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**Grout and Glass Performance in Support
of Stabilization/Solidification of
the MVST Tank Sludges**

**R. D. Spence
T. M. Gilliam**

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Chemical Technology Division

GROUT AND GLASS PERFORMANCE IN SUPPORT OF
STABILIZATION/SOLIDIFICATION
OF THE MVST TANK SLUDGES

R. D. Spence and T. M. Gilliam

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EXECUTIVE SUMMARY

Wastewater at Oak Ridge National Laboratory (ORNL) is collected, evaporated, and stored in the Melton Valley Storage Tanks (MVST) pending treatment for disposal. The waste separates into two phases: sludge and supernatant. Some of the supernatant from these tanks has been decanted, solidified into a grout, and stored for disposal as a solid low-level waste. The sludges in the tank bottoms have been accumulating for several years. Some of the sludges contain a high amount of gamma activity (e.g., ^{137}Cs concentration range of 0.013–11 MBq/g) and contain enough transuranic (TRU) radioisotopes to be classified as TRU wastes. Some Resource Conservation and Recovery Act (RCRA) metal concentrations are high enough in the available total constituent analysis for the MVST sludge to be classified as RCRA hazardous; therefore, these sludges are presumed to be mixed TRU waste.

Grouting and vitrification are two stabilization/solidification alternatives for mixed wastes. Grouting has been used to stabilize/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.

An envelope, or operating window, for grout and glass formulations for a surrogate MVST sludge was identified and is documented in this report. Surrogate wet sludge loadings up to 55 wt % in grout met all performance criteria, resulting in volume increases of 40–50 vol % with little or no secondary waste generation. Higher loadings may result in free water, which violates the waste acceptance criteria of potential disposal facilities. Dewatering the sludge to <52 wt % water allows higher waste loadings, with correspondingly lower volume increases, without sacrificing Toxicity Characteristic Leach Procedures (TCLP) performance or leach resistance. The grout strength declines as the sludge loading increases, but a strong monolithic solid is not usually a waste acceptance criterion. Grouts stabilized the RCRA metals, including mercury (potentially a problem species for the tank sludges), and passed the TCLP test.

The tank sludges can be stabilized in glass at a waste oxide loading of 40–50 wt %, resulting in a net volume decrease of 50–60 vol %. This is a threefold decrease in the volume of the final waste form compared with grout, not counting the secondary-waste-generation volume from off-gas treatment. The benefits of the lower glass volume compared with grout volume must be weighed against the generally higher capital and operating costs for vitrification, as well as the volume of secondary waste generated from both vitrification and grouting. RCRA metals incorporated into the glass matrix are stabilized and leach resistant, but mercury is volatilized and must be treated in the off-gas.

Confirmation of these results with actual hot sludge must be done prior to final acceptance of either technique.

GROUT AND GLASS PERFORMANCE IN SUPPORT OF STABILIZATION/SOLIDIFICATION OF THE MVST TANK SLUDGES

R. D. Spence and T. M. Gilliam

1. INTRODUCTION

Wastewater at Oak Ridge National Laboratory (ORNL) is collected, evaporated, and stored in the Melton Valley Storage Tanks (MVST) pending treatment for disposal. The waste separates into two phases: sludge and supernatant. Some of the supernatant from these tanks has been decanted, solidified into a grout, and stored for disposal as a solid low-level waste. The sludges in the tank bottoms have been accumulating for several years. Some of the sludges contain a high amount of gamma activity (e.g., ^{137}Cs concentration range of 0.013–11 MBq/g) and contain enough transuranic (TRU) radioisotopes to be classified as TRU wastes. Some Resource Conservation and Recovery Act (RCRA) metal concentrations are high enough in the available total constituent analysis for the MVST sludge to be classified as RCRA hazardous; therefore, these sludges are presumed to be mixed TRU waste.

Grouting and vitrification are two stabilization/solidification alternatives for mixed wastes. Grouting has been used to stabilize/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.

2. OBJECTIVE

The objective of this project is to define an envelope, or operating window, for grout and glass formulations for MVST sludges. This objective is to be accomplished using surrogates of the MVST sludges and supernates.

3. SURROGATES

The composition of the MVST sludges and supernates was estimated using the available characterization data.^{1,2} This characterization data mainly reports the elemental concentrations, although the inorganic carbon (IC) was reported for the sludge and some anions were reported for the supernates. For purposes of developing MVST surrogates, the IC was assumed to be carbonate. The other anions measured in the supernates were estimated for the sludges by assuming the water contained in the sludge had the same concentration of the anions. The soluble salts in the sludges were assumed to be sodium salts with the potassium as nitrate. The undissolved solids were assumed to be mainly alkaline carbonates and hydroxides. This approach accounted for the anions that were reported in the data. The remainder of the measured

elements were assumed to be oxides in an attempt to close the mass balance and determine whether a large unknown mass had not been characterized in the sludge.

3.1 MVST SLUDGES

Table 1 lists the calculated sludge compositions based on these assumptions in the attempt to close the mass balance. The row for unknown in Table 1 indicates that most of the mass was accounted for in the characterization data (with the assumptions discussed above). Only the sludges for tanks W-24 and W-25 had a significant unknown mass. Summarizing, the mass balance calculations accounted for 96, 102, 77, 85, 103, 100, 103, and 100 wt % of the sludge mass in tanks W-21, W-23, W-24, W-25, W-26, W-27, W-28, and W-31, respectively. The weighted average composition listed in Table 1 was obtained by taking into account the estimated mass of sludge in each tank to obtain an overall sludge composition if all of the sludges were mixed. This weighted average composition was the basis for the proposed surrogate MVST sludge.

The last column under the RCRA metals in Table 1 lists the sludge concentration of the RCRA compound required to potentially generate a TCLP extract concentration equal to the Universal Treatment Standard (UTS) limit assuming total extraction during the TCLP test. In other words, if the sludge concentration is below the value listed in this last column for the RCRA metals, then it cannot fail the UTS criteria. From Table 1, the concentrations for the compounds of arsenic and barium do not exceed this critical value for any of the tank sludges; therefore, these two RCRA metals are not included in the surrogate. Also, from Table 1, the nickel compound concentration exceeded this critical value only for Tank W-23 and only by 10%; plus, the weighted average did not exceed this critical value. Therefore, this RCRA metal is not included in the surrogate. In addition, thallium was not necessarily measured in the sludges; rather, the quantitation limit was high enough in most cases to prevent excluding thallium as a potential cause of failing the TCLP UTS limit, so thallium was included in the surrogate.

Table 2 lists the target composition for the surrogate MVST sludge. Table 2 lists HgCl_2 , rather than the HgO listed in Table 1, because HgCl_2 is much more soluble than HgO and would present much more of a challenge to stabilize, just in case the MVST sludges do fail the TCLP test for mercury. For similar reasons, Table 2 lists $\text{Al}(\text{OH})_3$, $\text{Sr}(\text{NO}_3)_2$, $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ rather than the Al_2O_3 , $\text{Sr}(\text{OH})_2$, ThO_2 , and UO_2 listed in Table 1, respectively.

3.2 MVST SUPERNATES

Table 3 lists the composition measured for the MVST supernates. The weighted average was obtained by using the quantity of supernate estimated for each tank. This weighted average forms the basis for the surrogate MVST supernate. The last column under the RCRA metals in Table 3 lists the UTS wastewater limits for these RCRA metals, unlike Table 1, which lists a value calculated from the nonwastewater UTS limits. The weighted average concentration did not

exceed these limits for Ag, As, Ni, or Se; therefore, these RCRA metals were not included in the surrogate MVST supernate.

Table 4 lists the compounds and their target concentrations for the surrogate MVST supernate. Table 5 lists the elemental or ionic concentrations of the Table 4 solution. The concentrations listed in Table 5 can be compared directly with the weighted average concentrations listed in Table 3.

4. GROUT

4.1 SELECTION OF THE DRY BLEND ADDITIVES FOR FURTHER EVALUATION

The inorganic additives historically used for stabilization/solidification are portland cement, fly ash, lime, and clay but also included are blast furnace slag, cement kiln dust, high alumina cements, natural pozzolans, masonry cements, special cements, and cement admixtures.^{3,4} Conner cites the following reasons for the widespread use of these materials in treating wastes:³

- "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 ten 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 lists the following advantages and disadvantages of cement for the solidification of radioactive wastes:⁴

"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 vapour 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.
- 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 reason for selection are presented in the following subsections for each material.

4.1.1 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.³⁻⁹ 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 interacting with and encapsulating the waste. Wastes are generally physically encapsulated heterogeneously in the calcium-silicate-hydrate (CSH) matrix, with the level of dispersion and homogeneity generally 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 wastewater treatment.

This high pH precipitation captures most of the RCRA metals and radionuclides. For example, the low solubility at high pH of Cu, Ni, Fe, Cd, Zn, Ag, and Pb is illustrated in the published solubility curves with pH.^{3,10} In general, these solubility curves pass through a minimum as the pH increases, meaning these metals actually start becoming more soluble as the pH passes a certain point, with the generation of complex hydroxide ions. The minimum solubility for these metals occurs in a pH range of 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 12–13, which is well above the minimum solubility for most of these metals.³ 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 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, (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–fly ash) reportedly have a pH of about 11, which is much better suited for minimizing metal solubility.³ 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 . . .”^{3, 11}

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 ASTM standards specify five standard portland cements with optional properties available within each type:^{3, 12}

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.

4.1.2 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.⁴ 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.^{3, 4, 13-17}

Using fly ash in concrete has many advantages in certain usages, the most important being cost, as it replaces 25–35 wt % of the portland cement normally used.³ Incorporating fly ash into cement lowers the heat of hydration, reducing curing temperature, an advantage in producing massive monoliths.^{4, 15-17} 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.³ However, such bulking does result in larger volume and weight increases than for portland cement alone, “. . . usually only justified where low handling, transportation, and disposal costs are encountered.”³ 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.”³

Since strontium chemically 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.^{13, 18-21}

The ASTM standards specify two fly ashes and one natural or calcined pozzolan for use in portland cement concrete:^{3, 22}

<u>ASTM Mineral Admixture Class</u>	<u>Description</u>
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, may contain lime contents >10 %

In general, a commercial industry has evolved to supply fly ash cheaply and with adequate QA/QC 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). The lime content of Class C fly ash can be 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, the fly ash lime content 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.

4.1.3 Indian Red Pottery Clay

Over the years, illite (IRPC), $(\text{OH})_4\text{K}_x(\text{Al}_4\text{Fe}_4\text{Mg}_4\text{Mg}_6)(\text{Si}_{8-x}\text{Al})\text{O}_{20}$, 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 .^{19, 20, 23-25} Illite has been known as an effective selective sorbent for ^{137}Cs for decades.²⁶⁻²⁸ 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), 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/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 rather 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 indicated by the high ANSI/ANS-16.1 leachability indexes reported for ^{137}Cs over the years for grouts containing IRPC.

4.1.4 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 an inert crystalline slag useful only 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."⁴ 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.⁴ 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."^{4, 29}

Slags have been substituted for cement for decades.³⁰ 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.^{4, 30-37}

- 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; that is, the presence of excess slag prevents buildup of this cement hydration product.⁴ This implies that the proper proportion of slag-cement can replace cement-fly ash to stabilize ⁹⁰Sr. In addition, a combination of 85:15 or higher slag produces a strong reducing environment within the matrix, suitable for reducing pertechnetates or chromates.^{38,39} Thus, slags have been used in grouts developed for radioactive and mixed wastes for a long time.³⁸⁻⁴⁸

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:⁴⁹

ASTM Slag Grade	Minimum Average Slag Activity Index, %	
	7 days	28 days
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 of commercially available slag, not their strength, are important to waste treatment and are generally not specified in the ASTM standard. Perhaps the most important property regarding waste treatment measured in the standard is the air permeability or Blaine fineness, although no limits are specified.⁵⁰ 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."^{4,36} Typically, portland cement has a Blaine fineness of 3000-4000 cm²/g and slag, a fineness of 4000-5000 cm²/g, but slag >5000 cm²/g, or even >6000 cm²/g, can sometimes be acquired. In general, the finer, the better, although it is unlikely that special requests for finer grinding is 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. In summary, ground granulated blast furnace slag with a Blaine fineness of >4000 cm²/g was selected for this study.

4.1.5 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, leaving a drainable liquid on the grout surface (phase separation, bleed water, freestanding liquid, or free water).⁵¹⁻⁵³ 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, such as 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 oilwell cements to decrease slurry weight and to increase slurry volume."^{54, 55} The individual clay particles of bentonite are plate-shaped. The particle faces are positively charged, while 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.^{53, 56} 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).^{53, 57}

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.⁵³ 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.⁵³ 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.^{53, 58}

The American Petroleum Institute (API) issued specifications for both bentonite and attapulgite.^{59, 60}

In general, the hazardous waste industry adopted a different strategy for the treatment of low solids wastes (i.e., waste waters 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.³ Sodium silicate forms a hydrogel, a three-dimensional polymeric structure incorporating up to 90 % water; that is, a little sodium silicate can accommodate a lot 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. Hydrogels are subject to frost or dessication damage, not unexpectedly with such a large water content, so care should be exercised about using hydrogels if the waste form will be stored aboveground (or the above the frost line) and/or exposed to freezing or drying conditions.

Another cheap, water sorptive bulking agent is perlite. "Perlite is a volcanic material that is mined, crushed, screened, and expanded by heat to form cellular product of extremely low bulk weight."⁵⁴ Water is absorbed by capillary action within the large volume of pore structure within this light, porous product.

In summary, the water sorptive agents selected for testing were bentonite, attapulgite, and perlite.

4.2 SELECTING GROUT COMPOSITION FOR EVALUATION

The initial basis for a dry blend were the cement-fly ash dry blends historically developed for treatment of radioactive wastes:

	weight %	
	<u>Hydrofracture ²³</u>	<u>Hanford ⁷²</u>
Type I portland cement	42	38
Class F fly ash	34	39
Attapulgite 150 drilling clay	16	15
IRPC	8	8

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.^{23,52} 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 combination of about 90:10 was maintained to enhance the reducing capability of the matrix. In general, IRPC was fixed in the dry blend at 8 wt % for ¹³⁷Cs stabilization. The fly ash was kept as a proven pozzolan for ⁹⁰Sr stabilization. (The main mobile radionuclides of interest in these tank sludges are ¹³⁷Cs and ⁹⁰Sr.) The fly ash content was allowed to float to compensate for the varying content of water sorptive agent.

Summarizing, the dry blend guidelines used to initiate experimental work were as follows:

	<u>wt %</u>
Slag-Type I-II portland cement (90:10)	40-50
Class F fly ash	25-50
Water sorptive agent	0-20
IRPC	8

Strong monoliths are expected with waste loadings up to 60 wt % or higher. In general, strength decreases with waste loading or clay content.

4.3 EXPERIMENTAL

4.3.1 Surrogate Preparation

The surrogate MVST wet sludge was prepared from reagent-grade chemicals according to the composition listed in Table 2. The chemicals were allowed to hydrolyze by mixing with the recipe water at least overnight. One-liter batches of the surrogate MVST supernate were prepared from reagent-grade chemicals according to the composition listed in Table 4 and used extra water as needed in the grout mixing.

4.3.2 Blending

The dry blends 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 6220 cm²/g from the Koch Minerals Co., (2) Type I-II portland cement (cement) from the Dixie Cement Co., (3) Class F fly ash (fly ash) from the American Fly Ash Co., (4) Grade H-200 perlite from the Harborlite Corp. (perlite), (5) IRPC from the American Art Clay Co., (6) Attapulgate 150 ground clay (attapulgate) from the Engelhardt Corp., and (7) bentonite clay (bentonite) from the Benton Clay Co. The dry blends were blended for 2 h in an 8-qt twin-shell blender (or V-blender) from the Patterson-Kelley Co.

4.3.3 Mixing

The grouts were mixed in a Model N-50 Hobart mixer using a wire whip. 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 (30-60 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 m, then adding the dry blend using the above procedure.

4.3.4 Curing

The freshly made grout was stored in a humidity cabinet and cured in a humid environment at $30 \pm 1^\circ\text{C}$. The samples were cured only 7 d for the scope testing, but the sensitivity samples were cured for the standard 28 days.

4.3.5 Performance Testing

The performance testing for the scope testing consisted of measuring the density, the penetration resistance, free water (or bleed water), and TCLP performance after only 7 d. The sensitivity testing consisted of measuring the density, 28-d unconfined compressive strength, 28-d free water, 28-d TCLP performance, and the 28-d leachability index of ^{85}Sr and ^{137}Cs .

The free water was measured by casting 250 mL of grout into a graduated cylinder and measuring the volume of free water standing over the solid grout. This property is reported as volume percent, calculated by dividing the observed free water volume, as measured in milliliters, by 250 mL and multiplying by 100.

The density of the freshly mixed grout was obtained by measuring the net mass in grams of the 250 mL of grout in the free water test and dividing by 250 mL to obtain the density in units of g/mL. The density of the surrogate grouts was also obtained using the graduated cylinders.

For penetration resistance, the force (lb_f) to push a flat rod with a cross-sectional area of $1/40 \text{ in.}^2$, a preset distance into the curing grout was measured. This force was divided by the cross-sectional area and reported as penetration resistance (psi). The gauge on the penetrometer read a maximum force of 200 lb_f , limiting measurements on penetration resistance to 8000 psi.

For the unconfined compressive strength, nominal 2-in. cubes of grout were cast and cured. After curing 28 d, the cube dimensions were measured and the force (lb_f) required to crush the cube measured on a Tinius-Olsen Machine. Dividing the crushing force by the cube cross-sectional area gave the unconfined compressive strength (psi).

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 extraction 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 procedure dictates which extractant to use based on the buffering capability of the sample when mixed with a hydrochloric acid solution.) After extracting 18 h, the undissolved solids are filtered from the extract and the extract is digested using a microwave digester. The concentrations of the inorganic RCRA metals in the extract, were then measured using a Thermo Jarrel Ash ICAP 61E Trace Analyzer (ICP). Although selenium and arsenic analyses by ICP are not usually accepted, EPA accepts the

higher sensitivity of the 61E. Some mercury analysis was also performed on the 61E, but mercury analysis by ICP is still not accepted by EPA, including the 61E.

For the leachability index, a semidynamic leach test was performed using a modification of the ANSI/ANS-16.1 test. (In a semidynamic test, the samples remain quiescent in the leachate for a set time interval and are then moved to a fresh leachate at zero concentration for the next time interval.) The grout samples were leached in deionized water. The concentration of the radionuclides were measured by gamma spectroscopy using a germanium detector with an efficiency of 10% and a background of 30 counts per 1000 s, or 0.03 counts per second (cps). After a 30-s rinse, the leachates were changed at cumulative times of 1, 2, 3, 4, and 7 d. The effective diffusion coefficient was estimated from the cumulative fraction leached with time, assuming diffusion-controlled leaching. The leachability index is the negative of the logarithm of the effective diffusion coefficient.

4.4 RESULTS AND DISCUSSION

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 waste form compositions meeting the performance criteria (<0.5 vol % free water, passes TCLP, and hardens into a monolithic solid waste form). After establishing this envelope, an acceptable formulation was selected for testing the sensitivity of the formulation to variations in the formulation and surrogate composition.

4.4.1 Scoping Tests

Table 6 lists the compositions of the grouts tested during the scoping tests. Table 7 lists the densities measured for these grouts and the ratios of the grout volume to wet sludge volume calculated from these grout densities, the wet sludge loadings, and the surrogate MVST sludge density (1.40 g/mL). Figure 1 illustrates the dependence of these grout densities on the W/S of these grouts. Figure 2 illustrates the dependence of the ratio of grout volume to wet sludge volume on the wet sludge loading in the grout. Table 8 lists the free waters and penetration resistances measured for these grouts. Table 9 lists the TCLP extract concentrations measured for the surrogate sludge, and Table 10 lists the TCLP extract concentrations measured for the scoping test grouts.

The first 12 grouts established the performance of two dry blends using no water sorptive agents: (1) 83, 0, 9, and 8 wt % and (2) 41, 46, 5, and 8 wt % of slag, fly ash, cement, and IRPC, respectively. The first two grouts established the water demand nature of the surrogate sludge and blends. First, the dry blends were added to the wet sludge until the resulting grouts were too dry (wet sludge loadings of 37 and 33 wt % and W/S of 0.24 and 0.21 for blends 1 and 2, respectively). Next, surrogate MVST supernate was added until the grouts were judged to be processable wet plastic masses (the final grout compositions listed in Table 6 for grouts 1 and 2). Prior work with wastewater treatment sludges had obtained satisfactory performance with wet

Fig. 1. Grout density as a function of the water-to-solids ratio (W/S).

Fig. 2. Volume ratio of grout-to-wet sludge as a function of the wet sludge loading.

sludge loadings of 67 wt %, so these two dry blends were tested at this loading, as well as testing the free water performance over a range of W/S, using the surrogate supernate to adjust the W/S. Figure 3 illustrates the free water obtained for these 12 grouts as a function of the W/S.

These results established that the W/S needs to be about 0.4 or more for the grout to be processable, but that free water can be a problem above W/S of 0.4. (The surrogate sludge consisted of two phases with a free water content of 15.6 vol %, so its free water performance may not be representative of the MVST sludges resting on the tank bottoms. The W/S of the surrogate sludge was 1.08, and to achieve a W/S of 0.4, enough dry blend must be added to make a grout with 55 wt % wet sludge loading.) Having no free water is a regulatory and waste acceptance criteria, and a major driver for establishing the grout composition and an acceptable operating envelope. Consequently, the next 20 grouts were devoted to testing water sorptive agents in an attempt to control the bleed water and allow higher wet sludge loadings (in lieu of dewatering). These grouts were made with a constant amount of dry blend (wet sludge loading of 67 wt % and W/S of 0.53) and varying amounts of different water sorptive agents in the dry blend, concentrating on dry blends with large amounts of fly ash (the traditional additive used to stabilize ⁹⁰Sr). Figure 4 illustrates the free water performance of these grouts as a function of the amount of water sorptive agent in the dry blend. The water sorptive agents tested were perlite, attapulgite, and bentonite. Perlite at 20 wt % in the dry blend proved to result in the lowest free water after 7 d for these water sorptive agents. This dry blend still resulted in significant free water at 7 d, so increasing the cement in this dry blend was tested to further reduce the free water (the dry blends contained 4 wt % cement to this point). As illustrated in Fig. 4, the minimum free water was obtained with 20 wt % cement and 20 wt % perlite in the dry blend. This dry blend (33, 20, 19, 20, and 8 wt % of slag, cement, fly ash, perlite, and IRPC, respectively) was selected as the standard for further testing.

The last seven grouts in the scoping tests used this dry blend at wet sludge loadings ranging from 27 to 90 wt %. Figures 5 and 6 illustrate the 7-d free water and 7-d penetration resistance, respectively, with wet sludge loading for these grouts. As Fig. 5 illustrates, some free water occurs as the wet sludge loading exceeds 55 wt %; therefore, the grout loading for this sludge is limited to 55 wt % because of the free water criteria, unless the wet sludge is dewatered. As Fig. 6 illustrates, all of the grouts hardened, except at a wet sludge loading of 90 wt %. The 7-d penetration resistance did decline significantly above wet sludge loadings of 60 wt %. (Note that measurement of penetration resistance was limited to 8000 psi, and the first four points plotted in Fig. 6 exceeded this value but were plotted at this limit.)

From Table 9, the surrogate MVST sludge would have been characteristically hazardous only for mercury by the RCRA characteristic limits and, similarly, would have passed the TCLP (Land Disposal Restrictions (LDR) criteria, except for mercury. However, the surrogate sludge did not meet the more stringent Universal Treatment Standard (UTS) criteria for Cd, Cr, Hg, or Tl. In general, the scoping test grouts not only stabilized the mercury to meet TCLP LDR criteria but also passed the more stringent UTS criteria, except for selenium. Although the surrogate sludge did not fail for selenium, the TCLP extract concentrations of selenium for several of the scoping

Fig 3. Free water as a function of the water-to-solids ratio (W/S) without water-sorptive agents. Blend 1: 83 wt % slag, 9 wt % cement, 8 wt % IRPC; Blend 2: 41 wt % slag, 46 wt % fly ash, 5 wt % cement, 8 wt % IRPC.

Fig. 4. Free water as a function of the percentage of water sorptive agent in the dry blend. Grout: 67 wt % wet sludge, 33 wt % dry blend; W/S = 0.53 (noncement blends contain 4 wt % cement).

Fig. 5. Free water as a function of sludge loading for the selected dry blend. Dry blend: 33 wt % slag; 20 wt % cement; 19 wt % fly ash; 20 wt % perlite; 8 wt % IRPC.

Fig. 6. Penetration resistance as a function of sludge loading for the selected dry blend. Dry blend: 33 wt % slag, 20 wt % cement, 19 wt % fly ash, 20 wt % perlite, 8 wt % IRPC.

grouts did exceed the limit set by UTS (although the extract selenium concentration never exceeded 0.5 mg/L). The later grouts do meet all of the UTS criteria, including selenium. More importantly, the UTS criteria was met for all of the last seven grouts testing the selected standard dry blend, including a wet sludge loading of 90 wt %. The consistently low concentrations of the RCRA metals did not exhibit any obvious correlations, but the extract uranium concentration varied with final extract pH, as illustrated in Fig. 7. Four data points at low pH (for grouts 29–32) are obvious outliers in Fig. 7. Since these grouts were made with more cement than the other grouts in the scoping tests, it makes no sense that the final TCLP extract pH would be as low as 5–6. Apparently, the reported extract pHs for these four grouts are in error.

4.4.2 Sensitivity Testing

Sensitivity testing is the evaluation of the sensitivity of a selected formulation to changes in waste composition and changes in concentration of the grout composition. Two grouts were selected for sensitivity testing: (1) to obtain the highest sludge loading and (2) to pass the NRC criteria. For the high sludge loading grout, the dry blend most successful at handling the free water in the scoping tests was 33, 20, 19, 20, and 20 wt % of slag, cement, fly ash, perlite, and IRPC, respectively. This dry blend was limited to a sludge loading of 55 wt %, because of the free water criteria. To better meet the NRC criteria, the sludge loading for the second grout was reduced to 40 wt %. At this waste loading, the enhanced water sorptive properties were not needed (in fact, some supernate was added to ensure processability), so the dry blend was altered to 41, 5, 46, and 8 wt % of slag, cement, fly ash, and IRPC, respectively. The standard grout compositions resulting from these two formulations are listed as Grout #1 for the high and low sludge loading in Table 11. In addition, Table 11 lists the four grouts selected for sensitivity testing of variation in the grout composition, taken from the $\pm 10\%$ variation in the formulation. The sensitivity testing consisted of measuring the performance of the grouts listed in Table 11 using the standard surrogate MVST sludge plus testing each Grout #1 with surrogate MVST sludge at the maximum water content listed in Table 1 and with surrogate MVST sludge at the minimum water content and the maximum concentration of bad actors listed in Table 1. Table 12 lists the three surrogate sludge compositions used in the sensitivity testing.

Tables 13–17 list the results for the sensitivity testing of the grouts, grout density and grout volume to sludge volume, free water, unconfined compressive strength, TCLP performance and cesium and strontium leachability indexes, respectively.

The high waste loading grout had a volume increase of 44%, no free water, an average compressive strength of 1663 psi, an acceptable TCLP performance, and cesium and strontium leachability indexes >9 . The variation in grout and surrogate composition made the volume increase vary from 36 to 55%. Although the composition variations affected the appearance of free water during cure and the rate at which the free water disappeared, none of the composition variations had any free water after curing 28 d. The composition variations significantly affected the compressive strength, ranging from 776 to 2,086 psi, but all were significantly >500 psi (the target for the NRC criteria). The composition variations had little effect on the TCLP

Fig. 7. Uranium concentration in TCLP extracts of the scoping test grouts as a function of pH.

performance or leachability indexes, and all extract concentrations were below the limiting values for RCRA characteristically hazardous, TCLP LDR, or UTS.

The low waste loading grout had a volume increase of 93%, no free water, an average compressive strength of 542 psi, and cesium and strontium leachability indexes >8. The TCLP performance was acceptable, except the selenium extract concentration exceeded the UTS limit. The variation in grout and surrogate composition made the volume increase vary from 57 to 111%. Although the composition variations affected the appearance of free water during cure and the rate at which the free water disappeared, none of the composition variations had any free water after curing 28 d. The composition variations significantly affected the compressive strength, ranging from 179 to 1888 psi, ranging around 500 psi (the target for the NRC criteria). The composition variations had little effect on the TCLP performance or leachability indexes, and all extract concentrations were below the limiting values for RCRA characteristically hazardous, TCLP LDR, or UTS (except the one selenium value exceeding the UTS limit). Substituting the zeolite sorptive agent used to remove ^{137}Cs from tank supernates for the IRPC in the dry blend decreased the effective diffusion coefficient by one to two orders of magnitude, increasing the leachability index of between 9 and 10 to >11 for both ^{137}Cs and ^{85}Sr .

In general, the high waste loading grout outperformed the low waste loading grout and is a better candidate for meeting the NRC criteria. The higher cement content in the high waste loading grout or slower activation of slag in the low waste loading grout may explain why the higher waste loading grout is stronger at 28 d, but this has not been definitively established.

Unfortunately, the high waste loading grout was difficult to process and handle, because of its apparent dryness from the water sorption of the perlite. This dry blend may be able to handle wet sludge loadings higher than 55 wt %, without bleed water at 28 d, and the extra water would assist in processing. Field operation with this drier grout (high waste loading) may require some water addition, depending on the mixing and handling equipment and the water content of the sludge being processed.

5. GLASS

5.1 SELECTION OF THE GLASS FORMING SYSTEM FOR FURTHER EVALUATION

There are numerous glass families that have been developed/evaluated on a commercial scale. Examples of these families include soda-lime-silicate, borosilicate, lead silicate, aluminosilicate, halide, borate, phosphate, sulfide, chalcogenide, chalcahalide, oxyhalide, oxynitride, and oxycarbide glasses.^{61, 62} However, of these families, three have received the most attention for the vitrification of wastes. Consequently, these three families, borosilicate, soda-lime-silica (SLS), and phosphate, were the initial candidates for further study within this project. Many phosphate glasses are known to be readily attacked by water⁶² and were quickly discarded as a candidate for further study. Borosilicate glasses, which have been used extensively for immobilization of high-level radioactive wastes, have a large known immiscibility gap in the

CaO-B₂O₃-SiO₂ system;⁶³ and a high calcium content is a characteristic of the waste in this study. The known immiscibility leads to the strong probability of multiple glass phases within the resulting vitrified product. The unknown distribution coefficients of the contaminants of interest (both radionuclides and the RCRA metals) makes a multiple phase product undesirable. Consequently, the experimental study, presented herein, focused on the SLS system. The SLS system has been evaluated previously for numerous low-level radioactive and chemically hazardous (i.e., mixed) waste sludges^{64,65} and has the advantage of utilizing the calcium content of the waste as a needed additive.

5.2 SELECTING GLASS COMPOSITION REGION FOR EVALUATION

A methodology for calculating the maximum composition range for formation of acceptable glass products has been developed previously.⁶⁶ A brief summary of the rationale for the methodology is presented, herein, for continuity.

5.2.1 The Basic System

The phase diagrams for the basic SLS system, those of the related ternary systems that contain common major waste constituents [e.g., alumina (Al₂O₃)], and the accompanying literature permit useful comparisons to be made between the conditions of composition and temperature for equilibrium systems and those used to vitrify mixed waste. These comparisons lead, in turn, to an understanding of the fundamental chemical issues that operate in the processing of these wastes.

The structures of silicate glasses are based on the polymerizing tendency of SiO₄ tetrahedra, which results, in part, from the bonding properties of Si(IV) and the small ionic size of silicon relative to that of oxygen. For present purposes, the bonding properties have been deemed to rely primarily on the electronic polarity of the Si-O bond and the coordination number of oxygen atoms that surround the silicon atoms. Based on electronegativity values,⁶⁷ the Si-O bond is approximately 88% ionic, indicating that the bond exhibits both ionic and covalent properties.

The 12% covalent character helps to maintain the tetrahedra in the melt, making them the basic "building blocks" in silicate melts and glasses. If crystalline silicates precipitate from the melt, the high ionicity leads to the well-known variety of crystallographic packing arrangements for Si⁴⁺ and O²⁻.

These concepts indicate that both the melt and its corresponding glassy state can be considered as differing only moderately from the crystalline silicates that possess similar chemical composition. Consequently, an improved understanding of silicate waste glasses can be gained from knowledge of the glass melt, the corresponding crystalline metal silicates, and the solidified glasses. Analogously, the structural properties of glasses that contain elements such as aluminum and boron would respectively resemble the corresponding crystalline aluminosilicates and borosilicates.

One molecular restriction that applies to the glassy and crystalline states of silicate materials and to their melts is particularly noteworthy. Neighboring tetrahedra that are linked to one another can share only corners; sides and faces of tetrahedra cannot be shared. Hence, two tetrahedra are linked to each other by the sharing of an oxygen atom. This arrangement means that a tetrahedral unit may be linked to two, three, or four other tetrahedra. Two such links per silicon yield, locally and on the average if they predominate, a somewhat linear polymer or chain of SiO_4 tetrahedra. Analogously, three bridging oxygens per silicon produce two-dimensional arrays that resemble cross-linked polymers, and four would generate a three-dimensional network.

Clearly, the oxygen-to-silicon ratio is an important parameter for the polymeric and network structures in silicate melts, their corresponding glasses, and the formation of the various crystalline phases that can precipitate during processing. This ratio is 2:1 for unary SiO_2 systems. Thus, crystalline SiO_2 (e.g., quartz) can be understood as composed of tetrahedral arrangements of close-packed ions; this situation explains the relatively high density of quartz. The ionic radii of silicon and oxygen are 0.041 nm and 0.138 nm, respectively. Hence, the corresponding size ratio for Si:O of 0.34:1 leads to the establishment or retention of the SiO_4 tetrahedra in the crystalline state: 2.65 kg m^{-3} , as compared with that of the high-temperature crystalline forms of SiO_2 —tridymite (2.26 kg m^{-3}), cristobalite (2.32 kg m^{-3}), and amorphous silica (2.2 kg m^{-3}).

These considerations suggest that the establishment of SiO_4 tetrahedra in a melt requires an additional source of oxygen in order to achieve the oxygen-to-silicon ratio needed to stabilize the two- and three-dimensional networks. Normally, alkali and alkaline oxides are used to provide the needed oxygen while maintaining charge balance between positive and negative ions. Oxides of other metals, such as the transition metals and some of those in Groups IIIB and IVB, can also be used. This function underscores the variety of silicate minerals and the prevalence of complex compositions for tailored glasses and ceramics.

5.2.2 Minimum Bridging Oxygens

Recognizing that the number of bridging oxygens (oxygens which can bond covalently to produce the glass structure) is a critical parameter (above and beyond the simple oxygen-to-silica ratio) suggests a methodology by which one of the boundaries to the range of acceptable compositions can be predicted. The methodology is based upon Stevels⁶⁸⁻⁷⁰ theory in which he calculated the mean possible number of bridging oxygens per SiO_2 based upon the oxygen-to-silica ratio. A minimum of one bridging oxygen is necessary for a plausible glass structure to form;⁶³ that is, at calculated bridging oxygens of less than one, ionic bonding is favored over covalent bonding. Consequently, there is, in effect, too much oxygen to promote the formation

of the basic tetrahedral structure necessary for glass to form. Thus, the region of acceptable glass compositions would be predicted to be bounded by

$$F = 8 - 2(\text{oxygen/silicon}), \quad (1)$$

where

F = the mean possible number of bridging oxygens and has a value ≥ 1 ,
oxygen = moles of oxygen within the glass melt,
silicon = moles of silicon within the glass melt.

5.2.3 Waste Composition on an Oxide Basis

The equation for bridging oxygens can be used to predict a region of acceptable glass formulations based upon the composition of the waste being vitrified. The waste composition has been described previously (Sect. 3). However, the chemistry of glass formation takes place at elevated temperatures ($>1000^\circ\text{C}$). Consequently, the waste is assumed to be calcined prior to the chemistry of glass formation taking place. This, in turn, leads to the chemistry of glass formation being more appropriately described on an oxide basis rather than an "as received" basis. Toward that end, the dried waste composition was calculated assuming that the majority of the constituents are converted to oxide form. The calculated composition of the dry waste on an oxide basis is shown in Table 18.

It should be noted that the summation of the resulting oxides represents approximately 475 g/kg of original dried waste. Thus, the conversion to oxide form or calcination of the waste leads to a significant reduction in the quantity of waste to be immobilized in the glass as compared with the original weight of the waste. The weight loss of the dried surrogate is primarily due to the thermal destruction of the nitrates and would be transferred to the off-gas treatment system of a melter.

5.2.4 The Operating Diagram

Historically, the SLS system has used the three-component operating diagram with units of weight percent to illustrate regions of acceptable glass formulations. However, it is well known that the chemistry of any system occurs on a mole basis rather than a weight basis. The primary reason that units of weight percent can successfully illustrate regions within the SLS system is that the molecular weights of the three components are so similar. The molecular weights of Na_2O , CaO , and SiO_2 are 62, 56, and 60 g/mole, respectively. Thus, a plot of composition in weight percent would accurately (to within a few percent error) reflect composition in mole percent. Obviously, as more components are introduced into the system, this comparison is no longer as accurate as the simple three-component system. Nonetheless, the operating diagram has proven to be an acceptable means of describing glass formulations containing mixed⁶⁴⁻⁶⁶ and is used herein.

The surrogate waste composition (on an oxide basis) is shown in the traditional ternary operating diagram in Fig. 8. The "three" components represented on the diagram include alkalis (e.g., Na_2O), alkaline earths (e.g., CaO), and glass formers (SiO_2 and Al_2O_3). Line A-A represents calculated bridging oxygens of ≈ 1 . Thus, line A-A is one of the boundaries of acceptable glass compositions and, in effect, represents the maximum allowable oxygen content in the melt for this application. Compositions to the right of line A-A are those with calculated F values greater than 1. The second boundary for acceptable glass compositions, also shown in Fig. 8, is line B-B. Line B-B is particularly noteworthy in that it represents a suspected phase-separation boundary based upon literature data for the $\text{CaO-Na}_2\text{O-SiO}_2$ system;⁷¹ that is, compositions beyond this boundary that are "deficient" in alkali and alkaline earth tend to form unary rather than ternary phases. Compositions to the right of line B-B would be expected to produce glass products characterized by phase separation and/or contained crystalline material. Line C-C represents the maximum alkaline earth (RO) composition supplied by the waste. One of the constraints imposed is the assumption that the waste supplies one of the major SLS glass-forming system components, thus necessitating only two additional additives. The resulting region bounded by lines A-A, B-B, and C-C represents the predicted region of acceptable compositions. The recipes or formulations for further evaluation are those additives which when combined with the waste result in compositions within the bounded region.

It is interesting to note that the line A-A, representing a minimum bridging oxygen of ≈ 1 , corresponds to a waste loading of approximately 50 wt % (on an oxide basis). Therefore, for this glass-forming system and surrogate composition a waste loading of 50 wt % represents the maximum achievable waste loading.

5.3 EXPERIMENTAL PROCEDURE

The aqueous surrogate MVST sludge was prepared as described in Sect. 4.1.1. The sludge was then dried at 105°C to a constant weight. The dried material was broken up with a hammer, followed by ballmilling for approximately 2 h. This dried, size-reduced material was passed through a 4.75-mm sieve. It is this dried, homogenized, and sieved material that became the waste feed for the vitrification studies.

Weight loss observed upon drying was 52.4 wt % (the water content, including waters of hydration, of the surrogate sludge was 52.0 wt %). Homogenization of the dried material proved difficult due to the presence of a hard white crust on the upper surface of the dried waste. This white crust was determined to be CaCO_3 .

A more detailed discussion of the procedures in preparing glass is presented elsewhere.⁶⁵ A brief summary of the procedure follows. The recipe of interest was selected from the predicted composition region, as described in Sect. 5.2.4. The ingredients were weighed, combined, and rolled in a ball mill for approximately 30 min. The material was then placed in a 99.8% pure $\alpha\text{-Al}_2\text{O}_3$ crucible with a loose fitting lid. The crucible and contents were placed in a high-temperature furnace to achieve melting. The furnace was programmed to ramp to the desired melt temperature at 300°C/h and hold at the melt temperature for 4 h, after which the fluid glass

Fig. 8. Calculated region of acceptable glass compositions.

was poured into a stainless steel pan and allowed to cool to ambient temperature. The resulting solidified glass product was then subjected to various characterization/analyses.

5.4 RESULTS AND DISCUSSION

5.4.1 Scoping Tests

Glass recipes/formulations evaluated in the scoping tests and calculated composition of the resulting products are presented in Table 19. The glass-product compositions are also shown on the traditional ternary diagram in Fig. 9.

5.4.1.1 Viscosity

All glasses poured easily from the crucible, indicating that removal of the glass from field-scale operations does not appear to be an issue of concern. Viscosity determinations (other than by visual observation) were beyond the scope of this project. However, glass viscosity models have been developed and can be used to qualitatively calculate the viscosity of the glass produced. [72, 73]

5.4.1.2 Leaching

All glasses were subjected to TCLP testing. Results are presented in Table 20. As shown by these data, all products were acceptable with respect to meeting RCRA LDR per this test. That is, none of the glasses produced would be designated as characteristically hazardous for Ag, As, Ba, Cd, Cr, Pb, or Se. Thus, it is assumed that glasses with compositions within the region bounded by compositions from experiments numbered V-1, V-5, V-6, and V-8 would produce products with acceptable TCLP values.

The question of "what constitutes good leaching performance" has been debated for decades. Numerous leach tests and acceptance criteria have been put forward.⁷⁴ The most widely used is ANS 16.1, and leach results for this test are presented in Sect. 5.1.2. It is widely recognized that leaching (or the release of constituents in a liquid environment) is a complex process which is impacted by leachant composition, available solid surface area, matrix composition, constituent speciation, anion associated with the constituent (i.e., chemical form of the constituent), soluble fraction of the constituent, etc. Nonetheless it is the TCLP that is the standard applied under RCRA. As stated previously, all glasses produced acceptable TCLP results as defined by regulation. However, within this region of glass composition, TCLP concentrations actually varied significantly. For example, uranium leachate concentrations ranged from 0.039 to 8.5 mg/L. Clearly, the TCLP, which is used to determine acceptable glass from a regulatory context, is not sufficient to identify and explain significant leaching differences at leachate concentrations below the regulatory threshold value.

Be that as it may, the TCLP leach values can be used to identify qualitative trends with respect to TCLP leachate values versus glass composition. Experiments V-1 through V-5 represent glass

Fig 9. Glass compositions presented on ternary diagram.

compositions with an approximately constant waste loading and silica content (70 wt %). The basic change in composition is that the CaO content is reduced with a corresponding increase in Na₂O content as the experiment number is increased from V-1 to V-5. As one would expect, the calcium leachate concentrations decreased as the calcium content of the glass decreased, as did the sodium. However, the potassium TCLP concentration steadily increased as the glass calcium content decreased, indicating that there may be a minimum calcium-to-sodium ratio necessary to significantly reduce leaching.

Runs V-6, V-7, and V-8 represent a similar series of runs with a constant silica content of approximately 55 wt %. Leachate concentrations were generally higher for all constituents for glass compositions with 70 wt % silica. Clearly silica, which is the basic building block of the glass structure, is beneficial. It should be pointed out, however, that the line representing a silica content of 55 wt % corresponds to the compositions where calculated bridging oxygens are constant at 2. At bridging oxygens of 2, the basic glass structure changes from group silicates to ring or chain silicates.⁷⁵ As bridging oxygens are increased, the structure further changes to layer silicates and ultimately network silicates. In simplest terms, as the number of bridging oxygens increase, so does the bonding between the various silicate building blocks, thus producing a stronger glass matrix which should offer greater leach (or release) resistance. It is this trend with bridging oxygens which best describes the observed TCLP data.

5.4.1.3 Material Characterization

Typically, a performance criterion for acceptable glass product is that it be amorphous. That is, no observable secondary phases. Devitrification (the formation of crystalline phases) during or within the melt process is unacceptable. The crystals formed can plug material transfer lines (or drains) and in some cases the melter itself. It should be noted that formation of crystals during the cooling process (assuming that cooling takes place external to the melter) is not necessarily detrimental and may actually improve leach performance.⁶⁵

In the compositional studies presented herein, it is assumed that the method of pouring glass into a steel pan at ambient conditions provides sufficient cooling to avoid the formation of crystalline phases during the cooling process. Therefore, any observed crystallinity in the glass product is considered to be formed during the melt process and constitutes an unacceptable glass. Toward that end, product samples were submitted for X-ray Diffraction (XRD) characterization.

XRD is a method for determining the presence and identity of the crystalline components of the glass product. The basic technique involves the bombarding of a crystal with a monochromatic beam of X-rays. Under these conditions, there exist a limited number of angles at which constructive diffraction occurs, and when a detector is moved past the cones of diffracted X-rays, a series of peaks is observed. The positions of these peaks are characteristic of individual crystalline compounds within the glass sample. An absence of peaks is indicative of an amorphous or glassy material.

Figures 10, 11, and 12 illustrate typical diffraction patterns of glasses that (by XRD) are deemed amorphous, slightly crystalline, and strongly crystalline. All glasses evaluated in this study were deemed amorphous via XRD.

5.4.2 Appearance of Glass Above the Melt Line

Recorded visual observations during the pouring of the glasses made during the scouting studies (Sect. 5.4.1) are presented in Table 19. In some cases, the glass was observed to have traveled up the crucible walls during the melting process. The presence of this thin layer, possibly indicating that foaming had occurred, could prove corrosive to melter components during actual full-scale operations. In essence, the glass is of low viscosity and can penetrate into the microcracks of the melter liner. This fluid melt is highly corrosive and can accelerate liner corrosion by this penetration. Consequently, it can significantly reduce the lifetime of a melter liner, thereby increasing cost and reducing operating time, and, in the worst case, present a safety hazard by corroding through the melter and allowing molten glass to flow out into the working environment. Unfortunately, there is little if any data on the increased rate of corrosion induced by this phenomenon.

It is significant to note that this phenomenon was observed for glass compositions with the highest waste loading. The high waste loading corresponds to glass melts with the highest nitrate content. Nitrates are known oxidants. Initially, it was assumed that the dominant decomposition products of the nitrate would be NO_2 and O , with the O combining with the cation to form its oxide. However, literature data have confirmed that to some extent the decomposition products are N_2 and O_2 , as described by Volf and presented in Eqs. (2) and (3).⁶³

The results of these decomposition reactions are twofold. First, these reactions indicate the presence of more gas generation than anticipated from the nitrate salts. This "excess" of gas bubbling through the melt could lead to a lower melt viscosity than anticipated, and its release (escape) at the melt line could induce foaming.

Second, the presence of this "excess" oxygen suggests that the melt chemistry takes place in the presence of more oxygen than envisioned in the bridging model used to calculate the expected range of acceptable compositions. This, in turn, would lead to fewer bridging oxygens to form the cohesive glass structure, producing a less viscous (more fluid) melt. In simplest terms, the basic glass building block is the ionic bond between silicon (Si) and oxygen (O). The bridging oxygens, which connect the building blocks to form a durable structure, do so by covalent bonding between oxygens. In the presence of "excess" oxygen, ionic bonding is favored over covalent bonding and the glass does not form the structure predicted. This "lack of structure" leads to a fluid of lower viscosity than predicted.

Fig. 10. Typical XRD pattern from amorphous glass.

ORNL DWG 95C-870

Fig. 11. Typical XRD pattern from glass that is slightly crystalline.

Fig. 12. Typical X-ray diffraction pattern for glass that is strongly crystalline.

Experience⁷⁶⁻⁸⁰ with borosilicate glasses developed for high-level radioactive wastes at Westinghouse Savannah River Company (WSRC) has shown that glass melt chemistry/behavior is a strong function of the oxidation-reduction (redox) equilibria, which is influenced by melt temperature and the presence of oxidizers such as nitrates or oxygen. In some cases, deoxygenation of salts can lead to foaming in waste glass melters, particularly as melt temperature increases. In order to mitigate these concerns, it has been recommended that routine operation of borosilicate glass at a melter temperature of 1150°C be performed in melt conditions with oxygen fugacity maintained between 10^{-2} and 10^{-9} (or percentage of reduced iron between 8 and 80). Foaming was observed at higher temperatures with oxygen fugacity as high as 10^{-4} (20% reduced iron).

In order to verify that the melts in the scouting studies were being formed under "extreme" oxidizing conditions, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple was determined in the glass products. The method used was developed previously by WSRC in support of the high-level nuclear waste vitrification program.⁷⁶⁻⁸⁰ In essence, the determination of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple allows the calculation of the oxygen fugacity of the melt conditions. This, in turn, allows the determination of other inorganic redox couples using available Electromotive Force (EMF) data. The wet-chemical technique used to determine the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple is summarized as follows:

- Dissolution of the glass sample in an $\text{H}_2\text{SO}_4/\text{HF}$ mixture containing ammonium vanadate.
- Addition of boric acid to destroy the iron-fluorine complexes.
- Addition of pH 5 buffer and Ferrozine with subsequent measurement of the magenta-colored ferrous-Ferrozine complex to determine the ferrous iron.
- Addition of ascorbic acid to reduce any ferric iron to ferrous.
- Remeasurement of the total absorbance of the ferrous Ferrozine complex to determine total iron. The difference between the two measurements is taken to be the ferric iron.

Resulting redox data are presented in Table 21. Experiments numbered V-18, -24, and -25 represent replicates of the same recipe. Although the percent reduced iron for V-24 and V-25 showed excellent consistency (23 and 20%, respectively), V-18 (11%) did not. The differing values may be attributed to sample heterogeneity, in spite of the efforts taken in sample preparation to achieve a homogeneous product. Conversely, the difference may be attributed to the accuracy/precision of the analytical technique at the low iron concentrations of this surrogate. In either case, comparisons of the relative percentage of reduced iron for the various samples must be assumed to be qualitative indicators rather than absolute values.

In general, the iron redox data indicate oxidizing conditions, with most values of the percentage of reduced iron being in the low 20s or teens (oxygen fugacity on the order of 10^{-4} and higher). Based upon the experience at WSRC, these values would suggest that the melt is too oxidizing

and conditions are favorable to observe foaming. For want of additional data, the observance of glass on the crucible walls above the melt line will be referred to hereafter as foaming.

The iron redox data indicate that the melts experience "excessive" oxidizing conditions and suggests the need for the addition of a reductant to the melt. The role of the reductant would be to react with the "excess" oxygen, thereby mitigating its effect on the melt chemistry. Numerous reductants are available. In determining the reductant of choice, it is important to understand the chemistry of the nitrate decomposition. Nitrate salts such as NaNO_3 and KNO_3 melt at temperatures on the order of 300 to 350°C, which is substantially below the melting point of the primary glass formers in the recipe. Although actual nitrate decomposition occurs over a range of temperatures, it is known to begin slightly above its melting temperature.⁶³ Thus, the reduction reaction can and should take place at temperatures significantly below that of the melt temperature (operating temperature in field-scale operations). During field-scale operations, this would indicate that the reducing reaction should take place in the melter working space above the glass melt. The glass melt would be maintained at operating temperatures of 1100 to 1400°C (depending on the formulation used), while the working space above the melt would experience a temperature gradient of feed temperature (near ambient) to that of the melt. Consequently, the reduction reaction would need to take place at a temperature on the order of 400°C (slightly above the nitrate melt temperature). This would suggest introducing a reductant, perhaps as second feed stream, into the working space above the melt in a regime of the desired temperature (~400°C). For reactions at this temperature, carbon-containing materials such as sugar appear to be a strong candidate.

5.4.2.1 Redox Experiments

Although redox studies were beyond the scope of this project, three simple experiments were performed in an attempt to assess the effects of carbon addition. Simplified assumptions as to the reduction reaction predict that 1 mole of carbon is needed for each mole of nitrate in the waste. This translates to approximately 5 g of carbon per 100 g of dried waste. In an effort to assess the effects of carbon, activated carbon was added to formulation V-9 in various quantities. Specifically, small quantities of activated carbon were placed on top of the V-9 blended ingredients after the ingredients had been placed in the crucible. The layered mixture (carbon on top) was then placed in the furnace and subjected to the normal heating profile described previously. Formulations V-10, V-11, and V-12 are identical to V-9 except that 1.2, 1.2, and 3 g of carbon, respectively, were added to the V-9 formulation. V-11 was identical to V-10 except that the carbon was blended in with the formulation ingredients rather than placed on top. As shown by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ data in Table 22, there is no indication of the carbon having any effect on the percentage of reduced iron. This lack of effect is attributed to the experimental procedure. That is, ramping to melt temperature at 300°C as in the procedure for the routine composition studies is not indicative of conditions to approximate reactions occurring above the melt. Future experiments to assess the effect of carbon on redox should be performed at melt temperature. That is, the furnace should be preheated to melt temperature before placing the crucible in the furnace. It is believed that this would better approximate the heat-up rates actually experienced

in the working area above the melt in field-scale operations and, thus, more accurately assess the effects of carbon addition.

Clearly the solution to the "excess" oxidizing conditions in the melt is to induce a reduction reaction. The reductant and the quantities needed are yet to be established. However, once established, the operating window or range of formulations which are acceptable should more closely approximate the predicted range (Sect. 5.1.4).

5.4.3 Sensitivity Testing

It must be recognized that the scouting studies described previously were not designed to identify an optimum formulation. The present studies have identified a potential problem with several of the glass formulas producing melts with glass adhering to the crucible wall above the melt line. Such a phenomenon could have serious consequences on melter operation at the field scale. As discussed in Sect. 5.4.2, it is believed that the cause of this phenomenon is known and can be overcome, thereby making the majority of the predicted acceptable composition regime available (or acceptable) during actual operations. However, this was not confirmed during this scouting study. Consequently, a recipe/formulation for further additional testing had to be selected from a much smaller region than that predicted. That is, the recipe for additional testing was selected based upon the limited data available and it was *not* assumed that the potential foaming problems identified with some of the glass formulations could be overcome. Thus, the formulation for additional testing was selected from the composition regime bounded by formulations V-1, V-3, V-17, and V-13, which did not exhibit foaming, and was arbitrarily taken to be the composition at the center of this region (i.e., V-18).

Table 21 lists the feed compositions and the ternary glass compositions for the sensitivity test glasses. The standard glass was tested in triplicate (V-18, V-24, and V-25). Four variations of the $\pm 10\%$ variations in the feed mix were picked for sensitivity testing (V-19–V-22). The remaining glass (V-23) used the standard glass recipe, but extra RCRA metal compounds were added to the dried sludge to simulate the maximum RCRA metals listed in the tank characterization data. Table 23 lists the solids composition of the standard MVST surrogate sludge used for seven of the eight glasses and the surrogate solids composition with maximum RCRA metals used for V-23. These eight glass melts poured readily into graphite molds. After filling with the melted glass, the graphite molds were placed in a furnace at 535°C for 2 h and then allowed to cool to room temperature in the furnace, to anneal the glass. This procedure resulted in clear glass cylinders for leach testing, tinted slightly green or amber with a cluster of gas bubbles trapped in the center. The cylinders were slightly rounded at the top (the result of the glass melt meniscus when the mold was filled with the viscous glass). The dimensions and masses of the cylinders were measured and used to calculate the glass densities listed in Table 24. Since the cylinders were not perfect right cylinders and contained gas bubbles, the densities listed in Table 24 are bulk densities. These bulk glass densities were used with the estimated volume of wet sludge used in making these glass cylinders and the cylinder masses to calculate the ratios of the resulting glass volume to the original wet sludge volume listed in Table 24. These values imply that one can expect a volume reduction by more than a factor of

2 upon vitrifying the wet sludge into SLS glass (not counting any off-gas or secondary waste volumes), compared with the volume increase of about 50 vol %, if grouted.

These glass cylinders were leached in deionized water at room temperature. Daily monitoring of the cesium and strontium concentration of one leachate indicated that no measurable concentrations accumulated in the leachates during the first week. After 6.85 d, the leachates were replaced with fresh deionized water and the cesium and strontium concentrations measured in these first leachates. Table 25 lists these leachate concentrations along with the cesium and strontium concentration measured in each glass by total dissolution analysis. Also listed in Table 25 are the percentages of the cesium and strontium spiked into the glass feed mix recovered by total dissolution analysis of the glass product. Some volatilization of cesium was expected, and Table 25 indicates a presence of at least 44 to 57 wt % of the original cesium in the glass product. However, not all of the unrecovered cesium necessarily vaporized, because some glass may not have dissolved in the total dissolution analysis. As Table 25 illustrates, less than 100% of the strontium was also recovered (except for V21 with 122% recovery), which may be indicative of the lack of total dissolution (since strontium is not expected to have the same volatility as cesium at the high vitrification temperatures). The 122% recovery for V-21 also introduces the possibility of heterogeneity in the glass, unless an error was made in spiking (the higher strontium leachate concentration for V-21 is consistent with the latter). Assuming the total dissolution analysis results as representative of the glass composition, one can expect that at least about 50 wt % of the cesium will remain with the glass in operations similar to the laboratory crucible melting.

These glass samples proved quite leach resistant, as illustrated by the low leachate concentrations, even after leaching for a week. Table 25 lists the leachability indexes estimated for cesium and strontium from these single leachate analyses, assuming diffusion-controlled leaching with zero leachate concentration. Further analyses of the leachates indicated the silicon concentrations were <0.02 mg/L, well below the solubility limit for silica at room temperature in a neutral pH, meaning that the leaching was not hampered by solubility limits of the glass matrix and diffusion control with zero leachate concentration over the leach interval of 6.85 d was a reasonable assumption. These results imply leachability indexes >18 for the sensitivity glasses, a challenge to measurement capability and well above the grout leachability indexes of 9–10.

6. SUMMARY AND CONCLUSIONS

An envelope, or operating window, for grout and glass formulations for a surrogate MVST sludge was identified and is documented in this report. Surrogate wet sludge loadings up to 55 wt % in grout met all performance criteria, resulting in volume increases of 40–50 vol % with little or no secondary waste generation. Higher loadings may result in free water, which violates the waste acceptance criteria of potential disposal facilities. Dewatering the sludge to <52 wt % water allow higher waste loadings, with correspondingly lower volume increases, without sacrificing TCLP performance or leach resistance. The grout strength declines as the sludge loading increases, but a strong monolithic solid is not usually a waste acceptance criterion.

Grouts stabilized the RCRA metals, including mercury (potentially a problem species for the tank sludges) and passed the TCLP test.

The tank sludges can be stabilized in glass at a waste oxide loading of 40–50 wt %, resulting in a net volume decrease of 50–60 vol %. This is a threefold decrease in final waste form volume compared with grout, not counting the secondary waste generation volume from off-gas treatment. The benefits of the lower glass volume compared with grout volume must be weighed against the generally higher capital and operating costs for vitrification, as well as the volume of secondary waste generated from both vitrification and grouting. RCRA metals incorporated into the glass matrix are stabilized and leach resistant, but mercury is volatilized and must be treated in the off-gas.

Confirmation of these results with actual hot sludge must be done prior to final acceptance of either technique. Hot testing of the grout and glass formulations with actual tank sludge samples was done subsequently to the work documented in this report. In addition, laboratory surrogate work continued at ORNL (grout) and the Savannah River Technology Center (glass) to apply this work to the sludges in other ORNL tank sets and to refine the formulations to allow higher waste loadings and lower volume increases.

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Table 1. Composition of the MVST sludges

Assumed species	Projected composition of the tank sludges (mass fraction)								Weighted average	20 x UTS TCLP limit ^a
	W-21	W-23	W-24	W-25	W-26	W-27	W-28	W-31		
RCRA metals										
Ag ₂ O	0.000054	0.000030	0.000008	0.000008	0.000032	0.000008	0.000018	0.000007	0.000019	0.000006
As ₂ O ₃	0.000055	0.000066	0.000055	0.000054	0.000086	0.000051	0.000036	0.000044	0.000060	0.000132
Ba(OH) ₂	0.000097	0.000079	0.000055	0.000074	0.000109	0.000061	0.000049	0.000021	0.000073	0.000190
CdO	0.000031	0.000037	0.000007	0.000013	0.000048	0.000015	0.000030	0.000002	0.000023	0.000004
Na ₂ Cr ₂ O ₇	0.000403	0.000479	0.000091	0.000149	0.000428	0.000164	0.000139	0.000068	0.000255	0.000043
HgO	0.000056	0.000019	0.000026	0.000037	0.000064	0.000011	0.000012	0.000014	0.000032	0.000001
NiO	0.000095	0.000140	0.000028	0.000043	0.000117	0.000034	0.000079	0.000022	0.000071	0.000127
PbO	0.000312	0.000485	0.000162	0.000237	0.000506	0.000129	0.000205	0.000183	0.000296	0.000008
SeO ₂	0.000035	0.000055	0.000074	0.000072	0.000078	0.000069	0.000041	0.000058	0.000066	0.000005
Ti ₂ O	0.000010	0.000017	0.000017	0.000017	0.000018	0.000021	0.000009	0.000014	0.000017	0.000002
Process Metals										
Al ₂ O ₃	0.0019	0.0053	0.0030	0.0053	0.0142	0.0081	0.0016	0.0026	0.0065	
CaCO ₃	0.1001	0.1373	0.0553	0.0327	0.0899	0.0438	0.0302	0.0118	0.0665	
Ca(OH) ₂	0.0091	0.0000	0.0127	0.0460	0.0000	0.0378	0.0830	0.0016	0.0221	
Fe ₂ O ₃	0.0033	0.0027	0.0009	0.0013	0.0033	0.0020	0.0009	0.0006	0.0020	
KNO ₃	0.0323	0.0465	0.0304	0.0266	0.0717	0.0158	0.0502	0.0329	0.0378	
MgCO ₃	0.0000	0.0115	0.0000	0.0000	0.0086	0.0000	0.0000	0.0000	0.0033	
Mg(OH) ₂	0.0232	0.0307	0.0135	0.0143	0.0206	0.0116	0.0362	0.0021	0.0182	
NaNO ₃	0.2379	0.2897	0.1284	0.2343	0.2176	0.2510	0.3337	0.3011	0.2384	
NaCl	0.0022	0.0029	0.0041	0.0042	0.0054	0.0048	0.0063	0.0056	0.0043	
NaF	0.0014	0.0011	0.0014	0.0013	0.0016	0.0017	0.0015	0.0018	0.0014	
Na ₂ SO ₄	0.0046	0.0058	0.0014	0.0016	0.0029	0.0018	0.0017	0.0019	0.0027	
Sr(OH) ₂	0.0003	0.0004	0.0002	0.0002	0.0002	0.0002	0.0002	0.0000	0.0002	
ThO ₂	0.0156	0.0137	0.0017	0.0044	0.0107	0.0022	0.0016	0.0032	0.0068	
UO ₂	0.0352	0.0193	0.0042	0.0054	0.0273	0.0031	0.0193	0.0034	0.0131	
TOC	0.0065	0.0041	0.0029	0.0023	0.0062	0.0024	0.0025	0.0004	0.0035	
Solids	0.4681	0.5684	0.2576	0.3783	0.4754	0.3844	0.5670	0.3690	0.4242	
Water	0.4890	0.4560	0.5130	0.4690	0.5510	0.6140	0.4670	0.6310	0.5204	
Total	0.9571	1.0244	0.7706	0.8473	1.0264	0.9984	1.0340	1.0000	0.9446	
Unknown	0.0429	-0.0244	0.2294	0.1527	-0.0264	0.0016	-0.0340	0.0000	0.0554	

^aCalculated from the UTS tCLP limit for nonwastewater by converting for the compound and multiplying by 20.

Table 2. Target composition for the surrogate MVST sludge

Compound	Mass fraction
RCRA metals	
Ag ₂ O	0.000019
CdO	0.000023
Na ₂ Cr ₂ O ₇	0.000255
HgCl ₂	0.000040
PbO	0.000296
SeO ₂	0.000066
TiNO ₃	0.000021
Process metals	
Al(OH) ₃	0.0099
CaCO ₃	0.0665
Ca(OH) ₂	0.0221
Fe ₂ O ₃	0.0020
KNO ₃	0.0378
MgCO ₃	0.0033
Mg(OH) ₂	0.0182
NaNO ₃	0.2790
NaCl	0.0043
NaF	0.0014
Na ₂ SO ₄	0.0027
Sr(NO ₃) ₂	0.0004
Th(NO ₃) ₄ ·4H ₂ O	0.0141
UO ₂ (NO ₃) ₂ ·6H ₂ O	0.0244
Total solids	0.4866
Water	0.5134
Sludge	1.0000

Table 3. Composition of the MVST supernates

Species	Measured composition of the tank supernates (mg/L)										UTS limit ^a
	W-21	W-23	W-24	W-25	W-26	W-27	W-28	W-31	Weighted average		
RCRA metals											
Ag	1.20	0.44	0.06	0.07	0.07	0.07	0.07	0.07	0.16	0.43	
As	3.80	3.00	0.25	0.25	0.25	0.25	0.25	0.25	0.56	1.40	
Ba	25.00	0.19	0.18	0.86	3.47	12.70	7.91	0.95	5.81	1.20	
Cd	2.00	1.70	0.82	0.67	0.65	0.31	0.31	0.81	0.72	0.69	
Cr	27.00	0.42	1.46	3.24	1.52	1.03	1.03	11.80	5.20	1.20	
Hg	0.92	0.07	0.05	0.13	0.09	0.64	0.14	0.71	0.34	0.15	
Ni	15.00	3.00	0.83	1.12	6.99	3.18	2.84	0.95	3.49	3.98	
Pb	7.10	2.70	2.00	2.71	2.20	2.20	2.20	2.20	2.59	0.69	
Se	2.30	2.30	0.50	0.50	0.50	0.50	0.50	0.50	0.67	0.82	
Tl	0.94	0.94	18.00	19.00	19.00	19.00	19.00	19.00	17.18	1.40	
Process metals											
Al	1	2	33	1	0	0	0	3	6		
B	1	10	1	2	1	1	1	1	1		
Be	0	0	0	0	0	0	0	0	0		
Ca	23,000	18	6	7	1,590	10,400	10,300	153	5,313		
Cs	0	0	0	1	0	0	1	0	0		
Co	0	0	0	0	0	0	0	0	0		
Cu	0	0	0	0	0	1	1	0	0		
Fe	240	1	0	0	0	0	0	0	17		
K	20,000	78,000	20,600	19,100	40,900	11,500	30,100	16,500	24,247		
Mg	5,600	3	0	0	145	1,090	1,870	0	938		
Mn	0	0	0	0	0	0	0	0	0		
Na	61,000	82,000	74,800	81,600	79,900	95,100	110,000	99,200	89,373		
Sb	0	0	3	3	3	3	3	3	2		
Si	1	1	53	69	21	25	21	21	30		
Sr	160	0	1	2	43	69	81	41	50		
Th	95	16	1	1	1	12	5	1	10		
U	750	17	6	3	1	503	234	2	169		
V	0	0	0	0	0	0	0	0	0		
Zn	0	0	24	1	1	2	1	1	5		
Cations	110,934	160,083	95,552	100,818	122,641	118,746	152,651	115,963	120,197		

Table 3. (continued)

Species	Measured composition of the tank supernates (mg/L)								Weighted average
	W-21	W-23	W-24	W-25	W-26	W-27	W-28	W-31	
	Anions								
CO ₃ ⁻ (IC)	5	41,668	5,651	1,869	75	450	220	2,443	2,464
Bromide	0	0	11	665	690	343	395	425	367
Chloride	2,092	3,545	4,380	4,730	4,800	3,800	5,950	4,370	4,524
Cyanide	0	0	0	0	0	0	0	0	0
Fluoride	1,007	1,007	1,080	1,100	1,040	975	1,070	1,050	1,049
Nitrate	310,025	200,276	197,000	239,000	299,000	342,000	425,000	311,000	308,210
Phosphate	5,033	5,033	11	10	10	10	10	10	474
Sulfate	4,995	7,781	1,720	1,950	2,940	1,570	1,750	1,670	2,247
Anions	323,157	259,311	209,853	249,324	308,555	349,148	434,395	320,968	319,334
Total ions	434,090	419,394	305,404	350,141	431,196	467,893	587,046	436,932	439,532
pH	0.6	12.8	13.0	13.0	9.3	7.2	7.2	11.9	12.0

^aThe UTS concentration limits for wastewater.

Table 4. Target composition for the surrogate MVST supernate

Compound	mg/L
RCRA metals	
Ba(OH) ₂	7.25
CdO	0.82
Na ₂ Cr ₂ O ₇	13.10
HgCl ₂	0.46
PbO	2.79
TiNO ₃	22.39
Process metals	
Ca(OH) ₂	6,780
KNO ₃	62,695
Mg(OH) ₂	2,249
NaNO ₃	369,782
CaCO ₃	4,109
NaBr	473
NaCl	7,458
NaF	2,318
Na ₂ SO ₄	3,322
pH	12.0

**Table 5. Ionic concentrations for the surrogate
MVST supernate in Table 4**

	mg/L
RCRA metals	
Ba	5.81
Cd	0.72
Cr	5.20
Hg	0.34
Pb	2.59
Tl	17.18
Process metals	
Ca	5,313
K	24,247
Mg	938
Na	106,126
Anions	
Carbonate	2,464
Bromide	367
Chloride	4,524
Fluoride	1,049
Nitrate	308,215
Sulfate	2,247

Table 6. Composition of the grouts tested during the scoping tests

Grout no.	Surrogate wet sludge (wt%)	Surrogate supernate (wt%)	Dry blend				Water sorptive agent (wt%)	W/S
			Slag (wt%)	Cement (wt%)	Fly Ash (wt%)	IRPC (wt%)		
1	33.1	10.6	46.7	5.1	0.0	4.5	0.0	0.39
2	27.8	16.7	22.8	2.8	25.6	4.4	0.0	0.45
3	66.7	0.0	27.7	3.0	0.0	2.7	0.0	0.53
4	67.0	0.0	13.5	1.7	15.2	2.6	0.0	0.53
5	54.9	0.0	37.4	4.1	0.0	3.6	0.0	0.40
6	38.5	30.0	26.2	2.8	0.0	2.5	0.0	1.00
7	30.8	44.0	20.9	2.3	0.0	2.0	0.0	1.50
8	25.6	53.3	17.5	1.9	0.0	1.7	0.0	2.00
9	54.9	0.0	18.5	2.3	20.7	3.6	0.0	0.40
10	38.5	30.0	12.9	1.6	14.5	2.5	0.0	1.00
11	30.8	44.0	10.4	1.3	11.6	2.0	0.0	1.50
12	25.7	53.3	8.6	1.1	9.7	1.7	0.0	2.00
13	67.0	0.0	12.5	1.3	14.9	2.6	1.7 ^a	0.53
14	67.0	0.0	12.5	1.3	13.2	2.6	3.3 ^a	0.53
15	67.0	0.0	10.9	1.3	13.2	2.6	5.0 ^a	0.53
16	67.0	0.0	10.9	1.3	11.6	2.6	6.6 ^a	0.53
17	67.0	0.0	12.5	1.3	14.9	2.6	1.7 ^b	0.53
18	67.0	0.0	13.2	1.3	13.2	2.6	2.6 ^b	0.53
19	67.0	0.0	12.5	1.3	12.5	2.6	4.0 ^b	0.53
20	67.0	0.0	12.2	1.3	11.9	2.6	5.0 ^b	0.53
21	67.0	0.0	10.9	1.3	11.6	2.6	6.6 ^a	0.53
22	67.0	0.0	10.9	3.3	9.6	2.6	6.6 ^a	0.53
23	67.0	0.0	10.9	5.0	7.9	2.6	6.6 ^a	0.53
24	67.0	0.0	10.9	6.6	6.3	2.6	6.6 ^a	0.53
25	67.0	0.0	12.5	1.3	14.9	2.6	1.7 ^c	0.53
26	67.0	0.0	13.2	1.3	13.2	2.6	2.6 ^c	0.53
27	67.0	0.0	12.5	1.3	12.5	2.6	4.0 ^c	0.53
28	67.0	0.0	12.2	1.3	11.9	2.6	5.0 ^c	0.53
29	67.0	0.0	7.9	7.9	7.9	2.6	6.6 ^a	0.53
30	67.0	0.0	6.9	9.9	6.9	2.6	6.6 ^a	0.53
31	67.0	0.0	5.9	11.9	5.9	2.6	6.6 ^a	0.53
32	67.0	0.0	5.0	13.9	5.0	2.6	6.6 ^a	0.53
33	27.4	20.5	17.2	10.4	9.9	4.2	10.4 ^a	0.53
34	32.9	24.3	14.1	8.6	8.1	3.4	8.6 ^a	0.71
35	42.9	16.7	13.3	8.1	7.7	3.2	8.1 ^a	0.64
36	56.3	6.1	12.4	7.5	7.1	3.0	7.5 ^a	0.55
37	70.0	0.0	9.9	6.0	5.7	2.4	6.0 ^a	0.57
38	80.0	0.0	6.6	4.0	3.8	1.6	4.0 ^a	0.71
39	90.0	0.0	3.3	2.0	1.9	0.8	2.0 ^a	0.88

^aPerlite^bAttapulgite^cBentonite

Table 7. The measured grout densities and grout volume relative to the surrogate MVST wet sludge volume for the scoping tests

Grout no.	Grout density (g/mL)	Volume ratio of grout to wet sludge ^a
1	1.90	2.22
2	1.84	2.74
3	1.62	1.29
4	1.63	1.28
5	1.73	1.47
6	1.63	2.23
7	1.58	2.88
8	1.54	3.54
9	1.73	1.47
10	1.58	2.30
11	1.52	2.99
12	1.45	3.76
13	1.61	1.30
14	1.63	1.28
15	1.60	1.30
16	1.60	1.30
17	1.63	1.28
18	1.63	1.28
19	1.63	1.28
20	1.62	1.29
21	1.61	1.30
22	1.60	1.30
23	1.62	1.29
24	1.62	1.29
25	1.63	1.28
26	1.64	1.27
27	1.64	1.27
28	1.65	1.26
29	1.68	1.24
30	1.69	1.23
31	1.66	1.26
32	1.68	1.24
33	1.72	2.96
34	1.70	2.50
35	1.69	1.92
36	1.71	1.45
37	1.62	1.23
38	1.53	1.14
39	1.49	1.05

^aCalculated from the wet sludge loading, grout density, and the measured surrogate MVST wet sludge density of 1.40 g/mL.

Table 8. Free water and penetration resistance measured for the scoping test grouts

Grout no.	Free water (vol%)				Penetration resistance (psi)			
	1 d	3 d	5 d	7d	1 d	3 d	5 d	7d
1	0.4	0.0		0.0	0	0		3,840
2	0.8	0.8		0.0	0	80		>8,000
3	8.0	8.0		7.2	0	1,280		5,960
4	6.0	8.0		7.2	0	160		2,520
5	0.8	0.0		0.0	0	3,000		>8,000
6	8.0	7.2		6.4	0	0		3,600
7	18.4	17.6		16.4	0	0		960
8	26.4	25.2		24.8	0	0		240
9	1.6	0.8		0.8	160			3,440
10	16.8	17.6		16.0	0			2,360
11	28.8	28.4		27.2	0			1,240
12	39.2	39.2		39.2	0	80		880
13	8.8	8.8		8.0	0	360		1,720
14	5.6	4.8		4.0	0	480		1,440
15	4.8	4.0		4.0	0	280		1,960
16	4.0	4.0		3.2	0	440		960
17	16.0	15.2		14.4	0	640		2,000
18	13.6	12.8		12.4	0	720		2,320
19	12.8	12.0		11.6	0	680		2,120
20	10.4	9.6		9.6	0	280		1,600
21	6.8	6.0		5.6	0	800		2,000
22	4.0	3.6		2.8	0	920		4,560
23	2.4	2.0		1.6	0	1,200		6,160
24	2.4	1.6		1.2	0	920		5,560
25	11.2		12.0	12.0	0		760	1,600
26	9.2		8.8	9.2	0		640	1,240
27	8.0		7.2	7.6	0		480	892
28	5.2		4.4	4.4	0		400	760
29	4.0	3.2		2.4		240		3,720
30	3.6	2.0		1.6		480		4,800
31	3.6	2.4		2.0		480		4,240
32	4.4	3.6		2.8		680		3,920
33	0.8	0.4		0.2		>8,000		>8,000
34	0.8	0.8		0.4		>8,000		>8,000
35	0.8	0.0		0.0		>8,000		>8,000
36	1.2	0.8		0.8		>8,000		>8,000
37	1.6	1.6		0.8		3,760		4,600
38	5.6	4.0		4.0		960		1,680
39	19.2	18.4		18.4		0		0

**Table 9. Concentrations of the RCRA metals and uranium in the TCLP
extract of the surrogate MVST sludge**

Analyte	TCLP extract concentration (mg/L)			
	Sludge sample	UTS limits ^a	RCRA characteristic limits ^b	TCLP LDR limits ^c
Cd	0.904	0.190	1.000	1.000
Cr	2.69	0.86	5.00	5.00
Hg	1.54	0.025	0.200	0.200
Pb	0.111	0.370	5.000	5.000
Se	0.118	0.160	1.000	5.700
Tl	0.486	0.078	N/A ^d	N/A
U	511	N/A	N/A	N/A
TCLP Fluid No.	2			
pH	6.75			

^aThe Universal Treatment Standard limits for the TCLP extract concentration.

^bToxicity limits for TCLP extract concentrations in determining whether a waste is characteristically hazardous by the RCRA.

^cThe TCLP extract concentration limits by the LDR of the RCRA.

^dNot applicable.

Table 10. Concentrations of the RCRA metals and uranium in the TCLP extract of the grouts from the scoping tests

Grout no.	TCLP extract concentration (mg/L)							TCLP fluid no.	pH
	Cd	Cr	Hg	Pb	Se	Tl	U		
1	<0.002	<0.002	<0.011	<0.004	0.173	<0.006	0.174	2	9.40
2	<0.002	<0.002	<0.011	<0.004	0.486	0.008	0.206	2	9.34
3	<0.003	<0.003	<0.022	<0.009	0.305	<0.011	0.170	2	9.06
4	<0.003	<0.003	<0.022	<0.009	0.334	0.014	107	2	8.37
5	<0.003	<0.003	<0.022	<0.009	0.245	<0.011	0.237	2	9.84
6	<0.003	<0.003	<0.022	<0.009	0.281	<0.011	0.376	2	9.54
7	<0.003	<0.003	<0.022	<0.009	0.373	<0.011	0.479	2	9.50
8	<0.003	<0.003	<0.022	<0.009	0.350	<0.011	0.376	2	8.95
9	<0.003	<0.003	<0.022	<0.009	0.287	<0.011	53.1	2	8.58
10	<0.003	<0.003	<0.022	<0.009	0.252	<0.011	96.7	2	8.31
11	<0.003	<0.003	<0.022	<0.009	0.220	<0.011	83.2	2	8.40
12	<0.003	<0.003		<0.009	0.198	0.042	117	2	7.48
13	<0.003	<0.003		<0.009	0.088	0.020	111	2	8.26
14	<0.003	<0.003		<0.009	0.082	0.018	122	2	8.29
15	<0.003	<0.003		<0.009	0.102	0.027	160	2	8.31
16	<0.003	<0.003		<0.009	0.109	0.033	225	2	8.21
17	<0.003	<0.003		<0.009	0.255	<0.011	138	2	8.31
18	<0.003	<0.003		<0.009	0.234	0.017	73.5	2	8.50
19	<0.003	<0.003		<0.009	0.206	<0.011	107	2	8.39
20	<0.003	<0.003		<0.009	0.207	0.020	98.7	2	8.39
21	<0.003	<0.003		<0.009	0.279	0.020	141	2	8.13
22	<0.003	<0.003		<0.009	0.178	<0.011	105	2	8.14
23	<0.003	<0.003		<0.009	0.164	<0.011	79.4	2	8.34
24	<0.003	<0.003		<0.009	0.157	<0.011	39.7	2	8.39
25	<0.003	<0.003		<0.009	0.065	0.014	67.3	2	8.43
26	<0.003	0.022		<0.009	0.063	0.020	59.3	2	8.40
27	<0.003	<0.003		<0.009	0.073	0.019	60.6	2	8.46
28	<0.003	<0.003		<0.009	0.073	0.032	38.3	2	8.34
29	<0.003	0.003		<0.009	0.025	0.041	1.21	2	6.45
30	<0.003	0.004		<0.009	0.022	0.039	4.17	2	5.53
31	<0.003	0.003		<0.009	<0.018	0.039	0.75	2	5.80
32	<0.003	0.008		<0.009	<0.018	0.042	4.43	2	5.48
33	<0.003	0.007		0.011	0.040	<0.011	<0.078	1	10.75
34	<0.003	0.006		0.013	0.040	<0.011	<0.078	1	10.60
35	<0.003	0.010		0.013	0.053	<0.011	<0.078	1	10.55
36	<0.003	0.015		0.013	0.073	<0.011	<0.078	1	10.74
37	<0.003	<0.003		<0.009	0.103	<0.011	13.7	2	8.63
38	<0.003	<0.003		<0.009	0.078	0.015	83.9	2	8.48
39	<0.003	<0.003		<0.009	0.090	0.053	379	2	8.32
TCLP	0.190	0.860	0.025	0.370	0.160	0.078	N/A ^a		
UTS ^b									

^aNot applicable.

^bThe UTS limits for the TCLP extract concentration.

Table 11. Grout compositions for sensitivity testing of grouting the surrogate MVST sludge

Grout component	Grout #1 (Std)	Grout #2	Grout #3	Grout #4	Grout #5
High waste loading (mass fraction)					
IRPC	0.036	0.032	0.040	0.038	0.034
Perlite	0.090	0.080	0.100	0.094	0.085
Fly ash	0.086	0.076	0.095	0.089	0.081
Slag	0.149	0.132	0.165	0.127	0.172
Cement	0.090	0.080	0.100	0.077	0.104
Wet sludge	0.550	0.599	0.500	0.575	0.522
Supernate	0.000	0.000	0.000	0.000	0.000
Total	1.000	1.000	1.000	1.000	1.000
W/S ^a	0.40 ^b	0.45	0.35	0.43	0.37
Low waste loading (mass fraction)					
IRPC	0.042	0.041	0.046	0.044	0.040
Perlite	0.000	0.000	0.000	0.000	0.000
Fly ash	0.240	0.238	0.263	0.251	0.228
Slag	0.214	0.212	0.234	0.183	0.248
Cement	0.026	0.026	0.029	0.022	0.030
Wet sludge	0.400	0.484	0.358	0.418	0.380
Supernate	0.078	0.000	0.070	0.082	0.074
Total	1.000	1.000	1.000	1.000	1.000
W/S ^a	0.40 ^c	0.34	0.34	0.43	0.37

^aFor the standard surrogate MVST sludge.

^bW/S = 0.53 for the surrogate MVST sludge with the maximum water; W/S = 0.33 for the surrogate MVST sludge with the minimum water and maximum bad actors.

^cW/S = 0.49 for the surrogate MVST sludge with the maximum water; W/S = 0.35 for the surrogate MVST sludge with the minimum water and maximum bad actors.

Table 12. Surrogate MVST sludge compositions used in sensitivity testing

Compound	Standard surrogate	Maximum water	Minimum water + maximum bad actors
RCRA metals (mass fraction)			
Ag ₂ O	0.000019	0.000014	0.000054
CdO	0.000023	0.000018	0.000048
Na ₂ Cr ₂ O ₇	0.000255	0.000193	0.000479
HgCl ₂	0.000040	0.000030	0.000080
PbO	0.000296	0.000224	0.000506
SeO ₂	0.000066	0.000050	0.000078
TiNO ₃	0.000021	0.000016	0.000026
Process metals (mass fraction)			
Al(OH) ₃	0.0099	0.0075	0.0110
CaCO ₃	0.0665	0.0504	0.1373
Ca(OH) ₂	0.0221	0.0168	0.0247
Fe ₂ O ₃	0.0020	0.0015	0.0022
KNO ₃	0.0378	0.0287	0.0423
MgCO ₃	0.0033	0.0025	0.0037
Mg(OH) ₂	0.0182	0.0138	0.0203
NaNO ₃	0.2787	0.2113	0.1887
NaCl	0.0043	0.0033	0.0063
NaF	0.0014	0.0011	0.0018
Na ₂ SO ₄	0.0027	0.0021	0.0058
Sr(NO ₃) ₂	0.0004	0.0003	0.0004
Th(NO ₃) ₄ ·4H ₂ O	0.0141	0.0107	0.0326
UO ₂ (NO ₃) ₂ ·6H ₂ O	0.0244	0.0185	0.0655
Total solids	0.4866	0.3690	0.5440
Water	0.5134	0.6310	0.4560
Sludge	1.0000	1.0000	1.0000

Table 13. The measured grout densities and grout volume relative to the surrogate MVST wet sludge volume for the sensitivity testing grouts

Surrogate MVST sludge	Grout no.	Grout density (g/mL)	Volume ratio of grout to wet sludge
High waste loading			
Standard	1	1.76	1.44
	2	1.72	1.36
	3	1.78	1.57
	4	1.75	1.39
	5	1.82	1.47
Minimum water + maximum bad actors	1	1.64	1.55
Maximum water	1	1.82	1.39
Low waste loading			
Standard	1	1.81	1.93
	2	1.84	1.57
	3	1.85	2.11
	4	1.80	1.86
	5	1.84	2.00
Minimum water + maximum bad actors	1	1.74	2.01
Maximum water	1	1.91	1.83

Table 14. Free waters measured for the sensitivity testing grouts

Surrogate MVST sludge	Grout no.	Free water (vol%)				
		1 d	3 d	5 d	7 d	28 d
High waste loading						
Standard	1	0.4		0.0		0.0
	2	1.6	0.8			0.0
	3	0.0	0.0			0.0
	4	0.4	0.0			0.0
	5	0.0	0.0			0.0
Minimum water + maximum bad actors	1	0.0		0.0		0.0
Maximum water	1	0.0				0.0
Low waste loading						
Standard	1	0.0				0.0
	2	0.4	0.0			0.0
	3	0.0	0.0			0.0
	4	1.2	1.6		0.8	0.0
	5	0.8	0.0			0.0
Minimum water + maximum bad actors	1	3.2		1.2		0.0
Maximum water	1	0.8		0.0		0.0

Table 15. Unconfined compressive strengths measured for the sensitivity testing grouts

Surrogate MVST sludge	Grout no.	Unconfined compressive strength (psi)				
		1	2	3	Avg.	Std. dev.
High waste loading						
Standard	1	1959	1367		1663	296
	2	373	992	964	776	286
	3	1688	1865	1485	1679	155
	4	720	2842		1781	1061
	5	2121	2191	1945	2086	103
Minimum water + maximum bad actors	1	1042	1560	1414	1339	218
Maximum water	1	899	2107	2425	1810	657
Low waste loading						
Standard	1	472	593	561	542	51
	2	158	40	340	179	123
	3	928	960	989	959	25
	4	464	543		504	39
	5	716	637		676	39
Minimum water + maximum bad actors	1	572	443		507	65
Maximum water	1	1276	2500		1888	612

Table 16. TCLP extract concentrations measured for the sensitivity testing grouts

Surr. MVST sludge	Grout no.	TCLP extract concentration, mg/L							TCLP fluid no.	pH
		Cd	Cr	Hg ^a	Pb	Se	Tl	U		
High waste loading										
Std.	1	<0.002	0.014	0.0002	0.009	0.053	<0.006	0.071	1	10.23
	2	<0.002	0.013	0.0003	0.016	0.028	<0.006	<0.039	1	10.50
	3	<0.002	0.011	0.0004	0.009	0.041	<0.006	<0.039	1	10.29
	4	<0.002	0.014	0.0004	0.008	0.130	<0.006	<0.039	1	10.36
	5	<0.002	0.010	0.0003	0.008	0.083	<0.006	<0.039	1	10.41
Min. water + max. bad actors	1	<0.002	0.022	0.0001	0.009	0.034	<0.006	<0.039	1	10.43
Max. water	1	<0.002	0.038	0.0002	0.012	0.019	<0.006	0.103	1	10.51
Low waste loading										
Std.	1	<0.003	<0.003	<0.0001	<0.009	0.234	<0.011	6.491	2	9.52
	2	<0.002	0.005	0.0003	0.009	0.058	<0.006	<0.039	1	10.47
	3	<0.002	0.005	0.0003	0.009	0.059	<0.006	<0.039	1	10.62
	4	<0.002	0.007	0.0002	0.010	0.187	<0.006	<0.039	1	10.56
	5	<0.002	0.007	0.0004	0.009	0.078	<0.006	<0.039	1	10.66
Min. water + max. bad actors	1	<0.002	0.005	0.0001	0.009	0.068	<0.006	<0.039	1	10.51
Max. water	1	<0.002	0.066	0.0002	0.015	0.107	<0.006	0.3	1	10.52
TCLP UTS ^b										
		0.190	0.860	0.025	0.370	0.160	0.078	N/A ^c		

^aMeasured by cold vapor atomic absorption; all other extract concentrations were measured by ICP.^bThe UTS limits for the TCLP extract concentration.^cNot applicable.

Table 17. The measured leachability indexes of ^{85}Sr and ^{137}Cs for the sensitivity testing grouts

Surrogate MVST sludge	Grout no.	Leachability index	
		⁸⁵ Sr	¹³⁷ Cs
High waste loading			
Standard	1	9.5 ^a	9.9 ^a
	2	9.4	9.7
	3	10.0	10.5
	4	9.4	9.9
	5	9.9	10.1
Minimum water + maximum bad actors	1	9.2	9.3
Maximum water	1	9.6	10.5
Low waste loading			
Standard	1	8.7 ^a	9.5 ^a
	2	8.7	9.4
	3	9.1	10.1
	4	8.0	8.7
	5	9.5	10.2
Minimum water + maximum bad actors	1	8.5	8.7
Maximum water	1	9.1	10.0

^aAverage of three.

Table 18. Calculated surrogate composition on an oxide basis

Species	g/kg dry-waste
Ag/Ag ₂ O	0.040
Al/Al ₂ O ₃	13.467
As/As ₂ O ₃	0.000
Au/Au ₂ O	0.000
B/B ₂ O ₃	0.000
Ba/BaO	0.000
Ca/CaO	112.500
Cd/CdO	0.048
Ce/Ce ₂ O ₃	0.000
Ce/CeO ₂	0.000
Co/CoO	0.000
Co/Co ₃ O ₄	0.000
Cr/Cr ₂ O ₃	0.309
Cs/Cs ₂ O	0.000
Cu/CuO	0.000
Fe/Fe ₂ O ₃	4.170
Fe/FeO	0.000
K/K ₂ O	36.712
La/La ₂ O ₃	0.000
Li/Li ₂ O	0.000
Mg/MgO	29.505
Mn/MnO	0.000
Mn/MnO ₂	0.000
Mo/MoO ₃	0.000
Na/Na ₂ O	221.655
Nd/Nd ₂ O ₃	0.000
Ni/NiO	0.000
P/P ₂ O ₅	0.000
Pb/PbO	0.617
Rb/Rb ₂ O	0.000
Ru/RuO ₂	0.000
Sb/Sb ₂ O ₃	0.007
Se/SeO ₂	0.138
Si/SiO ₂	0.000
Sn/SnO ₂	0.000
Sr/SrO	0.341
Tc/TcO ₂	0.000
Te/TeO ₂	0.000
Th/ThO ₂	15.987
Ti/TiO ₂	0.000
U/UO ₃	29.036
U/UO ₂	0.000
Tl/Tl ₂ O	0.035
Zn/ZnO	0.000
Zr/ZrO ₂	0.000
S/SO ₄	3.781
Cl/Cl ₂ O	6.793
F	1.300
Totals	475.141

Table 19. Scoping glass recipes tested

Sample ID & recipe	Pour date & temp	Pour description & (g loaded /g product) & density (d)	Melt description
MVST-V-1-1400 Waste: 31.57 CaCO ₃ : 56.76 Ott. Sand: 103.25	6-6-96 @ 1400°C	Poured fairly quickly, like STP, but very clumpy. (191.2 /149.3) d=2.6	Pan: glass is glossy and bright yellow with large amounts of white material both inside and the surface of the glass. The yellow portion is transparent. Crucible: pour is very thick. Glass looks like pan glass, except the pour portion has a thick white crust, particularly on the right. Glass in bottom has the same white crust ringed round the top. May be some very slight wicking (?). Pan: glass is smooth, glossy and a very bright neon-lime color. Crucible: glass looks just like pan glass. May be some very slight wicking (?).
MVST-V-5-1400 Waste: 31.58 CaCO ₃ : 54.30 Ott. Sand: 103.25	6-6-96 @ 1400°C	Beautiful, smooth, pour fast only, slightly slower than water. Kyanites from V-1 and V-5; both stayed in furnace. (188.8/149.0) d=2.5	
MVST-V-6-1100 Waste: 31.58 Na ₂ CO ₃ : 92.31 Ott. Sand: 81.01	6-12-96 @ 1100°C	Smooth pour; like thick STP. (NA) d=2.6	Pan: glass is bright yellow, glossy and smooth. Bubbles, single or in small groups can be seen inside the glass, which is transparent. Crucible: glass on pour side looks the same as the pan glass. The glass overflowed the alumina and the kyanite, leaving a very thin yellow glaze on both crucibles. It went onto the alumina "slab" on the bottom of the furnace, but didn't go through; it flowed over and only slightly into the slab.
MVST-V-7-1100 Waste: 129.60 Na ₂ CO ₃ : 20.43 Ott. Sand: 76.48	6-12-96 @ 1100°C	Whatever could be poured looked good, but this sample overflowed both crucibles in a big way. Like V-6, the overflow was not very corrosive and only made a shallow indentation where it flowed over the alumina slab. (NA) d=2.6	Pan: glass is bright yellow, smooth and glossy. It would be transparent except that each piece is full of bubbles. Bubbles can even be seen in the stringers. Crucible: the most colorful crucible to date! Pour side has glass similar to pan glass. The overflow on both the inside and outside of the crucible does not resemble glass; it's crumbly and not glossy, but rough. The colors are mostly orange, yellow, green-gray and brown in separate layers.
MVST-V-8-1100 Waste: 111.12 CaCO ₃ : 35.44 Ott. Sand: 77.37	6-12-96 @ 1100°C	No pour; sample crusted over. (223.5/148.0) d=2.6	Pan: no pour. Crucible: sample appears not to have melted, but it did shrink in volume. The material is segregated into the same colors as V-7, but it's very porous and crumbly-looking.

Table 19. (continued)

MVST-V-2-1400 Waste: 63.14 CaCO ₃ : 33.00 Ott. Sand: 101.55	6-17-96 @ 1400°C	Kyanite crucible cracked. Nice, smooth pour, like STP. No clumps or bubbles noted. (196.8/148.8)	d=2.6	<p>Pan: glass is very bright yellow-green; smooth, glossy and transparent. The side which hit against the pan is dull and translucent. There are small notches in the bottom glass which were probably air bubbles as the glass hit the surface. There are also some bubbles in the glass.</p> <p>Crucible: Pour glass looks like pan glass. There is a crust on top of the melt line which is white and extends around the crucible except where the pour glass is located. There is a thin layer of glass up the sides, but no higher than the original fill line.</p>
MVST-V-3-1400 Waste: 94.72 CaCO ₃ : 33.00 Ott. Sand: 101.55	6-17-96 @ 1400°C	Pour was slightly faster and thinner than V-2. Again, no clumps or bubbles. (203.0/147.6)	d=2.6	<p>Pan: glass is the same as V-2. The circle on the pan is slightly larger due to the lower viscosity.</p> <p>Crucible: pour glass appears the same as pan glass. The thin glass layer is again no higher than the original height of the sample. Glass in the bottom of the crucible really fractured.</p>
MVST-V-4-1400 Waste: 77.36 Na ₂ CO ₃ : 21.51 Ott. Sand: 100.69	6-17-96 @ 1400°C	Thinner still; getting close to water in viscosity. Nice smooth pour. (198.9/147.5)	d=2.6	<p>Pan: glass the same as the two previous pours. The circle on the pan is the largest of the three.</p> <p>Crucible: poured more of this glass, so the color of the remaining glass appears light yellow. No crust; no thin glass layer.</p>
MVST-V-6a-950 Waste: 31.58 Na ₂ CO ₃ : 92.31 Ott. Sand: 81.01	6-25-96 @ 950°C	No pour. (204.5/151.8)	d=NA	<p>Pan:</p> <p>Crucible: material texture like stiff cream of wheat. Pliable. Pale yellow in color with orange visible around top 1/2-in. edge of sample. Volume about the same as start.</p>
MVST-V-7a-950 Waste: 129.60 Na ₂ CO ₃ : 20.43 Ott. Sand: 76.48	6-25-96 @ 950°C	No pour. (226.1/150.3)	d=NA	<p>Pan:</p> <p>Crucible: crucible has material slightly over the top. Bottom has a porous crust of gold and orange with brown lumps. Sides have a color progression of gold crust (like bottom) over a brown layer, then an orange layer, orange-brown, dark brown (narrow band) and tan, yellow and orange at the top. Layers are porous and crusty up to the tan layer which is much smoother. Splatter on lid.</p>
MVST-V-8a-950 Waste: 111.12 Na ₂ CO ₃ : 35.44 Ott. Sand: 77.39	6-25-96 @ 950°C	No pour. (223.6/149.5)	d=NA	<p>Pan:</p> <p>Crucible: Sandy texture. Came out of crucible in a lump, but fairly easy to break apart. Grains of green, orange, yellow and white.</p>

Table 20. TCLP values (mg/L) from scoping glasses prepared with MVST surrogate

Species	V-1	V-2	V-3	V-4	V-5	V-6	V-7	V-9	V-10	V-11	V-12	V-13
Ag	0.002	0.004	0.004	0.004	0.002	0.004	0.004	0.002	0.002	0.002	0.002	0.002
Al	0.033	0.067	0.263	0.358	0.033	0.778	1.876	1.107	0.929	1.212	1.376	0.363
As	0.008	0.016	0.016	0.016	0.008	0.016	0.016	0.008	0.008	0.008	0.008	0.008
B	0.219	0.294	0.316	0.316	0.199	0.313	0.864	1.054	0.961	1.191	1.534	0.983
Ba	0.303	0.411	0.470	0.522	0.280	0.327	0.992	1.496	1.561	1.569	1.677	1.151
Be	0.001	0.002	0.002	0.002	0.001	0.002	0.002	0.001	0.001	0.001	0.001	0.006
Ca	2.265	1.850	1.700	1.880	0.681	0.600	136.4	390.0	395.0	396.0	390.0	1.220
Cd	0.002	0.003	0.003	0.003	0.002	0.003	0.034	0.012	0.013	0.012	0.015	0.007
Cr	0.003	0.007	0.012	0.060	0.056	0.033	0.041	0.104	0.100	0.102	0.112	0.009
Fe	0.066	0.079	0.320	0.139	0.064	0.136	0.158	0.336	0.311	0.354	0.399	0.153
K	0.635	0.152	0.263	0.552	4.280	31.60	10.85	21.67	23.21	22.13	21.83	0.711
Mg	0.049	0.040	0.040	0.092	0.075	0.271	8.710	14.02	14.90	14.32	14.89	0.181
Mn	0.001	0.018	0.023	0.385	0.004	0.007	0.008	0.007	0.005	0.010	0.004	0.009
Na	1087	1394	1417	1470	1411	2181	1645	1767	1790	1817	1735	1527
Ni	0.004	0.009	0.009	0.013	0.004	0.009	0.009	0.004	0.007	0.004	0.004	0.085
Pb	0.004	0.012	0.016	0.016	0.004	0.022	0.143	0.049	0.049	0.053	0.056	0.018
Se	0.009	0.018	0.018	0.018	0.009	0.018	0.046	0.009	0.009	0.009	0.009	0.012
Sb	0.006	0.011	0.011	0.011	0.006	0.011	0.011	0.006	0.006	0.006	0.006	0.008
Si	1.300	1.490	1.750	2.420	2.900	74.42	96.26	68.30	70.40	75.30	71.20	1.554
Ti	0.001	0.002	0.002	0.002	0.001	0.004	0.002	0.011	0.010	0.011	0.013	0.009
Tl	0.006	0.011	0.011	0.011	0.006	0.011	0.011	0.006	0.006	0.006	0.006	0.006
U	0.039	0.078	0.078	0.135	0.054	0.427	8.470	3.010	2.790	3.120	3.500	0.039
V	0.009	0.018	0.018	0.018	0.009	0.018	0.021	0.041	0.043	0.048	0.042	0.028
Zn	0.383	0.567	0.612	0.636	0.380	0.336	1.163	1.606	1.562	1.533	1.742	1.148
Zr	0.003	0.007	0.007	0.007	0.003	0.021	0.085	0.255	0.238	0.244	0.269	0.006

Table 21. Feed and glass compositions for the MVST glass sensitivity testing

MVST-V no.	Feed mix (mass fraction)			Ternary glass compositions (mass fraction)		
	CaCO ₃	Spiked dried waste	SiO ₂	Alkaline oxides	Alkali oxides	Glass former oxides
18 ^a	0.143	0.410	0.447	0.198	0.152	0.650
19 ^b	0.131	0.459	0.410	0.206	0.176	0.618
20 ^b	0.154	0.363	0.483	0.192	0.130	0.678
21 ^b	0.155	0.446	0.398	0.224	0.172	0.604
22 ^b	0.130	0.373	0.497	0.174	0.133	0.693
23 ^c	0.143	0.410	0.447	0.198	0.152	0.650
24 ^d	0.143	0.410	0.447	0.198	0.152	0.650
25 ^d	0.143	0.410	0.447	0.198	0.152	0.650

^aStandard glass selected for sensitivity testing.

^bOne of the ± 10 wt% variations in the feed mix picked for sensitivity testing.

^cStandard glass feed using the dried MVST surrogate sludge with maximum RCRA metals.

^dReplicate of MVST-V18, the standard glass.

Table 22. $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple determinations for glass products of sensitivity testing

Sample ID	Fe^{2+}	Fe total	$\text{Fe}^{2+}/\text{Fe}^{3+}$	% reduced Fe
MVST-V-9	0.007	0.028	0.33	25
	0.007	0.029	0.32	24.1
MVST-V-10	0.004	0.021	0.24	19
	0.007	0.026	0.37	26.9
MVST-V-11	0.005	0.022	0.29	22.7
	0.013	0.041	0.46	31.7
MVST-V-12	0.012	0.046	0.35	26.1
	0.016	0.061	0.36	26.2
MVST-V-18	0.002	0.014	0.2	14.3
	0.001	0.015	0.08	6.7
MVST-V-19	0.002	0.015	0.18	13.3
	0.003	0.017	0.27	17.6
MVST-V-20	0.001	0.012	0.1	8.3
	0.002	0.015	0.18	13.3
MVST-V-21	0.001	0.013	0.09	7.7
	0.002	0.016	0.17	15.5
MVST-V-22	0.004	0.02	0.33	20
	0.006	0.023	0.54	26.1
MVST-V-23	0.003	0.018	0.25	16.7
	0.004	0.02	0.33	20
MVST-V-24	0.006	0.025	0.46	24
	0.006	0.027	0.4	22.2
MVST-V-25	0.004	0.022	0.28	18.2
	0.006	0.027	0.4	22.2

**Table 23. Composition of the surrogate MVST sludge solids
used in the glass sensitivity testing**

Compound	Standard (mass fraction)	With maximum RCRA metals (mass fraction)
RCRA metals		
Ag ₂ O	0.000039	0.000099
CdO	0.000048	0.000088
Na ₂ Cr ₂ O ₇	0.000524	0.000881
HgCl ₂	0.000082	0.000147
PbO	0.000608	0.000930
SeO ₂	0.000135	0.000143
TiNO ₃	0.000043	0.000048
Process metals		
Al(OH) ₃	0.0203	0.0203
CaCO ₃	0.1367	0.1366
Ca(OH) ₂	0.0454	0.0454
Fe ₂ O ₃	0.0041	0.0041
KNO ₃	0.0777	0.0777
MgCO ₃	0.0068	0.0067
Mg(OH) ₂	0.0374	0.0374
NaNO ₃	0.5727	0.5722
NaCl	0.0089	0.0089
NaF	0.0029	0.0029
Na ₂ SO ₄	0.0056	0.0056
Sr(NO ₃) ₂	0.0008	0.0008
Th(NO ₃) ₄ ·4H ₂ O	0.0290	0.0290
UO ₂ (NO ₃) ₂ ·6H ₂ O	0.0502	0.0501
Total solids	1.0000	1.0000

Table 24. Glass bulk density and ratio of glass volume to wet sludge for the sensitivity testing

Glass leach sample	Calculated bulk density ^a (g/mL)	Calculated volume ratio of glass/wet sludge
MVST-V-18	2.80	0.42
MVST-V-19	2.45	0.43
MVST-V-20	2.50	0.54
MVST-V-21	2.58	0.42
MVST-V-22	2.57	0.50
MVST-V-23	2.54	0.47
MVST-V-24	2.51	0.47
MVST-V-25	2.57	0.46

^aBulk density calculated for leach samples assuming perfect right cylinders. With the slightly rounded tops, this includes some air volume at the top, in addition to the gas bubbles trapped inside the glass.