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# **Idaho Nuclear Technology and Engineering Center Low-Activity Waste Process Technology Program FY-99 Status Report**

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**IDAHO NUCLEAR TECHNOLOGY  
AND ENGINEERING CENTER  
LOW-ACTIVITY WASTE PROCESS  
TECHNOLOGY PROGRAM  
FY-99 STATUS REPORT**

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## **ABSTRACT**

The Low-Activity Waste Process Technology Program at the Idaho Nuclear Technology and Engineering Center (INTEC) anticipates that large volumes of low-level/low-activity wastes will need to be grouted prior to near-surface disposal. During fiscal year 1999, grout formulations were studied for transuranic waste derived from INTEC liquid sodium-bearing waste and for projected newly generated low-level liquid waste. Additional studies were completed on radionuclide leaching, microbial degradation, waste neutralization, and a small mockup for grouting the INTEC underground storage tank residual heels.

## SUMMARY

The general purpose of the Low-Activity Waste Process Technology Program is to solidify and stabilize the liquid low-activity wastes (LAW) generated at the Idaho Nuclear Technology and Engineering Center (formerly the Idaho Chemical Processing Plant). It is anticipated that LAW will be produced from the following: (1) chemical separation of the tank farm liquid sodium-bearing waste, (2) chemical separation of dissolved aluminum and zirconium calcines, and (3) facility decontamination and process equipment wastes. Grout formulation studies included cesium separated sodium-bearing waste and newly generated liquid wastes. Additional studies were completed in radionuclide leaching, microbial degradation, and pH adjustment. A small scale mockup test was completed for grouting the tank farm vessel residual heels.

Initial grout formulations were developed for the cesium separated sodium-bearing waste and the projected newly generated liquid waste. The cesium separated waste would be a transuranic waste that could be sent to the Waste Isolation Pilot Plant. A waste loading of up to 70% weight percent was successfully prepared. Grout formulations of up to 47% weight percent can be prepared for one projected newly generated liquid waste. Both of these formulations utilize the waste as the liquid for the cement powders. The small lab-scale mockup test for the closure of the underground storage tank residual heels demonstrated that Savannah River reducing grout will work with the acidic heels.

During FY-2000, the cesium separated sodium-bearing waste process will continue to be studied to refine the grout formulation and document its properties. For the newly generated liquid waste, research will continue to determine if a viable process can be demonstrated to divert the new waste from the tank farm. The international contract with AEA Technologies will continue in support of the newly generated liquid waste demonstration project. Additionally, the Tanks Focus Area plans to provide matching funds for this latter project.

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## NOMENCLATURE

<b>Acid Grout</b>	A grout formulation where the acidity of the waste is kept to a pH less than 1.0 and mixed with a 3:1:1 blend of blast furnace slag, portland cement, and fly ash.
<b>Alkaline Grout</b>	A grout formulation where the waste is rendered basic (pH > 12) and mixed with a 9:1 blend of blast furnace slag and portland cement.
<b>Blast Furnace Slag</b>	A finely ground non-metallic waste produce developed in the manufacture of pig iron, consisting basically of a mixture of lime, silica, and alumina, the same oxides that make up portland cement, but not in the same proportions or forms.
<b>Calcination</b>	The process of converting a liquid to a solid product called calcine.
<b>Calcine LAW</b>	Low-activity waste derived from dissolved, separated calcine solids.
<b>Cement</b>	Refers to type I/II portland cement.
<b>Denitration</b>	A thermal process to destroy the nitrate content of the waste.
<b>Fly Ash</b>	A pozzolan of finely divided residue that results from the combustion of ground or powdered coal. Class C fly ash may contain 10% lime, has cementitious properties, and reacts with water to form a solid. Class F fly ash does not use water and aids in grout flow.
<b>Grout</b>	A mixture of portland cement, other powdered additives, waste, and water. It may contain fine-grained sand and does not include large aggregate material. For this study, grouting is the process of solidifying and stabilizing low-level waste in cement based materials.
<b>Leaching</b>	The process whereby a liquid agent will dissolve hazardous materials within a waste mass and transport these materials through the mass and beyond. The most widely used laboratory leaching test is the TCLP (Toxic Characteristic Leaching Procedure) specified by the EPA in several regulations. For many treated and untreated wastes, the results of this test determine whether the EPA considers the material toxic or not.
<b>Low-Activity Waste</b>	Low-level waste derived from the solvent extraction, ion exchange, and chemical extraction separation processes on the tank farm sodium-bearing waste and on the dissolved calcines.
<b>Na LAW</b>	Low-activity waste derived from sodium-bearing waste.
<b>Portland Cement</b>	The product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates.

<b>Pozzolan</b>	A siliceous or siliceous and aluminous material that reacts with liquid calcium hydroxide in the cement gel to form compounds possessing cementitious properties.
<b>3-Way Blend</b>	A 1:1:1 blend of portland cement, blast furnace slag, and coal fired power plant fly ash on a mass basis.
<b>Solidification</b>	The process of producing from liquid, sludge, or loose solids a more or less monolithic structure having some integrity. Occasionally, solidification may refer to the process that results in a soil-like material rather than a monolithic structure. Solidification does not necessarily reduce leaching of hazardous materials. However, when a waste is solidified, its mass and structure are altered, decreasing migration of solutions within the mass.
<b>Stabilization</b>	Generally refers to a purposeful chemical reaction that has carried out to make waste constituents less leachable. This is accomplished by chemically immobilizing hazardous materials or reducing their solubility by a chemical reaction.
<b>Water-to-Cement Ratio</b>	Defined as the mass of the water divided by the mass of the cements used (portland cement plus cement additives). In the case of the three way blends of portland cement, blast furnace slag, and fly ash, the mass of the water was divided by the total mass of the three cementing agents. The mass of the waste is not included in this calculation.
<b>Waste Form</b>	The final product for long-term storage. This includes the solidified/stabilized waste as well as the container. The waste form must pass extensive qualification testing prior to release for storage.
<b>Waste Loading</b>	The mass weight percent of the waste in the total mass of the mixed grout.
<b>Vitrify</b>	The process of placing waste material in a glass form. This is a thermal process where the waste material is placed in a melter with glass beads or frit, then heated together, poured into a storage container, and cooled to a solid form.
<b><math>Vol_{grout} / Vol_{sim}</math></b>	The ratio of the volume of grout produced from a given volume of the original liquid low-level waste volume. For a ratio of 4, the volume of grout would be 4 times greater than the original volume of the liquid waste. If the ratio is less than 1.0, the volume of grout would be less than the original liquid waste volume. An objective of the preconditioning and grouting processes is to optimize (reduce) this ratio; thus, reducing final repository costs based on volume.

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# IDAHO NUCLEAR TECHNOLOGY AND ENGINEERING CENTER LOW-LEVEL WASTE PROCESS TECHNOLOGY PROGRAM FY-99 STATUS REPORT

## 1. INTRODUCTION

The High-Level Waste Program Plan for the Idaho Nuclear Technology and Engineering Center (INTEC) calls for the sodium-bearing liquid waste in the tank farm to be separated into high-activity and low-activity radioactive wastes.<sup>1</sup> The calcine in the storage bins will be retrieved, dissolved in nitric acid, and separated. The small volume, high-activity waste will be vitrified and disposed of in a geological repository. The large volume, low-activity waste (LAW) will be grouted and either returned to the tank farm vessels or disposed of in drums. In addition to the LAW derived from separations, facility decontamination and the process equipment waste system will continue to generate low-level waste (LLW) liquids to be grouted. These decontamination and process equipment solutions are also a form of sodium-bearing waste. This research, performed by the LAW Process Technology group, provides data on the various LAW/LLW alternatives being proposed by the Department of Energy (DOE) High-Level Waste and Facilities Disposition Environmental Impact Statement.

The fiscal year 1999 work is discussed in six main sections. The first two sections present grout formulation tests with sodium-bearing waste and newly generated waste simulants. The next section covers the lab-scale mockup test for underground storage tank heel closure and in particular the performance of Savannah River's reducing grout formulation with projected INTEC tank heels. Another section covers the radionuclide leach study, followed by the microbial degradation study. The final section covers the chemical neutralization of the INTEC acidic wastes for pretreatment options.

The criteria for an acceptable grout formulation and waste form are governed by the Department of Energy and augmented with guidelines from the U.S. Nuclear Regulatory Commission. These documents are Department of Energy Order 435.1, "Radioactive Waste Management,"<sup>2</sup> and the "Technical Position on Waste Form," published by the Low-Level Waste Management Branch of the U.S. Nuclear Regulatory Commission (NRC).<sup>3</sup> The NRC guidelines are specifically directed at grouted waste forms and contain definitive qualifications in the areas of compressive strength, leach resistance, thermal cycling, immersion testing, and irradiation. In the case of cesium separated sodium-bearing waste, a transuranic waste is produced for which the Waste Isolation Pilot Plant acceptance criteria applies.

## 2. CsIX WASTE GROUT DEVELOPMENT

In January 1990, the U.S. Environmental Protection Agency (EPA) issued to the Department of Energy (DOE) a Notice of Noncompliance because the Idaho Nuclear Technology and Engineering Center (INTEC) tank farm facility (TFF) did not meet the secondary containment requirements of the Resource Conservation and Recovery Act (RCRA). As a part of the Settlement Agreement between DOE and the State of Idaho, the TFF tanks are to be taken out of service by December 31, 2012. Two obvious elements of the TFF tanks closure are: 1) the removal, treatment and disposal of the remaining liquid mixed waste, and 2) the treatment and disposal of future-generated liquid mixed wastes. Currently the TFF contains a total waste inventory of approximately 1.5 million gallons from past reprocessing operations and decontamination efforts, HLW and sodium-bearing waste (SBW), respectively.

Several potential options have been proposed for dealing with both the current and future liquid wastes mentioned above. Of the options in which grouting technologies are used, perhaps the most preferred for the treatment and disposal of existing TFF waste includes: 1) separating the cesium from the liquid, 2) solidifying the liquid using alkaline cement-based grout additives, and 3) disposing of the solid as contact-handled transuranic (TRU) waste at the Waste Isolation Pilot Plant (WIPP). This cesium-separated waste will be referred to as CsIX waste throughout the remainder of this report.

Of the potential options for the treatment and disposal of the majority of future liquid mixed waste, the currently preferred option is to: 1) concentrate a major fraction of that waste in the PEW evaporator, 2) possibly remove (via separations technologies) specific radioisotopes from the concentrated waste, 3) solidifying the liquid using alkaline cement-based grout additives, and 4) disposing of the final solidified waste at Envirocare or a low-activity waste (LAW) disposal facility. This "newly generated liquid waste" will be referred to as NGLW waste throughout the remainder of this report.

Tests are being conducted to develop alkaline cement-based grout formulations for both CsIX and NGLW wastes. As both wastes are very similar in composition, development progress for one grout application is often very useful for the other. For this reason, grout development testing results and progress for both waste streams are included in a single report.

Grout development works for CsIX and NGLW wastes are presented below in separate sections of this report. Prior to these sections on actual testing, and as an aid in the understanding of grout solidification/treatment of wastes, a brief description of immobilization grout chemistry follows.

### 2.1 Immobilization Grout Overview

Complete detoxification of metals is impossible by chemical, biological, or other means. Thus, methods which isolate the hazardous metals and/or radioelements are necessary.<sup>4</sup> Grouting with alkaline chemicals is generally the most successful and widely used solidification/stabilization (S/S) technology for aqueous mixed waste treatment. Alkaline grout provides solidification of aqueous waste through hydration reactions of the cement components, and immobilization of waste species via two mechanisms: physical entrapment and chemical interaction.

In cement chemistry, the following nomenclature is used to designate the various reactive oxides: C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, H = H<sub>2</sub>O, and F = Fe<sub>2</sub>O<sub>3</sub>.

The four major components of clinker are tricalcium silicate, C<sub>3</sub>S (35 to 65%); dicalcium silicate, C<sub>2</sub>S (10 to 40%); tricalcium aluminate, C<sub>3</sub>A (0 to 15%); and calcium aluminoferrite,

C<sub>4</sub>AF (5 to 15%).<sup>5,6</sup> Ordinary portland cement (OPC) is a mixture of clinker and gypsum, the later component being added as a function of the concentration of calcium aluminate present in the clinker in order to control the rate of set. Although the cement components will each result in hydration products, they have significant differences in their rates of reaction with water, and the amounts of heat generated from those reactions. Heats of reaction associated with mixing each component with water are shown in Table 1. The reaction rate order correlates directly with the heats of reaction; the component with the highest heat of reaction (C<sub>3</sub>A) reacts with water the fastest, while the component with the lowest heat of reaction (C<sub>2</sub>S) reacts with water the slowest.

Another equally important and often overlooked property of cement and cementitious additives is solubility based on particle size and crystalline structure.

**Table 1.** Heats of Reaction With Water for Cement Components

<b>Clinker Component Reacted With Water</b>	<b>Heat of Hydration (cal/g)</b>
C <sub>3</sub> A	320
C <sub>3</sub> S	120
C <sub>4</sub> AF	100
C <sub>2</sub> S	60

OPC is produced in several different mass ratios of the above oxides. An OPC "type" identifies the general composition ranges of the various reactive oxides, and the cement particle size. Thus, as described above, the different OPC types vary by reaction properties (i.e., reaction rate, heat generation).

Cementitious additives (pozzolans), consisting of one or more of the same components in OPC, also vary significantly in solubility and reactivity. Thus, changes in a grout formulation generally result in differences in waste form density, compressive strength, alkaline capacity, etc. These property differences can be subtle (unnoticed) or significant. Typical compositions of the two types of OPC (Type I/II and Type V) and of other cementitious additives used in this testing are given in Table 2. A general description of the proposed benefits of major cementitious grout additives follows:

Calcium Oxide (CaO): Neutralizes acid, decreases water content, acts as the "binding" component in OPC, increases initial heat evolution, decreases mix fluidity, hastens grout set, and precipitates multiple waste species.

Fly Ash (FA): Slows hydration reactions, lowers initial heat evolution, increases mix fluidity, decreases permeability, and increases density.

Blast Furnace Slag (BFS): Slows hydration reactions, lowers initial heat evolution, increases mix fluidity, and improves the retention of reducible mobile species by lowering the internal solution redox potential (Eh).

Silica Fume (SF): Decreases permeability, increases sorption of metals, and decreases mix fluidity.

**Table 2.** Typical Composition of Cements and Cementitious Additives (wt%).

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>
Type I/II OPC	21.3	5.0	2.9	64.0	2.8	2.6
Type V OPC	25.0	3.4	2.8	64.4	1.9	1.6
BFS	34.0	10.0	0.8	41.0	11.0	
Fly Ash*	66.0	12.0	4.0	4.0		
Silica Fume	96.0					

\*Substantial fraction is non-reactive (insoluble).

For heavy (toxic) metal immobilization, hydroxide precipitation, which is inherent to alkaline grouts, is effective for Cd, Cr(III), and Pb. Sulfide precipitation is effective for Hg. Chemical reduction is effective for Cr, Hg, and Pb. The later two techniques (sulfide precipitation and reduction) are achieved in this testing by the addition of a sulfide into the grout mix, via the use of BFS in the grout makeup, or by direct chemical addition.

## 2.2 CsIX Waste Grout Development

The waste acceptance criteria (WAC) for WIPP includes several requirements with respect to both radioisotope concentrations and transportation to the disposal facility (i.e. truckload total weight). However, essentially the only requirement with respect to waste solidification is just that, the final waste product must be solid (<2 liters total residual liquid per 55-gallon drum). Unlike LAW disposal requirements, and primarily based on the acceptance of a "no-migration petition", TRU waste disposal at WIPP has no other legal physical or leach requirements. Nonetheless, political pressure may deem it prudent to produce TRU waste forms that meet self-imposed criteria more stringent than the WIPP WAC minimum.

In this light, two separate approaches have been implemented for the development of solidification methods for potential CsIX waste. The first approach deals with maximizing waste loading while simply satisfying the "no liquids" criteria of the WIPP WAC. The second approach deals with developing and optimizing grout formulations to produce a reasonable waste form monolith, satisfying both the RCRA land disposal requirements (LDR) for immobilizing toxic elements and the recommended requirements of the Nuclear Regulatory Commission (NRC) for LAW disposal.

The calculated average composition of CsIX waste (after Cs separation and waste concentration), without the radioactive components, is presented in Table 3.

### 2.2.1 CsIX Maximum Waste Loading Testing

Two groups of tests were performed for the CsIX waste maximum loading approach to WIPP disposal. The initial maximum waste-load (IMWL) samples were generated to determine the approximate upper waste-loading boundary of alkaline grout solidification, which is limited by the preliminary requirement of acid neutralization. IMWL tests were performed using a non-radioactive tank farm waste simulant that contained no toxic metals. The composition of this waste simulant solution is contained in Table 3.

**Table 3.** Compositions of Proposed CsIX Waste (Excluding Radioisotopes) and Test simulants

Species	Calculated CsIX Waste (M)	IMWL Test Simulant (M)	CsIX GO and SMWL Test Simulant (M)
H	1.94	1.57	1.94
Ag	$2.75 \times 10^{-5}$		
Al	$7.84 \times 10^{-1}$	$6.40 \times 10^{-1}$	$7.84 \times 10^{-1}$
As	$6.07 \times 10^{-5}$		
B	$1.91 \times 10^{-2}$	$1.80 \times 10^{-2}$	$1.91 \times 10^{-2}$
Ba	$7.23 \times 10^{-5}$		
Ca	$5.76 \times 10^{-2}$	$5.27 \times 10^{-2}$	$5.76 \times 10^{-2}$
Cd	$3.32 \times 10^{-3}$		$3.32 \times 10^{-3}$
Cl	$4.05 \times 10^{-2}$	$2.87 \times 10^{-2}$	$4.06 \times 10^{-2}$
Cr	$4.78 \times 10^{-3}$		$4.78 \times 10^{-3}$
Cs		$1.03 \times 10^{-5}$	
F	$7.12 \times 10^{-2}$	$6.90 \times 10^{-2}$	$7.12 \times 10^{-2}$
Fe	$2.71 \times 10^{-2}$	$2.20 \times 10^{-2}$	$2.71 \times 10^{-2}$
Hg	$1.60 \times 10^{-3}$		$1.60 \times 10^{-3}$
K	$2.45 \times 10^{-1}$	$2.04 \times 10^{-1}$	$2.45 \times 10^{-1}$
Mn	$1.59 \times 10^{-2}$	$1.22 \times 10^{-2}$	$1.59 \times 10^{-2}$
Mo	$8.43 \times 10^{-4}$	$6.17 \times 10^{-4}$	$8.43 \times 10^{-4}$
Na	2.36	1.89	2.36
Ni	$2.27 \times 10^{-3}$		$2.27 \times 10^{-3}$
NO <sub>3</sub>	6.95	4.22	6.80
Pb	$2.01 \times 10^{-3}$		$2.01 \times 10^{-3}$
PO <sub>4</sub>	$2.04 \times 10^{-2}$	$1.39 \times 10^{-2}$	$2.04 \times 10^{-2}$
Se	$3.20 \times 10^{-5}$		
Sr	$2.04 \times 10^{-5}$	$5.20 \times 10^{-6}$	$2.04 \times 10^{-5}$
SO <sub>4</sub>	$6.37 \times 10^{-2}$	$5.04 \times 10^{-2}$	$6.37 \times 10^{-2}$
Zr	$7.31 \times 10^{-3}$	$2.84 \times 10^{-3}$	$7.31 \times 10^{-3}$

Subsequent maximum waste-load (SMWL) samples were generated in attempts to improve the physical properties of the "sludges", while remaining at or near maximum waste loading. The SMWL tests were performed using a non-radioactive CsIX waste simulant. The composition of this waste simulant solution is also contained in Table 3.

Details of both groups of CsIX maximum waste loading test are presented separately below.

### 2.2.1.1 IMWL Testing

Scoping tests were performed to determine the approximate maximum weight percent loading of CsIX waste to attain a "solid", minimally satisfying the WIPP WAC.



Grout solidification of CsIX waste first requires neutralization of the acid component. Thus, the attainable percent loading of a waste is limited by its concentrations of acid and trivalent cations. Per calculation, and due largely to the acid buffering effect of the aluminum contained in the waste, approximately ten weight percent calcium oxide (CaO) must be added to attain a neutralized (pH 7) waste. Although considerable precipitation and hydration of the contained salts does occur upon neutralization, significant "water" still remains. Excess CaO will hydrate and take up some of the remaining water content of the waste ( $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$ ).

Although CaO is the "binding" component of OPC, grout "setting" will not occur in the absence of the other components to bind with ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ). Thus, for the samples prepared with CaO as the only additive to the waste simulant, the goal was simply to eliminate the "free liquid" aspect of the individual sample simulants, and not to produce a monolithic waste form. Other samples were prepared using minimal amounts of cementitious additives in an attempt to achieve a waste form with some strength.

### 2.2.1.2 IMWL Test Description and Results

Four waste solidification samples were prepared for this test using the IMWL test simulant of Table 3. Two additional samples (5A and 6A) were prepared after initially evaporating (boiling) the same waste simulant solution to approximately double the original concentration (1000 ml of simulant was boiled down to 490 ml).

For the preparation of each sample, the waste simulant was first poured into a stainless steel mixing bowl, followed by the addition and mixing of CaO for neutralization. Any additional ingredients (samples 4A and 6A) were added and mixed following the initial CaO mixing. The sample mixing was achieved using an electric kitchen-type mixer, periodically scraping the mix bowl sides manually with a rubber spatula. The sample mixture was then poured/scraped into a pint-sized plastic container with a snap-on lid, weighed, and allowed to set/cure. The compositions of the six samples prepared for this test are presented in Table 4. The samples were weighted and visually inspected after two different periods of "curing". These results are presented in Table 5.

**Table 4.** Composition of IMWL Grout Samples (wt%)

Sample	IMWL Waste Simulant	CaO	BFS	Silica Fume
1A	86.8	13.2		
2A	88.8	11.2		
3A	85.8	12.5		1.7
4A	82.4	14.3	3.7	
5A*	78.0	22.0		
6A*	75.4	18.0	6.6	

\* Waste simulant was concentrated by evaporation to 49% original volume

**Table 5.** IMWL Sample Inspection Results

Sample	Initial Mass	122 Days After Preparation			417 Days After Preparation		
		Mass	Mass Loss %	Observations	Mass	Mass Loss %	Observations
1A	209.1	206.4	1.29	little surface water, very soft	184.4	11.8	No free liquid, very soft
2A	217.4	215.0	1.10	Very soft, muddy	191.3	12.0	Same as 1A
3A	214.3	210.5	1.77	soft, muddy	186.0	13.2	Same as 1A
4A	216.1	212.7	1.57	soft/firm, layers formed	183.3	15.2	Firm but fairly easy to break (crumble)
5A	216.0	214.0	0.93	soft/firm, white spots forming	192.2	11.0	loose crystals formed on surface, firm
6A	233.8	231.4	1.03	soft/firm, dry, crystals forming	212.0	9.32	Loose crystals formed on surface, somewhat soft but firm below

### 2.2.1.3 IMWL Test Results Discussion

As expected, all of the samples prepared by just adding CaO to the waste simulant resulted in a soft "mud", having no monolithic properties. The samples prepared with small mass fractions of BFS did possess weak binding properties. The single sample prepared with a small mass fraction of SF had very minimal binding properties.

One potentially important observation for all samples is the significant weight loss after an extended curing period, indicating water diffusion through the plastic containers despite the assumed containment. Note, however, that the weight loss does not necessarily represent the evaporation and diffusion of "free" liquid (water), but more that of the "drying out" of a wet substance. Certainly even the best grout formulation will experience some weight loss over time due to the evaporation of pore water.

It is believed that even the worst of the samples prepared in this test (samples 1A and 2A) could potentially be acceptable for disposal at WIPP, per the criteria listed in the WAC, but depending on interpretation of that document. These worst-case samples of "treated" waste simulant had the consistency of a soft peanut butter, and still had some free liquid on the surface 4 months after preparation (exact amount not measured). However, the substance would likely pass a paint filter test and the volume of "free" liquid would likely be within the specified limits. Additionally, for a 55-gal drum of this substance, the addition of a few pounds of cement powder or other drying solid on the wet surface after the initial "curing" period would aid tremendously in alleviating any "free liquid" problem with little change in overall waste loading.

Test samples with the more favorable results (samples 4A and 6A) indicate that even at these extremely high loadings, some pozzolanic ingredients are beneficial, and further improvements can likely be made.

Test samples prepared using the concentrated waste (samples 5A and 6A) positively show that maximum waste loading is also limited by the water content of the waste. The volume of concentrated waste simulant used represents over twice that volume of waste simulant prior to concentration. The

increased mass of salts would likely effect the physical and chemical properties of a grout monolith. However, the absence of requirements on those properties for waste destined for WIPP encourages concentration efforts.

## 2.2.2 Subsequent Maximum Waste Loading

Although the IMWL test results indicated that waste forms containing approximately 80 wt% CsIX waste can be made that minimally meet the WIPP WAC, additional work was performed in an attempt to improve the high waste-loading grout formulation with respect to waste form strength and toxic metal leaching.

### 2.2.2.1 SWML Test Description and Results

For the SMWL tests, a waste simulant more closely representing the anticipated composition of CsIX waste was used. This simulant also contained the major toxic metals (Cr, Cd, Hg, and Pb) that will be in the CsIX waste, at the approximate same concentrations. The composition of this waste simulant is presented in Table 3.

For this testing, 50-gram samples were prepared, each having a waste loading of 70 or 80 weight percent. The formulations used in the preparation of these test samples are presented in Table 6. Each sample is identified with an "H", followed by a number. The "H" represents this SMWL testing. The number identifies the inscribed number on the respective Teflon container the sample was cured in.

For the preparation of each sample, the waste simulant was first poured into a pint-sized plastic container, followed by the addition and mixing of CaO for neutralization (for sample H-11, I/II OPC was added directly to the waste simulant). Any additional cementitious ingredients were then added and mixed. When used, CaS was added and mixed into the grout mixture last. The sample mixing was achieved manually, using a metal spatula. The sample mixture was then poured/scraped into a pre-weighed 60 cc Teflon container, which sealed upon tightening of the lid.

**Table 6.** Composition of SMWL Grout Samples (wt%)

Sample	SMWL Waste Simulant	CaO	BFS	I/II OPC	Silica Fume	CaS
H-26	80.0	16.0	4.0			
H-30	80.0	14.0		5.0		1.0
H-11	80.0			19.0		1.0
H-28	80.0	8.0		11.0		1.0
H-32	70.0	16.0	14.0			
H-20	70.0	12.0		17.0		1.0
H-27	70.0			29.0		1.0
H-7	70.0	16.0			13.0	1.0
H-8	70.0	14.0	16.0			

To expedite the testing process, all fluid grout samples (after placement in individual sealed

Teflon containers) were quick-cured for seven days in a 45°C water bath (instead of the standard 28-day cure period at ambient temperature). After curing, the samples were visually inspected, removed from their respective containers, and submitted for TCLP leach tests. (TCLP testing performed throughout this report was modified from the standard procedure; considerably smaller masses of the crushed grout were leached in proportionally smaller volumes of solution). Comments on sample appearance/physical properties immediately after the curing period, are presented in Table 7. TCLP leach results for the samples are presented in Table 8.

**Table 7.** SMWL Sample Observations Following Curing Period

<b>Sample</b>	<b>Comments/Observations</b>
H-26	Gray, soft, wet
H-30	Black, soft, no free liquid
H-11	Black, considerable free liquid
H-28	Black, soft and spongy, no free liquid
H-32	Black, somewhat hard, no free liquid
H-20	Black, slightly hardened, no free liquid
H-27	Brown at surface, remainder black, soft, no free liquid
H-7	Gray, soft, similar to molding clay, no free liquid
H-8	Black, soft, no free liquid

**Table 8.** TCLP Results for the SMWL Grout Samples.

<b>Sample</b>	<b>Hg</b>	<b>Cr</b>	<b>Cd</b>	<b>Pb</b>
RCRA LDR Limits	0.025	0.60	0.11	0.75
H-26	0.006	<0.04	<0.02	0.06
H-30	0.059	0.07	0.02	0.32
H-11	0.006	<0.04	<0.02	0.05
H-28	0.06	0.06	<0.02	0.27
H-32	0.009	<0.04	<0.02	0.34
H-20	0.023	<0.04	<0.02	0.03
H-27	0.12	0.16	0.06	0.22
H-7	0.009	<0.04	<0.02	0.10
H-8	0.007	<0.04	<0.02	0.07

### **2.2.2.2 SMWL Test Results and Discussion**

Considerable improvements over the physical properties of the IMWL test samples were shown attainable. Not only have the waste form physical properties been improved (in most sample cases), but

results indicate that RCRA LDR limits for toxic metals can also be met. These improvements have, however, been at the expense of a somewhat lower waste loading.

Results from the samples prepared in this testing with the highest waste loading (80 wt%) indicate that physically acceptable waste forms are produced when sufficient CaO is first mixed with the waste to achieve neutralization. The single sample with 80 wt% waste loading and prepared with no up-front CaO addition (sample H-11), is the same sole sample having significant free liquid after curing.

Following CaO neutralization, the addition of OPC and a chemical reducing agent (CaS) resulted in the most physically favorable product (sample H-30). However, LDR limits for mercury were not met with this approach (samples H-30 and H-28). In all cases, the 80 wt% waste loading "cured" samples grouts remained somewhat soft (little or no binding).

Results from 70 wt% waste loading grout formulations were considerably more favorable. The sample blended with a slight excess of CaO initially, and followed with just BFS (sample H-32), was the most favorable. This cured grout product was somewhat hard (likely to continue hardening with time), had no free liquid, and met LDR TCLP limits.

## **2.3 CsIX Grout Optimization Testing**

Several scoping tests were conducted to determine the effects of different grout additives in the effort to establish and optimize the CsIX waste grout formulation with respect to heavy metal leaching, absence of free water, and comparative strength.

### **2.3.1 CsIX Grout Optimization Test Description and Results**

Optimized grout testing for CsIX waste immobilization has thus far been scoping in nature. The composition of the waste simulant used in this testing is presented in Table 3. Multiple grout samples were prepared using the previously described cementitious ingredients in an effort to evaluate the effects of each ingredient, and to determine workable recipes for CsIX waste immobilization. For some samples, small amounts of various reducing chemicals were also added to enhance the immobilization of some toxic components.

As in the SMWL testing, 50-gram samples were generally prepared. Each CsIX GO test sample was prepared made with approximately the same waste loading of 40 wt%. Samples were prepared in groups, generally using results from prior tests as a guide. Early groups of samples were prepared with the intent to test and compare the capabilities of grout additives with respect to solidification, strength, TCLP leach results, processability, etc. Other, generally later sample groups were prepared to test or compare additive effects on specific criteria.

The formulations used in the preparation of the above described test samples are presented in Table 9. Each sample is identified with a prefix number and/or letters, identifying the respective sample group, followed by a second number identifying the inscribed number on the respective Teflon container the sample was cured in.

To expedite the testing process, all fluid grout samples were placed in individual sealed Teflon containers, and quick-cured for seven days in a 45°C water bath. After curing, the samples were visually inspected and then broken, using a screwdriver and hammer, to remove them from their respective

containers. Sample pieces were then crushed and submitted for TCLP leach tests. Also for each sample, 5 grams of the crushed grout was placed in 20 grams of distilled water. After allowing 24 hours to reach equilibrium, these solutions were measured for pH and redox potential (Eh).

Additional information concerning the preparation of specific samples in this testing includes:

1. Although samples 18-1 and 16-1 have the same formulation, the Na<sub>2</sub>S was added following the neutralization step but prior to the addition of the other cement powders for sample 18-1. The Na<sub>2</sub>S was added last for sample 16-1.
2. Although samples 13-2 and 21-2 have the same chemical formulation, no wait period was allowed after the NaOH addition, or after the Ca(OH)<sub>2</sub> addition. AEA, the company which has developed this specific grout immobilization formulation for CsIX waste, recommends considerable wait periods after the addition of both chemicals.
3. Although samples 15-4 and 28-4 have the same chemical formulation, the entire amount of CaO was added to the waste simulant as a first process step for sample 15.4. For sample 28-4, approximately one-half the CaO was added to the waste simulant initially, followed by the addition and mixing of the other cement powders, and finally followed by the addition of the remaining CaO.

Comments on sample preparation and sample appearance/physical properties immediately after the curing period are presented in Table 10. Also presented in Table 10 are the pH and redox results for the cured grout/deionized water equilibrium samples. TCLP leach results for the samples are presented in Table 11. It should also be noted here that in all sample preparation cases, significant heat is generated. This is due to both solution neutralization and grout powders hydration reactions.

### **2.3.2 CsIX Grout Optimization Test Results and Discussion**

With respect to heavy metal leaching, the most obvious and important result from this testing is that Pb, Cr, and Cd can all be easily and sufficiently immobilized (TCLP leach results below RCRA LDR limits) by hydroxide precipitation, for an alkaline grout with a CsIX waste loading of 40 wt%. Not a single sample made for this testing failed the LDR limits for these metals. Similarly, all samples prepared for this testing containing any sulfide were within the TCLP limits for mercury. Sample 17-1 was the sole sample that failed TCLP for mercury. Sample 17-1 was also the sole sample prepared with no form of sulfide mixed into it.

Based on TCLP results here, and in other samples, it is apparent that heavy metal leaching results do not always concur with expectations based on redox potential readings. TCLP results without verification (as in this test) are acknowledged only as indicative, certainly not conclusive.

With respect to the processability of the grouts, samples prepared using 50% NaOH solution for neutralization (samples 13-2, 21-2, and 26-6) are the most favorable for handling. These formulations produce a fluid grout that is easily mixed and pours well. Note, however, that considerable "expense" is paid for this convenience. The 50% NaOH solution is extremely alkaline (over 18M), hazardous, and somewhat difficult to handle. At such a high hydroxide concentration, it is extremely easy to overshoot or undershoot the required amount per waste volume. Furthermore, by neutralizing with 50% NaOH, additional and excess water is added to the mix (7% for sample 26-5). This excess water also must be included in the "liquid requiring solidification", and thus limits the potential for higher waste loading.

**Table 9.** CsIX Grout Optimization Sample Formulations (wt%)

Sample	CsIX Waste Simulant	CaO	OPC I/II	OPC V	BFS	FA	50% NaOH	Ca(OH) <sub>2</sub>	Na <sub>2</sub> S	CaS	FeS	Clay	SF
2-1	39.8	5.9		51.4					3.0				
17-1	39.9	5.9		54.2									
14-1	39.7	7.9			52.4								
13-1	40.0	5.9		25.6	25.6				2.9				
15-1	40.0	5.9	25.6			25.6			2.9				
22-1	39.5	5.9		25.8		25.8			3.0				
18-1	39.9	7.9		24.7		24.7			3.0				
16-1	39.5	7.9		24.8		24.8			3.0				
21-1	39.9	5.9		51.3					3.0				
13-2	37.1		5.5		30.3		22.0	5.1					
21-2	37.0		5.5		30.2		22.1	5.2					
18-2	40.8	8.0	46.2								5.0		
22-2	40.0		11.4		34.2	11.4	3.0						
17-2	34.7	5.2		9.5		25.9	13.6		2.6				8.6
17-3	39.5	13.7			46.8								
18-3	40.4	7.0		20.0	32.6								
21-3	40.6	8.0		21.7		21.7			8.0				
2-3	50.4	16.6			33.0								
15-4	40.4	14.0			22.8	22.8							
28-4	40.4	14.0			22.8	22.8							
26-5	40.0		4.4		39.0		13.8	2.8					
23-5	40.2		10.6		31.6	10.4	7.2						
27-5	40.0	8.0		24.6		24.2				3.0			
14-6	40.0	14.0	6.0			37.0			3.0				
2-6	40.0	8.0	6.0			44.0			2.0				
28-6	40.0	8.0	6.0			44.0				2.0			
16-6	33.4			64.9					1.7				
21-6	40.0	8.0	49.0							3.0			
15-6	40.0			58.0						2.0			
18-6	40.0		58.0							2.0			
17-6	67.0	16.7							3.0			13.3	

**Table 10.** CsIX Grout Sample Inspection Results

Sample	Preparation Comments	After Curing Comments	pH	Eh
2-1	Reasonable mixing	Hard	12.0	+66
17-1	Reasonable mixing	Hard		
14-1	Smooth	Soft	11.2	-196
13-1	Reasonable mixing	Moist, easier to break	11.7	-117
15-1	Reasonable mixing	Hard	11.5	+89
22-1	Reasonable mixing	Hard	11.7	+106
18-1	Reasonable mixing	Hard	11.5	+79
16-1	Reasonable mixing	Hard	11.5	+55
21-1	Reasonable mixing	Hard	12.0	+84
13-2	Soupy, easily mixed	Somewhat crumbly	12.8	-134
21-2	Soupy, easily mixed	Somewhat crumbly	12.9	-136
18-2	Reasonable, FeS insoluble	Hard	11.9	+74
22-2	Stiff	Softer, crumbly	11.0	+124
17-2	Extremely stiff, difficult to mix	Somewhat brittle, hard	12.0	-21
17-3	Extremely stiff, difficult to mix	Hard but wet	11.3	+59
18-3	Smooth, mixes well	Hard	11.6	-76
21-3	Reasonable mixing	Somewhat crumbly	11.7	-321
2-3	Smooth, mixes well	Hard	11.4	+31
15-4	Extremely stiff, difficult to mix	Somewhat hard	11.3	-81
28-4	Thick at end	Somewhat hard	11.0	-18
26-5	Soupy, easily mixed	Hard	12.5	-206
23-5	Little dry	Soft	11.0	+54
27-5	Dry	Hard	11.8	-261
14-6	Extremely stiff, difficult to mix	Somewhat hard	11.6	-186
2-6	Reasonable mixing	Somewhat hard, crumbly	11.3	-79
28-6	Reasonable mixing	Somewhat hard, crumbly	11.3	-126
16-6	Mixes well, but begins to set	Somewhat hard	12.1	-191
21-6	Somewhat stiff	Somewhat hard	12.0	-291
15-6	Smooth, mixes well	Somewhat hard	12.1	-291
18-6	Ok, but thicker than 15-6	Hard	12.0	-261
17-6	Extremely stiff, difficult to mix	Wet, crumbly	10.9	-266



**Table 11.** TCLP Results for the CsIX GO Test Samples

<b>Sample</b>	<b>Hg</b>	<b>Cr</b>	<b>Cd</b>	<b>Pb</b>
RCRA LDR Limits	0.025	0.60	0.11	0.75
2-1	<0.002	<0.05	<0.03	<0.2
17-1	0.104	<0.05	<0.03	<0.2
14-1*	0.004	<0.01	0.0006	0.005
13-1	<0.002	<0.05	<0.03	<0.2
15-1	0.013	<0.05	<0.03	<0.2
22-1	<0.002	<0.05	<0.03	<0.2
18-1	<0.002	<0.05	<0.03	<0.2
16-1	<0.002	<0.05	<0.03	<0.2
21-1	<0.002	<0.05	<0.03	<0.2
13-2	<0.002	0.08	<0.005	<0.008
21-2	0.007	0.03	<0.005	<0.008
18-2	<0.002	0.03	<0.005	<0.008
22-2	<0.002	0.1	<0.005	<0.008
17-2	<0.002	0.05	0.008	<0.008
17-3	<0.002	<0.01	<0.0005	<0.005
18-3	<0.002	0.03	<0.0005	<0.005
21-3	<0.002	0.088	0.0016	0.01
2-3	<0.002	0.012	<0.0005	<0.005
15-4	<0.002	<0.003	0.005	<0.009
28-4	<0.002	0.034	<0.002	<0.009
26-5	0.002	0.02	0.004	<0.01
23-5				<0.01
27-5	0.001	0.019	0.001	<0.01
14-6	0.007	0.018	0.006	<0.01
2-6	0.001	0.007	0.002	<0.01
28-6	0.002	0.015	0.001	
16-6	0.002	0.019	0.004	<0.01
21-6	0.01	0.015	0.001	<0.01
15-6	0.015	0.007	0.002	<0.01
18-6	0.009	0.013	0.006	<0.01
17-6	0.003	0.014	0.004	<0.01

\* 30 Days of additional curing at ambient conditions were required before sample 14-1 had set adequately and was submitted for TCLP testing

Samples 13-2 and 21-2 had also been prepared to verify the benefits of allowing reaction "wait periods" for NaOH and Ca(OH)<sub>2</sub> addition (AEA recommendations). From the test results, there was no evidence that any waste form advantage is gained by this practice with CsIX waste. However, larger scale samples and more rigorous testing will be required to verify this indication.

Other grout formulation samples, using CaO for waste neutralization, were also reasonably easy to mix. Use of high weight fractions of the more reactive cement components (CaO, silica fume, OPC) generally offers a quicker set rate and poor processability. The use of high weight fractions of less reactive cement components (FA, BFS) improves processability and decreases set time. The physical and chemical properties of the final waste form change with the inclusion (or omission) of each ingredient. Results of these tests certainly indicate that an acceptable balance between processability and grout waste form properties can be made. A near optimum 40 wt% CsIX waste loading grout will likely consist of initially adding only sufficient CaO to assure neutralization (6-8 wt%), using some OPC (2-10 wt%) to assure set reactions are initiated in a reasonable time period, and using BFS as the major final ingredient to provide sulfide reduction, eventually react with the other matrix components, and assure good processability (ease of mixing) with the decreased reactivity.

With respect to physical appearance and properties, all CsIX GO samples were essentially "liquid free" after the cure period. Although compressive strength or other related tests were not conducted on the cured samples, the physical examinations that were performed do give a reasonable indication on how they will perform with these tests. Generally, samples determined as "hard" will easily pass the 500 psi minimum compressive strength test for LAW disposal. Verification of this, as well as all other properties, will be required prior to final flowsheet recommendations are made.

## 2.4 REDOX TESTING

### 2.4.1 Redox Test Description

Although the CsIX GO testing results have established that the addition of a sulfide reducing agent greatly enhances the immobilization of Hg in grout, the longevity of that reduced effect is of interest. Unless a waste form is disposed of in a location free of oxygen, oxidation of that waste form will proceed. Testing was performed to subject grout samples containing different reducing agents (generally sulfides) to an aggressive oxidizing environment, to determine any differences in reducing state longevity.

To compare the buffering capacities for chemical reduction of the various sulfide sources used to date, several grout samples were prepared, each having essentially the same formulation except for the type of sulfide (or other reducing agent) used. (The sample containing BFS used proportionally less OPC). The formulations used in the preparation of the redox test samples are presented in Table 12.

**Table 12.** Redox Test Sample Formulations (wt%)

Sample	CsIX Waste Simulant	CaO	OPC I/II	BFS	Na <sub>2</sub> S	CaS	FeS	Powdered Fe
S2-13	40.0	8.0	50.0		2.0			
S2-29	40.0	8.0	51.4			0.6		
S2-8	40.0	8.0	51.2				0.8	
S2-22	40.0	8.0	6.0	46.0				
S2-31	40.0	8.0	52.0					
S2-25	40.0	8.0	50.0					2.0

All redox samples were prepared and cured in the same manner as were the GO samples (50-gram samples, accelerated curing). During preparation, all samples were somewhat dry and relatively difficult to mix, with the exception of sample S2-22, in which the majority of the OPC was replaced with BFS. After curing, the hard grout samples were broken, using a screwdriver and hammer, to remove them from their respective containers. Sample pieces were then crushed and submitted for TCLP leach tests. TCLP results are presented in Table 13.

Also for each sample, 5 grams of the crushed grout was placed in 20 grams of de-ionized (DI) water. After allowing 3 days to reach equilibrium, these leach solutions were measured for redox potential (Eh). After 4 additional days, the leach solutions were re-measured for Eh. The solid grout pieces were then filtered from the leach water, allowed to dry, and approximately 20 grams of new DI water was added. This process was repeated several times; measuring Eh twice every week, and changing DI water once every week. The Eh results for the various samples are plotted in Figure 1.

**Table 13.** TCLP Results for the Redox Test Samples

Sample	Hg	Cr	Cd	Pb
RCRA LDR Limits	0.025	0.60	0.11	0.75
S2-13	<0.002	<0.05	<0.05	<0.25
S2-29	0.011	<0.05	<0.05	<0.25
S2-8	0.017	<0.05	<0.05	<0.25
S2-22	0.022	<0.05	<0.05	<0.25
S2-31	0.049	<0.05	<0.05	<0.25
S2-25	0.064	<0.05	<0.05	<0.25

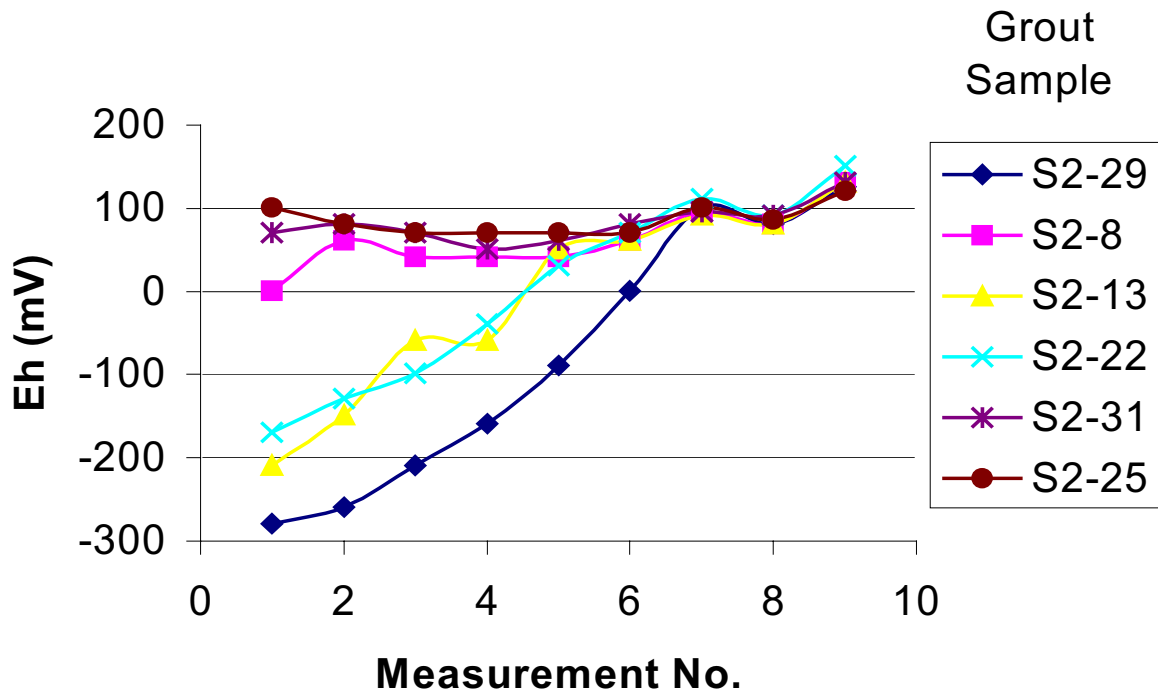
#### 2.4.2 Redox Test Results

The TCLP results in Table 13 verify the mercury leach problem for CsIX waste grout in the absence of an adequate reducing agent. The RCRA LDR limit for mercury was exceeded for the grout samples having no reducing agent (S2-31), and using powdered iron as a reducing agent (S2-25). Only samples formulated with some form of sulfide met the LDR limits for all toxic metals.

The redox test results of Figure 1 show sample S2-29, containing CaS, to have the strongest capacity for maintaining a chemically reducing environment. Samples S2-13 and S2-22, containing Na<sub>2</sub>S and BFS respectively, also demonstrate reasonable longevity of a reducing environment. Samples S2-25 and S2-31, containing no reducing agent and using powdered iron as a reducing agent, respectively, showed the approximate same and constant Eh throughout this testing. This strongly suggests that powdered iron provides minimal (if any) benefit in heavy metal immobilization. Sample S2-8, containing FeS, showed some improvement in reduction potential over samples S2-25 and S2-31. In fact, sample S2-8 TCLP results for Hg showed less leaching than that reported for the sample containing BFS (S2-22).

In all sample cases, there was no noticeable "buffering" of the reducing environment. Oxidation was constant and generally at the same slope (rate), regardless of the sulfide source. The sample containing CaS was only determined the most favorable because it started with the

**Figure 1.** Grout Redox Measurements for Various Sulfides



most reducing Eh. Nonetheless, the samples containing Na<sub>2</sub>S or BFS had lost their reducing advantage after approximately three water -change cycles, while four cycles were required before that advantage was lost in the sample containing CaS.

With respect to maintaining a reducing environment within the grout matrix, it is not certain at this point whether or not this actually presents any real advantage with respect to heavy metal immobilization. Test results have already shown that for CsIX waste treatment (grouting), LDR limits for Cd, Cr, and Pb can easily be met with hydroxide precipitation. Although sulfide addition does provide a reducing environment, it also reacts directly with mercury, forming relatively insoluble mercury sulfide. At this point, loss of the reduction potential (oxidation of the remaining sulfide not already reacted with mercury) may have no effect on Hg leaching. Further investigation will be required to make this determination.

## 2.5 Conclusions

Please refer to Section 3.3 for overall conclusions and recommendations on CsIX formulations.

### **3. NEWLY GENERATED LIQUID WASTE GROUT DEVELOPMENT TESTING**

Similar to the treatment and disposal of CsIX waste, there are at least two potential grouting options for NGLW waste. Waste solidification and disposal at Envirocare of Utah is being considered, assuming the concentrations of the various radioisotopes in the waste are within the stated limits. (At least some radioisotope separations treatment will be required to meet those limits). An alternative disposal option would be to simply solidify the waste (with or without radioisotope separations pre-treatment) and dispose of (or temporarily store) it at a LAW repository (location currently uncertain).

The WAC for Envirocare, similar to that of WIPP, requires solidification, allows a very small amount of free liquid, and does not require a monolithic waste form. Unlike the WIPP WAC, Envirocare also requires the solidified waste to meet RCRA LDR leach standards for toxic metals. The absence of any requirement for physical strength of the solidified waste allows for increased waste loading, provided the other requirements are still met.

Low-activity waste disposal criteria generally follows the recommended requirements of the NRC, requiring the grout waste form to possess a reasonable compressive strength (>500 psi), and also meet other physical standards (submersion test, thermal cycle test, etc.). LAW waste disposal sites also require the waste form to meet RCRA LDR leach standards for toxic metals. The waste form physical requirements generally limit waste loading.

Based on the above discussion, two separate grouting approaches are being investigated for the disposal of NGLW waste. The first approach deals with maximizing waste loading while satisfying both the "no liquids" and RCRA LDR criteria of Envirocare. The second approach deals with developing and optimizing grout formulations to produce a reasonable waste form monolith, satisfying requirements/guidelines of RCRA and the NRC, respectively. The two test approaches are referred to as NGLW MWL and NGLW GO, respectively, throughout the remainder of this report.

The calculated average composition of NGLW waste, without the radioactive components, is presented in Table 14.<sup>7,8</sup> The composition of the waste simulant used in all of the NGLW grout development tests is also presented in this table.

#### **3.1 NGLW Maximum Weight Loading Tests**

Two groups of samples were prepared as scoping tests to determine the approximate maximum weight percent loading of NGLW waste to attain a "solid" product. This waste product should be liquid-free, preferably have some compressive strength, and satisfying RCRA LDR leach limits for heavy metals.

Samples for the first group, individually identified by an "H2" followed with their cure bottle number, have formulations identical (except for the waste simulant type) to samples from the CsIX SMWL testing. These samples were prepared to enable a direct comparison of grout products from the two waste streams.

Samples for the second group, individually identified by an "N" followed with their cure bottle number, were prepared to further determine product changes with changes in mix composition. Both test

groups are presented together below.

**Table 14.** Compositions of Proposed NGLW Waste (Excluding Radioisotopes) and NGLW Test Simulant

Species	Calculated NGLW (M)	NGLW Test Simulant (M)
H	1.57	1.57
Ag (mg/l)	2.2	
Al	0.17	0.17
Ba (mg/l)	2.4	
Ca	0.13	0.13
Cd (mg/l)	<15	20
Cl	0.1	0.1
Cr (mg/l)	10	15
F	0.065	0.65
Hg (mg/l)	350	350
K	0.03	0.03
Na	1.7	1.7
Ni (mg/l)	<7	
NO <sub>3</sub>	4.2	4.2
Pb (mg/l)	6	10
Si (mg/l)	1500	1500
SO <sub>4</sub>	0.078	0.078

### 3.1.1 NGLW MWL Test Description and Results

Nine NGLW MWL grout samples were prepared for the H2 group test (same grout formulations used in CsIX SMWL testing). Seven additional NGLW MWL samples were prepared for the N group test. Compositions for the various samples are presented in Table 15.

Again for this testing, 50-gram samples were prepared, each having a waste loading of 70 or 80 weight percent (except for sample N-32, which had a waste loading of 60 wt%). For the preparation of each sample, the waste simulant was first poured into a pint-sized plastic container, followed by the addition and mixing of CaO for neutralization (for samples not using CaO, OPC was added directly to the waste simulant). Any additional cementitious ingredients were then added and mixed. When used, CaS or Na<sub>2</sub>S was added and mixed into the grout mixture last. The sample mixing was achieved manually, using a metal spatula. The sample mixture was then poured/scraped into a pre-weighed 60 cc Teflon container, which sealed upon tightening of the lid.

To expedite the testing process, the fluid grout samples were quick-cured for seven days in a 45°C water bath. After curing, the samples were visually inspected, removed from their respective containers, and submitted for TCLP leach tests (only two of the N-group samples were submitted for TCLP testing). Comments on sample appearance/physical properties immediately after the curing period, are presented in Table 16. TCLP leach results for the samples are presented in Table 17.

**Table 15.** NGLW High Waste-Loading Grout Sample Compositions (wt%).

Sample	Waste	CaO	I/II OPC	BFS	Na <sub>2</sub> S	CaS	Clay	SF
H2-24	80.0	16.0		4.0				
H2-1	80.0	14.0	5.0			1.0		
H2-38	80.0		19.0			1.0		
H2-4	80.0	8.0	11.0			1.0		
H2-3	70.0	16.0		14.0				
H2-35	70.0	12.0	17.0			1.0		
H2-2	70.0		29.0			1.0		
H2-5	70.0	16.0				1.0		13.0
H2-33	70.0	14.0		16.0				
N-28	80.0	15.0		4.0				1.0
N-29	80.0	16.0	4.0					
N-12	80.0	15.0	4.0					1.0
N-26	80.0		16.0		2.0			2.0
N-11	80.0	12.0		4.0			4.0	
N-27	80.0		12.0	4.0			4.0	
N-32	60.0		38.0		2.0			

**Table 16.** NGLW MWL Sample Observations Following Curing Period

Sample	Comments/Observations
H2-24	Gray, soft, small amount of free liquid
H2-1	Black, soft, wet
H2-38	Dark gray, soft, some free liquid
H2-4	Black, somewhat firm, some free liquid
H2-3	Green/black, somewhat firm, considerable amount of free liquid
H2-35	Black, spongy/hard, wet/damp
H2-2	Black, firm, damp
H2-5	Dark gray, soft, similar to molding clay, no free liquid
H2-33	Black, somewhat firm, considerable amount of free liquid
N-28	Gray, somewhat firm, considerable amount of free liquid
N-29	White, moderately soft, very little/no free liquid
N-12	Light gray, moderately soft, very little/no free liquid
N-26	Black/brown, soft, considerable amount of free liquid
N-11	Light brown/gray, moderately soft, considerable amount of free liquid
N-27	Light brown/gray, soft, considerable amount of free liquid
N-32	Black, somewhat firm, considerable amount of free liquid

**Table 17.** TCLP Results for the NGLW Grout Samples

SAMPLE	LEACHATE CONCENTRATION (MG/L)			
	Hg	Cr	Cd	Pb
RCRA LDR Limits	0.025	0.60	0.11	0.75
H2-24	0.017	<0.04	<0.02	<0.03
H2-1	0.002	<0.04	<0.02	0.07
H2-38	<0.002	<0.04	<0.02	<0.03
H2-4	0.019	0.04	<0.02	<0.03
H2-3	<0.002	<0.04	<0.02	0.06
H2-35	0.009	<0.04	<0.02	<0.03
H2-2	0.016	<0.04	0.02	<0.03
H2-5	0.078	<0.04	<0.02	0.06
H2-33	0.002	<0.04	<0.02	<0.03
N-29	0.019	<0.04	0.02	<0.03
N-12	0.12	<0.04	<0.02	<0.03

### 3.1.2 NGLW MWL Test Discussion

Following the accelerated curing period, NGLW MWL samples (H2) generally had somewhat more free liquid than did the CsIX SMWL samples (H) made with the same formulations. Nonetheless, several NGLW MWL samples did result in having minimal or no free liquid. Minor modifications to the more promising flowsheets will likely result in water-free products at these higher loadings.

Although most samples were within the RCRA LDR limits, two failed for Hg leaching. At least three others were uncomfortably close to the same failure. Further modifications and testing will be required to assure Hg leaching will be controllable.

## 3.2 NGLW Grout Optimization Testing

Four test samples were prepared with various NGLW simulant waste loadings (40-60 wt%), to explore the grouting of that waste using only CaO and BFS.

### 3.2.1 Grout Optimization Test Description and Results

These 50-gram samples were prepared and cured at the same time period as were the previously described CsIX GO group 4 samples. All preparation, curing, and data determination procedures were the same. The formulations used in the preparation of those samples are presented in Table 18.



**Table 18.** NGLW Grout Optimization Sample Formulations (wt%)

Sample	Waste	CaO	BFS
14-4	40.2	11.8	48.0
13-4	50.6	13.4	36.0
16-4	51.0	21.0	28.0
22-4	60.0	23.2	16.8

Comments on sample preparation, and sample appearance/physical properties immediately after the curing period, are presented in Table 19. Also presented in this table are the pH and redox results for the cured grout/deionized water equilibrium samples. TCLP leach results for the samples are presented in Table 20.

**Table 19.** NGLW GO Sample Inspection Results.

Sample	Preparation Comments	After Curing Comments	pH	Eh
14-4	Smooth	Dk gray, hard, dampish, little/no free liquid	11.7	-275
13-4	Soupy (pours)	Dk gray, crumbly, dampish, little/no free	11.8	-280
16-4	Smooth	Dk gray, hard but crumbly, dampish, little/no	11.9	-245
22-4	Smooth	Med-dk gray, very crumbly, dampish,	11.8	140

**Table 20.** TCLP Results for the NGLW GO Test Samples.

Sample	Hg	Cr	Cd	Pb
RCRA LDR Limits	0.025	0.60	0.11	0.75
14-4	0.016	0.005	0.005	0.018
13-4	0.011	<0.003	0.004	<0.009
16-4	0.020	0.11	<0.002	<0.009
22-4	0.004	0.01	<0.002	<0.009

As in all previous testing, significant heat was generated during the preparation of all samples. This is due to both solution neutralization and grout powders hydration reactions.

### 3.2.2 Grout Optimization Test Discussion

Test results strongly indicate that reasonable grout waste forms can be successfully produced using only CaO and BFS powders, at NGLW waste loadings up to 60 wt%. All four sample grout products produced in this manner likely meet the acceptance criteria for LAW disposal.

Although all samples produced in this testing were still damp following the accelerated curing period, this is likely due to BFS being considerably less reactive than OPC. As in sample 14-1 of the CsIX GO testing, significant further solidification reactions (grout setting) will occur with extended cure time. However, because of the lower reactivity of the BFS, it is uncertain whether adequate ambient temperature grout setting will occur within a reasonable time period without some assistance (i.e.: increased set temperature or use of some "more reactive" grout ingredients). This uncertainty will require further investigation.

With respect to heavy metal leaching, initial redox potential readings were not indicative of TCLP results. Sample 22-4, as expected with the higher waste loading, had the least reducing internal environment. Conversely, sample 22-4 had perhaps the most favorable leaching results. The leaching results for all samples from this testing were, however, within the RCRA LDR limits. Mercury leaching is generally close to the leaching limit, and is thus of concern.

### **3.3 Conclusions and Recommendations**

Grout formulation test results thus far strongly indicate that, regardless of the approach taken (maximum waste loading or optimized grout), successful grout formulations can and will be developed for both CsIX and NGLW wastes. The close chemical similarities of the two waste types makes grout development work for one at least somewhat applicable to the other.

Specific indications and conclusions from the maximum waste loading tests include:

1. Approximately 80 wt% waste loading is the maximum achievable for either CsIX or NGLW waste, to minimally meet the WIPP WAC or Envirocare WAC, respectively.
2. LDR TCLP limits can likely also be met at these high waste loadings (required for disposal at Envirocare).
3. Sulfide addition will be required to achieve adequate Hg immobilization.
4. Considerably better grout products, both chemically and physically, can be attained by slightly lowering the maximum achievable waste loading (to 70-75 wt%).
5. Initial waste neutralization with CaO is required to attain an acceptable product with these high waste loadings.
6. The use of BFS results in a superior grout product over the use of I/II OPC and CaS. The final formulation will likely require a small amount of OPC to assure product setting within a reasonable time period.
7. Heat generation from waste acid neutralization and cement powders hydration is significant. On a large-scale process, a mix system equipped with cooling coils (or other means of cooling) may be required, regardless of the grout formulation chosen.
8. Waste solution concentration (evaporation) greatly enhances maximum waste loading product properties when leach requirements are not of concern.

Specific indications and conclusions from the grout optimization tests include:

1. Multiple acceptable grout formulations are available to successfully immobilize either CsIX or NGLW waste to LAW disposal standards, for waste loadings of at least 40 wt%.
2. Pb, Cr, and Cd can all be sufficiently immobilized through hydroxide precipitation.
3. Hg immobilization will require sulfide (or another strong reducing agent) addition.
4. Of the various sulfide types (and other reducing agents) tested, calcium sulfide maintains a reducing environment for the longest time period under aggressively oxidizing conditions.
5. Formulations using NaOH for neutralization are preferred with respect to processability (ease of mixing). NaOH neutralization (with 50 wt% NaOH solution) is likely not applicable to maximizing waste loading.
6. Even at the lower waste loading of these tests (40 wt%), heat generation from waste acid neutralization and cement powders hydration is significant. On a large-scale process, a mix system equipped with cooling coils (or other means of cooling) may be required.

#### **4. TANK FARM CLOSURE GROUTING DEVELOPMENT UPDATE**

As a part of the Batt Agreement, closure of the INTEC Tank Farm Facility (TFF) is required. Two INTEC TFF tanks (WM-182 and WM-183) are to be closed by 2006 to meet the INEEL High Level Waste initiative. The feasibility study for the closure of these two tanks<sup>9</sup> was produced based on several assumptions, including: 1) any settled solids that might exist in the tank heels are of no environmental consequence; and 2) the network of cooling coils at the bottom of each tank and the limited access to the tank interiors provide sufficient restrictions to warrant no extra effort be made to remove any “incidental” high-level waste solids that might exist. All INTEC development work for the closure of these tanks has been performed within these assumptions.

Multiple tests have been performed to develop a heel solidification method and grout formulation for the closure of the two tanks. Based on initial closure testing, tank heel displacement with grout and removal was determined favorable to direct heel grouting, with respect to both economics and waste form quality<sup>10</sup>. It was also determined during this initial testing that the heel solutions should be diluted with water to no more than 12.5% original solution to prevent excessive chemical degradation of the grout. A second set of tests was performed to optimize the makeup of the displacement grout<sup>11</sup>. Of six grout formulations tested, a “reducing” grout developed for tank closures at the Savannah River Site (SRS) was determined to possess the most favorable qualities for this application. This SRS grout demonstrated the highest slump (most self-leveling) without the use of admixtures and the highest compressive strength of all grouts tested. As with all grouts tested except the WCF closure grout, the SRS grout uses sulfide-containing blast furnace slag (BFS). Sulfide addition to a solution having a relatively high oxidation potential, reduces that potential and causes most toxic metals to exist in a less soluble state. Finally, the SRS grout contains a large mass fraction of sand, which is a relatively cheap aggregate (the WCF grout contains an even higher mass fraction of sand).

Additional testing has been performed to demonstrate a small-scale tank closure grouting operation to verify the concept of displacing waste solution with grout for removal. The general tank closure steps

specified in the feasibility study are to: 1) pump the heel level down to approximately one inch, 2) wash the tank walls and dilute the heel solution, 3) displace and remove the remaining tank waste solution with a one-foot layer of grout, and 4) pour a one-foot layer of adsorption grout on top of the displacement grout. This testing demonstrated both grout pours, including the solution displacement and removal portions of the closure plan. The formulations for the WCF and SRS grouts, recommended by the feasibility study and used in this testing as the displacement and adsorption grouts, respectively, are presented in Table 21.

**Table 21.** Test Grout Formulations

<b>Grout Components (wt%)</b>	<b>WCF Grout</b>	<b>SRS Reducing Grout</b>
Type I/II Ordinary Portland Cement (OPC)	9.0	
Type V OPC		34.6
BFS		5.3
Type F Fly Ash (FA)	17.7	
Water	14.0	18.4
Sand	59.3	41.6
Mid-Range Admixture (Polyheed 997) (oz/yd <sup>3</sup> )	32	
Hi-Range Admixture (Rheobuild 1000) (oz/yd <sup>3</sup> )	64	
Water-to-(Cement+Pozzolan) Mass Ratio	0.52	0.46

## 4.1 Test Description

The small-scale tank heel solution displacement and removal demonstration was conducted in an open-top 16"x24" stainless steel test pan, 8 inches deep. This pan was filled to a liquid depth of approximately 2.5 inches with 13.24 liters of dilute tank farm simulant (12.5 volume percent non-toxic tank farm waste simulant and 87.5 volume percent water). The chemical composition of the tank farm simulant (prior to dilution) is presented in Table 22. Approximately 200 g of sand was spread evenly over the test pan bottom (settled in the solution) to simulate settled solids in the tanks. The suction end of a Masterflex pump plastic tubing was taped in place in one corner of the test pan so that it was parallel to and just touching the solution surface. For the initial solution displacement, 1200 in<sup>3</sup> of WCF grout was mixed in a separate plastic bucket. With the pump turned on, grout was poured through a 1.5-inch outlet diameter funnel into the test pan solution at the corner opposite that of the pump tubing. The funnel outlet elevation was maintained at approximately 2 inches above the solution during the pour. As the solution level rose due to grout displacement, it was pumped out of the test pan to maintain a relatively constant level. After the grout pour, a plastic sheet was placed over and taped to the test pan to prevent evaporation of the remaining solution. The grout was allowed to cure for 2 days.

**Table 22.** Tank Farm Simulant Chemical Composition (Prior to Dilution)

<b>Chemical Species</b>	<b>Concentration (Molar)</b>
H+	1.57E+00
Al	6.39E-01
B	1.80E-02
Ca	5.27E-02
Cl	2.87E-02
Cs	1.05E-05
F	6.89E-02
Fe	2.20E-02
Mn	1.22E-02
Mo	6.37E-04
K	2.04E-01
Sr	5.10E-06
Na	1.89E+00
NO <sub>3</sub>	5.17E+00
PO <sub>4</sub>	1.40E-02
SO <sub>4</sub>	5.04E-02

After the initial curing period for the WCF grout, 1000 in<sup>3</sup> of SRS grout was mixed and poured on top per the above procedure. This step allows for further solution displacement and removal, and provides an additional “cap” to the waste solids remaining of the tank bottom. Following this second pour, the test pan was again covered with a plastic sheet to prevent evaporation loss.

## 4.2 Test Results

**Initial Pour-** During the initial pour with WCF grout, several problems were encountered. The grout, made per the recommended recipe including the admixtures, was far too viscous to flow through the funnel without significant physical assistance. To increase the “flowability” of the grout, 100 ml of additional water was mixed into it. Although this considerably improved the ability to flow the grout through the funnel, continuous tapping on the funnel (vibrating) and probing the grout with a screwdriver were still required to move it through the funnel. Additionally, the grout level in the test pan where the grout was being introduced rapidly built up to the funnel outlet, hindering further flow. The grout had to be continuously scraped away from the funnel outlet to allow the flow to continue.

The solution displacement by the WCF grout allowed for 11.9 of the original 13.2 liters of dilute tank farm simulant to be pumped out. During the grout pour, it was visually observed that the layer of loose sand on the pan bottom was increasing in depth at the grout flow interface. This indicates that the sand can be at least partially moved with the flow of a relatively low-slump grout.

**Second Pour-** After 2 days curing for the WCF grout, and just prior to the second grout addition, the test system was examined. The remaining solution was cloudy and had a pH of approximately 7 (by pH paper). The grout depth was 4 1/2 inches at the pour corner, was approximately

4 inches at the closest corner directly across from the pour corner (16 inches), was approximately 2 inches at the furthest corner directly across from the pour corner (24 inches), and was approximately 1 ½ inch diagonally across at the pump corner.

The SRS grout had an extremely high slump, and had no problems flowing immediately through the grout addition funnel. In fact, while preparing the grout for this test, and before the total recommended amount of water had been added (several hundred milliliters of water still remained to be added), it was commented that the grout was already “thin enough” to pour easily through the funnel. (Note, however, that a "new batch" of sand had been used for the SRS grout makeup. It was obvious that this sand had a higher moisture content than that used preparing the WCF grout. Furnace drying a sample of this new sand indicated it had a moisture content of 6.4 wt%. This is equivalent to a total water addition of 14.5% above that stated in the SRS grout recipe.) When the grout was poured, it flowed easily over the rough and uneven WCF layer, and self-leveled in the test pan near-perfectly. The solution displacement by the SRS grout allowed for approximately 600 ml of additional simulant solution to be pumped out of the test pan. Only a small volume (approximately 200 ml) was visually evident as left on the grout surface, predominantly all located towards the pump corner.

A brief inspection was conducted on the test grout monolith 3 days after the second pour. The grout surface appeared damp, and condensate was present on the inner side of the plastic sheet that had been covering the test pan. Signs of discoloration were evident on the monolith surface, where the remaining solution had been setting. There was no visible free liquid on the grout surface.

**Monolith Inspection-** A final inspection on the test grout monolith was conducted 22 days after the initial pour and 20 days after the second pour. The monolith surface was dry, and no condensate was present on the plastic sheet covering. A thin powdery white layer was present where the remaining solution had set.

With much effort, the grout monolithic slab was removed from the test pan for further inspection. The removal effort did cause several smaller pieces to be broken off from the main grout slab. Inspection of the removed slab showed that the sand, which had been initially spread evenly over the solution-containing test pan bottom to represent settled solids in the tanks, had been almost entirely “pushed” in front of the WCF grout flow. This was evident by the extremely smooth grout surface where it had contacted the test pan bottom, except for the test pan wall areas away from the grout pour location. When the grout monolith was removed from the test pan, loose sand spilled out. The grout had solidified on top of the piled sand. There was no evidence of any of the sand having mixed, or even sticking to the cured grout. Figure 2 depicts views of the monolith from the bottom and each side, indicating the levels of the sand and the two grout types at those locations. The top view (not illustrated) is simply SRS grout throughout. The bottom view identifies each test pan corner with respect to the side views, and also illustrates the general area at the bottom of the test pan that the sand had been pushed to. Note that although the depths of sand depicted on the pan side and end views are relatively significant (up to 1 1/2 inches), those depths tapered off rapidly from the pan walls.

Other interesting observations made with respect to the broken monolith include:

1. The two grouts, and particularly the SRS grout, were not entirely cured. At the break surfaces, both grouts felt cool and damp.
2. The major break occurred at the interface between the two grout types, at the slab end where the unremoved solution had remained after the initial grout pour. A thin (approximately 1/8-inch) layer of soft, easily removed solid material was present at the grout interface break where solution had set during the curing of the WCF grout. This powder material was sampled and analyzed.

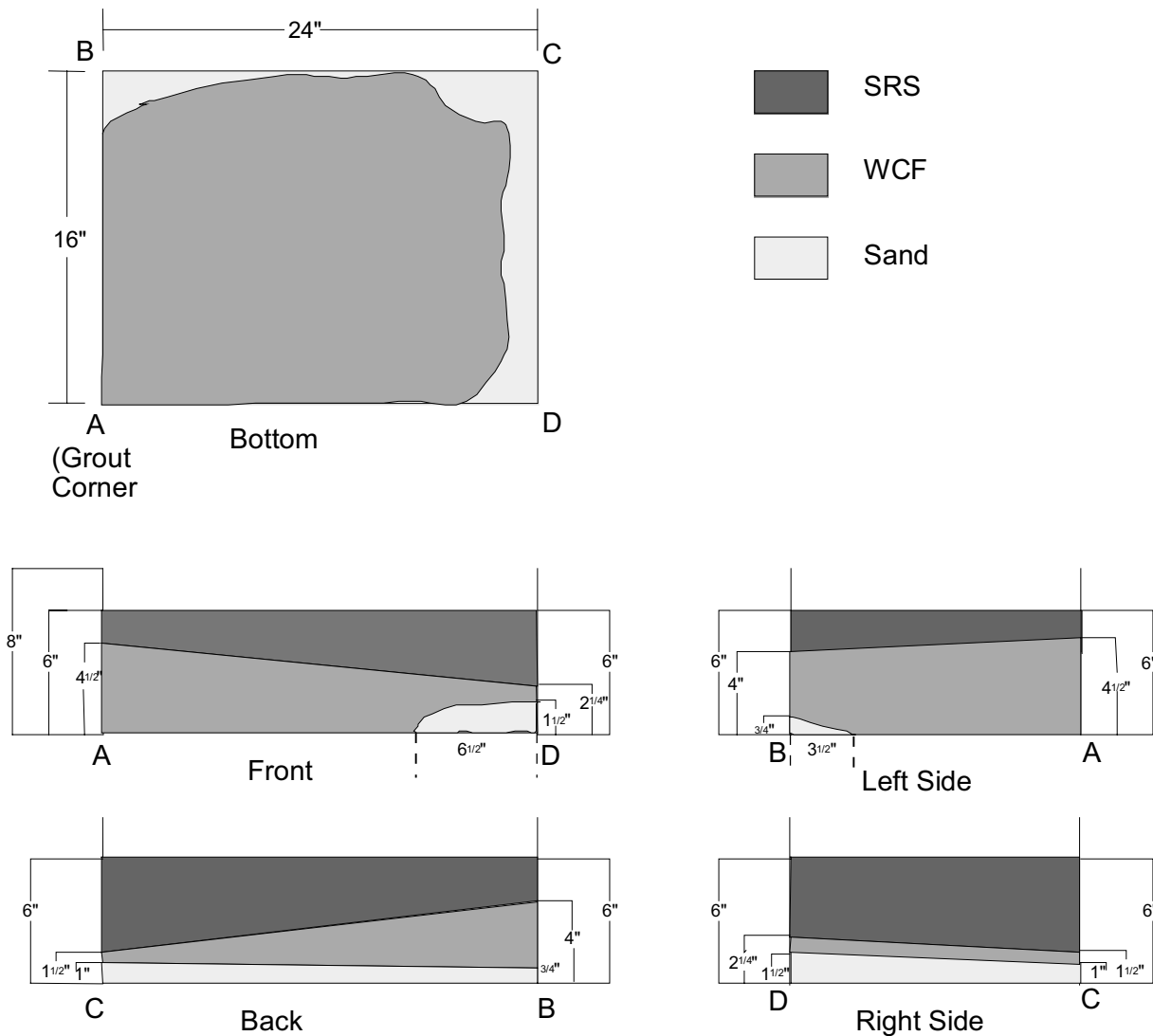
The results of this analysis are presented in Table 23. It is evident from the results of this analysis that the majority of the solids composition comes from the grout mixture, and not from the waste simulant. This strongly suggests that the acidic waste solution reacted at the surface of the fluid grout with alkaline components, leaving a layer of non-binding solids.

**Table 23.** Grout Interface Substance Composition

Chemical Species	Concentration (Wt%)
Al	4.7
Ca	11.2
Fe	1.2
K	0.83
Mg	1.2
Na	1.0
Si	11.7
NO <sub>3</sub>	0.66
SO <sub>4</sub>	0.94
CO <sub>3</sub>	1.0
	25.1
Solids Insoluble in 6 <u>M</u> HNO <sub>3</sub> (likely sand)	18.0

### 4.3 Results Discussion

**Grout Flow-** WCF grout flow and associated difficulties experienced in this tank closure demonstration are only slightly indicative of what will happen on a full-scale tank closure. The combined small scale of this testing and the vessel corner restrictions at the grout pour location, did significantly contribute to the grout flow problems experienced in this test, and would not occur to the same magnitude on a full-scale tank closure operation. However, it is very likely that using the WCF grout (per the blend ratios given in the feasibility study) for the displacement of tank heel solution will result in a significant grout buildup (several feet of depth) at the pour location(s) to achieve flow to the opposite end of a 50-foot diameter tank. An increased slump for the WCF grout can likely be achieved by increasing either the quantity of the super-plasticizer admixture(s) used or the grout water content. Either strategy should be looked at carefully for detrimental effects before implementation. Specifically, excess water in a grout is known to result in a decrease in the quality of the monolith (larger pore size, less dense, decreased strength), and also increases the potential for resulting bleed water.



**Figure 2.** Approximate Grout Layer Dimensions from Small-Scale Tank Closure Demonstration

SRS grout was excellent for its role as the “cap” over the WCF displacement grout. The extremely high slump of the SRS grout enabled it to easily fill in all surface irregularities of the initial WCF pour, and proved to be almost perfectly self leveling. This grout formulation will self-level equally well on a large scale (50-ft diameter tank), likely leaving a monolith depth differing by only a couple of inches from one end to the other. Although some extra water had been added to the SRS grout in this testing via the use of "damp" sand, the extremely high slump of this grout has been verified during previous tests.

As previously recommended, the SRS grout could also be used as the displacement grout. With respect to flow, it is likely that a slightly lower slump would be more desirable. This could easily be



achieved by using less water in the mix blend. This action would only have positive effects on the grout, the inverse of those stated above for adding excess water. Additionally, SRS grout formulated with less water would contribute to the absorbing capabilities advertised for this grout blend.

**Solids Moving-** The WCF grout was able to entirely “push” a 1/8-inch layer of submerged loose sand a distance of 2 feet. Although this may be suggestive of achieving the same on a larger scale, it is in no way conclusive. With respect to moving solids with grout flow across 50-ft diameter tanks, that feat would be dependent on many factors, including solids density, grout density, solids quantity, and tank bottom friction factor. Additionally, if solids are pushed by the grout flow, they will go in the direction of the flow. Thus, to achieve a successful movement of solids to a desired area in this way, controlled grout pours from multiple locations will likely be necessary. Removal of these potential solids from the tanks will require somewhat more than a stationary pump.

Conversely, solids accumulation caused by grout flow has the potential to be a significant problem. Depending on the quantity and radioisotope composition of existing solids, an accumulation may have the potential of reaching a critical mass. This issue will need to be addressed and resolved in a separate study.

## 4.4 Conclusions and Recommendations

Based on the small-scale tank closure testing, a significant percentage of dilute liquid heel remaining in the existing waste tanks can be removed using grout displacement techniques. Although WCF grout can successfully be used for this purpose, adjustment of the water and/or admixture content may be required to achieve the desired degree of "self-leveling". Careful planning of grout injection locations and sequence will allow a maximum amount of liquid displacement and removal before extraction capabilities are halted by grout interference to the pump.

The capability to remove waste solids in the tanks by grout displacement is highly questionable, and will likely be only very minimally achieved with the current plan. Even if all solids could be pushed to within the general vicinity of the planned stationary pump, no means of getting them directly to the pump is in place. Use of WCF grout for waste displacement will result in at least some solids being “pushed” outward from the grout injection area with the grout flow. The extent of solids movement is unknown, is dependent on currently unknown factors (i.e. solids quantity, solids density), and requires further study to determine. With the current closure plan, regardless whether solids are moved by the grout flow or not, the majority of any existing tank solids will remain in the closed tanks. Further, the majority of these remaining tank solids will not be mixed with the grout, will not be immobilized, but will be “sandwiched” between the displacement grout monolith and the tank bottom. Depending on the quantity of any existing solids, their radioisotope content, and the extent of solids accumulation from the grout flow, a criticality issue may exist. Actual tank heel samples are being taken from at least one of the existing tanks. It is hoped that analysis results from these samples will give a strong indication on whether or not a solids problem does exist.

As previously reported, the acid in the heel solution will react with the fluid grout in contact with it. Any grout surface area cured while in contact with this acidic solution will form a thin solid layer that will be relatively unreactive to another grout poured on top. This grout interface where liquid waste had previously set will allow for little chemical bonding, and will be the weakest area of the total monolith.

Also previously reported, the SRS grout, developed specifically for Savannah River Site tank closures, possesses better qualities and properties for use as either a displacement grout or as an in-tank cap:

- a) This formulation provides the most “self-leveling” (highest slump) grout of all tested.
- b) The “advertised” reducing nature of this grout will likely cause any contacted hazardous cations to be less soluble than will the WCF grout.
- c) The compression strength of this grout exceeds that of all others tested.
- d) The proposed tank closure application is very similar to the Savannah River tank closure, for which it has already been used.
- e) The slower overall rate of reaction realized in the Type V OPC (SRS grout), as compared to the Type I/II OPC (WCF grout) lessens any concerns with heat dissipation and/or pre-mature cement setting.

To use SRS grout for waste solution displacement, it is likely that a grout slump lower than that achieved with the given recipe would be more desirable. This could be achieved by reducing the water content. This lowering of the water content would enhance the advertised "water adsorbing" quality of the grout.

Regardless of the grout recipe used, and as previously recommended, potential solids buildup could be eliminated by actually mixing waste remnants with the grout by means of high-pressure grout injection<sup>12</sup>.

## 5. RADIOACTIVE TRACER LEACH STUDY

In order to characterize the performance of various grouted waste formulations, a standard test was completed to measure the simultaneous release of cesium, strontium, technetium and nitrate in accordance with a standard test procedure, ANSI/ANS 16.1-1986.<sup>13</sup> This procedure requires that grout samples be immersed in successive baths of purified water for specific lengths of time.

Waste simulants were prepared to duplicate the latest composite flowsheets. The LAW (low-activity waste) simulants duplicated Concentrated Sodium Bearing Waste before separations and Composite Calcine raffinate after TRU extraction. To reduce exposure and allow for contact handling, the three elements tested were traced with Cs-137, Sr-85, Tc-95 and Tc-99. It was planned to use Hg-203 but the amount of the nuclide available was inadequate for test work. In the calcine flowsheet grout the total amount of the Cs and Sr were increased to the non-separated flowsheet values to more easily obtain leachability index values for a potential Class-C waste concentration.

It was initially planned to use five different pre-treatments on the simulants before grouting: 1) Grouting directly the concentrated liquid (Sp.Gr. < 1.2), 2) Neutralization of the concentrated simulant to a pH between 1 and 2 with sodium hydroxide, 3) denitrating at 650 ° C and grouting the crushed powder, and, two new grout forms. These treatments are designated as groups. A coupon group will contain four tracer coupons and at least one property check coupon. The designation acronyms for each treatment group are:

**Group 1, CTWA**-Calcine Low Level Waste Acid Grout.

**Group 2, CTWB**-Calcine Low Activity Waste Basic Grout.

**Group 3, SBWA**-Sodium Bearing Low Activity Waste Acid Grout.

**Group 4, SBWB**- Sodium Bearing Low Activity Waste Basic Grout.

**Group 5, SBWMc**-Sodium Bearing Low Activity Waste Special Grout.

**Group 6, SBWMcS**-Sodium Bearing Low Activity Waste Special Sulfide Grout.

**Group 7, CTWHT**-Calcine Low Activity Waste (heat-treated @ 650 °C for denitration)

**Group 8, SBWCHT**- Sodium Bearing Low Activity Waste (heat-treated @ 650 °C for denitration) Grout.

**Group c, SBWBWCST** - Added in near the end of the preparation phase. Group 4 with crystalline silicotitanate (CST) added to retain Cs.

Because all the initial formulations failed the quick three-day immersion test and the acid grout formulation re-adjustments also failed, as discussed below, Groups 1 and 3 were eliminated from further test work. All the other groups required adjustment to the original formulation to pass the initial immersion test during the preparation checks.

## 5.1 Experimental Process

The laboratory testing was divided into six time ordered phases of activity:

Simulant preparation and equipment setup.

Grout preparation checks without tracers.

Simulant treatment and grouting with tracers.

Grout curing phase and pre-counting.

Water leach testing and radioactive tracer analysis.

Property Testing of Grout Treatments.

### 5.1.1 Simulant Preparation and Equipment Setup

Equipment for the preparation of the grout coupons was setup in the south hood of Laboratory 111 in CPP-637. The grout mixing, grout curing, denitrating and leach testing was performed in this hood. Gamma scanning, scintillation counting and ICP-MS analysis for Tc on the leach solutions was done in the radiochemical labs of CPP-602.

The chemical constituent concentrations of the two simulants are shown in Table 24. The sodium bearing waste (SBW) values represent evaporation of blended tank farm waste after the planned concentration per Charles Barnes flowsheet dated 12/9/98. The values used do not include blending in of newly generated waste. The calcine constituent concentrations represent evaporated LAW after separations from the blended calcine. It is based on Charles Barnes calcine LAW flowsheet dated 1/2/99. The acid concentration of the evaporated LAW is less than the dissolved calcine acid concentrations used in past work. This is a result of the modifications in the separations flowsheet.

**Table 24.** Concentrated Low Activity Waste Simulant Compositions (gmol/L)

	<b>SBW 2008 2x Flow Sheet</b>	<b>SBW- LAW Average</b>	<b>Composite Calcine- LAW</b>	<b>Stock Chemicals Used for Mixing the Simulants</b>
Acidity	1.54	1.94	1.68	HNO <sub>3</sub> , HBF <sub>4</sub> , etc
Ag	2.42 E-5	----	---	AgNO <sub>3</sub>
Al	0.674	0.784	0.724	Al(NO <sub>3</sub> ) <sub>3</sub> sol'n
B	0.0189	0.0191	0.0779	HF, ZrF <sub>4</sub> , HBF <sub>4</sub>
Ba	6.42 E-5	7.23 E-5	--	Ba(NO <sub>3</sub> ) <sub>2</sub>
Ca	0.0558	0.0576	0.599	CaO
Cd	0.0029	0.0001	0.0001	Cd(NO <sub>3</sub> ) <sub>2</sub> • 4H <sub>2</sub> O
Cl	.0304	0.0405	0.00214	HCl
Cr	0.0039	0.0001 <sup>1</sup>	0.0001 <sup>1</sup>	Cr(NO <sub>3</sub> ) <sub>3</sub> • 9H <sub>2</sub> O
Cs	1.16 E-9	2.76 E-5	3.34 E-5	CsNO <sub>3</sub> & <sup>137</sup> CsCl
F	.0726	0.0712	1.013	HF, ZrF <sub>4</sub> , HBF <sub>4</sub>
Fe	.0232	0.0271	0.00821	Fe(NO <sub>3</sub> ) <sub>3</sub> • 9H <sub>2</sub> O
Hg	1.15 E-3	0.0001 <sup>1</sup>	0.0001 <sup>1</sup>	Hg(NO <sub>3</sub> ) <sub>2</sub> • H <sub>2</sub> O
K	0.216	0.245	0.0129	KNO <sub>3</sub>
Mg	--	--	0.0232	MgO
Mn	0.0168	0.0159	0.00083 <sup>2</sup>	Mn(NO <sub>3</sub> ) <sub>2</sub> sol'n
Mo	0.000736	0.000843	0.0008 <sup>2</sup>	MoO <sub>3</sub>
Na	2.20	2.36	1.463	NaNO <sub>3</sub>
Ni	0.00168	0.00227	0.000942	Ni(NO <sub>3</sub> ) <sub>2</sub> • 6H <sub>2</sub> O
NO <sub>3</sub>	5.96	6.95	5.753	HNO <sub>3</sub> , Ca(NO <sub>3</sub> ) <sub>2</sub> , NaNO <sub>3</sub> , etc
Pb	0.00147	0.0001 <sup>1</sup>	0.0001 <sup>1</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>
PO <sub>4</sub> <sup>-3</sup>	---	0.0204	0.00037	H <sub>3</sub> PO <sub>4</sub>
Sr	---	2.04 E-5	1.01 E-4	Sr(NO <sub>3</sub> ) <sub>2</sub>
SO <sub>4</sub> <sup>-2</sup>	0.0526	0.0637	0.0101	H <sub>2</sub> SO <sub>4</sub>
TcO <sub>4</sub> <sup>-</sup>	---	1.17 E-5	1.024 E-5	NH <sub>4</sub> TcO <sub>4</sub>
ZrOF <sup>-</sup>	0.00105	0.00731	0.132	ZrF <sub>4</sub>

<sup>1</sup> Amount added to be below possible RCRA concern.

<sup>2</sup> Estimated- no value provided in spreadsheet.

Many different flowsheet compositions have been used to produce grout formulations for the SBW. Included in the first column of Table 24 above is the 2008 concentrated flowsheet used for some

of the recent grout work. The major difference between it and the new SBW-LLW compositions is the nitrate. It is considerably higher in the new calculated blended composition than in the 2008 flowsheet. This is probably because better values for the tank farm compositions are now available and the fact that nitrate adjustments were used to balance the species charge in the calculations. The nitrate is also one of the difficult anions to analyze for in waste solutions containing so many different species. Because of the higher nitrate, using the newer compositions may slightly affect leachability and some of the mechanical properties of the direct grouted waste options. Control grout coupons, without tracer, were therefore prepared to verify grout set and to run cross checks on other properties.

Simulants were made up in 3.0 liter batches by dissolving the reagents shown in Table 24 with the acids and added water. The hazardous metals and tracers were added later in the appropriate phase of the coupon preparation.

While preparing the composite calcine simulant a voluminous precipitate formed immediately upon the addition of the phosphoric acid. The volume of the precipitate after settling overnight was about two percent of the three liters. A sample was taken, washed two times with distilled water using a centrifuge for separation, and submitted for analyses. A result summary is presented in Table 25 below.

**Table 25.** Analysis Result Summary of CTW Simulant Precipitate

Precipitate Condition	X-ray Diffraction	SEM
Washed - Air Dried	Amorphous-Very Little Crystalline material present-Some $\text{Na}_2\text{Zr}(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ and other phosphates may be present	Zr major-Others detected: Ca, S, P and O.
Dried at 90°C Overnight	Mostly Amorphous $\text{Na}_2\text{Zr}(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ and other phosphates likely present.	Zr major - Na, Ca, P, Si, and O detected.
Dried at 700°C for Two Hours	$\text{NaZr}_2(\text{PO}_4)_6$ and $\text{CaZr}_2(\text{PO}_4)_6$ are the major crystalline components. $\text{ZrO}_2$ and $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ were detected as minor components. Some unidentified crystalline material and amorphous material is also present	Zr major - Na, Ca, P, Si, and O detected.

It appears that the precipitate is primarily a hydrated zirconium phosphate associated with many possible cations. The precipitate fraction remaining with the simulant for over six months appears to still be fluffy and suspends with relative ease and takes hours to resettle.

### 5.1.2 Grout Preparation Checks

Each of the grout types was prepared using formulations provided from past work. These formulations are shown as Table 26. To verify mechanical properties and preparation method the coupons had to have enough strength to hold onto the hanger while immersed in water. Proven mixtures and methods had to assure that the handling of the radioactive materials were kept to a minimum.

**Table 26.** Initial Proposed Formulations as Weight Percent of Simulant (As Liquid)

	<b>Group 1</b>	<b>Group 2</b>	<b>Group 3</b>	<b>Group 4</b>	<b>Group 5</b>	<b>Group 6</b>	<b>Group 7</b>	<b>Group 8</b>
Simulant	CTW	CTW	SBW	SBW	SBW	SBW	CTW	SBW
<b>Pre-Adjustants</b>							(14.7) <sup>1</sup>	(20.9) <sup>1</sup>
NaOH 50%	5.8	45.1	6.1	22.1				
CaO					19	13		
Water							13.9	19.7
Ca(OH) <sub>2</sub>		10.5		12.7				
<b>Cement Powders</b>								
OPC Type	34.9	12.1	34.8	7.9			6.8	9.6
BFS <sup>3</sup>	104.1	109.1	103.7	71.3	140		6.8	9.6
Fly Ash	34.9		34.8			100.6	6.8	9.6
CaO					16.1	33		
<b>Waste Loadings %</b>								
Total Grout Mass g/100g Liquid Sim.	279.7	276.6	279	208.7	275.2	247	49	69.6
Liquid Mass	35.8	36.2	35.8	47.9	36.3	40.5	204.1	143.7
Dry Basis as TDS <sup>4</sup> Mass	13.9	14.1	14.4	19.3	14.6	16.3	79.6	56

<sup>1</sup> Mass of dried solid/100g simulant. <sup>2</sup> OPC is Ordinary Portland Cement. <sup>3</sup> BFS is Blast Furnace Slag. <sup>4</sup> TDS is Total Dissolved Solids (includes dissolved acid gases).

None of the formulations initially provided worked well. Most were very difficult to mix and none held together properly when immersed in water for three days. Some of the compositions were reformulated several times until a successful grout was made. The successful formulations are shown as Table 27. For the AEA formulations, Groups 2 and 4, the sodium nitrate to total cement powders ratio was adjusted to 0.2 as per the AEA report. The balance of the formulation was adjusted to give a grout that could be mixed and handled in a radiation work setting and that would pass the immersion test. Initially, the Group 4 formulation was very dilute and shank to about 80% of the original volume when it finally setup. It miserably failed the immersion test.

**Table 27.** Actual Grout Formulations Used--Weight Percent of Simulant (As Liquid)

	<b>Group 2</b>	<b>Group 4</b>	<b>Group 5</b>	<b>Group 6</b>	<b>Group 7</b>	<b>Group 8</b>	<b>Group c</b>
Simulant	CTW	SBW	SBW	SBW	CTW	SBW	SBW
<b>Pre-Adjustants</b>	<i>(16.7)<sup>1</sup> (19.1)<sup>1</sup></i>						
CST <sup>2</sup>							0.027
NaOH 50%	23.7	27.4					27.4
Water	4	4.3			15.8	10.9	
Na <sub>2</sub> S				5.0			
CaO			20	20			
Ca(OH) <sub>2</sub>	12.4	12.7					12.7
<b>Cement Powders</b>							
OPC Type III <sup>3</sup>	16.7	21.2			7.7	12.5	21.2
OPC Type V <sup>3</sup>			25	62.5			
BFS <sup>4</sup>	150.8	190.6	100		7.7	9.9	190.6
Fly Ash				60	7.7	7.5	
Na <sub>2</sub> S				2.4			
CaO							
<b>Waste Loadings %</b>							
Total Grout Mass g/100g Liquid Sim.	307.6	356.2	245	250	55.6	59.6	351.9
Liquid Mass	32.5	28.1	40.8	40.0	180	170	28.4
Dry Basis as TDS <sup>5</sup> Mass	12.9	11.4	16.2	16.1	70.2	67.3	11.5
Volume %	44.3	40.3	56.3	52.6	285.5	246.6	

<sup>1</sup> Mass of dried solid/100g liquid. <sup>2</sup> CST is Crystalline Silicotitanate. <sup>3</sup> OPC is Ordinary Portland Cement. <sup>4</sup> BFS is Blast Furnace Slag. <sup>5</sup> TDS is Total Dissolved Solids (includes dissolved acid gases).

For Groups 5 and 6 the formulations were completely changed to produce a suitable grout. The initial compositions were very thick and couldn't be molded into the small cylinders without large air pockets. They had a tendency to soften, with some expansion, during the immersion test.

Groups 7 and 8 feeds were evaporated powders heated to 650 °C. The grouting of the denitrated simulants required that the liquid be evaporated and the resulting solids heated to 650 °C to "decompose" the nitrate. The temperature for the total calcine simulant was held at 650 °C for two hours. For the sodium bearing waste the temperature was held at 400 °C for two hours for reasons stated below. The resulting solids were mixed with the appropriate amount of water and the other cement powders blended in. The denitrating apparatus was a tube furnace that had the offgas condensed and collected for subsequent analysis. Cold testing of this apparatus was conducted using each of the simulants.

A separate test was ran on the evaporation-"denitration" of both liquid simulants to determine the degree of weight loss versus temperature for each. Table 28 shows these results. From this test it was concluded that little denitration would be gained going higher than 400 °C with the SBW-LAW simulant.

**Table 28.** Mass Loss at Temperature for Tested Simulants

<b>Temperature °C/time @ Temp.</b>	<b>SBW %Mass Remaining</b>	<b>CTW %Mass Remaining</b>
250 / 8 hr.	22.1	22.6
314 / 4 hr.	21.8	22.3
400 / 4 hr.	20.9	19.3
500 / 2 hr.	19.2	18.2
650 / 2 hr.	19.2	14.7

The initial Group 7 formulation was a little thick and with extra water did form a grout that hardened but had a marginal immersion test. Group 8 formed an extremely dilute grout that took days to set and then failed the immersion test. Adjustments were made to the formulations by checking a series of waste loadings. The choices made are included with the other formulations shown as Table 27.

The direct grouts, Groups 1 and 3 did not pass the immersion tests even with the modifications tried. Because of this and time factors in finding a good formulation they were eliminated from the tracer leach test. If time would have permitted perhaps satisfactory formulations could have been found. Waste loadings, however, would have to had been reduced to about the same level as the AEA grout type formulations, Groups 2 and 4.

Check grouts were made up for Groups 2, 4, 5, and 6 to be examined for mechanical properties and microbial attack. (Section 6) The mechanical test specimens were two-inch cubes and the microbial test coupons were the same size as the tracer coupons, 8.4 cm<sup>3</sup> cylinders. Results of the mechanical testing are shown in Table 29.

The results are good for all four of the treatments tested. Groups 7 and 8 were not tested because it has been determined that processing the waste at high temperature may not be a desirable option and because these groups did not perform well during the leach testing.

The results are good for all four of the treatments tested. Groups 7 and 8 were not tested because it has been determined that processing the waste at high temperature may not be a desirable option and because these groups did not perform well during the leach testing. The freeze thaw has a common tendency to strengthen the grouts. It can be noted that the group 2 90 day immersion cube indicated about half of the base case strength.



**Table 29.** Load Test Results for Mechanical Testing of Tracer Formulation Grouts-Two Inch Cubes PSI @ Failure

Group	Regular After 28 days of Cure	After Freeze/Thaw	After 90 Day Immersion
2	1362	1440	750
4	1186	1910	1240
5	1159	1860	1340
6	771	1710	950

### 5.1.3 Simulant Treatment and Grouting with Tracers

Four radioactive tracers were used in various concentrations in the simulants. Stock dose solutions were made up from the vendor supplied radionuclide solutions to facilitate supplying 1.0 to 2.0 micro-curies per grout coupon for both the Cs-137 and Sr-85. Stock solution for Tc-95m was planned out such that all of it was used for the six groups. The Tc-99 supply was diluted such that 1.0 ml was equivalent to  $1.0 \times 10^{-5}$  gmol Tc. The actual concentration that each treatment group was dosed with is shown in Table 30. The Tc-99 was added as an element of concentration with Tc-95m being the tracer for gamma scan purposes. As mentioned above, test coupons were prepared in groups of four or three for each grout treatment. Each treatment group was prepared one at a time in the same manner as proved out above. Except for the high temperature denitrated waste, one coupon out of the four had only Tc-99 as a radionuclide. This was measured successfully using ICP-MS as a crosscheck to the gamma emitter Tc-95m because of the expected low concentration in the leachate. The presence of Cs-137 would prevent this possibility.

Groups 7 and 8 did not have the fourth coupon made up because at a temperature of 650 °C and in the oxidizing conditions, much of the Tc was expected to vaporize and be collected with the condensate. This did not occur as expected. Over 68 % of the Tc-95m stayed with solids. Less than 1.0% showed up in the collected condensate and from the acid washed surfaces of the apparatus. It is assumed that the balance adhered chemically to the glassware. The strontium indicated a similar situation with 70 to 75% of the Sr-85 being detected in the solids. Over 93% of the cesium was indicated by gamma scan to be with the solids and less than 1% collected from the overheads.

Extra grout had to be made up to assure that the molds were fully loaded. The last column of Table 30 shows the percentage of the grout mixture that was used. These values were used to calculate the actual decayed dose from the gamma scan measurements made on the coupons. Group 7 has indicated loss for all three nuclides. As discussed above, this is a result of the 650 °C temperature and interaction with the quartz tube. Group 6 shows a lower than intended value for Sr-85 and Group 5 a much higher value. Apparently Group 5 was dosed with the amount intended Group 6 second dose round was applied. A note was made of the possibility when the treatments were dosed.

**Table 30.** Tracer Amounts Added to Grouted Simulant Volumes and Percentage Grout Used

Treatment Group	Volume ml	Cs-137 $\mu\text{Ci}$	Sr-85 $\mu\text{Ci}$	Tc-95m $\mu\text{Ci}$	Tc-99 $\mu\text{mol}$	% Grout Used
		Dose Intended / Decayed Actual	Dose Intended / Decayed Actual	Dose Intended / Decayed Actual		
2	15.2	6/6	6/3.6	3/1.9	0.157	67.7
4	14	6/5.7	6/3.6	3/2	0.162	79.2
5	18.3	6/5.8	6/5.4	3/2	0.212	77.2
6	18	6/6.1	6/1.7	3/2	0.209	79.4
7-Evap.	116	6/4.4	6/4.3	3/1.3	1.346	65.6
8-Evap.	100	6/6.1	6/4.8	Bal/0.275	1.16	61.9
C	14	6/5.4	6/5.4	none	0.162	80.8

#### 5.1.4 Grout Curing and Pre-counting

The numbered coupon molds were placed aside in an unused area of the hood for a minimum cure of 30 days. When cured, the coupons were removed from the mold, attached to a bottle lid and the bottle screwed on. The hanging coupons contained by the 250 ml bottles were then submitted in two separate groups for the record gamma scan. This was necessary because of cure time, instrument availability and to avoid confusion. Groups 2,4,5 and 6 had the coupons counted on April 16, 1999 and groups 7, 8, and c on April 22. All of the leachate samples were referenced to the coupon scans as the zero time. The values determined at this point were adjusted for the exact height of the coupons within the bottle and this value used as  $A_{0 + \text{rinse}}$  in the leach index calculations.

#### 5.1.5 Water Leach Testing and Radioactive Tracer Analysis

The coupons were leached according to the ANSI/ANS 16.1 Short test. Leaching of the coupons in one solution after another normally lasts 128 hrs in seven strategic intervals. The leaching was done in eight separate intervals. Fresh distilled water of a measured conductivity 1.4 megohm was used for each interval with the first being the 30 second rinse. This experiment differed slightly on the length of some of the intervals, but the overall time was 128 hours. This sequence was not a rigid time order but was planned to avoid conflicts and to assure that the leach solutions are removed at about the proper time. All exposure time was recorded within 10 minutes. The leach water was left in the bottle used for that leach interval and the grout coupon removed as it was being rinsed with a small amount of distilled water. The bottle was then capped and submitted for gamma scan or liquid scintillation. The grout coupon and attached bottle lid were transferred to the next bottle containing leach solution. After the final leach solution has been capped, the coupon and lid of the sample were screwed onto an empty bottle and submitted for simultaneous gamma scan of all three radionuclides. The bottles containing the leach solutions were returned to Lab 111 after the gamma scans. After the final leach solution had been capped, the coupon and lid of the sample were screwed onto an empty bottle and submitted for simultaneous post leach gamma scan.

For the Tc-99 only coupons, the leach water was evaporated to less than 10 ml from approximately 240 ml at ambient temperature in the hood. The bottles were rinsed into the evaporating beakers with dilute nitric acid followed by aqueous ammonia. The resulting samples were rinsed from the evaporation beakers into 15 ml bottles in the same manner as above and diluted to 15 ml. The samples were first submitted for liquid scintillation, but a successful analysis was not possible. Apparently the original supply of Tc-99 was contaminated or it became contaminated with another beta emitter during the makeup of the stock solutions at analytical. To achieve the desired analysis the samples were submitted for ICP-MS.

After the gamma scan analysis each of the treatment leachates was measured for nitrate using a specific ion probe. A leach index was also provided for the nitrate. The apparatus was calibration checked before and after each group of readings. Conductivity of each leachate was also run at the same time. The leachates from each coupon were then poured into 4.0 liter beakers and air evaporated to below 250ml. This concentrate was poured into 250 bottles diluted to approximately 250 ml and submitted for gamma scan. This was done as a summing cross check on earlier values. There was no serious discrepancy. The differences would have affected the leach indexes by less than 2%. The cesium and strontium showed less in the composite and the technetium was variable. Nuclide losses as a result of the evaporation of the solutions is very likely. The Tc differences could have been also been enhanced by the fact that the actual counts in both the original sum of eight bottles and the evaporated composite were small; thus, amplifying any other variabilities. The counting standard deviations for the composited samples were from 10 to 15 %

## 5.2 Leach Index Results

The leach index results are shown as Tables 31 and 32. The values in Table 31 were calculated based strictly on the ANSI 16.1 standard. The ANSI formula used to calculate the individual  $D_n$ , effective diffusivity, for each leach interval is:

$$D_n = \Pi \left[ \frac{a_n / A_0}{(\Delta t)_n} \right]^2 \left( \frac{V}{S} \right)^2 T \quad (\text{Eq. 1})$$

Where:

- $D_n$  is the effective diffusivity in  $\text{cm}^2/\text{sec}$ .
- $a_n$  is the amount of substance released from the specimen during leach interval n. Corrected for decay if a radionuclide (selected units).
- $A_0$  is the total original amount of the substance of concern at the beginning of leach interval 1 (selected units).
- $(\Delta t)_n$  is the duration of the  $n^{\text{th}}$  time interval ( $t_n - t_{n-1}$ ) in seconds.
- $V$  is the volume of the coupon in  $\text{cm}^3$ .

S is the coupon surface area in cm<sup>2</sup>.

T is the mean time of the leaching interval in seconds.

$$T = \left( 0.5 \left( t_n^{1/2} - t_{n-1}^{1/2} \right) \right)^2 \quad (\text{Eq. 2})$$

The composite leach index is calculated by averaging the logs of the reciprocals of the D<sub>n</sub>'s :

$$LI = \frac{1}{n} \log \left( \frac{1}{D_n} \right) \quad (\text{Eq. 3})$$

When the total amount of a specie leached out reaches is over 20 % of the original value, A<sub>0</sub>, then a graphical procedure is used. The D used in Equation 3 for the first interval which the total leached out was over 20 % and each of the following intervals is computed from:

$$D_n = \frac{G_n d^2}{t_{total}} \quad (\text{Eq. 4})$$

The G value used in the above equation comes from an interpolation of the ANSI table, derived from a graphical solution. The interpolations are based upon the length to diameter ratio of the cylinder and the fraction of component leached out. The l/d ratio was fixed in our case so a curve fitting of the table values was used for interpolation. For the purposes of this report the values of G were derived from the following equation:

$$G = 0.000822e^{4.8998F} \quad (\text{Eq. 5})$$

When the G values were necessary the leach index shown in Table 31 is followed by a number in italics indicating how many of the seven leach intervals had D computed using Equation 5.

**Table 31.** ANSI Leach Test Results Summary

Group	Cs-137 Leach Index			Sr-85 Leach Index			Tc-95m Leach Index			Tc-99 Leach Index			Nitrate Leach Index		
	Index	SD <sup>1</sup>	Cinv <sup>3</sup>	Index	SD <sup>1</sup>	Cinv <sup>3</sup>	Index	SD <sup>1</sup>	Cinv <sup>3</sup>	Index	GSD <sup>2</sup>	Cinv <sup>3</sup>	Index	SD <sup>1</sup>	Cinv <sup>3</sup>
2	8.2	0.05	0.23	9.5	0.09	0.18	11.3	0.07	0.48	11.2	0.25	0.39	7.6(5)	0.07	0.44
4	8.8	0.10	0.40	10.3	0.06	0.13	11.7	0.10	0.36	11.1	0.24	0.38	7.8(4)	0.03	0.48
5	7.8	0.07	0.26	8.5	0.07	0.29	10.3	0.10	0.43	11.4	0.23	0.36	7.6(5)	0.04	0.54
6	7.1	0.05	0.41	7.9(7)	0.06	1.04	9.8	0.12	0.35	9.8	0.44	0.69	7.3(6)	0.07	0.41
7	6.6(7)	0.04	0.33	8.7	0.09	0.21	6.6(7)	0.04	0.33	---	---	---	6.9(7)	0.01	0.20
8	6.6(7)	0.01	0.34	8.5	0.10	0.26	6.3(7)	0.09	0.33	---	---	---	7.1(6)	0.03	0.56
c	8.9	0.12	0.37	11.2	0.06	0.36	---	---	---	---	---	---	7.7(5)	0.04	0.64

<sup>1</sup>SD is the standard deviation of the ANSI method leach index of the three coupons in the Group. <sup>2</sup>GSD is the global standard deviation of all individual indexes measured for the Group (in the Tc-99 case, seven leachates and for the others, 21 leachates.) <sup>3</sup>Cinv is the Confidence Interval (+/- Cinv)

From Table 8 it is evident that groups 7 and 8 did not retain very well any of the four measured components except for strontium. The high pH of the grout systems would tend to hold the strontium precipitated as the hydroxide. The evaporated powders had the highest waste loading so good retention of nitrate and cesium would not have been expected. The poor performance on the technetium was a surprise. It is surmised that the Tc was tied up in the powder in a form that was not available for dissolution when the cement powders were mixed in. That form was perhaps also in the +7 Oxidation State which then could not have been reduced by the cement powders, and, as a result leached out during the leach test. Most of the technetium was removed during the first three intervals. Based on past leaching results, these two groups should have performed well. The differences were that the "dry" waste loadings were higher but not by much and the fact that the tracers were added to the simulant before evaporation-"denitration" instead of to the mixture at the time grout formulation.

Groups 4 and c performed the best overall. Group c was a modification of group 4 by the addition of CST. The crystalline silicotitanate was added to inhibit the leaching of cesium. The leachability was not statistically different from group 4. It was not known at that very high pH solutions would release the cesium from the CST. The AEA formulation requires that 14.9 molar caustic be added to the solution to neutralize the acid and to precipitate aluminum, iron, and other metals that can interfere with a high strength grout set. Leachability of the strontium, however, was improved by over a factor of seven. For a high pH this was expected.

Because the ANSI procedure does not take into account the change in the original value by the amount leached it tends to over predict the leach index except when the value leached out is small. To compensate for this the G, or graphical dimensionless time factor is used. It appeared during the initial evaluation of the data that possibly this could be an over prediction of the leach index. To examine other possibilities the formula for the effective diffusivity, D, was modified to compensate for the amount leached from the coupons by subtracting from A<sub>0</sub> the total amount leached from the coupon prior to each leach interval. Equation 6 reflects this change:

$$D_n = \Pi \left[ \frac{\frac{a_n}{\left( A_0 - \sum_{i=0}^{n-1} a_i \right)}}{(\Delta t)_n} \right]^2 \left( \frac{V}{S} \right)^2 T, \quad a_0 = 0 \quad (\text{Eq. 6})$$

The mean effective diffusivity then is driven by the amount remaining in the coupon at the beginning of each leach interval. It is felt that this formula more accurately reflects the physical situation than the original ANSI formula. This modification is called the "delta" modification of the ANSI leach effective diffusivity. This formula can be used without resorting to interpolation of the graphical solution. The leach index results using the Delta modification are summarized as Table 32.

**Table 32.** Modified "Delta" ANSI Leach Test Results Summary

Group	Cs-137 Leach Index			Sr-85 Leach Index			Tc-95m Leach Index			Nitrate Leach Index		
	Index	GSD <sup>2</sup>	Cinv <sup>3</sup>	Index	GSD <sup>2</sup>	Cinv <sup>3</sup>	Index	GSD <sup>2</sup>	Cinv <sup>3</sup>	Index	GSD <sup>2</sup>	Cinv <sup>3</sup>
2	8.1	0.14	0.23	9.5	0.07	0.11	11.2	0.34	0.53	6.7	0.48	0.75
4	8.7	0.25	0.39	10.3	0.06	0.09	12.1	0.37	0.58	7.1	0.37	0.58
5	7.6	0.16	0.25	8.4	0.16	0.25	10.9	0.59	0.93	6.9	0.25	0.39
6	6.8	0.27	0.42	7.6	0.10	0.16	9.7	0.27	0.42	6.4	0.28	0.44
7	5.8	0.21	0.33	8.7	0.13	0.20	6.2	0.81	1.27	6.1	0.25	0.39
8	6.2	0.23	0.36	8.5	0.17	0.27	6.1	0.86	1.35	6.9	0.79	1.24
c	8.8	0.22	0.35	11.2	0.22	0.35	---	---		7.2	0.16	0.25

<sup>2</sup>GSD is the global standard deviation of all leach index calculations made for each group. (In the case of the values above 21 leach indexes) <sup>3</sup>Cinv is the Confidence Interval (+/- Cinv)

Leach indexes that have values over 8.0 in Table 31 are not changed too much by the modification. For all leach index values that required the graphical solution for  $D_n$ , the leach index values are lower. Some values by as much as 0.8. This is a logarithmic difference that can be translated to mean an increase by a factor of about 6.0 in the calculated leachability.

Graphs showing the individual leach indexes in sequence are shown as Figures 3 through 6. A discussion of each figure is included below each. Both ANSI calculated and modified "delta" calculated values are shown. The delta values are the solid lines and the ANSI are broken lines.

Figure 7 shows the sequential leach results for the conductivity. It is noted that group 8 is the most conductive, followed by groups 7, 6, 5, 2, 4, and c. This is, as could be expected, the inverse order as the nitrate or cesium leach indexes.

### 5.3 Conclusions

This test clearly shows that leachability of a component is strongly dependent on waste loading. To increase the leach index special effort must be made to chemically bind the component within the grout matrix to decrease its solubility. In some of the treatments used during this testing attempts were made to do just that. Some improvements were definitely made but nothing over an order of magnitude.

The test re-iterates the difficulty restricting the leaching of cesium and nitrate from grouts. Nitrate is one of the most mobile anions in crustal formations and one of the problematic contaminants in both surface and ground water. Nitrates will not be simply tied up. The strontium leaching was successfully restricted in all groups except group 6 where the formulation contained too much excess calcium. The technetium leaching was essentially constrained in all but the evaporated powders. The reason for such a low performance of groups 7 and 8, Tc ANSI leach indexes of 6.6 and 6.3 respectfully, is not totally understood. Additional investigation is needed.

The ANSI leach test method provides a gross indication of the true nature of leachability contained grout components. By using the initial concentration for each leach interval and using the graphical solution developed for infinite mediums, which the fraction leached is greater than 0.2, some information is not expressed. It would also perhaps be more informative to report all of the interval leach

indexes for evaluation. Graphs as presented in this report show the trends and quickly indicate suspicious data points.

For practical usage any leach index below about 8.0 should not be considered acceptable. A leach index of 8.0, the indicated diffusivity is  $1.0 \text{ e-}8 \text{ cm}^2/\text{ sec}$ . This value is only about a 1000 times less than the diffusivity of ethanol in water. Using 8.0 as the minimum passing basis and the computed confidence interval, a hypothetical passing limit can be applied to each of the groups for each level. Table 33 summarizes the passing leach indexes at the 99.9 % confidence level.

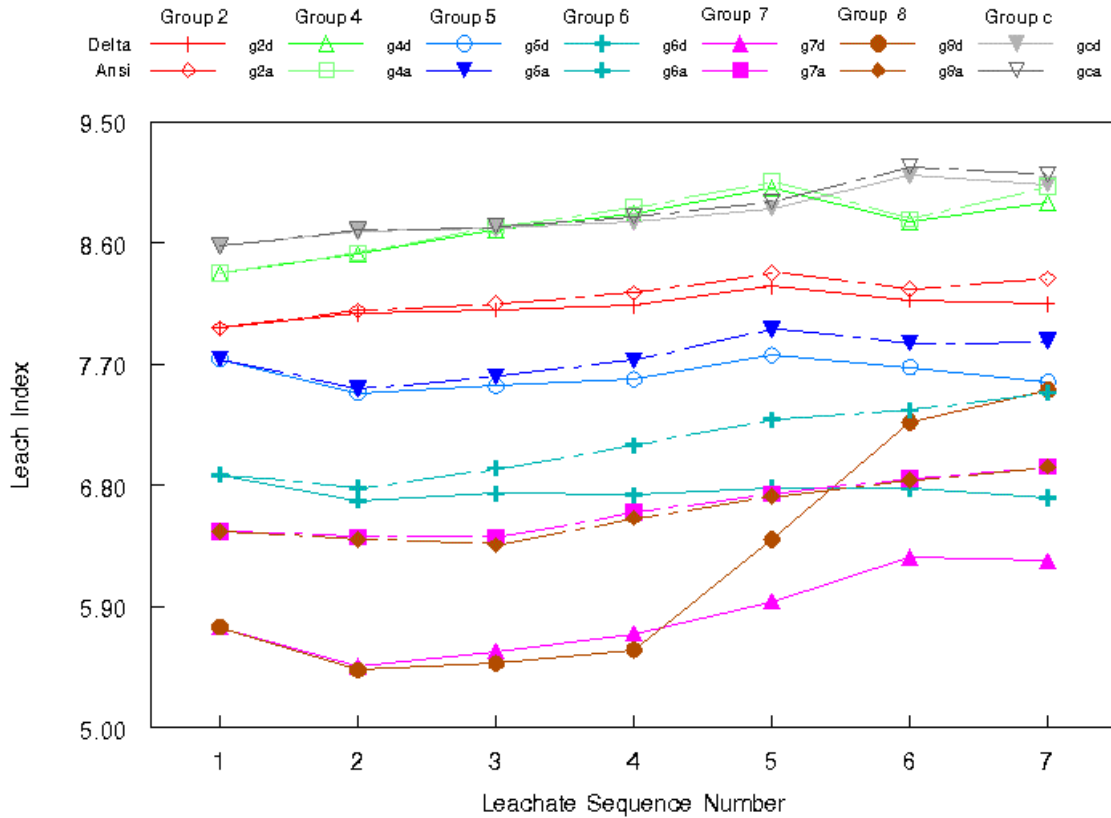
**Table 33.** Passing Leach Indexes Summary at 99.9 % Confidence

Group	Cesium	Strontium	Technetium
2	Fail	9.3	10.8
4	8.4	10.2	10.7
5	Fail	8.2	9.9
6	Fail	Fail	9.5
7	Fail	8.5	Fail
8	Fail	8.2	Fail
c	8.5	10.8	----

None of the groups retained nitrate well enough to pass the stipulated criteria. Only groups 4 and c passed all the other three components tested. All but group 6 passed for strontium and all but groups 7 and 8 passed for technetium. The CST containing AEA grout was not tested for technetium. Only the AEA formulation was reliable enough of the formulations tested to adequately contain all three radionuclides.

Future test work should definitely further examine possible methods of binding the desired components chemically. It appears that our efforts are lacking since the leach index of all four of the measured components can be correlated to dry waste loading. If most of a component was chemically bound the leach index would rise on each subsequent leach from a high value to a higher one without receding. The data from this test do not indicate this on any component except when the specie is nearly leached out.

### Cs Leach Index by Sequence (Delta and ANSI)

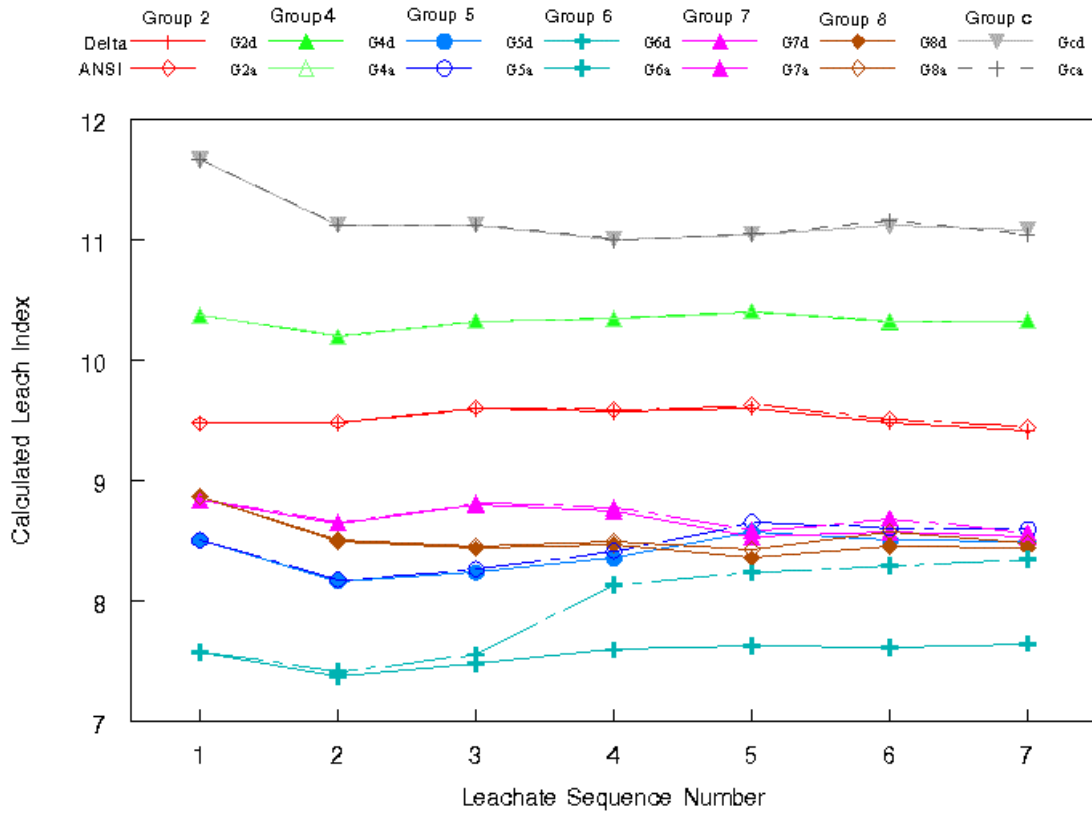


**FIGURE 3.**

Discussion of Figure 3: None of the individual cesium leach indexes reach 9.0. Above 7.0 the ANSI and Delta values are close with the ANSI values a little higher as mentioned earlier. With groups 7 and 8 the difference between the Delta and ANSI values is about 1.0. The Delta values of both 7 and 8 are grouped together as are the ANSI values. It is noted that the entire series of ANSI individual indexes for groups 7 and 8 were from the graphical solution. The group 8 Delta values rise quickly for leaches 5, 6, and 7. This is because there is less than 1.0% of the original amount of cesium left. The small amount left becomes much more difficult to leach. This effect is not demonstrated by the ANSI values. The diversion of the ANSI from the Delta for groups 5 and 6 becomes pronounced as more of the cesium becomes leached out.



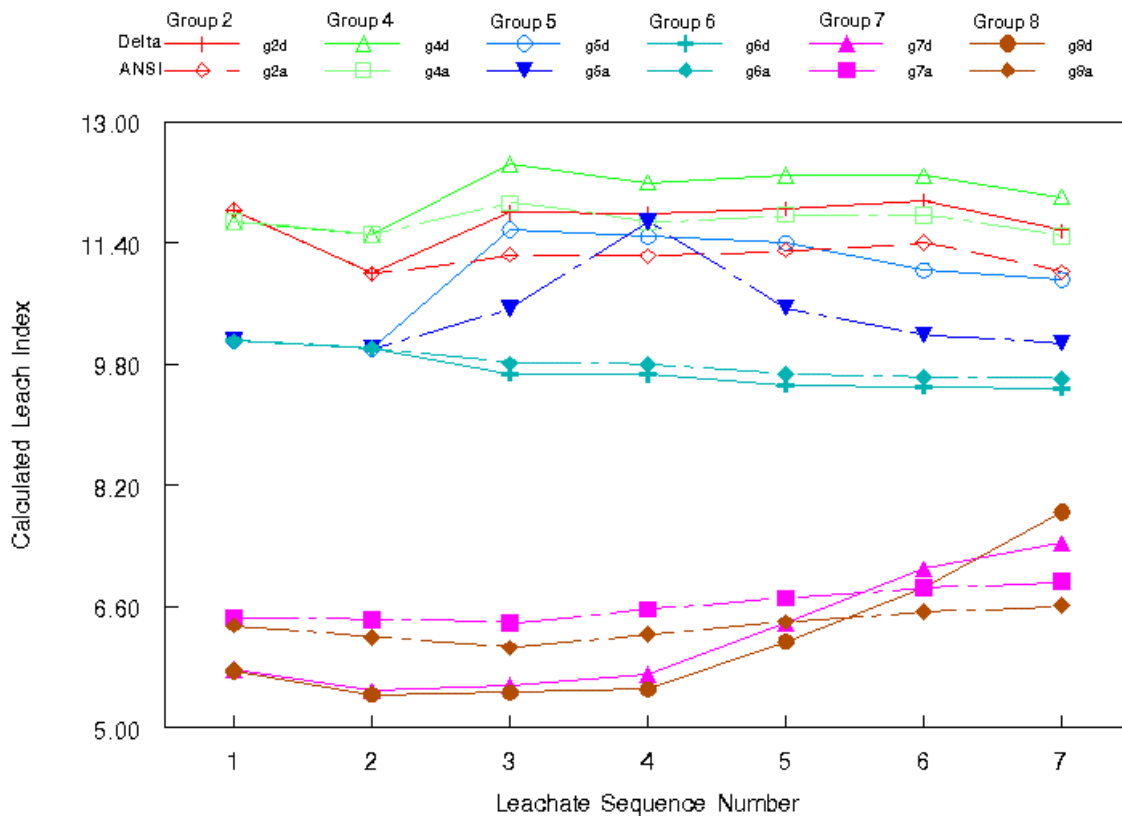
### Sr Leach Index by Sequence (Delta and ANSI)



**FIGURE 4.**

Discussion of Figure 3: All of the strontium leach indexes are over 7.0. Above values of 9.0 the ANSI and Delta values are essentially the same. Below a leach index of 9.0 a divergence of the values is evident. Note that for group 6, which is unexpectedly below 8.0, that the ANSI values jump up at leach number 4. At this point the calculation of D is graphical. It is believed that Group 6 is lower than the others because of the presence of too much calcium in the cement powders blend.

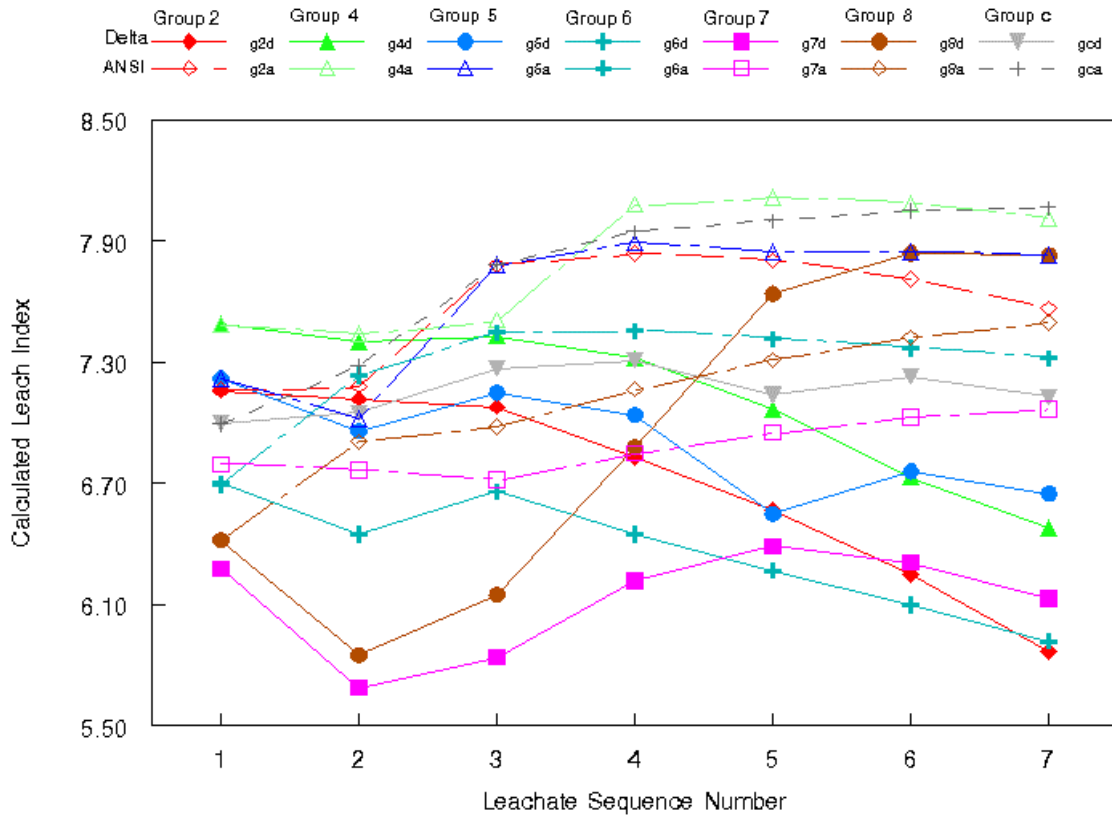
### Tc Leach Index by Sequence (Delta and ANSI)



**FIGURE 5.**

Discussion of Figure 5: Most of the technetium leach indexes were high as expected. The exception being groups 7 and 8. As discussed earlier this was not as desired and is difficult to adequately explain. It is noted that above a leach index of about 10, ANSI values are lower than the delta. This shows again loss of sensitivity in the use of the ANSI values. All of the indexes for the group 7 and ANSI values were determined from graphical Ds. The Delta values increase sharply at leach number 5. This increase reflects the fact that both groups had over 90% of the Tc leached out at leach number 4.

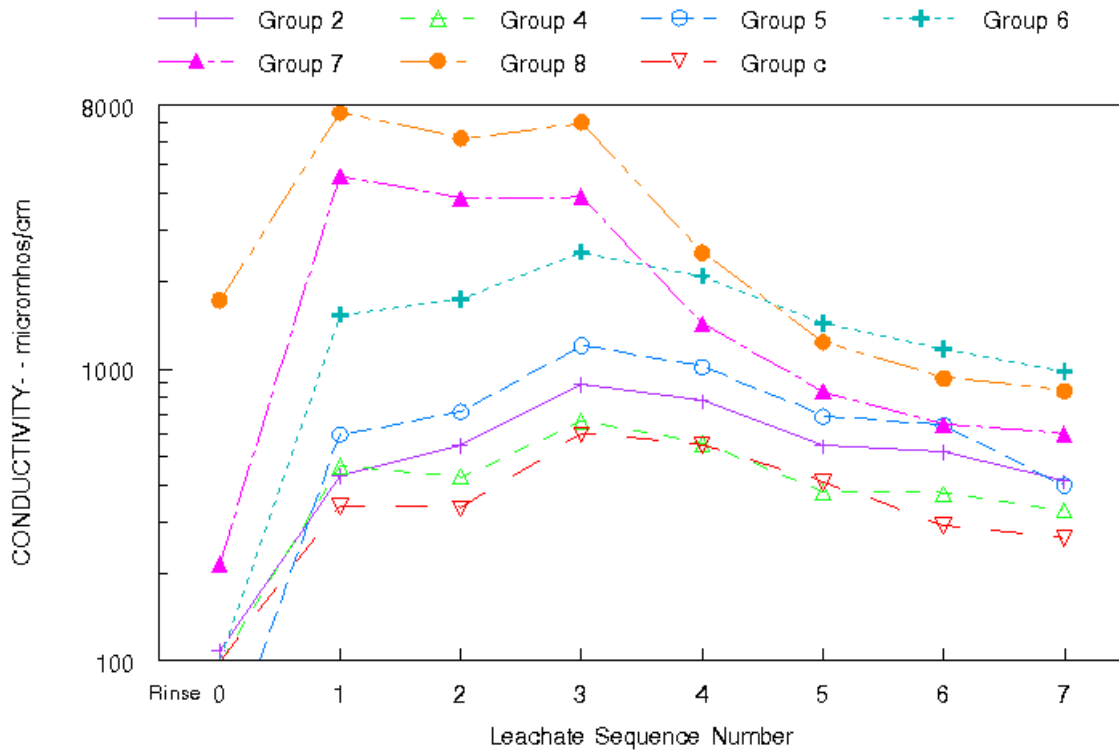
### Nitrate Leach Index by Sequence (Delta and ANSI)



**FIGURE 6.**

Discussion of Figure 6: None of the nitrate sequential leach indexes reached 8.0. For all groups the nitrate leached easily from the grout coupons. None of the Delta values are higher than 7.5 and groups 7 and 8 are essentially leached out by leach number 4. The rise in the group 8 Delta again reflects a very small amount of nitrate remaining in the group 8 coupons.

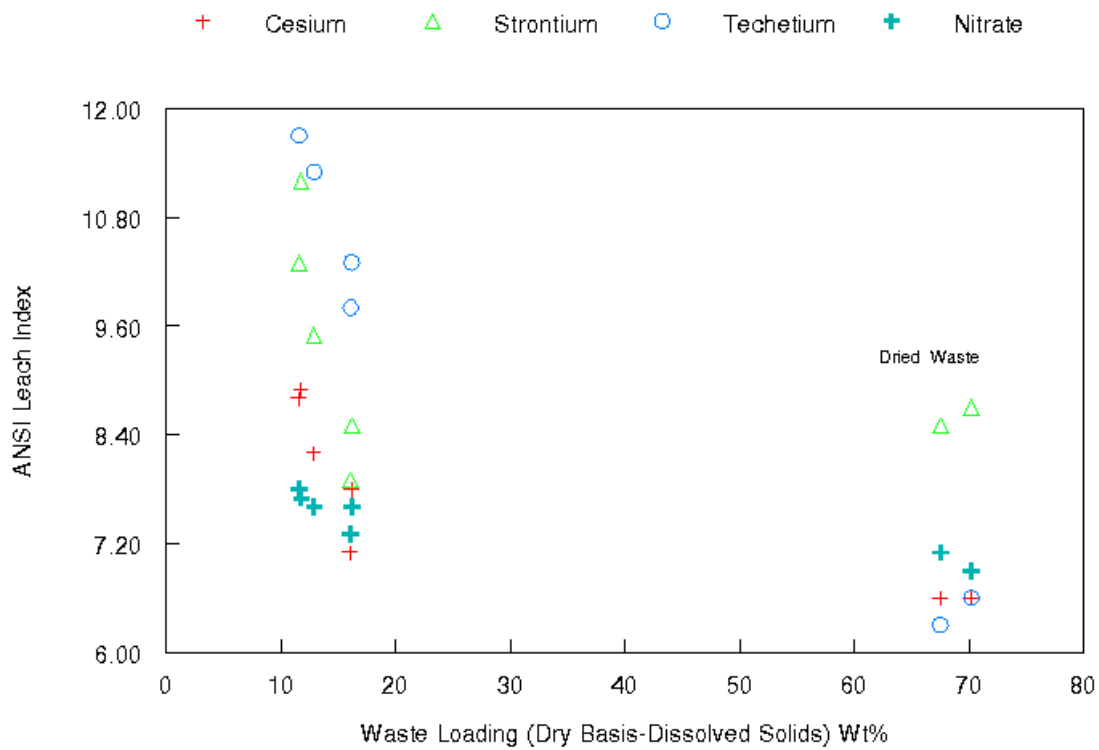
## Average Conductivity of Leach Solutions



**FIGURE 7.**

A discussion of Figure 7 also appears in the general text. The figure shows the trend that is followed by most of the leach indexes. Group 8 leached the most and has a lower leach index in most of the components. Group 7 is the next worst followed in order by 6, 5, 2 4, and c. Conductivity reflects the trend in nitrate leachability.

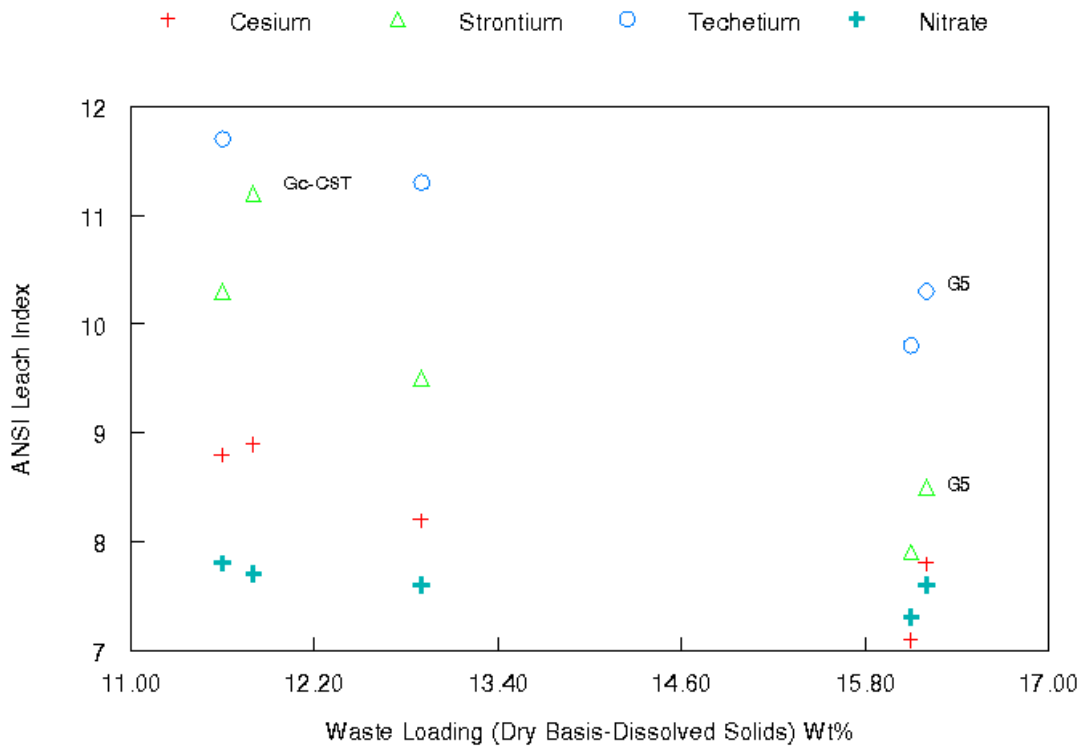
### Leach Index vs Dry Basis Waste Loading



**FIGURE 8.**

Discussion of Figure 8: It can be seen that the leach index of all four measured components decrease sharply with dry waste loading of the grouts. Only one component has a higher index at a higher waste loading and that is strontium in the dried waste forms. The reason is not definitely known at this time.

## Leach Index vs Dry Basis Waste Loading (Lower Range)



**FIGURE 9.**

Discussion of Figure 9: The lower waste loading portion of Figure 8 is shown here as Figure 9. Leach index values almost inversely proportional to waste loading even with the variety of treatment mixtures used on the liquid waste forms. Linear equations were derived for each of the four measured components and are shown below:

Cesium             $LI = 12.29 - 0.301 * (\text{wt\% dry waste loading})$

Strontium         $LI = 16.65 - 0.544 * (\text{wt\% dry waste loading})$

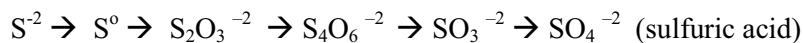
Technetium       $LI = 15.98 - 0.368 * (\text{wt\% dry waste loading})$

Nitrate             $LI = 8.48 - 0.0644 * (\text{wt\% dry waste loading})$

## 6. MICROBIAL DEGRADATION OF GROUT STUDY

Microbial influenced degradation of low-level waste forms was tested on the acid grout and alkaline grout formulations of sodium-bearing waste forms. The test is to determine the structural stability of the waste form following microbial exposure. The Code of Federal Regulations [10 CFR 61.56(b)(1) ] states, “Waste must have structural stability. A structurally stable waste form will generally maintain its physical dimensions and its form, under the expected disposal conditions such as weight of overburden and compaction equipment, the presence of moisture, and microbial activity, and internal factors such as radiation effects and chemical changes. Structural stability can be provided by the waste form itself, processing the waste to a stable form, or placing the waste in a disposal container or structure that provides stability after disposal.” The Nuclear Regulatory Commission in their Low-Level Waste Management Branch Technical Position on Waste Form (1991) requires a biodegradation test if the waste form contains carbon. However, a recent contract report (NUREG/CR-6641, June 1996)<sup>14</sup> recommends that a sulfur-oxidizing bacteria be used since this bacteria is common in landfill soils. Thus, this experiment follows the more recent recommended test procedure.

*Thiobacillus* is an autotrophic organism which means that it uses something else for energy rather than organic carbon – for example as you know a tree is an autotroph because it uses sunlight for energy and CO<sub>2</sub> for the carbon it needs to produce new cells. *Thiobacilli* obtain their energy by oxidizing reduced sulfur compounds and like the trees use CO<sub>2</sub> for biomass production. The sequence of sulfur (S) usage starting with a sulfide is as follows:



Sulfides and elemental sulfur are not soluble in water so they are not suitable for reduced sulfur sources for continuous, liquid culture solutions. Thiosulfate has been used but tetrathionate (S<sub>4</sub>O<sub>6</sub><sup>-2</sup>) is very soluble in water at high concentrations; thus, it's use in this experiment. Now when the cells are not using S<sub>4</sub>O<sub>6</sub><sup>-2</sup> it can either auto reduce or biologically reduce to elemental sulfur. As a result, elemental sulfur can sometimes be found in the growth medium. Because *thiobacilli* are capable of withstanding high concentrations of acid the production of sulfuric acid is not a problem for them, hence the continued growth at low pH.

The bacteria *Thiobacillus thiooxidans* was used to determine the extent of microbially induced degradation (MID) of cement specimens formed from sodium bearing waste simulant, portland cement, blast furnace slag. These grout specimens will be evaluated under conditions of intermittent immersions in T. thiooxidans lixiviant and compared to the same waste forms under intermittent immersion in sterile growth media.

The bacteria *T. thiooxidans* will be grown in a two liter, continuous flow bioreactor and lixiviant will be pumped to the Soxhlet contact cells at a rate of approximately 100 ml/day/cell. Sterile growth media will be pumped to the other contact cells at the same rate. Each contact cell consisted of a Soxhlet apparatus containing the grout waste form attached to a 500 ml Erlenmeyer flask with a stopcock valve at the base to allow sampling and draining to the appropriate collection container. This solution was sampled weekly for toxic metals and pH. The pH of the bioreactor solution was taken each day during working hours. The experiment ran continuously and was left unattended over the weekends.

## 6.1 Description

The two liter bioreactor (self contained) was set up and operated, growing the bacteria T. thiooxidans, with a sterile growth mineral salts and potassium tetrathionate media. Neither the constituents of the growth media nor the bacteria themselves, pose any safety or health hazards. Glass 19 liter carboys containing the sterile growth media consisting of the formulation given in Table 1 was brought into the experimental area as needed to supply feed to the bioreactor; where it came in contact with the culture media. Similar sterile growth media was fed directly from a similar glass carboy to the sterile soxhlets by the same pump setting and flow rate as used to feed the microbial Soxhlets. The experiment consists of 12 Soxhlet contact cells. The bioreactor effluent was distributed to six of the Soxhlet contact cells. Sterile growth media was pumped to the other six Soxhlet contact cells using the same pump setting and flow rate used to pump the bioreactor effluent to the microbe Soxhlet cells. Eight of the twelve cells contained grout specimens containing a spike of toxic metals (Cd, Cr, Pb, Hg and Ni) simulating actual grout characteristics. The other four cells contained nonhazard grout specimens. Effluent (or media) was distributed to the Soxhlets; where it passed over the grout waste form specimens and accumulated in the Soxhlets filling to the overflow point; then auto dumping into 500 ml flasks located beneath each soxhlet. This auto dumping from the soxhlet to the flask below occurred at approximate 8 to 9 hour intervals. The solutions collected in the flasks were drained into labeled containers; where a pH was taken and sampled weekly. The solutions remaining after sampling were placed into an authorized (SAA) Satellite Accumulation Area. The first experiment was expected to run 60 days continuously; but was terminated after 55 days operation due to roof repair in the Low Bay Laboratory. The experiment was taken out of the LBL and placed in the High Bay Lab; where a second 60 day test was started. At the conclusion of the test all waste was taken out of the SAA, neutralized, sent to service waste or shipped to a Licensed Disposal Facility (LDF). Placement of waste depends on toxic metals sampling and proper pH (2 to 12). The waste used in nonhazard specimens will be neutralized to the proper pH and sent to service waste. Any waste found to contain toxic metals above the RCRA treatment standard is be sent to a LDF.

**Table 34.** Sterile Growth Media Composition per 1 liter deionized water.

Component	Quantity (grams)
MgSO <sub>4</sub> · 7H <sub>2</sub> O	0.4
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.5
CaCl <sub>2</sub>	0.20.25
KH <sub>2</sub> PO <sub>4</sub>	3.0
FeSO <sub>4</sub>	0.01
K <sub>2</sub> H <sub>4</sub> O <sub>6</sub>	3.0

The test used grout specimens with the cement powders ratio of blast furnace slag (BFS): ordinary portland cement (OPC): pulverized fly ash (PFA) at 3 : 1 : 1 at 30 wt% and 45 wt% waste loading using the acid and alkaline formulations. Additionally, a second set of grout specimens were tested which were made with the alkaline formulation at 45 wt% waste loading and a cement powders ratio of 9 : 1 : 0 (no fly ash). Each formulation utilized a specimen on the control side and on the microbe side.

Each grout specimen was formed in a mold sized into a cylinder form with an average diameter of 0.737 inches and an overall height of 1.23 inches. The average grout density was 1.8 g/cc and an



average weight of 15.0 g. The grout specimens were allowed to cure in a plastic bag environment for greater than 30 days prior to microbial testing.

The experiment and apparatus was set up in CPP 637 Laboratory inside a module. This module has an air supply (20 lbs.), 110 volt electrical receptacles, air temperature control and isolation from temperature and air variance. Figure 10 shows the setup of the apparatus. The test is based on an intermittent immersion. This was accomplished by using 125 ml Soxhlet extraction columns. Figure 11 shows several of the columns set up, including attachment to effluent 500 ml collection flasks. Each specimen was placed on top of a teflon pedestal inside an individual Soxhlet column. Filling of the column was controlled by the effluent flow rate. It required 8-9 hours for a specimen to become immersed. After the liquid level rose to a predetermined height, the column was emptied by the activation of a siphon.

**Figure 10.** Setup of the Microbial Test Apparatus.



**Figure 11.** View of the 125 ml Soxhlets and the 500 ml Erlenmeyer Collection Flasks with the Grout Samples Residing on the Teflon Pedestals.



## 6.2 Results and Conclusions

Figure 12 is illustrative of the test results. Specimen 1MH represents the samples exposed to the bacteria and specimen 1CH represents the control side that was not exposed to the bacteria. Note how the 1MH sample deteriorated compared to the control sample. The control specimens had an approximate compressive strength of 1500 psi; whereas, the microbe samples could generally be broken by with simple finger pressure. Such was the case for all exposed and control specimens.

In addition to studying the structural degradation of the waste form, the effluent was analyzed for toxic metals to determine if the microbial degradation would cause their release. During the 60 day test no RCRA metals leached from either the exposed or control samples above the RCRA limits.

The microbial degradation test showed that the bacteria, Thiobacillus thiooxidans, can and will attack the cement based structure of these sodium-bearing waste forms. Even though the structure of the grout waste form degraded, the toxic / hazardous metals did not leach greater than the RCRA treatment limits. Further studies are needed to test the long term microbial degradation and leach resistance of these waste forms. Also, the new DOE Order 435.1 requires checking for gaseous releases due to microbe activity. This test will need to be redesigned to meet the new requirement.

**Figure 12.** Comparison of the Microbe Test Sample (1MH) and the Control Sample (1CH)



## 7. pH ADJUSTMENT STUDY OF INTEC WASTE STREAMS

### 7.1 Introduction and Background

In the INTEC High-Level Waste program, one feasible option is to grout the liquid low-activity waste (LAW) and newly generated liquid waste (NGLW) streams. The proposed treatment process<sup>11</sup> is to adjust the solution pH to an appropriate level (>11); allow the mixture to stabilize 1 to 3 days (depending on solution composition), add additional chemicals if necessary (e.g.,  $\text{Ca}(\text{OH})_2$  to precipitate fluoride ion), and grout the resulting solution. The physical characteristics of the resulting mixture from pH adjustment could affect the equipment and grout performance. However, if long term storage is required and the pH adjustment of the waste streams is necessary (due to regulatory and equipment constraints), the potential deposition of sludge in tanks and plugging of line/valves etc. are a major concern. The process and storage equipment must be compatible with the products resulting from pH adjustment. This report

summarizes an effort to estimate the amount and characteristics of the precipitates/sludges of the LAW and the chemicals used for pH adjustment.

Spent nuclear fuel was reprocessed at the Idaho Nuclear Technology and Engineering Center (INTEC) from 1953 through the 1980s. A significant quantity of liquid waste was generated and stored in tanks at the INTEC. Over the last 36 years, approximately 4071 cubic meters of calcine solids were generated and stored in stainless steel bins at INTEC. Approximately 1.5 million gallons of high sodium content, intermediate-level radioactive wastes are stored in tank farms. This liquid waste is referred to as sodium-bearing waste (SBW). The high sodium content of SBW makes it difficult to process in the existing calciner system.

A feasibility study (FS) on waste treatment was performed in 1997 for the U. S. Department of Energy (DOE). The FS addressed a concept for a new waste treatment facility (WTF) to retrieve and treat stored calcine and liquid waste; producing immobilized waste forms suitable for disposal. The FS evaluated a WTF option using efficient separation processes to partition SBW and calcine into two product streams: a small volume, high-activity waste (HAW) stream to be vitrified and disposed in a geologic repository; and a relatively large volume, low-activity waste (LAW) stream to be immobilized in grout for near surface disposal.

To aid in the future closure of the INTEC tank farms, current plans are to segregate, and separately treat and dispose of many waste streams that normally go to these tanks. This newly segregated waste will consist of spent decontamination solutions, flushes, storm water run off, etc., and has been designated as Newly-Generated Liquid Waste (NGLW or type 2 LLW). Proposed plans are to combine these NGLW streams, concentrate resultant solution in the Process Equipment Waste Evaporator (PEWE), and store it until a grouting or other treatment facility is available. Another newly-generated waste stream is also being evaluated for potential grouting. Due to the relatively high chloride content in the PEWE bottoms from a blend of high level liquid waste evaporator (HLLWE) condensate and INTEC-603 basin water, this waste stream, referred to as NGLW-2000, was evaluated separately.

## 7.2 Objectives

The primary objective of the pH adjustment study was to develop and evaluate a flowsheet for adjusting the pH of individual LAW streams to be compatible with grout formulations. The options for the product after pH adjustment are (1) storing the resulting mixture in tanks for future treatment, or (2) grouting the product immediately. The quantity of the precipitates/sludge resulting from waste stream pH adjustment is critical to selecting process equipment and determining the feasibility of achieving a given pH. Additional objectives of this laboratory bench test were:

1. To determine the amount and characteristics of the resulting precipitates from the pH ranges tested
2. To minimize chemical addition and volume increase of the resulting mixture during pH adjustment
3. To produce an easily transferable LAW product with minimal quantities of undissolved solids
4. To identify any problems inherent with LAW pH adjustment.

## 7.3 Chemistry

pH adjustment of all LAW involves an initial reaction between the acid in the waste solution and the added base. Further increases of solution pH may result in precipitation of metals. Metal hydroxides precipitate at various pH levels, depending on such factors as the speciation, oxidation state, and the presence of complexing agents such as citric acid, ethylenediamine tetraacetate (EDTA), etc. The solubility of a metal in solution is dependent not only on obvious variables, such as pH and temperature, but also on metal concentration, time (which affects crystal form/stability and poly-nuclear complex formation), and particle size. The typical reaction for the formation of hydroxide is as follows:



Where  $M^{n+}$  is a metallic cation.

If no complexing agents other than hydroxide ion are present, the simple metal cation ( $M^{n+}$ ) will often hydrolyze to form complexes with the hydroxide ion as function of pH. These complexes can be cations ( $M(OH)_{n-1}^+$ ), neutral molecules ( $M(OH)_n$ ), or anions ( $M(OH)_{n+1}^-$ ), where n is the oxidation state of the metal. In addition to these mononuclear complexes, polynuclear species containing more than one metal atom (e.g.,  $M_k(OH)_{kn-2}^{+2}$ ) may also form. All of these hydrolysis reactions play a significant role in the aqueous chemistry and solubility of metals in water.

As hydrolysis of metal ion occurs, the sizes and surface charge of the ionic species increase. When the surface becomes charged, a charged double layer surrounding the ion is formed. The existence of these double layers around ions inhibits their close approach to each other. Thus, the hydrated metal ions may be stabilized and remain suspended in solution as a colloid.

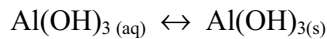
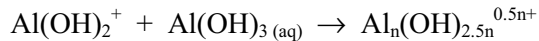
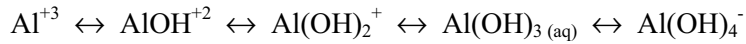
In order to precipitate metal ions as salts out of a waste solution, the stability of the colloidal suspension must be overcome. The destabilization of colloids can be achieved by adding iron salts, aluminum salts, calcium salts or polyelectrolytes to the solution and by adjusting pH. The thickness of the double layer and the surface charge density are sensitive to both pH and concentration of the ions in solution.

The precipitation process of metal hydroxides may be regarded as a sequence of interacting steps that destabilize the colloids as both pH and metal ion concentration are increased. Table 35 presents the order of precipitation from dilute solution as the pH increases:

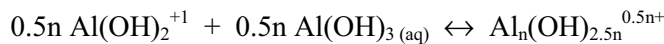
**Table 35.** Order of Ion Precipitation from Dilute Solution as pH Increases.

Ion	pH	Ion	pH
Zr <sup>+4</sup>	2.0	Ni <sup>+2</sup> , Cd <sup>+2</sup>	6.7
Fe <sup>+3</sup>	2.5	Co <sup>+2</sup>	6.9
Al <sup>+3</sup>	4.1	Zn <sup>+2</sup>	7.0
Cr <sup>+3</sup> , Cu <sup>+2</sup>	5.3	Hg <sup>+2</sup>	7.3
Fe <sup>+2</sup>	5.5	Mn <sup>+2</sup>	8.5
Pb <sup>+2</sup>	6.0		

Due to high concentration of aluminum in most of the waste streams, most of discussion will revolve around this metal. AEA Technology PLC<sup>15</sup> proposed that a better grout could be produced from the waste solution containing solid/crystal aluminum, instead of amorphous or gel like aluminum precipitates. As the solution pH increases, the first precipitate is generally of colloidal size and of low crystalline order. Colloidal aluminum hydroxide is hydrophilic and easily coagulates to form gels. Many different forms of aluminum are thought to exist over a wide pH range. The following simplified aluminum hydrolysis scheme was chosen by Clark<sup>16</sup> to incorporate five equilibrium aluminum species ( $\text{Al}^{+3}$ ,  $\text{AlOH}^{+2}$ ,  $\text{Al(OH)}_2^{+1}$ ,  $\text{Al(OH)}_3(\text{aq})$ , and  $\text{Al(OH)}_4^{-1}$ ) and amorphous aluminum hydroxide ( $\text{Al(OH)}_3(\text{s})$ ):



The equilibrium species are well supported by equilibrium data in the literature.<sup>17</sup> Due to the lack of agreement in the literature on the structure of aluminum polymers, Clark<sup>16</sup> proposed an “average” aluminum polymer,  $\text{Al}_n(\text{OH})_{2.5n}^{0.5n+}$ :



At pH values below 10 and temperature below 60°C, the solids are found to be either amorphous or microcrystalline bayerite.<sup>18</sup> The amorphous and microcrystalline precipitates consist of very small particles that are difficult to separate from liquid phase by filtration.<sup>18</sup> At pH 10 and temperature below 60°C, well crystallized bayerite is then present. If a precipitate is formed at 60°C and pH of 10, gibbsite is formed.

Recycling of sludge (chemical seeding) to induce the formation of more crystalline and less amorphous precipitates was studied by Knocke and Kelly.<sup>19</sup> The results showed that less water was incorporated into the metal hydroxide sludge floc matrix when sludge recycling was used.

Vermeulen<sup>18</sup> proposed that during aluminum precipitation mixing, one must avoid localized hydroxide ion concentrations that are much higher than the overall concentrations of hydroxide ions, to minimize localized  $\text{OH}^-$  variations. Vermeulen also noted that if the  $\text{OH}^-$  concentration is rapidly and nonuniformly added to the system, different types of products were formed. Rapid neutralization of aluminum salt solutions with bases leads to gels rich in water which contain variable amounts of residual acid ions.

During Clark's<sup>16</sup> study of aluminum precipitation, he noticed that mixing at different speeds causes variations in solid and polymeric species. Therefore the competition between polymeric and solid species is mixing sensitive. Clark concluded that “good mixing” – more intense mixing, higher local turbulence intensities and faster circulation times is produced stable solid species; more desirable solid and less undesirable polymer is formed.

The reverse reaction, adding the acid to the caustic solution, was studied by Stol<sup>20</sup>. The authors showed that if the rate of acid titration is slow enough, it should be possible to obtain complete reversibility. However, at  $\text{OH}/\text{Al}$  ratios exceeding 2.5, the acid titration curves suggested that the dissolution process is simply not a reverse of the precipitation process. Stol also observed the effect of increasing ionic strength. The results indicated that increased polymerization on addition of salts is

incurred by a more effective screening of the high positive charge of the ionic aggregates by the anions  $\text{NO}_3^-$  and  $\text{Cl}^-$ .

Gelatinous aluminum hydroxides prepared by neutralization of concentrated aluminum salt solutions at temperature below  $17^\circ\text{C}$  have low crystalline order and very small particle size. This “active” form of amorphous precipitates will often undergo changes while aging. Either the active form becomes inactive or a more stable crystalline modification is formed. Usually, the time for aging is hours or days, rather than months or years. However, the presence of anions in the solution could retard the aging process.<sup>21</sup> If the “amorphous” solid remains in contact with the liquid, it will transform into one of the ordered hydroxides or oxide hydroxides. The rate and path of this transformation are complex functions of the chemistry of precipitation during aging.<sup>21</sup>

Very little research information was available about the precipitation and sludge properties of waste solutions with high ionic content. Novak<sup>22</sup> studied what effects of reverse addition may have on the sludge properties by adding SBW simulant ( $\text{Al}^{+3}$  at  $0.66\text{ M}$ ) to  $2\text{ M NaOH}$ . The process produced a sludge which had poorer dewatering characteristics than the sludge created by adding the base into the SBW. However, when a similar process was used by SBW simulant spiked with additional calcium, the dewatering characteristics improved considerably. While calcium addition, combined with reverse addition encouraged crystal formation and improved dewatering rates, the improved dewatering rates were due to the presence of more stable aluminum precipitates in solution.

## 7.4 Materials and Methods

The research was performed to evaluate the precipitates resulting from the pH adjustment of waste simulant. Due to INTEC’s limited tank farm capacity, it has been a common practice to minimize the waste volume sent to tank farm by using an evaporating process to achieve maximum liquid waste reduction. In addition, a similar approach was adopted for HLW, where waste streams from INTEC’s operations are to be combined and concentrated. If necessary, a diluent will be added to these concentrated waste streams in order to be compatible with the downstream treatment processes and equipment. A total of six concentrated LAW streams were evaluated for this study. All LAW simulants and a listing of the representative chemical composition are shown in Table 36. To simplify waste disposal, toxic metals were not used in the simulants. The concentrations of the constituents in NGLW are typical of what would be sent to the tank farm after concentration in the PEWE. High acid NGLW-2000 was evaluated because of the potential variation of blend feed for NGLW-2000. The two concentrated LAW streams from solvent extraction flowsheets will be referred to as Na-LAW (from SBW), and Al/Zr-LAW (from Al/Zr calcines). In addition, pH adjustment of concentrated SBW, subsequent to cesium removal, was tested.

The chemicals most frequently used for pH adjustment are lime, caustic and sodium carbonate. There are three types of limes available: quicklime ( $\text{CaO}$ ), dolomitic lime ( $\text{CaO.MgO}$ ), and hydrated lime ( $\text{Ca(OH)}_2$ ). Quicklime requires protective clothing for workers since it can cause severe burns. It must be stored in air-tight bins to prevent air-slaking, and plugging of pipes. Dolomitic lime reacts more slowly than quicklime and hydrated lime. Hydrated lime is less irritating than quicklime, but it tends to bulk and bridge in storage tanks, and requires special agitating systems on cone bottom tanks. Caustic (sodium hydroxide) is available in either liquid or dry form. Liquid caustic soda is usually preferred because of ease handling. Since 50% NaOH freezing occurs at  $53^\circ\text{F}$ , indoor or heated storage is required. Sodium carbonate has superior handling characteristics, but it is very difficult to dissolve. Only hydrated lime and 50% NaOH were used in this study, because of a high salt content in all six simulants.

**Table 36.** Compositions of Simulated Wastes (*M*)

Component	NGLW	NGLW-2000	High Acid HGLW-2000	Conc. SBW	Na-LAW	Al/Zr LAW
H	2.00E+00	1.57E+00	3.00E+00	1.82E+00	1.55E+00	2.30E+00
Al	1.00E+00	1.70E-01	5.00E-01	7.84E-01	6.74E-01	6.37E-01
Ca	2.49E-01	1.30E-01	2.50E-01	5.76E-02	5.60E-02	5.36E-01
Cl	2.70E-02	1.00E-01	1.40E-01	4.05E-02	3.10E-02	3.00E-03
F	1.24E-01	6.50E-02	2.10E-01	7.12E-02	7.30E-02	9.36E-01
Fe	5.00E-02	1.20E-03	5.00E-03	2.71E-02	2.30E-02	5.00E-03
K	1.54E-01	3.00E-02	5.00E-02	2.45E-01	2.16E-01	1.00E-02
Na	1.54E+00	1.70E+00	1.70E+00	2.36E+00	2.20E+00	1.56E-01
NO <sub>3</sub>	7.14E+00	3.75E+00	6.27E+00	6.75E+00	5.96E+00	4.64E+00
SO <sub>4</sub>	2.00E-02	7.80E-02	7.40E-02	6.37E-02	5.20E-02	8.00E-03
Zr	----	----	----	7.31E-03	----	6.90E-02
Total Anions	7.31E+00	3.99E+00	6.69E+00	6.93E+00	6.12E+00	5.59E+00
Sp. G.	1.33	1.17	1.28	1.31	1.26	1.19
Reference	23	8	8	24	25	25

#### 7.4.1 Base Addition Study

The bench top experiments consisted of neutralizing 70 ml of LAW simulant in a glass beaker with a pre-determined amount of either 50% sodium hydroxide solution or hydrated lime that was added slowly to the simulant. The mixture was stirred at moderate speed using a magnetic stirrer. If a significant precipitation occurred during mixing, a higher stirring speed was used to overcome the viscosity of the slurry. The base was added to the simulant over 5 to 10 minutes interval. The solution pH was varied from 2 to 14 to ascertain the effects on the LAW precipitate characteristics.

#### 7.4.2 Reverse Addition Study

The addition of LAW simulant to a given volume of base was performed to determine what effect this reverse addition would have on the characteristics of the precipitates and precipitation process. Only 50% sodium hydroxide solution was used for the study. For each sample, a pre-determined amount of 50% NaOH was placed in a glass beaker, and 60 ml of LAW was added to the base in 8-10 minutes. The pH ranges of this study were between pH 12 and pH 14.

After completion of chemical addition (base or simulant), the mixtures were stirred for 2 to 6 hours until the pH stabilized and the pH readings were recorded. Each sample was transferred into two separate 50-ml centrifuge tubes and centrifuged for approximately 20 minutes. The total sample volume and the volume of precipitates were then recorded. After the experiment, each sample was allowed to stand in the tubes for 5 to 7 days. The product characteristics were then evaluated and recorded.



## 7.5 Results and Discussion

Data obtained during this study were significant in that they clearly indicated the effect of pH on the quantity and properties of resulting precipitates. The data not only show the quality of the precipitate and whether the gel or more stable crystalline product was formed, but also the relative amount of precipitates formed in the mixture. Because it is generally difficult to dewater on amorphous (gel) particle structure, filtration of precipitates was not performed. Instead, the precipitated volumes were determined after centrifugation. The measured volumes will be used to trend the amount of precipitation as the solution pH changed. However, it should not be considered the mass of precipitate, because the density of the hydroxide precipitates between test samples may be different. The results are discussed below and listed in Tables 37-42. Some samples show a larger difference from the expected total volume. This is probably due to that portion of the sample lost while transferring from the glass beaker into centrifuge tubes. Additionally, some of the solution mixture may have evaporated because of the heat released during neutralization.

### 7.5.1 Base Addition Study

The base addition was studied to see how the different base materials effected the precipitation of the simulant species. Either 50% NaOH or  $\text{Ca}(\text{OH})_2$  was added to the glass beaker containing the simulant over a 5-10 minutes period. The amounts of base were previously determined earlier to obtain pH values ranging from 2 to 14. When the test was completed and pH reading stabilized, the volume and characteristics of the resulting precipitates were determined after centrifugation.

NGLW – The results (see Table 37) are very similar when either 50% NaOH or  $\text{Ca}(\text{OH})_2$  was used to adjust the pH of NGLW stream. A relative small amount of precipitate formed at  $\text{pH} < 3$ . As the solution pH became greater than 3, a significant quantity of precipitates formed. A further increase of solution pH to approximately 4 resulted in a substantial quantity of precipitation. Unless a diluent was used, attempts to increase the pH further were difficult due to the formation of a thick, viscous sludge.

NGLW-2000 – NGLW-2000 is the most dilute solution of the six streams tested. By using either 50% NaOH or  $\text{Ca}(\text{OH})_2$ , the pH of NGLW-2000 stream could be adjusted from less than 2 to greater 13. However, less precipitate was formed by using  $\text{Ca}(\text{OH})_2$  than 50% NaOH. Only a small amount of precipitate was formed when solution pH values were less than 3. The results are presented in Table 38.

High Acid NGLW-2000 – For the highly acidic NGLW-2000 flowsheet, extra base was needed to neutralize the acid before the solution pH increased (Table 39). At  $\text{pH} < 3$ , the results were similar to NGLW with a minimal amount of precipitation. More and more precipitate formed when the solution pH was increased to above 3. However, the fluid-like, non-viscous mixture allows the solution pH increased to greater than 12 by adding more 50% NaOH. The test was terminated at a pH of 5.1 when  $\text{Ca}(\text{OH})_2$  was used. A large amount of precipitate was observed in the solution, but the resulting mixture is still fluid-like.

Conc. SBW – For concentrated SBW samples with pH values between 2 and 3, the volume of precipitate increased slightly (Table 40), compared with the three simulants discussed above. This is probably due to the presence of zirconium in the simulated solution. For sample pH values greater than 3.2, a significant amount of precipitate formed. While using 50% NaOH, approximately 20 ml of precipitate was initially observed in the sample. However, after 3 days, the solution turned into liquid-free, gelatinous material.

Na-LAW – With sample pH values between 2 and 3, only a small amount of precipitate formed using either 50% NaOH or Ca(OH)<sub>2</sub> (Table 41). A large amount of precipitation was formed at pH values greater than 3.4, when Ca(OH)<sub>2</sub> was used. The resulting mixture was a thick sludge with a small amount of free liquid. When 50% NaOH was used to adjust solution pH, the mixture remained fluid even though a significant quantity of precipitate formed; probably due to dilution of the simulant by the NaOH solution.

Al/Zr-LAW – The results (Table 42) are similar to the test on Conc. SBW simulant, where a small amount of precipitate was formed when the sample pH was adjusted up to 3, probably due to the presence of zirconium in the solution. The simulant characteristics permitted the pH values to be adjusted over 10 without undue difficulty when NaOH was used, but when Ca(OH)<sub>2</sub> was used, a thick sludge formed at a pH of 8.8, with only a small amount of free liquid remaining in the sample. The formation of thick sludge at this pH range makes further pH adjustment difficult.

Except for samples in Conc. SBW and NGLW streams, which formed a gelatinous material, and few samples that formed thick sludge mixtures, most other samples of the simulants showed that the precipitates were stable solids with some colloidal flocculant on top. The amount of the total precipitates and its stability depend on its composition, the base used and an aging effect. Most of the stable solid precipitates in test samples formed gradually. All six simulants have a relatively high content of anions. The presence of anions could retard aging and growth of stable crystalline solids. No attempt was made to quantify the exact amounts of crystalline and amorphous precipitates. However, it is not clear what effect the age, whether for hours, days, weeks or even longer, had on the precipitate. The exact amount of the stable solids (crystal) and polymer material (amorphous) in the precipitate is very difficult to quantify.

It may be stated that hydrated lime addition is advantageous relative to NaOH addition because a smaller final waste volume is achieved. However, liquid NaOH is usually preferred because of easy handling. In addition, longer mixing times are required to dissolve Ca(OH)<sub>2</sub> into the simulant and a portion of Ca(OH)<sub>2</sub> remains undissolved when the solution pH is above 3.

## **7.5.2 Reverse Addition Study**

The addition of simulant to base (50% NaOH) rather than adding base to the simulant was studied to see what effects this may have on the precipitate properties. The reverse addition could avoid the pH ranges that form thick sludges while allowing higher pH values to be achieved.

Most of the waste simulants formed stable solids as the sample pH ranged between 12 to 14 (Tables 37-42) after several days of aging. The stable solid precipitates settled quickly after agitation. As the solution pH approached 14, a large amount of precipitates for NGLW samples were formed. The resulting mixtures were thick sludges with only small amounts of free liquid after centrifuging. For NGLW and Conc. SBW flowsheets, the samples formed stable solid precipitates with some flocculant from reverse addition. This is probably due to the relatively high anion and aluminum concentrations in both simulants (Table 36). Except in the NGLW stream, all other flowsheets have shown the general trend that the higher solution pH (between 12 to 14), the less precipitate that is formed in the mixture from reverse addition.

**Table 37.** Bench-Scale pH Adjustment Test Results - NGLW

Add 50% NaOH into 70 ml NGLW	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	8.5	2.1	2	78	1
	10	2.2	2	81	1
	13	2.6	4	83	2
	14.5	2.8	4	84	2
	15	3.0	5	83	2
	16	4.1	81	84	6
Add Ca(OH) <sub>2</sub> into 70 ml NGLW	<b>Ca(OH)<sub>2</sub> (g)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (g)</b>	<b>Mixture Description *</b>
	8.3	1.8	<1	71	1
	11.7	2.6	5	71	3
	14.4	2.7	12	71	3
	15.0	NA	NA	NA	6
	16.0	4.2	NA	NA	6
Add 60 ml NGLW into 50% NaOH	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	17.5	12.3	55	65	6
	18.5	13.4	56	73	2
	21.5	13.7	60	75	6
	25.	14.	72	83	6

\* Remarks: 1. Very small amount of precipitates. 2. Flocculant with stable solid precipitates, clear supernate. 3. Gel like precipitates, clear supernate. 4. Gel like precipitates, cloudy supernate, some suspended materials difficult to settle. 5. Stable solid precipitates, clear supernate. 6. Thick sludge.

**Table 38.** Bench-Scale pH Adjustment Test Results - NGLW-2000

Add 50% NaOH into 70 ml NGLW 2000	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	5.5	3.0	<1	72	1
	6.4	3.7	18	73	2
	6.9	6.9	25	71	2
	7.5	10.3	49	67	6
	8.5	12.9	52	73	6
	9.5	13.3	23	73	5
	10.5	13.4	24	77	5
Add Ca(OH) <sub>2</sub> into 70 ml NGLW 2000	<b>Ca(OH)<sub>2</sub> (g)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (g)</b>	<b>Mixture Description *</b>
	4.0	0.7	4	66	2
	4.3	2.8	4	66	2
	5.0	3.4	4	67	2
	5.6	7.1	26	65	2
	6.2	8.6	28	67	2
	7.2	9.9	23	67	2
	8.2	11.6	34	67	2
	10.3	11.5	33	70	2
Add 60 ml NGLW 2000 into 50% NaOH	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	7	12.5	50	56	6
	8	13.1	17	63	5
	9	13.4	18	63	5
	10.5	13.5	22	63	5

\* Remarks: 1. Very small amount of precipitates. 2. Flocculant with stable solid precipitates, clear supernate. 3. Gel like precipitates, clear supernate. 4. Gel like precipitates, cloudy supernate, some suspended materials difficult to settle. 5. Stable solid precipitates, clear supernate. 6. Thick sludge.

**Table 39.** Bench-Scale pH Adjustment Test Results - High Acid NGLW-2000

Add 50% NaOH into 70 ml High Acid NGLW-2000	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	9.5	2.3	1.	77	1
	10.5	2.6	3.	78	2
	12.5	3.0	29.	80	2
	13.5	3.5	29.	81	2
	14.	4.3	32.	82	2
	15.	8.2	36.	81	2
	17.	12.7	42.	79	2
Add Ca(OH) <sub>2</sub> into 70 ml High Acid NGLW-2000	<b>Ca(OH)<sub>2</sub> (g)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (g)</b>	<b>Mixture Description *</b>
	7.8	2.3	5.	69	2
	8.5	2.5	6.	70	2
	9.3	2.8	6.	70	2
	9.5	2.9	8.	70	2
	9.9	3.1	46.	64	2
	10.7	5.1	53.	67	2
	Add 60 ml High Acid NGLW-2000 into 50% NaOH	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>
13		8.2	32	68	2
14		12.5	45	60	5
15		13.0	40	69	5
16.5		13.4	38	70	5
17.5		13.4	56	72	5
18.5		13.6	17	76	5
20		13.6	26	76	5
25		13.6	10	81	2
30		13.5	8	86	2
37.5		13.5	4	92	2

\* Remarks: 1. Very small amount of precipitates. 2. Flocculant with stable solid precipitates, clear supernate. 3. Gel like precipitates, clear supernate. 4. Gel like precipitates, cloudy supernate, some suspended materials difficult to settle. 5. Stable solid precipitates, clear supernate. 6. Thick sludge

**Table 40.** Bench-Scale pH Adjustment Test Results - Conc. SBW

Add 50% NaOH into 70 ml Conc. SBW	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	7.5	2.0	7	75	3
	9.	2.4	9	76	3
	11.4	2.8	9	78	3
	12.	3.0	15	79	3
	12.5	3.1	20	79	3
	13.	3.2	20 (81)	81	7
	13.5	3.5	45	79	2
15.	7.1	48	79	8	
Add Ca(OH) <sub>2</sub> into 70 ml Conc. SBW	<b>Ca(OH)<sub>2</sub> (g)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (g)</b>	<b>Mixture Description *</b>
	6.4	2.0	6	70	3
	7.5	2.2	8	68	3
	8.5	2.5	9	68	3
	9.	2.6	9	69	3
	9.6	2.8	9	68	3
	10.8	3.2	NA	NA	6
Add 60 ml Conc. SBW into 50% NaOH	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	14.5	12.3	24	72	2
	16.	12.9	24	72	2
	18.	13.3	10	76	2
	20.	13.5	9	78	2
	24.	13.6	7	81	2
	25.	13.6	7	82	2

\* Remarks: 1. Very small amount of precipitates. 2. Flocculant with stable solid precipitates, clear supernate. 3. Gel like precipitates, clear supernate. 4. Gel like precipitates, cloudy supernate, some suspended materials difficult to settle. 5. Stable solid precipitates, clear supernate. 6. Thick sludge. 7. Sample has 20 ml precipitates initially, but the whole sample turn into liquid free, gel like material after 3 days. 8. Flocculant with gel like precipitates.

**Table 41.** Bench-Scale pH Adjustment Test Results - Na-LAW

Add 50% NaOH into 70 ml Na-LAW	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	6.	2.3	2	73	1
	8.	2.8	2	76	1
	9.	3.0	2	72	1
	10.	3.2	15	78	3
	11.5	4.0	36	78	2
	12.	6.1	45	77	2
	13.	11.2	37	78	2
	14.5	12.7	22	80	2
Add Ca(OH) <sub>2</sub> into 70 ml Na-LAW	<b>Ca(OH)<sub>2</sub> (g)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (g)</b>	<b>Mixture Description *</b>
	4.6	2.3	2	70	1
	5.0	2.4	2	67	1
	5.7	2.6	2	71	1
	6.4	2.7	2	71	1
	7.1	2.9	2	70	1
	7.5	2.9	4	66	2
	7.8	3.4	59	67	6
8.1	3.9	63	68	6	
Add 60 ml Na-LAW into 50% NaOH	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	11	8.3	33	66	2
	12	12.5	21	69	2
	12.5	12.9	18	70	2
	15	13.3	25	73	2
	20	13.7	14	76	5
	24	13.7	9	81	5

\* Remarks: 1. Very small amount of precipitates. 2. Flocculant with stable solid precipitates, clear supernate. 3. Gel like precipitates, clear supernate. 4. Gel like precipitates, cloudy supernate, some suspended materials difficult to settle. 5. Stable solid precipitates, clear supernate. 6. Thick sludge.

**Table 42.** Bench-Scale pH Adjustment Test Results - Al/Zr-LAW

Add 50% NaOH into 70 ml Al/Zr-LAW	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	8.	0.9	15	74	3
	8.5	2.7	15	74	2
	9.	3.2	13	78	2
	11.	3.6	15	77	2
	13.	4.3	41	79	2
	14.	5.9	39	77	2
	15.	8.3	39	81	2
	16.	10.7	39	83	2
Add Ca(OH) <sub>2</sub> into 70 ml Al/Zr-LAW	<b>Ca(OH)<sub>2</sub> (g)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (g)</b>	<b>Mixture Description *</b>
	5.9	1.4	18	69	2
	6.5	2.7	8	70	4
	7.3	2.8	10	70	4
	8.	3.2	11	70	4
	8.8	3.3	13	66	2
	9.5	3.7	42	70	2
	10.5	6.7	39	69	2
	12.5	8.8	48	65	6
Add 60 ml Al/Zr-LAW into 50% NaOH	<b>50% NaOH (ml)</b>	<b>Solution pH</b>	<b>Precipitates Volume (ml)</b>	<b>Total Volume (ml)</b>	<b>Mixture Description*</b>
	14.	11.7	30	65	2
	17.	13.0	19	73	5
	20.	13.5	19	69	5
	28.	13.7	20	82	5

\* Remarks: 1. Very small amount of precipitates. 2. Flocculant with stable solid precipitates, clear supernate. 3. Gel like precipitates, clear supernate. 4. Gel like precipitates, cloudy supernate, some suspended materials difficult to settle. 5. Stable solid precipitates, clear supernate. 6. Thick sludge.



## 7.6 Conclusions and Recommendations

The purpose of this study was to evaluate the pH adjustment procedure that would treat the INTEC low-activity waste for storage or immobilization in grout. The laboratory test results show that the adjustment process was very sensitive to pH, especially that all six LAW streams have high concentration of aluminum. A small pH increases from less than 3 to greater than 3 could result in a significant amount of precipitation. Too much precipitate in the mixture could cause plugging of valves, pumps, pipes, and other process equipment. In addition, without special equipment, the resulting thick sludge will be difficult to retrieve from the storage tanks. Between a pH value of 2 and 3, only small amounts of precipitates (mostly iron) were formed in the adjusted mixture solutions. However, the amount of precipitates in Conc. SBW and Al/Zr-LAW streams were slightly higher than the other four waste streams, probably due to the presence of zirconium in both flowsheets. On the other hand, the results have shown that the stable precipitates (mostly from aluminum) could be formed as the simulant was adjusted to pH>12. For the INTEC LAW tested, because a substantial amount of precipitates could form between pH values of 3 to 12, the reverse addition method plays an important role in pH adjustment. Reverse addition (pH>12) not only provides the benefit of producing acceptable product for grout, but also could avoid potential mixing problems for those waste streams that form a substantial amount of precipitate between the pH ranges of 3 to 12.

Based on the results of this study, the following conclusions were made:

1. A low rate of addition (either base addition, or reverse addition) is required to minimize heat generation rate. The high rate of heat released during mixing could evaporate some product.
2. The caustic demands for pH adjustment are highly variable and will differ from waste stream to waste stream and batch to batch.
3. Unless pH value below 3 is acceptable, adjusting the LAW pH and storing in tanks for future treatment is not a viable option, because a significant amount of diluent that will be needed to increase sludge fluidity and a much bigger waste volume will be generated. Otherwise, the large amount of precipitates formed in the mixture will cause numerous retrieval and product transfer problems.
4. At pH values greater than 12, more stable solid and less gelatinous material are formed. The stable solid products are more desirable for grout formulation.

In principle, pH adjustment appears to be a simple process; however, in reality the efficiency of the treatment process performance is affected by a number of parameters. These include such factors as the chemical solubility of the solid phase, the crystal structure of the solid phase, aqueous phase complex formation, ionic strength, temperature and the reaction time. In order to provide the optimum treatment, the composite effect of all such parameters must be identified, and accounted for.

Based on the test results of this study, the following items are recommended for future research and development efforts for both storage and grout options:

1. The required pH should be determined taking into account the possible regulatory restrictions and equipment limitations, temporary storage, retrieval/transfer, and immobilization for each LAW flowsheet. If a target pH between 6 and 8 is necessary (to be compatible with concrete container), a diluent and complexing agent will be needed to minimize the amount of precipitate that forms.

2. Determine the optimum flowsheets solids content and the viscosity of the resulting slurry mixture that will be acceptable for the retrieval/transfer process operations. (storage option)
3. The pH adjustment was very sensitive to the constituents of the waste solution. Further studies should use the simulated solution with all components and the actual LAW, after all the operating parameters were determined. (both options)
4. A small cylindrical, baffled mixing chamber is recommended to minimize the variations of local reactant concentration and wall effects by intense mixing. (both options)
5. For the mixing chamber selected, the rate of base addition and the speed of mixer should be evaluated for each waste solution to be treated. (both options)
6. An all-purpose container for mixing, aging/stabilization, and grouting should be evaluated to eliminate product transfer problems and maximize waste loading in the grout product. (grout option)

## **8. FUTURE TESTING**

### **8.1 CsIX Grouting**

The scoping tests performed to date have provided significant insight for optimized grout formulations, resulting in basic preferred grout formulations for both CsIX and NGLW wastes regardless of waste-loading approach. Considerable understanding of the expected effects from using (or not using) the various grout ingredients has also resulted. Significant further development work is still necessary for optimization. For CsIX waste grout treatment, future optimization efforts will concentrate on the maximized waste loading flowsheet, making minor flowsheet changes to assure a liquid-free grout product while maintaining processability. Flowsheet adjustments will also consider improved product physical properties and heavy metal leaching.

Verification testing of optimized grout formulations will also be required. The scoping tests described above were generally conducted by curing 50-gram samples at an elevated temperature (45 °C) for seven days. Grout formulation verification tests will be performed with much larger samples, and ambient temperature curing for at least 28 days. Ambient curing may force some changes in an optimized flowsheet, increasing the addition of more reactive ingredients (OPC) at the expense of those less reactive (BFS).

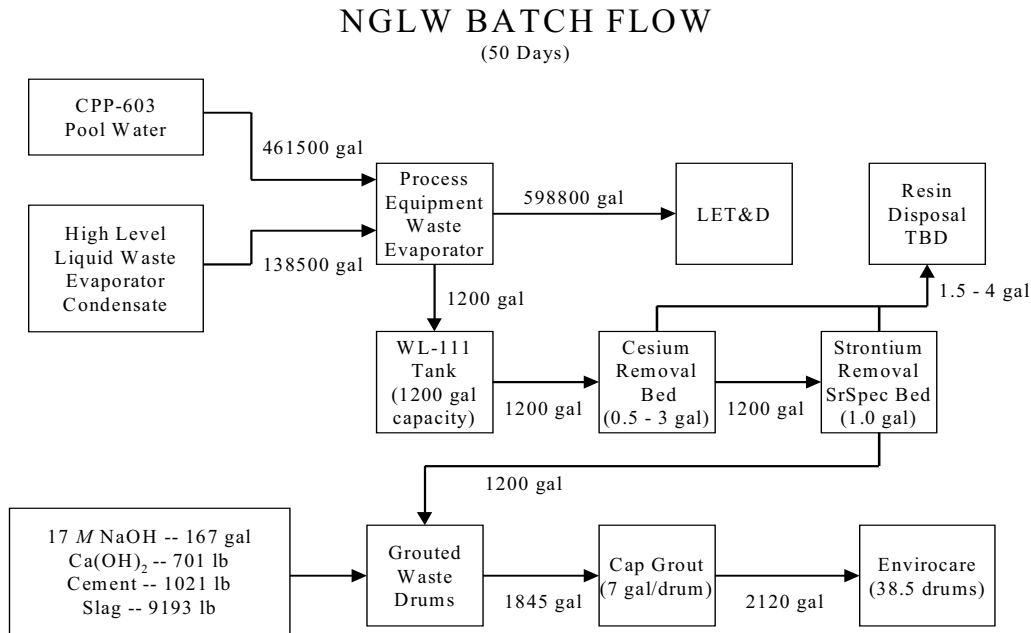
Additional anticipated testing includes investigating preventive measures for radioisotope leaching. Scoping efforts have already been initiated to investigate strontium leaching. Results indicate that Sr leach rate is proportional to that of calcium. Some exploratory tests will be performed to minimize the overall Ca concentration in grout samples (by neutralizing the waste simulant with MgO instead of CaO) to determine if Sr leaching can be reduced. Some minor increase in maximum waste loading could potentially also result using this approach.

## 8.2 NGLW Grouting Demonstration Project

A major area of future study is the diversion of low-level and low-activity waste from the tank farm. Currently, all process equipment waste evaporator (PEWE) bottom solutions are sent to the tank farm. During the years 2001 to 2003, the High-Level Liquid Waste Evaporator (HLLWE) will be used to reduce the tank farm inventory. The HLLWE bottom solution will be returned to the tank farm; however, the overhead condensate stream will be sent to the PEWE for further concentration. It is proposed to combine this condensate stream with CPP-603 pool water to control nitrate and chloride content. The PEWE overhead condensate would be sent to LET&D and the bottom solution would be sent to a LAW grout rather than back to the tank farm. Such a process could help to break the cycle of tank farm use.

The combined HLLWE condensate and CPP-603 pool water would be boiled down about 500 times in the PEWE. The projected bottom waste was modeled<sup>7,8</sup> and a simulated waste composition prepared. In examining this projected NGLW and its disposal at the Envirocare site in Utah, it was found that the cesium and strontium content are too high to meet the very low-level waste acceptance requirements. Thus, it is proposed that separation unit operations be added for cesium and strontium removal. Figure 1 illustrates the proposed pretreatment and grouting processes for a 50 day operation. The grouting steps are based on AEA Technology's recommended formulation. The pretreatment separation is based on INTEC separation projections using ion exchange media which must be verified.

During FY-2000, a project will be initiated to determine the feasibility of such a process in CPP-604. If feasible, further design and research will be conducted for construction in FY-2001.



**Figure 13.** 50 Day Batch Flow Diagram for Newly Generated Liquid Waste

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