PNWD-2455
BNFL-RPT-012, Rev. 0

Hanford Tank Waste Simulants Specification and Their Applicability for the Retrieval, Pretreatment, and Vitrification Processes

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March 2000

Prepared for BNFL, Inc. under
Project 29953
Battelle, Richland, Washington, 99352

DISCLAIMER

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Summary

This report provides a detailed review of the existing reports on simulated wastes for the remediation of single-shell and double-shell tank wastes at the Hanford reservation. In this review, we have compiled all the simulants used over the past decade in testing for the retrieval, pretreatment, and vitrification processes. The retrieval and transport simulants may be useful for testing in-plant fluidic devices and in some cases for filtration technologies. The pretreatment simulants, which include simulants for envelopes A, B, C, and D, will be useful for filtration, Sr/TRU removal, and ion exchange testing. The vitrification simulants will be useful for testing melter, melter feed preparation technologies and for waste form evaluations.

All of these simulants, their representative chemical and physical characteristics, and their preparation specification are summarized. We have reviewed the TWRS privatization mass and activity balance for the proposed low-activity waste and high-level waste feeds and addressed the application of simulants that mimic these types of waste composition. From this review, we have evaluated the appropriateness of using simulants for specific chemical and physical properties associated with each envelope.

Acronyms

ACS	**American Chemical Society**
ANL	**Argonne National Laboratory**
BNFL	**British Nuclear Fuel Limited, Inc.**
CC	**complexant concentrate**
DOE	**U.S. Department of Energy**
DSSF	**double-shell slurry feed**
DST	**double-shell tank**
EDTA	**ethylene diaminetetra acetic acid**
HEDTA	**N-(2-hydroxyethyl) ethylenediaminetetraacetic acid**
HLW	**high-level waste**
HWVP	**Hanford Waste Vitrification Project**
IC	**ion chromatography**
ICP	**inductively coupled plasma**
IPM	**initial pretreatment module**
LANL	**Los Alamos National Laboratory**
LAW	**low activity waste**
NCAW	**neutralized current acid waste**
PAS	**PUREX acidified sludge**
PNNL	**Pacific Northwest National Laboratory**
PUREX	**plutonium uranium extraction**
PVC	**polyvinyl chloride**
RFP	**request for proposal**
RI	**remaining inventory**
RSM	**research-scale melter**
SIPT	**slurry integrated performance testing**
SST	**single-shell tank**
TD	**to deliver**
TIC	**total inorganic carbon**
TOC	**total organic carbon**
TRAC	**Track Radionuclide Components**
TRU	**transuranic**
TRUEX	**transuranic extraction**
TWRS	**Tank Waste Remediation System**
TWRS-P	**TWRS-Privatization**
UST	**underground storage tank**
USTID	**UST integrated demonstration**
WHC	**Westinghouse Hanford Company**
XRD	**X-ray diffraction**

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1.0 Introduction

1.1 Background

Millions of gallons of radioactive waste are stored in 177 underground storage tanks (USTs) at the U.S. Department of Energy (DOE) Hanford reservation in Eastern Washington. The waste was generated from the production of nuclear materials for national defense and waste management operations. Approximately 37 million gallons of waste is stored in 149 single-shell tanks (SSTs) in the form of saltcake, semi-wet sludge, hardened sludge, and alkaline supernatant liquid. The remainder of the waste (approximately 25 million gallons) is stored in 28 double-shell tanks (DSTs) as a mixture of sludge and alkaline supernatant liquid. Within a given tank, the waste is frequently not uniform and contains layers of sludge, saltcake, and supernatant that are complex mixes of radioactive and chemical products.

In many of these tanks, the supernatant is a highly basic (pH 10 to >14) solution of sodium nitrate/nitrite salt of 1 to 10 M concentration with smaller quantities of other hydroxides, aluminate, carbonate, sulfate, chloride, fluoride and phosphate anions. The saltcake was generated by extensive evaporation of supernatant solution, and it largely consists of nitrate, aluminate, nitrite, carbonate, phosphate, hydroxide, and sulfate. The bulk of soluble radionuclides, such as ^{137}Cs and ^{99}Tc, are contained in the dissolved saltcake and supernatant solutions. The insoluble sludge fraction consists of metal oxides/hydroxides and contains the bulk of ^{90}Sr and many of the transuranic (TRU) radionuclides.

The Tank Waste Remediation System (TWRS) has been established to retrieve, treat, immobilize, and dispose of radioactive wastes stored in USTs at the Hanford Site. These wastes will be disposed of either as high-level waste (HLW) in a deep geological repository or as low-activity waste (LAW) onsite in a near-surface burial ground. Before being solidified for permanent disposal, the waste in SSTs and DSTs will be retrieved using a water-jet based technology and transferred to pretreatment facilities. The first stage in the pretreatment process is to separate the supernatant and dissolved saltcake from the sludges. It is envisioned that cesium, technetium, and sulfates will be removed from the aqueous solutions using ion exchange unit operations, and the decontaminated solutions will be immobilized as LAW. The tank sludges, on the other hand, which contain the bulk of radionuclides, will be vitrified and disposed of as HLW.

Recently, DOE elected to privatize several elements of the TWRS program. This privatization has been divided into two phases. Phase 1 is a proof-of-concept/commercial demonstration phase and will involve the pretreatment and LAW vitrification of approximately 6 to 13 percent of the total waste volume using a pilot-scale system. Phase 1 also allows for immobilization of a fraction of the HLW sludges. Phase 2 will be the full-scale production phase. Facilities will be sized so all of the remaining waste from the 177 tanks can be processed and immobilized.

The British Nuclear Fuel Ltd., Inc. (BNFL) has prepared a Development Requirement Document for Part A of Phase 1 TWRS Privatization (TWRS-P) project. In Phase 1-B, detailed process virification and product qualification tests will be conducted. Battelle is funded by BNFL Inc. to conduct various process testing for both simulated and actual LAW and HLW tank waste samples.

1.2 Purpose of Document

A wide variety of waste simulants were developed over the past few years to test various retrieval pretreatment and waste immobilization technologies and unit operations. Tank waste simulants are often used to test candidate waste retrieval, treatment, and immobilization processes when tests cannot be feasibly conducted using actual radioactive waste. Experiments can be performed cost-effectively using non-radioactive waste simulants in open laboratories that significantly decrease development costs and eliminate worker exposure associated with radioactive material. Use of simulants also allows large-scale trials to be carried out at an acceptable cost, thus reducing the potential for scale-up problems that can be experienced when full-scale process performance is extrapolated on the results of small-scale trials alone.

This document reviews the composition of many previously used waste simulants for remediation of SST and DST wastes at the Hanford reservation. In this review, the simulants used in testing for the retrieval, pretreatment, and vitrification processes are compiled, and the representative chemical and physical characteristics of each simulant are specified. The retrieval and transport simulants may be useful for testing in-plant fluidic devices and in some cases for filtration technologies. The pretreatment simulants, which include simulants for envelopes A, B, C, and D, will be useful for filtration, Sr/TRU removal, and ion exchange testing. The vitrification simulants will be useful for testing melter, melter feed preparation technologies and for waste form evaluations.

This work is conducted at Battelle for BNFL. Inc. and is referenced in the Development Requirements Document.

Finally, it is hoped that future simulant development efforts will benefit from the collection of simulant compositions and properties provided in this report.

2.0 Simulant Classification

Given the complexity and radioactivity of actual tank wastes, simulants are designed to emulate specific types of chemical or physical behavior of actual radioactive wastes. In this context, simulants can be developed to exhibit only a limited set of important properties specific to a process or may be tailored to exhibit a broader range of physical, rheological, and/or chemical properties of actual waste. In all cases, an important part of simulant development effort is the selection of the waste properties that are applicable and should be matched to support the needs of a technology or a unit operation.

2.1 Chemical Versus Physical Simulants

Two general types of simulants are used for testing: chemical and physical. Chemical simulants are used when it is necessary to mimic certain chemical properties of the waste. These simulants are usually prepared by following a series of chemical additions and procedures that approximate those used to originally create the actual waste with the exception that radioactive materials are not used. Chemical simulants are needed to evaluate processes such as vitrification and certain separations. When the chemistry of the waste governs process performance, chemical simulants are typically used. Chemical simulants relative to physical simulants are expensive to produce and dispose of, and, in most cases, hazardous. Thus, they are used when other testing methods are inadequate.

Physical simulants are used when the waste's chemical properties are of little or no relevance. In such cases, it is the physical properties of the waste that must be matched by the simulant. It is true that many physical properties depend on chemical properties, so it is important to know the waste's physical properties under the chemical conditions that are relevant to the process being tested. Physical properties, such as the rheological behavior, also can depend on the history of the waste, which can affect the size distribution of agglomerates and the degree of compaction of agglomerates as well as other factors. Consequently, chemical simulants do not always (or even often) exhibit the appropriate range of physical properties because the history of the tank waste and the chemical simulants differs significantly (e.g., the waste may have been aging in a tank for decades).

Despite the differences between chemical and physical simulants, they are designed and used in the same way. The process to be tested is carefully considered to decide which chemical and/or physical properties must be matched between the simulant and the waste. This often requires an iterative approach in which experiments are used to identify which properties are most relevant and which can be ignored.

2.2 Simulant Applications

As discussed before, simulants are used to test or develop processes, and testing needs must be the basis for selecting simulant properties. Based on this criterion, in this document all the waste simulants used in the past for the Hanford tank wastes are classified into three major categories in the TWRS mission. These are: simulants used for retrieval and transport, simulants used for pretreatment processes, and simulants used for melter feed preparation and vitrification applications.

The tank waste simulants for testing retrieval processes and slurry transport monitoring are described in Section 3.0. Because most retrieval-operation tests are conducted at relatively large scales, chemical simulants are undesirable. Thus, most of the simulants used for retrieval-system testing (i.e., those included in this report) are physical rather than chemical simulants. Others have developed chemical waste simulants (Elmore et al. 1992; LaFemina 1995c).

In Section 4.0 tank waste simulants for various pretreatment unit operations are discussed. Over the past few years, a large volume of simulant recipes were developed for a wide range of treatment operations. In this section, only simulant specifications applicable to current planned pretreatment technologies of: solid-liquid separation, caustic leaching and sludge washing, Sr/TRU removal, cesium and technetium ion exchange, sulfate ion exchange, and evaporation are described. The majority of simulants presented in this section are chemically based simulants, and studies were conducted in laboratory and bench scale operations.

The waste simulants for melter feed and vitrification applications are reviewed in Section 5.0. The majority of simulant development efforts discussed in this section assumed that the tank waste slurry was caustic leached and water washed before this treatment. Thus, simulants were formulated to make waste compositions following sludge washing. Furthermore, some simulants presented in this section were developed based on the chemical processing flow sheets used for producing of nuclear materials.

3.0 Simulant Description for Retrieval and Transport

Since the purpose of this document is to review previous reports on simulant waste for the Hanford site, the majority of the discussions presented in this section are extracted from the following reports:

M.R. Powell, G. R. Golcar, J. G. H. Geeting. 1997b. *Retrieval Process Development and Enhancement Waste simulants Compositions and Defensibility*. PNNL-11685, Pacific Northwest National Laboratory, Richland, Washington.

G. R. Golcar, J. R. Bontha, J. G. Darab, M. R. Powell, P. A. Smith, and J. Zhang. 1997. *Retrieval Process Development and Enhancements Project Fiscal Year 1995 Simulant Development Technology Task Progress Report.* PNNL-11103, Pacific Northwest National Laboratory, Richland, Washington.

As described in Section 2.0, an important part of simulant development for the retrieval processes is to select of the waste physical properties that will be matched by the simulant. Selecting these properties requires a careful consideration of the retrieval process to be tested. Different processes often require that different simulants be used.

Physical simulants are prepared using relatively non-hazardous and inexpensive materials rather than matching the chemical composition of the tank waste. Consequently, only some of the waste properties are matched by the simulant. Deciding which properties need to be matched and which do not requires a detailed knowledge of the physics of whatever process is to be tested using the simulant. Developing this knowledge requires reviews of available literature, consultation with experts, and parametric tests. Once the relevant properties are identified, waste characterization data are reviewed to establish the target ranges for each relevant property. Simulants are then developed that possess the desired ranges of properties. In Section 3.1, the simulant development strategy adopted for the retrieval and transport processes and the sequence of steps needed to validate a simulant are discussed.

3.1 Simulant Development Strategy

The methodology used to develop physical simulants for testing waste retrieval processes is illustrated in Figure 3.1 (Golcar et al. 1997). The first step is to identify the retrieval process or processes for which the simulant is to be developed. Because simulants are designed with a specific retrieval process in mind, a simulant that is appropriate for testing one process might be inappropriate for another. For example, hard saltcake simulants prepared from potassium-magnesium sulfate were designed specifically for the testing of high-pressure waterjet scarifiers (Hatchell et al. 1996). The mechanical strength and porosity of this simulant can be related to waste characterization data. Other properties such as its dissolution rate, solubility, and thermal conductivity were not matched, so it is inappropriate to use the potassium-magnesium sulfate simulants to test processes for which these other properties are relevant.

The second step is to identify the waste properties that are expected to determine the process performance. A combination of literature reviews, consultation with experts, and reviews of existing test data is used to understand of the mechanisms by which the process operates. An understanding of the relevant mechanisms is needed to develop a list of expected key physical properties. If all the relevant mechanisms have been identified and the associated key properties

matched between the waste and the simulant, then process tests using the simulant are expected to predict process performance against the tank waste.

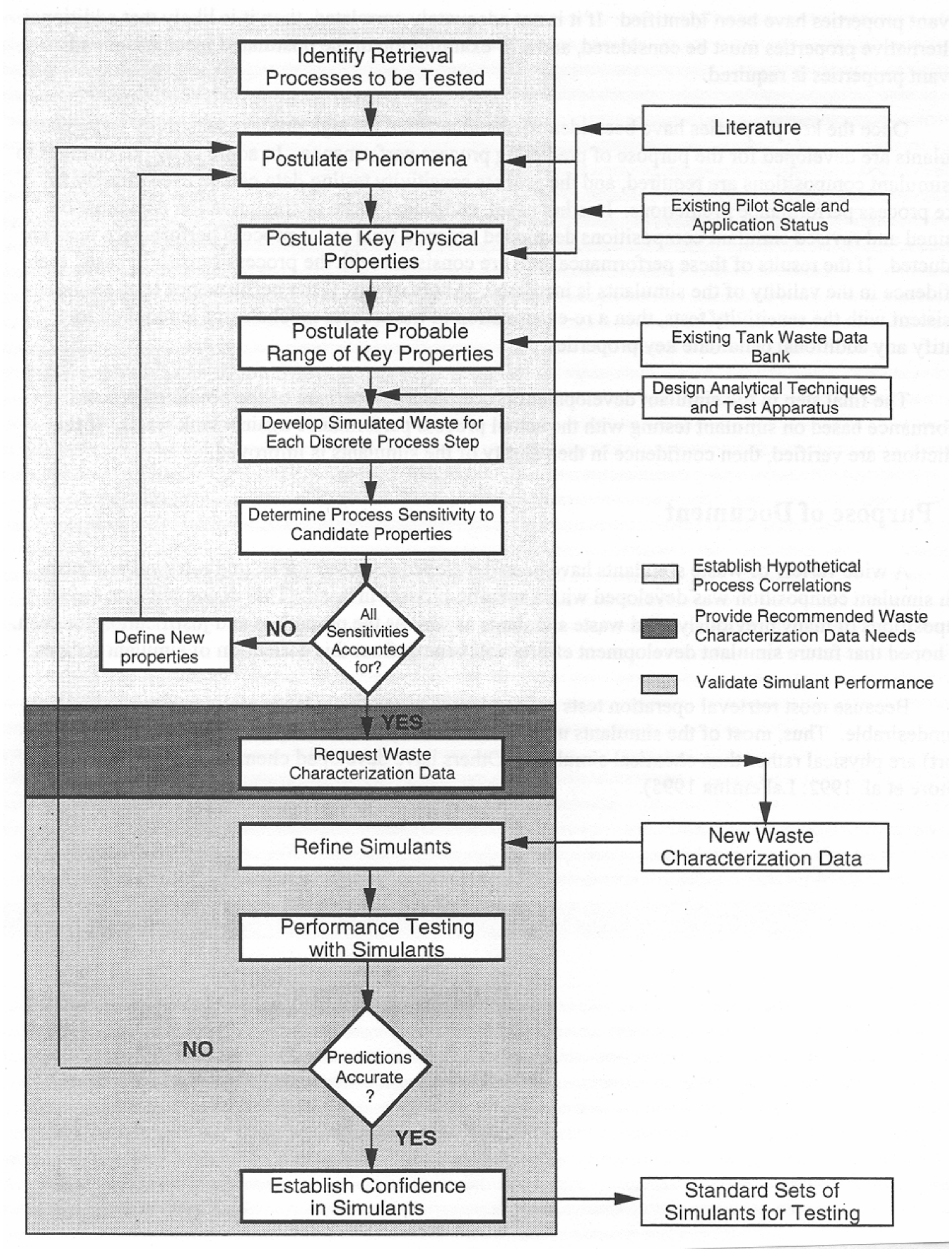

Figure 3.1. Simulant Development Strategy Logic Diagram (from Golcar et al. 1997)

An estimated range for the magnitude of each hypothesized key property is needed to establish target ranges for the simulant(s). Waste characterization data obtained from samples and *in situ* measurements often can be used to establish the target ranges for certain properties (e.g., viscosity, density, and shear strength). However, these data are not available for the waste in many tanks. Further, available data are sometimes unreliable. In such instances, the waste process history, the measurements that have been made on wastes thought to be similar, and any available qualitative descriptions of the waste are examined. These data are used to select a suitably conservative range of values for each of the postulated key waste properties.

Simulants are developed with properties that fall within the desired ranges for each key property. Because it is not always practical to match all the key properties simultaneously, compromises are sometimes required. Where possible, compromises are made such that the simulants yield conservative test results. The sensitivity of the process to changes in each of the key properties is then determined using tests designed to approximate specific aspects of the waste retrieval process. The data from these tests provide an indication of the relative importance of each of the key properties. Simulants used for process testing are then designed to match only the most important key properties and not the less important properties.

Process sensitivity testing involves testing the process (or a specific aspect of the process) against a variety of different simulant compositions. If the process performance against all the simulants is adequately correlated with the postulated key properties, then there is improved confidence that all of the relevant properties have been identified. If it is not adequately correlated, then it is likely that additional or alternative properties must be considered, and a re-examination of the postulated mechanism and relevant properties is required.

Once the key properties have been identified and verified through process-sensitivity tests, waste simulants are developed for the purpose of predicting process performance. In some cases, no changes to the simulant compositions are required, and the process-sensitivity testing data can be used directly to predict process performance. In other cases, additional waste characterization data must be obtained and revised simulant compositions developed before final testing of process performance. If the results of these performance tests are consistent with the process-sensitivity tests, then confidence in the validity of the simulants is increased. Alternatively, if the performance tests are not consistent with the sensitivity tests, then the process mechanisms must be re-examined to identify any additional candidate key properties.

The final step in the simulant development process is to compare the predicted process performance based on simulant testing with the actual process performance against tank waste. If the predictions are verified, then confidence in the validity of the simulants is improved.

3.2 Simulant Descriptions For The Retrieval Process

Tank waste can be divided into six general categories: sludge, hardpan, saltcake, supernatant, slurry, and miscellaneous. Many of the simulants that have been used for each waste type are described in this section. Because of the large number of different waste simulant recipes that have been used for various test programs, some waste simulant recipes are not included.

3.2.1 Sludge Simulants

The waste properties that are expected to have the greatest influence on the retrieval of sludge are discussed in Section 3.2.1.1. This is followed in Section 3.2.1.2 by a listing of many of the sludge simulant compositions, that have previously been used and the justification for each.

3.2.1.1 Relevant Properties for Sludge Retrieval

The sludge properties postulated to be relevant for determining the performance of various candidate waste retrieval technologies are identified in this section. The selection of these properties is based on a combination of testing results and literature reviews. Additional or alternate relevant properties may be selected, based on future testing results.

The key sludge properties for determining the performance of waterjet-based sludge-retrieval methods is thought to be sludge shear strength, sensitivity, cohesiveness, density, and water-absorption rate. Sludge shear strength provides a measure of the capability of the sludge to resist the impinging waterjet. Sludge sensitivity is an indication of the effect of mechanical disruption on the sludge strength. A sludge with a high sensitivity will undergo a drastic decrease in shear strength upon disruption. Cohesiveness[1] measures the tendency of the wet sludge to adhere to both itself and to pieces of process equipment. The rate of water absorption affects the rate that the large pieces of dislodged waste disintegrate and form a pumpable slurry. If the sludge contains an appreciable fraction of soluble solids, the solubility and dissolution rate of these solids may be important. In general, it is expected that soluble sludge will be retrieved at a greater rate than insoluble sludge, all other properties being equal. Sludge density is important because it influences the rate at which the pieces of dislodged sludge settle either within the tank or within the conveyance line.

Tests using a variety of simulants indicate that the sludge-mobilization performance of *submerged*-jet-based retrieval methods (e.g., mixer pumps) is determined primarily by the sludge cohesiveness (Powell et al. 1995). For many sludge-like materials, the maximum expected sludge cohesiveness is a function of the shear strength. The submerged-jet tests also show the importance of partial sludge solubility, but no significant dependence on sludge sensitivity has been found. Sludge

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[1] Cohesiveness is the tendency of a material to stick to other pieces of the same material. The kaolin simulant, for example, is cohesive because separate pieces of kaolin readily stick together. Adhesiveness is the tendency of a material to stick to a different material. For a sludge waste to stick to process equipment, it must be both adhesive and cohesive. If the waste is only adhesive, then only a thin film would form on the process equipment. If the waste is only cohesive, then not even a film will form. The nature of both the waste and the kaolin simulant make them tend to be *both* adhesive and cohesive.

sensitivity is expected to be more important for the non-submerged waterjet-retrieval methods.[1] Tests using low-pressure (100-psi) water-in-air jets also imply a strong correlation between shear strength and the jet pressure of incipient mobilization.

To investigate the relationship between low-pressure waterjet sludge mobilization and shear strength, several different sludge simulants were subjected to an impinging water-in-air waterjet. With the jet directed perpendicularly onto the flat sludge simulant surface, the jet flow rate was gradually increased until continuous removal of sludge was observed. The jet flow and pressure required to mobilize the sludge was then correlated with the sludge shear strength.

The data from these tests are plotted in Figure 3.2. The data show that shear strength has a significant effect on the required waterjet pressure. Further, it appears that different simulants can follow different, apparently linear, relationships. The kaolin and bentonite simulant data are reasonably well fit by a line with a slope of 4.0. The kaolin/plaster simulant, however, follows a different line, which has a slope of about 1.2. The kaolin/plaster data are consistent with the results of previous sluicing pressure tests using kaolin/plaster simulant (Powell 1996). The reason for the difference in behavior observed with the kaolin/plaster simulant is not yet known. Regardless, the importance of matching the sludge shear strength when designing sludge simulants is evident.

For high-pressure waterjet applications, the sludge shear strength is not thought to be important for determining whether the waterjet will cause mobilization. The waterjet pressures are orders of magnitude higher than the typical sludge strengths, so rapid penetration of the waterjet into the sludge is expected regardless of sludge shear strength. However, waterjet cutting of hardpan materials, which are thought to have shear strengths in excess of 10 kPa, is likely affected by the hardpan strength.

Shear strength is still thought to be important for high-pressure waterjet applications because the transport of the cut sludge depends strongly on the ability of the waterjets to reduce the size of the dislodged sludge. Stronger sludge resists the slurrying action of the waterjets more effectively than does weaker sludge. For this reason, efforts are made to match the sludge shear strength when designing simulants for retrieval processes that use high-pressure waterjets.

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[1] **In mixer-pump-based retrieval systems (submerged waterjet), the dislodged pieces of sludge are broken down into a slurry through the combined action of the mixer pump jet turbulence and travel of the dislodged pieces through the mixer pump volute. The shear stresses imposed on the sludge pieces within the mixer pump are likely much higher than either the disturbed or undisturbed sludge strength. Thus, it is not expected that the decrease in strength of a disrupted sensitive sludge will be of any consequence. In the non-submerged jet applications being considered (e.g., sluicing), the dislodged sludge is broken up into slurry by the impacting sluice-jet turbulence. In this case, the stresses imparted to the dislodged sludge pieces are likely to be much lower. The decrease in sludge strength upon disruption may then accelerate the rate of slurry formation.**

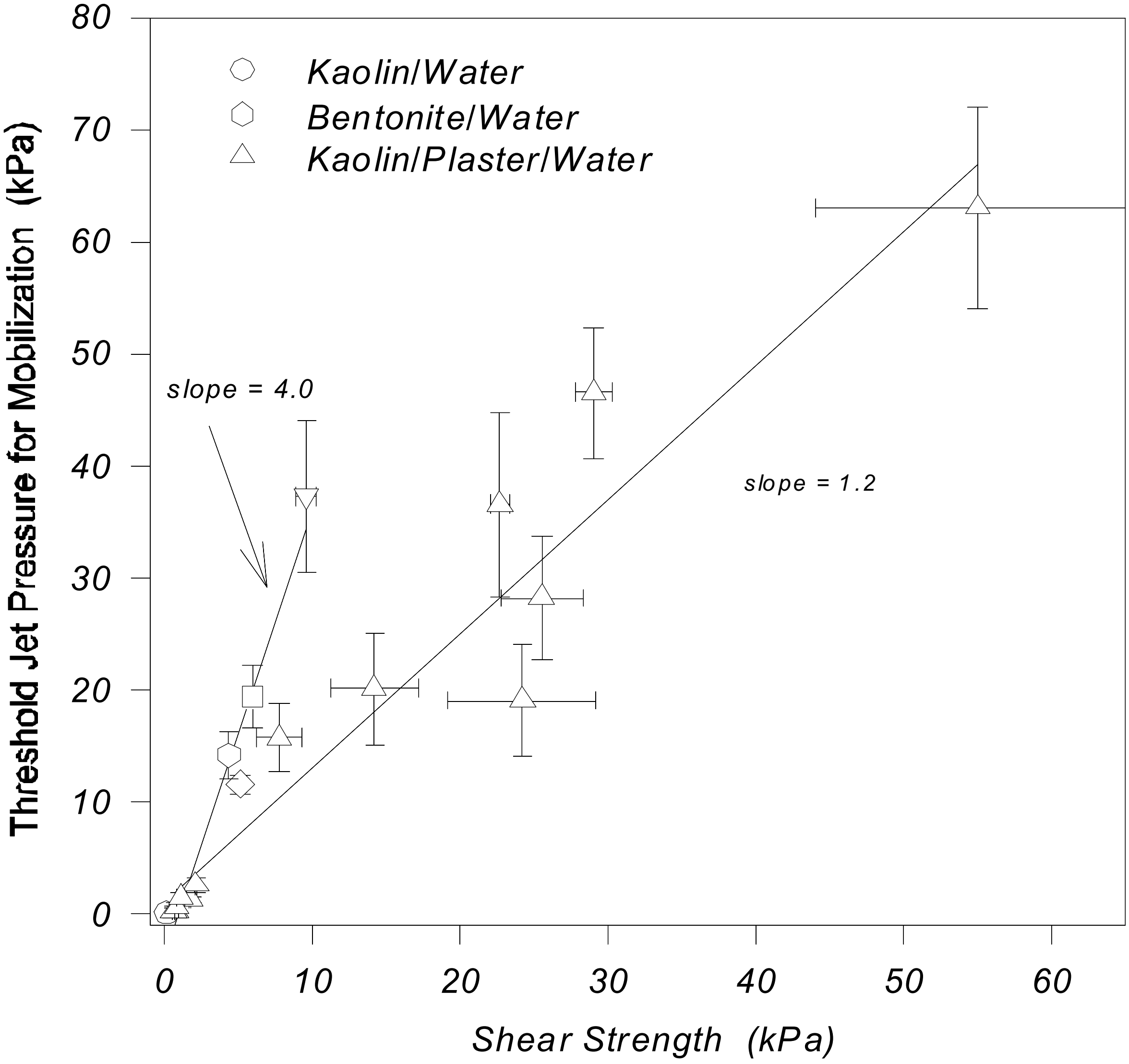

Figure 3.2. Waterjet Pressure Required for Sluicing vs. Shear Strength

Whether the list of postulated key sludge properties given above also applies to non-waterjet-based retrieval techniques is not certain. The exact nature of the candidate retrieval technique must be specified before such a determination can be made. It seems reasonable, however, that for techniques using mechanical cutting/dislodging blades, the sludge shear strength, sensitivity, and cohesiveness would be quite important. Dissolution effects are probably of reduced or negligible importance, depending on the type of conveyance system employed.

With respect to designing a wet sludge-retrieval conveyance system, the greatest concern is that of conveyance-line plugging. Shear strength, cohesiveness, and water-absorption rate are all relevant for conveyance systems. The justification for these key properties is described in Golcar et al. (1997).

The compositions and properties of many of the sludge simulants that have been used for retrieval process testing are given in the following sections. The range of simulants discussed is not intended to encompass all the sludge simulants that have been used at Hanford, but most of the principal physical-property simulants are included.

3.2.1.2 Kaolin Clay Simulants

One of the sludge simulants used most often is a mixture of kaolin clay and tap water. Kaolin clay is composed of the mineral kaolinite. Kaolinite forms plate-shaped particles with diameters in the 0.3 to 3 micron range and thickness in the 0.03 to 1 micron range (Lambe and Whitman 1969). The specific surface area of kaolin clay is typically in the range of 10 to 20 μ^2/g.

There are several properties of kaolin that make it a reasonable simulant for tank sludge. Comparisons of waste properties with those of kaolin/water mixtures are given below.

The particle-size distribution of EPK Pulverized kaolin clay has been measured using the same instrument as is used for waste samples, and the results are similar (see Figures 3.3 and 3.4).[1] Effects of particle morphology are not addressed by such a comparison, but the plate-like shape of the kaolin particles is expected to render the kaolin conservatively cohesive (i.e., more sticky and difficult to retrieve than the waste).

The kaolin clay shear strength and cohesiveness are thought to be reasonably similar to that of wet tank sludge, based on hot-cell measurements of shear strength and particle-size as well as on qualitative descriptions of waste behavior (e.g., “The solids were sticky...”)[2]. Tank sludge is observed to rinse off of hot-cell spatulas and glassware more readily than the kaolin simulant. This is further evidence that the kaolin simulant is conservatively adhesive.

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[1] The particle-size distribution data given in Figure 3.3 were taken from W. J. Gray, M. E. Peterson, R. D. Scheele, and J. M. Tingey. 1990. *Characterization of the Second Core Sample of NCAW from DST 101-AZ.* Letter report prepared for Westinghouse Hanford Company by Pacific Northwest Laboratory, Richland, Washington.

[2] J. M. Tingey, R. D. Scheele, M. E. Peterson, and M. R. Elmore. 1990. *Characterization of Waste from Double-Shell Tank 103-AW.* Letter report prepared for Westinghouse Hanford Company by Pacific Northwest Laboratory, Richland, Washington.

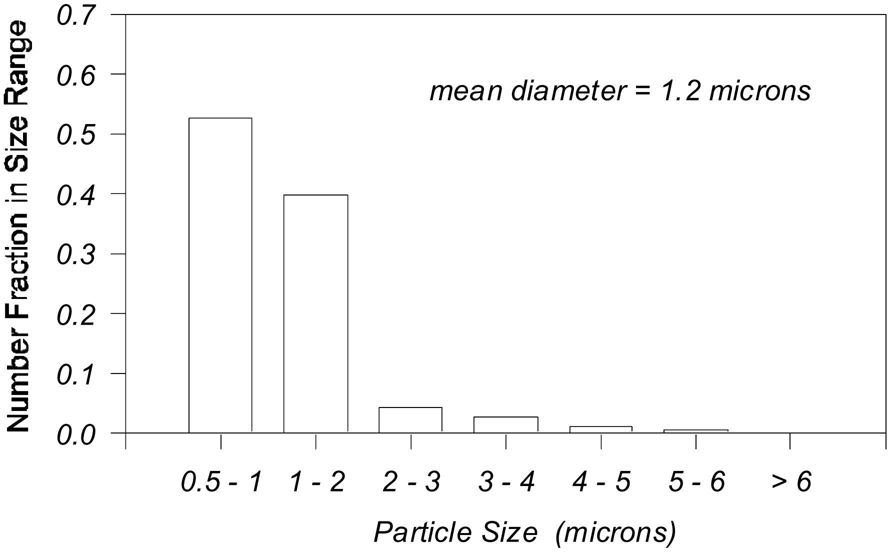
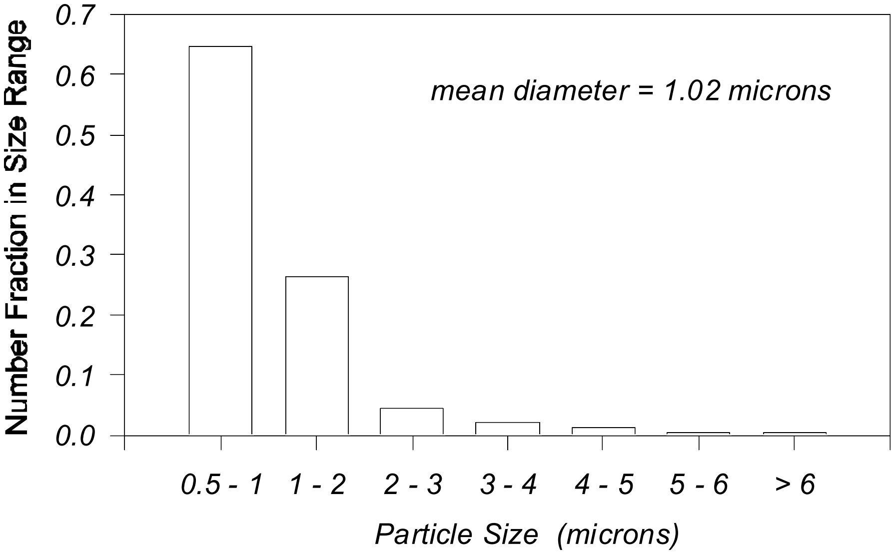


Figure 3.3. Particle-Size Distribution of NCAW Core Sample #2



At a solids concentration of 66 wt% in water, the kaolin simulant shear strength is about 3.5 kPa. The shear strength of sludge samples from various Hanford waste tanks ranges from zero to near 5.0 kPa (Willingham 1994). This is shown in Figure 3.5 Stronger sludge is expected in tanks where the waste has dried and/or reached high temperatures, but this waste type is addressed by the hardpan/dried-sludge simulants in Section 3.2.2. The dependence of the shear strength of kaolin/water mixtures on weight percent solids is shown in Figure 3.6. Rheology data (yield stress and plastic viscosity) are shown for selected kaolin clay/water slurries in Figure 3.7.

The shear strength of sludge simulants is due to the combination of cohesive and frictional forces. Cohesive forces arise from colloidal attractive forces and bonding between adjacent particles. Frictional forces result when particles encounter each other when the simulant is deformed.

The shear strength of kaolin sludge simulants at relatively high solids fractions (i.e., above about 60 wt%) is principally due to frictional forces. Measurements indicate that roughly 7% of the shear strength of a 68 wt% kaolin/water mixture is due to cohesive forces, and 93% is due to friction (Gibson 1953). Decreasing the clay/water ratio is expected to alter this split such that cohesive forces become relatively more important because the increased space between adjacent particles will decrease friction. The cohesion of kaolin clay is primarily due to edge-to-face, electrostatic alignment of clay particles rather than to van der Waals attractive forces as is the case for bentonite. The total amount of cohesion obtained from these edge-to-face bonds is expected to be linearly related to the total number of such bonds per unit volume of clay. As the weight percent of clay is decreased, fewer particles are available for bond formation, so the total cohesion decreases.

The sensitivity of the waste to disruption is known to be significant. That is, mechanical disruption is known to decrease the shear strength of wet sludge. The amount of this decrease in strength varies depending on the waste type. The kaolin clay simulant has a relatively low sensitivity to disruption. This difference between waste and simulant may make the simulant more difficult to retrieve than the waste in some circumstances.

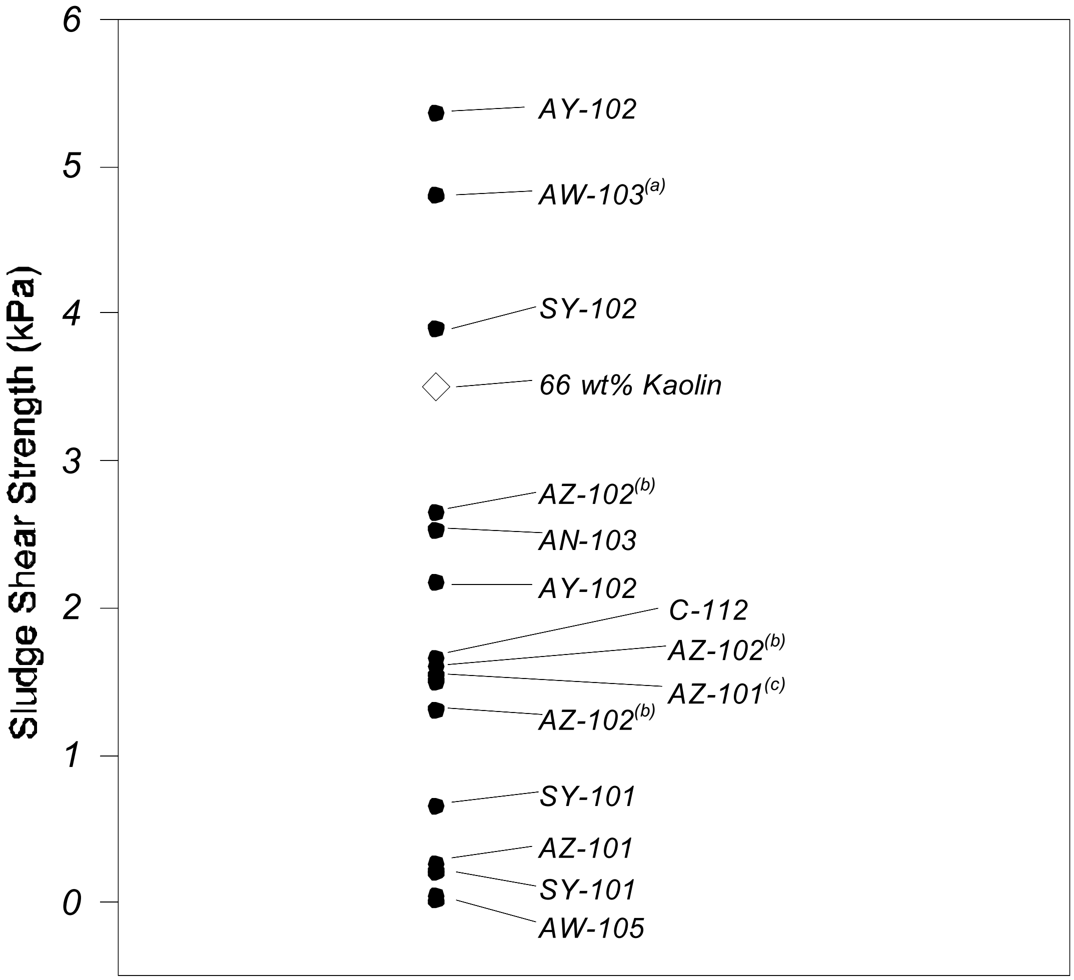


Figure 3.5. Plot of Sludge Shear Strengths

Note: The data used to generate this plot were taken from Willingham (1994) except as noted by superscripts a, b, and C. The data for the superscripted tanks are from:

(a) Tingey, J. M., R. D. Scheele, M. E. Peterson, and M. R. Elmore. 1990. *Characterization of waste from Double Shell Tank 103-AW.* Letter report prepared by Westinghouse Hanford Company by Pacific Northwest Laboratory, Richland, Washington.

(b) Gary, W. J., M. E. Peterson, R. D. Scheele, and J. M. Tingey. 1991. *Characterization of the First Core Sample of NCAW from DST 102-AZ.* Letter report prepared by Westinghouse Hanford Company by Pacific Northwest Laboratory, Richland, Washington.

(c) Gary, W. J., M. E. Peterson, R. D. Scheele, and J. M. Tingey. 1990. *Characterization of the second Core Sample of NCAW from DST 101-AZ.* Letter report prepared by Westinghouse Hanford Company by Pacific Northwest Laboratory, Richland, Washington.

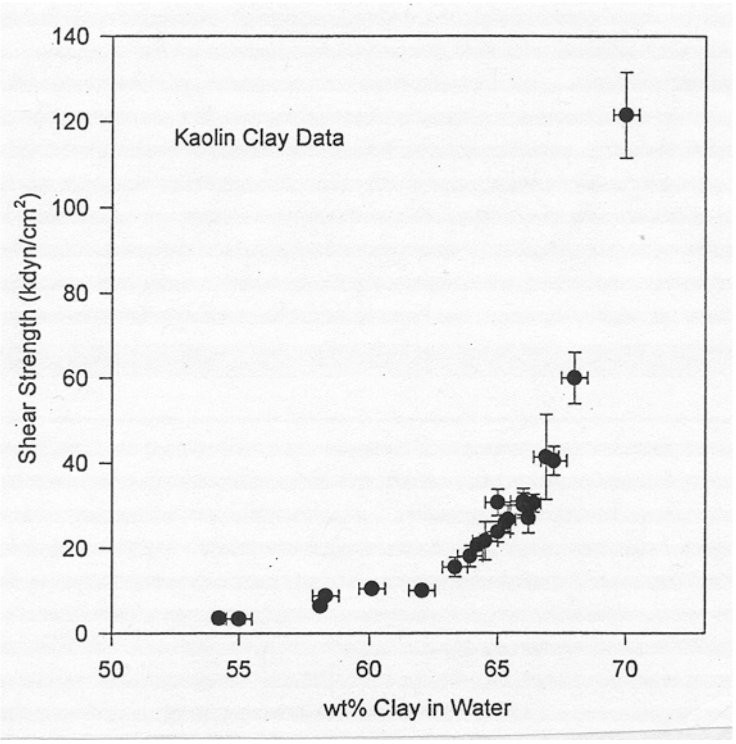


Figure 3.6. Kaolin Clay/Water Shear Strength vs. Wt% Kaolin

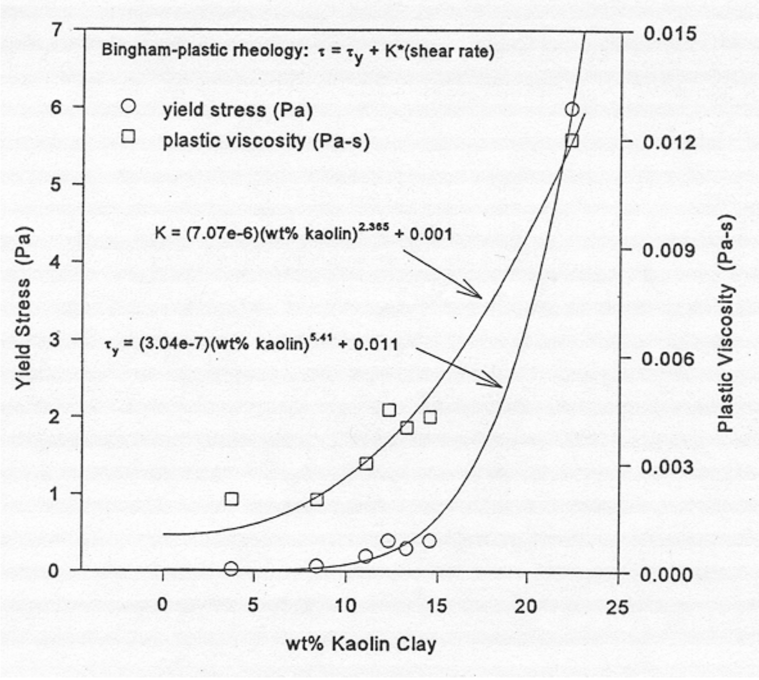


Figure 3.7. Kaolin Slurry Rheology Data

There are many factors that complicate simple comparisons of waste property data to simulant-property data. For example, the disruption effects of core sampling may decrease the shear strength measured in the hot cell considerably, depending on the properties of the waste. Similarly, the fact that the particle-size distributions, as given by the Brinkmann Model 2010 Particle-size Analyzer, are similar does not necessarily mean that the distributions actually are similar. The Brinkmann is not sensitive to particles smaller than about 0.5 microns, so any differences in the concentrations of these small particles will not be detected. It should be clear that some refinement to the waste simulants may be required as more waste characterization data become available.

3.2.1.3 Bentonite Clay in Water

Bentonite clay is composed primarily of montmorillonite clay particles. The atomic mineralogical structure of montmorillonite allows the formation of very small, very thin, plate-shaped particles. Typical particles of bentonite clay range from 0.1 to 1 micron in diameter with thickness of about 0.001 to 0.01 microns, which is smaller and thinner than kaolin clay (see Section 3.2.1.2).

Various mixtures of bentonite clay and water have been used to produce sludge simulants. The smaller particles of the bentonite give the bentonite-based simulants somewhat different properties than the kaolin/water simulants. The shear strength, for example, is higher for a given weight percent solids. A plot of shear strength versus weight percent solids is shown in Figure 3.8.

In many respects, bentonite-based sludge simulants behave similarly to the kaolin simulants, provided that equal shear strengths are used for comparison. The bentonite simulants, however, have two properties that make them distinct from kaolin simulants. First, bentonite undergoes osmotic swelling when exposed to water. Second, the bentonite clay simulants are highly elastic and owe only a small portion of their shear strength to interparticle friction. Each of these properties is discussed below.

The degree to which a clay will imbibe water due to osmotic swelling depends on the average double-layer thickness compared to the distance between adjacent clay particles. Double-layer thickness is determined by the clay's surface charge density, which is a function of its mineralogical composition, and by the ionic strength of the fluid surrounding the clay. The distance between clay particles is a function of the weight fraction of clay in the clay/fluid mixture. White and Pichler (1959) studied the rate of water absorption of several different clay types. Beyond the liquid limit of each clay, osmotic swelling was small or nonexistent for illite clay, kaolin clay, and calcium-bentonite clay. Sodium-bentonite, however, showed continuing osmotic swelling, even when the weight percent clay had fallen to about 12 wt%. The swelling of sodium-bentonite is expected to cease when the particles are so far apart that double-layer repulsions are balanced by the attractive van der Waals and edge-to-face cross-linking forces (van Olphen 1977). Calcium-bentonite does not show the same continuous swelling as the sodium-bentonite due to the ability of the calcium cations to compress the double layers. In calcium-bentonite, the weight percent at which the double layers cease to overlap is higher than for sodium-bentonite.

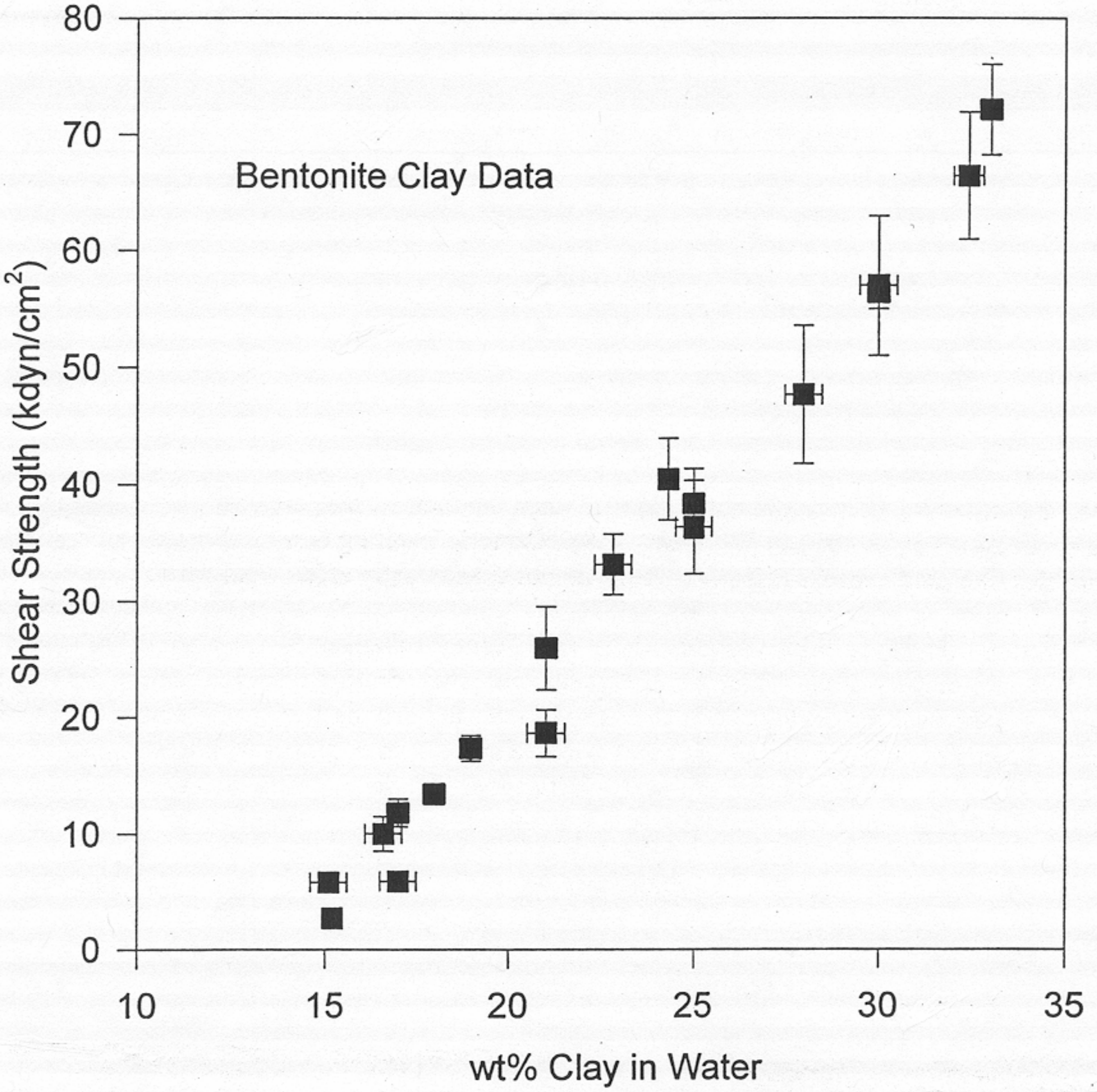


Figure 3.8. Bentonite Clay/Water Mixture Shear Strength vs wt% Bentonite Clay

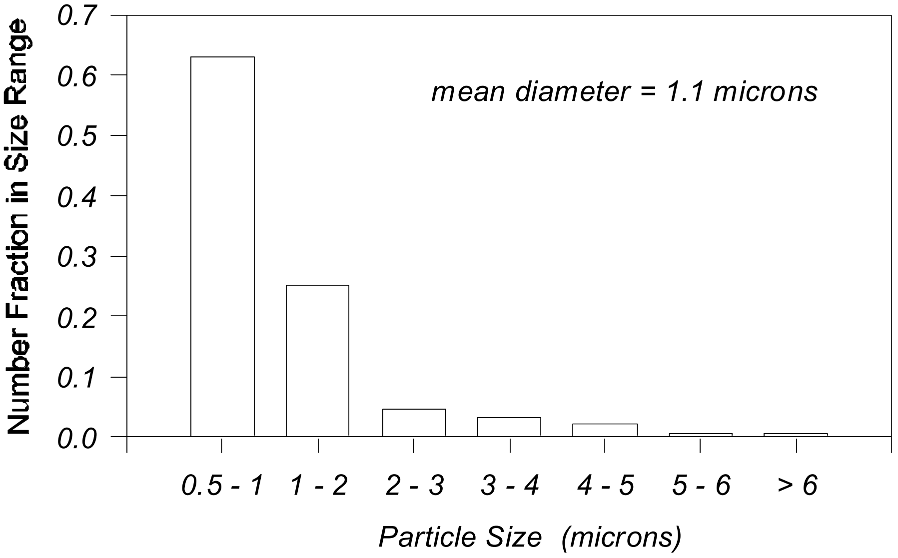


Figure 3.9. Particle-size Distribution for Bentonite Clay

Osmotic swelling up to about the liquid limit is commonly observed in concentrated dispersions like clay pastes when colloidal effects principally govern the behavior of the particles. It has been

suggested that colloidal effects dominate behavior when the total surface area per unit mass of particles exceeds about 25 μ^2/g (Lambe and Whitman 1969). Osmotic swelling is not observed in dispersions of large particles like sand because colloidal effects do not significantly affect sand particles.

Whether osmotic swelling is a potentially significant mechanism for retrieving of sludge is not known. The permeability of the sludge and the osmotic-pressure driving force will determine the rate at which any osmotic swelling could occur. The osmotic-pressure driving force will be a function of both the specific surface area of the sludge and the difference in ionic strength between the eroding and interstitial fluids. For osmotic swelling to be a significant effect, the swelling rate of the sludge must be high enough that an appreciable waste retrieval rate is obtained.

Bentonite sludge simulants exhibit considerable elasticity. The elasticity results from the house-of-cards structure the bentonite particles form. This structure allows the bentonite suspensions to respond elastically to much greater strain than can kaolin suspensions. Viscoelastic characterization of bentonite simulants confirms the high bentonite elasticity and relatively low kaolin elasticity (Powell et al. 1995).

The particle-size distribution of CS-50 Bentonite clay (from American Colloid Co.) was measured using the Brinkmann Model 5050 particle-size analyzer. The data from this analysis are presented in Figure 3.9. The bentonite particles are thin sheets rather than spheres, as is implicitly assumed by the particle-size analyzer, so this particle-size distribution is not necessarily representative of the actual particle-sizes. The Brinkmann particle-size analyzer uses a laser-chopping technique to determine the particle-size distribution. The sample is slurried with water and subjected to a rapidly moving laser-beam. A sensor detects when the laser is blocked by a

particle. Using the rate of laser beam movement and an assumed particle geometry (e.g., spherical), the particle-size distribution can be estimated based on the range of laser occlusion times.

3.2.1.4 Bentonite/BaSO$_4$ Sludge Simulants

As discussed in Section 3.2.1.3, bentonite-based sludge simulants are highly cohesive and achieve shear strengths similar to that of tank sludge at relatively low solids concentrations. As a result, the bulk density of the bentonite/water simulants is typically lower than that of tank sludge. A 25 wt% bentonite/water mixture, for example, has a shear strength of about 4000 Pa, but a density of only 1.18 g/cm^3.

To increase the density of bentonite-based sludge simulants, powdered barium sulfate can be added. Barium sulfate, also known as barite, is a naturally occurring high density salt, which is used extensively in the oil-well drilling industry as a slurry densifier. The particle density of barite is typically between 4.25 and 4.5 g/cm^3 (Brady and Clauser 1991). The natural barite crystals are polymorphous; thus a range of densities is typically observed.

Bentonite/BaSO$_4$ sludge simulants were used as part of the waterjet-based end-effector development work at Hanford (Thompson et al. 1993).

3.2.1.5 Kaolin/Bentonite Sludge Simulants

Mixtures of kaolin and bentonite clays with water have been used as sludge simulants for the scaled testing of jet mixer pumps (e.g., Powell et al. 1995a). For some applications, these simulants are preferred to the kaolin/water and bentonite/water simulants.

Kaolin/bentonite sludge simulants have a higher density than the bentonite/water simulants for a given shear strength. By adjusting the ratio of kaolin to bentonite and the total solids fraction in the mix, the sludge density and shear strength can be varied independently over a range of values. The bulk density of a kaolin/bentonite simulant can be estimated using Equation 3.1 where x_k is taken to be the sum of the kaolin and bentonite weight percentages. The particle density of kaolin clay or bentonite clay is about 2.65 g/cm^3 (Lambe and Whitman 1969).

No easily used correlation of shear strength with kaolin/bentonite simulant composition has been developed. The shear-strength data for several compositions are shown in Table 3.1.

Another advantage of the kaolin/bentonite simulant is that it has a negligible water absorption rate. The kaolin/bentonite simulants apparently owe most of their shear strengths to cohesive rather than frictional forces. In this sense, the kaolin/bentonite simulants are like the bentonite/water simulants. However, as discussed in Section 3.2.1.3, the bentonite/water simulants absorb water. Water absorption can be undesirable for some applications. In these cases, the kaolin/bentonite simulants offer high cohesion along with minimal water absorption and independently adjustable density and shear strength. The improved flexibility of the

kaolin/bentonite simulants allows the simulant density and strength to more closely match those of the waste.

Table 3.1. Kaolin/Bentonite Sludge-Simulant Properties

Simulant No.	Composition (wt%)	Kaolin to Bentonite Ratio	Bulk Density (g/cm^3)	Shear Strength (kPa)
1	18% bentonite 36% kaolin --> 54% solids 46% water	2.00	1.50	6.64 ± 5.5
2	14.4% bentonite 28.9% kaolin --> 43.3% solids 56.7% water	2.01	1.37	2.44 ± 1.6
3	12.1% bentonite 24.8% kaolin --> 36.9% solids 63.1% water	2.05	1.30	0.63 ± 0.4
4	1.33% bentonite 65.0% kaolin --> 66.3% solids 33.7% water	48.9	1.70	3.71 ± 1.7
5	1.27% bentonite 62.08% kaolin --> 63.4% solids 34.0% water	48.9	1.65	2.01 ± 2.1
6	1.22% bentonite 59.87% kaolin --> 61.1% solids 38.91% water	49.1	1.61	0.71 ± 0.7

3.2.1.6 Kaolin/Plaster Sludge Simulants

Mixtures of kaolin clay and plaster of Paris have been used to create sludge simulants that obtain their shear strengths via a different mechanism than either the kaolin/water or bentonite/water simulants. Most of the shear strength for these simulants results from the curing of the plaster of Paris; the kaolin clay helps to absorb the excess water and to increase the bulk density. This is advantageous for two reasons. First, the preparation of high-shear-strength simulants is made easier when the simulant can be prepared as a pumpable slurry that subsequently cures. High-shear-strength kaolin and bentonite simulants require a special mixer to prepare, and the simulant is usually transported by hand.

Second, it is important to test candidate retrieval processes against simulants that obtain their properties through a variety of different mechanisms. As was discussed in Section 3.1, these kinds of tests will often reveal whether the retrieval process performance depends on sludge properties in addition to (or instead of) those that have been selected as the "key properties."

The kaolin/plaster simulant has a shear strength on the order of 25% to 50% of its cured strength when it is first prepared (i.e., before significant curing takes place). This initial strength is due to the combination of the kaolin clay cohesion and friction as well as the frictional contribution of the plaster particles. As the plaster of Paris cures, the calcium sulfate hemihydrate ($2CaSO_4 \cdot H_2O$) dissolves and reprecipitates with additional complexed water molecules to form interlocking crystals of gypsum ($CaSO_4 \cdot 2H_2O$). These crystals precipitate between and around the kaolin particles as they grow together and interlock. The growth of interlocking crystals between insoluble sludge particles has been suggested as a possible mechanism for strength development in some tank sludges. This is

based on the observation that the shear strength from Hanford DST 101-SY decreased markedly as the temperature increased (Herting 1992a). The increase in temperature, it is postulated, causes some of the salts to dissolve, thereby decreasing the degree of interlocking.

The kaolin/plaster sludge simulants are not without drawbacks. The properties obtained once the simulant cures can be quite sensitive to small variations in the simulant preparation procedure. Under some conditions, for example, mixing for 15 minutes instead of 10 minutes can result in a much lower ultimate strength. The additional mixing breaks down the calcium sulfate dihydrate crystals that begin forming once the plaster of Paris contacts water. Thus, careful attention to the simulant preparation procedure is needed to ensure that multiple batches of kaolin/plaster simulant have similar properties.

Physical properties for several kaolin/plaster simulants are given in Table 3.2. Again, the shear strengths for the kaolin/plaster simulants will vary depending on mixing time and temperature, so the values given in Table 3.2 will not be obtained in some circumstances. Clearly, when using the kaolin/plaster simulants, it is necessary to characterize each batch of simulant once it cures.

The bulk density of kaolin/plaster sludge simulants can be predicted based on the known densities of kaolin clay particles (2.65 g/cm^3), water (0.998 g/cm^3), calcium carbonate (2.83 g/cm^3), and calcium sulfate dihydrate (2.32 g/cm^3). According to the manufacturer, the plaster of Paris contains 20% ± 5% by weight of calcium carbonate as a nonreactive filler.

Table 3.2. Properties of Kaolin/Plaster Sludge Simulants

Composition (wt%)	Shear Strength (kPa)	Density (kg/m^3)
50.0% kaolin 10.0% plaster of Paris 40.0% water	0.97 ± 0.09	1610
50.0% kaolin 12.0% plaster of Paris 38.0% water	2.12 ± 0.22	1640
50.0% kaolin 13.0% plaster of Paris 37.0% water	2.9 ± 0.4	1660
50.0% kaolin 14.0% plaster of Paris 36.0% water	4.0 ± 0.7	1680

3.2.1.7 Kaolin/Ludox® Sludge Simulants

Mixtures of kaolin clay, water, salt, and Ludox have been used to simulate DST sludge for scaled mixer-pump tests conducted in fiscal years 1988 and 1994 (see Powell et al. 1997a). Following a series of fiscal year 1987 1/12-scale sludge mobilization tests using a silica/soda ash simulant, a series of additional 1/12-scale tests were performed using a kaolin/Ludox sludge simulant. It was desired that these mobilization tests be conducted using sludge simulants with higher shear strengths than those practically attainable using the silica/soda ash sludge simulant. To meet this need, a new simulant was developed. This simulant used the gelation of colloidal silica to create strength. The colloidal silica chosen is sold under the trade name Ludox HS-30. Kaolin clay was added to give the gel the target sludge density of 1.5 kg/L. This simulant was convenient to use for the 1/12-scale tests because it could be mixed as a slurry and pumped into the tank where it cured to form a sludge. The shear strength of the sludge and curing time are predictably controlled by the Ludox and salt concentrations used.

The mechanism for strength development in the kaolin/Ludox sludge simulant is similar in some respects to bentonite clay, but different in others. The Ludox HS-30 is purchased in the form of a 30 wt% mixture of very small amorphous silica particles (roughly 12 nm) in water. The particles are small enough to be maintained in suspension by Brownian motion, and they do not flocculate because of their high surface charge. Adding salt (sodium chloride) suppresses the interparticle electrostatic repulsions, which allows the particles to aggregate and form a three-dimensional gel structure that gives the simulant strength. Similarly, bentonite/water mixtures obtain strength from the gel structure formed by the colloidal bonded bentonite particles.

Where the kaolin/Ludox simulant differs, however, is in the reversibility of the interparticle bonds. The Ludox particles undergo a condensation reaction at the interparticle contact points that results in a chemical bond between the particles. These bonds form relatively slowly and can be broken by an applied strain. Further, once broken, these bonds do not readily reform. Thus, kaolin/Ludox sludge simulants lose their shear strength when mixed after they have been allowed to cure. Bentonite sludge simulants in the concentration range typically used lose comparatively little of their strength even upon vigorous mixing.

The kaolin in the kaolin/Ludox simulant mixture does not contribute appreciably to the shear strength of the cured simulant. The kaolin is included in the mixture primarily to increase the simulant density and to absorb the free water inside the cured simulant.

Kaolin/Ludox simulants are highly elastic and have been described qualitatively as a cross between thick mud and Jell-O®. Viscoelastic rheometry has not been performed on samples of kaolin/Ludox, but it is expected that such samples would exhibit a very small loss tangent, which implies that very little of its strength is due to interparticle friction. Viscoelastic characterization of bentonite simulants, which are similar in this respect, is described in Golcar et al. (1997).

Table 3.3. Kaolin/Ludox Sludge Simulant Properties

Composition	Target Shear Strength (kPa)	Measured Shear Strength (kPa)	Bulk Density (kg/L)
48.6% kaolin 17.0% Ludox 33.7% water 0.71% NaCl	10.0 10.0	8.0 ± 2.0 (24 h) 8.3 ± 1.4 (48 h)	1.50
47.4% kaolin 25.0% Ludox 26.9% water 0.69% NaCl	23 30	47.4 ± 2.3 (24 h) 64.2 ± 2.3 (48 h)	1.50
47.1% kaolin 27.0% Ludox 25.2% water 0.69% NaCl	30 40	75.8 ± 4.2 (24 h) 95.2 ± 5.3 (48 h)	1.50

Shear-strength data for several kaolin/Ludox compositions are shown in Table 3.3. For two of the compositions shown in the table, the target shear strength differs significantly from the measured shear strength. The reason for this difference is not known, but was likely due to a variation in the simulant preparation procedure and/or variations in the quality of the Ludox used.[1]

3.2.2 Hardpan Waste Simulants

Many Hanford tanks are known to contain a layer of sludge-like material that has solidified. Layers of hard sludge were encountered during past tank-sluicing campaigns. The sluice jets were found to be largely ineffective at removing this layer of "hardpan" waste. In some cases, the hardpan layer could be sluiced if fresh water was used as the sluice stream. It was hypothesized that some of the hardpan layers were composed of insoluble sludge particles and crystals of sodium uranyl carbonate (Rodenhizer 1987). In other tanks, the sludge has been allowed to dry and, in some cases, reach temperatures in excess of 100°C. Bonding reactions between adjacent sludge particles are accelerated at higher temperatures and when the sludge is dried. It is postulated that these reactions have resulted in the formation of very hard sludge in some tanks. No samples of high-strength sludge have yet been obtained and characterized, so the extent to which these reactions may have affected the waste can only be speculated.

3.2.2.1 Relevant Properties for Hardpan/Dried Sludge

Retrieval technologies are needed to recover the hardpan sludge wastes. Simulants have been developed so that candidate retrieval technologies can be evaluated against simulated hardpan wastes. The recipes for these test materials are given in Section 3.2.2.3. The hardpan/dried sludge properties that control the performance of retrieval processes are not yet known.

It is hypothesized that waterjet-based and mechanical-cutting-based retrieval approaches for hardpan and dried sludge are most strongly dependent on the mechanical strength of the undisturbed waste. The sensitivity to disruption and waste density is also judged to be important,

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[1] Ludox properties can be significantly altered by exposure to freezing weather. It is not known whether the Ludox used for theTable 3.3 samples had been affected in this way.

as both affect settling and the rate of slurry formation. Salt dissolution may also be important, but this effect cannot yet be adequately predicted, so it has not been included in the hardpan simulants. The extent to which the hardpan wastes are soluble is not known. Because it is possible that at least some of the hardpan wastes are wholly insoluble, it was judged prudent to formulate nondissolving hardpan simulants. Retrieval rates obtained from testing these simulants may be lower than those that would be obtained from a partially soluble hardpan simulant. Testing of these materials is needed to establish whether all the relevant properties are addressed by the simulants.

3.2.2.2 Hardpan Simulant and Waste Property Comparison

The development of defensible hardpan/dried-sludge simulants is hindered by the complete lack of physical property data from hardpan waste samples. Some defensibility, however, can be obtained if the waste simulants are designed to develop strength through the same (or similar) mechanisms that operate in the tank waste. For the purpose of the present and past simulant-development efforts, the mechanisms operating in the hardpan and dried-sludge waste types were assumed to be the binding together of insoluble sludge particles by interstitial salt crystals (hardpan) and chemical bonding of sludge particles at their contact points.

The kaolin/plaster hardpan simulants described in Section 3.2.2.3 obtain mechanical strength via the formation of interlocking hydrated calcium sulfate crystals in the voids between kaolin clay particles. Adjusting the plaster concentration in the initial mix controls the strength of the cured simulant. The kaolin particles do not add significantly to the simulant strength, but instead serve to dilute the plaster (thereby limiting its strength) and to absorb the water that remains following the completion of the hydration reaction.

Because the interlocking salt crystals determine the strengths of the kaolin/plaster simulants, mixing this simulant (after it is cured) will greatly reduce its apparent strength. Mixing breaks down the calcium sulfate dihydrate crystals into small, non-interlocking pieces. The simulant strength remaining after extended mixing will be determined largely by the amount of free water that remains in the simulant mixed with kaolin clay. The simulants specified here have a relatively high water content to facilitate simulant preparation. As a result, the hardpan simulant residual strength after disruption is quite low. The residual strength can be increased by increasing the fraction of kaolin (or, equivalently, decreasing the fraction of water) in the simulant recipe.

The tendency for the apparent viscosity of a fluid or paste to decrease with continued mixing is called thixotropy. This type of rheological behavior is common in slurries that obtain their shear resistance via the formation of gel structures or the interlocking of particles and crystals. Sludge-like materials that develop mechanical strength using these mechanisms are expected to be thixotropic. Materials that develop strength exclusively via interparticle attractive forces (e.g., van der Waals attraction) and interparticle friction are expected to not exhibit significant thixotropy.

The hardpan/dried sludge in the Hanford waste tanks is expected to develop its mechanical strength via a combination of interparticle attractions, friction, interlocking salt crystals, and chemical reactions at particle contact points. Mechanical disruption of this waste, then, should result in a decrease in its strength. The tank hardpan/dried sludge should exhibit some degree of thixotropy. The extent to which the strength is reduced by the disruption will depend on the fraction of the strength that is due to disruptable forces (e.g., interlocking salt crystals and interparticle reactions). Since these relative fractions are not yet known, the amount of thixotropy expected from tank waste is unknown. Adjustments to the relative fractions of kaolin and water, which control the residual strength, may be required as hardpan characterization data become available.

There are only two sources of semi-quantitative hardpan physical property data available. First, it has been noted that the Hanford sluicing jets used in the past were not capable of mobilizing the hardpan wastes at a significant rate. Second, samples of the hardpan layer have been described as having the "consistency of blackboard chalk" (Rodenhizer 1987).

Some Hanford sluicing campaigns in the past were conducted using a flow rate of 300 to 350 gpm out of a 1-inch nozzle (Rodenhizer 1987). The nozzle pressure required to obtain this flow with

water is approximately 140 psig. It was found that the hardpan wastes in some tanks were capable of resisting the mobilizing force of these sluice jets. Accurate correlations between sludge strength and the jet pressure required to induce mobilization have not yet been developed. However, the tests described in Section 3.2.2 imply that the threshold impact pressure for mobilization is on the order of the sludge shear strength or perhaps a factor of 4 higher. The data in Figure 3.2 show that the kaolin/plaster hardpan simulants require a waterjet impact pressure of about 1.2 times the shear strength before significant mobilization occurs. It is not yet known why the bentonite and kaolin clay simulants follow a different relationship.

If the jet-impact pressure exceeds the threshold pressure for mobilization, it is expected that mobilization will take place. Mobilization probably takes place at lower pressures as well, but it is not yet known how much lower these pressures may be. The sluice jets lose some of their impact force as the jet breaks up in the air before impacting the sludge. At a typical sluicing distance of 30 feet, for example, the remaining maximum jet impact pressure is approximately 22% of the nozzle pressure.[1] Since the 140 psig sluice jets were not capable of mobilizing the hardpan wastes, it seems reasonable that the minimum penetration resistance of the hardpan is probably around (0.22)(140 psi) = 31 psi (214 kPa). Assuming the relationship shown in Figure 3.2 between the threshold waterjet impact pressure and shear strength holds for the hardpan waste, the shear strength of the hardpan is estimated to be between (1/4)(31 psi) = 7.8 psi = 53 kPa and (1/1.2)(31 psi) = 25.8 psi = 178 kPa.

A sample of the hardpan layer in Hanford SST 106-C was obtained via rotary mode core sampling in 1986 (Weiss 1988). The bottom-most section of the core sample was a hard white material that did not break up under the action of a plastic "masher" (i.e., a hand-held device used in the preparation of mashed potatoes).

3.2.2.3 Kaolin/Plaster Hardpan Simulants

Only a single type of simulant has been used to simulate the physical properties of hardpan wastes for the testing of retrieval systems. Mixtures of kaolin clay and plaster of Paris are used to simulate hardpan. The fraction of plaster of Paris used for the hardpan simulants is much higher than those of the sludge simulants described in Section 3.2.1.5.

Two hardpan simulant recipes have been used to test several different waste retrieval processes (Bamberger et al. 1997). The compositions and properties of these simulants are given in Table 3.4.

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[1] This is estimated using the empirical relationship between jet-impact pressure and standoff distance given by Summers (1995).

Table 3.4. Kaolin/Plaster Hardpan Simulant Compositions and Properties

Material	Concentration (wt%)	Shear Strength (kPa)	Bulk Density (g/cm^3)
kaolin clay plaster of Paris water	30.0 27.5 42.5	32 ± 6	1.56 ± 0.05
kaolin clay plaster of Paris water	40.0 22.5 37.5	150 ± 25	1.65 ± 0.05

The shear strengths given in Table 3.4 were measured after 24 hours of curing. As was noted in Section 3.2.1.5, the shear strength of kaolin/plaster simulants not only changes with time, but is sensitive to variations in the preparation procedure and conditions. Further, even though the cured hardpan simulants are relatively hard (the stronger hardpan can be walked upon), their strength will decrease when they are subjected to mixing or are otherwise disturbed. Consequently, insertion of a shear vane into the cured simulant can decrease the shear strength of the simulant surrounding the vane, which will result in the shear strength measurement being biased low. The preferred way to measure the shear strength of kaolin/plaster hardpan simulants is to insert the vane into the simulant before it cures. This method results in more reliable shear-strength data.

The kaolin clay appears to have the unintended effect of causing the simulant strength to reach a peak and then decrease to a stable value. A plot of the 40% plaster hardpan simulant shear strength versus time is shown in Figure 3.10. It is hypothesized that this behavior may be due to a cation exchange reaction between the plaster (calcium sulfate) and the naturally occurring sodium ions in the clay. Alternatively, the strength decrease may be due to disruption of the simulant structure by

he small volume change that accompanies the hydration of plaster. While interesting, this tendency is not expected to be relevant to the simulant defensibility

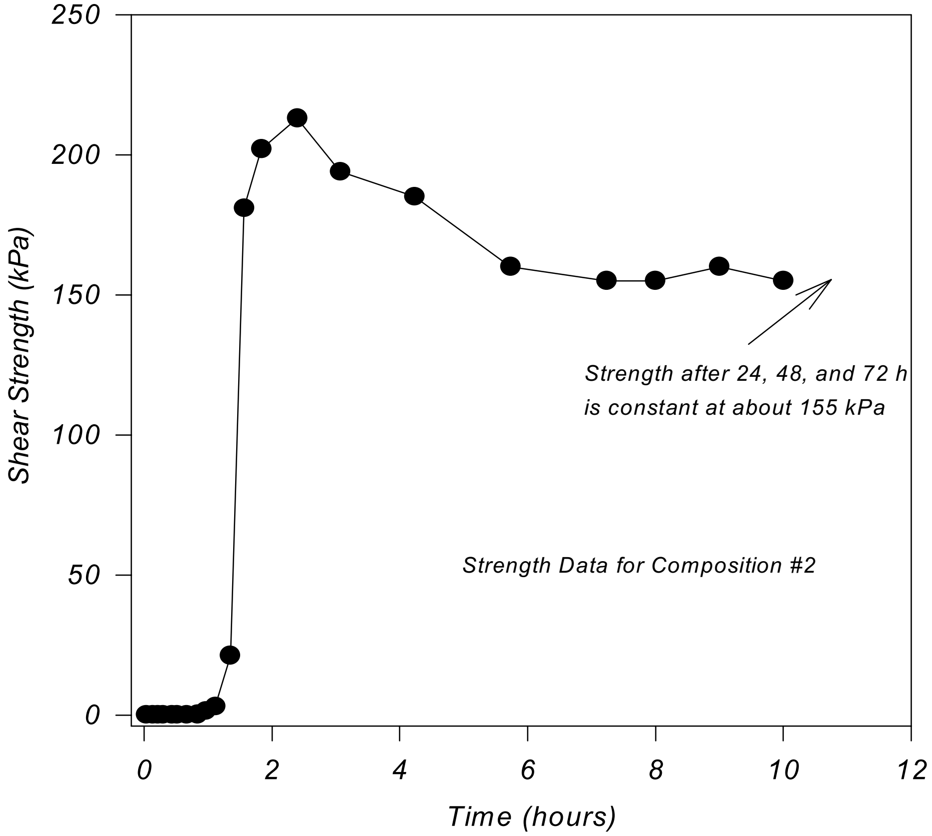

Figure 3.10. Shear Strength vs. Time for 40% Plaster Hardpan Simulant

3.2.3 Saltcake Waste Simulants

The saltcake present in the Hanford tanks consists largely of sodium salts of nitrate, aluminate, nitrite, carbonate, phosphate, hydroxide, and sulfate. The exact compositions vary according to which process generated the waste and according to the subsequent history of waste in each tank. These differences are expected to give rise to a wide variety of physical and chemical properties. The mechanical strength of the saltcake, for example, is expected to vary over a range of perhaps 2 or more orders of magnitude, depending on the saltcake composition and history.[1] Several different techniques have been proposed for saltcake retrieval at Hanford. These processes and the saltcake properties that determine the performance of these processes are described in this section. Composition and property data are also given for some of the saltcake simulants that have been used at Hanford.

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[1] **Some chemically simulated saltcake has been found to have compressive strengths as high as 28 MPa (4000 psi) (Wanner 1993). Samples of hard saltcake have not been taken from the tanks and analyzed to verify this estimated strength. Samples of soft saltcake, however, have been described as having a "snow-cone" consistency, which would imply a very low compressive strength (i.e., < 10 psi).**

3.2.3.1 Relevant Properties for Saltcake Retrieval

There are several saltcake properties known to influence the performance of saltcake retrieval systems. Which properties are most important, of course, depends on the type of retrieval process being considered. The performance of mechanical chopping techniques, for example, will be strongly dependent on the shear, compressive, and tensile strengths of the saltcake, but insensitive to the rate of saltcake dissolution. Waterjet-based techniques, however, are affected by saltcake dissolution rates as well as by selected mechanical strength and saltcake structure properties. The saltcake properties expected to have the greatest influence on several different saltcake retrieval techniques are discussed below.

A considerable effort has been made by EM-50 DOE to develop high-pressure, waterjet-based saltcake retrieval techniques (Rinker et al. 1997). Small diameter jets of high-pressure water (between 1,000 and 60,000 psi) are used to cut the hard saltcake materials into small chunks roughly 1 cm in size. The cuttings are gathered as they are produced by a vacuum-based air conveyance or jet-pump driven pumping system. The conveyance system gathers both the cuttings and the water from the waterjets so that significant amounts of water are not added to the waste. This is desired to minimize the chance that tank waste could leak from the tanks during retrieval.

The rate at which the high-pressure waterjets cut hard saltcake is thought to be a function primarily of the salt-crystal grain size, bulk porosity, pore connectedness, and tensile strength. Other factors that may be important include salt solubility,[1] dissolution rate, and fracture toughness. This list of physical and chemical properties was developed through consultation with waterjet cutting experts and a consideration of the physics of waterjet cutting. A detailed discussion of the reasons for selecting each of these properties is given in Golcar et al. (1997).

To better understand the relationship between saltcake properties and waterjet cutting, tests were conducted in which a variety of hard saltcake simulants were subjected to high-pressure waterjets. This work described in Powell et al. (1997b), is being used to establish correlations between waterjet cutting and selected physical properties of saltcake simulants.

Lower-pressure, waterjet-based saltcake retrieval methods are also receiving attention. It is currently planned that sluicing will retrieve the waste in many of the Hanford SSTs. The baseline sluicer design uses a 2.5-cm (1-inch) diameter nozzle discharging liquid (either a dilute slurry or inhibited water) at an exit velocity of about 46 m/s (150 ft/s). This high volumetric flow, low-pressure technique will rely primarily on dissolution to effect the retrieval of hard saltcake. The impacting jet, in addition to dissolving, may dislodge softer saltcake wastes.

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[1] Recent testing at the University of Oklahoma implies that the dissolution of the K-Mag saltcake simulants may be significant during high-pressure (1 to 5 kpsi) waterjet cutting (*Performance Analysis of Water-Jet Cutting Technology on Saltcake Erosion as a Function of Temperature, Pressure, and Stand-off Distance.* Baeza, Scopel, and Gremillion of the University of Oklahoma, December 14, 1995). Increasing the temperature of the waterjet fluid was found to increase the rate of cutting. Whether this is due solely to enhanced K-Mag dissolution kinetics or to other, less obvious factors is not yet known. For example, the higher temperature waterjet fluid may have a reduced interfacial tension (between the saltcake and the water) or decreased viscosity, which will tend to improve performance by allowing the waterjet to penetrate into the saltcake pores more readily. It is not known whether water temperature effects are significant for > 5 kpsi waterjets.

The retrieval rate of saltcake sluicing is expected to be a function primarily of the dissolution rate of the saltcake. The dissolution rate will likely be increased if the sluice jet is powerful enough to overcome the mechanical strength of the soft saltcake, but this is unlikely to occur for the hard saltcake. The dissolution rate of saltcake-like materials is a function of the saltcake composition, porosity, grain size, and grain shape, as well as the properties of the sluicing fluid (e.g., fluid composition, flow rate, and temperature [Helgeson et al. 1984; Aagaard and Helgeson 1982]).

3.2.3.2 Saltcake Simulant and Waste Property Comparison

Very little characterization of Hanford saltcake physical properties has been completed. Some chemical composition data have been developed, based on a combination of measurement and process flowsheet analyses (e.g., Kupfer 1981), but physical-property data are qualitative at best. No measurements of saltcake tensile strength, compressive strength, porosity, or fracture toughness have been made. However, the need to support retrieval-system testing with defensible saltcake simulants remains. At present, only qualitative comparisons between simulant and saltcake properties can be made for most of the key properties discussed in Section 3.2.3.1. The quantitative and qualitative comparisons that can be made are described below.

Mechanical Strength Properties

The physical properties of tank saltcake have not been measured, but it is suspected that there is wide variation in those properties (Krieg 1992). In-tank photographs and operational experiences indicate that some tanks contain relatively soft saltcake while others contain very hard saltcake. It has been suggested that the soft saltcake waste was formed when solids-laden evaporator effluent slurry was pumped into the tanks. Pumping and evaporation, leaving a loosely bound matrix of salt crystals, subsequently removed the interstitial liquor. The hard saltcake supposedly formed via a slow, in-tank crystallization that resulted as water evaporated from the liquid tank waste.

Much of the previous saltcake simulant work has been focused on the development of simulants for the hard saltcake wastes (Golcar et al. 1997). The potassium-magnesium sulfate (K-Mag) simulants described in Section 3.2.3.3 were developed for testing high-pressure waterjet-based retrieval methods. The retrieval systems being designed had to be robust enough to retrieve all waste types at the target waste retrieval rate successfully. Because the hard saltcake was judged to represent the greatest challenge to these high-pressure waterjet systems, an effort was made to develop a simulant for the hard saltcake. If the waterjet systems could be designed to handle the hard saltcake simulant, then it was expected that they would also be able to handle the other waste types (e.g., sludge, hardpan, and soft saltcake).

To support the development of the high-pressure waterjet system, saltcake simulants similar to the hard saltcake waste were needed. No samples of hard saltcake were available for characterization, so the physical properties of some chemically based simulants were measured (Wanner 1993). The compressive strengths of these chemical simulants were used to establish the target compressive strengths for the K-Mag saltcake simulants. The chemical simulants could not be used directly because of the hazards and associated disposal costs. The 84% K-Mag simulant was developed to produce the target hard saltcake compressive strength of about 21 MPa (3000 psi).[1]

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[1] Wanner (1993) measured the compressive strengths of both chemical saltcake simulants and several K-Mag simulant samples. The K-Mag strengths reported by Wanner are considerably lower than those found by

The 10 MPa (1500 psi) K-Mag simulants (88% and 75% K-Mag in water) were developed to allow testing of high-pressure waterjet-based retrieval methods on simulants with different mechanical strengths and porosities. The porosity of the 88% K-Mag saltcake is much greater than that of the 75% saltcake (Golcar et al. 1997). Developing an understanding of the hard saltcake physical properties that control high-pressure waterjet effects is an ongoing effort in the Retrieval Process Development and Enhancements Project.

The simulants made from rock salt and plaster of Paris were developed to provide test materials expected to be similar to the soft saltcake. No quantitative sample-characterization data are available on which to base the target mechanical strength of soft saltcake simulants. There are recent indications that some of the soft saltcake may be soft enough to allow the emplacement of in-tank probes with a minimal amount of force. What this means in terms of measurable strength properties (e.g., compressive strength) must be evaluated. However, there are qualitative descriptions indicating the soft saltcake is a very weak material ("slushy snow cone" consistency; Wong 1990). This qualitative description was used as the basis for selecting mechanical strength target values for the weak salt/plaster simulants.

Saltcake Dissolution Rate

It must be stressed that the K-Mag simulants were not originally developed to model the dissolution characteristics of hard saltcake. The dynamics of high-pressure waterjet cutting were thought to be fast enough that dissolution would be of secondary importance compared to properties like tensile strength, granularity, porosity, and fracture toughness.[1] K-Mag simulants, however, do dissolve slowly and, therefore, may have some usefulness as simulants for high-volumetric-flow sluicing-based retrieval methods that rely on waste dissolution. The dissolution rate of K-Mag, however, is considerably slower than that of the sodium nitrate and nitrite salts that compose the bulk of the actual saltcake wastes.

Whether or not K-Mag simulants can be used to model actual hard saltcake dissolution is not yet known and requires further study. However, for retrieval methods that do not rely heavily on salt-dissolution effects (e.g., high-pressure waterjets or mechanical choppers/cutters), the K-Mag simulants are reasonable. Efforts are being made to identify materials that can be used to formulate representatively soluble simulants for hard saltcake. This effort is made more difficult by the requirement that the simulants not be too expensive to prepare and/or dispose of.

Porosity

The porosity of Hanford saltcake has not been measured, but estimates range between 10% and 50% (Krieg 1992). The porosity of the K-Mag saltcake simulants has been measured using a mercury porosimeter. The K-Mag porosity is found to vary between about 10% and 20%, depending on the water content in the initial mix. The porosity of the rock salt/plaster saltcake

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more recent testing at PNNL. The discrepancy is due to differences in the K-Mag curing procedure. Wanner allowed the samples to dry while curing, which decreased the extent of langbeinite hydration. Much lower compressive strengths resulted.

[1] The University of Oklahoma study mentioned earlier provides evidence that K-Mag dissolution may be significant for high-pressure waterjet-based retrieval techniques.

simulants (compositions 4 and 5) is estimated to be approximately 40%, based on the known plaster, salt, and simulant densities. The K-Mag saltcake simulants are near the lower end of estimated saltcake porosities, and the rock salt/plaster simulants are near the upper end.

3.2.3.3 Hard Saltcake Simulants (K-Mag)

The hydration chemistry of potassium-magnesium sulfate (K-Mag) and its relationship to the physical properties of the saltcake simulants has been extensively studied as part of the EM-50 simulant development efforts. For a detailed discussion of the chemical and physical properties of K-Mag saltcake simulants, see Golcar et al. (1997).

Table 3.5 gives the physical properties of eight different K-Mag simulant compositions. The compressive strength data are plotted versus water content in Figure 3.11, which shows that the peak compressive strength occurs at around 86 wt% K-Mag. Porosity and average pore size data obtained by a mercury intrusion method are plotted in Figures 3.12 and 3.13. The variations in compressive strength and porosity with water content are discussed in Golcar et al. (1997).

Table 3.5. Hard Saltcake Simulant (K-Mag) Compositions and Properties

Composition Wt%	Bulk Density g/cm^3	Porosity %	Compressive Strength MPa (psi)
10 water 90 K-Mag	2.08	17.2	9.8 (1420)
12 water 88 K-Mag	1.94	18.9	18.1 (2620)
14 water 86 K-Mag	2.22	10.5	29 (4140)
16 water 84 K-Mag	2.25	13.7	19 (2750)
18 water 82 K-Mag	2.19	14.8	15 (2190)
20 water 80 K-Mag	2.27	6.8	15 (2220)
25 water 75 K-Mag	2.56	12.5	13 (1840)
30 water 70 K-Mag	2.33	4.0	12 (1720)

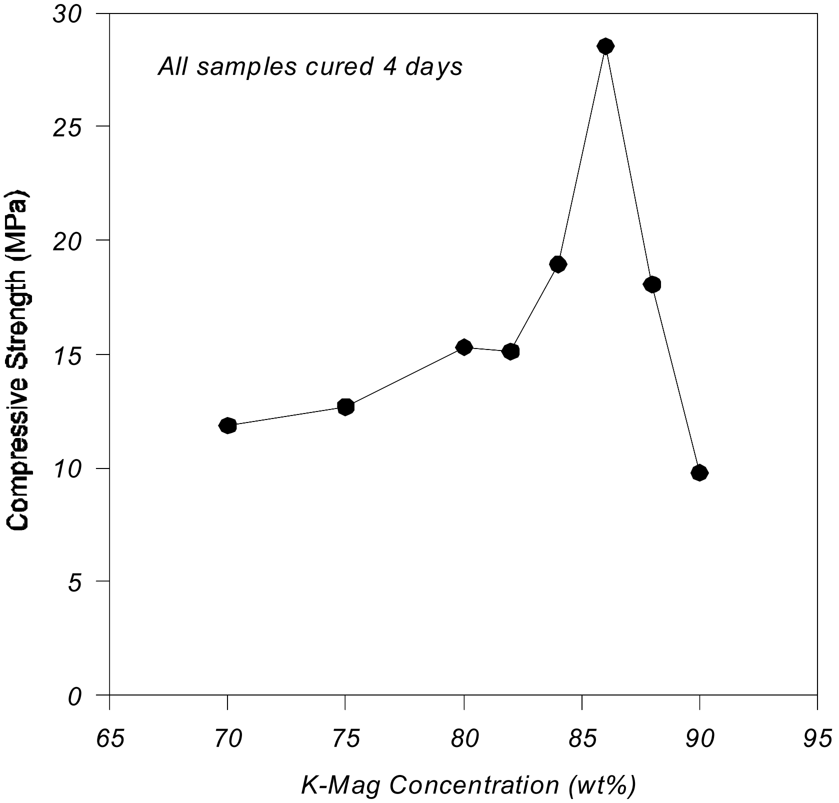

Figure 3.11. Hard Saltcake Simulant (K-Mag) Compressive Strengths

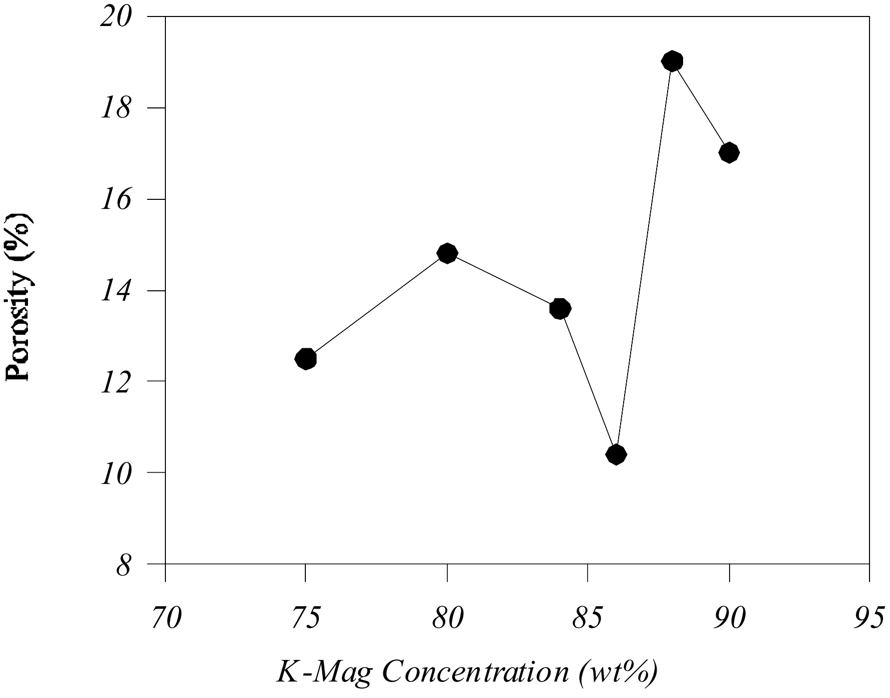

Figure 3.12. K-Mag Porosity vs. Concentration

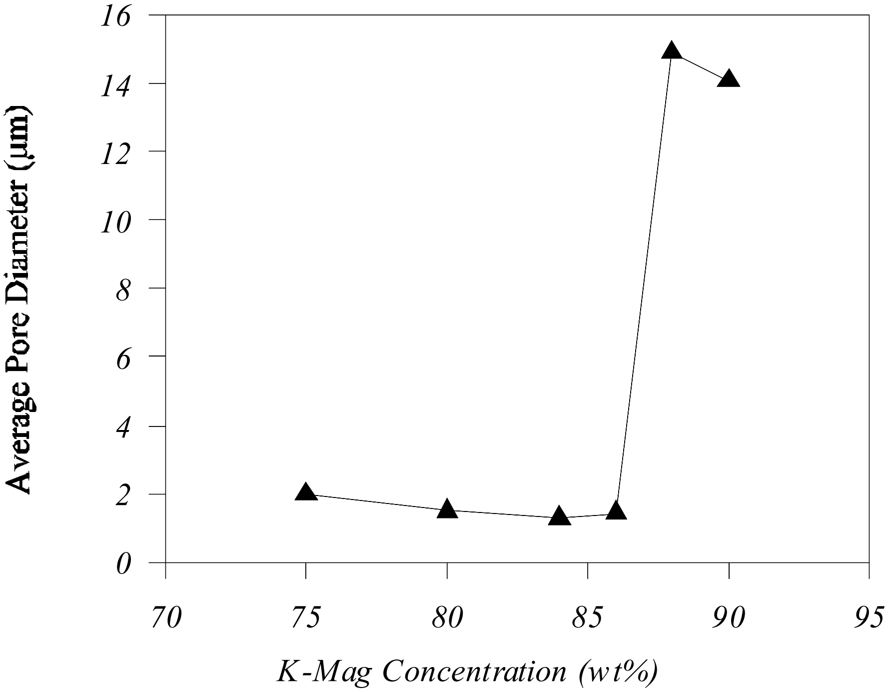

Figure 3.13. K-Mag Average Pore Diameter vs. Concentration

3.2.4 Supernatant Liquid and Slurry Simulants

Efforts have been made to develop simulants specifically for the purpose of studying the transport of waste slurries in pipelines. Long-distance waste transport is of concern at all the DOE waste sites, but particularly so at Hanford where some wastes must be transported through a six-mile-long pipeline for processing. Both chemical simulants (e.g., Fow et al. 1986a, 1986b; Carleson et al. 1987) and physical simulants (Reynolds et al. 1996) have been formulated for rheological and pipe-loop testing.

For the development and testing of most waste retrieval methods, however, the properties of the waste slurries and supernatant liquids are of secondary importance. The greater challenge is usually the initial mobilization and breakup of the waste solids. Waste slurry properties can be important for evaluating how readily the mobilized waste is transported to the inlet of a waste transfer pump, but this problem is usually considered when designing the sludge and saltcake simulants (see Section 3.2.1.1). Because waste slurry properties are of reduced importance for retrieval system development and testing, slurry and supernate simulants will not be discussed further in this document. Refer to Reynolds et al. (1996) and Hudson (1996) for descriptions of slurry simulants and their relationship to tank waste.

3.3 Simulant Preparation and Characterization

The simulant recipes given in Section 3.2 will not always yield simulants with the expected properties. The properties of some simulants are sensitive to variations in the preparation procedure, while others are relatively insensitive. This variability can be reduced by strict adherence to the recommended simulant-preparation procedures given in Section 3.3.1. Section 3.3.1.1 describes the preparation of simulants that are relatively insensitive to variations in preparation conditions, and Section 3.3.1.2 addresses the simulants that are sensitive to preparation conditions.

The methods and standards used to characterize the waste simulants are described in Section 3.3.2. Brand names and manufacturers for the simulant materials are given in Section 3.3.3.

3.3.1 Simulant Preparation Procedures

The procedures used to prepare the waste simulants described in Section 3.2 are given in this section.

3.3.1.1 Insensitive Simulants

Many of the waste simulants show relatively little sensitivity to changes in preparation procedure. These "insensitive" simulants are

kaolin/water
bentonite/water
bentonite/$BaSO_4$/water
bentonite/kaolin/water.

These simulants are prepared simply by mixing together the desired quantities of materials until a uniform mixture is obtained. No cure time is associated with these simulants, and they may be used immediately after preparation or weeks afterward without significant changes in their properties, provided that no water evaporates from the mixture.[1]

Any type of mixer that will result in a uniform product is acceptable for use with these simulants. Simulants with relatively high shear strengths (> 1 kPa) may require the use of special mixing equipment designed for mixing pastes. PNNL uses a Littleford (Florence, Kentucky) paste mixer to prepare 20-gallon batches of high-shear-strength simulants.

3.3.1.2 Sensitive Simulants

The properties of the simulants listed in this section are sensitive to changes in the simulant-preparation procedures.

The kaolin/plaster (both sludge and hardpan) and rock salt/plaster simulants must not be mixed any longer than necessary after being added to the plaster of Paris. Once the plaster of Paris comes in contact with the water, the hydration reaction begins. Prolonged mixing can hinder the growth of the gypsum crystals, and this will decrease the cured strength of the simulant. High-shear mixers should not be used for preparing these simulants. Rolling-drum concrete mixers have provided suitable mixing for the kaolin/plaster, rock salt/plaster, and K-Mag simulants.

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[1] These simulants should not be allowed to freeze as this will dramatically alter their properties. The simulants will also be affected by prolonged contact with water or salt solutions.

Kaolin/plaster sludge and hardpan simulant should be prepared as follows. The required quantities of kaolin and water are first mixed to form a uniform slurry. If large quantities are being prepared or if the ambient temperature exceeds about 20°C, it is advisable to substitute ice for a portion of the water in the mix. This will ensure that the kaolin/water slurry is cold before the plaster of Paris is added. The plaster of Paris hydration reaction is greatly accelerated by elevated temperature, so premature curing of the simulant can occur if the slurry temperature is too high. This is especially problematic when large quantities of hardpan are being prepared. Once the kaolin/water slurry is uniform, the plaster of Paris should be added as rapidly as possible while continuing to mix. Batches should be sized so that the plaster of Paris is uniformly mixed into the slurry, and the slurry is placed into its curing mold no more than about 10 minutes after the plaster of Paris is added. Mixing for longer periods can result in markedly lower strengths for the cured simulant.

Rock salt/plaster saltcake simulant is prepared by first mixing the plaster of Paris and water to form a uniform slurry and then adding the rock salt. Mixing should be continued only as long is necessary to ensure that the rock salt particles are uniformly coated with plaster of Paris. This simulant should not be prepared when the ambient temperature is high (i.e., greater than 25°C).

The remaining waste simulants can be prepared without undue regard for the ambient temperature, and they have less sensitivity to mixing time. Silica/soda ash, kaolin/Ludox, and the K-Mag saltcake simulants are prepared by mixing the components together until uniform, and then the resulting slurry is placed in a mold to cure.

All the waste simulants must be covered to prevent water loss during curing.

3.3.2 Characterization Procedures

The simulant characterization procedures are described in the sections below.

3.3.2.1 Shear Strength

The shear strength of sludge and hardpan simulants is measured using a shear vane and a Haake rheometer. This technique is a standard method for measuring shear strength. It is most often used to characterize soils. ASTM standard D4648-94 describes the proper use of shear vanes for measuring shear-strength.

The Haake rheometer M5 allows the vane torque to be accurately measured as the vane is rotated at a constant, slow rate equal to or less than 0.3 rpm. For field measurements, a hand-held shear vane (Model CL-612 from ELE International, Inc.) is used. The hand-held vane spring is calibrated to accurately read the vane torque, but it is difficult to maintain a steadily increasing torque and maintain the vane perfectly vertical. For this reason, the Haake system is preferred when shear strengths must be accurately measured.

3.3.2.2 Compressive Strength

The compressive strength of the saltcake simulants is measured using the ASTM C39 specifications for the compressive strength testing of concrete cylinders. It is preferred that samples for compressive and tensile strength testing be removed from the simulant bed using a core drill, but when this is not practical, cylindrical test molds are filled at the time of simulant preparation.

3.3.3 Simulant Material Suppliers

Simulant properties will vary from those listed in this report if alternative sources for simulant components are used. The properties of kaolin clay, for example, vary considerably depending on where the clay was mined. The brand names of each of the simulant components used for the waste simulants described in Section 3.2 are given in Table 3.6 below.

Table 3.6. Simulant Material Specifications

Simulant Material	Manufacturer	Product Name
kaolin clay	**Feldspar Corporation Edgar, Florida**	**EPK Pulverized Kaolin Clay**
bentonite clay	**American Colloid, Inc. Upton, Wyoming**	**CS-50 bentonite clay**
plaster of Paris	**DAP, Inc. Dayton, Ohio**	**Plaster Wall Patch - Long Working Time Plaster of Paris**
K-Mag	**Western Ag-Minerals Co. Houston, Texas**	**Feed Grade Dynamate potassium-magnesium sulfate**
rock salt (NaCl)	**Morton International, Inc. Chicago, Illinois**	**Extra Coarse White Crystal Solar Salt**
Ludox® colloidal silica	**DuPont Specialty Chemicals Wilmington, Delaware**	**Ludox® HS-30**
silica powder	**U.S. Silica Pacific, Missouri**	**Min-U-Sil® 30**

4.0 Simulants for Pretreatment Processes

Pretreatment strategies include using processes and equipment to separate and/or destroy waste components to minimize treated waste volumes and to produce waste fractions compatible with final waste forms and their disposal criteria. Because of the difficulties in obtaining and working with actual tank wastes, many pretreatment studies performed to date have used simulated wastes developed to mimic the critical chemical and, in some instances, physical properties that affect individual pretreatment processes. This section relates simulated wastes to different pretreatment unit operations and provides available information for preparing the simulants.

Following are important caveats for working with simulants that are best mentioned up front:

- While simulant names in many cases refer to specific tank wastes, the chemical and physical behaviors observed for these simulants may not necessarily be representative of the specified wastes.

- Simulant solutions that contain only selected organic constituents may not necessarily be representative of actual supernatant wastes that contain organic complexes.

- In spite of careful preparation, solids may precipitate from simulant solutions. As a result, solution compositions may not reflect compositions provided with the recipes.

In general, simulants can play a valuable role *when they are characterized as to their own chemical and physical properties and then used to evaluate a range of processing parameters and/or conditions.*

4.1 Background

In 1990, the primary mission at the Hanford Site changed from plutonium production to environmental restoration. The baseline pretreatment scenario for the treatment and disposal of Hanford wastes involved partitioning the wastes into a small volume of HLW and a relatively large volume of LAW. Removal of radionuclides from the LAW stream was intended to minimize leaching of these constituents from the low-level final waste form into the surrounding environment. Separation of the TRUs from sludge materials was anticipated to reduce the bulk of the sludge that would be vitrified as HLW. Initially, one of the options for reducing HLW volumes was acidic dissolution of the sludge and extraction of the TRUs from dissolved sludge solutions using the TRUEX process.

Under the Underground Storage Tank Integrated Demonstration (USTID) program, a chemical simulant was developed in 1992 to evaluate pretreatment equipment and processes, including acid dissolution, for sludge type wastes. This simulant was extensively characterized, and the results from these analyses were compared with analytical results for two actual wastes from SSTs 241-B-110 and 241-U-110 (Elmore et al. 1992). While the elemental composition of this simulant compared favorably with actual waste sample compositions, only a few of the chemical phases in the simulant were similar to those observed in analyzed wastes. Subsequent acid dissolution studies performed in 1992 with B-110 and U-110 wastes (Lumetta et al. 1993) demonstrated how wastes with different chemical phases can exhibit very different dissolution behaviors. Specifically, the bulk of the solids in B-110 sludge readily dissolved in nitric acid, while the bulk of the solids in U-110 sludge did not dissolve with the same treatment.

In 1994, the pretreatment scheme for reducing HLW volumes began transitioning from acid-based to alkaline-based processing. The alkaline-side pretreatment plan included washing tank sludges with retrieval solutions, followed by at least one caustic or caustic permanganate wash to remove aluminum, phosphorous, and chromium. This separation scheme relied on separating bulk components based on their dissolution behaviors. Because results from earlier studies showed that different chemical phases exhibited very different dissolution behaviors, tank-specific sludge washing and alkaline leaching studies have been performed with actual Hanford tank wastes. Refer to Table 4.1. A few studies at Tennessee Technology University used the USTID benchmark simulant to investigate conditions, i.e., time, temperature, and NaOH concentration, for aluminum and metal removal by alkali washing.

Table 4.1. Data Sources for Washing/Leaching Studies

Tank	Reference
B-101	**Lumetta et al. (1998)**
B-104	**Temer and Villarreal (1996)**
B-106	**Temer and Villarreal (1997)**
B-110	**Lumetta and Rapko (1994)**
B-111	**Rapko et al. (1995)** **Rapko et al. (1996)**
B-201	**Lumetta and Rapko (1994)**
B-202	**Temer and Villarreal (1995)**
BX-103	**Temer and Villarreal (1997)**
BX-105	**Temer and Villarreal (1995)**
BX-107	**Rapko et al. (1995)**
BX-109	**Temer and Villarreal (1996)**
BX-110	**Lumetta et al. (1998)**
BX-112	**Lumetta et al. (1998)**
BY-104	**Lumetta et al. (1996)**
BY-108	**Lumetta et al. (1997)**
BY-110	**Rapko et al. (1997)** **Lumetta et al. (1996)**
C-102	**Lumetta et al. (1998)**
C-103	**Rapko et al. (1995)**
C-104	**Spencer et al. (1998)** **Temer and Villarreal (1997)**
C-105	**Spencer et al. (1998)** **Temer and Villarreal (1997)**
C-106	**Brooks et al. (1997)**
C-107	**Spencer et al. (1997)** **Temer and Villarreal (1995)** **Lumetta and Rapko (1996)**
C-108	**Temer and Villarreal (1995)**
Continue	
C-109	**Lumetta and Rapko (1994)**

Tank	Reference
C-112	**Lumetta and Rapko (1994)**
S-101	**Spencer et al. (1998)** **Lumetta et al. (1997)** **Lumetta et al. (1998)**
S-104	**Spencer et al. (1998)** **Lumetta et al. (1997)** **Temer and Villarreal (1995)** **Rapko et al. (1995)**
S-107	**Brooks, et al. (1998)** **Rapko et al. (1997)** **Lumetta et al. (1996)**
S-111	**Lumetta et al. (1997)**
SX-108	**Rapko et al. (1997)** **Lumetta et al. (1996)**
SX-113	**Spencer et al. (1998)** **Temer and Villarreal (1997)**
T-104	**Temer and Villarreal (1995)** **Rapko et al. (1995)**
T-107	**Temer and Villarreal (1995)**
T-111	**Rapko et al. (1995)**
TY-104	**Temer and Villarreal (1995)**
U-110	**Lumetta and Rapko (1994)**

During 1994 and 1995, activities under the Tank Waste Treatment Science task (TWRS Pretreatment Technology Development Project) focused on identifying the major solid phases in sludge-type wastes, both before and after alkaline leaching, and on determining how colloidal interactions in tank waste impact solid-liquid separations and filtration. Based on results from the phase studies, early colloid studies used colloidal suspensions of boehmite (AlOOH) and gibbsite [$Al(OH)_3$]. Aluminum phases were deemed important from a processing standpoint because of the large aluminum inventory. Later studies investigated suspensions containing iron hydroxide [$Fe(OH)_3$] and also a simple physical/chemical simulant (C-103). The results from settling and filtration studies performed with these one- and two- component suspensions and with the simple C-103 simulant are given in LaFemina et al. (1995a, 1995b, 1995c). After 1995, the last year for the science task, phase studies continued as part of the washing/leaching studies. In 1995 and 1996, the washing/leaching studies also looked at settling rates for the washed/leached solids.

While processing scenarios aimed at reducing HLW volumes have changed substantially over the past years, pretreatment schemes for removing contaminants from LAW streams have not. These schemes generally have focused on using processes or materials to remove contaminants from alkaline supernatant wastes. Studies to evaluate these processes and materials have used alkaline supernatant simulants that attempt to replicate inorganic cation and anion concentrations and solution pH and densities determined for actual supernatants or diluted supernatants. Selected organic components have been added to these simulant solutions in varying concentrations. While knowledge of organic constituents in actual tank wastes has improved over the years, many organic constituents have not yet been characterized.

4.2 Applications

The currently envisioned baseline pretreatment strategy is depicted schematically in Figure 4.1. This strategy includes solid/liquid separation, contaminant removal (e.g., Cs and Tc ion exchange, etc.), washing and leaching, filtration, and evaporation unit operations. Simulants previously used in studies to evaluate these different types of unit operations are listed in Table 4.2. Most of these simulants attempt to replicate supernatant or diluted versions of supernatant wastes, while a few attempt to mimic mixtures of poorly soluble metal compounds, salts, and liquids. Only one simulant (C-103) is designed with regard to controlling physical properties.

In Table 4.2, solution simulants are categorized by applicable unit operation and by waste envelope specification (soluble fraction). The remaining simulants are categorized only by the unit operation that was studied with that particular simulant. Corresponding studies performed with actual tank wastes also are referenced.

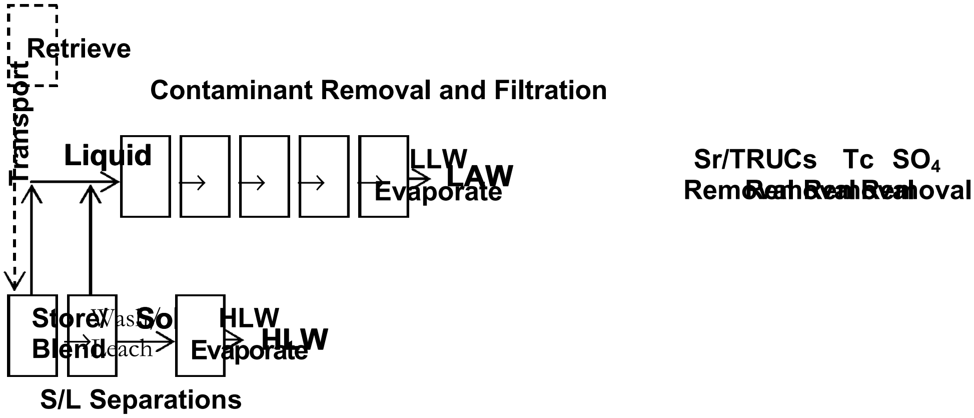

Figure 4.1. Schematic of Generic Pretreatment Unit Operations

4.3 Recipes

Recipes for preparing individual simulants are provided on the following pages. Where possible, each simulant is referenced to a document that contains results from the study performed with that particular simulant. Available background information for individual simulants is also provided. Recipes for the notorious “burping” tank, SY-101, are provided first for two reasons: 1) to show variations among simulants for a particular tank waste and 2) to introduce useful guidelines for preparing simulants that may be applicable to other recipes that are not described in as much detail.

Supernatant simulants are categorized first by waste type, e.g., CC, DSSF, etc., and then by the specific tank waste the simulant composition attempts to replicate. *While a simulant name infers a composition for a specific tank waste, the chemical and physical behaviors observed for that particular simulant may not necessarily reflect specific waste behaviors; to do so, the simulant would need to contain identical chemical and physical properties as the specified waste. In general, simulants are most valuable when they are characterized as to their own chemical and physical properties and then used to evaluate a range of processing parameters and/or conditions.*

Table 4.2. Simulated Wastes for Pretreatment Unit Operations

Simulant Reference	Studies with Actual Waste	Cs Removal	Tc Removal	Sr Removal	Sulfate Removal	Other
4.3.1. CC-SY-101 Simulated Wastes – provided for information. These simulants were used in early studies related to tank safety concerns, e.g., gas generation studies.						
Simulated Solutions (Chemical)						
4.3.2. CC SY-101 (SY1-SIM-93A)		A,C	–	A,B	A	O, E
4.3.3. CC SY-101 Diluted, Treated Solutions					A	O, E, TRU
4.3.4. CC SY-101 Solution (5M Na)		A,C	–	A,B	A	O, E
4.3.5. CC AN-102 Stock Solution (10M Na)		A,C	–	>C	A	O, E
4.3.6. CC AN-102 Solution (5M Na)		A,C	–	A,B	A	O, E
4.3.7. CC AN-102 Diluted, Treated Solutions					A	O, E, TRU
4.3.8. CC AN-107 Solution (5M Na)		A,C	–	A,B	A	E
4.3.9. CC SY-103 Solution (5M Na)		A,C	–	A,B	A	O, E
4.3.10. DSSF-7 Solution (7M Na)		A,C	–		A	E
4.3.11. DSSF-7 Solution with Radiotracers		A,C			A	E
4.3.12. DSSF A-101 Solution (5M Na)			–	–	B	O, E, TRU
4.3.13. DSSF AW-101 Solution (5M Na)		A,C	–	A,B	A	O, E
4.3.14. Composite Supernatant Solution (AN-102, -104, -105, 107)			–			E
4.3.15. NCAW Stock Solution		<A,C to >B	–		B	E
4.3.16. NCAW AZ-102 Solution (5M Na)		A,C	–		B	E
4.3.17. NCAW AZ-102 Solution (5M Na with Radiotracers)		A,C			B	E, TRU
4.3.18. PFP SY-102 Solutions			–			
Simulated Slurries and Sludges (Chemical)						
4.3.19. NCAW Slurry Simulant		S/L Separation				
4.3.20. SST BY-104 Chemical Simulant		developed for FeCN Destruction				
4.3.21. SST C-106 Chemical Simulant	[1]	S/L Separation; Alkaline Leach				
4.3.22. SST C-112 Chemical Simulant		developed for FeCN Destruction				

Simulant Reference	Studies with Actual Waste	Cs Removal	Tc Removal	Sr Removal	Sulfate Removal	Other
4.3.23 SST Variable Chemical Composite		Alkaline Leach				
4.3.24. Calcined Composite Simulated Waste		developed for Calcination Studies				
4.3.25. PUREX Acidified Sludge (SYM-PAS-95)		developed for Energetic Studies				
Simulated Sludge (Simple Chemical/Physical)						
4.3.26. SST "C-103" Chemical/Physical Simulant	**[2]**	S/L Separation				

Key:

[1] **Brookes, et al. (1997)**

[2] Rapko et al. (1995) and Lumetta et al. (1996) contain settling rates for different tank wastes, although no rates are reported for C-103

A Meets Envelope A Specification (soluble fraction)

B Meets Envelope B Specification (soluble fraction)

C Meets Envelope C Specification (soluble fraction)

O Contains organic compounds

TRU Contains spiked concentrations of transuranic elements

4.3.1 Complex Concentrate SY-101 Chemical Simulants

Reference: Bryan, S. A. and L. R. Pederson. 1994. *Composition, Preparation, and Gas Generation Results from Simulated Wastes of Tank 241-SY-101*, PNL-10075, Pacific Northwest Laboratory, Richland, Washington.

4.3.1.1 SY1-SIM-91A

Purpose: Previously used to evaluate flammable gas generation and crust growth phenomena (Delegard, 1980).

This simulant contains all the major inorganic chemicals contained in Tank 241-SY-101, which are sodium hydroxide, sodium nitrate, sodium nitrite, sodium aluminate, and sodium carbonate. A single compound generally represents organic components.

Preparation Guidelines: The simulant is prepared by evaporating (under reduced pressure) excess water from a dilute feedstock solution.

Feed Solution

1. For 1L solution in a 2-L beaker, start with about 500mL water. A round Teflon stir bar works better than the standard cigar-shaped stir bar for stirring thick slurries.
2. Heat the water to about 90ºC and add the sodium aluminate. Stir and heat until the solution is almost clear; waiting too long results in precipitation of aluminum hydroxide.
3. Turn off heat and SLOWLY (to avoid boil-over) add NaOH pellets.
4. Add the sodium carbonate and stir until dissolved. Solution may need to be cooled somewhat to get al the carbonate into solution. If all carbonate doesn't go into solution at this point, don't panic. (See step 8).
5. Turn heat back on and add remaining ingredients in any order (see step 6 regarding organic addition), stirring to dissolve solids and keeping solution hot.
6. Always add the organic as the fully deprotonated sodium salt if possible (sodium salts are more readily soluble that the free acids and no hydroxide correction is needed). With EDTA and HEDTA, solubility is not a problem; however, for others, addition of the organic earlier than last in the order of addition may help with complete dissolution.
7. Add water at any point during solids additions that seems appropriate; however try to end up with close to 900mL total volume. Filter solution while hot (around 50ºC) through a medium, glass-frit filter funnel. While filtering hot caustic through glass frit is not an ideal course of action, paper filters dissolve, and Teflon filters require solvent wetting. Filtration is ~10x faster with hot solution than a cool one.
8. If significant solids remain in the filter, transfer the solids to a 150mL beaker and add water until the total volume is a little under 100mL. Transfer slurry back to the filter.
9. Cool solution to room temperature; then transfer to a volumetric flask and dilute to 1L. Mix well and recheck volume; dilute again if necessary.
10. Analyze final solution.

Slurry Preparation

1. Prepare appropriate solution.
2. Set up a vacuum still that can be controlled to a constant pressure of 60 Torr. Evaporate 100 mL of feed solution at a constant 60 Torr until volume of slurry remaining is 70mL. The solution nucleates not long before the end of the volume reduction and is more pronounced when organics are present.

Note: Standard TD (to deliver) pipettes are not reliable for concentrated solutions. When calibrated with concentrated solutions, air displacement pipettes provide reproducible results.

Table 4.3. SY1-SIM-91A Component Concentrations and Composition

Component	Feed Solution (M)	Concentrated Solution (M)	Wt%
NaOH	1.61	2.3	5.9
$NaAl(OH)_4$	1.54	2.2	16.3
$NaNO_3$	2.59	3.7	20.3
$NaNO_2$	2.24	3.2	14.3
Na_2CO_3	0.42	0.6	4.1
Organic[a]	0.21	0.3	7.4
H_2O			31.7
Total			**100.0**

[a] Added as Na_3HEDTA

4.3.1.2 SY1-SIM-91B

Purpose: Previously used for experiments requiring homogeneous solution.

Preparation: With the exception of NaOH, concentrations are the same as the feed solution used to prepare -91A. Refer to preparation guidelines under SY1-SIM-91A.

Table 4.4. SY1-SIM-91B Component Concentrations /Composition

Component	Concentration (M)	Wt%
NaOH	2.00	6.4
$NaAl(OH)_4$	1.54	14.2
$NaNO_3$	2.59	17.7
$NaNO_2$	2.24	12.4
Na_2CO_3	0.42	3.6
Organic[a]	0.21	6.4
H_2O		39.4
Total		**100.0**

[a] Added as HEDTA.

4.3.1.3 SY1-SIM-91C

Purpose: Homogeneous solution used to study gas generation.

Gas generation work performed at ANL focused on evaluating radiolytic yield (G) values and mechanisms for generating gases within SY-101 waste. Homogeneous solutions were required to avoid the complications of solids interfering with gas release from solution. Measuring gas release was used to quantify radiolytic and radiolytically-induced generation of gases

Differences between this simulant and -91B are few: the sodium aluminate concentration is approximately half that in -91B, and no sodium carbonate is added to this simulant. A typical formulation involved sequential addition of each ingredient at room temperature. Organics are added at various levels as required. Care must be taken to add the sodium aluminate after adding sodium hydroxide to prevent precipitation of aluminum hydroxide.

Preparation: Refer to preparation guidelines under SY1-SIM-91A.

Table 4.5. SY1-SIM-91C Component Concentrations /Composition

Component	Concentration (M)	Wt%
NaOH	2.3	8.6
$NaAlO_2$	0.86	9.2
$NaNO_3$	2.8	22.2
$NaNO_2$	2.2	14.2
H_2O		45.8
Total		**100.0**

4.3.1.4 SY1-SIM-92A

Purpose: Chemical simulant attempting to match inorganic components and concentrations present in actual waste (Strachan and Schulz, 1993).

Based on Window C core sampling and analysis (Herting et al., 1992a), this simulant contains all the major inorganic components plus many of the minor constituents at chemically significant levels. When this simulant was developed, the inorganic components were reasonably well understood; however, the same could not be said about the organic components.

Preparation: This simulant is made by adding each ingredient in the order given in Table 4.6 and by adding one organic component at approximately the TOC concentration of actual waste. First, the required amount of water (except what was needed to dissolve transition metal salts) is added to the mixing container. Transition metal salts are dissolved in a minimal amount of water before adding them to the formulation. Vigorously and continuously mix the ingredients by mechanical stirring. Batches should be stirred at room temperature for several days prior to use. Use of glass containers and all glass surfaces should be avoided.

Table 4.6. SY1-SIM-92A Component Concentrations/Composition

Component	grams (g)	Concentration (M)	Wt%
$Na_3C_6H_5O_7 \cdot 2H_2O$ (citrate)[a]	99.99	0.340	4.99
NaCl	30.74	0.526	1.97
$Na_3PO_4 \cdot 12H_2O$	68.04	0.179	4.36
$NaAlO_2.0.21NaOH \cdot 1.33H_2O$	235.75	2.05	15.1
$NaNO_2$	272.55	3.95	17.45
$NaNO_3$	186.98	2.20	11.97
Na_2CO_3	42.4	0.400	2.71
NaF	4.20	0.100	0.27
NaOH	98.00	2.45	6.28
$Cr(NO_3)_3 \cdot 9H_2O$	42.06	0.105	2.69
$Cu(NO_3)_2 \cdot 2.5H_2O$	0.05	0.00021	0.003
$Fe(NO_3)_3 \cdot 9H_2O$	2.99	0.0074	0.19
$Ni(NO_3)_2 \cdot 6H_2O$	0.61	0.0021	0.04
Na_2SO_4	4.55	0.032	0.29
$CaCl_2$	0.92	0.0083	0.06
KCl	10.89	0.146	0.69
H_2O	483.00		30.5
Total	1583.71		100

[a] Na_4EDTA
Na_3HEDTA
[b] Density = 1.58g/mL

4.3.1.5 SY1-SIM-93B

Purpose: Homogeneous waste simulant developed for round-robin type testing among research groups.

A homogeneous waste was needed to ensure each site had identical simulants that could be simply prepared and reproduced. Eliminating the solid phase greatly simplifies this task; therefore, this simulant contains only the major inorganic components found in SY-101, but at lower concentrations than in the actual waste.

This simulant contains carbonate, and nitrate and nitrite concentrations are close to Window C and E analyses. This simulant differs from earlier simulants mostly in the replacement of sodium aluminate with aluminum nitrate [$Al(NO_3)_3$]. The relative ease of dissolution and the ability to procure a certified grade of aluminum nitrate made this source of aluminum advantageous compared with sodium aluminate. Large quantities of sodium aluminate tend to be sold as technical grade and have to be analyzed prior to use.

Preparation: The $Al(NO_3)_3$ is added after adding NaOH to prevent precipitation of aluminum hydroxide.

Table 4.7. SY1-SIM-93B Component Concentrations/Composition

Component	Concentration (M)	Wt%
Na_3HEDTA	0.21	6.04
$Al(NO_3)_3\ 9H_2O$	0.43	12.49
$NaNO_2$	2.0	10.69
$NaNO_3$	0.4	2.63
Na_2CO_3	0.2	1.64
NaOH	3.4	10.53
H_2O		55.98
Total		**100.0**

4.3.1.6 SY1-SIM-94A and SY1-SIM-94B

Purpose: Previously used in waste aging studies.

Simulant SY1-SIM-94A was prepared by adding trace noble and transition metals to the base SY1-SIM-93A simulant composition. This simulant was replaced by a modified composition designated SY1-SIM-94B.

Table 4.8. SY1-SIM-94B Component Concentrations/Composition

Component	Concentration (M)	Wt%
Na_4EDTA	0.1	2.24
Hexadecanoic acid	0.1	1.43
$Na_3Citrate \cdot H_2O$	0.092	1.59
Tributyl phosphate	0.1	1.57
Dibutyl phosphate	0.1	1.24
Hexone	0.1	1.0
NPH	0.1	1.0
$Na_3PO_4 \cdot 12H_2O$	0.1078	2.41
$NaNO_2$	3.6517	14.83
$NaNO_3$	2.4563	12.29
Na_2CO_3	0.8399	5.24
Na_2SO_4	0.0666	0.56
NaCl	0.3555	1.22
NaF	0.0253	0.06
$Ce(NO_3)_3\ 6H_2O$	0.0031	0.08
$Ca(NO_3)_2\ 4H_2O$	0.0092	0.13
KNO_3	0.1334	0.79
$ZnCl_2$	0.0005	0.004

Component	Concentration (M)	Wt%
$CsNO_3$	0.0002	0.002
$Sr(NO_3)_2$	0.00001	0.0002
NaOH	2.35	5.53
$Cr(NO_3)_3\ 9H_2O$	0.1262	2.97
$Fe(NO_3)_3\ 9H_2O$	0.008	0.19
$Ni(NO_3)_2\ 6H_2O$	0.0041	0.07
$RuCl_4\ 5H_2O$	0.0001	0.002
$Rh(NO_3)_3 \cdot H_2O$	0.0001	0.002
$Mn(NO_3)_2$	0.01	0.11
$Pb(NO_3)_2$	0.01	0.19
Zr Citrate	0.008	0.13
$Pd(NO_3)_2$	0.0001	0.001
$NaAlO_2\ 021NaOH \cdot 1.33H_2O$	1.9098	12.93
H_2O		30.58
Total		**100.4**

References Cited in Section 4.3.1:

Delegard, C. 1980. *Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241 SY-101*, RHO-LD-124, Rockwell International, Richland, Washington.

Herting, D. L., D. B. Bechtold, B. A. Crawford, T. L. Welsh, and L. Jensen. 1992a. *Laboratory Characterization of Samples Taken in May 1991 from Hanford Waste Tank 241-SY-101*, WHC-SD-WM-DTR-024, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Herting, D. L., D. B. Bechtold, B. E. Hey, B. D. Keele, L. Jensen, and T. L. Welsh. 1992b. *Laboratory Characterization of Samples Taken in December 1991 (Window E) from Hanford Waste Tank 241-SY-101*, WHC-SD-WM-DTR-026, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Orth, R. J., A. J. Schmidt, M. R. Elmore, T. R. Hard, G. G. Neuenschwander, S. R. Gano, R. W. Lehmann, J. A. Momont. 1995a. *Removal of Strontium and Transuranics from Hanford Waste via Hydrothermal Processing – FY 1994/95 Test Results*, PNL-10765, Pacific Northwest Laboratory, Richland, Washington.

Orth, R. J., A. H. Zacher, A. J. Schmidt, M. R. Elmore, K. R. Elliott, G. G. Neuenschwander, S. R. Gano. 1995b. *Removal of Strontium and Transuranics from Hanford Tank Waste via Addition of Metal Cations and Chemical Oxidant – FY 1995 Test Results*, PNL-10766, Pacific Northwest Laboratory, Richland, Washington.

Reynolds, D. A. 1992. *Window C Results and Interpretation,* WHC-EP-0589, Westinghouse Hanford Company, Richland, Washington.

Strachan, D. M., and W. W. Schulz. 1993. *Minutes of the Tank Waste Science Panel Meeting January 12-13, 1993*, PNL-8845, Pacific Northwest Laboratory, Richland, Washington.

4.3.2 Complex Concentrate SY-101 (SY1-SIM-93A), 3:1 Dilution

Reference : Hohl, T. M. 1993. ***Synthetic Waste Formulations for Representing Hanford Tank Waste*, WHC-SD-WM-TI-549, Rev. 0, Westinghouse Hanford Company, Richland, Washington.**

Purpose: **TWRS benchmark simulant for evaluating equipment and processes.**

This simulant was developed by WHC for the TWRS program as a benchmark simulant so laboratories within the program could baseline performance tests with the same formulation. Baseline performance tests included Sr and TRU removal tests via hydrothermal treatment and via metal cation/chemical oxidant addition (Orth et al., 1995a; Orth et al., 1995b).

This simulant is based on "Window E" analyses of core samples taken during December 1991 (Herting, 1992b). Cesium and strontium concentrations are based on ^{137}Cs and ^{90}Sr analyzed concentrations adjusted to include their common isotopes, ^{135}Cs, ^{133}Cs, and ^{88}Sr. Based on ORIGEN2 model data and 35 years of decay, the ^{137}Cs and ^{90}Sr concentrations were multiplied by factors of 4.01 and 2.46, respectively, to establish the total cesium and strontium in the waste.

A Window E-based formulation developed by Delegard (1993) was modified to include cesium and strontium nitrates and EDTA in its sodium salt form as the source of TOC. Delegard's formulation also was modified by diluting the simulant with three parts water by volume (the accepted estimate of the dilution ratio for this waste after retrieval). The diluted EDTA simulant (SY1-SIM-93A) is the baseline composition for testing; other organic sodium salts, e.g., HEDTA, citrate, oxalate, acetate, and formate, may be substituted for EDTA in tests for other purposes.

Table 4.9. Tank 241-SY-101 Waste Compositions

Component	SY-101[a] wt%	SY-101[b] wt%
TOC	1.58	1.53
Na	20.5	20.7
Al	3.5	3.2
Cr	0.37	0.41
Fe	0.03	0.03
Ni	0.01	0.02
Ca	0.02	0.02
K	0.37	0.03
Cl^-	1.5	0.79
PO_4^{3-}	1.1	0.64
NO_2^-	11.5	10.5
NO_3^-	10.0	11.7
CO_3^{2-}	1.6	3.15
F^-	0.1	0.03
OH^-	3.1	2.47
SO_4^{2-}	0.19	0.4
H_2O	38.0	35.5

Component	SY-101[a] wt%	SY-101[b] wt%
Total	**100.9**	**91.1**

[a] Calculated from Herting et al. (1992a) and Reynolds (1992).

[b] **Calculated from Herting et al. (1992b).**

Preparation: The formulation presented below is for 3.8L of diluted 101-SY simulant (based on 1.0L of undiluted simulant). For larger quantities, refer to Appendix A of Hole 1993.

1. **Tare a 4L stainless steel or plastic beaker with a large Teflon-covered stir bar.**

2. **Add 1000mL H_20 to the beaker and begin stirring.**

3. **Add 156.55g of $NaAlO_2$ in the form of a commercially available solution and stir. Determine how much NaOH was added to the commercial solution, and while stirring, slowly add additional NaOH to bring the total NaOH added to 110.16g. (Caution: Addition of NaOH will cause the solution to heat up).**

4. **In a separate container, add 200 mL H_20. Then, with stirring, slowly add the following metal salts in the order shown:**

50.50g	**$Cr(NO_3)_3 \cdot 9H_2O$**
2.17g	**$Ca(NO_3)_2 \cdot 4H_2O$**
3.23g	**$Fe(NO_3)_3 \cdot 9H_2O$**
13.49g	**KNO_3**
1.19g	**$Ni(NO_3)_2 \cdot 6H_2O$**
0.068g	**$ZnCl_2$**
0.0331g	**$CsNO_3$**
0.0023g	**$Sr(NO_3)_2$**

When the salts are dissolved, slowly add the metal salt solution to the $NaAlO_2$/NaOH solution. (Caution: the heat of neutralization causes the solution to heat up).

5. **While stirring, slowly add the following salts to the solution in the order shown:**

208.77g	**$NaNO_3$**
251.95g	**$NaNO_2$**
89.02g	**$Na2CO_3$**
40.98g	**$Na_3PO_4 \cdot 12H_2O$**
9.46g	**Na_2SO_4**
20.78g	**NaCl**
1.06g	**NaF**

While stirring, add one of the following organic compounds, depending on the test to be performed:

84.83g	**tetrasodium EDTA (baseline)**	**$Na_4C_{10}H_{12}N_2O_8 \cdot 2H_2O$ (MW=415.20)**
77.50g	**trisodium HEDTA**	**$Na_3C_{10}H_{15}N_2O_7 \cdot 2H_2O$ (MW=380.24)**
99.90g	**trisodium citrate**	**$Na_3C_6H_5O_7 \cdot 2H_2O$ (MW=294.10)**
136.55g	**disodium oxalate**	**$Na_2C_2O_4$ (MW=134.00)**
83.60g	**sodium acetate**	**$NaC_2H_3O_2$ (MW=82.03)**
138.61g	**sodium formate**	**$NaCHO_2$ (MW=68.01)**

6. While stirring, add H_2O to aid dissolution described in Step 6 until 4600g total chemical weight has been attained. This amount is based on the assumption that the density of undiluted simulant is 1.60 g/mL and the dilution factor is 3 parts water to 1 part waste. With these assumptions, a liter of waste would have a mass of 1600g and 3 liters of water would have a mass of 3000g. The simulant may be stored at ambient temperature in the beaker or transferred to polyetheylene, polypropylene, or polyvinyl chloride (PVC) bottles. Use the stirrer or agitator to homogenize samples before and during transfer.

Table 4.10. Composition of SY1-SIM-93A

Component[a]	Weight percent undiluted[b]	Weight percent SY1-SIM-93A	Concentration (M) SY-SIM-93A
Na	20.7	7.05	3.69
Al	3.2	1.12	0.50
Cr[c]	0.41	0.14	0.033
Ca	0.023	0.0080	0.0024
Fe	0.028	0.0097	0.0021
K	0.326	0.11	0.035
Ni	0.015	0.0052	0.0011
Zn	0.002	0.00071	0.00013
Cs	0.00145[d]	0.00049	0.000044
Sr	0.000058[d]	0.000021	0.0000029
NO_3	11.7	4.07	0.79
NO_2	10.5	3.65	0.96
OH[e]	2.47	1.02	0.72
TIC[f]	0.63	0.22	0.22
PO_4	0.64	0.22	0.028
SO_4	0.40	0.14	0.017
Cl	0.79	0.27	0.093
F	0.030	0.010	0.0067
TOC[f]	1.53	0.53	0.53
H_2O	35.5	78.46	--

[a] Non-sodium metals added as nitrate salts (except $ZnCl_2$). Anions added as sodium salts.
[b] Based on information in WHC-SD-WM-DTR-026, Rev. 0, Table 5-4.
[c] Cr(VI) is small compared to total Cr and is not added.
[d] Concentrations of Cs and Sr are based on data from WHC-SD-WM-DTR-026, Rev. 0, Tables 5-7 and 5-8. These concentrations were adjusted to add in the more stable forms of these two elements. Based on ORIGEN2 model data and 35 years of decay, the ^{137}Cs and ^{90}Sr concentrations were multiplied by factors of 4.01 and 2.46, respectively to arrive at total Cs and Sr.
[e] To neutralize acidic hydrolyzable metal salts of Cr, Ca, Fe, Ni, Zn, Cs and Sr: 0.443M "extra" NaOH added per liter of undiluted simulant.
[f] TIC, TOC wt% reported as C. Carbonate is used for TIC. TOC is made up using EDTA, the baseline organic.

Table 4.11. Physical and Chemical Properties of SY1-SIM-93A

Property		Acceptable Range
Density (g/mL)		1.20 ± 0.03, at 20°±1°
Moisture (wt%)		76.0 ± 4.0
OH^-		1.02 ± 0.2
TOC (wt%)		0.53± 0.2
ICP	Na (wt%)	7.05 ± 0.70
	Al (wt%)	1.12 ± 0.11
	Cr (wt%)	0.14 ± 0.014
	Ca (wt%)	0.008 ± 0.0008
	Fe (wt%)	0.010 ± 0.0010
	K (wt%)	0.11 ± 0.011
	Ni (wt%)	0.0052 ± 0.0005
	Zn (wt%)	0.00071 ± 0.00007
	Sr (wt%)	0.000021 ± 0.000002
Cs (wt%)		0.00049 ± 0.00007
nitrate by IC (wt%)		4.07 ± 0.41
nitrite (wt%)		3.65 ± 0.37

References Cited in Section 4.3.2:

Delegard, C. H. 1993. *Test Plan for Ozone Oxidation of 241-SY-101 Waste Materials*, WHC-SD-WM-TP-156, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Herting, D. L., D. B. Bechtold, B. A. Crawford, T. L. Welsh, and L. Jensen. 1992a. *Laboratory Characterization of Samples Taken in May 1991 from Hanford Waste Tank 241-SY-101*, WHC-SD-WM-DTR-024, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Herting, D. L., D. B. Bechtold, B. E. Hey, B. D. Keele, L. Jensen, and T. L. Welsh. 1992b. *Laboratory Characterization of Samples Taken in December 1991 (Window E) from Hanford Waste Tank 241-SY-101*, WHC-SD-WM-DTR-026, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Orth, R. J., A. J. Schmidt, M. R. Elmore, T. R. Hard, G. G. Neuenschwander, S. R. Gano, R. W. Lehmann, J. A. Momont. 1995a. *Removal of Strontium and Transuranics from Hanford Waste via Hydrothermal Processing – FY 1994/95 Test Results*, PNL-10765, Pacific Northwest Laboratory, Richland, Washington.

Orth, R. J., A. H. Zacher, A. J. Schmidt, M. R. Elmore, K. R. Elliott, G. G. Neuenschwander, S. R. Gano. 1995b. *Removal of Strontium and Transuranics from Hanford Tank Waste via Addition of Metal Cations and Chemical Oxidant – FY 1995 Test Results*, PNL-10766, Pacific Northwest Laboratory, Richland, Washington.

Reynolds, D. A. 1992. *Window C Results and Interpretation,* WHC-EP-0589, Westinghouse Hanford Company, Richland, Washington.

4.3.3 Complex Concentrate SY-101 Diluted and Treated Solutions

Reference: Marsh, S. F., Z. V. Svitra, S. M. Bowen. 1995. *Effects of Soluble Organic Complexants and Their Degradation Products on the Removal of Selected Radionuclides from High-Level Waste, Part II: Distributions of Sr, Cs, Tc, and Am onto 32 Absorbers from Four Variations of Hanford Tank 101-SY Simulant Solution*, Los Alamos National Laboratory, Los Alamos, New Mexico.

Purpose: Used for measuring sorption in the presence of organic complexants and their degradation products.

This simulant was used at LANL to measure sorption (distribution coefficients, Kd) of Sr, Cs, Tc, and Am onto 32 absorbers in the presence of organic complexants and their degradation products. These studies used four variations of 101-SY simulated solution: 1) 3:1 dilution with EDTA; 2) 3:1 dilution with EDTA with γ-irradiation to 34Mrads; 3) unirradiated simulant after treatment with a hydrothermal organic destruction process; and 4) irradiated simulant after treatment with a hydrothermal organic destruction process. Because gamma spectrometry was used to measure Kd values, appropriate quantities of radiotracers for strontium, cesium, technetium, and americium were added to each simulant.

Preparation:

<u>Unirradiated/untreated</u>
Follow procedure for SY1-SIM-93A (Refer to 4.3.2). Degradation of the initial EDTA into other organic compounds is to be expected if there are many months between simulant preparation and experimental testing.

<u>Irradiated/untreated</u>
γ-irradiate SY1-SIM-93A while exposed to air, at 1.35 Mrads/h to a total of 34Mrads with ^{60}Co. Irradiation is known to degrade most organic compounds into simpler compounds and CO_2, which forms carbonate in alkaline solutions. Moreover, the solution heating that occurs during the γ -irradiation also may contribute to organic degradation.

<u>Unirradiated/hydrothermal-treated</u>
SY1-SIM-93A treated with hydrothermal organic-destruction processing. The small-scale hydrothermal unit used to process the solution in the LANL studies consisted of a 5-ft reactor that operated at 450ºC and 15,000 psi. The typical residence time of solution passing through the reactor was approximately 25 seconds.

<u>Irradiated/hydrothermal-treated</u>
Irradiated SY1-SIM-93A treated with hydrothermal organic-destruction processing. Each simulant solution is passed through an Acrodisc™ LC13 PVDF 0.45-μm filter to remove any insoluble materials, and the four radiotracers are then added. The simulant and radiotracers are stirred thoroughly and left undisturbed for at least one week to allow adequate time for soluble complexes or insoluble compounds to form. The variations of the simulant solution differ significantly in appearance—the unirradiated solution appears green; the γ-irradiated portion appears more yellow, and hydrothermal-treated solutions are bright yellow.

Table 4.12. Composition of Four Variations of SY-101 Simulant

	Concentration (M)			
Constituent	Unirradiated/ untreated	Irradiated/ untreated	Unirradiated/ hydrothermal	Irradiated/ hydrothermal
Na	3.45	3.82	3.85	3.69
K	0.035	0.035	0.041	0.037
Rb	5E-07	3E-07	5E-07	4E-07
Cs	9E-05	9.8E-05	9.8E-05	9.8E-05
Al	0.37	0.48	0.48	0.37
Ca	0.001	0.001	0.001	0.001
Cr	0.0062	0.0035	0.0083	0.0042
Fe	2.7E-04	1.0E-04	4.5E-05	3.8E-05
Sr	3.1E-06	1.5E-06	7E-08	1E-07
F	--	--	--	--
Cl	0.096	0.091	0.089	0.091
NO_3	0.67	0.67	0.55	0.54
NO_2	0.89	1.03	0.48	0.59
PO_4	0.027	0.028	0.023	0.023
SO_4	0.016	0.016	0.015	0.015
CO_3	1.64	1.63	2.03	2.18
oxalate	<DL[a]	0.005	<DL[a]	<DL[a]
TOC	0.71	0.59	0.13	0.16
pH	13.7	13.7	13.6	13.5

Radiotracer	**γ-Energy (MeV)**	**Estimated Concentrations**
^{85}Sr	0.514	3 μg/L
^{137}Cs	0.662	6 μg/L
^{95m}Tc	0.204	2 pg/L
^{241}Am	0.0595	3 μg/L to 30 μg/L

[a] Less than detection limit

4.3.4 Complex Concentrate SY-101 Solution (5M Na)

Reference: Not available

Purpose: Batch distribution and column experiments.

This simulant represents a complex concentrate supernatant diluted to 5M Na. The composition approximates diluted waste from Tank 241-SY-101.

Preparation: Add components in the order listed below while continuously stirring. For batch distributions and column experiments, spike the final solution with 1 μL ^{137}Cs tracer per liter, and stir for four hours. This simulant should be soluble at room temperature.

Table 4.13. SY-101 5M Na Solution

Component	FW,g	M	g/L	g/4.0 L
H_2O			400 mL	1600 mL
$Ni(NO_3)_2\cdot 6H_2O$	290.80	2.49E-04	0.07	0.289
$Ca(NO_3)_2\cdot 4H_2O$	236.16	4.20E-03	0.99	3.967
$Zn(NO_3)_2\cdot 6H_2O$	297.50	5.00E-04	0.15	0.595
MoO_3	143.94	4.20E-04	0.06	0.242
$Fe(NO_3)_3\cdot 9H_2O$	404.02	1.96E-04	0.08	0.317
$CsNO_3$	194.92	4.19E-05	8.18E-03	3.27E-02
$RbNO_3$	147.47	4.20E-06	6.19E-04	2.48E-03
$Sr(NO_3)_2$	211.63	2.86E-07	6.06E-05	2.42E-04
Na_4EDTA	380.20	5.00E-03	1.90	7.604
$Na_3HEDTA\cdot 2H_2O$	344.20	3.75E-03	1.29	5.163
Na_3ED3A	300.10	3.75E-03	1.13	4.502
Citric acid$\cdot H_2O$	210.16	5.00E-03	1.05	4.203
Nitrilotriacetate (Na_3NTA)	257.10	2.50E-04	0.06	0.257
Iminodiacetic acid (IDA)	133.10	3.05E-02	4.06	16.238
Sodium gluconate	218.14	1.25E-02	2.73	10.907
Na_2SO_4	142.05	4.75E-03	0.67	2.699
$Na_2HOP_4\cdot 7H_2O$	268.07	2.04E-02	5.46	21.848
$NaOH$	40.00	3.78E+00	151.13	604.507
$NaNO_3$	85.00	0.00E+00	0.00	0.0000
KF	58.10	3.38E-02	1.96	7.844
$Al(NO_3)_3\cdot 9H_2O$	375.15	4.15E-01	155.69	622.749
Na_2CO_3	105.99	3.75E-02	3.97	15.899
NaF	41.99	5.80E-02	2.44	9.742
$NaNO_2$	69.00	1.09E+00	75.04	300.150
H_2O (up to volume)				

Table 4.14. SY-101 Simulant Composition Compared with Actual SY-101 Compositions

	Concentration (M)		
Species, Total	Simulant SY-101	Actual SY-101	Diluted w/ 2 M NaOH
Na	5.05E+00	1.23E+01	5.00E+00
K	3.38E-02	1.35E-01	3.38E-02
Rb	4.20E-06	NA	4.20E-06
Cs	4.19E-05	1.68E-04	4.19E-05
Ca	4.20E-03	1.68E-02	4.20E-03
Sr	2.86E-07	1.15E-06	2.86E-07
Al	4.15E-01	1.66E+00	4.15E-01
Ni	2.49E-04	9.95E-04	2.49E-04
Fe	1.96E-04	7.84E-04	1.96E-04
Mo	4.20E-04	1.68E-03	4.20E-04
Zn	5.00E-04	2.00E-03	5.00E-04
CO_3	3.75E-02	1.50E-01	3.75E-02
F	9.18E-02	3.67E-01	9.18E-02
NO_2	1.09E+00	4.35E+00	1.09E+00
NO_3	1.29E+00	3.79E+00	9.48E-01
OH (added)	3.78E+00	NA	NA
OH (free)	2.11E+00	2.42E+00	2.11E+00
Theoretical pH	1.47E+01	1.49E+01	1.43E+01
SO_4	4.75E-03	1.90E-02	4.75E-03
PO_4	2.04E-02	8.15E-02	2.04E-02
TOC (g/L)	3.42E+00	1.37E+01	3.42E+00
Na/Cs Ratio:	1.20E+05	7.33E+04	1.19E+05
K/Cs Ratio:	8.05E+02	8.05E+02	8.05E+02
Na/Sr Ratio:	1.76E+07	1.07E+07	1.75E+07
K/Sr Ratio:	1.18E+05	1.18E+05	1.18E+05

4.3.5 Complex Concentrate AN-102 Stock Solution (10M Na)

Reference: Bray, L. A., K. J. Carson, R. J. Elovich, D. E. Kurath. 1992. *Equilibrium Data for Cesium Ion Exchange of Hanford CC and NCAW Tank Waste*, TWRSPP-92-020, Pacific Northwest Laboratory, Richland, Washington.

Kurath, D. E., L. A. Bray, K. P. Brooks, G. N. Brown, S. A. Bryan, C. D. Carlson, K. J. Carson, J. R. DesChane, R. J. Elovich, A. Y. Kim. 1994. *Experimental Data and Analysis to Support the Design of an Ion Exchange Process for the Treatment of Hanford Tank Waste Supernatant Liquids*, TWRSPP-94-094, Pacific Northwest Laboratory, Richland, Washington.

Purpose: High sodium waste containing organic complexants for ion-exchange studies.

Preparation: Add components in the order listed in Table 4.15 while continuously stirring. This simulant should be soluble at room temperature. For batch distribution and column experiments, spike the final solution with 1μL ^{137}Cs tracer per liter, and stir for four hours.

Table 4.15. CC Stock Solution

Component	FW, g	M	g/L
$NaNO_3$	85	2.74	232.9
Na_2SO_4	142.05	0.1	14.2
KNO_3	101.11	0.05	5.0
$Na_2CO_3 \cdot H_2O$	124.0	0.64	79.4
$NaNO_2$	69.0	1.5	103.5
$Na_2HPO_4 \cdot 7H_2O$	268.07	0.03	8.0
$Al(NO_3)_3 \cdot 9H_2O$	375.15	0.5	188
$Ca(NO_3)_2 \cdot 4H_2O$	236.16	0.02	4.7
NaF	42.0	0.15	6.3
NaCl	58.45	0.1	5.85
NaOH (0.5M free)	40.0	3.46	138.5
$Fe(NO_3)_3 \cdot 9H_2O$	404.02	0.06	24.2
$La(NO_3)_3 \cdot 6H_2O$	371.0	0.001	0.37
$Mg(NO_3)_2 \cdot 6H_2O$	256.4	0.01	2.6
$Mn(NO_3)_2$, 50%	8.64M	0.02	2.3mL
MoO_3	169.43	0.005	0.85
$Ni(NO_3)_2 \cdot 6H_2O$	290.8	0.01	2.9
SiO_2	60.08	0.005	0.3
$Sr(NO_3)_2$	211.63	0.0007	0.15
$Zn(NO_3)_2 \cdot XH_2O$	297.5	0.002	0.59
$ZrO(NO_3)_2 \cdot 2H_2O$	267	0.002	0.53
Na_4EDTA	292.24	0.03	8.8

Component	FW, g	M	g/L
Citric Acid	210.14	0.064	13.5
$Na_3HEDTA\ 2H_2O$	344	0.038	13.1
Na_3NTA	191.1	0.0074	1.41
Na Gluconate	218	0.30	65.4
Iminodiacetic	133.1	0.23	30.6
The stock solution is spiked with non radioactive cesium (^{133}Cs) so that the Na/Cs mole ratio ranges from 500 to 50000. Trace amounts of ^{137}Cs was added for analytical purposes.			

Table 4.16. Composition for CC Stock Solution

Component	M
Al	0.5
Ca	0.02
Cs	a
Fe	0.06
K	0.05
La	0.001
Mg	0.01
Mn	0.02
Mo	0.005
Na	10.00
Ni	0.01
Si	0.005
Sr	0.0007
Zn	0.002
Zr	0.002
CO_3	0.64
F	0.15
Cl	0.10
NO_2	1.50
NO_3	4.62
PO_4	0.03
OH (free)	0.5
TOC	46 g/L
[a] Na/Cs ratios 500, 5000, 50000	

4.3.6 Complex Concentrate AN-102 Solution (5M Na)

Reference: Not available

Purpose: Ion exchange batch distribution and column experiments.

This simulant represents a complex concentrate supernatant diluted to 5M Na. The composition approximates Tank 241-AN-102.

Preparation: Add components in the order listed in Table 4.17 while continuously stirring. This simulant should be soluble at room temperature. For batch distribution and column experiments, spike the final solution with 1μL ^{137}Cs tracer per liter, and stir for four hours.

Table 4.17. AN-102 5M Na Solution

Component	FW,g	M	g/L	g/4.0 L
H_2O			400 mL	1600 mL
$Mn(NO_3)_2$, 50%	8.46 M	6.57E-03	2.175 mL	8.70 mL
$La(NO_3)_3·6H_2O$	433.06	4.07E-04	0.18	0.705
MoO_3	143.94	3.20E-03	0.46	1.840
$Mg(NO_3)_2·6H_2O$	256.40	1.28E-04	0.03	0.131
$Ni(NO_3)_2·6H_2O$	290.80	2.30E-03	0.67	2.671
$Ca(NO_3)_2·4H_2O$	236.16	4.39E-03	1.04	4.150
$Zn(NO_3)_2·6H_2O$	297.50	1.51E-04	0.04	0.179
$ZrO(NO_3)_2·2H_2O$	267.28	6.18E-04	0.17	0.661
$Fe(NO_3)_3·9H_2O$	404.02	6.43E-04	0.26	1.039
$CsNO_3$	194.92	3.10E-05	6.04E-03	2.41E-02
$RbNO_3$	147.47	3.10E-06	4.57E-04	1.83E-03
$Sr(NO_3)_2$	211.63	1.77E-05	3.75E-03	1.50E-02
Na_4EDTA	380.20	1.12E-02	4.26	17.055
Na_3HEDTA·$2H_2O$	344.20	1.34E-02	4.61	18.439
Na_3ED3A	300.10	6.39E-03	1.92	7.674
Citric acid·H_2O	210.16	2.30E-02	4.83	19.335
Nitrilotriacetate (Na_3NTA)	257.10	2.62E-03	0.67	2.692
Iminodiacetic acid (IDA)	133.10	6.71E-02	8.94	35.747
Sodium Gluconate	218.14	6.96E-02	15.19	60.768
Na_2SO_4	142.05	4.07E-02	5.78	23.134
$Na_2HPO_4·7H_2O$	268.07	1.69E-02	4.53	18.114
NaOH	40.00	2.26E+00	90.37	361.499
$NaNO_3$	85.00	1.35E+00	114.75	459.000
KF	58.10	1.90E-02	1.10	4.407

Component	FW,g	M	g/L	g/4.0 L
$Al(NO_3)_3 \cdot 9H_2O$	375.15	1.92E-01	71.95	287.794
Na_2CO_3	105.99	3.00E-01	31.80	127.188
NaF	41.99	2.32E-02	0.97	3.893
$NaNO_2$	69.00	4.71E-01	32.53	130.114
H_2O (up to volume)				

Table 4.18. AN-102 Simulant Composition Compared with Actual AN-102 Compositions

	Concentration (M)		
Species, Total	Simulant AN-102	Actual AN-102	Diluted w/ 2 M NaOH
Na	5.00E+00	1.04E+01	5.00E+00
K	1.90E-02	5.31E-02	1.90E-02
Rb	3.10E-06	8.67E-06	3.10E-06
Cs	3.10E-05	8.67E-05	3.10E-05
Mg	1.28E-04	3.57E-04	1.28E-04
Ca	4.39E-03	1.23E-02	4.39E-03
Sr	1.77E-05	4.96E-05	1.77E-05
Al	1.92E-01	5.37E-01	1.92E-01
Fe	6.43E-04	1.80E-03	6.43E-04
La	4.07E-04	1.14E-03	4.07E-04
Mn	6.57E-03	1.84E-02	6.57E-03
Mo	3.20E-03	8.95E-03	3.20E-03
Ni	2.30E-03	6.43E-03	2.30E-03
Zn	1.51E-04	4.22E-04	1.51E-04
Zr	6.18E-04	1.73E-03	6.18E-04
CO_3	3.00E-01	8.40E-01	3.00E-01
F	4.21E-02	1.18E-01	4.21E-02
NO_2	4.71E-01	1.32E+00	4.71E-01
NO_3	1.96E+00	3.61E+00	1.29E+00
OH (added)	2.26E+00	NA	NA
OH (free)	1.36E+00	2.01E-01	1.36E+00
Theoretical pH	1.43E+01	1.33E+01	1.41E+01
SO_4	4.07E-02	1.14E-01	4.07E-02
PO_4	1.69E-02	4.73E-02	1.69E-02
TOC (g/L)	11.20E+01	3.37E+01	1.20E+01
Na/Cs Ratio:	1.62E+05	1.20E+05	1.61E+05
K/Cs Ratio:	6.12E+02	6.12E+02	6.12E+02
Na/Sr Ratio:	2.83E+05	2.10E+05	2.82E+05
K/Sr Ratio:	1.07E+03	1.07E+03	1.07E+03

Table 4.19. Composition of AN-102 Simulant Compared with Actual AN-102 Waste under Various Dilution Conditions

	Concentration (M)				
Species, Total	Simulant AN-102	Actual AN-102	Dilution w/ Water	Dilution w/1M NaOH	Dilution w/2M NaOH
Na_4EDTA	1.12E-02	3.14E-02	1.51E-02	1.34E-02	1.12E-02
Na_3HEDTA - 2 H_2O	1.34E-02	3.75E-02	1.80E-02	1.60E-02	1.34E-02
Na_3ED3A	6.39E-03	1.79E-02	8.61E-03	7.62E-03	6.39E-03
Citric acid - 1 H_2O	2.30E-02	6.44E-02	3.10E-02	2.74E-02	2.30E-02
Nitrilotriacetate	2.62E-03	7.33E-03	3.52E-03	3.12E-03	2.62E-03
Iminodiacetic acid	6.71E-02	1.88E-01	9.04E-02	8.00E-02	6.71E-02
Sodium Gluconate	6.96E-02	1.95E-01	9.38E-02	8.30E-02	6.96E-02
Na	5.00E+00	1.04E+01	5.00E+00	5.00E+00	5.00E+00
K	1.90E-02	5.31E-02	2.55E-02	2.26E-02	1.90E-02
Rb	3.10E-06	8.67E-06	4.17E-06	3.69E-06	3.10E-06
Cs	3.10E-05	8.67E-05	4.17E-05	3.69E-05	3.10E-05
Mg	1.28E-04	3.57E-04	1.72E-04	1.52E-04	1.28E-04
Ca	4.39E-03	1.23E-02	5.91E-03	5.23E-03	4.39E-03
Sr	1.77E-05	4.96E-05	2.38E-05	2.11E-05	1.77E-05
Al	1.92E-01	5.37E-01	2.58E-01	2.29E-01	1.92E-01
Fe	6.43E-04	1.80E-03	8.65E-04	7.66E-04	6.43E-04
La	4.07E-04	1.14E-03	5.48E-04	4.85E-04	4.07E-04
Mn	6.57E-03	1.84E-02	8.85E-03	7.83E-03	6.57E-03
Mo	3.20E-03	8.95E-03	4.30E-03	3.81E-03	3.20E-03
Ni	2.30E-03	6.43E-03	3.09E-03	2.74E-03	2.30E-03
Zn	1.51E-04	4.22E-04	2.03E-04	1.80E-04	1.51E-04
Zr	6.18E-04	1.73E-03	8.32E-04	7.36E-04	6.18E-04
CO_3	3.00E-01	8.40E-01	4.04E-01	3.57E-01	3.00E-01
F	4.21E-02	1.18E-01	5.67E-02	5.02E-02	4.21E-02
NO_2	4.71E-01	1.32E+00	6.35E-01	5.62E-01	4.71E-01
NO_3	1.29E+00	3.61E+00	1.74E+00	1.54E+00	1.29E+00
OH (added)	NA	NA	NA	NA	NA
OH (free)	1.36E+00	2.01E-01	9.66E-02	6.60E-01	1.36E+00
Theoretical pH	1.41E+01	1.33E+01	1.30E+01	1.38E+01	1.41E+01
SO_4	4.07E-02	1.14E-01	5.48E-02	4.85E-02	4.07E-02
PO_4	1.69E-02	4.73E-02	2.27E-02	2.01E-02	1.69E-02
TOC (g/L)	1.20E+01	3.37E+01	1.62E+01	1.43E+01	1.20E+01
Na/Cs Ratio:	1.61E+05	1.20E+05	1.20E+05	1.36E+05	1.61E+05
K/Cs Ratio:	6.12E+02	6.12E+02	6.12E+02	6.12E+02	6.12E+02
Na/Sr Ratio:	2.82E+05	2.10E+05	2.10E+05	2.37E+05	2.82E+05
K/Sr Ratio:	1.07E+03	1.07E+03	1.07E+03	1.07E+03	1.07E+03

4.3.7 Complex Concentrate AN-102 Diluted and Treated Solutions

Reference: Marsh, S. F., Z. V. Svitra, S. M. Bowen. 1995. *Effects of Soluble Organic Complexants and Their Degradation Products on the Removal of Selected Radionuclides from High-Level Waste. Part III: Distributions from Four Variations of a 3:1 Dilution of Hanford Complexant Concentrate (CC) Simulant Solution. Part IV: The Effects of Varying Dilution Ratios on the Distributions of Sr, Cs, Tc, Pu, and Am onto 12 Absorbers from Hanford Complexant Concentrate (CC) Simulant Solutions.* LA-13000, Los Alamos National Laboratory, Los Alamos, New Mexico.

Purpose: Batch distribution and column experiments

Studies performed at LANL measured the distribution of strontium, cesium, technetium, plutonium, and americium onto selected absorbers. These studies used four variations of generic CC simulant solution: 1) 3:1 dilution of CC simulant solution described above in 4.3.5; 2) 3:1 dilution with γ-irradiation to 34Mrads; 3) 3:1 unirradiated simulant after treatment with a hydrothermal organic destruction process; and 4) 3:1 irradiated simulant after treatment with a hydrothermal organic destruction process. Because gamma spectrometry was used to measure Kd values, appropriate quantities of radiotracers for strontium, cesium, technetium, plutonium, and americium were added to each simulant.

Preparation:

Unirradiated/untreated
Use 3:1 dilution of standard composition (refer to 4.3.5). Preparation procedures are the same as described for making SY1-SIM-93A (refer to 4.3.2). Degradation of the initial EDTA into other organic compounds is to be expected if there are many months between simulant preparation and experimental testing.

Irradiated/untreated
γ-irradiate 3:1 CC simulant while exposed to air, at 1.35 Mrads/h to a total of 34Mrads with ^{60}Co. Irradiation is known to degrade most organic compounds into simpler compounds and CO_2, which forms carbonate in alkaline solutions. Moreover, the solution heating that occurs during the γ -irradiation also may contribute to organic degradation.

Unirradiated/hydrothermal-treated
3:1 CC simulant treated with hydrothermal organic-destruction processing. The small-scale hydrothermal unit used to process the solution in the LANL studies consisted of a 5-ft reactor that operated at 450ºC and 15,000 psi. The typical residence time of solution passing through the reactor was approximately 25 seconds.

Irradiated/hydrothermal-treated
Irradiated 3:1 CC simulant treated with hydrothermal organic-destruction processing. Each simulant solution is passed through an Acrodisc™ LC13 PVDF 0.45-µm filter to remove any insoluble materials, and the five radiotracers are then added. The simulant and radiotracers are stirred thoroughly and left undisturbed for at least one week to allow adequate time for soluble complexes or insoluble compounds to form. The variations of the simulant solution differ significantly in appearance – the unirradiated solution appears light tan; the γ-irradiated portion appears darker, and hydrothermal-treated solutions are nearly colorless.

Table 4.20. Composition of Four Variations of Diluted CC Simulant Solutions

	Concentration (M)			
Constituent	Unirradiated/ untreated	Irradiated/ untreated	Unirradiated/ hydrothermal	Irradiated/ hydrothermal
Na	2.2	2.1	1.9	1.6
K	0.009	0.009	0.013	0.014
Rb	1.3E-05	1.2E-05	9E-06	1.0E-05
Cs	1.4E-04	1.3E-04	1.0E-04	1.3E-04
Al	0.16	0.16	0.024	0.012
Ca	0.002	0.002	0.0001	0.0001
Fe	0.003	0.005	6E-05	7E-05
Sr	1.3E-04	1.3E-04	3E-05	3E-05
Cl	0.04	0.012	0.012	0.013
NO_3	0.9	0.9	0.5	0.7
NO_2	0.3	0.3	0.1	0.1
PO_4	0.009	0.009	<DL[a]	<DL[a]
SO_4	0.006	0.007	0.003	0.003
CO_3	0.19	0.23	0.49	0.62
TOC	1.0	0.9	0.13	0.14
pH	13.2	13.2	11.9	12.1

Radiotracer	**γ-Energy (MeV)**	**Estimated Concentrations**
^{85}Sr	0.514	3 μg/L
^{137}Cs	0.662	6 μg/L
^{95m}Tc	0.204	2 pg/L
^{238}Pu	0.152	10 mg/L
^{241}Am	0.0595	30 μg/L

[a] Less than detection limit

4.3.8 Complex Concentrate AN-107 Solution (5M Na)

Reference: Not available

Purpose: For batch distributions and column experiments.

This simulant represents a complex concentrate supernatant diluted to 5M Na. The composition approximates Tank 241-AN-107.

Preparation: Add components in the order listed in Table 4.21 while continuously stirring. This simulant should be soluble at room temperature. For batch distribution and column experiments, spike the final solution with 1μL ^{137}Cs tracer per liter, and stir for four hours.

Table 4.21. AN-107 5M Na Solution

Component	FW,g	M	g/L	g/4.0 L
H_2O			400 mL	1600 mL
$Mn(NO_3)_2$, 50%	8.46 M	2.30E-03	2.175 mL	8.70 mL
$La(NO_3)_3 \cdot 6H_2O$	433.06	9.89E-05	0.04	0.171
MoO_3	143.94	2.22E-04	0.03	0.128
$Mg(NO_3)_2 \cdot 6H_2O$	256.40	3.71E-04	0.10	0.381
$Ni(NO_3)_2 \cdot 6H_2O$	290.80	3.14E-03	0.91	3.656
$Ca(NO_3)_2 \cdot 4H_2O$	236.16	6.18E-03	1.46	5.837
$Zn(NO_3)_2 \cdot 6H_2O$	297.50	2.23E-04	0.07	0.265
$ZrO(NO_3)_2 \cdot 2H_2O$	267.28	2.85E-04	0.08	0.305
$Fe(NO_3)_3 \cdot 9H_2O$	404.02	1.18E-02	4.78	19.104
$CsNO_3$	194.92	4.49E-05	8.76E-03	3.50E-02
$RbNO_3$	147.47	4.49E-06	6.63E-04	2.65E-03
$Sr(NO_3)_2$	211.63	2.11E-05	4.47E-03	1.79E-02
Na_4EDTA	380.20	1.12E-02	4.26	17.055
$Na_3HEDTA \cdot 2H_2O$	344.20	1.34E-02	4.61	18.439
Na_3ED3A	300.10	6.39E-03	1.92	7.674
Citric acid·H_2O	210.16	2.30E-02	4.83	19.335
Nitrilotriacetate (Na_3NTA)	257.10	2.62E-03	0.67	2.692
Iminodiacetic acid (IDA)	133.10	6.71E-02	8.94	35.747
Sodium Gluconate	218.14	7.14E-02	15.58	62.326
Na_2SO_4	142.05	2.26E-02	3.21	12.845
$Na_2HPO_4 \cdot 7H_2O$	268.07	8.32E-03	2.23	8.923
$NaOH$	40.00	1.74E+00	69.41	277.622
$NaNO_3$	85.00	1.75E+00	148.75	595.000
KF	58.10	1.57E-02	0.91	3.644
$Al(NO_3)_3 \cdot 9H_2O$	375.15	7.07E-02	26.53	106.114
Na_2CO_3	105.99	4.54E-01	48.07	192.296

Component	FW,g	M	g/L	g/4.0 L
NaF	41.99	6.36E-02	2.67	10.683
$NaNO_2$	69.00	2.96E-01	20.43	81.716
H_2O (up to volume)				

Table 4.22. AN-107 Simulant Composition Compared with Actual AN-107 Compositions

	Concentration (M)		
Species, Total	Simulant AN-107	Actual AN-107	Diluted w/ 2 M NaOH
Na	5.00E+00	1.01E+01	5.00E+00
K	1.57E-02	4.39E-02	1.57E-02
Rb	4.49E-06	1.26E-05	4.49E-06
Cs	4.49E-05	1.26E-04	4.49E-05
Mg	3.71E-04	1.04E-03	3.71E-04
Ca	6.18E-03	1.73E-02	6.18E-03
Sr	2.11E-05	5.92E-05	2.11E-05
Al	7.07E-02	1.98E-01	7.02E-02
Fe	1.18E-02	3.31E-02	1.18E-02
La	9.89-05	2.77E-04	9.89E-05
Mn	2.30E-03	6.44E-03	2.30E-03
Mo	2.22E-04	6.21E-04	2.22E-04
Ni	3.14E-03	8.80E-03	3.14E-03
Zn	2.23E-04	6.23E-04	2.23E-04
Zr	2.85E-04	7.98E-04	2.85E-04
CO_3	4.54E-01	1.27E+00	4.54E-01
F	7.93E-02	2.22E-01	7.39E-02
NO_2	2.96E-01	8.92E-01	2.96E-01
NO_3	2.02E+00	3.54E+00	1.26E+00
OH (added)	1.74E+00	NA	NA
OH (free)	1.30E+00	4.00E-02	1.30E+00
Theoretical pH	1.43E+01	1.26E+01	1.41E+01
SO_4	2.26E-02	6.33E-02	2.26E-02
PO_4	8.32E-03	2.33E-02	8.32E-03
TOC (g/L)	1.22E+01	4.43E+01	1.58E+01
Na/Cs Ratio:	1.11E+05	8.03E+0	1.11E+05
K/Cs Ratio:	3.49E+02	3.49E+02	3.49E+02
Na/Sr Ratio:	2.37E+05	1.71E+05	2.37E+05
K/Sr Ratio:	7.42E+02	7.42E+02	7.42E+02

4.3.9 Complex Concentrate SY-103 Solution (5M Na)

Reference: Not available

Purpose: Batch distribution and column experiments.

This simulant represents a complex concentrate supernatant diluted to 5M Na. The composition approximates Tank 241-SY-103.

Preparation: Add components in the order listed below while continuously stirring. For batch distributions and column experiments, spike the final solution with 1 μL ^{137}Cs tracer per liter, and stir for four hours. This simulant should be soluble at room temperature.

Table 4.23. SY-103 5M Na Solution

Component	FW,g	M	g/L	g/4.0 L
$Ni(NO_3)_2\cdot 6H_2O$	**290.80**	**3.95E-04**	**0.11**	**0.459**
$Ca(NO_3)_2\cdot 4H_2O$	**236.16**	**3.16E-03**	**0.75**	**2.983**
$Zn(NO_3)_2\cdot 6H_2O$	**297.50**	**6.32E-04**	**0.19**	**0.752**
MoO_3	**143.94**	**3.95E-04**	**0.06**	**0.227**
$Fe(NO_3)_3\cdot 9H_2O$	**404.02**	**2.48E-04**	**0.10**	**0.400**
$CsNO_3$	**194.92**	**5.30E-05**	**1.03E-02**	**4.13E-02**
$RbNO_3$	**147.47**	**5.30E-06**	**7.81E-04**	**3.13E-03**
$Sr(NO_3)_2$	**211.63**	**9.10E-07**	**1.93E-04**	**7.70E-04**
Na_4EDTA	380.20	9.47E-03	3.60	14.408
Na_3HEDTA_2 H_2O	344.20	6.32E-03	2.17	8.696
Na_3ED3A	300.10	6.32E-03	1.90	7.581
Citric acid_H_2O	210.16	1.58E-02	3.32	13.273
Nitrilotriacetate (Na_3NTA)	257.10	3.16E-04	0.08	0.325
Iminodiacetic acid (IDA)	133.10	2.53E-02	3.36	13.450
Sodium Gluconate	218.14	2.87E-02	6.27	25.075
Na_2SO_4	142.05	3.60E-02	5.11	20.455
Na_2HPO_4_7H_2O	268.07	9.47E-03	2.54	10.158
NaOH	40.00	3.68E+00	147.05	588.186
$NaNO_3$	85.00	8.00E-02	6.80	27.200
KF	58.10	2.84E-02	1.65	6.605
$Al(NO_3)_3$_9H_2O	375.15	4.74E-01	177.70	710.811
Na_2CO_3	105.99	2.08E-01	22.90	88.362
NaF	41.99	5.68E-02	2.39	9.547
$NaNO_2$	69.00	6.76E-01	46.63	186.518
H_2O (up to volume)				

Table 4.24. SY-103 Simulant Composition Compared with Actual SY-103 Compositions

	Concentration (*M*)		
Species, Total	SimulantSY-103	Actual SY-103	Diluted w/ 2M NaOH
Na	5.00E+00	1.15E+01	5.00E+00
K	2.84E-02	9.00E-02	2.84E-02
Rb	5.30E-06	NA	5.30E-06
Cs	5.30E-05	1.68E-04	5.30E-05
Ca	3.16E-03	1.00E-02	3.16E-03
Sr	9.10E-07	2.88E-06	9.10E-07
Al	4.74E-01	1.50E+00	4.74E-01
Ni	3.95E-04	1.25E-03	3.95E-04
Fe	2.48E-04	7.84E-04	2.48E-04
Mo	3.95E-04	1.25E-03	3.95E-04
Zn	6.32E-04	2.00E-03	6.32E-04
CO_3	2.08E-01	6.60E-01	2.08E-01
F	8.53E-02	2.70E-01	8.53E-02
NO_2	6.76E-01	2.14E+00	6.76E-01
NO_3	1.54E+00	3.61E+00	1.14E+00
OH (added)	3.68E+00	NA	NA
OH (Free)	1.77E+00	1.27E+00	1.77E+00
Theoretical pH	1.46E+01	1.41E+01	1.42E+01
SO_4	3.60E-02	1.14E-01	3.60E-02
PO_4	9.47E-03	3.00E-02	9.47E-03
TOC (g/L)	6.34E+00	2.01E+01	6.35E+00
Na/Cs Ratio:	9.43E+04	6.85E+04	9.44E+04
K/Cs Ratio:	5.36E+02	5.36E+02	5.36E+02
Na/Sr Ratio:	5.49E+06	3.99E+06	5.49E+06
K/Sr Ratio:	3.12E+04	3.12E+04	3.12E+04

4.3.10 Double Shell Slurry Feed (DSSF-7)

Reference: Carson, C. D., S. R. Adami, L. A. Bray, G. N. Brown, S. A. Bryan, K. J. Carson, J. R. DesChane, R. J. Elovich, M. R. Telander. 1994. *Supernatant Treatment Technology Development*, TWRSPP-94-006, Pacific Northwest Laboratory, Richland, Washington.

Kurath, D. E., L. A. Bray, K. P. Brooks, G. N. Brown, S. A. Bryan, C. D. Carlson, K. J. Carson, J. R. DesChane, R. J. Elovich, A. Y. Kim. 1994. *Experimental Data and Analysis to Support the Design of an Ion Exchange Process for the Treatment of Hanford Tank Waste Supernatant Liquids*, TWRSPP-94-094, Pacific Northwest Laboratory, Richland, Washington.

Purpose: Challenging simulant for ion-exchange studies.

This simulant is based on the analytical results from all of the DSS tank wastes and, but most closely simulates waste from 241-AW-101. It contains the highest Na/Cs ratio (10^5) and the lowest Na/K ratio found in DSS tanks. Because anticipated plant operations are at temperatures less than the 40ºC waste, the simulant is prepared at 50ºC and diluted with water to the extent that all of the compounds present remain in solution at slightly lower than room temperature.

Several difficulties that may be important to the overall cesium ion exchange removal process were encountered while formulating the DSSF simulants. These problems related to the aluminum solubility, the actual meaning of the OH^- analytical data, and the specific gravity of the DSSF solution. Initially, the hydroxide result from the tank analysis was used as the total hydroxide; this lead to the initial preparation of a simulant that had a pH of 13.75. Upon dilution, the pH dropped to a value where $Al(OH)_3$ (gibbsite) was formed. As a compromise, a second simulant was formulated with a higher hydroxide content.

Preparation: The simulant is prepared at 50ºC and diluted with water to the extent that all of the compounds present remain in solution at slightly lower than room temperature.

Table 4.25. Target Composition for DSSF-7

Component	M
Na	7.0
K	0.945
Cs	7.0E-05
Al	0.721
SO_4	0.008
OH^-(total), OH^-(free)	4.63, 1.75
CO_3	0.147
Cl	0.10
PO_4	0.014
NO_2	1.51
NO_3	3.52
Mole Ratio Na/Cs: 1.05E+05 Na/K: 7 Na/Al: 10	

4.3.11 DSSF Solution (DSSF-7) with Radiotracers

Reference: Marsh, S. F. Z. V. Svitra, S. M. Bowen. 1994. *Distributions of 15 Elements on 58 Absorbers from Simulated Hanford Double-Shell Slurry Feed (DSSF)*, LA-12863, Los Alamos National Laboratory, Los Alamos, New Mexico.

Purpose: Used to evaluate absorber materials for their ability to recover selected elements.

Preparation: DSSF-7 (refer to Table 4.26) is passed through a 0.45-μm filter to remove any suspended solids and then filtered again after adding radiotracers to remove any portion not truly in solution. Each portion of pre-contacted and post-contacted simulant solution is again passed through a 0.45-μm filter before γ-spectrometric assay.

Table 4.26. Composition of DSSF-7
Solution with Radiotracers

Constituent	Concentration (M)
Na	7.0
K	0.945
Cs	7.0E-05
Al	0.721
Cl	0.102
NO_3	3.52
NO_2	1.51
PO_4	0.014
SO_4	0.008
CO_3	0.147
OH^-(total), OH^-(free)	4.63, 1.75
pH	14.0

Radiotracer	**γ-Energy (MeV)**	**Est. Conc.**
^{241}Am	0.0595	30 μg/L
^{141}Ce	0.145	50 pg/L
^{237}U	0.208	20 mg/L
^{56}Ni	0.158	60 pg/L
^{95m}Tc	0.204	2 pg/L
^{51}Cr	0.320	0.3 μg/L
^{88}Zr	0.394	50 μg/L
^{85}Sr	0.514	3 μg/L
^{137}Cs	0.662	6 μg/L
^{54}Mn	0.835	3 μg/L
^{88}Y	0.898	50 μg/L
^{48}V	0.983	80 pg/L
^{59}Fe	1.099	20 μg/L
^{65}Zn	1.115	6 μg/L
^{60}Co	1.173	2 μg/L

4.3.12 Double Shell Slurry Feed A-101 Solution (5M Na)

Reference: Not available

Purpose: Previously used in salt-splitting studies.

This simulant represents a Double Shell Slurry Feed supernatant diluted to 5M Na. The composition approximates Tan 241-A-101.

Preparation: Weigh and tare feed container and fill with about 2/3 volume of distilled water. Add the components listed below in order while stirring. Add all components relatively quickly with the exception of KOH and NaOH. The components will cause the solution to heat up. Monitor the temperature so that it doesn't boil and splash. After adding the $Al(OH)_3$, heat the solution and maintain the temperature at 95ºC until solids dissolve. (No mention is made as to whether the solution is maintained hot or subsequently cooled).

Table 4.27. A-101 5M Na Solution

Component	FW,g	Molarity	g/L	g for 10L
$NaNO_3$	85.00	9.20E-01	78.20	782.000
KOH	56.11	3.70E-02	2.08	20.761
NaOH	40.00	1.56E+00	62.40	624.000
$Al(OH)_3$	78.00	4.23E-01	32.99	329.940
Na_2CO_3	105.99	6.50E-01	68.89	688.935
Na_2SO_4	142.05	1.30E-01	18.47	184.665
$Na_2HPO_4 \cdot 7H_2O$	268.07	2.20E-02	5.90	58.975
NaCl	58.45	5.60E-02	3.27	32.732
NaF	41.99	2.06E-02	0.86	8.650
EDTA	292.24	9.00E-03	2.630	26.302
Citric Acid	210.14	9.00E-03	1.891	18.913
Na_2oxalate	136.00	9.00E-03	1.224	12.240
$NaNO_2$	69.00	8.30E-01	57.27	572.700

Table 4.28. A-101 Simulant Composition Compared with Actual A-101 Composition (Diluted to 5M Na)

	Concentration (M)		
Species, Total	Simulant A-101	Actual A-101 Diluted	Target
Na^+	5.01E+00	5.01E+00	5.00E+00
K^+	3.70E-02	3.70E-02	3.70E-02
$Al(OH)^{4-}$	4.23E-01	4.23E-01	4.23E-01
SO_4^{2-}	1.30E-01	1.30E-01	1.30E-01
OH^-	1.60E+00	1.60E+00	
OH^- (free)	1.09E+00	1.09E+00	1.10E+00
Theoretical pH	1.41E+01	1.41E+01	1.41E+01
Cl^-	5.60E-02	5.60E-02	5.60E-02
CO_3^{2-}	6.50E-01	6.50E-01	6.50E-01
NO_2^-	8.30E-01	8.30E-01	8.30E-01
NO_3^-	9.20E-01	9.20E-01	9.20E-01
F^-	2.06E-02	2.06E-02	2.06E-02
PO_4^{3-}	2.20E-02	2.20E-02	2.20E-02
EDTA	9.00E-03	9.00E-03	
Citrate	9.00E-03	9.00E-03	
oxalate	9.00E-03	9.00E-03	8.60E-03
TOC (g/L)	1.94E+00	1.94E+00	1.97E+00

4.3.13 Double Shell Slurry Feed AW-101 Solution

Reference: Not available

Purpose: Previously used in salt-splitting studies.

This simulant represents a Double Shell Slurry Feed supernatant diluted to 5M Na. The composition approximates Tank 241-AW-101.

Preparation: Weigh and tare feed container and fill with about 2/3 volume of distilled water. Add the components listed below in order while stirring. Add all components relatively quickly with the exception of KOH and NaOH. These components will cause the solution to heat up; try not exceed temperature >70ºC if using a poly container.

Table 4.29. AW-101 5M Na Solution

Component	FW,g	Molarity	g/L	g for 10L
EDTA	292.24	3.70E-03	1.081	10.813
Citric Acid	210.14	3.70E-03	0.778	7.775
$Na_3HEDTA\cdot 2H_2O$	344.00	3.70E-03	1.273	12.728
Na_3NTA	257.10	3.70E-03	0.951	9.513
Na Gluconate	218.00	3.70E-03	0.807	8.066
Na_2Iminodiacetic	177.07	3.70E-03	0.655	6.552
$Cd(NO_3)_4\cdot H_2O$	308.00	0.00E+00	0.00E+00	0.000
$Fe(NO_3)_3\cdot 9H_2O$	404.02	5.00E-05	2.02E-02	0.202
$Mg(NO_3)_2\cdot 6H_2O$	256.40	1.50E-03	0.385	3.846
$Mn(NO_3)_2$, 50%	8.46	6.63E-05	0.561 mL	5.609 mL
MoO_3	143.95	2.86E-04	4.12E-02	0.412
$Ni(NO_3)_2\cdot 6H_2O$	290.80	1.33E-04	3.87E-02	0.387
SiO_2	60.08	2.93E-03	0.176	1.760
$BaNO_3$	261.38	1.33E-04	3.48E-02	0.348
$Ca(NO_3)_2$	236.16	4.13E-04	0.098	0.975
$Sr(NO_3)_2$	211.65	1.30E-05	2.75E-03	0.028
$RbNO_3$	147.47	1.00E-05	1.47E-03	0.015
$CsNO_3$	194.92	6.40E-05	1.25E-02	0.125
$NaNO_3$	85.00	0.00E+00	0.00	0.000
KNO_3	101.11	0.00E+00	0.00	0.000
$LiNO_3$	69.00	5.51E-04	0.04	0.380
KOH	56.11	4.30E-01	24.13	241.273
NaOH	40.00	3.89E+00	155.60	1556.000
$Al(NO_3)_3\cdot 9H_2O$	375.15	5.06E-01	189.83	1898.259
Na_2CO_3	105.99	1.00E-01	10.60	105.990
Na_2SO_4	142.05	2.36E-03	0.34	3.352
$Na_2HPO_4\cdot 7H_2O$	268.07	1.73E-03	0.46	4.638
NaCl	58.45	6.93E-02	4.05	40.506
NaF	41.99	1.10E-02	0.46	4.619
$NaNO_2$	69.00	7.90E-01	54.51	545.100

Table 4.30. AW-101 Simulant Composition Compared with Actual AW-101 Composition (Diluted to 5M Na)

	Concentration (M)		
Species, Total	Simulant AW-101	Actual AW-101 Diluted	Target
Na	5.00E+00	5.00E+00	5.00E+00
K	4.30E-01	4.30E-01	4.30E-01
Li	5.51E-04	5.51E-04	5.51E-04
Rb	1.00E-05	1.00E-05	1.00E-05
Cs	6.40E-05	6.40E-05	6.40E-05
Ba	1.33E-04	1.33E-04	1.33E-04
Ca	4.13E-04	4.13E-04	4.13E-04
Cd	0.00E+00	0.00E+00	5.40E-06
Fe	5.00E-05	5.00E-05	5.00E-05
Mg	1.50E-03	1.50E-03	1.50E-03
Mn	6.63E-05	6.63E-05	6.63E-05
Mo	2.86E-04	2.86E-04	2.86E-04
Ni	1.33E-04	1.33E-04	1.33E-04
Si	2.93E-03	2.93E-03	2.93E-03
Sr	1.30E-05	1.30E-05	1.30E-05
$Al(OH)^{4-}$	5.06E-01	5.06E-01	5.06E-01
SO_4^{2-}	2.36E-03	2.36E-03	2.36E-03
OH^-	4.32E+00	4.32E+00	4.32E+00
OH^- (free)	2.27E+00	2.27E+00	2.30E+00
Theoretical pH	1.48E+01	1.48E+01	1.48E+01
Cl^-	6.93E-02	6.93E-02	6.93E-02
CO_3^{2-}	1.00E-01	1.00E-01	1.00E-01
NO_2^-	7.90E-01	7.90E-01	9.45E-01
NO_3^-	1.52E+00	1.52E+00	1.06E+00
F^-	1.10E-02	1.10E-02	1.10E-02
PO_4^{3-}	1.73E-03	1.73E-03	1.73E-03
EDTA	3.70E-03	3.70E-03	
Citrate	3.70E-03	3.70E-03	
HEDTA	3.70E-03	3.70E-03	
NTA	3.70E-03	3.70E-03	
Gluconate	3.70E-03	3.70E-03	
Iminodiacetate	3.70E-03	3.70E-03	
TOC (g/L)	1.86E+00	1.86E+00	1.97E+00

4.3.14 Composite Supernatant (102-AN, 104-AN, 105-AN, and 107-AN)

Reference : **TWRSPP-94-072, Letter Report from L. K. Holton to K. A. Gasper**

Purpose: **A mixture of supernatant from Tanks AN-102, -104, -105, and –107 for Organic Destruction Technology Development testing.**

In order to develop this simulant composition, all available sample data were obtained on each tank. An average weight concentration of each constituent was determined except for TOC, Cs, Sr, Am, and Pu, where maximum concentrations were used to establish a high concentration case. Engineering, safety, and productivity considerations for developing this simulant included: 1) the method of preparation must be applicable to making large quantities, e.g., 100 gallons, and 2) preparation should not generate secondary waste.

The approach uses sodium for anionic species and nitrate for cationic species. As a result, there is an excess of NO_3 in the simulant; however, this was not expected to cause problems for organic destruction testing purposes. Although the use of dissolved solids may not accurately simulate parameters such as particle sizes, shapes, and morphologies, this approach simulates relevant analyte concentrations, is reproducible, and minimizes secondary waste generation.

Europium nitrate was selected as a surrogate for americium and plutonium (Norton, 1993). To simulate aluminum hydroxide, a mixture of 10% boehmite and 90% gibbsite (Colton, et al. 1993) was assumed. To simulate the particle size distribution of the gibbsite, a 1:1 weight ratio of 1μm and 7.5μm diameter particles. For TOC makeup, a 2:1 molar ratio of EDTA and HEDTA was determined based on the recipe developed by Delegard et al. (1993). ^{137}Cs and ^{90}Sr values were multiplied by factors of 4.01 and 2.46, respectively, to simulate the total concentrations of Cs and Sr (Hohl, 1993).

Preparation: Although this simulant has not been prepared in a lab, the recipe is very similar to other simulants, using essentially the same compounds in varying concentrations. Before using this simulant, it is recommended that ICP, IC, and particle size distribution tests be performed and results compared to actual tank waste data. It should also be noted that the OH^- concentration was used to determine the amount of NaOH to add, rather than pH. pH should be monitored while preparing the simulant, but unless the pH value varies significantly from the expected values of 12 – 13, the added amount should be sufficient. In preparing this simulant, glassware should be avoided due to caustic leaching and dissolution of chemical species from glass.

1. Container A: To 100 mL H_2O, add:

2.32g	$Fe(NO_3)3\ 9H_2O$; stir until dissolved
62.36g	NaOH; stir
4.38g	AlO(OH) (boehmite); stir
51.25g	1-μm $Al_2O_3\ 3H_2O$ (gibbsite); stir
51.25g	7.5-μm $Al_2O_3\ 3H_2O$ (gibbsite); stir

2. Container B: To 100 mL H_2O, add:

2.32g	$Fe(NO_3)_3\ 9H_2O$; stir until dissolved
5.67g	$Na_3PO_4\ 12H_2O$; stir

3. Add the contents of Container B to Container A, stir, and then add:

1.290g	$Ca(NO_3)_2\ 4H_2O$	0.180g	$Zr(NO_3)_4\ 5H_2O$
0.650g	$Mn(NO_3)_2\ 4H_2O$	8.700g	KNO_3
0.490g	$Ni(NO_3)_2\ 6H_2O$	0.039g	$CsNO_3$
0.040g	$Ba(NO_3)_2$	0.006g	$Sr(NO_3)_2$
2.120g	$Cr(NO_3)_3\ 9H_2O$	0.032g	$Eu(NO_3)_3\ 6H_2O$

4. Container C: To 45mL H_2O, add one-by-one and stir (heat gently) until dissolved before adding the next component:

107.16g	$Na_4(EDTA)\ 2H_2O$	7.29g	Na_2SO_4
48.67g	$Na_3(HEDTA)\ 2H_2O$	49.47g	Na_2CO_3
84.11g	$NaNO_2$	0.35g	NaF
263.15g	$NaNO_3$	7.02g	NaCl

5. Add contents of Container C to Container A, stir.

Table 4.31. Composite Supernatant (Molar and Mass Concentrations)

Constituent	M	g/L	Constituent	M	g/L
$Na_4(EDTA)\ 2H_2O$	0.255	107.16	$Ca(NO_3)_2\ 4H_2O$	0.0055	1.29
$Na_3(HEDTA)\ 2H_2O$	0.127	48.67	NaCl	0.1201	7.02
$NaNO_2$	1.219	84.11	$Cr(NO_3)_3\ 9H_2O$	0.0053	2.12
$NaNO_3$	2.568	263.15	NaF	0.0084	0.345
NaOH	1.559	62.36	$Fe(NO_3)_3\ 9H_2O$	0.0057	2.32
$Na_3PO_4\ 12H_2O$	0.015	5.67	KNO_3	0.0860	8.70
Na_2SO_4	0.051	7.29	$Mn(NO_3)_2\ 4H_2O$	0.0026	0.65
Na_2CO_3	0.306	49.47	$Ni(NO_3)_2\ 6H_2O$	0.0017	0.49
AlO(OH)	0.073	4.38	$Zr(NO_3)_4\ 5H_2O$	0.0004	0.18
1-μm $Al_2O_3\ 3H_2O$	0.329	51.25	$CsNO_3$	0.0002	0.039
7.5-μm $Al_2O_3\ 3H_2O$	0.329	51.25	$Eu(NO_3)_3\ 6H_2O$	7.13e-05	0.032
$Ba(NO_3)_2$	0.0001	0.04	$Sr(NO_3)_2$	2.93e-05	0.006

References Cited in Section 4.3.14:

Colton, N. G., G. J. Lumetta, A. R. Felmy, J. A. Franz. 1993. *ESPIP Alkaline Tank Sludge Treatment: Fiscal Year 1993 Annual Report* (unpublished), Pacific Northwest Laboratory, Richland, Washington.

Delegard, C. H., A. M. Stubbs, and S. D. Bolling. 1993. *Laboratory Testing of Ozone Oxidation of Hanford Site Waste from Tank 241-SY-101*, WHC-EP-0701, Westinghouse Hanford Company, Richland, Washington.

Hohl, T. M.. 1993. *Synthetic Waste Formulations for Representing Hanford Tank Waste*, WHC-SD-WM-TI-549, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Norton, M. V. 1994. *Selective Separation of Eu^{3+} Using Polymer-Enhanced Ultrafiltration*, PNL-9339, Pacific Northwest Laboratory, Richland, Washington.

4.3.15 Neutralized Current Acid Waste (NCAW) Stock Solution

Reference: Bray, L. A., K. J. Carson, R. J. Elovich, D. E. Kurath. 1992. *Equilibrium Data for Cesium Ion Exchange of Hanford CC and NCAW Tank Waste*, TWRSPP-92-020, Pacific Northwest Laboratory, Richland, Washington.

Purpose: Represent a high sodium waste containing a low organic content for ion-exchange studies.

Table 4.32. NCAW Stock Solution

Component	FW, g	M	g/L
$NaNO_3$	85	0.310	26.3
Na_2SO_4	142.05	0.18	25.7
KNO_3	101.11	0.14	14.3
$RbNO_3$	147.47	1.3E-04	0.02
Na_2CO_3 H_2O	124.0	0.24	29.7
$NaNO_2$	69.0	0.52	35.8
Na_2HPO_4 $7H_2O$	268.07	0.03	8
$Al(NO_3)_3$ $9H_2O$	375.15	0.52	196.3
NaF	42.0	0.107	4.48
NaOH	40.0	4.08	163
The stock solution is spiked with tracer quantities of ^{137}Cs so that the Na/Cs mole ratio ranges from 50 to 5000.			

Table 4.33. Composition of NCAW Stock Solution

Component	M
Na	5.92
K	0.14
Rb	1.3E-04
Cs	a
Al	0.52
SO_4	0.18
OH (free)	2.0
CO_3	0.24
F	0.107
NO_2	0.52
NO_3	1.87
[a] Na/Cs ratios 50, 500, 5000	

4.3.16 Neutralized Current Acid Waste AZ-102 Solution (5<u>M</u> Na)

Reference: Kurath, D. E., L. A. Bray, K. P. Brooks, G. N. Brown, S. A. Bryan, C. D. Carlson, K. J. Carson, J. R. DesChane, R. J. Elovich, A. Y. Kim. 1994. *Experimental Data and Analysis to Support the Design of an Ion Exchange Process for the Treatment of Hanford Tank Waste Supernatant Liquids*, TWRSPP-94-094, Pacific Northwest Laboratory, Richland, Washington.

Purpose: Ion exchange studies.

This simulant represents a Neutralized Current Acid supernatant diluted to 5<u>M</u> Na and should be soluble at room temperature. The composition approximates Tank 241-AZ-102.

Preparation: Weigh and tare feed container and fill with about 1/2 volume of distilled water. Add the components listed below in order while stirring. Add all components relatively quickly with the exception of KOH and NaOH. These components will cause the solution to heat up; try not exceed temperature >70ºC if using poly container.

Table 4.34. AZ-102 5<u>M</u> Na Solution

Component	FW,g	<u>M</u>	g/L	g/5 L
$NaNO_3$	85.00	0.258	21.93	109.650
KNO_3	101.11	0.120	12.13	60.666
KOH	56.11	0.000	0.00	0.000
NaOH	40.00	3.400	136.00	680.000
$Al(NO_3)_3$·9H2O	375.15	0.430	161.31	806.573
Na_2CO_3	105.99	0.230	24.38	121.889
Na_2SO_4	142.05	0.150	21.31	106.538
$Na_2HPO_4 \cdot 7H_2O$	268.07	0.025	6.70	33.509
NaF	41.99	0.089	3.74	18.686
$NaNO_2$	69.00	0.430	29.67	148.350
$RbNO_3$ (from 0.1M)	147.47	5.00E-05	0.50 mL	2.50 mL
$CsNO_3$ (from 0.1M)	194.92	5.00E-04	5.00 mL	25.00 mL

Table 4.35. AZ-102 Simulant Composition Compared with Actual AZ-102 Composition (Diluted to 5M Na)

	Concentration (M)	
Species, Total	AZ-102 Simulant	Actual AZ-102 Diluted
Na	4.987	4.90
K	0.120	0.12
Rb	5.00E-05	
Cs	5.00E-04	6.00E-04
Al	0.430	0.48
SO_4	0.150	0.15
OH	3.400	
OH (free)	1.680	1.10
Theoretical pH	14.52	
CO_3	0.230	0.21
NO_2	0.430	0.44
NO_3	1.669	1.80
F	0.089	0.09
PO_4	0.025	<0.028
Na/Cs Ratio	9.97E+03	
K/Cs Ratio	2.40E+02	
OH/Cs Ratio	6.80E+03	
Na/K Ratio	4.16E+01	

4.3.17 Neutralized Current Acid Waste AZ-102 Solution (5M Na) with Radiotracers

Reference: Svitra, Z. V., S. F. Marsh, S. M. Bowen. 1994. *Distributions of 12 Elements on 64 Absorbers from Simulated Hanford Neutralized Current Acid Waste (NCAW)*, LA-12889, Los Alamos National Laboratory, Los Alamos, New Mexico.

Purpose: For measuring the distribution coefficients.

Preparation: Neutralized Current Acid Waste AZ-102 5M Na solution is passed through a 0.45-μm filter to remove any suspended solids and then refiltered after adding radiotracers to remove any portion not truly in solution. Each portion of precontacted and postcontact simulant solution is again passed through a 0.45-μm filter before γ-spectrometric assay.

Table 4.36. Composition of 5M Na AZ-102 Solution

Constituent	Concentration (M)
Na	4.987
K	0.120
Rb	5.0E-05
Cs	5.0E-04
Al	0.43
F	0.089
NO_3	1.669
NO_2	0.43
PO_4	0.025
SO_4	0.15
CO_3	0.23
OH^-(total)	3.4
OH^-(free)	1.68
pH	14.2

Radiotracer	**γ-Energy (MeV)**	**Est. Conc.**
^{56}Ni	0.158	60 pg/L
^{95m}Tc	0.204	2 pg/L
^{51}Cr	0.320	0.3 μg/L
^{88}Zr	0.394	50 μg/L
^{85}Sr	0.514	3 μg/L
^{137}Cs	0.662	6 μg/L
^{54}Mn	0.835	3 μg/L
^{88}Y	0.898	50 μg/L
^{48}V	0.983	80 pg/L
^{59}Fe	1.099	20 μg/L
^{65}Zn	1.115	6 μg/L
^{60}Co	1.173	2 μg/L

4.3.18 Plutonium Finishing Plant SY-102 Solutions

Reference: Marsh, S. F., Z. V. Svitra, S. M. Bowen. 1994. *Distributions of 14 Elements on 63 Absorbers from Three Simulant Solutions (Acid-Dissolved Sludge, Acidified Supernatant, and Alkaline Supernatant) for Hanford HLW Tank 102-SY*, LA-12654, Rev., Los Alamos National Laboratory, Los Alamos, New Mexico.

Purpose: Previously used to evaluate absorber materials.

The compositions of these simulant solutions were based on consultation with and recommendations from WHC and PNNL personnel. Assumptions about tank contents were checked against composition data obtained by reconstructing the tank contents from all available records for transfers into and out of each tank during its entire operating history.

The sludge composition was based on the assumption that soluble components had been leached out during thorough mixing with the supernatant solutions. These soluble components were subtracted from the best estimate of the initial sludge composition. The alkaline supernatant and acidified supernatant solutions are similar in their initial composition, but the alkaline supernatant solution contains substantially more hydroxide and generates much more precipitate.

Preparation: Dissolve the components assumed to remain in the sludge in a minimum quantity of nitric acid and filter to remove insoluble residue. To ensure the alkaline supernatant solution is truly saturated with relatively insoluble salts, dilute the initial liter of solution/solids with another three liters of water and heat until the diluted solution reduced to the initial one liter. Separate bulk solids by centrifugation, and remove any remaining suspended solids by passing the alkaline supernatant solution through a 0.45-µm filter.

Table 4.37. Compositions of SY-102 Simulant Solutions

Constituent	Acid-Dissolved Sludge (M)	Acidified Supernatant (M)	Alkaline Supernatant (M)
Na	0.65	1.4	2.2
Mg	0.060	0.032	none
Al	0.43	0.44	0.16
Si	0.125	0.29	0.0024
Ca	0.044	0.028	0.0069
Cr(III)	0.33	0.072	none
Cr(VI)	none	0.007	0.0051
Mn	0.143	0.043	none
Fe	0.36	0.101	0.0061
Ni	0.010	<DL[a]	<DL[a]
Cu	0.016	<DL[a]	<DL[a]
Se	0.027	<DL[a]	<DL[a]
Sr	0.0009	<DL[a]	<DL[a]
Pb	0.012	<DL[a]	<DL[a]
Th	0.027	<DL[a]	<DL[a]

Continued			
U	0.023	<DL[a]	<DL[a]
^{239}Pu	3 g/L	--	<DL[a]
^{238}Pu	60 mg/L	60 mg/L	none
F	0.027	0.024	0.21
Cl	0.006	0.021	0.102
NO_3	5.24	1.95	1.31
PO_4	0.006	<0.002	0.061
SO_4	0.009	0.015	0.022
pH	0.58	3.5	13.85
calculated H^+	0.5	--	--
Calculated OH^-	--	--	0.7

[a] Less than detection limit.

4.3.19 Neutralized Current Acid Waste Slurry Simulant

Reference: Norton, M. V. and F. Torres-Ayala. 1994. *Laboratory Testing In-Tank Sludge Washing*, PNL-10153, Pacific Northwest Laboratory, Richland, Washington.

Purpose: Previously used to study waste settling behavior.

This simulant was originally made by WHC and stored for several years. Simulant composition and particle size data were comparable with data obtained from Tank 241-AZ-101 core samples. The recipe provided below is the original recipe for the simulant (Elmore and Smith, 1990).

Preparation:

1. Add to 30 gal (~115L) of water and mix until dissolved:

5.33kg	$NaNO_3$	1.82kg	$Cr(NO_3)_3\ 9H_2O$
90.89kg	$Al(NO_3)_3\ 9H_2O$	0.19kg	SiO_2
12.40kg	$Fe(NO_3)_3\ 9H_2O$	7.04kg	$Ni(NO_3)_2\ 6H_2O$
8.99kg	$Fe_2SO_4)_3\ 9H_2O$	0.46kg	$ZrO(NO_3)_2$

2. Add: 12.05L HNO_3 (70% solution)
   2.57L H_2SO_4 (98.6% solution)
   1.72L HF (50% solution)

3. Over an 8-hr period, starting at ~92ºC to 95ºC, slowly meter in 25L of sucrose solution (6.64 kg sucrose and 48g NaOH in 23.54L H_2O).

4. Add makeup H_2O to maintain level of 66 gal (~250L); digest at a minimum temperature of ~50ºC to 60ºC; then "neutralize" to pH~13 with 19M NaOH caustic solution.

5. Add 3.15kg K_2CO_3. Add H_2O as needed to bring mixture to 100 gal (~380L). Boil for 5 days; then store at ~40ºC.

Table 4.38. Composition of Simulated NCAW Slurry and Actual NCAW AZ-101 Slurry

Component	Simulated NCAW Slurry		Actual AZ-101 Slurry	
	Supernatant (mmol/g)	Solids (mmol/g)	Supernatant (mmol/g)	Solids (mmol/g)
Al	0.19	2.81	0.33	1.46
Cr	0.006	0.047	0.013	0.055
Fe	0.0001	1.15	0.0002	1.50
K	0.103	<0.001	0.088	<0.27
Na	3.89	7.92	3.76	3.42
NO_3	2.05		1.04	
SO_4	0.16		0.13	
Specific Gravity (g/mL)	1.24		1.2	

Reference Cited in Section 4.3.19:

Elmore, M. R. and H. D. Smith. 1990. *Erosion-Corrosion of Carbon Steel in Simulated Neutralized Current Acid Waste Slurry,* (unpublished) Pacific Northwest Laboratory, Richland, Washington.

4.3.20 Single-Shell Tank BY-104 Chemical Simulant

Reference : **Not available.**

Purpose: Developed to demonstrate ferrocyanide destruction with ozone.

This simulated waste composition is based on a 1976 analysis of BY-104 waste and assumes ~30% sludge. Waste ingredients believed to affect ozonation of ferrocyanide include transition metals, nitrite, and carbonate. A small quantity of simulant was prepared. Initially, the brown solution produced ~30% fine-grained solids. A 2-mm crust formed over the top of the wide mouth beaker. After two weeks, white crystals grew up and over the beaker edge. The top crust thickened to 1 cm, and the rest of the waste was thick brown goo with the consistency of toothpaste.

Preparation:

1. Dissolve the following chemicals into 974mL of 8M HNO_3:

199.3g	$NaAlO_3$	3.945g	$NiSO_4\ 6H_2O$
8.34g	$FeSO_4 \cdot 7H_2O$	5.106g	$Na_2HPO_4 \cdot H_2O$
4.72g	$Ca(NO_3)_2 \cdot 4H_2O$	26.13g	$Na_2SiO_3\ 9H_2O$
2.676g	$Mg(ClO_4)_2$	0.212g	$Sr(NO_3)_2$
0.783g	MnO_2	0.84g	CsCl

2. While blending the solution, slowly add 1M NaOH to pH 12.
3. Add the following chemicals to the solution:

30.74g	Na_2CO_3
29.4g	$Na_2NiFe(CN)_6$
113.85g	$NaNO_2$

   Note: The ferrocyanide was made based upon the Sloat Flowsheet.

4. Blend the solution at 90ºC.
5. Place solution into a 200ºC oven and boil down to 1L.
6. Cover and let cool.

Table 4.39. Composition of BY-104 Chemical Simulant

Constituent	gmol/L	Constituent	gmol/L
NO_3	7.79	Mn	0.009
NO_2	1.65	Ni	0.015
CO_3	0.29	PO_4	0.037
OH	0.01	Si	0.092
Al	2.43	$NaNiFe(CN)_6$	0.100
Fe	0.03	Sr	0.001
Ca	0.02	Cs	0.005
Mg	0.012	Na	(not provided)

4.3.21 Single-Shell Tank C-106 Chemical Simulant

Reference: Hyatt, M. G., M. V. Norton, F. Torres-Ayala, K. A. Zaniboni. 1995. *Laboratory Testing In-Tank sludge Washing/Settling Mixer Pump Simulations with NCAW Simulant*, TWRSPP-94-108, Pacific Northwest Laboratory, Richland, Washington.

Purpose: Waste settling studies.

Settling investigations, similar to those performed earlier with NCAW, were conducted using C-106 simulant. Alkaline leach tests also were performed using this particular simulant. The following recipe was based on tank composition data assuming a 3X-volume dilution.

Preparation:

1. Start with 7.7L deionized water. Add the following compounds slowly in order. After each addition, stir the solution until all compounds are dissolved.

Table 4.40. SST C-106 Chemical Simulant (40L)

Compound	Mass added (g)	Required Ion	Required (μg/g)
Al_2O_3 (gibbsite)	997.49	Al^{3+}	9738
AlOOH (boehmite)	110.62		
$Fe(NO_3)_3$ $9H_2O$	4171.89	$Fe(III)^{3+}$	14230
$Ba(NO_3)_2$	85.60	Ba^{2+}	1110
$Ca(NO_3)_2$ $4H_2O$	727.64	Ca^{2+}	3048
$La(NO_3)_3$ $6H_2O$	350.04	La^{3+}	2771
$Mg(NO)_3$ $6H_2O$	409.66	Mg^{2+}	958
$Mn(NO_3)_2$	551.74	Mn^{2+}	2089
$Sr(NO_3)_2$	4.10	Sr^{2+}	42
$Cr(NO_3)_3$ $9H_2O$	174.11	$Cr(III)^{3+}$	558
$Na_2SO_4 \cdot 10H_2O$	544.51	SO_4^{2-}	5324

2. Neutralize the solution to pH 7 with NaOH pellets. Take care to *add the NaOH slowly to prevent gel formation*, or use a 50/50 NaOH/water weight percent solution. Continue to stir for several hours.

3. Add: 1223.16g Na_2HPO_4 (PO_4^{3-} concentration of 30450 μg/g). Stir the solution for 24 hours. Continue with NaOH addition to a pH around 10. Then add:

Na_2CO_3	620.09	CO_3^{2-}	13041
$NaNO_3$	338.47	Na^+	65675
		NO_3^-	36969
Na_2SiO_3 $9H_2O$	4705.50	Si^{4+}	49220

4. Continue with NaOH addition to a pH around 12. When the solution has reached a pH of 12, add sufficient deionized water to 40L.

5. Stir the solution for 24 hours and then allow it to settle. For settling tests, stir the solution adequately to suspend all particles.

4.3.22 Single-Shell Tank C-112 Chemical Simulant

Reference : Memo from N. G. Colton to A. J. Schmidt (February, 1994)
Milestone 60505A, Subtask 0604, "Simulant Development and Documentation"

Purpose: For evaluating the suitability of organic destruction technologies for destroying ferrocyanide compounds.

An estimated composition for C-112 sludge is given in Table 4.41. This composition shows that approximately 8 wet wt% (13 dry wt%) of the actual tank sludge is calcium uranium (U^{+6}) oxide compound. Using this estimated composition as a guideline, a recipe was developed and a preliminary simulant was prepared. Uranium compounds were not included because of no known suitable substitute for U^{+6}; addition of depleted uranium was not an option as it defeated the purpose of non radioactive testing. (Depleted uranium is viewed at the Hanford Site in the same light as uranium).

A sample of the simulant was evaluated using transmission electron microscopy techniques that also were being used at that time to evaluate samples of C-112 sludge. While chemical phases may have been similar, particle sizes, shapes, and morphologies definitely were not. In addition, the waste minimization consideration of not generating a secondary waste was not achieved because the calcium pyrophosphate species in the simulant was prepared by a precipitation method that required the precipitate to be washed to remove excess sodium nitrate. (Note that scientists have since questioned whether phosphate associated with calcium would/could be in the pyrophosphate form that was proposed following XRD analyses of C-112).

Again using the estimated composition for C-112 as a guideline and excluding the uranium compounds, a second recipe was prepared. While this method of preparation meets the considerations listed above, the simulant has certain shortcomings. Since the simulant is prepared mostly by adding dry solids (without grinding) to water, particle sizes are larger that in the preliminary simulant. As a result, larger particles settle out rapidly and are then followed by smaller species prepared by precipitation. Colton recommended that before spending addition funds to chemically and physically characterize the simulant, e.g., ICP, IC, and particle size, the organic destruction task provide input as to whether testing with a chemical simulant that had few physical characteristics of actual C-112 sludge would effectively verify organic destruction technologies.

Table 4.41. Estimated Composition of 241-C-112 (Composite Cores 34, 35, 36; pH 11 – 12.3[a])

Constituent	Weight %	Constituent	Weight %
$NaNO_3$	9.8	CaU_2O_7	7.9
$NaNO_2$	8.1	FeOOH	2.5
Na_3PO_4[b]	5.6	$FePO_4$[c]	1.5
Na_2CO_3	5.3	$Mg_2P_2O_7$	0.3
NaF	0.1	$Ni(OH)_2$	1.4
NaCl	0.2	$Al_2(OH)_4Si_2O_5$[d]	0.3
$NaAlO_2$	0.2	$Al(OH)_3$	5.7
Na_2SO_4	2.0	$USiO_4$	0.7
$Na_2NiFe(CN)_6$/$CsNiFe(CN)_6$	2.8	SiO_2	0.2
$NaAlSi_3O_8$	0.4	$Ca_2P_2O_7$[e]	5.8
Organic Salts	0.9	H_2O	~38

[a] pH of 1g sludge in 100mL H_2O = 9.0 – 10.3; pH of supernatant in tank June, 1975 was 11.7 – 12.1. Therefore pH of sludge estimated to be 11.0 – 12.3.

[b] Sodium phosphate species is pH dependent. If the pH of the sludge is less than 12.3, Na_2HPO_4 most likely would be present.

[c] An iron phosphate phase was tentatively identified in C-112 by TEM techniques. Investigation of C-112 is continuing to verify that this phase is present, and if so, in what form.

[d] An aluminum silicate (1:1) species was identified with SEM. While cancrinite has been identified in U-110 and C-109 using XRD, none was identified in C-112. Therefore, kaolin is being assumed for this estimated composition.

[e] This compound may exist as $Ca_3(PO_4)$; however, since the magnesium phosphate compound was identified by XRD as a pyrophosphate, calcium is assumed to be in the same form for this estimated composition.

Preparation: Method for preparing 250g of 3:1 diluted (by volume) C-112 chemical simulant.

1. Tare Container A.

Container A: To 10g H_2O, add:
11.31g $Fe(NO_3)_3\ 9H_2O$; stir until dissolved
8.4 mL $10\underline{N}$ NaOH; stir until gelatinous mass flows freely.

Add the following compounds one-by-one to Container A while stirring:

5.71g	$Al_2O_3\ 3H_2O$ (gibbsite; particle size 50/50 mix of 1µm and 7.5µm particles)
5.78g	$Ca_2P_2O_7$
0.32g	$Mg_2P_2O_7$
0.26g	Kaolin
2.00g	30wt% colloidal SiO_2 in H_2O

2. To container B: To ~45g H_2O, add one-by-one and stir (heat gently) until dissolved before adding the next component:

13.05g	$Na_3PO_4 \cdot 12H_2O$
8.12g	$NaNO_2$
0.45g	Na_2EDTA
0.53g	$Na_3Citrate$
2.05g	Na_2SO_4
5.15g	Na_2CO_3
0.15g	NaF
0.18g	NaCl
0.16g	$NaAlO_2$ (may form precipitate)

Add Container B to A; stir.

3. Container C: To 5g H_2O, add 3.94g $Fe(NO_3)_3\ 9H_2O$; stir until dissolved.

4. Container D: Dissolve 3.71g $Na_3PO_4 \cdot 12H_2O$ in ~10g H_2O. Add Container C to D; stir until tan colored gelatinous mass flows freely. Then add contents of Container D to A; stir.

5. Add to Container A: 2.94g $Na_2NiFe(CN)_6$. The $Na_2NiFe(CN)_6$ used in this recipe was supplied by WHC to Mike Lilga for the Ferrocyanide Project. The compound was apparently prepared offsite using sulfate salts and was washed at WHC. The material consisted of black, glass-type chunks that were ground with a mortar and pestle to a powder. Particle sizes remained large enough so that these solids are the first to settle out.

6. Add H_2O to 145g total (approximate 1:1 dilution by volume). Stir and let solids settle overnight. Take pH of supernatant; pH should be around 10.8. If a pH >10.8 is required, pH may be adjusted with NaOH at this time.

7. Add H_2O to 250g total mass (approximate 3:1 dilution by volume).

4.3.23 Single-Shell Tank Variable Chemical Composite

Reference: Elmore, M. R., N. G. Colton, and E. O. Jones. 1992. "*Development of Simulated Tank Wastes for the U. S. Department of Energy's Underground Storage Tank Integrated Demonstration*," Spectrum '92 International Topical Meeting, Nuclear & Hazardous Waste Management, August 23-27, 1992, Boise, Idaho (Published Proceedings).

Purpose: USTID benchmark simulant for evaluating equipment and processes.

At the time this simulant was developed, the waste pretreatment scenario at the Hanford site for sludge-type wastes included acid dissolution followed by radionuclide removal with the TRUEX process. This simulant was Developed by PNL for the Underground Storage Tank Integrated Demonstration (USTID) program as a benchmark simulant for evaluating equipment and processes e.g., acid dissolution; sensor technologies; fiber optics for in-situ chemical analyses; steam reforming for organic destruction; magnetic separation for actinide removal from wastes. When the pretreatment scenario switched from acid dissolution to alkaline leaching, actual tank wastes were used for the most part to investigate waste chemical and physical properties. However, this simulant was used at Tennessee Technology University to investigate optimum conditions, i.e., time, temperature, and NaOH concentration, for aluminum and metal removal by alkali washing (Callahan, et al., 1994; Ensor, et al., 1994).

Procedures for preparing the waste were derived from Kupfer (1981) and the mean concentrations of 18 analyzed SST sludge wastes. A thermally aged simulant, prepared by refluxing the simulant at 105°C for 5 days, was prepared and compared with an unaged simulant to determine what effect thermal aging had on speciation. Chemical properties of the simulant were characterized using ICP, IC, and XRD techniques. XRD analyses indicated the major crystalline phases in the aged and unaged samples were sodium nitrate and bismuth phosphate. These phases are present in the two wastes, B-110 and U-110, used for comparison. A sodium aluminum silicate phase, which is present in B-110 was present in the thermally aged simulant sample. Waste in Tank 241-B-110 originated from second decontamination cycle Bismuth Phosphate waste streams, and waste in Tank 241-U-110, from first decontamination cycle Bismuth Phosphate and REDOX waste streams.

Procedure: In this procedure, metal oxide/hydroxide/phosphate and sodium salt simulants are prepared individually and then mixed together at varying ratios depending on the specific tank waste to be simulated or on the test being conducted. *Note that a lot of secondary waste is generated with this procedure unless the wash solution is analyzed, dried, and the salts reused in other simulant batches.*

<u>Metal oxide/hydroxide (without phosphate)</u>

1. Solution 1: To a 4-L beaker filled with 600mL water, add while stirring:

143.35g	$Al(NO_3)_3\ 9H_2O$

Continue stirring and add:

2.31g	$Ca(NO_3)_2\ 4H_2O$	0.09g	$Zr(O)(NO_3)_2\ 2H_2O$
0.30g	$Pb(NO_3)_2$	0.36g	$Ce(NO_3)_3\ 6H_2O$
0.80g	$Mg(NO_3)_2\ 6H_2O$	14.73g	$Fe(NO_3)_3\ 9H_2O$
0.04g	$AgNO_3$	0.95g	$Cr(NO_3)_3\ 9H_2O$
0.14g	$Zn(NO_3)_2\ 6H_2O$		

2. Solution 2: To 100mL water, dissolve while stirring.

0.21g	$KMnO_4$
0.20g	$Mn(NO_3)_2$ dissolved in 2mL water

3. Add well-stirred Solution 2 to Solution 1. Stir 1 hour and adjust pH to ~9.5.

<u>Metal oxide/hydroxide (with phosphate)</u>

4. Solution 3: To a 1-L beaker filled with 400mL water, add while stirring:

13.6g	$Fe(NO_3)_3\ 9H_2O$
1.48g	$Cr(NO_3)_3\ 9H_2O$
0.98g	$La(NO_3)_3\ 6H_2O$

Dissolve 0.21g $Mn(NO_3)_2$ in 2mL water. Add to above solution while stirring. Mix 10 minutes. Continue to stir and add 3.45g 85% H_3PO_4. Stir until dissolved.

Add 7.82g $Bi(NO_3)_3\ 5H_2O$ (precipitate will form). Mix 10 minutes. While stirring, add:

10.09g	$Na_3PO_4\ 12H_2O$
2.07g	$Ce(NO_3)_3\ 6H_2O$
0.49g	$Zr(O)(NO_3)_2\ 2H_2O$

Adjust pH to ~10 with 25% NaOH. While stirring add:

0.38g	$Ni(NO_3)_2.6H_2O$
0.09g	$Sr(NO_3)_2$

Stir 1 hour; adjust to pH 10.

5. Add contents of Container C to Container A.

6. Wash: Add pH 10 water to the 3.5L mark; mix. Let settle overnight; pump off clear liquid. Repeat wash two more times. Add:

0.17g	NaF
1.42g	K_2SO_4
27.99g	30% SiO_2 Solution
0.62g	EDTA (MW=372.2)
0.53g	Citric Acid

Mix well. Mixture may be dried if particle size is unimportant or may be maintained wet. Dry yield equivalent is 62g metal oxide/hydroxide/phosphate simulant.

7. <u>Sodium Salt Mixture</u>:

	<u>Dry Wt%</u>
$NaNO_3$	75.2
$NaNO_2$	4.8
$Na2SO_4$	2.4
$Na2CO_3$	4.3
$NaAlO_2$	4.3
Na_3PO_4	4.6
NaOH	4.4

7. Composite simulated Waste = (x) metal oxide/hydroxide/phosphate + (1−x)salt mixture

where x is dry weight equivalent. For example, adding 51g dried sodium salt mixture to the metal oxide/hydroxide/phosphate mixture (62g dry equivalent) results in a composite 55% metal oxide/hydroxide/phosphate:45% sodium salt simulated waste.

Table 4.42. Summary of ICP and IC Results (Dry Weight %) for a Composite Simulated Waste (55% metal oxide/hydroxide/phosphate:45% sodium salts) and Two Actual Tank Wastes

Element	Aged Simulant	Unaged Simulant	B-110 Waste	U-110 Waste
Al	8.2	8.5	0.29	20.6
Ag	0.02	0.01	0.005	NR
Ba	--	--	0.003	0.006
Bi	3.1	3.1	4.3	NR
B	--	--	<DL	0.02
Ca	0.35	0.35	0.21	0.10
Cr	0.25	0.25	0.20	0.10
Cu	0.02	0.02	<DL	0.005
Fe	3.4	3.3	4.8	2.6
La	0.28	0.27	0.01	NR
Pb	0.16	0.15	0.28	NR
Mg	0.07	0.06	0.05	0.08
Mn	0.14	0.14	0.02	0.64
Ni	0.06	0.05	NR	0.02
P	2.5	2.6	4.0	NR
K	<DL	<DL	NR	NR
Si	3.3	3.5	2.3	9.1
Na	17.9	17.5	23.8	13.2
Sr	0.03	0.02	0.05	0.08
Zn	0.03	0.03	0.02	0.03
Zr	0.004	<DL	<DL	0.01
NO_3^-	27.2	28.6	39.7	8.1
NO_2^-	1.5	1.6	2.4	0.007
TOC	0.18	0.18	0.10	0.17
PO_4^{3-}	1.4	3.0	6.2	7.1
SO_4^{2-}	0.73	0.89	2.6	2.0
U	--	--	0.06	1.1
Ce	0.65	0.64	NR	NR
F^-	0.34	0.34	0.40	1.5
Cl^-	0.005	0.005	0.13	0.16

DL: Detection Limit
NR: No data reported

References Cited in Section 4.3.23:

Callahan, P. S., D. D. Ensor, and B. Z. Egan. 1994. *"Aluminum Removal from Simlated Waste,"* presented at the 207th National Meeting of the American Chemical Society, San Diego, California, March 13-18, 1994.

Ensor, D. D., P. S. Callahan, and B. Z. Egan., "Metal Removal from Simulated Radioactive Sludge by Alkali Washing," presented at the 18th Annual Actinide Separations Conference, Durango, Colorado, May 23-26, 1994.

Kupfer, M. J. 1981. *Preparation of Non radioactive Substitutes for Radioactive Wastes*, DOE/ET/41900-8, Richland, Washington.

4.3.24 Calcined Composite Simulated Waste

Reference: Knight, R. C. 1993. *Calcine Residue Treatment Summary Report*, WHC-SD-WM-PE-052, Westinghouse Hanford Company, Richland, Washington.

Purpose: For calcination/dissolution studies.

The composition for this composite Hanford simulated waste was developed from a comprehensive literature review of all existing tank waste chemistries performed by the chemistry development subtask for this project. Small quantities of bismuth, strontium, cerium, and manganese were included in this composition to act as surrogates for radionuclides. A 35g sample reduces to ~1g insoluble residue following calcination and aqueous dissolution.

Procedure:

Table 4.43. Calcined Composite High-Level Simulated Waste

Compound	Formula Wt.	Mole Fraction	Mass, g
$Al(OH)_3$	78	0.0553	4.313
Fe_2O_3	159.6	0.0049	0.782
KOH	56.1	0.0098	0.550
NaOH	40	0.8170	32.680
SiO_2	60.09	0.0060	0.360
NaCl	58.44	0.0041	0.240
Na_2CO_3	106	0.0370	4.922
NaF	42	0.0193	0.830
$Na_3PO_4 \cdot 12H_2O$	380	0.0314	11.932
Na_2SO_4	138	0.0070	0.966
CeO_2	172	0.0010	0.172
$SrCl_2 \cdot 6H_2O$	266.5	0.0010	0.267
$Ni(OH)_2$	93	0.0010	0.093
$NaBiO_3$	280	0.0010	0.280
MnO_2	87	0.0010	0.087
ZrO_2	123.2	0.0010	0.123
$Na_2CrO_4 \cdot 4H_2O$	234	0.0010	0.234
$CaCO_3$	100	0.0010	0.100
		Total Sample Weight	**58.93g**

4.3.25 PUREX Acidified Sludge (SYM-PAS-95)

Reference: Carlson, C. D. and H. Babad. 1996. *Test Plan for Fauske and Associates to Perform Tube Propagation Experiments with Simulated Hanford Tank Wastes*, PNNL-10970, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Purpose: Previously used to test reactivity and energetics.

This simulant is a modified PUREX Acidified Sludge (PAS) simulant with added transition metals. Various organic species can be added to simulate those found in waste tanks. The ratios of the organic constitutes are based on estimated inventories added during operations.

Table 4.44. Modified SYM-PAS-95 (no organic added)

Component	Concentration (M)
NaOH	3.5500
$NaNO_2$	1.2650
$Fe(NO_3)_3\ 9H_2O$	0.0720
$Cr(NO_3)_3\ 9H_2O$	0.0013
$Ni(NO_3)_2\ 6H_2O$	0.0026
$Mn(NO_3)_2$	0.0019
KNO_3	0.0038
$Pd(NO_3)_2$	5.0E-05
$RuCl_4\ 5H_2O$	5.0E-05
$Rh(NO_3)_3\ 2H_2O$	5.0E-05
$Ce(NO_3)_3\ 6H_2O$	0.0041
$Bi(NO_3)_3\ 5H_2O$	0.0031
$Na_2SiO_3\ 9H_2O$	0.0031
$NaNO_3$	2.200
$Pb(NO_3)_2$	0.0079
Na_2SO_4	0.0081
$Na_3PO_4\ 12H_2O$	0.0081
$Al(NO_3)_3\ 9H_2O$	0.0850
NaF	0.1036

Preparation:

1. Make sure all chemicals are ACS Reagent grade.
2. To make a 1-L batch, add 500mL deionized water to a 1.5L (or larger) beaker with an appropriate stirrer.

3. Add:

142g	NaOH
31.89g	$Al(NO_3)_3.9H_2O$
0.88g	$Na_2SiO_3.9H_2O$
186.98g	$NaNO_3$
4.35g	NaF
1.15g	Na_2SO_4
3.08g	$Na_3PO_4.12H_2O$

Each compound should dissolve completely before the next compound is added.

4. Add: 29.09g $Fe(NO_3)_3\ 9H_2O$

Addition will cause a dark red precipitate to form. Stir solution for two hours before adding:

87.29g $NaNO_2$

Failure to stir in between these additions will result in evolution of N2O4, a red gas. Evolution of N_2O_4 indicates destruction of NO_2^-, and the solution needs to be remade.

5. Dissolve remaining metal nitrates in 50mL of deionized water:

0.38233g	KNO_3	0.01601 g	$RuCl_4\ 5H_2O$
0.52g	$Cr(NO_3)_3\ 9H_2O$	0.01557g	$Rh(NO_3)_3\ 2H_2O$
0.76g	$Ni(NO_3)_2\ 6H_2O$	1.79469 g	$Ce(NO_3)_3\ 6H_2O$
0.34g	$Mn(NO_3)_2$	1.49287g	$Bi(NO_3)_3\ 5H_2O$
0.01153 g	$Pd(NO_3)_2$	2.62g	$Pb(NO_3)_2$

Add 50mL solution to beaker.

6. Add remaining water to bring the solution up to 1L.

7. Place in 50°C vacuum oven and dry to a constant weight, which should be around 1225g.

8. After drying, grind and homogenize the sample to less than 100 mesh.

Procedure for Adding Organic to Modified SYM-PAS-95

1. Weigh 20g modified SYM-PAS-95 into a 150mL beaker with a stirring apparatus. Add 100mL deionized water.

2. Mix the following components together; grind to less than 50 mesh; then add to solution.

29.34g	Na_3HEDTA	33.59g	$Na_3citrate\ H_2O$
7.41g	Na_4EDTA	29.66g	Na-glycolate

3. Stir and heat solution (<50ºC) until free liquid is removed.

4. Place mixture in a 50ºC vacuum oven and dry to constant weight.

5. Homogenize and grind to less than 100 mesh.

4.3.26 Single-Shell Tank C-103 Chemical/Physical Simulant

Names: **C-103-4; C-103-6; C-103-7**

Reference: LaFemina, J. P. (Task Leader) et al. 1995. *Tank Waste Treatment Science Task Quarterly Report for January – March 1995*, PNL-10763, Pacific Northwest Laboratory, Richland, Washington.

Purpose: Investigating how slurries behave as a function of particle types and solution conditions, e.g., sedimentation, viscosity, agglomeration.

Simple chemical simulants for C-103, developed in the IPM Solid-Liquid Separations Simulant Development Task, were used in sedimentation and agglomeration studies. These simulants were prepared using commercial colloidal phases. Components include $Fe(OH)_3$, SiO_2, $Al(OH)_3$, AlOOH, and $Ca_5(PO_4)_3OH$ (apatite). The presence or absence of apatite has a significant impact on the colloidal behavior of mixed systems. The constituents were added in ratios similar to those indicated in the chemical analysis of actual C-103 sludge. Phases present in C-103 were not know at the time, so the phases present in the simulant may not represent the phases present in the actual waste.

Preparation:

Materials

- $NaNO_3$
- NaOH
- $Fe(OH)_3$, primary particle size 0.1μm (e.g., Iron(III) Hydroxide, 13% slurry, code #18863, NOAH Tech Corporation)
- Colloidal SiO_2, primary particle size 0.1μm (e.g., Nyacol Silica Sol 9950, 50wt%)
- $Al(OH)_3$ (gibbsite), primary particle size 0.25μm (e.g., Alcoa Space Rite S-11)
- AlOOH (boehmite), primary particle size 20nm (e.g., boehmite, Vista Catapal D)
- $Ca_{10}(OH)_2(PO_4)_6$, (hydroxyapatite or HAP), primary particle size 0.1μm (e.g., tribasic calcium phosphate, Aldrich Chemicals or GFS Chemicals)
- HNO_3

Table 4.45. Estimated Compositions for Simulants C-103-4, C-103-6, and C-103-7

Constituent	Primary Particle Size (nm)	C-103-4 (wt%)	C-103-6 (wt%)	C-103-7 (wt%)
$Fe(OH)_3$	10	3.5	3.0	2.6
SiO_2	60	3.5	3.0	2.6
$Al(OH)_3$	250	0.75	0.65	0.57
AlOOH	20	0.23	0.2	0.17
$Ca_{10}(OH)_2(PO4)_6$	50	0	1.2	2.1
Total Solid		7.9	8.0	8.0
$NaNO_3$		1.2<u>M</u>	1.0<u>M</u>	0.8<u>M</u>

Instructions for three variants of C-103 Simulant

1. Add B* of 50 wt% SiO_2 to A* of 13 wt% $Fe(OH)_3$ slurry; stir.

2. Add C* of $NaNO_3$; stir.

3. Add D* of $Al(OH)_3$, E* of AlOOH, and F* of $Ca_{10}(OH)_2(PO4)_6$; stir.

4. Add 5M NaOH slowly with stirring until pH 12. Stir vigorously for 24 hours.

5. Add 5M HNO_3 slowly with stirring until pH 10. Add deionized water until the total volume is 200L. Stir for 3 hours.

*The amount to add depends on which simulant is being synthesized. Refer to Table 4.46 for values.

Table 4.46. Variants of C-103 Simulant

Constituent	"Small" Particle Size Variant	"Medium" Particle Size Variant	"Large" Particle Size Variant
A. $Fe(OH)_3$	158.66 kg (8.7 wt%)	135.33 kg (7.5 wt%)	117.28 kg (6.5 wt%)
B. SiO_2	41.29 kg (8.7 wt%)	35.19 kg (7.5 wt%)	30.40 kg (6.5 wt%)
C. $NaNO_3$	17.00 kg (1.0M)	17.00 kg (1.0M)	17.00 kg (1.0M)
D. $Al(OH)_3$	4.39 kg (1.9 wt%)	3.78 kg (1.6 wt%)	3.32 kg (1.4 wt%)
E. AlOOH	1.36 kg (0.6 wt%)	1.18 kg (0.5 wt%)	1.00 kg (0.4 wt%)
F. $Ca_{10}(OH)_2(PO4)_6$	0	7.03 kg (0.3 wt%)	12.31 kg (5.2 wt%)
Estimated total solids loading	20 wt%	20 wt%	20 wt%
Estimated slurry density (g/cm^3)	1.1 to 1.2	1.1 to 1.2	1.1 to 1.2

5.0 Simulant Description for Vitrification

In vitrification operations, it is assumed that the waste is taken from holding tanks, either in the form of solutions or slurry precipitates of metal hydroxides, mixed with glass precursor material (e.g., H_3BO_3, SiO_2, $CaCO_3$, etc.) or with glass frit, and then fed to a melter. Depending on the melter design and final processing steps, the feed can be introduced directly into the melter, dried first, then melted or dried, calcined, and melted. Section 5.1 discusses parameters in developing simulants for pretreated slurry, melter feed slurry and vitrification operations. Sections 5.2 and 5.3 describe simulants for HLW and LAW, respectively. The vitrification simulants are elaborated in section 5.4. Note that the following processes are often interrelated and there is not a clear distinction.

5.1 Parameters in Simulant Development for Vitrification Testing

In the following sections, the important aspects of actual waste properties appropriate in designing simulants for each sequence of the vitrification process step are explained. The general features of simulants and the important chemical and physical parameters applicable for developing tank waste simulants for various steps of vitrification processes are presented in three categories: 1) slurry simulants, 2) melter feed simulants, and 3) vitrification simulants.

5.1.1 Slurry Simulants

Regardless of the final vitrification unit operations to be employed, the constituents of the solution or slurry will be subjected to elevated temperatures while it is still in the liquid stage. A critical issue in designing these simulants is to accurately mimic the necessary chemical activity of the actual waste. The importance of including nitrate/nitrite, catalytic metal species and organic reductants as well as using the correct particle size distribution and mineralogical phase distributions of the precipitates are often critical to properly investigating the sludge packing factor, redox, volatility, and foaming issues encountered in the vitrification process. Emulation of chemical activity, as opposed to chemical composition, often allows researchers to substitute non-radioactive, less expensive, or less complex species as surrogates for the myriad of constituents that are present in the actual waste. For example, for the series of lanthanide ions present in some actual wastes, which in their entirety may complicate the experimental results, a single lanthanide ion can be used to represent the activity of all lanthanide ions present. Note that this approach does not exclude using the chemical composition of a given waste as a basis for designing simulants.

The importance of adequately simulating the activity of actual waste is illustrated by the following example. Hydrogen generation during the formating of Hanford Waste Vitrification Plant feed was first observed using a simulant that contained noble metals (Wiemers et al. 1993). Also, melter evaluations using insufficiently validated simulants can result in poor melter selection or design, or melter operation flaws such as those experienced by the PAMELA melter (Powell et al. 1995b). The real waste melt contained noble metals and had a higher viscosity and liquidus temperature. The resulting flow dynamics allowed the noble metals to settle in the flat-bottomed melter and shorted it out.

5.1.2 Melter Feed Simulants

Simulants for mimicing melter-feed at this stage require inclusion of glass precursor compounds or glass frit to the slurry simulants discussed in Section 5.1.1 or ones related to them. One of the issues in this case relates to the rheological properties encountered in transporting actual melter feed in pipelines. The important slurry transport properties are the mean particle size, particle size distribution, density of particles, concentration of solid particles, density of the carrier

solution, the yield stress and viscosity of the slurry, and the effect of temperature on the viscosity/rheology. A combination of these properties will affect the transport velocity and the pressure drop across the pipeline. For example, in slurry transport a robust turbulence is desired to keep all particle sizes suspended, or at a minimum, a moving bed of sediment in the lower portion of the pipeline should be maintained. Assuming fully suspended transport, the pressure drop across the transfer pipeline depends on the apparent viscosity of transported slurry. This slurry viscosity depends primarily on the carrier liquid viscosity and the slurry solids loading.

Another issue is properly allowing for the reactions that occur between waste species and glass precursor compounds or frit. These reactions dictate the sequence of melting events that occur during vitrification, which in turn determine how the feed material transforms to a molten phase. For example, the sodium nitrate and nitrite that occur in some dried melter feeds will melt at temperatures near 300 °C and later decompose to form nitrogen oxide gaseous compounds, such as NO and NO_2, and sodium oxides, which then react with silicates to form sodium silicates and oxygen gas. The generation of offgas from these reactions and the presence of lower melting sodium silicates produce an increase in the melt volume, which is an important process parameter that needs to be considered. If a proper simulant is not used in these evaluations, such issues can not be taken into account.

5.1.3 Vitrification Simulants

The vitrification simulants are used to make laboratory crucible melt feeds for the purpose of preparing glass for waste form evaluations. At this stage, duplicating the target elemental composition of the glass derived from the actual waste with simple oxides, carbonates, and other salts with appropriate substitutions of radioisotopes (if required) will give an appropriate glass. This is because when all the feed reactions and offgas events described in Section 5.1.2 are completed and the oxide melt is collapsed into a dense liquid, memory of the starting materials is lost. Simulants at this stage are designed to expedite the glass preparation process so that the effects of final glass composition on chemical durability, solubility limits, melt viscosity, etc. can be studied extensively. Using these simulants, the volatility of components can also be studied in many cases; however, caution must be used because the volatility of certain components (e.g., technetium, iodine, etc.) is dictated by what occurs in the melter feed at much lower temperatures.

5.2 HLW Processing

The HLW simulants were prepared by either using an anticipated "reference" composition of a blend of tank wastes or using the elemental composition of a pretreated actual waste core sample. For example, a HLW blend simulant for use in vitrification tests was based on estimates of the pretreated HLW sludge composition for tanks AZ-101, AZ-102, C-106 and AY-102 (Russell and Smith 1996). These simulants were a slurry precipitate of metal hydroxides, which in some cases were mixed with glass pre-cursor material (e.g., H_3BO_3, SiO_2, $CaCO_3$, etc.) or with glass frit. In most of the simulants discussed below, the acutely toxic and radioactive species were either replaced by appropriate surrogates or eliminated from the waste composition.

5.2.1 Slurry Simulant

The critical issues in designing slurry simulants were discussed in Section 5.1.1. The waste slurry simulants presented in the following sections were prepared by emulating historical chemical processing flow sheets used for producing neutralized current acid waste (NCAW) at the Hanford site. This method was used to prepare NCAW simulant (Wiemers et al. 1993). The procedure involved the addition of sodium hydroxide to metal nitrate solutions to form precipitates and to adjust the concentration of other components by directly adding the oxides, hydroxides, fluorides, and sulfates of those elements to match the chemical composition of the NCAW waste. Similar

procedures were used to prepare double shell tank/single shell tank waste blend (Tracy et al. 1995) and request for proposal blend (RFP) (Russell and Smith 1996). In the following sections, the simulant specification for these three types of HLW slurry waste simulants is presented.

5.2.1.1 NCAW Slurry Simulant

The NCAW simulant was designed to mimic the elemental composition of a target NCAW waste that was subjected to washing and pretreatment steps. The basic procedure to prepare NCAW simulant slurry was coprecipitating an oxyhydroxide stock slurry by adding sodium hydroxide to a nitrate solution containing major waste oxide elements (Fe, Ni, Zr, and Mn). The aluminum hydroxide was prepared by adding an $Al(NO_3)_3$ solution to a sodium hydroxide solution and adding the resulting slurry to the stock slurry. The soluble/slightly soluble salts (halides, hydroxides, nitrates, nitrites, sulfates, borates, phosphates, oxides, and oxalate) were added dry to the major oxide slurry. Two other slurries were added to the major oxides and soluble/slightly soluble slurry: 1) minor components of oxides and fluorides as an insoluble compound slurry, and 2) precipitated nitrates of noble metals (Rh, Pd, Ru) either added directly to the stock slurry simulant or coprecipitated in a separate step. Excess nitrate and sodium were removed by washing. These anions and cations were added in various concentrations with other elements, and the volume was reduced or water was added during various stages of simulant preparation to obtain an appropriate concentration. A schematic of the NCAW simulant preparation flowsheet is presented in Figure 5.1.

The reference composition for NCAW simulant was a target pretreated NCAW feed composition defined in FY 1991. In Table 5.1 (Wiemers et al. 1993) the anticipated composition of the NCAW simulant is compared with the composition of FY 1991 pretreated NCAW. Also, in this Table, the composition of the NCAW feed and NCAW simulant are presented as an equivalent of 125 grams of waste oxides per liter of slurry before adding the glass precursor material to the slurry. Note that the FY 1991 pretreated NCAW feed composition assumes a sludge washing factor for actual NCAW waste during the pretreatment processes and represent an anticipated composition.

There are several aspects of the NCAW simulant described that make it a reasonable HLW simulant for vitrification unit operations. Comparisons of actual AZ-101 and AZ-102 core sample properties with those of NCAW slurry simulant in the context of similar processing schemes were investigated extensively by Morrey et al. (1996). These studies are summarized below.

The chemical composition of washed-solids slurries from the three core samples (AZ-101 Core 1, AZ-101 Core 2, and AZ-102 Core 1) and two NCAW slurry simulants indicated that the composition of the actual NCAW waste is accurately emulated. With a few exceptions (e.g., Ag and Cr) the NCAW simulant accurately represented the chemical composition of the washed solids actual NCAW waste (Morrey et al. 1996). Issues such as the effects of volatility, redox chemistry, and hazardous offgas generation from various components of the actual NCAW slurry on the vitrification process can be accurately addressed using the NCAW simulant.

The physical properties of the core samples and the simulants were partially characterized. The oxide basis concentration in the two NCAW simulants fell within the range of the core samples. Centrifugation studies showed that when the slurry samples at similar solids loading (14 to 18 wt%) were centrifuged, the NCAW simulant had a significantly lower centrifuged solids density than the core samples (Morrey et al. 1996). These results indicate that the NCAW simulant soilds experience less compaction than the actual waste under the same conditions. Thus, the NCAW simulant form a greater height, lower density solids layer compared to actual NCAW core samples. A lower compaction of simulant suggest that at the same conditions the solids content in the

centrifuged layer of actual waste slurry/sludge is underestimated using a NCAW simulant. The compaction characteristics of the solids are important for filter processing and for sludge buildup and suspension in the slurry transport line.

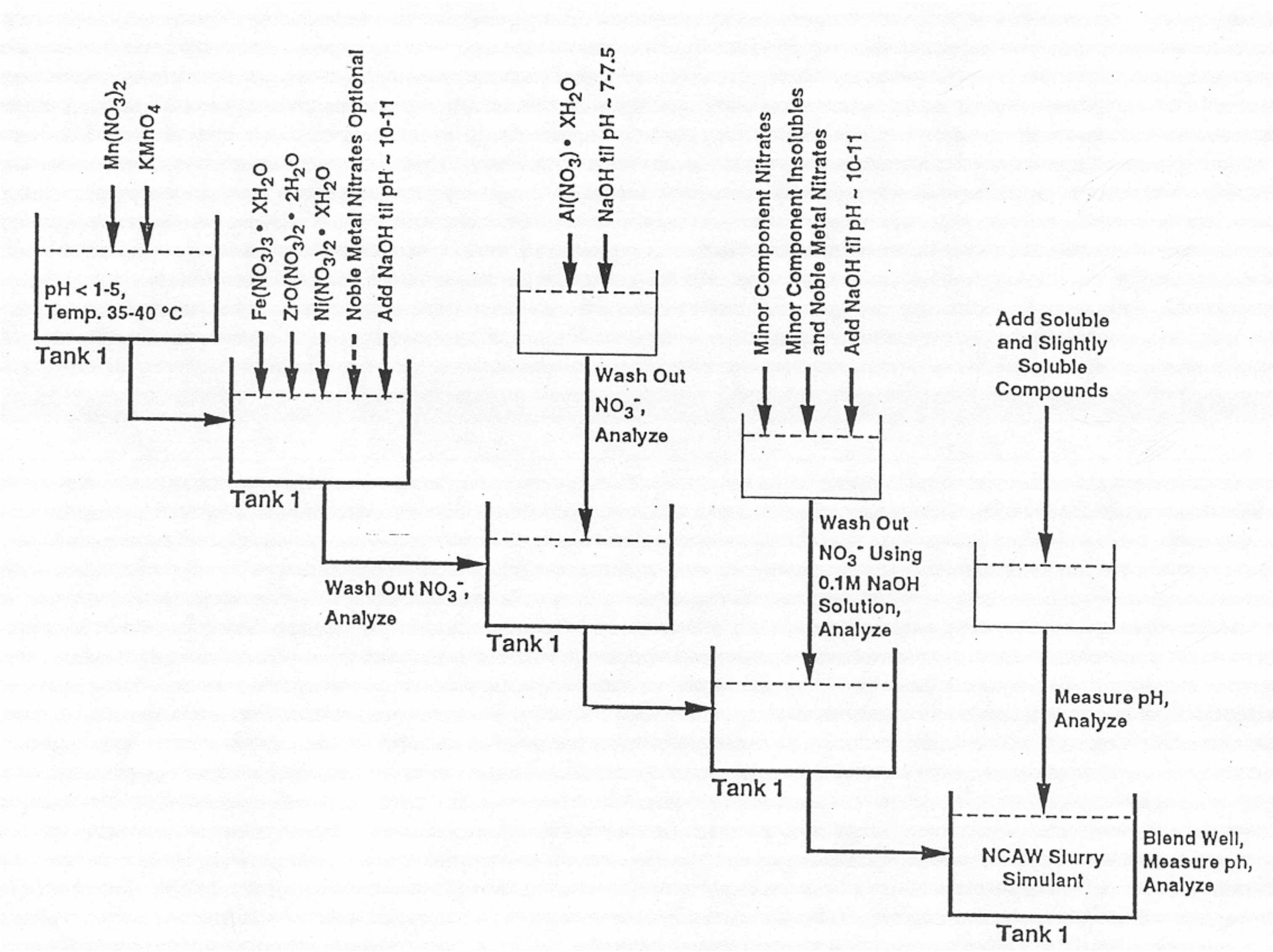

Figure 5.1. Schematic of the NCAW Simulant Preparation

Table 5.1. NCAW HLW Reference and Simulant Composition

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5.2.1.2 Scaled NCAW Slurry Simulant

The NCAW slurry simulant was prepared for various scales of process development testing for the Hanford Waste Vitrification plant (HWVP) project. Depending on the scale of testing, the outlined procedure was simplified or modified to meet specific HWVP testing objectives. The flowsheet for preparing laboratory scale simulant (see Figure 5.1) was used to make up to 50 liters of simulant. Similar procedures were used to prepare simulants for the research scale melter (RSM) and slurry integrated performance testing (SIPT).

Several hundred gallon batches of NCAW slurry simulant were prepared for the RSM testing. Since at this scale, the production of major components of the stock slurry would generate a lot of waste wash solution (several thousand gallons), the Optima Chemical Company was contracted to fabricate mixed hydroxide slurry in a slightly diluted form using a similar procedure as the laboratory scale flowsheet. Thus, the waste disposal problem was diminished. The addition of the rest of the components, including the soluble/slightly soluble components, noble metals, and minor components (Cooper et al. 1993) is similar to the laboratory scale procedure. The simulant preparation was carried out with one large mixing tank. The RSM simulant preparation flowsheet is presented in Figure 5.2.

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Figure 5.2. Research Scale Melter Waste Simulant Preparation Flowsheet

The procedure TP92-SIPT-100 (Kronschnabel 1992) was written to make 3900 gallons of NCAW slurry simulant at a time for SIPT testing activities. This procedure is similar to RSM procedure; however, at this scale, the chemicals were purchased in bulk quantities, which required additional composition adjustments and analyses to offset the lower chemical purity of the bulk materials. Also, the difference between the particle size of bulk materials and the laboratory grade minerals introduced grinding, pre-slurrying, pre dissolving steps to reach similar solids loading and composition as the RSM or laboratory scale simulants. In summary, additional preparation steps and analyses were required to qualify the SIPT simulant properties, and simulant preparation at this scale become more approximate.

5.2.1.3 Double Shell Tank/Single Shell Tank Waste Blend simulant

The double shell tank/single shell tank waste blend (waste blend) simulant (Tracy et al. 1995) was developed to emulate an anticipated composition of HLW feed representing a blend of the waste from 177 single shell and double shell tanks. The waste blend composition shown in Table 5.2 was based on the normalized Track Radionuclide Components (TRAC) inventory, historical tank data, and assumptions on the pretreatment of the waste. The waste simulant specification was written to prepare 1000 L of waste simulant. The procedure to prepare waste-blend simulant is included in Appendix A.

The waste blend simulant specification uses a procedure similar to that used for preparing the NCAW simulant. However, the elements Bi, W, Co, Np, Re, Th, Tl, Hg, V, and Cm, and the anion CN, which are present in the waste blend composition are not included in NCAW simulant composition. As with the NCAW, the organic component of the waste blend simulant was added as oxalate.

The waste blend preparation differs from the NCAW simulant preparation in that mineral phases such as boehmite, cancrinite, sodium silicate, and silica were used as sources of Al and Si. Also, Cyanide (CN^-) addition as $Na_2NiFe(CN)_6$ was proposed. Because of uncontrollable exothermic reactions of $Na_2NiFe(CN)_6$ in the presence of sodium nitrate it was suggested that the use of $Na_2NiFe(CN)_6$ in simulants should be employed only to meet specific testing objectives and its necessity should be carefully considered (Tracy et al. 1995).

Note that the chemical and physical properties of the waste blend simulant have not been measured due to discontinuation of the project. Thus, the application of this simulant for actual waste slurry has not yet been evaluated. However, this work formed the basis for future simulant development (e.g., RFP simulant) which not only accurately simulates elemental composition, but also the distribution of elements within different mineral phases.

Table 5.2. HLW Blend Reference and Simulant Composition

Table 5.2. HLW Blend Reference and Simulant Composition (contd)

Table 5.2. HLW Blend Reference and Simulant Composition (contd)

5.2.1.4 Request for Proposal Blend

This feed specification describes a method for preparing a waste simulant which corresponds to the high level waste (HLW) slurry composition provided in the privatization draft request for proposal (RFP). The simulant composition emulates the elemental composition of a calculated pretreated waste blend from tanks 101-AZ, 102-AZ, 106-C and 102-AY. The composition of this simulant is reported in Russell and Smith 1996. The blended waste simulant specification is written to prepare 1000 L of simulant slurry at 100 g waste oxide/L.

The RFP simulant composition in terms of batching chemicals and oxide compounds is shown in Table 5.3. In Table 5.4 the anionic composition of the RFP slurry simulant is presented. The procedure to prepare this simulant is described in detail in Appendix B. In this specification, boehmite (AlOOH) was used as a source of aluminum hydroxide precipitate. The boehmite phase has been identified in some actual HLW sludges. For example, it is reported that most (>50%) of the crystalline phase in actual sludge sample from tank S-104 is boehmite phase (LaFemina 1995c).

Other minerals such as cancrinite {$Na_8(AlSiO_4)_6(HCO_3)_2$} can be added to the RFP simulant composition as another source for Al and Si. Some aluminosilicate phases are reported to remain in HLW sludges even after caustic leaching processes (LaFemina 1995c) and the zeolite-like feature of cancrinite make it to be a reasonable aluminosilicates phase that resist dissolution in tank sludges. The procedure to prepare cancrinite is described in detail in Appendix A for waste-blend simulant specification. As more knowledge is gained about the mineral phases that are present in the actual waste, more appropriate simulants can be developed in the future.

Table 5.3. RFP Simulant Composition at 100 g oxide/L

Element	Batched Oxide Wt%	Source Chemical	Formula Wt. (incl. water)	Oxide Factor	Chemicals g/L (100 g oxide)
Ag	0.060	$AgNO_3$	169.87	0.682	0.088
Al	17.870	Al(OOH)	59.98	0.850	21.024
As	0.000	deleted	0.000	0.000	0.000
B	0.139	H_3BO_3	61.83	0.563	0.247
Ba	0.610	$Ba(OH)_2 \cdot 8H_2O$	315.48	0.486	1.255
Bi	0.060	$Bi(NO_3)_3 \cdot 5H_2O$	485.07	0.480	0.125
Ca	2.000	$Ca(NO_3)_2 \cdot 4H_2O$	236.16	0.237	8.439
Cd	1.290	$Cd(NO_3)_2 \cdot 4H_2O$	308.47	0.416	3.101
Ce	0.119	$Ce(NO_3)_3 \cdot 6H_2O$	434.23	0.378	0.315
Cl	0.090	NaCl	58.44	0.590	0.153
Cr	0.328	$Cr(NO_3)_3 \cdot 9H_2O$	400.15	0.190	1.726
Cs	0.617	$CsNO_3$	194.91	0.723	0.853
Cu	0.070	$CuSO_4 \cdot 5H_2O$	249.68	0.319	0.219
F	0.090	NdF_3	201.24	0.283	0.318
Fe	24.626	$Fe(NO_3)_3 \cdot 9H_2O$	404.00	0.198	124.374
K	0.430	KOH	56.11	0.839	0.513
La	0.507	$La(NO_3)_3 \cdot 5H_2O$	414.91	0.393	1.290
Mg	1.194	$Mg(NO_3)_2 \cdot 6H_2O$	256.41	0.157	7.605
Mn	0.770	$Mn(NO_3)_2$	178.95		0.950
		$KMnO_4$	158.04		0.560
Mo	0.010	MoO_3	143.95	1.000	0.010
Na	23.820	NaOH	40.00	0.775	30.735
Nd	1.020	$Nd(NO_3)_3 \cdot 6H_2O$	438.35	0.384	2.656
Ni	1.030	$Ni(NO_3)_2 \cdot 6H_2O$	290.81	0.257	4.008
P	1.040	Na_3PO_4	163.94	0.433	2.402
Pb	0.340	$Pb(NO_3)_2$	331.20	0.674	0.504
Pd	0.020	$Pd(NO_3)_2$	230.41	0.531	0.038
Pu	0.000	deleted	0.00	0.000	0.000
Re	0.570	ReO_2	218.21	1.000	0.570
Rh	0.050	$Rh(NO_3)_3$	288.92	0.439	0.114
Ru	0.060	$RuNO(NO_3)_3$	317.09	0.395	0.152
Sb	0.150	Sb_2O_3	291.50	1.000	0.150
Se	0.200	SeO_2	110.96	1.000	0.200
Si	16.120	SiO_2 (quartz)	60.09	1.000	16.120
Sr	0.080	$Sr(NO_3)_2$	211.63	0.490	0.163
SO3	0.470	Na_2SO_4	142.04	0.564	0.833
Tc	0.000	Subst NH_4ReO_4	484.40	1.000	0.000
Te	0.140	TeO_2	159.60	1.000	0.140
Ti	0.060	TiO_2	79.90	1.000	0.060
Tl	0.000	subst. $Nd(NO_3)_3 \cdot 6H_2O$	438.35	0.384	0.000
U	0.000	subst. $Nd(NO_3)_3 \cdot 6H_2O$	438.35	0.384	0.000
V	0.000	deleted	0.00	0.000	0.000
Zn	0.040	$Zn(NO_3)_2 \cdot 6H_2O$	297.47	0.274	0.146
Zr	3.910	$ZrO(NO_3)_2 \cdot 2H_2O$	267.26	0.533	7.336
Total	100.000				

Table 5.4. Nitrogen and Carbon Components of the RFP Simulant

Component	g/100 g WO	Source Chemical	Anion Equivalent	Source Chemical
			g/g	g/100g WO
NO_2^-	2.588	$NaNO_2$	0.667	3.880
NO_3^-	1.540	$NaNO_3$	0.729	2.112
TOC	0.732	$Na_2C_2O_4$	0.179	4.089 as carbon
TIC	5.988	Na_2CO_3	0.566	10.580

5.2.2 HLW Vitrification Step Simulant

See section 5.4 for a combined discussion on HLW and LAW vitrification step simulants.

5.3 LAW Processing

The Hanford Site LAW is characterized by high nitrate, nitrite, and hydroxide concentrations. Nitrogen-containing offgas products will naturally be of concern during the LAW processing. For example, NO_x is environmentally damaging and can affect the volatility of certain radionuclides via gas-phase entrainment at elevated temperatures.

The LAW simulants are solutions that may contain a residual amount of suspended solids. These simulants are developed to emulate the chemical composition of the LAW waste. In contrast to the HLW simulant development, the LAW simulant efforts are considerably less complex due to the lack of issues encountered with emulating the correct particle size distribution, mineralogical phase distributions of the precipitates, or mimicing the catalytic characteristics of metals in slurry systems. The chemical composition of LAW simulants is defined as an overall "volume-weighted" average composition based on a combination of waste tank analysis and process knowledge.

5.3.1 Supernatant Slurry

In the first phase of developing LAW vitrification simulant development for evaluating LAW melter technology evaluation, two waste stream compositions were used. The first waste simulant was based on the analyses of six tanks of DSSF waste and the projected composition of the LAW waste exiting the pretreatment unit operations. The chemical composition of this simulant was normalized to 6 M sodium to mimic an anticipated chemical composition after initial ion exchange and solid-liquid separation. The same simulant at 10 M sodium was prepared to represent the chemical composition of DSSF waste that was concentrated by evaporation to reduce the overall volume. The second LAW simulant, referred to as the remaining inventory (RI), encompassed the entire inventory of tank wastes except for that included in the DSSF waste stream discussed above. In Table 5.5, the chemical composition of these three LAW simulant solutions and the chemical compound used in these formulations are presented. Detailed preparation procedures for laboratory scale and large scales of approximately 13,000 liters are described in Lokken (1995).

The DSSF simulant is intended to be a surrogate for the DST wastes. Excluding the radionuclide components, comparison between the DSSF at 10 M sodium and the actual supernatant composition of the Hanford DST Tank AW-101 (which is already at 10 M sodium

concentration) shows reasonable agreement (within a factor of 2) of nearly all the components at 10 M sodium listed in Table 5.5. The RI supernatant is intended to simulate the larger volume of SST supernatants. The chemical composition variability analyses using the tank inventory data files indicated that the concentration of minor component Cl^- and F^- in the DST sources was higher than the DSSF surrogate, and the concentration of SO_4^{2-} and PO_4^{4-} was above those of RI supernatant (Lokken 1996). The concentration of these minor

Table 5.5. Composition of LAW Tank Waste Simulants Tested During Phase 1. (from Lokken 1995)

Component	DSSF 6 M Na (moles/L)	DSSF 10 M Na (moles/L)	IR (moles/L)	Compound Used in Formulation
$Al(OH)^{4-}$	0.61	1.0	0.16	$Al(NO_3)_3.9H_2O$
Ca^{2+}	0.00063	0.0010	0.0004	$Ca(NO_3)_2.4H_2O$
$Cr(OH)^{4-}$	0.0052	0.0087	0.0042	$Cr(NO_3)_3.9H_2O$
Fe^{3+}	0.00046	0.00077	0.00024	$Fe(NO_3)_3.9H_2O$
K^+	0.30	0.50	0.0058	KOH
Mg^{2+}	0.00062	0.0010	0.0000011	$Mg(NO_3)_2.6H_2O$
Mn^{2+}	0.00025	0.00042	0.001	$Mn(NO_3)_2$
MoO^{4-}	0.01	0.017	0.01	$NaMoO_4.H_2O$
Na^+	6.0	10.0	6.0	$NaNO_3$
Sr^{2+}	0.01	0.017	0.01	$SrCl_2$
Cs^+	0.01	0.017	0.01	$CsNO_3$
PO_4^{3-}	0.026	0.043	0.11	$NaH_2PO_4.H_2O$
IO_3^{3-}	0.01	0.017	0.01	$NaIO_3$
CO_3^{2-}	0.16	0.27	0.05	Na_2CO_3
Cl^-	0.096	0.16	0.0092	NaCl
F^-	0.15	0.25	0.13	NaF
SO_4^{2-}	0.026	0.043	0.038	Na_2SO_4
NO^{3-}	1.9	3.1	3.5	$NaNO_3$
NO^{2-}	1.0	1.7	0.26	$NaNO_2$

OH^-	**2.3**	**3.8**	**1.5**	**NaOH**
TOC	**0.81**	**1.4**	**0.11**	**$Na_4EDTA.2H_2O$**

components in the glass (typically as SO_3 and P_2O_5) strongly influence the glass durability (Li et al. 1995a,b). Therefore, matching the composition of these components to that of the actual waste should be carefully considered while designing the LAW simulants.

5.3.2 LAW Melter Feed Step

In LAW melter feed slurry, glass precursor material (e.g., SiO_2, H_3BO_3, etc.) or frit is added to the LAW solution to bring the final glass composition to waste form specification. For example, one of the proposed final waste glass compositions "LD6-5412" is based on 26.7 wt% oxide equivalent loading of DSSF LAW feed (e.g., K^+, SO_4^{2-}, F^-, etc., ions in the LAW are converted to K_2O, SO_3, F, etc., in the final glass). The glass precursor material or frit is combined with LAW (e.g., DSSF) to form a slurry, which is then vitrified.

One particular concern, which also helps illustrate the need for developing proper simulants, during LAW vitrification is the volatilization of minor components, such as technetium and iodine. For example, it is still not clear how much and in what form technetium is in the Hanford tank wastes; thus, it is not yet fully known how much of the technetium needs to be removed from the waste stream during pretreatment. Furthermore, the mechanism of technetium removal (in both pertechnetate and non-pertechnetate form) is not yet clear, e.g., ion-exchange for pertechnetate removal in conjunction with deliberate volatilization and collection for non-pertechnetate (DOE Technetium Workshop 1997).

For this latter scenario, emulating the chemical behavior of technetium in potential LAW simulants will thus be an important issue for evaluating volatility. In many instances, the chemistry of technetium and rhenium compounds are similar enough that rhenium can be successfully used as a non-radioactive surrogate for technetium (since there are no non-radioactive isotopes of Tc) (Darab 1996).

It is not only important to emulate the chemical activity of technetium and other troublesome minor components, but also the major components, such as sodium. In evaluating the volatility of technetium and rhenium from dried LAW streams during vitrification, the simulant composition, and hence chemistry, becomes an important consideration. For a desired simulated waste glass composition, the final material can be derived using a variety of chemical reagents. A glass composition having a certain fraction of Na_2O, for example, can be made from simulants containing Na_2CO_3 or $NaNO_3$.

The composition of the initial liquid and the temperature at which it forms during vitrification will depend on the compounds that are used to make up the simulant. This, in turn, will govern how the simulant densifies from a collection of liquid-coated glass precursor particles having open porosity, through which volatilized and/or entrained species can readily escape through the melt to a consolidated form in which volatility will most typically be controlled by diffusion through the melt. For example, attempts to evaluate technetium/rhenium volatility using LAW simulants derived from higher melting oxides, carbonates, sulfates, phosphates, and halides yield unrealistically greater volatility results compared to those obtained using simulants more akin to the actual waste (i.e., containing nitrates, nitrites, hydroxides, phosphates, sulfates, and halides along with glass precursors) (Darab 1996).

5.3.3 LAW Vitrification Step Simulant

See section 5.4 for a combined discussion on HLW and LAW vitrification step simulants.

5.4 HLW and LAW Vitrification

Processing a chemically complex melter feed simulant, whether it is a HLW or LAW simulant, containing water, metal cations, nitrates, nitrites, hydroxides, etc. to sufficiently high temperatures will eventually yield a dense molten oxide phase that would be essentially the same as one prepared from simple oxides, carbonates, and other salts processed at similar temperatures. This is because the melting process essentially wipes out material memory of how it was batched. At this stage of processing, the important parameters include such aspects as melt viscosity, component solubility, settling of insoluble components, crystallization, and chemical durability of the final waste form. Simulants readily made from simple oxides, carbonates, sulfates, phosphates, and halides will usually suffice (Hrma et al. 1994, Li et al., 1995a, Li et al., 1995b).

For example, to investigate the chemical durability of LAW glasses, containing a high concentration of minor components (Cl, F, P_2O_5, SO_3 and Cr_2O_3) Li et al. (1995b) prepared a simple LAW simulant. This simulant was prepared by using L6-5412 baseline glass (with 26 wt% waste loading) composed of SiO_2 (0.568), B_2O_3 (0.05), Na_2O(0.2), CaO (0.04), Al_2O_3 (0.12) and others (0.022) based on a mass fraction. Others were a sum of Bi_2O_3, Cl, Cr_2O_3, F, Fe_2O_3, K_2O, MnO, Nd_2O_3, P_2O_5, SO_3, and ZrO_2. Glass batch materials were made using chemical regents: oxides, boric acid, carbonates, and sodium-containing salts (Li et al. 1995a).

Using these simulants the volatility of components can also be studied in many cases (Li et al. 1995b), however, as discussed above, caution must be used as certain components (e.g., technetium) have their volatility dictated by what occurs in the melter feed at much lower temperatures (Darab 1996).

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