increase of 13 vol %, no bleed water, no penetration resistance, and an acceptable TCLP performance. The variation in grout and surrogate composition made the density vary from 1.16 to 1.29 g/mL and the volume increase vary from 8 to 14 vol %. None of the sensitivity grouts exhibited either bleed water or penetration resistance. Although the dry blend and sludge composition variations significantly affected the TCLP performance, all extract concentrations were below the limiting values for UTS.

5.5 Discussion of the Surrogate Tank Sludge Results

The previous sections documented the results in this report for the grouts targeted at specific surrogate sludges at high loadings, with plots illustrating the stabilization effectiveness for chromium and lead. These results are fairly specific to the particular combinations of surrogates and stabilizing agents being tested. To obtain a more general idea of the stabilization potential of these grouts, the data documented in this report were combined with the data from the two previous reports[1,2] and evaluated for trends or correlations. Figures 12–20 illustrate some of the trends found in this data set. These data include variations not apparent in the plots; for example, the attempts to use sodium sulfide and potassium permanganate in the current data set, both of which had deleterious effects on performance, are included. In other words, the plots should be viewed as illustrating upper limits of performance with improvements possible in a given case.

In general, chromate and mercury ions are not stabilized by high pH, as are many of the RCRA metals. Slag is a proven stabilizing agent for these two mobile RCRA metals. Figures 12 and 13 confirm the dependence of chromium and mercury TCLP performance on the grout slag content. Both appear effectively stabilized at grout slag contents of 15 wt % or higher. As the slag content is reduced to 10 wt %, the possibility of leaching begins increasing. Even then, effective stabilization occurred at slag contents below 5 wt %, depending on the compositional variations. To maximize the waste loading, a slag content as low as 5 to 6 wt % could be effective, but at a higher risk.

The effectiveness of pH control was evaluated for the other RCRA metals. Figure 14 illustrates that lead was effectively stabilized if the grout was tailored to yield a final TCLP extract pH >6. The rise in lead concentration at the highest pH values is consistent with lead hydroxide solubility. Several hydroxides exhibit a minimum solubility in the pH range of about 9 to11, becoming more soluble at the higher pH values.[8,15] Lead hydroxide passes through a minimum solubility at a pH of about 9.3 (see refs. 8 and 15). In other words, if a given formulation is having trouble stabilizing lead, just adding a caustic (e.g., lime) may solve the problem, but one can add too much.

Similarly, Figs. 15 and 16 illustrate cadmium and silver stabilization with pH. The cadmium concentration appears to increase as the pH approaches 5. The silver concentration appears to increase as the pH passes below 7.

Figure 17 illustrates that the behavior of selenium is more complex, consistent with its amphoteric nature. This plot is consistent with the behavior of more than one species. The selenium appears to be increasing in solubility at the highest pH values and decreasing at the lowest pH values, but potentially passing through both a minimum and a maximum in between, with a transition at a pH of about 9. It is important not to oversimplify this behavior, as these are not simple solutions of metal hydroxides. The surrogate sludges are complex water slurries of several compounds. These sludges are mixed with cement, slag, fly ash and clay, which are complex heterogeneous materials themselves. This complex mixture of solids and solution (grout) is then extracted with acetic acid, a chelating agent. Thus, these are not simple solubility plots. In general, the observed TCLP extract concentrations are significantly different from the published metal hydroxide solubilities. Thus, it is unclear exactly how to interpret Fig.17, except to note that grouts did meet the UTS limits across the pH regime and failures are somewhat difficult to predict.

Figures 18 and 19 illustrate thorium and uranium, the two main radioactive constituents in the surrogates, leachability with the final extract pH. The thorium behavior was straightforward, with leachability increasing as the pH approached 6. The behavior of the uranium was more complex, consistent with its more varied valence states. Carbonate forms of uranium are known to be somewhat soluble around a pH of about 9. Figure 19 would be consistent with more than one species of uranium (likely with the mixed bag of surrogates and grouts plotted), with one specie possibly being carbonate (the carbonate content varied, but was a significant part of the surrogates). These suppositions are by no means definitive, as the extracts are complex mixtures.

The dependence of leachability on pH raises the obvious question of the dependence of the pH on the stabilizing agents. Strong caustics, such as lime or cement, will have the strongest tendency to increase pH. Pozzolans, such as slag and fly ash, consume calcium hydroxide and tend to have a moderating effect on pH. They still form calcium silicate hydrates (CSH), which have calcium oxide as one of their major constituents, and are still bases. In other words, the mix of compositions in these data should not have a simple effect on pH. It was decided to plot the pH as a function of the sum of the grout cement, slag, and fly-ash content, defined as the pozzolan content. Figure 20 illustrates the expected upward trend with increasing pozzolan content. Considerable scatter is noted in this plot, which is not surprising, considering the wide variation in composition that includes high-cement grouts and caustic activation.

6. TESTING OF THE ACTUAL TANK SLUDGE SAMPLES

6.1 WASTE SLUDGE COMPOSITION AND PROPERTIES

The actual sludge samples, as removed from the tanks, had densities of 1.29, 1.36, and 1.17 g/mL for the GAAT W4, BVEST W23, and OHF T3 sludges, respectively. Tables 1, 3, and 5 list the composition measured for the W4, W23, and T3 sludge samples, respectively, and compare this measured composition with that of its corresponding surrogate. The W23 and T3 samples develop significant amounts of bleed water, if left quiescent. The W4 sample developed little or no bleed water, if left quiescent, resulting in no need to add Stergo™ to control bleed water when this sample was mixed into a grout.

6.2 EQUIPMENT AND SETUP

A walk-in hot cell equipped with manipulators was decontaminated and set up for dedicated use in the preparation of both cement-based and vitreous waste forms during FY 1997. The cell, designated as cell-D, is located in a complex of four walk-in cells in building 4501 at ORNL. After completing the vitrification part of the hot tests during the current work, another hot cell, cell-B, was decontaminated and all the equipment moved to this cell prior to hot testing the grouts. In other words, the vitrification hot test was conducted in cell-D, and the grout hot test was conducted in cell-B. The interior of both cells is 6 × 9 × 16 ft in height and is designed for easy entry.

6.3 GROUTING STUDIES WITH ACTUAL TANK SLUDGES

6.3.1 Modification of the Hobart Mixing Equipment

Standard equipment normally used for the preparation of cement-based grouts had to be modified for use with manipulators within the confines of the hot cell. A standard Hobart mortar mixer was modified by placing an enclosure over the mixing bowl, with two tubes above for placing dry solids and waste inside without forming too much dust that might spread contamination . Additionally, the base of the mixer was modified such that it stood approximately 6 in. higher so that the mixing bowl could be more easily removed using manipulators. When mixing was in progress, the mixer was completely covered to eliminate possible cell contamination from the dry solids component of the grout. The bowl and enclosure locked against each other by way of a rubber gasket seal.

The mixer was operated with a wire-wisk-type blade. A special tool was designed to remove this blade without contaminating the manipulator hand and working area.

6.3.2 Funnel and Cylinder Setup

Since bleed water formation was of interest, a means for placement of grout slurry into a plastic bottle was devised for use in the cell. (Plastic bottles were substituted for the graduated cylinder used last year, because of the problem of air incorporated into the thick grouts in these cylinders.) This seemingly simple task was significantly more complex since it had to be performed remotely.

A stainless steel funnel with "all-thread" adjustable legs and pick-up grips attached was fabricated such that it could fit inside the top of the bottle. The mixer pot was locked above the funnel, and the slurry was scraped into the bottle using a plastic cake spatula. When the bottle had received enough of the slurry the bottle was placed on a vibratory mixer to settle the slurry and remove any pockets where potential bleed water could be trapped. When the slurry was settled and free of visible voids, the bottle was sealed using its lid.

An additional test of interest for the cement-based grout waste form was the TCLP test. In order to prepare grout for this test, grout slurry remaining inside the pot of the Hobart mixer was scraped into a plastic "zip-lock" bag and the contents of the bag was flattened after sealing the bag. The flattened sample was allowed to cure for 7 d in this bag. After curing, the flattened grout "pancake" was broken while still in the bag, using a piece of wood and extra bags. The broken pieces were screened through a 9.6-mm screen in preparation for removal from the cell and use in the TCLP test. As will be seen, a 7-d cure may not have been enough for the hydration reactions to stabilize all the RCRA metals, and a 28-d cure was attempted to improve performance.

6.3.3 Penetration Resistance

A penetrometer with a wire penetrator tip of 1-in.^{2} was used to follow the rate of set. As the tip penetrated the grout samples, pounds force was displayed by a marker dial. Penetration resistance, which indicates the state of set, was calculated by multiplying the dial value by 1 to obtain the resistance in units of pound-per-square-inch (psi). The handle of the apparatus was modified with a swivel for the manipulator hand to allow movement forward in the confines of the hot cell.

Forms to contain the cured grout were fabricated from 2-in. PVC pipe caps epoxied to a piece of wood. Grout slurry from the mixing pot was spooned into the caps and vibrated to remove voids. The top of the wet grout in these caps was troweled with a soft plastic cake spatula to produce a flat surface. The filled forms were placed inside a "zip-lock" bag, along with a wet sponge and sealed. The sponge was checked periodically to ensure it was always wet, to keep the air in the bag saturated with water vapor. After various intervals, the cap-molded apparatus was removed from the bag and placed beneath the penetrometer and the test performed. Penetrometer readings were obtained after 7 d.

6.3.4 Cement-Based Grout Formula

The dry-solid blend was premixed in a V-blender and placed in preweighed bottles for use in the hot cell. The basic dry-solid blend used in the preparation of our cement grout was as follows:

Indian Red Pottery Clay	8.0 wt %
Blast Furnace Slag	84.0 wt %
Portland Type II Cement	8.0 wt %

The test work with grout utilized a basic grout recipe of 90, 8, and 2 wt % wet sludge, the above dry blend, and Stergo™, respectively. The sludge and dry blend were mixed for 10 min at low speed and 2 min at high speed in the Hobart mixer prior to use. The Stergo™ was added last and mixed for only a few minutes, as it thickens the grout considerably, making it more difficult to mix. The differences among the samples revolved around this basic recipe, consisting of the following: (1) for the W4 sample, no Stergo™ was required and sodium chloride was mixed with sludge at least 20 min prior to adding the dry blend; (2) for the W23 sample, the basic recipe was used with no modification; and (3) for the T3 sample, sodium hydroxide was mixed with the sludge at least 20 min prior to adding the dry blend to adjust the sludge pH for the purpose of activating the slag.

6.3.5 Cement-Based Grouts Test Results

Tables 32 and 33 list the results of the hot test with actual sludge samples from W4, W23, and T3. When Stergo™ was added to the W4 grout mix, the resulting product was dry and crumbly, not a wet mixable paste. This implies that addition of the hydrogel for bleed water control should be optional for field application, depending on the judgement of the operator as to whether a bleed control agent is needed. The W4 test was rerun without adding the Stergo™, leading to a higher sludge loading. The performance of this latter grout is listed in Tables 32 and 33. The W23 and T3 samples were judged to need the Stergo™ in the other two hot tests. To compare the grout performance for the actual sludge with the surrogate prepared similarly, compare the actual sample results to those of sensitivity grout No. 1 for each tank set.

6.3.5.1 Density and Volume Increase

The grout density for the actual W23 sample was comparable to that of its surrogate, but varied significantly for the W4 and T3 samples. The volume increases for the actual samples were significantly less than for the surrogate, 4.5, 2.1, and 4.9 vol % compared with 9, 7, and 13 vol % for W4, W23, and T3, respectively.

6.3.5.2 Bleed Water

None of the grouts produced in these hot tests produced bleed water, in agreement with the surrogate work. In fact, as stated above, the W4 grout with Stergo™ was judged too dry and not processable and, hence, was rerun without Stergo™ and still did not produce any bleed water.

6.3.5.3 Penetrometer

None of the grouts reached very high penetration resistances after only 7 d. Grouts containing the actual wastes achieved penetration resistances of 57, 92, and 135 psi at 7 d compared with 20, 106, and 0 psi at 7 d for the W4, W23, and T3 surrogates, respectively.

6.3.5.4 Toxicity Characteristic Leaching Procedure (TCLP)Test

Untreated waste sludge submitted to the TCLP test failed the UTS test for silver, chromium, and beryllium for W4, cadmium, mercury, lead, and zinc for W23, and mercury and lead for T3.

Grout samples cured 7 d containing actual tank sludge failed the UTS limits for silver for W4, cadmium and lead for W23, and lead for T3. Table 33 lists the results. In the sensitivity surrogate tests with the selected formulations, the W4 surrogate had trouble with chromium and lead, not silver as the actual sludge did. The other two surrogates met UTS limits, including lead, which was the problem for the actual sludge. The sodium dichromate in the surrogates proved to be the driver for formulation development and determining the sludge loading limit, but were not necessarily the driver for the actual samples. In pushing to the maximum sludge loading to pass TCLP, the grout apparently turned out to be specific for the surrogate, with significant differences from the actual sludges requiring fine tuning of the formulation to meet UTS limits. The effect of cure time was checked by resubmitting the samples for TCLP testing after curing at least 28 d. Table 34 lists these results. Although the silver performance improved to meet UTS limits for W4 with further curing, the lead and cadmium for W23 did not. (GFAA results were not available and the detection limits were too high to tell if OHF met the lead UTS limits after curing 28 d.)

The formulations with the hot sludges were tailored in an attempt to improve grout TCLP performances to meet UTS limits (see Table 34). The grouted hot sludges were immediately submitted for TCLP testing, with no time allowed for curing (because this testing occurred so close to the end of the project). Since the W4 sludge did not require any Stergo, sodium chloride or sodium sulfide were substituted for the 2 wt % allowed in the recipe for Stergo in two separate grouts, to improve silver stabilization. Since no Stergo was added previously, the sludge loading decreased from 92 wt % to 90 wt % with the addition of 2 wt % of either compound. The TCLP performance improved by more than an order of magnitude, with the extract silver concentration decreasing from 0.382 mg/L with 0.1 wt % sodium chloride after a 7-day cure to <0.0117 mg/L with the addition of 2 wt % of sodium chloride or of sodium sulfide after practically no cure.

For the other two sludges, 1 wt % lime was added to the grout to increase the pH and stabilize lead and cadmium. The dry blend was decreased by 1 wt %, keeping the sludge at 90 wt %. For caustic activation of the OHF grout, 1.5 g of solid sodium hydroxide (rather than 10 N sodium hydroxide) was added to the sludge per 100 g of grout, diluting the grout components slightly (i.e., the composition of the W23 grout was 0.56, 5.88, 0.56, 1.00, 90.00, and 2.00 wt % of IRPC, slag, cement, lime, sludge, and Stergo, respectively, and of the OHF grout 0.55, 5.79, 0.55, 0.99, 88.67, 1.97, and 1.48 wt % of IRPC, slag, cement, lime, sludge, Stergo, and sodium hydroxide, respectively). The TCLP performance for W23 improved, with the cadmium concentration decreasing to <0.132 mg/L, lower than the UTS limit of 0.19 mg/L. The analytical laboratory had difficulty with their graphite atomic absorption analysis (GFAA) for these later samples (unable to obtain an analysis for the samples cured 28 d and resulting in higher quantitation limits than usual for the hot samples tailored with sodium chloride, sodium sulfide or lime addition). The results in Table 34 show that the TCLP extract lead concentration decreased to 0.433 and <0.0835 mg/L from tailored treatment of the W23 and OHF samples, respectively, with little or no curing. These results prove the tailored treatment met the lead UTS limit of 0.37 mg/L for the OHF sample, but still not for the W23 sample. A longer cure, further tailoring, or lower sludge loading is needed for the treated W23 sludge sample to meet UTS limits.

6.4 VITRIFICATION STUDIES WITH ACTUAL TANK SLUDGES

6.4.1 Glass Preparation and Testing

This phase of the test work involved four glass formulas: a borosilicate reference glass provided by SRTC (known as the ARM) glass and three soda-lime glasses—each prepared from actual W4, W23, and T3 tank sludge. The ARM glass contains neither actual nor simulated waste. Rather, it is a reference glass used as a control for the Product Consistency Test (PCT). The ARM glass was provided as a single chunk of glass and was therefore not melted, but rather size-reduced, prior to leaching (PCT). The leaching performance of this glass has been well documented at SRTC and is therefore used as a control.[69] The soda-lime glasses were developed for a surrogate sludge composition representative of each tank sludge sample. The formulations vitrified in the hot tests for performance testing are listed in Table 35.

For each test, the actual sludge was weighed into new, 90-cc platinum crucibles and precipitated silica and finely powdered limestone were blended to the desired homogeneity based upon color, using a spatula with manipulator grips attached. The glass formulation developed by SRTC was used to prepare each glass (see Table 35). The platinum crucibles were set into clay crucibles inside the furnace to protect the oven refractory. The furnace was started at ambient temperature in the cell (27 to 29°C) with the crucible inside and the furnace programmed to ramp at 15°C/min to 1300°C and then hold this temperature for a minimum of 4 h. The surrogate blend used a hold time of 4 h; however, for the glass formed from actual waste, the hold time of 4.75 h was used because it was more difficult to mix the ingredients in the hot cell.

The 1300°C crucibles were removed from the furnace using special tongs adapted for use with the manipulator. Once removed they were quickly quenched in ice water, hoping that the thermal shock would loosen the glass from the crucible.

After removing the glass samples from the furnace, they were handled in accordance with the Product Consistency Test (PCT) procedure.[69] Implementing this procedure required modification of equipment necessary to pulverize, screen to the proper mesh size, wash and separate the glass samples so that cross contamination would not occur.

A small pulverizer using tungsten carbide blades was mated to a support stand that cradled it. An attached handle with a swivel permitted the manipulator hand to tilt the whole pulverizer forward to empty its contents of ground glass onto a series of screens, with a catch pan underneath. For pieces of glass that were thought to be too large for the pulverizer, small chunks were placed inside a stainless steel cylinder and hammered with a heavy steel tube. The size-reduced glass was then poured directly into the top of the pulverizer.

A stainless steel funnel, that tightly fits inside the screening pans, was used to transfer the 100-to-200 mesh glass particles into a plastic bottle, which was screwed onto the funnel spout.

Properly screened and washed glass was eventually placed into precleaned, Parr bombs for use in the PCT leaching test. The details of the complete test are described in ASTM C 1285.[70] The bombs received approximately 1.6 g of glass each, and the tops were torqued to 40 ft-lb, the maximum recommended by the manufacturer.

6.4.2 Soda-Lime-Based Glass Test Results

6.4.2.1 Product Consistency Test (PCT)

Tables 36–39 list the elemental leachate concentrations from the PCT tests. The PCT test required that a high-purity standard be carried through the test procedures and then analyzed. A standard solution was purchased from High-Purity Standards of Charleston, South Carolina, marked as lot No. 691218 and prepared in 2% (v/v) nitric acid. The concentrations are certified to within ± 0.5% at the ppm level. Table 40 lists the standard concentrations and blanks. These solutions were analyzed by a TJA 61E trace ICP, with 3 burns each and data reported at the 95% confidence interval.

6.4.2.2 Toxicity Characteristic Leaching Procedure (TCLP) Test

The TCLP extract concentrations for the glass made by vitrifying the sludge samples are listed in Table 41. The TCLP extract concentrations for the vitrified sludge samples were well below the UTS limits.

7. SUMMARY AND CONCLUSIONS

Sludge loadings of around 90 wt % are possible with minimal volume increases of <10 vol %. Hydrogels allow such high loadings without any bleed water during short-term processing, although the grouted waste does not form a strong monolithic waste form at such high loadings, that is, the grout can support overburden but is weak. However, it may be best to judge in the field the potential of a treated waste to generate bleed water before adding a hydrogel. If the treated waste is already fairly stiff, adding hydrogel can result in a fairly dry, crumbly waste form that may not be desirable. TCLP performance proved to be the limiting factor in sludge loading, with the more aggressive TCLP fluid 2 being used exclusively in the present work. Developing the formulation to maximize the loading while still passing TCLP tailored the grout fairly specifically for the sludge being tested. Although the surrogates served adequately for predicting actual sludge performance at more robust loadings, pushing the loading too close to UTS limits is risky because the differences between the surrogate and actual sludge could lead to field performance failure. Stabilizing the dichromates in the surrogates established the loading limits for the surrogates. The chromium appeared less leachable in the actual sludges, implying a different species, and conservatively making the surrogates more challenging to stabilize, as intended. However, other RCRA metals were limiting for the actual sludges (silver for W4 and lead for W23 and T3) and apparently were less leachable from the surrogates than from the actual sludges. This difference between the surrogates and actual sludges required further tailoring of the grout formulations in order to meet the UTS limits.

In summary, performance of the grout decreases as the waste loading increases, becoming weaker and more leachable. Apparently simple addition of a hydrogel will eliminate free water, a typical waste acceptance criterion. Meeting TCLP limits is not a criterion for deep geological disposal, for example, WIPP, but is for shallow land disposals. Sludge loadings up to about 85 wt % appear to form leach-resistant monolithic waste forms with fair strength. Above 85 wt %, the grouts continue to become less consolidated and more like soil.

Grout and vitrification treatment are inherently different. Grouting adds stabilizing agents directly to the wet sludge, inevitably increasing the volume unless evaporation or other pretreatment reduces the sludge volume. For vitrification, the sludge is inevitably dried and calcined into its refractory oxides with the accompanying mass and volume decrease and then its composition adjusted to make a suitable glass melt. The mass loss and densification accompanying vitrification usually result in net volume decreases. The key to maximizing the waste oxide loading and this volume decrease is the amount of glass formers-modifiers present in the waste. The key glass ingredients must be within a bounded region to make a "good" glass melt. If the waste doesn't contain the proper composition, then the major constituents must be added to adjust the composition. In addition to the major glass constituents, components that act as nucleation sites and/or have low solubility in the glass melt must be identified in the waste characterization and accounted for in the glass formulation development. In general, these two groups—the major glass-forming components and the minor troublesome components—dictate what waste oxide loading is achievable. A small fraction of wastes can be vitrified directly into glass without any additional ingredients. Typically, a large fraction of glass components must be added to the waste to achieve the desired composition. Theoretically, a low-waste oxide loading could be required if the waste contains little or no glass constituents and has a large fraction of a troublesome nucleating agent or low-solubility material. However, most wastewater treatment sludges and ashes appear to be good candidates for vitrification with good loadings and volume decreases possible. The ORNL tank sludges contain a lot of sodium and calcium; thus, mainly silica had to be added for making a soda-lime glass waste form. The glass melt solubility of the thorium and uranium present in these sludges had to be taken into account, but the SRTC developed glasses with 40 to 45 wt % waste oxide loadings with less than half the volume of the original wet sludges. Vitrification converted the tank sludge samples into dense, leach-resistant final waste forms. Off-gas treatment must be addressed in any field vitrification, but was not addressed in these laboratory hot tests. Apparently, the difference in volume between grouting and vitrifying these tank sludges was a key factor in the economic analysis performed in a separate report.

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Table 1. Composition of the W4 sludge sample and the surrogate GAAT sludge from ref. 2

Component	Concentration (mg/kg)			
	GAAT W4 sludge sample			Surrogate GAAT sludge from ref. 2
	1	2	Avg	
Ag	92.20	107.00	99.60	
Al	10,300.00	7,870.00	9,085.00	15,022.97
B	5.53	3.00	4.27	
Ba	25.30	14.10	19.70	
Be	15.30	18.00	16.65	
Ca	1,160.00	1,580.00	1,370.00	11,473.59
Cd	< 7.01	<6.60	<6.81	
Chloride	16.70	13.90	15.30	1,073.07
Co	5.72	6.71	6.22	
Cr	259.00	228.00	243.50	447.92
Cu	7.78	4.15	5.97	
Fluoride	<4.6	< 4.6	<4.6	2,022.32
Fe	627.00	443.00	535.00	7,676.57
Hg				91.53
K	358.00	339.00	348.50	4,429.85
Mg	<2.03	<1.91	<1.97	2,889.03
Mn	114.00	122.00	118.00	
Na	18,900.00	22,400.00	20,650.00	28,257.50
Ni	83.80	92.50	88.15	
Nitrate	956.00	939.00	947.50	30,006.42
Pb	<7.40	<6.97	<7.19	1,320.70
Phosphate	789.00	920.00	854.50	2,985.33
Si	2,370.00	1,460.00	1,915.00	3,686.96
Sulfate	1,180.00	1,150.00	1,165.00	5,406.62
Sr	15.60	15.60	15.60	
Th	<13.8	<13.0	<13.4	7,373.91
TIC	<1000	<1000	<1000	3,403.09
TOC	<1000	<1000	<1000	4,530.65
Carbonate	<5000	<5000	<5000	17,002.37
U	149,000.00	180,000.00	164,500.00	42,468.79
V	8.16	8.65	8.41	
Zn	55.00	74.20	64.60	
Water (wt %)	71.2%		71.2%	72.7%
pH	10.53	10.55	10.54	

Table 2. Composition of the surrogate GAAT W4 sludges

Compound	Concentration (mg/kg)			
	Standard		Maximum water (ref. 2 basis)	Minimum water-maximum bad actors from ref. 2
	With halides	Without halides		
$Al(OH)_3$	43,414	44,418	18,521	67,352
$Ca(OH)_2$	21,202	21,692	9,045	32,893
$Na_2Cr_2O_7.2H_2O$	1,284	1,312	547	6,877
Fe_2O_3	10,970	11,224	4,680	17,020
$HgCl_2$	124	126	53	563
K_2CO_3	7,826	8,006	3,338	12,141
$Mg(OH)_2$	4,788	4,900	2,043	7,429
NaOH	20,742	21,222	8,849	32,178
Na_2CO_3	24,016	24,572	10,246	37,259
PbO	1,422	1,456	607	7,885
SiO_2	7,884	8,066	3,363	12,232
$Th(NO_3)_4.4H_2O$	17,538	17,944	7,482	27,209
$UO_2(NO_3)_2.6H_2O$	89,547	91,620	38,203	96,068
NaCl	1,714	0	0	4,540
NaF	4,468	0	0	26,300
Tributylphosphate	8,368	8,562	3,570	22,153
Na_2SO_4	7,999	8,176	3,409	13,899
Ag_2O	100	102	43	0
Total	273,405	273,399	114,000	424,000
		wt %		
Compounds	27.3	27.3	11.4	42.4
H_2O	72.7	72.7	88.6	57.6

Table 3. Composition of the BVEST W23 sludge sample, the surrogate from ref. 1, and the surrogate used in the work documented in this report

	Concentration (mg/kg)		
Component	BVEST W23 sludge sample	MVST-BVEST surrogate from ref. 1	BVEST W23 surrogate
Ag	7	18	21
Ba	52		
Cd	24	20	28
Cr	161	89	189
Hg		30	35
Ni	118		
Pb	705	275	828
Se		47	55
Tl		16	19
Be	14		
V	<0.73		
Zn	579		680
Al	1,730	3,418	2,031
B	15		
Ca	56,900	38,593	66,810
Carbonate		43,623	7,744
Fe	1,730	1,399	2,031
K	12,900	14,627	15,147
Mg	10,900	8,534	
Na	58,200	78,870	68,337
Nitrate	79,800	238,531	107,134
Nitrite	8,490		
Cl	5,220	2,636	6,129
F	814	646	956
Sulfate	9,110	2,030	10,697
Sr	275	153	323
Th	16,400	5,932	19,256
U	7,990	11,577	9,382
Phosphate	2,920		3,429
Si	2,140		2,513
TC	2,870	8,731	3,370
TIC	1,320	8,731	1,550
TOC	1,550		1,820
Water (wt %)	54.2	51.3	54.2
pH	11.4		

Table 4. Composition of the surrogate BVEST W23 sludges

Compound	Standard	Maximum water (ref. 1 basis)	Minimum water-maximum bad actors from ref. 1
	RCRA metals		
Ag_2O	22	18	54
CdO	32	25	48
$Na_2Cr_2O_7.2H_2O$	542	436	479
$HgCl_2$	47	38	80
PbO	892	718	506
SeO_2	77	62	78
$TlNO_3$	24	20	26
ZnO	846	682	
	Process metals		
$Al(OH)_3$	5,873	4,731	11,049
$CaCO_3$	12,500	10,071	137,300
$Ca(OH)_2$	114,257	92,054	24,713
Fe_2O_3	2,904	2,340	2,236
KNO_3	39,165	31,555	42,286
$MgCO_3$			3,674
$Mg(OH)_2$	30,699	24,733	20,345
$NaNO_3$	78,385	63,153	188,737
$NaOH$	61,221	49,325	
$NaCl$	10,083	8,124	6,300
NaF	2,112	1,702	1,800
Na_2SO_4	14,267	11,495	5,800
$Sr(NO_3)_2$	780	628	413
$Th(NO_3)_4 \cdot 4H_2O$	45,819	36,916	32,621
$UO_2(NO_3)_2 \cdot 6H_2O$	19,790	15,945	65,455
$Na_3PO_4.12H_2O$	8,923	7,189	
SiO_2	5,376	4,331	
Tributylphosphate	3,363	2,709	
Total	458,000	369,000	544,000
	wt %		
Compounds	45.8	36.9	54.4
Water	54.2	63.1	45.6

Table 5. Composition of the OHF T3 sludge sample and the surrogate from ref. 2, and the surrogate used in the work documented in this report

	Concentration (mg/kg)		
Component	OHF T3 sludge sample	OHF surrogate from ref. 2	OHF T3 surrogate
Al	8,540	13,560	8,967
As	1		
Ba	59		
Be	39		
Ca	17,000	27,690	17,850
Cd	7	10	10
Cr	42	98	103
Fe	3,340	4,920	3,507
Hg	19	111	117
K	4,340	3,102	4,557
Mg	2,320	2,610	2,436
Na	13,200	14,286	13,860
Ni	43		
Pb	196	390	410
Si	15,300	13,034	16,065
Sr	125	480	131
Th	54,100	81,092	56,806
U	2,910	9,603	3,056
Zn	<84.9	157	
Zr	1,970		
Bromide	<4.77	24	
Chloride	1,650	501	1,733
Fluoride	800	209	840
Nitrate	3,840	5,683	4,032
Nitrite	8,220	2,042	8,631
Phosphate	6,680	6,242	7,014
Sulfate	4,110	1,417	4,316
Oxalate		78	82
Total organic carbon	7,340	9,472	7,707
Inorganic carbon	2,870	10,484	3,014
Total carbon	10,210	19,956	10,721
H_2O (wt %)	75.5	64.3	75.5
pH	10.2		

Table 6. Composition of the surrogate OHF T3 sludges

	Concentration (mg/kg)		
Compound	Standard	Maximum water (ref. 2 basis)	Minimum water-maximum bad actors from ref. 2
$Al(OH)_3$	25,924	29,416	41,802
$CaCO_3$	19,280	21,877	73,644
$Ca(OH)_2$	18,658	21,171	
CdO	12	13	19
$Na_2Cr_2O_7.2H_2O$	295	335	691
Fe_2O_3	5,014	5,690	7,502
$HgCl_2$	158	180	792
K_2CO_3	8,054	9,139	5,847
$Mg(OH)_2$	5,844	6,631	
$MgCO_3$			9,655
NaOH	6,768	7,680	
PbO	441	501	705
SiO_2	34,369	38,998	29,733
$Sr(NO_3)_2$	317	360	1,237
Th(NO3)4.4H2O	5,019	5,695	
ThO_2	62,240	70,623	36,726
$UO_2(NO_3)_2.6H_2O$	6,445	7,313	21,602
ZnO			294
NaBr			90
NaCl	2,856	3,241	5,710
NaF	1,857	2,107	601
$NaNO_2$	12,944	14,688	3,266
$Na_3PO_4.12H_2O$	7,748	8,791	80,788
Na_2SO_4	6,381	7,241	4,377
Na_2CO_3			4,045
Calcium Oxalate	135	154	137
Tributylphosphate	14,241	16,159	51,737
Total	245,000	278,000	381,000
	wt %		
Compounds	24.5	27.8	38.1
H_2O	75.5	72.2	61.9

Table 7. Composition of the screening test grouts for the surrogate GAAT W4 sludge

		Grout composition (wt %)									
		Dry blend							Other additives		
GAAT SG No.	Wet sludge	IRPC	Fly ash	Slag	Cement	Other dry blend additives		Total	Water-sorptive agent		10 N NaOH solution
					High cement grouts testing sodium silicate						
1	50.0	3.9	9.8	3.4	31.9	0.0		49.0	1.0	Sodium silicate solution	0.0
2	50.0	3.8	9.6	3.4	31.2	0.0		48.0	2.0	Sodium silicate solution	0.0
3	50.0	3.6	9.0	3.1	29.2	0.0		45.0	5.0	Sodium silicate solution	0.0
4	90.0	0.7	1.8	0.6	5.9	0.0		9.0	1.0	Sodium silicate solution	0.0
5	90.0	0.6	1.6	0.6	5.2	0.0		8.0	2.0	Sodium silicate solution	0.0
6	90.0	0.4	1.0	0.4	3.3	0.0		5.0	5.0	Sodium silicate solution	0.0
					High slag grouts testing hydrogels						
7	90.0	0.8	1.9	6.6	0.7	0.0		10.0	0.0		0.0
8	90.0	0.7	1.7	5.9	0.6	0.0		9.0	1.1	Sodium silicate solution	0.0
9	90.0	0.6	1.5	5.3	0.6	0.0		8.0	2.0	Sodium silicate solution	0.0
10	89.9	0.7	1.7	5.9	0.6	0.0		9.0	1.0	Sodium silicate powder	0.0
11	90.0	0.7	1.5	5.3	0.6	0.0		8.0	2.0	Sodium silicate powder	0.0
12	90.0	0.5	1.2	4.3	0.5	0.0		6.5	3.5	Stergo	0.0
13	89.9	0.7	1.7	6.0	0.6	0.0		9.1	1.0	Stergo	0.0
14	90.0	0.6	1.5	5.3	0.6	0.0		8.0	2.0	Stergo	0.0
15	90.0	0.6	1.5	5.3	0.6	0.0		8.0	2.0	Water works SP-400	0.0
					Caustic activation						
16	88.9	0.0	0.0	7.0	0.8	0.0		7.8	2.0	Stergo	1.3
17	89.0	0.0	0.0	7.9	0.0	0.0		7.9	2.0	Stergo	1.2
					Sodium sulfide premixed into sludge						
18	90.0	0.0	0.0	7.1	0.8	0.1	Na_2S	8.0	2.0	Stergo	0.0
19	90.0	0.0	0.0	7.1	0.8	0.1	Na_2S	8.0	2.0	Stergo	0.0
20	90.0	0.0	0.0	6.3	0.7	1.0	Na_2S	8.0	2.0	Stergo	0.0
					Sodium sulfide in dry blend						
21	90.0	0.0	0.0	7.2	0.8	0.1	Na_2S	8.0	2.0	Stergo	0.0
22	90.0	0.0	0.0	7.1	0.8	0.1	Na_2S	8.0	2.0	Stergo	0.0
23	90.0	0.0	0.0	6.3	0.7	1.0	Na_2S	8.0	2.0	Stergo	0.0
					Varying sludge loading using a cement-slag dry blend						
24	84.0	0.0	0.0	12.6	1.4	0.1	NaCl	14.1	1.9	Stergo	0.0
25	86.0	0.0	0.0	10.8	1.2	0.1	NaCl	12.1	1.9	Stergo	0.0
26	88.0	0.0	0.0	9.0	1.0	0.1	NaCl	10.1	1.9	Stergo	0.0
27	90.1	0.0	0.0	7.2	0.8	0.1	NaCl	8.0	1.9	Stergo	0.0
28	92.0	0.0	0.0	5.4	0.6	0.1	NaCl	6.1	1.9	Stergo	0.0
29	94.0	0.0	0.0	3.6	0.4	0.1	NaCl	4.1	1.9	Stergo	0.0
30	96.0	0.0	0.0	1.8	0.2	0.1	NaCl	2.1	1.9	Stergo	0.0
					Add fly ash and IRPC back to dry blend						
31	90.1	0.6	1.5	5.2	0.6	0.1	NaCl	8.0	1.9	Stergo	0.0
					Replace fly ash with slag and test with beryllium in surrogate						
32	89.9	0.6	0.0	6.7	0.6	0.1	NaCl	8.1	2.0	Stergo	0.0

Table 8. Grout density, grout:sludge volume ratio, and water:solids ratio for the GAAT W4 screening tests

GAAT-SG No.	Density (g/mL)	Grout vol:sludge vol	Water:solids	Comments
		High-cement grouts		
1	1.68	1.47	0.57	Slightly wet
2	1.67	1.48	0.57	Slightly wet
3	1.64	1.51	0.57	Soupy
4	1.25	1.10	1.89	Extremely soupy
5	1.25	1.10	1.89	Very extremely soupy
6	1.20	1.14	1.89	Very extremely soupy
		High-slag grouts		
7	1.25	1.10	1.89	Pourable
8	1.25	1.10	1.89	Pourable
9	1.23	1.11	1.89	Pourable
10	1.24	1.10	1.89	Pourable
11	1.23	1.11	1.89	Pourable
12	1.24	1.10	1.89	Pourable , but with little gel bits
13	1.23	1.11	1.89	Pourable
14	1.24	1.10	1.89	Pourable , but with little gel bits
15	1.25	1.09	1.89	
16	1.25	1.11	1.84	
17	1.25	1.11	1.84	
18	1.25	1.10	1.90	
19	1.25	1.10	1.89	
20	1.24	1.11	1.90	
21	1.24	1.10	1.89	
22	1.24	1.10	1.90	
23	1.24	1.10	1.89	
24	1.30	1.13	1.57	
25	1.28	1.12	1.66	
26	1.27	1.11	1.78	
27	1.26	1.09	1.90	
28	1.24	1.08	2.02	
29	1.22	1.07	2.16	
30	1.21	1.06	2.27	
31	1.25	1.09	1.92	
32	1.25	1.10	1.89	

Table 9. Bleed water results for the surrogate GAAT W4 screening tests

GAAT SG No.	Bleed water (vol %)					
	1 d	2 d	3 d	4 d	5 d	7 d
High-cement grouts						
1		0.0				
2		0.0				
3		0.0				
4		7.5				
5		8.3				
6		18.3				
High-slag grouts						
7					23.4	
8					8.1	
9					24.9	
10					22.8	
11					21.5	
12					0.0	
13					0.4	
14					0.0	
15	0.0					0.0
16		0.0				0.0
17		0.0				0.0
18		0.0				0.0
19		0.0				0.0
20		0.0				0.0
21		0.0				0.0
22		0.0				0.0
23		0.0				0.0
24				0.0		
25				0.0		
26				0.0		
27			0.0			
28				0.0		
29				0.0		
30				0.0		
31			0.0			
32	0.0				0.0	

Table 10. Penetration resistance results for the surrogate GAAT W4 screening tests

GAAT SG No.	Penetration resistance (psi)					Size and factor[a]
	2 d	3 d	4 d	5 d	7 d	
			High-cement grouts			
1	5200					40
2	5200					40
3	4800					40
4	0					40
5	0					40
6	0					40
			High-slag grouts			
7				0		40
8				0		40
9				0		40
10				0		40
11				0		40
12				0		40
13				0		40
14				0		40
15						
16	0				62	1
17	0				98	1
18	0				62	1
19	0				42	1
20	0				42	1
21	0				2	1
22	0				2	1
23	0				2	1
24			64			1
25			42			1
26			24			1
27		14				1
28			10			1
29			4			1
30			0			1
31		0				1
32				12		1

[a] Penetrator number that is the inverse of the tip area in in.^{2}. Thus, this number is also the factor multiplied times the measured penetrating force in lb to obtain the penetration resistance in psi.

Table 11. TCLP extract concentrations for the surrogate GAAT W4 screening tests

GAAT SG No.	TCLP extract concentrations (mg/L)								
	Cr	Hg	Pb	Ag	V	Be	Th	U	pH
Raw surrogate with halides									
	217	4.37	23.5	0.268			8.18	1766	5.60
Raw surrogate w/o halides									
	189	2.4	16.9	0.922			10.4	2021	5.65
High-cement grouts									
1	0.897		<0.014	<0.005			0.98	0.3	12.04
2	1.1	0.00300	0.219	0.011			1.98	7.5	11.95
3	3.13	0.00090	0.029	<0.005			1.16	1.3	11.78
4	7.06	0.00900	0.272	0.095			6.33	1180	5.97
5	7.23	0.00300	0.168	0.095			6.77	1343	5.99
6	7.96		0.442	0.157			26.55	1367	5.43
High-slag grouts									
7	0.432	0.00040	<0.014	0.069			0.76	921	6.35
8	0.723	0.00100	<0.014	0.083			1.79	1043	6.07
9	0.224	0.00200	<0.008	0.079			0.62	1022	6.40
10	1.46	0.00070	0.016	0.077			4.17	982	5.97
11	1.025	0.00100	<0.014	0.071			1.68	924	6.19
12	1.9	0.00060	0.225	0.08			<0.26	958	5.67
13	1.12	0.00100	0.113	0.062			1.18	819	5.80
14	0.685	0.00100	0.181	0.062			0.27	781	5.69
15	0.52	0.00050	0.56	0.081			6.32	1031	5.74
16	4.04	0.00103	0.558	0.111	0.18		11.1	1089	5.03
17	4.23	0.00041	0.551	0.075	<0.020		12.5	861	4.96
18	3.3	0.00013	0.4	0.103	0.12		9.4	1158	5.04
19	4.14	0.00011	0.345	0.078	<0.020		12.3	943	4.96
20	2.67	0.00027	0.083	0.09	0.21		12.1	964	5.97
21	1.16	<0.00005	0.024	0.079	<0.020		4.4	980	5.97
22	7.44	0.00005	0.668	0.119	0.48		16.8	1194	5.08
23	4.63	0.00213	1.313	0.106	0.18		21.2	1228	5.08
24	0.027	<0.00005	<0.014	<0.005	<0.020		3.86	600	7.18
25	0.043	<0.00005	<0.014	<0.005	<0.020		4.41	743	6.91
26	0.22	0.00011	<0.014	0.007	<0.020		5.78	896	6.12
27	0.52	0.00016	<0.014	0.013	<0.020		6.96	1080	5.94
28	0.635	0.00043	0.137	<0.005	<0.020		7.46	1014	5.42
29	3.27	0.00006	0.769	0.006	0.08		8.92	1057	5.19
30	10.16	0.00040	0.67	<0.005	0.07		13.1	1221	5.00
31	0.86	0.00058	0.07	0.072	0.08		4.55	1161	5.43
32	0.88	0.00081	0.079	0.19	0.07	0.017	<0.3	889	5.97
UTS									
	0.86	0.025	0.37	0.3	0.23	0.014	N/A	N/A	

Table 12. Composition of the sensitivity test grouts for the surrogate GAAT W4 sludge

			Grout (wt %)								
				Dry blend						Other additives	
GAAT SEN No.	Sludge	Grout	Wet sludge	IRPC	Slag	Cement	Other dry blend additives		Total	Water sorptive agent	
1	Std	Std	90.0	0.6	6.7	0.6	0.1	NaCl	8.1	1.9	Stergo
2		Var	91.6	0.5	5.6	0.5	0.1	NaCl	6.7	1.6	Stergo
3			88.0	0.8	8.0	0.8	0.1	NaCl	9.7	2.3	Stergo
4			91.2	0.6	5.6	0.5	0.1	NaCl	6.8	1.9	Stergo
5			88.5	0.6	8.1	0.8	0.1	NaCl	9.6	1.9	Stergo
6	Max water		90.0	0.6	6.7	0.6	0.1	NaCl	8.1	1.9	Stergo
7	Min water max bad actors	Std	90.0	0.6	6.7	0.6	0.1	NaCl	8.1	1.9	Stergo

Table 13. Grout density, grout:sludge volume ratio and water:solids ratio for the surrogate GAAT W4 sensitivity test grouts

GAAT-SEN No.	Density (g/mL)	Grout vol:sludge vol	Water:solids
1	1.25	1.09	1.89
2	1.24	1.09	2.00
3	1.26	1.11	1.78
4	1.24	1.09	1.97
5	1.26	1.11	1.80
6	1.12	1.08	3.94
7	1.41	1.07	1.08

Table 14. Bleed water and penetration resistance results for the surrogate GAAT W4 sensitivity test grouts

GAAT-SEN No.	Bleed water (vol %)			Penetration resistance (psi)		
	2 d	7 d	20 d	2 d	7 d	Size and factor[a]
1	0.0	0.0	0.0	0	20	1
2	0.0	0.0	0.0	0	22	1
3	0.0	0.0	0.0	0	38	1
4	0.0	0.0	0.0	0	34	1
5	0.0	0.0	0.0	0	46	1
6	0.0	0.0	0.0	0	0	1
7	0.0	0.0	0.0	0	46	1

[a] Penetrator number that is the inverse of the tip area in in.^{2}. Thus, this number is also the factor multiplied times the measured penetrating force in lb to obtain the penetration resistance in psi.

Table 15. TCLP extract concentrations for the surrogate GAAT W4 sensitivity test grouts

GAAT SEN No.	TCLP extract concentrations (mg/L)							
	Cr	Hg	Pb	Ag	V	Th	U	pH
1	0.619	0.0003	0.361	0.027	<0.020	<0.3	853	6.17
2	1.13	0.00142	0.48	0.027	<0.020	0.55	1058	5.67
3	0.43	0.0002	0.228	0.027	0.11	<0.26	697	6.57
4	0.71	0.00105	0.41	0.022	<0.020	<0.26	906	5.78
5	0.419	0.0003	0.246	0.016	<0.020	<0.26	722	6.57
6	0.624	0.00207	0.333	0.01	0.026	<0.26	427	5.33
7	54.8	0.00119	0.247	0.019	<0.020	0.28	660	7.63
				UTS				
	0.86	0.025	0.37	0.3	0.23	N/A	N/A	

Table 16. Composition of the screening test grouts for the surrogate BVEST W23 sludge

W23-SG No.	Grout (wt %)						
		Dry blend					
	Wet sludge	IRPC	Slag	Cement	Total	Water-sorptive agent	
1	90.1	0.6	6.7	0.7	8.0	1.9	Stergo
2	92.1	0.5	5.0	0.5	6.0	1.9	Stergo
3	94.0	0.3	3.4	0.4	4.1	1.9	Stergo
4	96.1	0.2	1.7	0.2	2.0	1.9	Stergo
5	88.0	0.8	8.4	0.8	10.1	1.9	Stergo
6	86.0	1.0	10.1	1.0	12.1	1.9	Stergo
7	84.0	1.1	11.8	1.2	14.1	1.9	Stergo

Table 17. Grout density, grout:sludge volume ratio, and water:solids ratio for the BVEST W23 screening tests

W23-SG No.	Density (g/mL)	Grout vol:sludge vol	Water:solids
1	1.44	1.07	0.95
2	1.42	1.06	1.00
3	1.41	1.05	1.04
4	1.38	1.05	1.13
5	1.45	1.09	0.91
6	1.47	1.10	0.87
7	1.51	1.09	0.84

Table 18. Bleed water and penetration resistance results for the BVEST W23 screening tests

W23-SG No.	7-d Bleed water (vol %)	7-d Penetration resistance (psi)	7-d Penetration resistance Size and factor[a]
1	0.0	100	1
2	0.0	60	1
3	0.0	20	1
4	0.0	0	1
5	0.0	140	1
6	0.0	165	1
7	0.0	195	1

[a] Penetrator number that is the inverse of the tip area in in.^{2}. Thus, this number is also the factor multiplied times the measured penetrating force in lb to obtain the penetration resistance in psi.

Table 19. TCLP extract concentrations for the BVEST W23 screening tests

W23 SG No.	TCLP extract concentrations (mg/L) Cr	Hg	Pb	Ag	Cd	Se	Tl	Zn	Th	U	pH
					Raw surrogate						
	33.5	1.682	28	0.023	<0.009	6.48	<0.074	56.6	<1.2	0.66	12.61
					Grouts						
1	<0.010	0.00022	<0.014	<0.005	<0.002	0.21	<0.016	3.85	<0.3	0.17	11.94
2	0.171	<0.00005	<0.014	<0.005	<0.002	0.223	<0.020	3.35	<0.3	0.31	12.20
3	4.19	0.00010	0.148	<0.005	<0.002	0.282	0.04	2.45	<0.3	0.46	12.54
4	6.75	0.00034	0.56	<0.005	<0.002	0.32	0.042	2.99	<0.3	0.59	12.53
5	<0.100	<0.00005	<0.140	<0.050	<0.020	0.232	<0.160	3.55	<2.6	<1.0	12.11
6	<0.010	<0.00005	<0.014	<0.005	<0.002	0.22	<0.016	3.99	<0.3	0.2	11.88
7	<0.010	0.00007	<0.014	<0.005	<0.002	0.21	<0.02	6.1	<0.3	<0.10	11.78
					UTS						
	0.86	0.02500	0.37	0.3	0.19	0.16	0.078	5.3	N/A	N/A	

Table 20. Composition of the sensitivity test grouts for the surrogate BVEST W23 sludge

W23-Sen No.	Sludge	Grout	Grout (wt %) Wet sludge	Dry blend IRPC	Dry blend Slag	Dry blend Cement	Dry blend Total	Water sorptive agent	
1	Std	Std	90.0	0.6	6.7	0.6	8.0	2.0	Stergo
2		Var	91.7	0.5	5.6	0.5	6.7	1.7	Stergo
3			88.1	0.8	8.0	0.8	9.6	2.4	Stergo
4			91.2	0.6	5.6	0.5	6.7	2.0	Stergo
5			88.6	0.6	8.1	0.8	9.5	2.0	Stergo
6	Max water		90.1	0.6	6.7	0.6	8.0	2.0	Stergo
7	Min water max bad actors	Std	90.0	0.6	6.7	0.6	8.0	2.0	Stergo

Table 21. Grout density, grout:sludge volume ratio, and water:solids ratio of the surrogate BVEST W23 sensitivity test grouts

W23-Sen No.	Density (g/mL)	Grout vol:sludge vol	Water:solids
1	1.44	1.07	0.95
2	1.43	1.06	0.99
3	1.46	1.08	0.91
4	1.42	1.07	0.98
5	1.45	1.08	0.93
6	1.33	1.09	1.33
7	1.53	1.06	0.70

Table 22. Bleed water and penetration resistance results of the surrogate BVEST W23 sensitivity test grouts

W23-Sen No.	Bleed water (vol %)			Penetration resistance (psi)	
	2 d	7 d	20 d	7 d	Size and factor[a]
1	0.0	0.0	0.0	106	1
2	0.0	0.0	0.0	60	1
3	0.0	0.0	0.0	114	1
4	0.0	0.0	0.0	65	1
5	0.0	0.0	0.0	120	1
6	0.0	0.0	0.0	44	1
7	0.8	0.8	0.8	0	1

[a] Penetrator number that is the inverse of the tip area in in.^{2}. Thus, this number is also the factor multiplied times the measured penetrating force in lb to obtain the penetration resistance in psi.

Table 23. TCLP extract concentrations of the surrogate BVEST W23 sensitivity test grouts

W23 Sen No.	TCLP extract concentrations (mg/L)										
	Cr	Hg	Pb	Ag	Cd	Se	Tl	Zn	Th	U	pH
1	0.086	0.00011	<0.014	<0.005	<0.002	<0.02	<0.016	<0.010	<0.26	0.33	11.45
2	0.029	0.00016	0.036	<0.005	<0.002	0.031	<0.016	<0.010	<0.26	0.44	11.73
3	0.023	0.00102	0.049	<0.005	<0.002	<0.02	<0.016	0.062	1.28	0.88	11.71
4	0.024	0.00041	0.06	<0.005	<0.002	0.06	<0.016	0.034	<0.26	0.58	11.56
5	0.013	0.00042	0.016	<0.005	<0.002	0.043	<0.016	0.023	<0.26	0.43	11.19
6	0.013	0.00023	<0.014	<0.005	<0.002	<0.02	<0.016	<0.010	<0.26	0.321	11.39
7	0.18	0.00007	0.122	0.064	<0.002	0.21	0.15	<0.010	0.43	1183	
						UTS					
	0.86	0.025	0.37	0.3	0.19	0.16	0.078	5.3	N/A	N/A	

Table 24. Composition of the screening test grouts for the surrogate OHF T3 sludge

	Grout (wt %)									
		Dry blend						Other additives		
OHF SG No.	Wet sludge	IRPC	Slag	Cement	Other dry blend additives		Total	Water-sorptive agent		10 N NaOH solution
Varying sludge loading										
1	89.9	0.6	6.7	0.6	0.0		8.0	2.0	Stergo	0.0
2	92.0	0.5	5.0	0.5	0.0		6.0	2.0	Stergo	0.0
3	94.0	0.3	3.4	0.3	0.0		4.0	2.0	Stergo	0.0
4	96.0	0.2	1.7	0.2	0.0		2.0	2.0	Stergo	0.0
5	88.0	0.8	8.4	0.8	0.0		10.0	2.0	Stergo	0.0
6	86.0	1.0	10.1	1.0	0.0		12.0	2.0	Stergo	0.0
7	84.0	1.1	11.8	1.1	0.0		14.0	2.0	Stergo	0.0
Varying sludge loading with caustic activation										
8	88.4	0.6	6.6	0.6	0.0		7.9	2.0	Stergo	1.7
9	90.8	0.5	5.0	0.5	0.0		5.9	2.0	Stergo	1.4
10	92.4	0.3	3.3	0.3	0.0		3.9	2.0	Stergo	1.7
11	94.4	0.2	1.6	0.2	0.0		1.9	1.9	Stergo	1.8
12	86.5	0.8	8.3	0.8	0.0		9.8	2.0	Stergo	1.7
13	84.5	0.9	9.9	0.9	0.0		11.8	2.0	Stergo	1.8
14	82.5	1.1	11.6	1.1	0.0		13.8	2.0	Stergo	1.7
Testing other dry blend additives										
15	84.5	0.4	4.1	0.4	6.8	$KMnO_4$	11.7	1.5	Stergo	2.3
16	88.1	0.6	5.8	0.6	1.5	$FeCl_3$	8.3	1.5	Stergo	2.1
17	86.9	0.6	6.3	0.6	1.8	$Al_2(SO_4)_3$	9.3	1.5	Stergo	2.3
Testing without TBP in surrogate										
18	88.9	0.6	6.6	0.6	0.0		7.8	2.0	Stergo	1.2
19	88.8	0.6	6.6	0.6	0.0		7.8	2.0	Stergo	1.3

Table 25. Grout density, grout:sludge volume ratio, and water:solids ratio for the OHF T3 screening tests

OHF-SG No.	Density (g/mL)	Grout vol:sludge vol	Water:solids
1	1.17	1.11	2.12
2	1.15	1.11	2.27
3	1.13	1.11	2.44
4	1.11	1.10	2.63
5	1.18	1.12	1.98
6	1.21	1.12	1.85
7	1.23	1.13	1.73
8	1.19	1.11	2.01
9	1.17	1.10	2.18
10	1.15	1.10	2.31
11	1.13	1.10	2.53
12	1.21	1.12	1.88
13	1.23	1.13	1.76
14	1.27	1.12	1.65
15	1.26	1.10	1.76
16	1.22	1.09	1.99
17	1.19	1.13	1.91
18	1.22	1.08	2.12
19	1.23	1.08	2.04

Table 26. Bleed water and penetration resistance results for the OHF T3 screening tests

OHF-SG No.	Bleed Water (vol %)		Penetration Resistance (psi)		
	2 d	7 d	2 d	7 d	Size and factor[a]
1		0.0		0	1
2		0.0		0	1
3		1.7		0	1
4		3.7		0	1
5		0.0		0	1
6		0.0		0	1
7		0.0		0	1
8	0.8	0.0	0	4	1
9	0.0	0.0	0	2	1
10	4.0	3.2	0	0	1
11	2.0	1.6	0	0	1
12	0.0	0.0	0	6	1
13	0.0	0.0	0	8	1
14	0.0	0.0	0	12	1
15	0.0	0.0	0	0	1
16	0.0	0.0	0	28	1
17	0.0	0.0	0	10	1
18	0.0	0.0	0	0	1
19	0.0	0.0	0	0	1

[a] Penetrator number that is the inverse of the tip area in in.^2. Thus, this number is also the factor multiplied times the measured penetrating force in lb to obtain the penetration resistance in psi.

Table 27. TCLP extract concentrations for the OHF T3 screening tests

OHF-SG No.	TCLP extract concentrations (mg/L)						
	Cr	Hg	Pb	Cd	Th	U	pH
				Raw surrogate			
	9.95	2.508	6.29	0.716	<0.588	95.7	5.42
				Grouts			
1	1.6	0.03170	1.02	0.024	<0.26	86	4.82
2	1.58	0.05930	1.28	0.063	<0.26	84.2	4.77
3	1.71	0.08470	1.4	0.056	<0.26	74.2	4.65
4	2.7	0.17000	1.15	0.043	<0.26	57.2	4.51
5	1.2	0.00363	0.839	0.055	<0.26	89.5	5.01
6	0.84	0.00246	0.375	0.019	<0.26	73.3	5.03
7	0.474	0.00204	0.244	0.015	<0.26	70	5.09
8	0.585	0.00265	0.112	0.0032	<0.3	80.9	5.58
9	1.2	0.02530	0.48	0.0281	<0.26	61.9	5.11
10	1.36	0.08340	0.738	0.022	<0.26	63.7	5.00
11	1.36	0.15800	0.58	0.04	<0.26	54.2	4.81
12	0.32	0.00155	0.05	<0.002	<0.26	71.8	5.84
13	0.04	0.00087	<0.014	<0.002	<0.3	102	6.58
14	<0.01	0.00147	<0.014	<0.002	<0.3	120	7.38
15	3.44	0.87400	<0.07	<0.01	1.5	5.6	5.20
16	0.29	0.00406	0.21	0.0396	<0.3	98.5	5.16
17	0.76	0.00193	0.191	0.0068	<0.3	85.4	5.37
18	0.063		0.071	<0.003	5.5	62.2	6.55
19	0.05		0.046	<0.003	2.97	105	7.85
				UTS			
	0.86	0.025	0.37	0.19	N/A	N/A	

Table 28. Composition of the grouts for the sensitivity testing of the surrogate OHF T3 sludge

			Grout (wt %)							
				Dry blend				Other additives		
OHF SEN No.	Sludge	Grout	Wet sludge	IRPC	Slag	Cement	Total	Water sorptive agent		10 *N* NaOH solution
1	Std	Std	88.5	0.6	6.6	0.6	7.8	2.0	Stergo	1.7
2		Var	89.9	0.5	5.5	0.5	6.5	1.6	Stergo	2.0
3			86.4	0.7	7.8	0.7	9.3	2.3	Stergo	2.0
4			89.2	0.6	5.4	0.5	6.6	2.0	Stergo	2.2
5			86.8	0.6	7.9	0.8	9.3	1.9	Stergo	2.0
6	Max water		88.3	0.6	6.6	0.6	7.8	2.0	Stergo	1.9
7	Min water max bad actors	Std	87.0	0.6	6.5	0.6	7.7	2.0	Stergo	3.3

Table 29. Grout density, grout:sludge volume ratio, and water:solids ratio of the surrogate OHF T3 sensitivity grouts

OHF-SEN	Density (g/mL)	Grout vol:sludge vol	Water:solids
1	1.17	1.13	2.02
2	1.16	1.12	2.11
3	1.19	1.14	1.90
4	1.20	1.09	2.07
5	1.23	1.10	1.90
6	1.26	1.08	1.76
7	1.29	1.13	1.17

Table 30. Bleed water and penetration resistance results of the surrogate OHF T3 sensitivity grouts

	Bleed water (vol %)			Penetration Resistance (psi)		
OHF-SEN No.	4 d	7 d	19 d	4 d	7 d	Size and factor[a]
1	0.0	0.0	0.0	0	0	1
2	0.0	0.0	0.0	0	0	1
3	0.0	0.0	0.0	0	0	1
4	0.0	0.0	0.0	0	0	1
5	0.0	0.0	0.0	0	0	1
6	0.0	0.0	0.0	0	0	1
7	0.0	0.0	0.0	0	0	1

[a] Penetrator number that is the inverse of the tip area in in.^{2}. Thus, this number is also the factor multiplied times the measured penetrating force in lb to obtain the penetration resistance in psi.

Table 31. TCLP extract concentrations of the surrogate OHF T3 sensitivity grouts

OHF SEN No.	TCLP extract concentrations (mg/L)						
	Cr	Hg	Pb	Cd	Th	U	pH
1	0.066	0.00144	0.024	<0.002	<0.26	85.8	6.72
2	0.066	0.00051	0.057	<0.002	<0.26	84.9	6.43
3	0.068	0.00307	0.056	<0.002	<0.26	106	7.50
4	0.12	0.00041	0.017	<0.002	<0.26	61.4	6.40
5	0.051	0.00078	0.022	<0.002	<0.26	81.9	7.39
6	0.344	0.00039	0.016	<0.002	<0.26	64.9	6.42
7	0.053	0.00008	<0.014	<0.002	<0.26	43.4	6.49
				UTS			
	0.86	0.025	0.37	0.19	N/A	N/A	

Table 32. Miscellaneous density and penetration resistance data for the grout hot tests

Waste or grout parameter	W-4	W-23	OHF
Waste bulk density, g/cc	1.29	1.36	1.17
Grout bulk density, g/cc	1.46	1.48	1.27
Grout:sludge volume ratio	1.045	1.021	1.049
Bleed water, vol %	0.0	0.0	0.0
Average penetration resistance, psi[a]	57	92	135
Wet sludge loading, %	92.6	90.0	87.8

[a] Using a circular penetration bob with a surface area of 1 in.^{2}.

Table 33. TCLP test results of the various grouted waste sludge cured 7 d

TCLP/UTS element	W-4		W-23		OHF		TCLP/UTS limits, mg/L
	Sludge	Grout	Sludge	Grout	Sludge	Grout	
Silver	2.95	0.382	0.227	0.0902	0.0651	0.0200	0.30
Arsenic	<0.00835	<0.0167	<0.00835	<0.0167	<0.0835	<0.0167	5.0
Barium	0.373	0.277	0.746	0.638	0.179	0.134	7.6
Cadmium	<0.125	<0.125	0.526	0.212	<0.125	<0.125	0.19
Chromium	1.60	0.436	0.563	0.139	0.574	0.0401	0.86
Mercury	<0.00501	<0.00334	0.0337	<0.00481	0.0942	0.0140	0.025
Nickel	1.66	0.112	2.47	1.74	0.671	0.0768	5.0
Lead	0.101	<0.190	0.680	1.11	1.49	1.41	0.37
Selenium	<0.00835	<0.0167	<0.00835	<0.0167	<0.0835	<0.0167	0.16
Thallium	<0.00835	<0.0167	<0.0919	<0.0167	<0.0835	<0.0167	0.078

Table 34. TCLP test results of the grouted waste sludge cured 28 d or tailored for stabilization

TCLP/UTS Element	W-4			W-23		OHF		TCLP UTS Limits, mg/L
	Cured 28 d	More NaCl added	Na_2S added	Cured 28 d	Lime added	Cured 28 d	Lime added	
Silver	0.254	<0.0117	<0.0117	<0.0701	0.0484	<0.0117	<0.0117	0.3
Arsenic		<0.132	<0.0835		<0.100		<0.0835	5.0
Barium	0.329	0.184	0.120	0.765	0.683	0.152	0.240	7.6
Cadmium	<0.129	<0.107	<0.107	0.342	<0.132	<0.129	<0.107	0.19
Chromium	0.466	<0.0117	<0.0134	0.205	<0.120	0.110	<0.0234	0.86
Mercury	<0.00334	<0.0835	<0.0835	0.00588	<0.0835	0.0498	<0.0835	0.025
Nickel	<0.0902	0.0668	<0.0668	1.80	1.49	<0.0902	<0.0668	5.0
Lead	<0.346[a]	<0.0835	<0.0835	1.31[a]	0.433	<1.39[a]	<0.0835	0.37
Selenium		<0.0835	<0.0835		<0.0835		<0.0835	0.16
Thallium		<0.0835	<0.0835		<0.239		<0.134	0.078

[a] By ICP analysis. No GFAA analysis available for the sample cured 28 days.

Table 35. Waste and glass formulation data

Glass or sludge parameter	OHF glass	W-23 glass	W-4 glass
Waste loading, %	40	45	45
Calcine ratio,[a] %	0.189	0.300	0.280
Total solids, %	24.5	45.8	28.8
SiO_2, %	62	62	62
Fe_2O_3, %	22	22	22
CaO, %	16	16	16

[a] Dry calcine weight divided by the starting wet sludge weight after 4 h at 850°C .

Table 36. PCT Test results for the ARM glasses (mg/L)

	ARM-17	ARM-23	ARM-27
Silver	<0.003 ± 0.004	<0.003 ± 0.002	<0.003 ± 0.001
Aluminum	6.114 ± 0.119	4.553 ± 0.049	4.536 ± 0.095
Arsenic	<0.010 ± 0.007	<0.010 ± 0.005	<0.010 ± 0.002
Boron	14.796 ± 0.221	16.522 ± 0.230	15.793 ± 0.431
Barium	0.001 ± 0.000	0.002 ± 0.000	0.001 ± 0.000
Beryllium	<0.001 ± 0.000	<0.001 ± 0.000	<0.001 ± 0.000
Calcium	<0.040 ± 0.024	<0.040 ± 0.009	<0.040 ± 0.047
Cadmium	<0.001 ± 0.000	<0.001 ± 0.000	<0.001 ± 0.000
Chromium	<0.005 ± 0.002	<0.005 ± 0.001	<0.005 ± 0.001
Copper	0.026 ± 0.008	0.015 ± 0.013	0.016 ± 0.005
Iron	<0.050 ± 0.035	<0.050 ± 0.025	<0.050 ± 0.005
Potassium	0.176 ± 0.022	0.154 ± 0.021	0.163 ± 0.030
Magnesium	<0.020 ± 0.010	<0.020 ± 0.013	<0.020 ± 0.021
Manganese	0.007 ± 0.000	0.011 ± 0.000	0.007 ± 0.000
Sodium	31.267 ± 0.595	33.906 ± 0.546	33.437 ± 0.918
Nickel	0.009 ± 0.001	0.019 ± 0.001	0.008 ± 0.004
Lead	<0.007 ± 0.001	<0.007 ± 0.002	<0.007 ± 0.003
Selenium	<0.010 ± 0.003	<0.010 ± 0.006	<0.010 ± 0.002
Antimony	<0.010 ± 0.004	<0.010 ± 0.006	<0.010 ± 0.003
Silicon	49.955 ± 0.802	55.310 ± 0.619	53.667 ± 1.223
Strontium	<0.001 ± 0.000	0.001 ± 0.000	<0.001 ± 0.000
Thorium	<0.130 ± 0.284	<0.130 ± 0.316	<0.130 ± 0.353
Titanium	0.007 ± 0.000	0.007 ± 0.001	0.007 ± 0.000
Thallium	<0.008 ± 0.004	<0.008 ± 0.002	<0.008 ± 0.008
Uranium	<0.050 ± 0.056	0.060 ± 0.049	<0.050 ± 0.049
Vanadium	<0.010 ± 0.012	<0.010 ± 0.008	<0.010 ± 0.011
Zinc	0.120 ± 0.002	0.121 ± 0.002	0.112 ± 0.003
Zirconium	<0.010 ± 0.011	<0.010 ± 0.012	<0.010 ± 0.016

Table 37. PCT test results for glass containing OHF waste sludge (mg/L)

	OHF-04			OHF-05			OHF-06		
Silver	<0.003	±	0.000	<0.003	±	0.002	<0.003	±	0.002
Aluminum	1.504	±	0.007	1.557	±	0.039	1.396	±	0.008
Arsenic	<0.010	±	0.011	<0.010	±	0.006	<0.010	±	0.001
Boron	<0.020	±	0.025	<0.020	±	0.006	<0.020	±	0.004
Barium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Beryllium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Calcium	2.218	±	0.017	2.199	±	0.064	2.097	±	0.017
Cadmium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Chromium	<0.005	±	0.001	0.006	±	0.001	0.007	±	0.001
Copper	0.011	±	0.019	0.014	±	0.011	0.012	±	0.010
Iron	0.096	±	0.026	0.078	±	0.027	0.058	±	0.018
Potassium	2.009	±	0.007	1.983	±	0.053	2.066	±	0.029
Magnesium	0.032	±	0.013	0.031	±	0.004	0.026	±	0.001
Manganese	0.004	±	0.000	0.002	±	0.000	<0.001	±	0.000
Sodium	17.896	±	0.041	18.049	±	0.454	18.108	±	0.119
Nickel	0.004	±	0.000	<0.004	±	0.002	<0.004	±	0.001
Lead	<0.007	±	0.002	<0.007	±	0.003	<0.007	±	0.005
Selenium	0.019	±	0.004	0.036	±	0.003	0.039	±	0.006
Antimony	<0.010	±	0.008	<0.010	±	0.003	<0.010	±	0.003
Silicon	20.159	±	0.059	20.275	±	0.501	20.912	±	0.101
Strontium	0.006	±	0.000	0.006	±	0.000	0.006	±	0.000
Thorium	<0.130	±	0.095	<0.130	±	0.273	<0.130	±	0.280
Titanium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Thallium	<0.008	±	0.001	<0.008	±	0.006	<0.008	±	0.005
Uranium	0.073	±	0.019	0.099	±	0.022	0.083	±	0.051
Vanadium	<0.010	±	0.002	<0.010	±	0.015	<0.010	±	0.004
Zinc	0.025	±	0.000	0.029	±	0.001	0.030	±	0.000
Zirconium	<0.010	±	0.004	<0.010	±	0.012	<0.010	±	0.012

Table 38. PCT test results for glass containing W-4 waste sludge (mg/L)

	W4-11			W4-14			W4-16		
Silver	<0.003	±	0.002	<0.003	±	0.002	<0.003	±	0.001
Aluminum	4.244	±	0.377	4.917	±	0.139	4.274	±	0.115
Arsenic	<0.010	±	0.004	<0.010	±	0.004	<0.010	±	0.004
Boron	<0.020	±	0.009	<0.020	±	0.007	<0.020	±	0.004
Barium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Beryllium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Calcium	<0.040	±	0.053	<0.040	±	0.004	<0.040	±	0.010
Cadmium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Chromium	0.006	±	0.000	<0.005	±	0.001	<0.005	±	0.001
Copper	0.016	±	0.007	0.012	±	0.013	0.010	±	0.009
Iron	0.151	±	0.031	0.158	±	0.015	0.142	±	0.018
Potassium	0.207	±	0.005	0.172	±	0.020	0.192	±	0.018
Magnesium	<0.020	±	0.003	<0.020	±	0.011	<0.020	±	0.012
Manganese	0.003	±	0.000	0.003	±	0.000	0.003	±	0.000
Sodium	25.645	±	2.134	24.062	±	0.512	25.075	±	0.502
Nickel	0.005	±	0.001	<0.004	±	0.002	<0.004	±	0.002
Lead	<0.007	±	0.001	<0.007	±	0.002	<0.007	±	0.002
Selenium	<0.010	±	0.009	<0.010	±	0.003	<0.010	±	0.002
Antimony	<0.010	±	0.003	<0.010	±	0.001	<0.010	±	0.002
Silicon	35.975	±	2.605	31.929	±	0.686	35.135	±	0.741
Strontium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Thorium	<0.130	±	0.209	<0.130	±	0.149	<0.130	±	0.106
Titanium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Thallium	<0.008	±	0.006	<0.008	±	0.004	<0.008	±	0.007
Uranium	0.318	±	0.034	0.271	±	0.026	0.290	±	0.028
Vanadium	<0.010	±	0.005	<0.010	±	0.012	<0.010	±	0.012
Zinc	0.031	±	0.002	0.037	±	0.001	0.030	±	0.001
Zirconium	<0.010	±	0.009	<0.010	±	0.006	<0.010	±	0.004

Table 39. PCT test results for glass containing W-23 waste sludge (mg/L)

	W23-07			W23-08			W23-09		
Silver	<0.003	±	0.002	<0.003	±	0.003	<0.003	±	0.002
Aluminum	0.322	±	0.033	0.278	±	0.006	0.274	±	0.015
Arsenic	<0.010	±	0.001	<0.010	±	0.002	<0.010	±	0.005
Boron	<0.020	±	0.002	<0.020	±	0.002	<0.020	±	0.003
Barium	0.003	±	0.000	0.003	±	0.000	0.004	±	0.000
Beryllium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Calcium	9.431	±	0.387	9.285	±	0.178	9.601	±	0.190
Cadmium	<0.001	±	0.000	<0.001	±	0.001	<0.001	±	0.000
Chromium	0.021	±	0.002	0.025	±	0.001	0.022	±	0.001
Copper	0.008	±	0.007	0.009	±	0.022	0.010	±	0.002
Iron	<0.050	±	0.028	<0.050	±	0.022	<0.050	±	0.014
Potassium	6.006	±	0.255	6.039	±	0.142	5.931	±	0.116
Magnesium	<0.020	±	0.008	<0.020	±	0.012	<0.020	±	0.006
Manganese	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Sodium	54.194	±	2.511	54.174	±	1.086	53.051	±	0.925
Nickel	<0.004	±	0.000	<0.004	±	0.002	<0.004	±	0.000
Lead	<0.007	±	0.001	<0.007	±	0.004	<0.007	±	0.000
Selenium	<0.010	±	0.003	<0.010	±	0.001	<0.010	±	0.004
Antimony	<0.010	±	0.002	<0.010	±	0.003	<0.010	±	0.001
Silicon	23.797	±	0.909	23.406	±	0.397	23.489	±	0.388
Strontium	0.048	±	0.002	0.050	±	0.001	0.051	±	0.001
Thorium	<0.130	±	0.257	<0.130	±	0.121	<0.130	±	0.361
Titanium	<0.001	±	0.001	<0.001	±	0.000	<0.001	±	0.000
Thallium	<0.008	±	0.006	<0.008	±	0.001	<0.008	±	0.004
Uranium	0.082	±	0.031	0.063	±	0.073	0.093	±	0.042
Vanadium	<0.010	±	0.009	<0.010	±	0.010	<0.010	±	0.019
Zinc	0.033	±	0.001	0.031	±	0.010	0.034	±	0.001
Zirconium	<0.010	±	0.011	<0.010	±	0.005	<0.010	±	0.016

Table 40. PCT test results for the analytical standard and blanks (mg/L)

	STANDARD			BLANK			BLANK		
Silver	<0.003	±	0.002	<0.003	±	0.000	<0.003	±	0.001
Aluminum	4.075	±	0.157	<0.030	±	0.006	<0.030	±	0.030
Arsenic	<0.010	±	0.005	<0.010	±	0.001	<0.010	±	0.032
Boron	21.035	±	0.718	<0.020	±	0.003	<0.020	±	0.009
Barium	0.009	±	0.000	0.001	±	0.000	<0.001	±	0.002
Beryllium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Calcium	<0.040	±	0.126	0.082	±	0.018	0.101	±	0.014
Cadmium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Chromium	<0.005	±	0.001	<0.005	±	0.002	0.012	±	0.003
Copper	0.007	±	0.005	0.042	±	0.003	0.027	±	0.003
Iron	4.159	±	0.112	<0.050	±	0.033	<0.050	±	0.075
Potassium	10.472	±	0.302	0.225	±	0.006	0.239	±	0.019
Magnesium	0.021	±	0.005	<0.020	±	0.003	0.027	±	0.012
Manganese	<0.001	±	0.000	0.104	±	0.004	0.108	±	0.011
Sodium	79.002	±	2.740	0.088	±	0.003	0.067	±	0.024
Nickel	<0.004	±	0.002	0.054	±	0.001	0.055	±	0.008
Lead	0.012	±	0.003	<0.007	±	0.001	<0.007	±	0.001
Selenium	<0.010	±	0.001	<0.010	±	0.006	<0.010	±	0.021
Antimony	<0.010	±	0.013	<0.010	±	0.008	<0.010	±	0.017
Silicon	49.984	±	1.607	0.190	±	0.029	0.189	±	0.034
Strontium	<0.001	±	0.000	<0.001	±	0.000	<0.001	±	0.000
Thorium	<0.130	±	0.106	<0.130	±	0.224	<0.130	±	0.312
Titanium	0.004	±	0.000	0.001	±	0.001	<0.001	±	0.001
Thallium	<0.008	±	0.003	<0.008	±	0.000	0.016	±	0.059
Uranium	<0.050	±	0.066	0.058	±	0.016	<0.050	±	0.327
Vanadium	<0.010	±	0.021	<0.010	±	0.007	<0.010	±	0.013
Zinc	0.038	±	0.002	0.040	±	0.002	0.043	±	0.004
Zirconium	<0.010	±	0.003	<0.010	±	0.011	<0.010	±	0.012

Table 41. TCLP test results for the various glasses

TCLP/UTS elements	OHF (mg/L)		W-23 (mg/L)		W-4 (mg/L)		UTS limits (mg/L)
	Sludge	Glass	Sludge	Glass	Sludge	Glass	
Silver	0.0651	0.0067	0.227	0.00668	2.95	<0.00501	0.30
Arsenic	<0.0835	<0.017	<0.00835	<0.0167	<0.00835	<0.0167	5.0
Barium	0.179	0.195	0.746	0.504	0.373	0.202	7.6
Cadmium	<0.125	<0.125	0.526	<0.125	<0.125	<0.125	0.19
Chromium	0.574	<0.0084	0.563	<0.00835	1.60	<0.00835	0.86
Mercury	0.0942	<0.00334	0.0337	<0.00334	<0.00501	<0.00334	0.025
Nickel	0.671	<0.0534	2.47	0.125	1.66	<0.0534	5.0
Lead	1.49	<0.021	0.680	<0.134	0.101	<0.0167	0.37
Selenium	<0.0835	<0.0167	<0.00835	<0.0167	<0.00835	<0.0167	0.16
Thallium	<0.0835	<0.0167	<0.0919	<0.0167	<0.00835	<0.0167	0.078

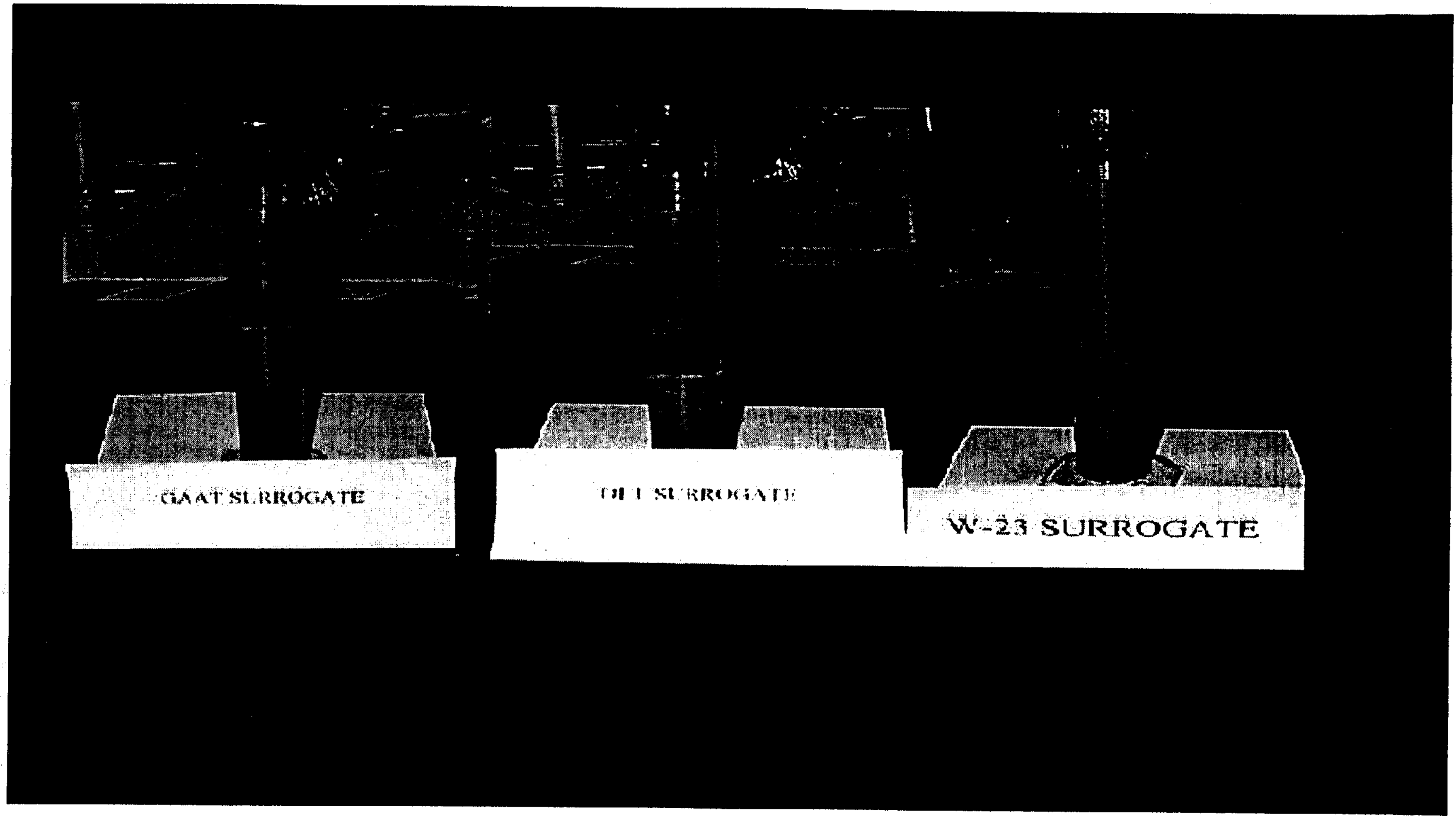

Fig. 1. Photographs of the surrogate GAAT W4, OHF T3, and BVEST W23 sludges.

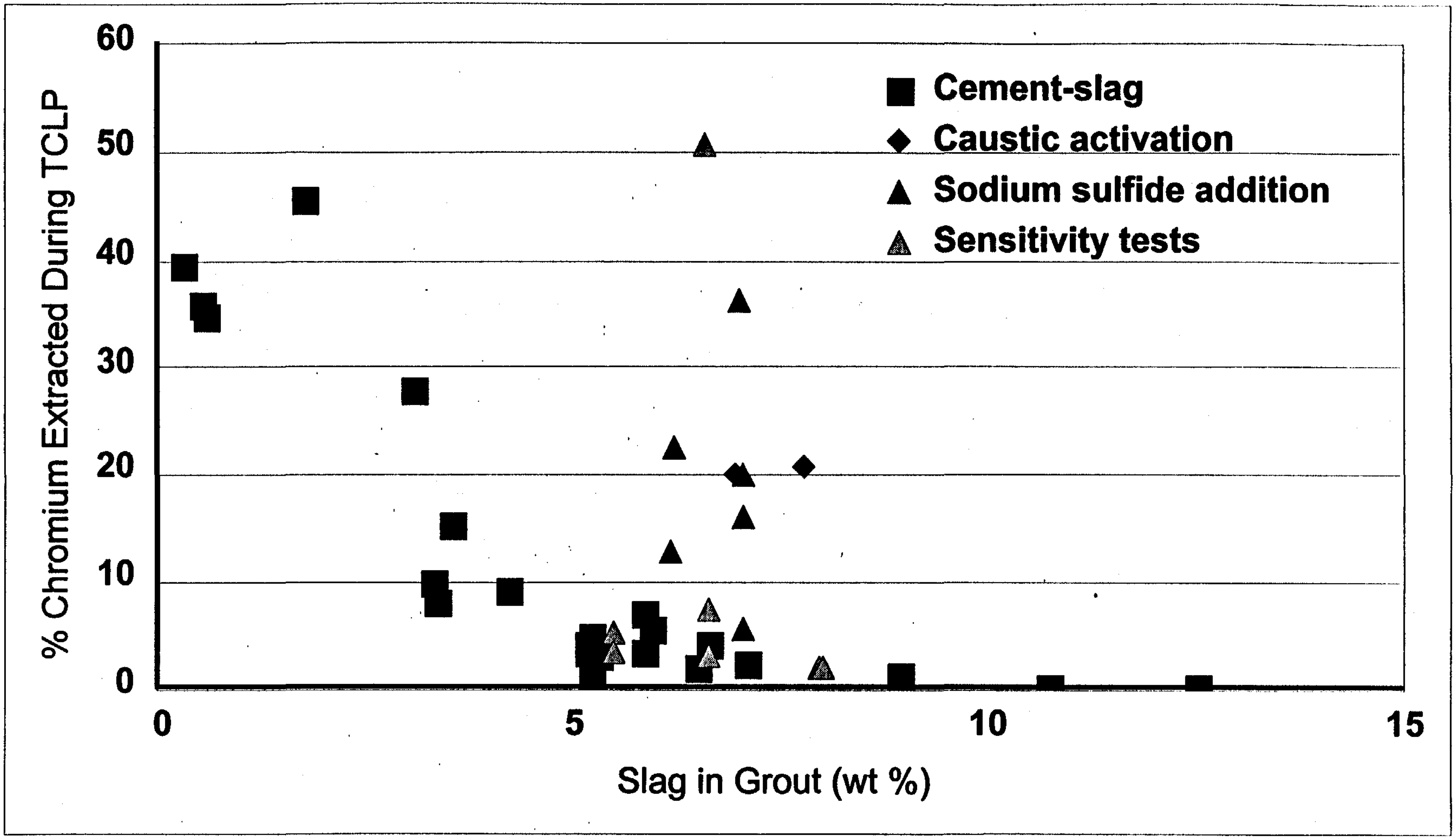

Fig.2. Plot of % chromium extracted during TCLP as a function of the grout slag content for the surrogate GAAT W4 sludge.

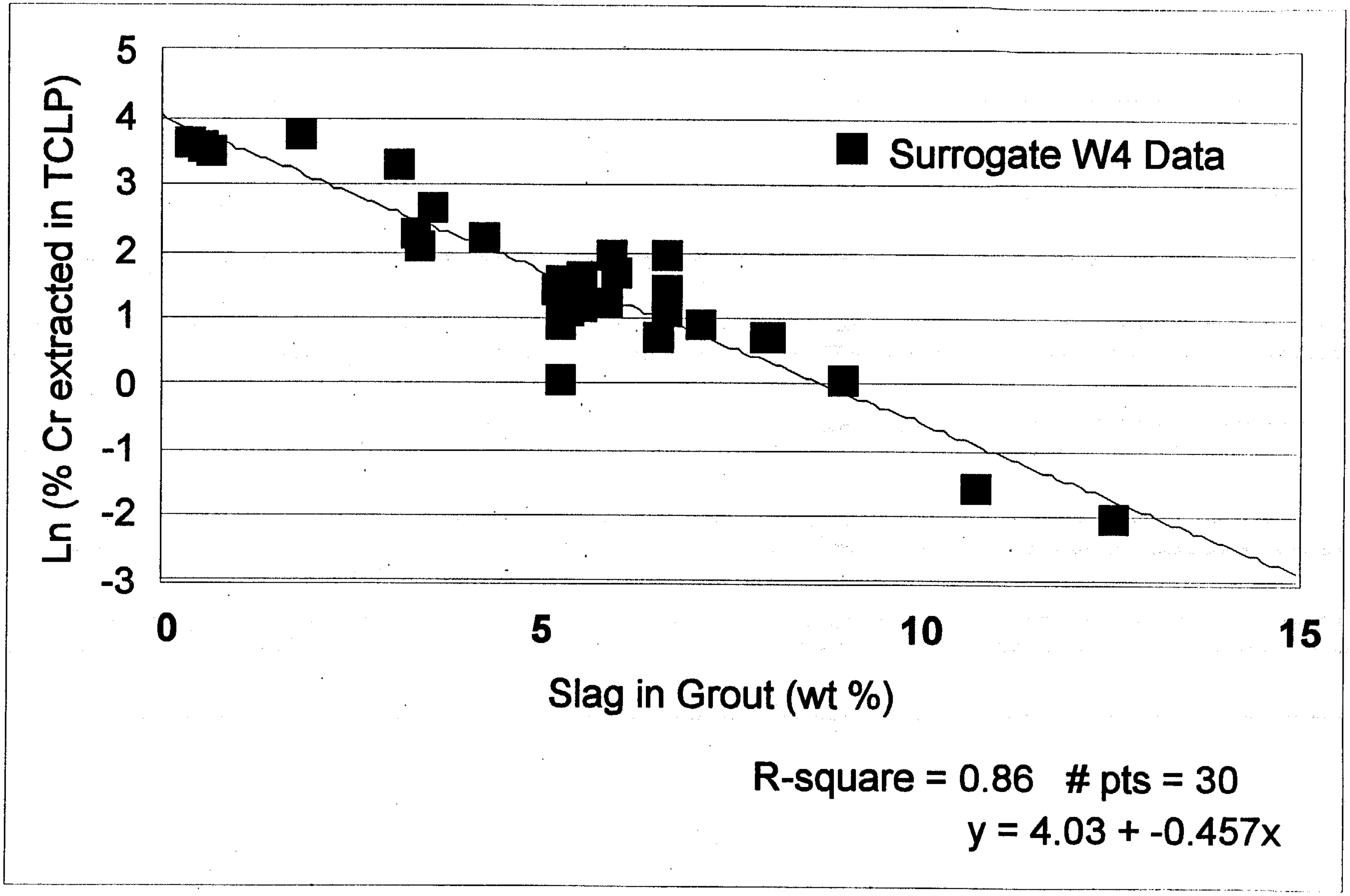

Fig. 3. Plot of ln(% Cr extracted) vs grout slag content for selected surrogate GAAT W4 data (regression equation and line shown).

Fig. 4. Maximum chromium concentration with slag loading calculated to equal UTS (0.86 mg/L) from regression.

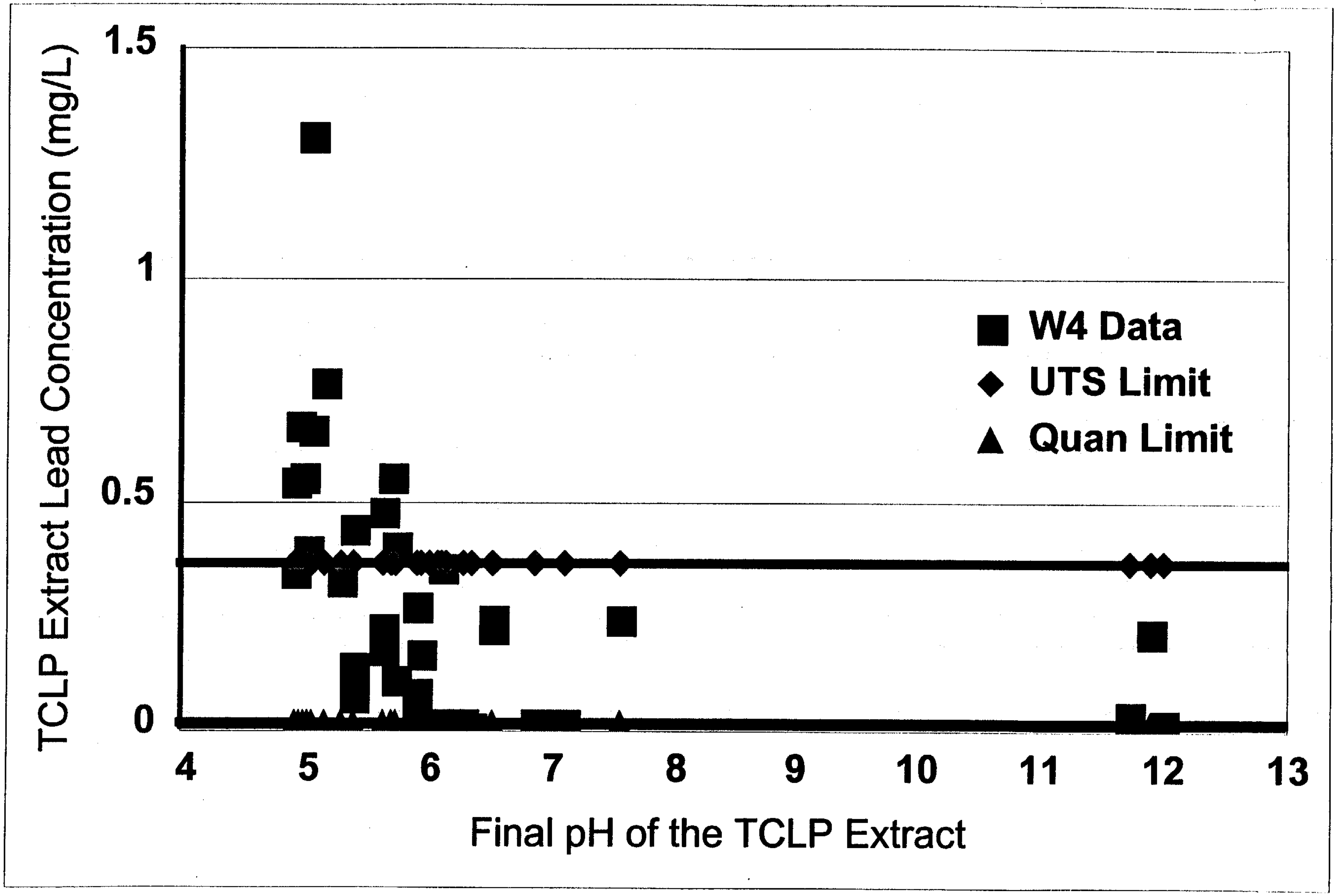

Fig. 5. Plot of TCLP extract lead concentration with final extract pH.

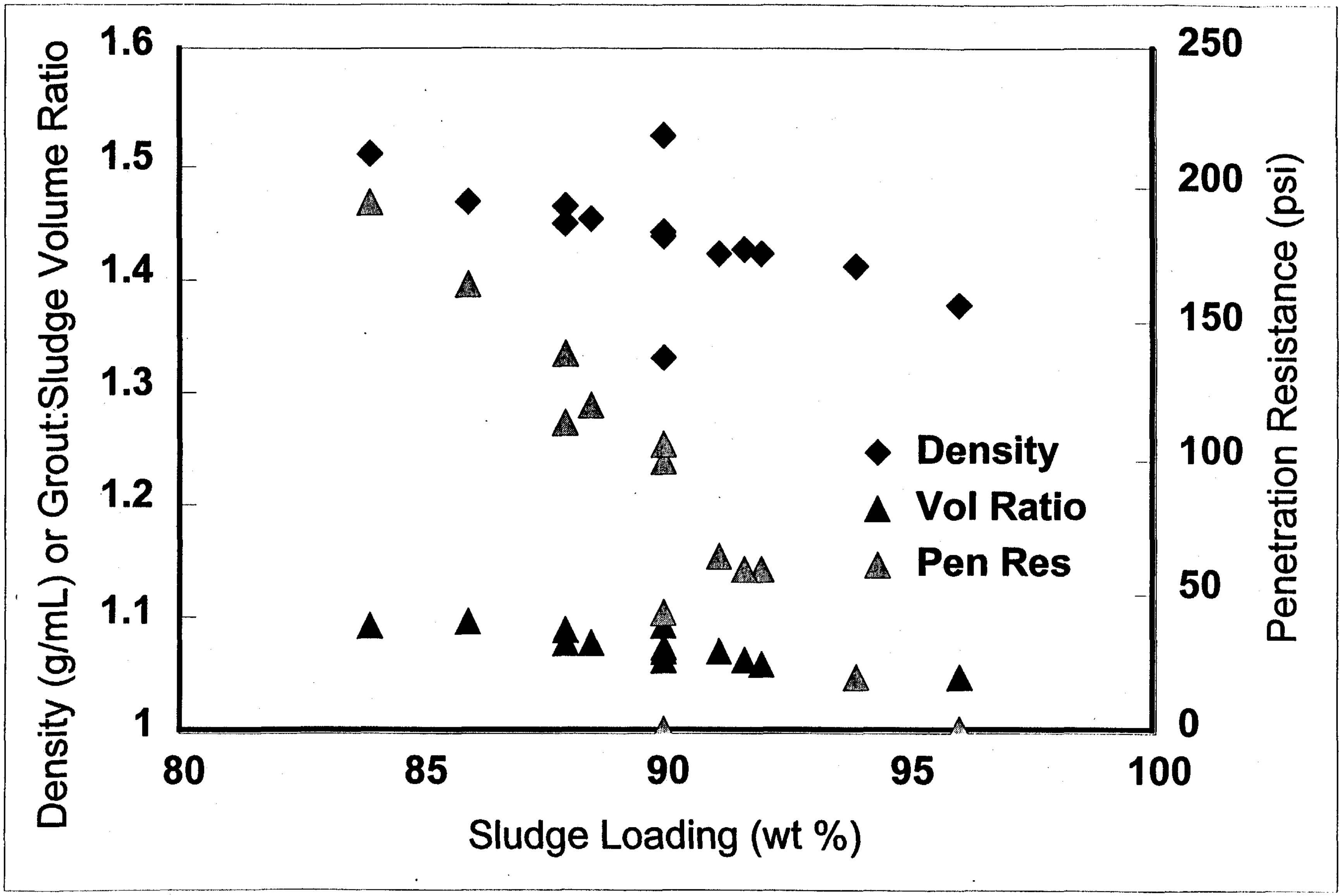

Fig. 6. Plot of grout density, grout:sludge volume ratio, and penetration resistance with sludge loading for the surrogate BVEST W23 sludge.

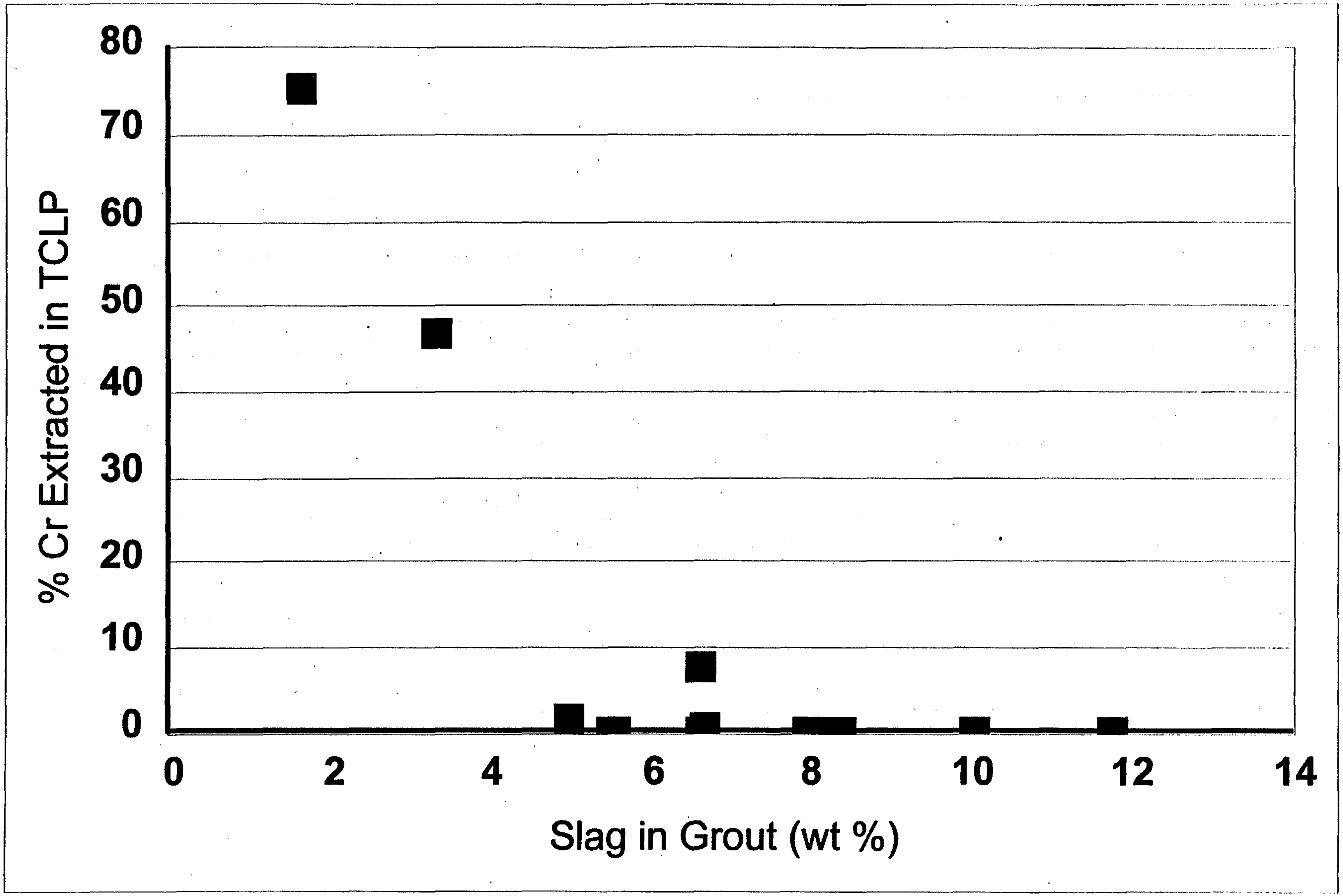

Fig. 7. Plot of % chromium extracted during TCLP as a function of the grout slag content for the surrogate BVEST W23 sludge.

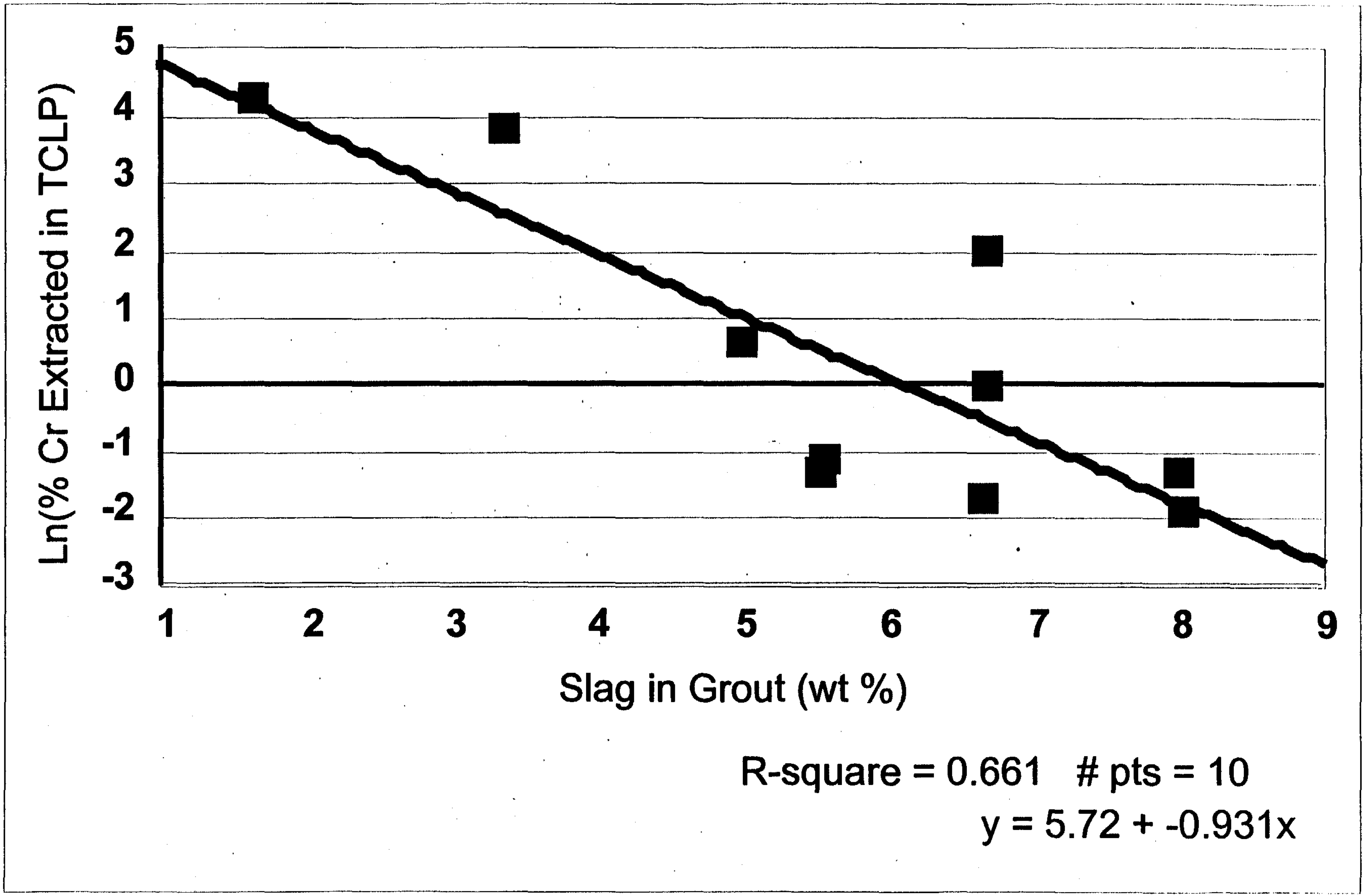

Fig. 8. Plot of ln(% Cr extracted) vs grout slag content for selected surrogate BVEST W23 data (the regression equation and line shown).

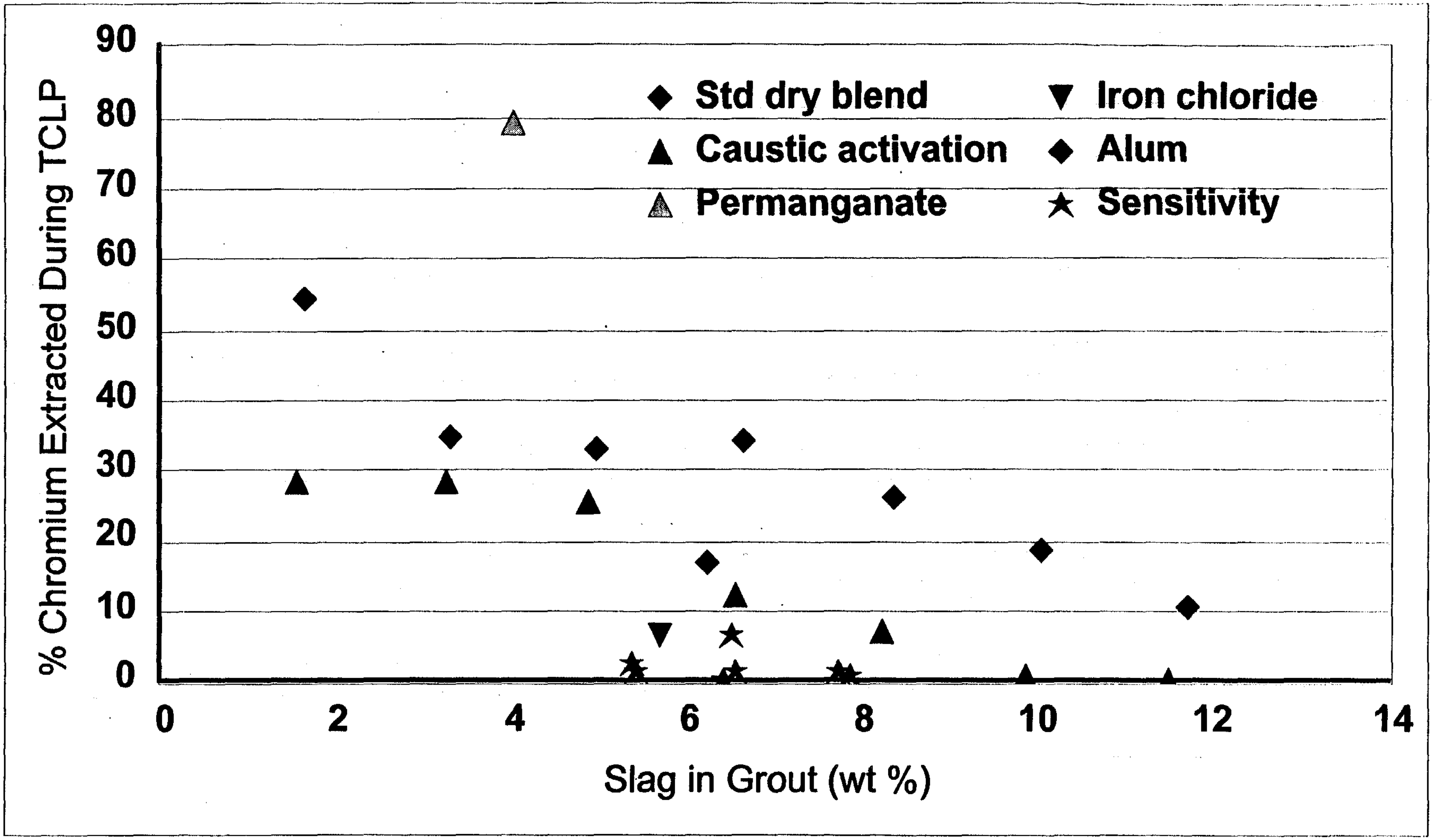

Fig. 9. Plot of % chromium extracted during TCLP as a function of the grout slag content for the surrogate OHF T3 sludge.

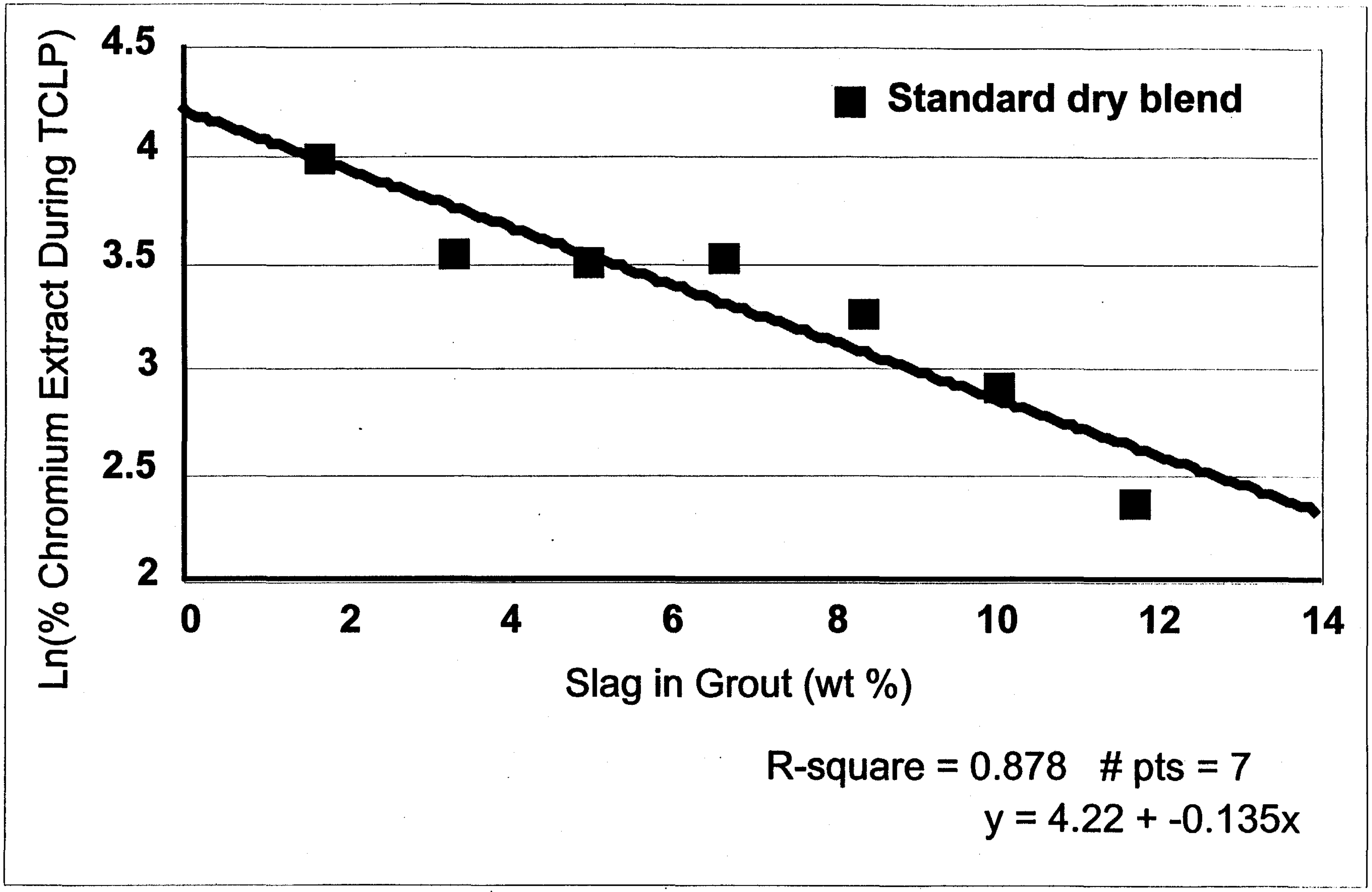

Fig. 10. Plot of ln(% Cr extracted) vs grout slag content for the surrogate OHF T3 with the standard dry blend from the scoping studies (the regression equation and line shown).

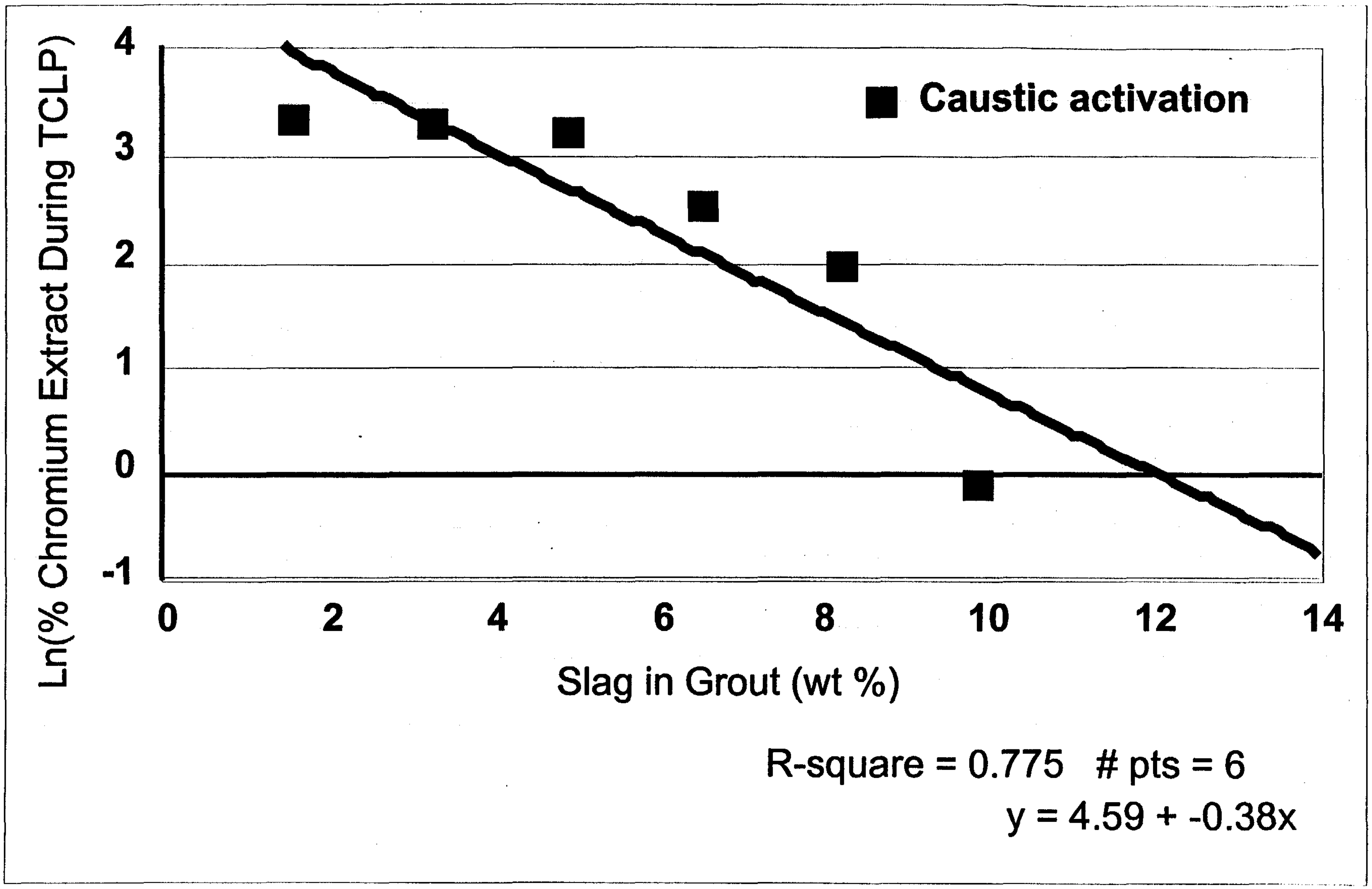

Fig. 11. Plot of ln(% Cr extracted) vs grout slag content for the surrogate OHF T3 with caustic activation from the scoping studies (the regression equation and line shown).

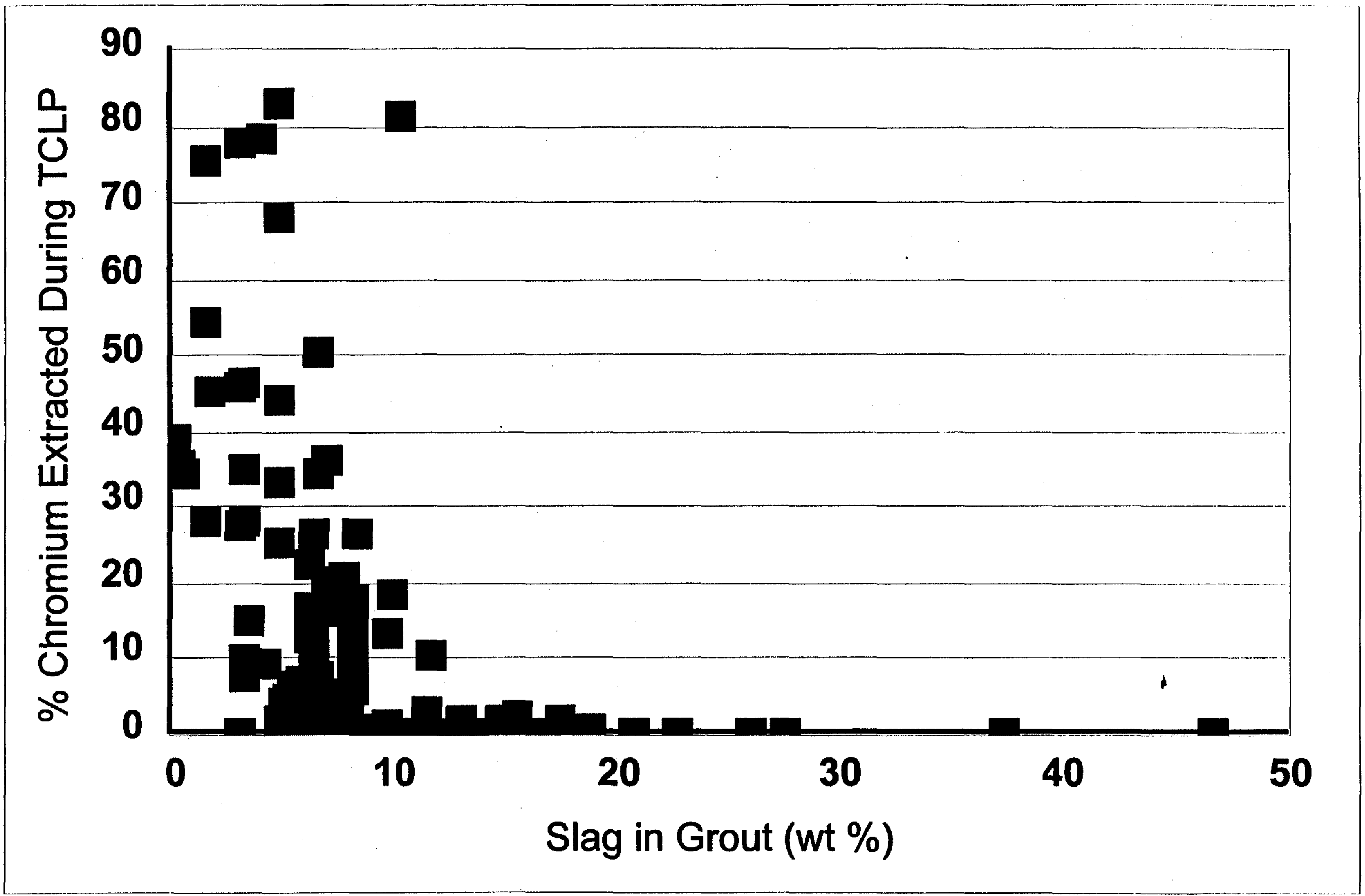

Fig. 12. Plot of the % chromium extracted during TCLP with grout slag content for all the grouts of ORNL surrogate sludges from FY 1996–FY 1999 (MVST-BVEST, GAAT, OHF, and overall weighted average).

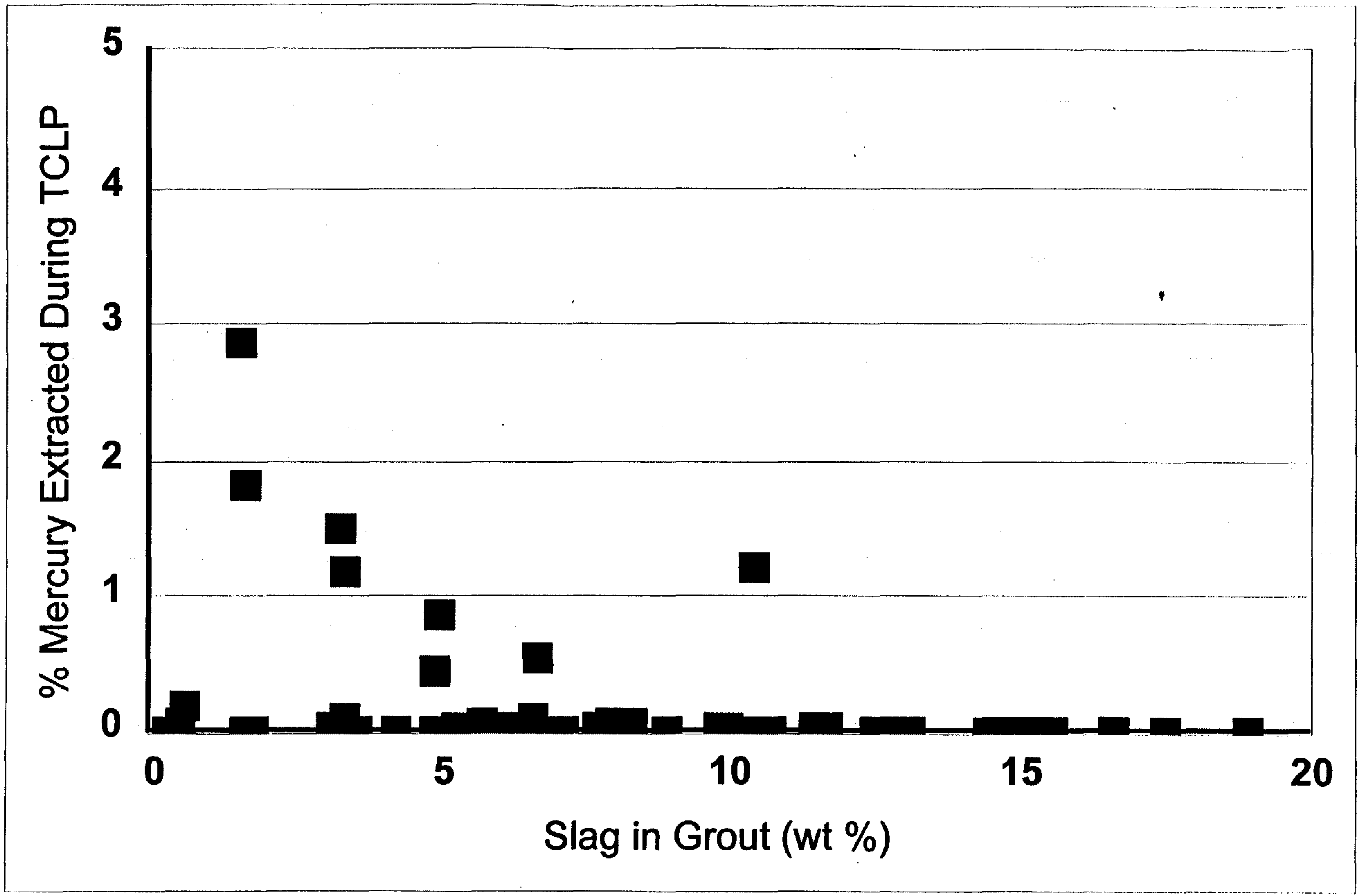

Fig. 13. Plot of the % mercury extracted during TCLP with grout slag content for all the grouts of ORNL surrogate sludges from FY 1997 and FY 1998 (MVST-BVEST, GAAT, OHF, and overall weighted average).

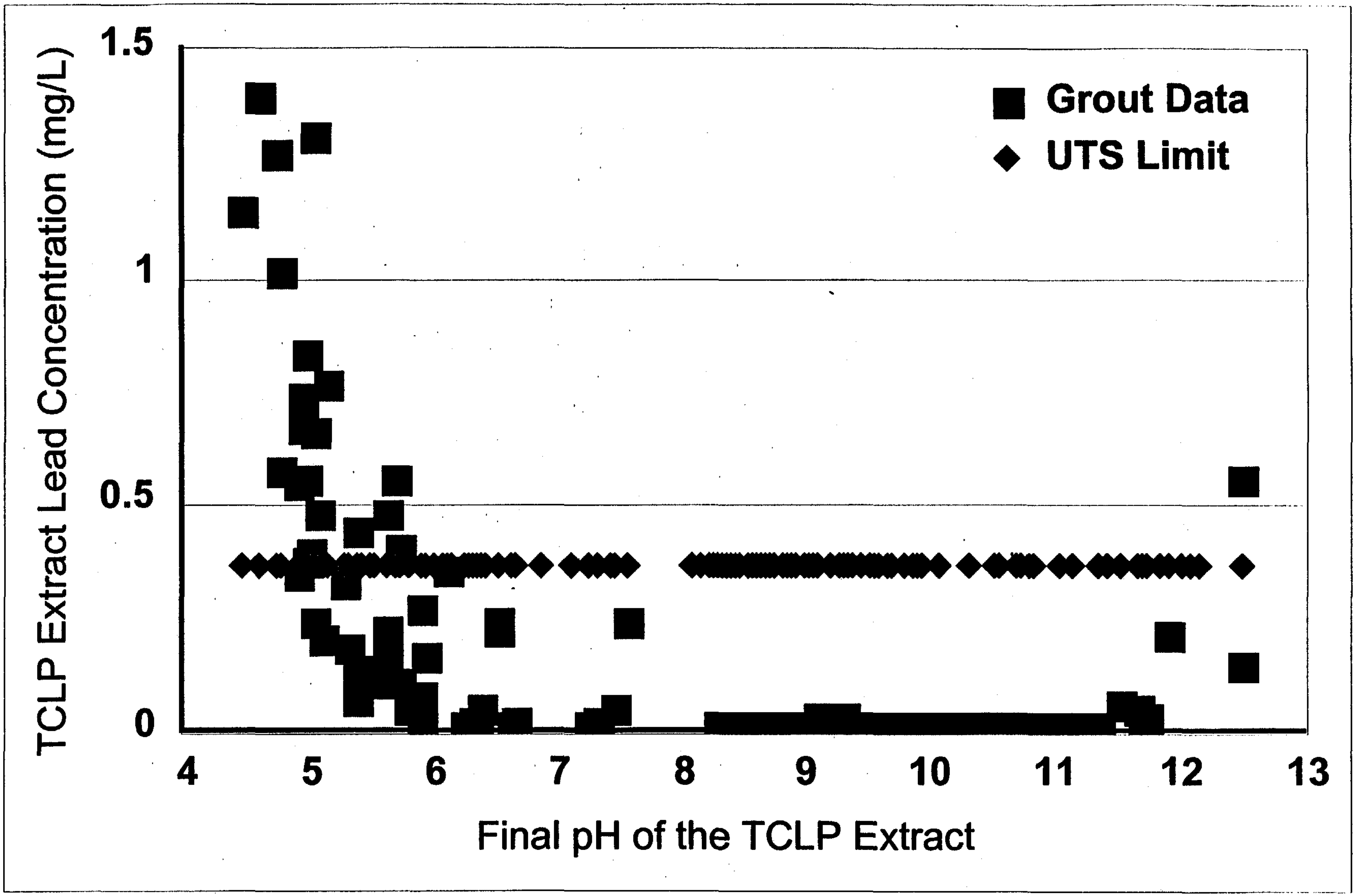

Fig. 14. Plot of the TCLP extract lead concentration with final extract pH for all the grouts of ORNL surrogate sludges from FY 1996–FY 1998 (MVST-BVEST, GAAT, OHF, and overall weighted average).

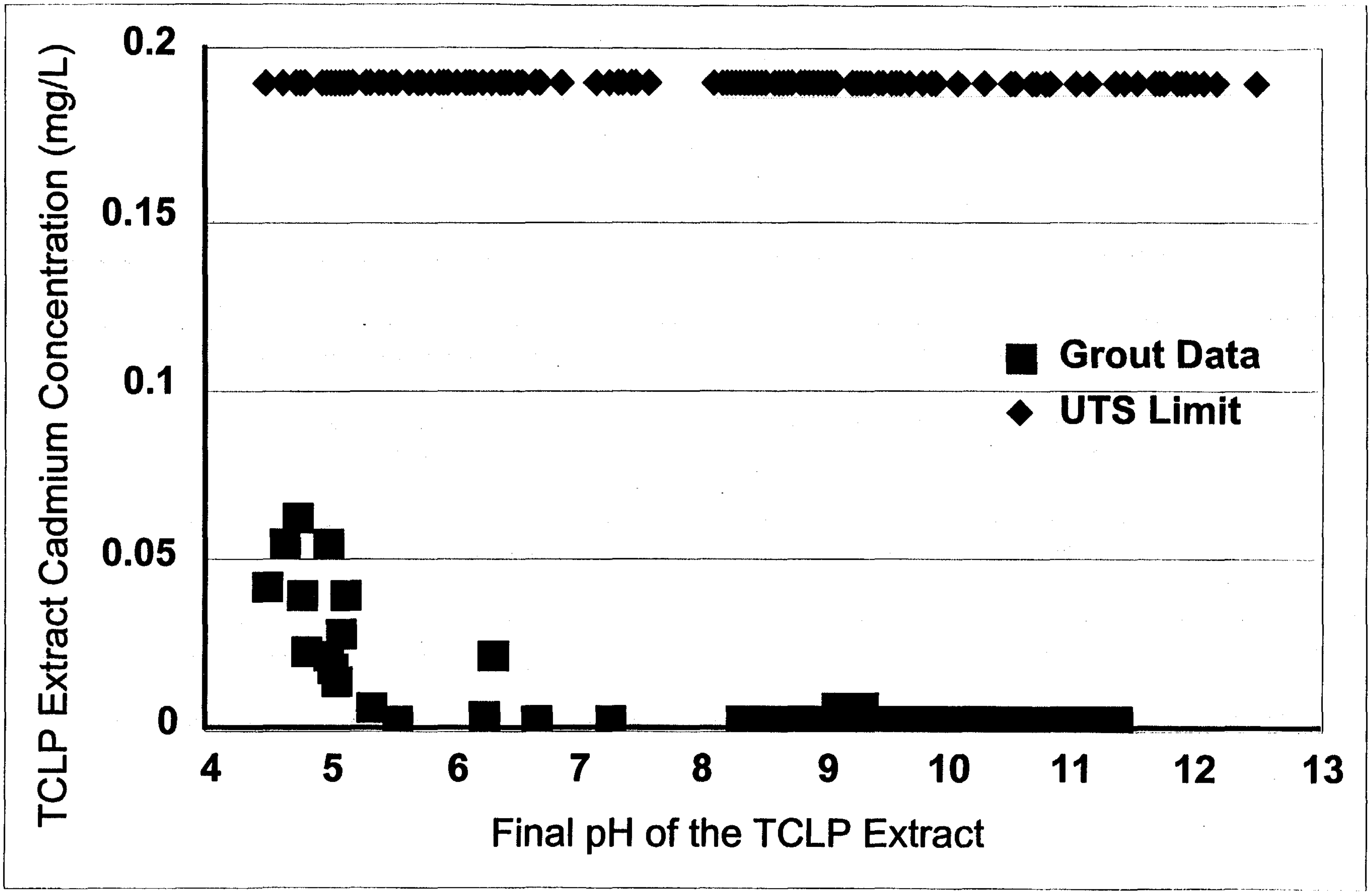

Fig. 15. Plot of the TCLP extract cadmium concentration with final extract pH for all the grouts of ORNL surrogate sludges from FY 1996–FY 1998 (MVST-BVEST, GAAT, OHF, and overall weighted average).

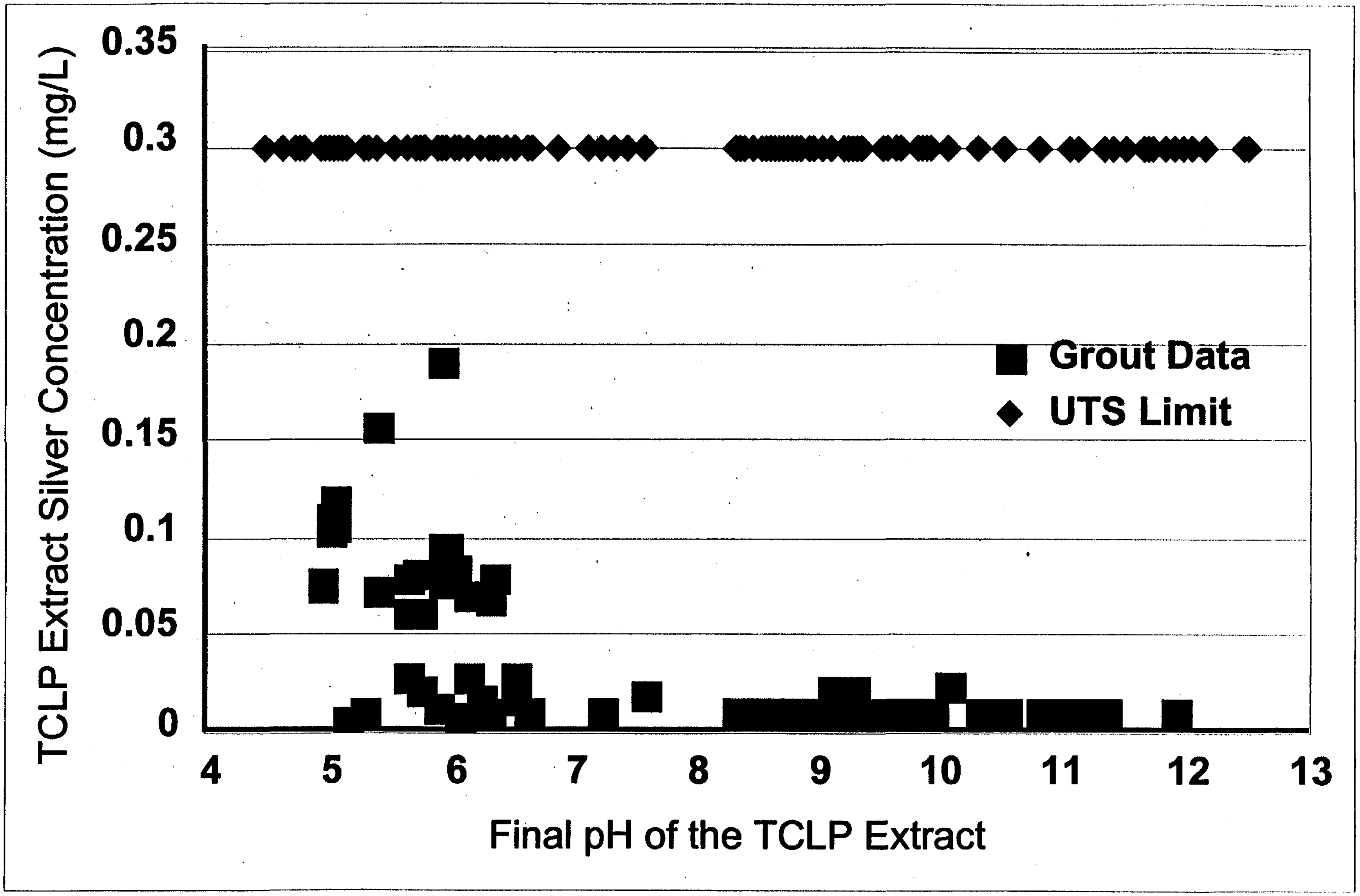

Fig. 16. Plot of the TCLP extract silver concentration with final extract pH for all the grouts of ORNL surrogate sludges from FY 1996–FY 1998 (MVST-BVEST, GAAT, OHF, and overall weighted average)

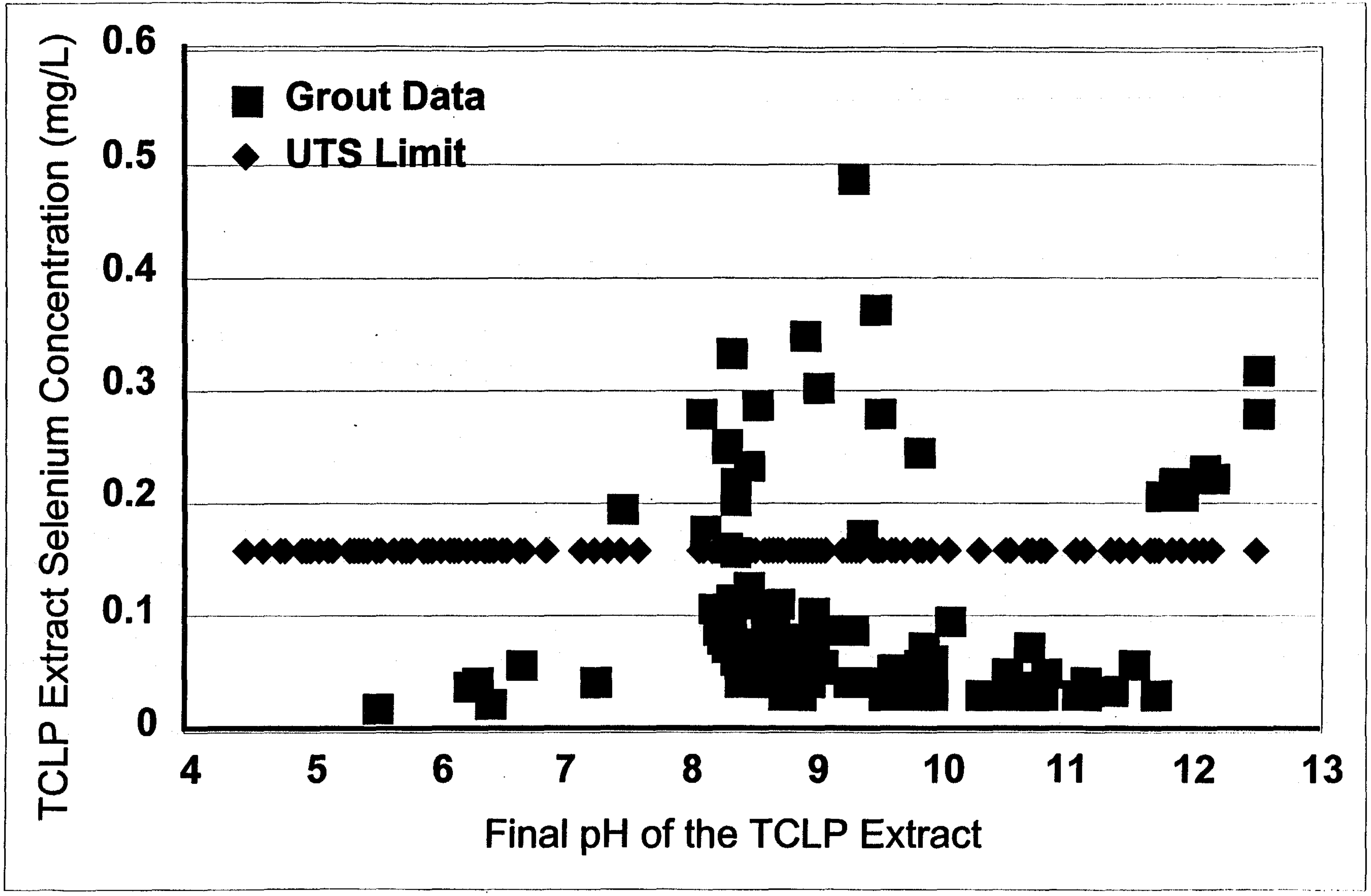

Fig. 17. Plot of the TCLP extract selenium concentration with final extract pH for all the grouts of ORNL surrogate sludges from FY 1996–FY 1998 (MVST-BVEST, GAAT, OHF, and overall weighted average).

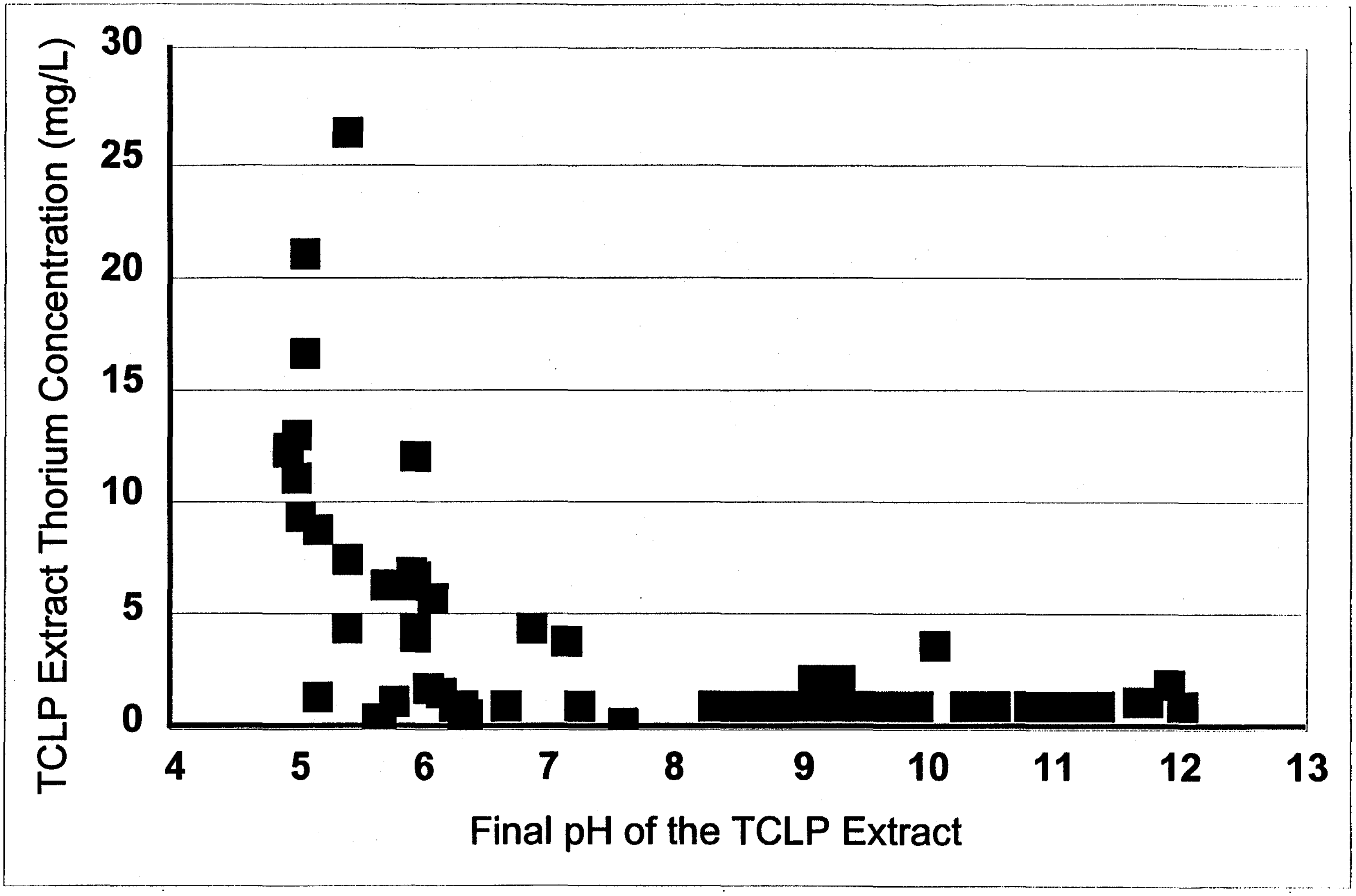

Fig. 18. Plot of the TCLP extract thorium concentration with final extract pH for all the grouts of ORNL surrogate sludges from FY 1996–FY 1998 (MVST-BVEST, GAAT, OHF, and overall weighted average).

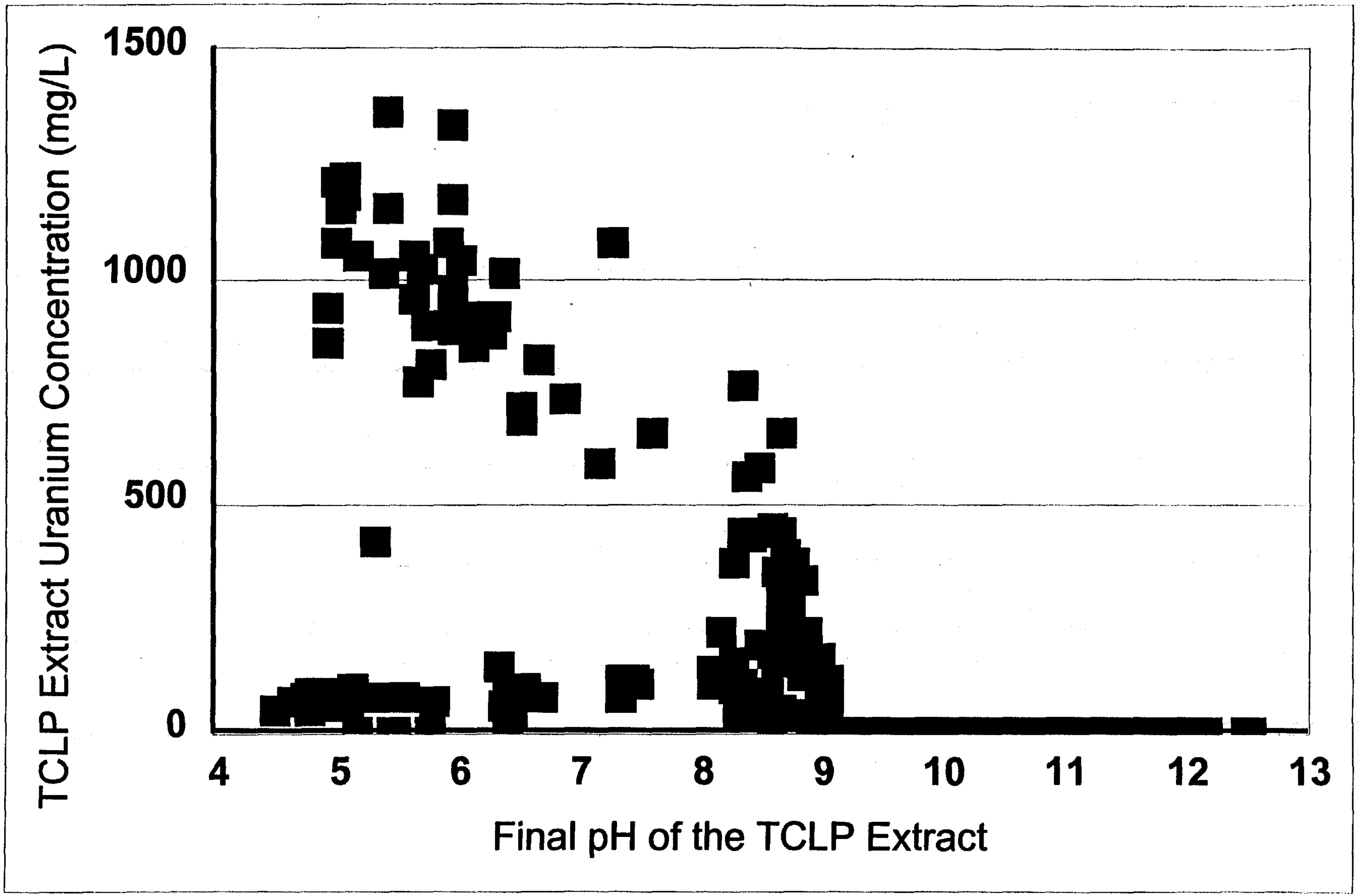

Fig. 19. Plot of the TCLP extract uranium concentration with final extract pH for all the grouts of ORNL surrogate sludges from FY 1996-FY 1998 (MVST-BVEST, GAAT, OHF, and overall weighted average).

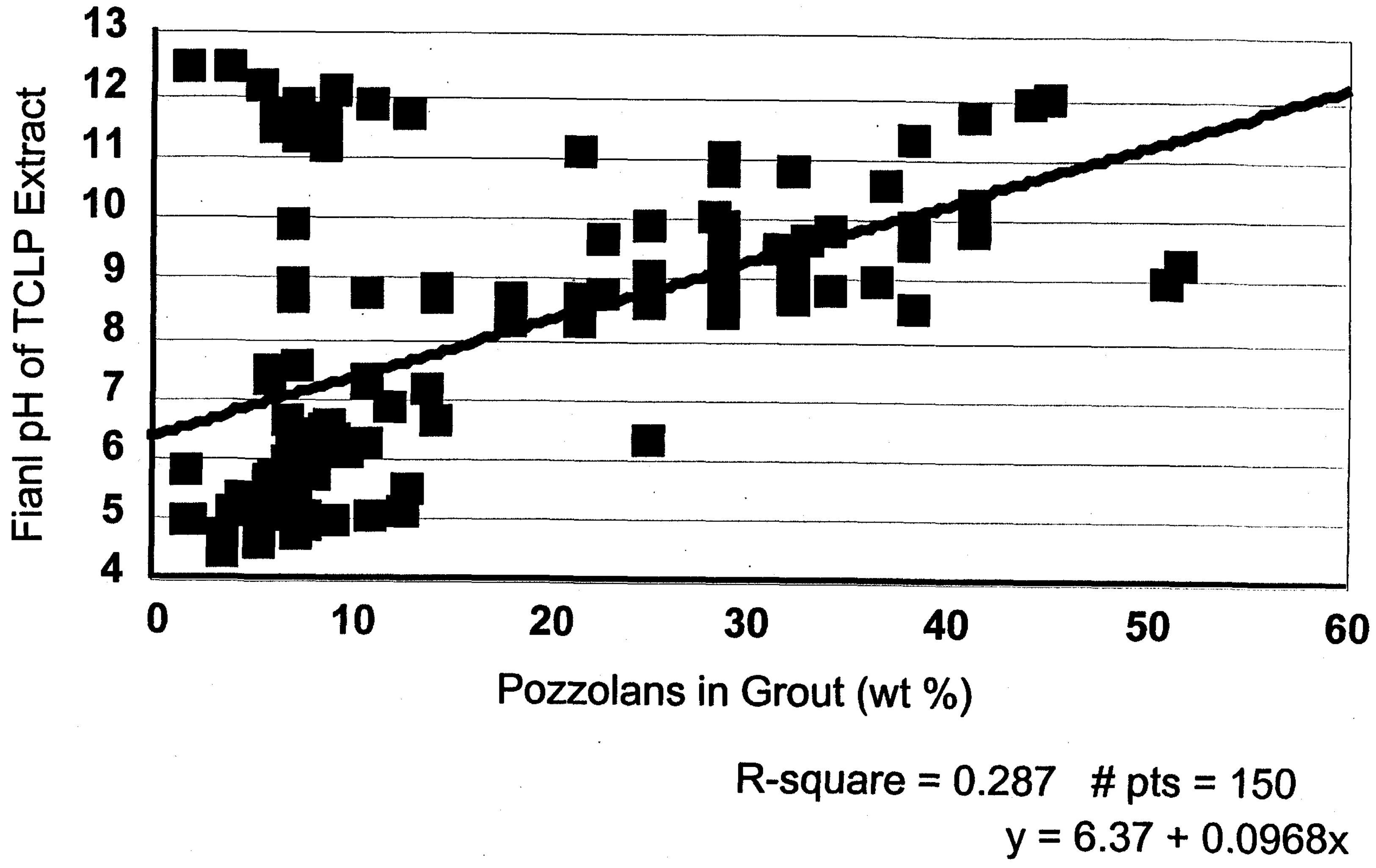

Fig. 20. Plot of the TCLP extract final pH with grout pozzolan content for ORNL surrogate sludges from FY 1996–FY 1998 (MVST-BVEST, GAAT, OHF, and overall weighted average).

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