

# **SAND REPORT**

SAND2002-0627

Unlimited Release

Printed July 2002

## **Occurrence, Characterization and Synthesis of Hanford and SRS Tank Heel Materials**

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**Abstract**

The long-range objective of this study was to develop chemically assisted technologies for removing heels from tanks. In FY 01, the first two steps toward this objective were taken: (1) catalogue the occurrence and nature of tank heels and assess which materials are available for study and (2) develop methods for synthesizing non-radioactive surrogate heel materials for use in testing potential removal technologies.

The chief finding of Task 1 was the existence of "heels", depending on the definition used. Hard materials that would be almost impossible to remove by sluicing are all but absent from the records of both Savannah River and Hanford. Historical usage suggests that the term "heel" may also apply to chunky, granular, or semi-solid pasty accumulations. These materials are documented and may also be difficult to remove by conventional sluicing technologies. Such heels may be comprised of normal sludge components, dominantly iron and aluminum hydroxides, or they may result from added materials which were not part of the normal fuel reprocessing operations: Portland cement, diatomaceous earth, sand and soil and spent zeolite ion exchange "resins". The occurrence and chemistry of the most notable "heel", that of the zeolite mass in Tank 19F at Savannah River, is reviewed in some detail. Secondly, no clear correlation was found between high tank temperatures and difficulties encountered in removing materials from a tank at a later date; nor did the sludges from these tanks give any indication of being particularly solid.

Experimental studies to develop synthetic heel materials were carried out using a number of different approaches. For normal sludge materials settling, even when assisted by a centrifuge, it proved ineffective. The same result was obtained from drying sludge samples. Even exposing sludges to a molten salt melt at 233°C, only produced a fine powder, rather than a resilient ceramic which resisted disaggregation. A cohesive material, however, was produced by wicking the pore fluid out of a sludge gel (into packed diatomaceous earth), while simultaneously applying pressure to compact the sludge as it dehydrated. Osmotic gradients could provide the same function as the capillary forces provided by the diatomaceous earth sorbant placed in contact with the sludge. Tests on the anomalous materials added to the tanks all indicated potential problems. Hard granules, and maybe chunks, may be encountered where Portland cement was added to a tank. Sand, spent zeolite resin, and diatomaceous earth, will all react with the tank fluids to produce a sodalite/cancrinite material. The degree of reaction determines whether the grains become cemented together. SRS activities showed that heels formed when spent zeolites were added to

tanks can be readily dislodged and it is expected that heels from sand would possess equal or less cohesion. Diatomaceous earth may form more resilient crusts or masses.

To summarize, the existence of "hard" heels has yet to be documented. A broader definition suggests inclusion of poorly cohesive cancrinite-cemented masses and dense past-like accumulations of abnormally compacted "normal" sludges. Chemical treatments to remove these materials must focus on agents that are active against aluminosilicates and hydrous oxides of iron and aluminum. Exploiting the high pore-water content of these materials may provide a second avenue for dislodging such accumulations. Techniques were developed to produce synthetic sludges on which various removal technologies could be tried.

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## 1.0 Introduction

The DOE complex contains numerous underground tanks filled with high level nuclear wastes (HLW) derived from Cold War weapons production activities. Although it is generally accepted that the tanks cannot be cleaned completely prior to decommissioning, there is a strong incentive to remove as much waste as possible. For most tanks, the balance of the wastes can be extracted using dilute NaOH fluids to dissolve the soluble salts, mostly sodium nitrate, nitrite, hydroxide and aluminate and amorphous aluminum phosphates (Lumetta, et al., 1997; TFA, 2000). In conjunction with mild agitation, most of the insoluble "sludge" particles (largely iron hydroxides with a host of minor components), can also be removed as a dilute suspension.

However, more resilient materials have occasionally been encountered adhering to the walls and bottoms of tanks that could not be removed by conventional sluicing techniques. There is speculation that more of these features may be encountered as additional tanks are readied for closure. Over the years, such accumulations have come to be referred to as "heels". This term lacks rigorous definition, but occasionally is used to imply a material with considerable strength. In other instances, the term may refer to a semi-solid sludge ranging from "the consistency of margarine", to something that is described as "firm" (Agnew, et al., 1993). In this instance, the "firm" material is a white, presumably Al-rich layer, that probably originated from decladding operations. Recorded tank temperatures never approached boiling, so presumably, the "firm" condition can be achieved while the sludge remains hydrated. It is probable that similarly wet mixtures of hydrous iron and aluminum oxides are responsible for the numerous heels reported at Hanford by Agnew, et al., 1995.

Radionuclides associated with heels may either be entrained in the solids or dissolved in the substantial amounts of pore fluid (Georgeton and Hester, 1995). In terms of developing removal technologies, it is important to identify the relevant source phase for the radionuclide in question. Cs, for example, will largely reside in the pore fluids, while Sr will principally be associated with the iron oxide component in the sludge. Where several inches (or more) of a heel cover the bottom of a tank, the radionuclide inventory may be great enough to preclude decommissioning of the tank without first removing the heel. Although some radionuclides may, in fact, reside as nuggets of a minor phase in the mass of the heel, it is presumed that these nuggets cannot be accessed for either chemical or mechanical removal until the heel has been disrupted.

***The long-term objective of this program is to develop chemical technologies to significantly decrease the cost of heel removal.***

Thus key steps toward this end objective are:

- (a) identifying the primary heel-forming materials by surveying site documents [Current FY],
- (b) developing techniques for making synthetic, non-radioactive heel materials [Current FY],
- (c) developing and testing novel chemical removal technologies on the synthetics before incurring the cost and risk of performing validation tests on the very limited amounts of actual heel materials, which presently reside in the sample inventories at the various sites where wastes are stored (principally Savannah River and Hanford National Laboratories) [to be addressed in out years].

Because "heel" is a catchall term, it is likely that many different materials could be involved. In some cases, heels may form from normal waste constituents, (principally the sludge component) that have been subjected to unusual conditions. Alternatively, certain tanks may have additions of special materials, notably spent zeolites, used to scavenge Cs (Fowler and Wallace, 1980, Caldwell, et al. 2001). At Hanford, Portland cement, soil, or diatomaceous earth (intended to stabilize the waste and slow leakage), may have contributed to heel formation. At both sites, the key to predicting heel formation is to understand the interactions between the normal waste fluids and the unusual materials which may have been placed in the tank.

## ***2.0 Review of Waste Production Activities:***

### *2.1 Normal sludges:*

It is not the intent of this report to provide a comprehensive overview of the waste producing processes. Excellent reviews are already provided by Cleveland, 1970, and Agnew, 1996; however, this brief discussion is provided as a basis for understanding the multiple origins of “heel” materials. It is also important to note that the historical development of operations at Hanford differed significantly from that at Savannah River. The first major fuel reprocessing (and Pu recovery) operations were conducted at Hanford; consequently, the chemical technology used at Hanford evolved over time. The three primary reprocessing technologies used at Hanford were: the Bismuth Phosphate Process, the REDOX process and the PUREX process, (though in reality, each technology also involved process modifications as experience was gained). In addition, after their primary production, Hanford wastes were reworked to recover various constituents. The need to recover uranium from bismuth phosphate wastes led to the development of the tri-butyl phosphate (TBP) process. Sr and Cs were also recovered by specialized processes from a subset of the wastes. Processing at Savannah River came later and was restricted to just PUREX process wastes. Other operations at both sites have, over the years, introduced significant amounts of oxalate into certain waste tanks.

In spite of the extreme complexity inherent in the individual processes, there are regularities that impart a degree of similarity to all the wastes. The primary aqueous waste streams were all generally nitric acid solutions. Since the intent was to place these wastes in underground mild steel tanks, all of the wastes were rendered highly caustic by adding NaOH and the nitrate to nitrite ratio was adjusted to preclude stress corrosion cracking of the tanks, Goslen, 1986. Although at the minor trace amount levels, the insoluble precipitates produced by adding base are highly variable, almost all sludges are dominated by either iron or aluminum hydrous oxides. Lesser amounts of Ni, Cr, Bi, U and  $\text{PO}_4^{3-}$  may also occur. Generic sludge recipes in the literature contain, individually, less than 15% of each of these components (by weight of insoluble solids). After being rendered caustic, some wastes were placed directly in tanks. Others were concentrated by evaporation prior to being placed in tanks and still others were either allowed to self-heat or artificially heated in order to eliminate water. Thus, most of the fluids remaining in tanks are highly concentrated salt solutions that are close to saturation, with one (or more) of the main salts in the waste ( $\text{NaNO}_3$ ,  $\text{NaNO}_2$ , NaOH, Na aluminate. Although the wastes have been mixed often in subsequent years, much of the phase chemistry of the insoluble “sludge” components, was fixed at a time when the wastes were initially neutralized. Thus, subsequent blending of the contents of various tanks often merely resulted in nothing more than the mechanical mixing of the insoluble sludge components. An exception is boehmite “freezing”, where mixing the contents of different tanks lowers the pH leading to additional boehmite precipitation and causing the mass to set up as a gel.

### *2.2 Cladding Wastes:*

The early reprocessing technologies started with removing the cladding, which held the uranium pellets together in fuel pins. For the most part, fuel was clad with Al alloys, though a lesser amount of zircalloy clad fuel was also processed (Kupfer, et al. 1997). Wastes from cladding removal are distinct from those which evolved from various Pu/U recovery operations. Not only was the principal element make-up significantly different, but the radionuclide loading was significantly less, since most of the fission and activation products remained sequestered inside the fuel pellets. Most cladding wastes are rich in aluminum and were derived by dissolving the metal in concentrated NaOH solutions (Lumetta, 1994). However, in the latter stages of Savannah River operations, it was found that the caustic treatment could be avoided by treating the aluminum cladding with an Hg catalyst. At this point, the separate cladding waste stream disappeared and instead, the aluminum was included in the main waste stream from U/Pu recovery operations (Caldwell et al., 2001). It is also noteworthy that, in the early days of Hanford reprocessing, some of the cladding wastes were commingled with  $\text{BiPO}_4$  fuel reprocessing wastes to producing sludges with elevated Al levels.

A further complication is the small amount of zircalloy fuel that was declad by a separate process. Wastes from this process would, in addition to zirconium, have been rich in fluoride. The active agent in dissolving Zr-cladding was not sodium hydroxide. Instead, the process used  $\text{NH}_4\text{F}$  with minor  $\text{NH}_4\text{NO}_3$  (Swanson, 1958). No obvious heel-forming interactions can be identified with this process, although in an environment rich in both sodium and aluminum, the mineral cryolite ( $\text{Na}_3\text{AlF}_6$ ) should form at least in small quantities. General chemistries for decladding waste streams are found in Table 1.

**Table 1 - Cladding Waste Stream Chemistry (from Anderson, 1990)**

Waste	Components	Concentration (molar)
Aluminum-Clad Fuel Coating	$\text{NaAlO}_2$	1.2M
	$\text{NaOH}$	1.0M
	$\text{NaNO}_3$	0.6M
	$\text{NaNO}_2$	0.9M
	$\text{Na}_2\text{SiO}_3$	0.02M
	Pu	0.4%
	U	0.4%
Zircalloy-clad Fuel Coating	$\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$	0.1M
	$\text{NaF}$	0.7M
	$\text{NaNO}_3$	0.02M
	$\text{KF}$	0.01M
	U	0.001 lb/gallon
	Pu	0.001 lb/gallon
	pH	10

### 3.0 Theoretical Considerations

The first step in understanding the potential for heel development from normal sludges is to address the colloidal chemistry of such materials (Rector and Bunker, 1995). On a mass balance basis, sludges are predominantly mixtures of hydrous iron and aluminum oxides, with a large percentage of entrained pore fluid, "supernate". Al occurs on three major sludge phases: less than 10 nm "primary particles" of boehmite, 1-40 micron particles of gibbsite and submicron-sized aluminosilicate "clay-like" materials. Studies of Savannah River sludges suggest that gibbsite is only stable in sludges that remain significantly below boiling, since elevated temperatures drive the dehydration reaction which change  $\text{Al}(\text{OH})_3$  to  $\text{AlO}(\text{OH})$ . The "clay-like" aluminosilicates are, in fact, equi-dimensional granular zeolites. To form significant amounts requires an "anomalous" silica source, with silica added in excess of that normally present in fuel reprocessing waste streams. In contrast to the platy nature of gibbsite and fibrous habit of boehmite, iron-rich sludges are made up of equi-dimensional grains of various, very poorly crystalline, hydrous iron oxides. Primary particle grain sizes are similar to boehmite (5-10 nm).

Sludge formation takes place in three steps: (1) the aggregation of the primary precipitate particles formed when acid wastes are neutralized prior to being placed in tanks (2) the settling of aggregate particles in the tanks and, finally (3) the effects of post-settling compaction processes.

The aggregation of primary particles is best described as a fractal process, where the geometric characteristics of the particle are replicated on successively larger scales, as the particle size increases. The primary particles, typically 5-10 nm across (except where gibbsite is involved), come together forming clusters ranging from a fraction of a micron to several microns. These, in turn, can further coalesce to larger masses, ranging from tens of microns to millimeters in size. Primary particles interact because of electrostatic and van der Waals forces. The latter dominates over very short distances (less than 10 nm). In dilute solutions, the electrostatic term acts over substantially greater distances and provides a substantial potential energy barrier to the approach of two particles with like surface charges. However, with increasing ionic strength, the effective range of this potential term decreases, so that in brines, particles can readily approach each other although they formally have like surface charges.

Electrostatic interactions also depend on the surface charge of the particle that is, in turn, directly related to the pH of the solution. Hydrous iron and aluminum oxides will have positive surface charges below pH 9-10 and negative surface charges above this range. Thus, in most waste fluids, the surface charge will be distinctly negative. However, as precipitates formed during the initial neutralization of the nitric acid waste fluids there may have been a brief time when positive surface charges existed. At this stage, anions such as pertechnetate, may have been incorporated into the cores of some grains (Zhang et al, 2000). As neutralization progressed, however, the surface charge would switch signs, and cations rather than anions, would sorb on the surfaces of the growing particles. The strong negative surface charge acquired in typical pH 13 tank fluids, implies that the particles should repel and remain in suspension. However, this is more than offset by the high ionic strength of such fluids, so particles always flocculate into clusters and settle to form a sludge on the bottom of the tank.

The volume of any particle, fractal or not, scales with  $r^3$  (where  $r$  is the particle radius); however, the amount of solid included in fractal particles typically increases with  $r^x$  where  $x$  assumes values less than 3. Thus, as particle radius increases, the density of the particle decreases rapidly. In high ionic strength supernates (where there is no electrostatic potential barrier causing the particles to repel each other), every interparticle collision increases the size of the aggregate. This produces a relatively loose packing so the mass of solid in the particle increases only at rates which scale with  $r^{1.8-2.1}$ . Ionic strengths may have been lower than typical late stage tank supernates, when the wastes were initially neutralized. This would have the effect of slightly increasing the upper limit on the value of  $x$ . However, a value of  $x = 2.25$  is about as high as can be expected. In practical terms, these constraints dictate that a 100 nm  $\text{Fe}(\text{OH})_3$  aggregate will only have about 18% as much hydrous iron oxide as a (completely solid) primary particle of the same size. For 1000 nm (1 micron) aggregate particles, the figure drops to 0.6%.

The second step in the formation of a sludge layer involves aggregate particles settling to the bottom of the tank. Settling of an  $\text{Fe}(\text{OH})_3$  suspension, having more than 4 wt% solids, produces a well-defined interface between clear supernate and a region made opaque with suspended particles. The particle-rich layer slowly collapses until the gel limit is approached. The gel limit is the point where particles come in contact to the degree they support their own mass. When this was achieved, further settling only occurs under the influence of applied stresses (mechanically stresses or the weight of the overlying sludge), or when pore water is removed by a chemical potential gradient.

With a lower loading of colloidal particles, a third relatively high density-layer of particles appears below the layer of suspended particles. This dense bottom layer forms quickly because, at the lower colloid loading, individual aggregates fall with far less interference from other particles and reach the bottom relatively quickly.

The nature of gels is such that the volume percent solid of the gel increases with decreasing aggregate size (at the same primary particle diameter) and increases with the size of the primary particles in the aggregate. Typically, the gel point for sludge materials ranges between a fraction of a percent to about 10 wt% solids (assuming  $\text{Fe}(\text{OH})_3$  based materials). Al is lighter, so the upper limit would be somewhat less for Al-based solids. Even in extreme cases, with a 100 micron primary particle size (e.g., gibbsite) and 100 micron aggregates, a gel can be expected when the mass contains only reach 16% solids (again expressed as wt %  $\text{Fe}(\text{OH})_3$ ).

Implicit in the preceding discussion is the conclusion that the many different results can be obtained, depending on the conditions under which sludge initially settles to the bottom of a tank. A further complication is, that under laboratory testing, sludge characteristics may change in response to changing experimental environments (Rector and Bunker, 1995). Large aggregate particles formed in concentrated colloidal suspensions can break down when the colloid loading is lowered. As a case in point, it was found that diluting a suspension of colloidal gold particles with an initial aggregate particle, distribution centered on 45 microns resulted in a suspension where the aggregate particle distribution centered on 1.6 microns.

The impact of all these factors probably explains why it is so difficult to prepare artificial sludges, which match the settling behavior of actual sludges (Morrey and Tingley, 1996). In this study, sludges were produced as a consequence of neutralizing nitric acid solutions with similar chemistries, to the real sludges; however, the artificial preparations usually fail to settle as fast as the real sludge particles. Actual sludges in the conditions of the experiment, had particles in the 1-5 micron particles and an additional distribution in the 75-120 micron range. The synthetic sludge also had a small distribution of particles centered on 5 microns, but the balance of the particles was in the 35-45 micron range. Thus, differences in the preparation or subsequent history of the colloids, produced different settling behaviors. In addition, the degree to which the initial particle size distribution of the tank sludge by earlier washing operations is not known.

The final, and most important point to be made however, is, not the great potential for variability in sludge formation. Rather, it is that once formed, the gels may possess modest strength (Fig. 1) without there being significant bonding of the aggregate particles. Thus, one would expect they could be re-suspended with modest agitation. Further, in spite of their resilience, such materials are not naturally dense enough to qualify as what is commonly perceived as a "heel".

Relatively complex models exist for predicting how fluids might be expelled from sludge suspensions in response to externally applied pressure (Rector and Bunker, 1995). For present purposes, it is merely sufficient to note the necessity for such a process and identify situations where this may have occurred. Expulsion of pore fluids may, in fact, occur widely in high-level waste (HLW) tanks because insoluble solids concentrations near 20% seem to be the norm for Savannah River sludges (Eibling and Fowler, 1982; Hay and Bibler, 1994; Hay, 1997).



**Fig. 1 - Pencil supported by paste-like Savannah River "PUREX" sludge simulant.**

Thus, one key to identifying possible heel locations may be to identify tanks which contain enough salt cake to compact sludges, which happen to have settled to the bottom of the tanks. Agnew, et al., 1995, provides estimates of the solids contained in the Hanford tanks. From this, it is possible to identify candidate tanks with large amounts of sludge (Table 2); however, it is not a foregone conclusion that the sludge has all settled to the bottom of the tanks where it could be compacted. Many of the Hanford tanks have, at one time or another, also achieved significant temperatures. This might have the effect of allowing the primary particles in agglomerates to rotate and find more favorable packing arrangements, in effect, increasing the fractal numbers of the aggregates. Thus in some tanks, this is an additional factor that could ultimately lead to a dense sludge layer, with the potential for heel formation.

Ongoing glass production (and the subsequent continued evolution of tank contents) at Savannah River, makes it more difficult to locate tanks with the appropriate proportions of sludge and salt to possibly form heels. However, a 1995 Waste Tank Level summary sheet indicates that only one tank (47-F) seemingly contains abundant sludge, as well as enough salt cake to potentially compact the sludge. Additional records (Chandler et al., 1994) indicate continual filling between 1981 and 1986, when the tank contained 600,000 gallons. With a continual addition of materials that subsequently set up as salt cake, it is probable that the sludge failed to settle or form a layer that was subsequently compacted. Hence, if heel-like materials do exist in the tank, they may not reside on the bottom of the tank.

**Table 2 - Tanks that combine thick accumulations of wastes likely to be rich in sludges and significant amounts of additional salt cake: Hanford and Savannah River**

Tanks	Max. Temp. – °C	Comments
T 104 T-110 T-111	90° 91° 98°	All - thick accumulations of BiPO <sub>4</sub> cladding wastes rich in Al
TX-109 TX-113	168° 129°	Cladding waste Cladding waste with abundant salt cake
U-101 U-103 U-105 U-108	92° 132° 146° 130°	Metal waste with abundant salt cake Same Same Same
SX-101 SX-103 SX-104	320° 225° 300°	REDOX waste REDOX waste with abundant salt cake REDOX waste with abundant salt cake
S-101 S-104 S-107	300° (11/53) 300° 240°	REDOX waste REDOX waste REDOX waste
C107 C110	170° 110°	Cladding waste Cladding waste
BX-107	88°	Metal waste
47-F - SRS	?	<i>Thick later stage (richer in Al) PUREX sludge with salt cake.</i>

#### 4.0 Tank Heel Search Strategy:

As outlined in the introduction, the term “heel” is poorly defined and has been used in a variety of contexts, depending on the individual(s) involved; however, in all cases, a degree of resiliency and insolubility is implied. In some cases, such as the zeolite “heels” at Savannah River, the origins can be traced to the anomalous addition of a component not normally included in the waste. Thus, anomalous additions became one search criteria. Another line of inquiry was whether subjecting “normal” tank contents to unusual conditions might produce a resilient heel; here identifying tanks with elevated temperatures was the obvious choice. We also employed process knowledge at the main sites (Hanford and Savannah River) to survey the specialized, often in-house documentation on the tank contents. One particularly useful piece of documentation was the records of waste levels in the tanks over the years. Only a few tanks have been emptied for closure, but a larger number have been almost emptied during various tank farm activities. A number of tanks have also been cored to various depths and the samples subjected to rather extensive testing. Often coring did not approach the bottom of the tank (where a heel might most logically be postulated to occur), but these samples do provide limited confirmation of inferences gained from other sources regarding the physical state of sludges in various environments.

To summarize, the various in-house and public domain documents on in-tank conditions were surveyed for (1) unusual chemistry, often tied to anomalous additions (2) the impact of elevated temperature, particularly with regards to drying (3) recorded instance of “heels” or other resilient solid materials found in the tanks (4) the difficulty of retrieving waste from the tanks and (5) the condition of core materials from the tanks.

#### 4.1 Summary of Savannah River Heel Search Results

In the early history of Savannah River, a number of tanks reached temperatures in excess of 150° C (Table 3), although in a few cases, the high-temperature condition is inferred rather than recorded. It should also be noted that some information from these documents is still restricted and they are not generally available to the public.

**Table 3 - Peak Tank Temperatures At Savannah River Site**

Tank	Peak Temperature	Year
1F	344° C	1964
4F	190° C	1962
5F	190° C	1960
7F	Inferred high temperature	---
8F	Inferred high temperature	---
12H	150° C	1957

Details of tank 1F history are instructive because they set the theme for the other high temperature tanks at Savannah River and provide an example of the sort of information that is available:

***Tank 1F served as a Purex high heat receipt tank from October 1954 until October 1961. In January 1962, it received low heat waste for several months. The low-heat supernate was decanted in October 1962 and the tank began receiving high heat waste again in April 1963. Sludge temperatures appeared uniform throughout the tank up until this time (ca. 120 deg C). Tank temperatures began rising and cooling water flow rates were increased. Temperatures continued to increase and one region of the sludge reached a peak temperature of 344 deg C in November 1964. Temperatures in this region of the tank slowly decreased back to ca. 120 deg C by December 1965. Waste additions to the tank were stopped in 1964 and resumed in November 1966. In 1969,***

*all of the supernate was removed in preparation of sludge removal. Sludge removal occurred in May and August 1969. In September 1969, the tank began receiving evaporator concentrat; this continued until mid 1972. About 400 Kgal of salt cake was produced during this time. Records indicate about 7 kgal of sludge remain in the tank. After completion of sludge removal operations, the sludge height was recorded at 11.5 inches, down from a height of about 30 inches, thus, it is concluded that about 2/3 of the sludge was removed from the tank. There are no indications that the fresh waste introduced at the time of the temperature increase was different from that previously produced from Purex processing. There was a layer of supernate over the sludge during the high temperature excursion.*

Although the detailed histories of the other high-temperature tanks differ, the general picture that emerges is that no unusual difficulties were encountered in emptying the sludge from the tanks. This strongly suggests that if a heel formed in these tanks at all, it cannot be more than a few inches thick. Further, to hypothesize such a feature would require an explanation of why the bottom few inches of sludge should have evolved differently from that which had already been removed with ease.

A variety of unusual additions to the tanks have also been noted, and indeed, it is the result of adding spent zeolitic ion exchange “resins” (predominantly Linde AW-500, now available as UOP’s IE-95), to some tanks, which provides the most widely cited example of a heel. Table 4 summarizes the unusual additions noted at Savannah River.

**Table 4 - Anomalous Additions at Savannah River**

Tank	Anomalous Additions
5 F	Chloride waste from Curium Tramax process
7 F	4545 kg of sand 3178 kg of coal 366 tons of sodium oxalate
8 F	Chloride waste from Curium Tramax process
13 H	Sodium oxalate
12 H	Fluoride from Th and ThO <sub>2</sub> dissolution wastes
15 H	Fluoride from Th and ThO <sub>2</sub> dissolution wastes
19 F	Zeolite (mostly Linde AW-500) from Cs recovery activities, 5.4x10 <sup>4</sup> lbs
24 H	Zeolite (mostly Linde AW-500) from Cs recovery activities, 1.9x10 <sup>5</sup> lbs
24 H	DWPF recycle frit, Zeolites

Although not strictly a heel within a tank, a related problem results from the leakage of tank fluids which accumulated in annulus between the inner and outer containment vessels (Table 5). These fluids have had an opportunity to interact with sand on the floor of the containment space, as well as dry out and deposit salts. Hard, insoluble nodules of dried salts have been observed to form on the sides of the tanks and residues have been noted on the floors of the containment spaces. In one case (16H), there is evidence that such accumulations contain a significant amount of radioactivity. The fact that these nodules apparently contain some dried zeolitic material, makes them not only mechanically hard, but also implies that they may not dissolve readily.

A further discussion of the “heel” derived from adding zeolites to tank fluids is merited because this is the largest anomalous addition at Savannah River and because it is the most often cited example of a heel. Considerable physical and chemical characterization has been done (Fig. 2-4). Although the material is

often referred to as a "resin", it is in fact, wholly inorganic and consists of the zeolites chabazite and erionite with a clay binder. When exposed to the typical highly caustic Al-rich fluids supernate fluids, these phases become unstable and react to form more aluminum-rich phases, such as sodalite and cancrinite-group zeolites, of which natrodavyne is a member. Although they have different crystal structures, both cancrinite and sodalite have Na, Al and Si in the same proportions:

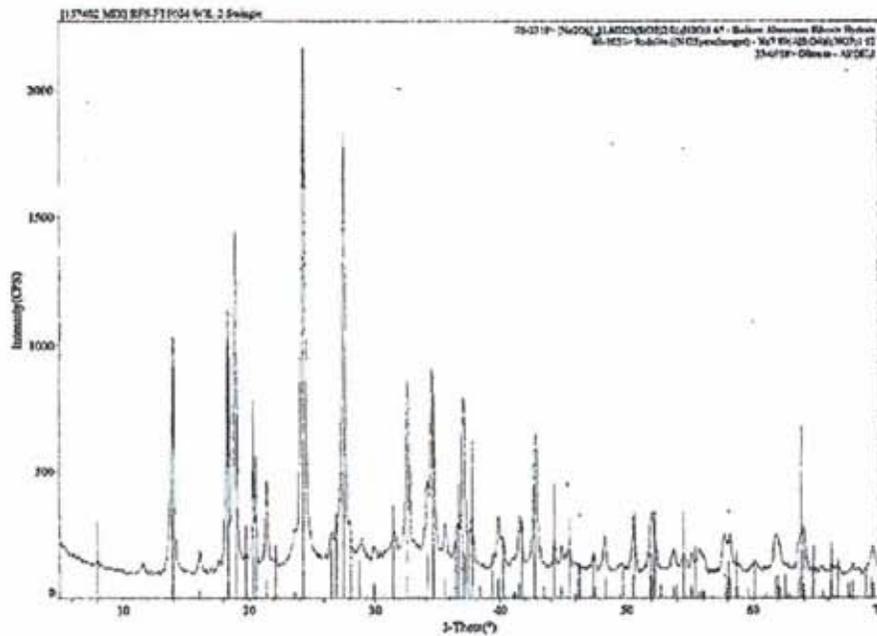
$2(\text{NaNO}_3) \cdot \text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot n\text{H}_2\text{O}$ . Because of this coincidence, it is possible to estimate the zeolite content of a heel sample from a silicon analysis. Other sludge phases may be mixed in, so the proportion of zeolite in the heel is variable. A sample of the Tank 19 F heel taken in 1996 contained about 50% zeolite by weight, while one taken in 2000 (after the heel had already been broken up) contained about 77% zeolite, the difference being the amount of normal HM sludge which happened to be mixed in with the altered Linde AW-500. The 2000 sample had the consistency of "moist dirt" and appeared to be agglomerations of smaller particles with a diameter in the 1000-2000 micron range. The dominant source of radioactivity was  $^{137}\text{Cs}$ , though lesser amounts of  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$  and  $^{238-239}\text{Pu}$  were detected. Many radionuclides, notably Pu and Sr, partition strongly into Fe-rich sludge phases (Georgeton and Hester, 1995), while the ability of the cancrinite zeolite to partition radionuclides (even Cs) appears to be limited (Nyman, et al., 2000). As a consequence, it was found that the more sludge-rich (e.g., Fe rich) 1996 sample had a greater activity than that of the 2000 (zeolite-rich) sample.

**Table 5 - Savannah River Double Shelled Tanks Having Accumulations in the Annulus.**

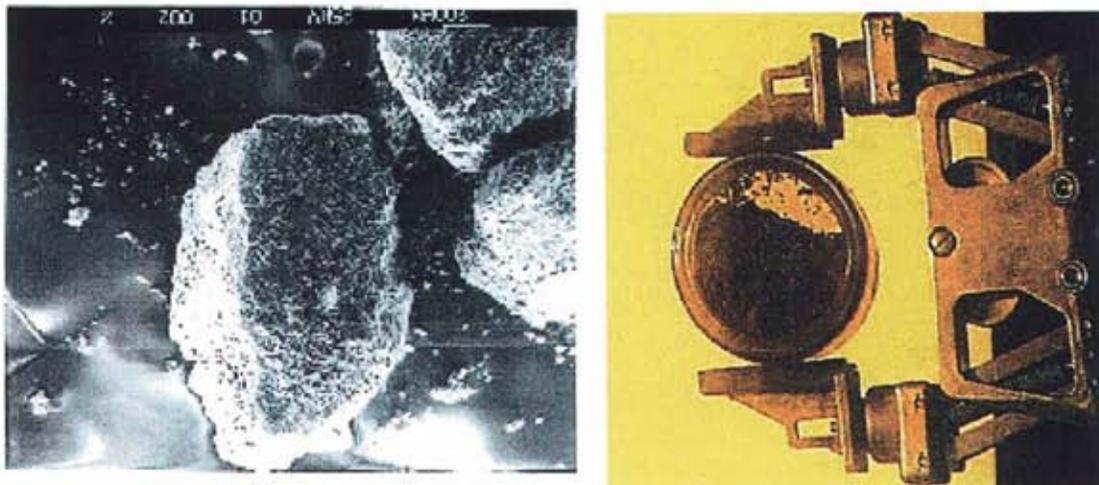
Tank	Comments
1 F	Small amount
5 F	1 gallon
6 F	92 gallons
9 H	8-10 inches
10 H	2 inches
11 H	Nodules on tank wall and residue on the floor
12 H	Nodules on tank wall and residue on the floor
13 H	Nodules on tank wall and residue on the floor
14 H	13-14 inches
15 H	Nodules on tank wall and residue on the floor
16 H	Heel in annulus, 30,000 curries of $^{137}\text{Cs}$



**Fig. 2 - Zeolite Heel Scanning Electron Microphotograph From Tank 19F, SRS**



**Fig. 3 - X-ray diffraction trace of the zeolite heel material from Tank 19F**



**Fig. 4 - (Right) Visual observation of the tank 19F sludge shows a dried loose material, similar to soil. (Left) Scanning electron microscope photo of altered zeolite resin grains demonstrating that in spite of the conversion to cancrinite/sodalite the grains generally retain their integrity. Current hot-cell inventory indicates that approximately 50 grams of this material are available.**

Finally, an inventory was taken of available sludge and heel materials at Savannah River (Table 6). Nothing in this inventory provides direction as to the occurrence of heels, except the entry for Tank 19. Note, two of the tanks in this list are from the tabulation of high-temperature Savannah River tanks, though there is no guarantee that these samples came from the high temperature part of the tank waste.

**Table 6 - Inventory of available Savannah River sludge and potential heel materials**

<u>Tank</u>	<u>Description</u>	<u>Amount</u>
Tank 8 F (sludge)	moist solids	
Tank 8F	dried sludge	
Tank 11H	dried sludge	
Tank 11H	sludge	
Tank 12H	sludge	
Tank 16H (Annulus)		
Tank 19F	solid sample	
Tank 22H	dried solids	
Tank 38H (core sample)	sludge	68 g
Tank 40	sludge slurry	125 ml
Tank 40	dried sludge	
Tank 41H (salt cake)	solids	
Tank 42H (old sludge)	dry	3kg
Tank 42H (washed)	sludge	
Tank 42H	dried sludge	
Tank 48H	washed solids	
Tank 51H (old sludge)	dry	3kg
Tank 51H (combined sludge)	wet	
Tank 51H (new sludge)	dry	3kg

*4.2 Summary of Hanford Heel Search Results:*

The search for potential heel-like materials at Hanford was conducted by Lenna Mahoney and her report is presented as Appendix A. What follows is a summary of these findings. This study followed the same general format as the Savannah River study; first we postulated circumstances likely to lead to heel formation and then searched the databases for evidence of problems, or a lack thereof. As with the Savannah River activity, it also proved particularly helpful to examine operations records to see to what degree it was possible to empty the tanks at various times in their service. Key findings of this inquiry were:

(1) Difficulties were *not* generally encountered in removing waste from “high temperature” (greater than 180° F or 82° C) tanks. In fact, it was often possible to remove waste to within several inches of the tank bottoms. Thus, the tie between heel development and elevated temperatures is not evident at either Hanford or SRS.

However, in a third of the sampled high temperature tanks, “chunks” or “flakes” are described that would be (were) difficult to sluice out. These would meet the broader concern of identifying materials that might be potentially troublesome to remove by sluicing the tanks. Coarser grained materials from these tanks are described as follows:

A-101	204° C	Sampled 1976, Chunks high in Al, Si;
A-102	216° C	Sampled 1996, Pebble-like pieces;
AX-104	160° C	Sampled 1997, Flakes and coarse particles, high Fe, Ca;
BY-105	82° C	Sampled 1998, Dark gravel-like chunks;
BY-106	93° C	Sampled 1995, Crumbly white solids;
BY-110	96° C	Sampled 1995, Yellow crystalline solids;
C-111	88° C	Sampled 1994, Clay-like material; Hard gray-black granular solids, brown chunks;
S-107	116° C	Sampled 1995, Hard black chunks;
SX-108	160° C	Sampled 1993, Large gray chunks;
SX-115	127° C	Sampled 1998, Clumps of black material.

(2) Twenty five low-temperature tanks also gave indications of having chunky or coarsely granular residues which did not form monolithic heels, but might meet the broader definition of a “heel” by being difficult to sluice:

White materials -	10 entries;
Black to dark brown materials -	19 entries;
Yellow to gray materials -	6 entries;
Rocks -	2 entries;
Uncharacterized -	9 entries;
Dense black sludge -	4 entries.

Both the sporadic occurrence and variable colors recorded suggest an essentially serendipitous origin for these materials that cannot be tied to bulk chemistry or operating conditions which are recorded in the site archives. Given that these tanks apparently did not receive anomalous additions, it is reasonable to infer that the white materials must be essentially pure aluminum-containing compounds while the darker ones would be richer in iron. The black coloration may reflect the influence of manganese dioxide; however, this is such a strong coloring agent, that only a small amount would be needed to dominate the appearance of a sludge sample. Yellow coloration may represent trace amounts of iron in an aluminum oxide matrix or entrainment of uranium compounds. In the course of recovering uranium from the “metal waste” produced by the BiPO<sub>4</sub> process, crusts and heels rich in uranium were encountered; however, sluicing with fresh water was found effective at removing them.

Hanford also has a few tanks in which it is possible to verify the presence of anomalous additions. Small amounts of zeolite were also added to the Hanford tanks, but it is trivial in comparison to the amounts of silica added in the form of diatomaceous earth (Table 7) and Portland cement (Table 8). Because of the desert nature of the site, it is also likely that a fair amount of soil and sand may have sifted down into some tanks over the years, but this is difficult to quantify. Neither tanks containing diatomaceous earth or Portland cement have been sampled extensively so, unfortunately, the physical state of the tank contents is largely unknown.

**Table 7 - Hanford tanks containing diatomaceous earth**

Tank #	Date of Addition #	Peak Temp. (°F)*	Range*
BX-102	1971	83° (in 1977)	Usually 60-65°F
SX-113	1972	92° (in 1989)	Usually 70-85°F
TX-116	1970	117° (?)	
TX-117	1970	191 (suspect)	
TY-106	1972	72° (in 1988)	Usually 60-65°F
U-104	1972	65° (1998-1994)	

**Table 8 - Hanford tanks containing Portland Cement**

Tank #	Date #	Peak Temp. (°F)	Range
BY-105	1977	140° (in 1978)	Usually 110-115 °F
SX-103	1965-66	470° (spike, 1992)	Usually 170-180 °F
SX-107	1965	230° (1989)	Usually 170-180 °F
SX-108	1965	220° (1989)	Usually 190-200 °F
SX-110	1995	190° (1989)	Usually 170-180 °F

# Agnew, et al., 1995, LA-UR-94-4296, page 5

\* Flanagan, 1994 WHC-SD-WM-TI-591, Appendix E

## ***5.0 Experimental Studies:***

The second general objective of this project was to develop methods for fabricating artificial heel materials to be used in developing novel chemical removal technologies. If one narrowly constrains the problem to that of mimicking "hard" materials, then apparently one would be trying to duplicate a material that does not exist. If one broadens the scope to cover semi-solid or granular materials, then a rationale for proceeding with the second phase of the study exists. In starting such tests, one obvious choice was to expose the AW-500 zeolite added to the Savannah River tanks, to an appropriate supernate simulant and observe whether the resulting reaction products resemble what was found in the tanks. By logical extension, similar testing should be done on diatomaceous earth and Portland cement. Hanford records suggest that normal sludge components may also be implicated in forming granular materials if not large cohesive masses. Thus, the behavior of normal sludge components under various conditions was also investigated.

A related issue was to ask why hard heels had not been found. Experimentally, this question becomes one of what actually has to be done to produce a hard or cohesive mass of material, starting with a normal sludge. Such results suggest where future problems may yet be encountered, or rule out the occurrence of heels in some settings.

### ***5.1 Behavior of Normal Sludge Components:***

In detail, sludges contain a host of minor and trace components. However, if a heel is to form from a particular component, it must at least locally, comprise a significant fraction of the sludge present. Most of the major waste streams from the different Hanford processing technologies have been defined (see Kupfer, 1997) and the major types of Savannah River sludge have also been documented. The procedure followed in preparing sludge stock solutions was to mix acid salts of the desired components and then neutralize them. The one exception was the addition of silicon as sodium silicate, which was dissolved in the NaOH solution added to the salt solution, to precipitate the insoluble sludge phase. Thus, for each entry (Table 9), the compositions of both pre-mix solutions are given. In a few cases, the amounts of NaOH (computed to just satisfy the base capacity of the metals), did not result in a strongly basic solution. In this case, additional NaOH pellets were added to produce the desired pH (as indicated by the ability of the solution to render pH paper a dark blue). In some lots, the concentrations in these mixes are multiples of the actual concentrations in the waste streams. This was necessary in order to produce reasonable amounts of sludge without producing many liters of waste solution. The last column in Table 9 gives the ideal mole percent of metal, assuming that all of the aluminum in the mix also precipitated.

**Table 9 - Recipes for Artificial Sludges and Estimated Precipitate Compositions**

Component	Grams Added	Mole % Metal In Mix (As Mixed)
<i>BiPO4 Process - Mix 1</i>		
Al(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	30.74	41.6
Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	12.72	16.0
Cr(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	1.28	1.6
Bi(NO <sub>3</sub> ) <sub>3</sub> .5H <sub>2</sub> O	5.58	5.8
MnSO <sub>4</sub>	1.18	3.5
HF (Conc. - 50%)	6.44	
H <sub>3</sub> PO <sub>4</sub> (Conc. - 85%)	28.6	
CaCl <sub>2</sub> .2H <sub>2</sub> O	4.28	
HNO <sub>3</sub> (Conc. - 71%)	20.27	
DI Water	126.62	
<i>BiPO4 Process - Mix 2</i>		
NaOH	82.91	
Na <sub>2</sub> SiO <sub>3</sub> .9H <sub>2</sub> O	17.06	31.5
DI Water	100	
<i>TBP Process - Mix 1</i>		
Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	27.97	84.0
Cr(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	1.95	5.9
Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	0.69	2.9
CaCl <sub>2</sub> .2H <sub>2</sub> O	6.48	
H <sub>3</sub> PO <sub>4</sub> (Conc. - 85%)	27.69	
HNO <sub>3</sub> (Conc. - 71%)	6.66	
DI Water	50.84	
<i>TBP Process - Mix 2</i>		
NaOH	38.76	
Na <sub>2</sub> SiO <sub>3</sub> .9H <sub>2</sub> O	1.68	7.2
DI Water	58.55	
<i>PUREX, Al Clad - Mix 1</i>		
Al(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	30.0	78.6
Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	4.8	11.6
Cr(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	0.32	0.79
MnSO <sub>4</sub>	0.51	2.99
Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	0.28	0.98
H <sub>3</sub> PO <sub>4</sub> (Conc. - 85%)	0.284	
HNO <sub>3</sub> (Conc. - 71%)	6.61	
DI Water	51.31	
<i>PUREX, Al Clad - Mix 2</i>		
NaOH	15.06	
Na <sub>2</sub> SiO <sub>3</sub> .9H <sub>2</sub> O	1.42	4.92
DI Water	23.15	
<i>REDOX - Mix 1</i>		
Al(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	20.6	87.3
Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	1.02	3.9
Cr(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	1.40	5.6

CaCl <sub>2</sub> .2H <sub>2</sub> O	0.21	
HNO <sub>3</sub> (Conc. - 71%)	6.37	
DI Water	51.4	
<i>REDOX – Mix 1</i>		
NaOH	11.33	
Na <sub>2</sub> SiO <sub>3</sub> .9H <sub>2</sub> O	0.568	3.1
DI Water	24.3	
<i>SRS-HLW Average - Mix 1</i>		
Al(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	29.8	75.2
Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	5.29	12.4
MnSO <sub>4</sub>	0.83	4.7
Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	0.29	0.96
HNO <sub>3</sub> (Conc. - 71%)	6.37	
DI Water	49.5	
<i>SRS-HLW Average - Mix 2</i>		
NaOH	16.84	
Na <sub>2</sub> SiO <sub>3</sub> .9H <sub>2</sub> O	1.99	6.6
DI Water	23.36	
<i>SRS-PUREX Average-Mix 1</i>		
Al(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	5.28	19.0
Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	18.15	60.3
MnSO <sub>4</sub>	1.34	10.7
Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	1.26	6.1
DI Water	61	
<i>SRS-PUREX Average-Mix 2</i>		
NaOH	11.2	
Na <sub>2</sub> SiO <sub>3</sub> .9H <sub>2</sub> O	0.80	3.8
DI Water	26.9	

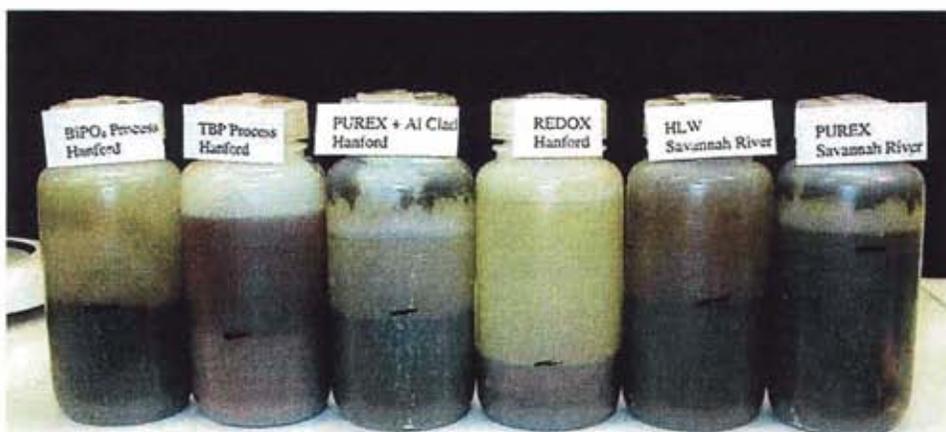
After the metal salts dissolved and the NaOH-sodium silicate solution was added, the slurries were aged for two weeks at 90° C. At the conclusion of this time, a well-defined separation had taken place between an upper sludge-free layer of supernate and a lower layer containing the synthetic sludges (Fig 5). Samples were then washed free of soluble salts and slurries placed on glass slides for X-ray diffraction analysis (Table 10).

**Table 10 - Phase chemistry of synthetic sludges after aging for two weeks at 90° C**

Sludge Type	Phases – by X-ray Diffraction
BiPO <sub>4</sub> Process	Zeolite Ferrihydrite – trace*
Tri-Butyl Phosphate Process	Ferrihydrite Zeolite - trace
PUREX-Hanford	Boehmite Bayerite Zeolite – trace Ferrihydrite – trace*
REDOX	Boehmite Zeolite Ferrihydrite – trace*

	Ferrihydrite – trace*
HM – Savannah River	Zeolite Boehmite Ferrihydrite – trace*
PUREX – Savannah River	Ferrihydrite Zeolite-trace

\* Ferrihydrite is very poorly crystalline compared to other sludge components. Thus, it may actually be present in significant amounts compared to other more crystalline materials and still appear as a minor phase on an X-ray diffraction trace.



**Fig. 5 - Synthetic sludges after two weeks settling at 90° C. Black lines on each bottle mark the interface between supernate and settled sludge. Note: in this synthesis run, the amounts of salts in the PUREX-Al Clad run were increased by a factor of 8/5, the REDOX salt loading was tripled and the SRS PUREX recipe was tripled compared to what is put forth in Table 10.**

### 5.1.1 Mechanical effects

Having developed methods for preparing synthetic sludges the question then became whether they could be transformed into synthetic heels. The operational definition settled upon to define a successful heel synthesis was that the material not be resuspended by mild, though prolonged, agitation. In this case, two week-aged precipitates (Fig. 5), a few shakes showed that after settling for two weeks, none of the recipes were consolidated to the point of becoming an artificial heel.

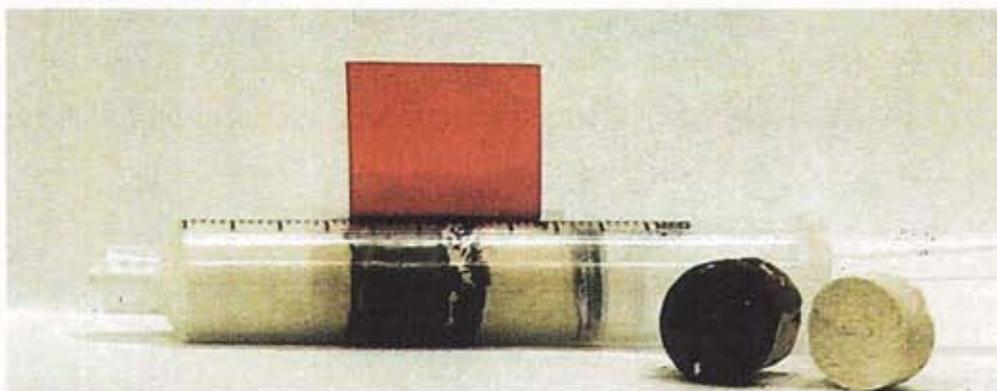
Settling alone, did not produce a heel, so the next step was to assess the effects of mild compaction. To achieve this, the sludges were cooled to room temperature and a portion transferred to a centrifuge tube. After running for 15 minutes at a speed that, according to the instrument documentation, should have exerted a force of 3,700 G's, a clear solution resulted with a more compact layer of sludge on the bottom of the tube (Fig. 6). Longer centrifuge treatments up to an hour, were also tried, but no additional compaction was observed. After this treatment, only the very fine material on the top of the layer could be resuspended by simply shaking the tube. To fully resuspend the mass, required placing the half empty tubes on a shaker table overnight, in contact with a solution of 1N NaOH.



**Fig. 6 - Synthetic sludge samples consolidated by 15-minute centrifuge treatment. Note also the layering of different phases; particularly in the PUREX-Al Clad test tube.**

Drying of centrifuge-compacted sludges at 107° C produced a 50-60% weight loss. Accounting for the dissolved salts left by evaporation, this weight loss implies they contained less than 10% sludge solids, even though there appeared to be relatively dense agglomerations of material. This seemingly anomalous result was confirmed qualitatively, while preparing samples for X-ray diffraction analysis. It seemed like more than enough material was added when a thoroughly opaque millimeter-thick layer of wet sludge was spread on a glass slide. However, when it dried, the residual coating of sludge particles was so tenuous as to be translucent. These observations are, however, in agreement with the earlier theoretical considerations advanced regarding moisture contents at the gel limits for sludges. Since the high G forces of the centrifuge evidently did not compact the material, it is apparently unlikely that mechanical forces alone can produce densely compacted sludges from the gels which naturally settle.

Gels apparently do not relinquish their fluids readily by mechanical means. The alternative to trying to mechanically drive the water out of such a material, is to wick the fluid out by capillary action. To assess the effectiveness of this, a syringe was partly filled with compacted diatomaceous earth (as a sorbant) and then a plug of sludge (SRS PUREX sludge, the same material used in Fig. 1), was introduced into the syringe. Finally the top of the syringe was sealed with a second plug of diatomaceous earth (Fig. 7). It was then put in a jig that compacted the sandwich until the plunger on the syringe started to deform. Pressure was maintained for three days.



**Fig 7-Rigid plug of sludge prepared at room temperature by dewatering in contact with a sorbant (diatomaceous earth). Note slight discoloration in the light-colored diatomaceous earth due to fluid wicking out of the sludge (dark brown). Red tab shows the initial length of the sludge plug.**

Almost as soon as the pressure was applied, a discoloration appeared in the diatomaceous earth indicative of a moisture front migrating into the sorbant. The size of the brown sludge plug also decreased. In three hours, a 53% volume decrease was observed and after five hours, a slight additional compaction had taken place resulting in a final 58% volume decrease (Fig. 7). Disassembly was achieved (with ease) by sawing the end off the syringe and extruding the mass. The sludge plug emerged intact, had a shiny surface, and gave no indication of deforming under its own weight or bleeding fluid. Although soft enough to be scratched by a fingernail, the sludge plug was, in fact, brittle and able to sustain a fracture. The diatomaceous earth was also compacted to the degree that a fracture could be maintained. Half of the plug with an adhering end cap of diatomaceous earth was then placed in a test tube half full of 1N NaOH and agitated. The compacted diatomaceous earth immediately disaggregated, leaving the sludge plug intact. It then took an additional 6 hours on the shaker table before the agitating fluid disaggregated the sludge pellet completely; thus, this procedure provided the most resilient heel-like material yet fabricated.

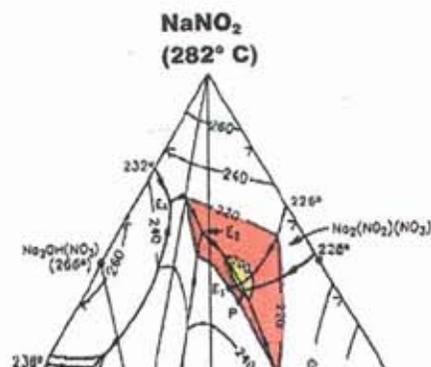
### 5.1.2 Thermal Effects

Thermal dehydration is obviously an alternative method of removing the fluid phase from a gel. At extreme conditions, it also holds the prospect of causing chemical changes which might facilitate cementing particles together. A simple first step in appraising this potential was to dry a portion of the centrifuge-compacted sludge samples (three days at 107° C) and then perform a resuspension test. The drying process produced relatively hard, dense, chips of sludge which retained their integrity for a few hours, when shaken in a 1N NaOH solution; however, after being shaken overnight, they too, lost their integrity.

Evaporation of pore water leaves a porous mass, with a residue of dried salts intermixed with the sludge particles. If it were possible to remove the open porosity, then a much more cohesive material might result. To test this dried sludge, samples were compacted in a pellet press designed for making salt tablets for X-ray diffraction studies. Nominal pressure was about  $1.3 \times 10^4$  psi, although the uniformity of the stress distribution in the pellet is questionable. During the compaction, the sludge-salt mix flowed plastically to the extent that most porosity was eliminated. The resulting pellets could be dropped for several feet without even chipping. Nonetheless, when placed in a 1N NaOH solution, the pellets came apart in less than an hour without any shaking. Again, just bringing the solid components in the mixture together failed to initiate the sort of cementing process that would produce a hard heel, once the interstitial salts had dissolved.

An extreme case of thermal treatment, appropriate only to the highest temperature tanks, is exposing previously dried chips of sludge to a molten salt bath. Both Savannah River and Hanford had one tank with recorded temperatures in excess of 300° C and several tanks at both sites had recorded temperatures approaching 200° C. These extremes occurred as localized hot spots and do not represent the temperature for an entire tank. Other tanks could have had similar unrecorded extremes and there is no guarantee that the recorded temperatures were the actual peak temperature that existed in the tank. If it can be shown generically, that such treatment does not produce heels, this would remove a potentially wide-ranging concern.

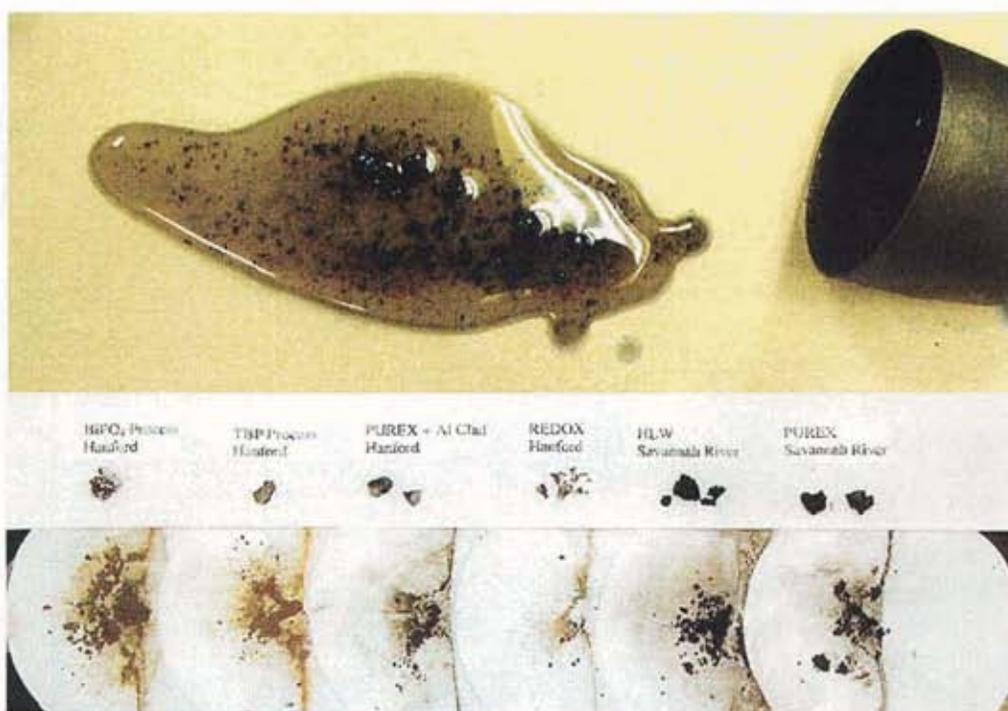
Salt cake consists principally of a mixture of sodium nitrate, nitrite and hydroxide. The NaOH-NaNO<sub>3</sub>-NaNO<sub>2</sub> salt system has a number of ternary eutectic compositions with surprisingly low melting points: 188°, 195°, 212°, 218° and 228° C. The minimum melting point in the simpler NaOH-NaNO<sub>3</sub> system is just 246° C (Fig. 8). Although drying did not provide a cemented ceramic heel, there is no guarantee that exposure to such a flux would not create conditions conducive to forming aggregates of interlocking or sintered particles.



**Fig. 8 - Phase diagram showing melting points of different mixes in the NaOH-NaNO<sub>3</sub>-NaNO<sub>2</sub> system: from Cook and McMurdie, 1989**

In fact, exposing large cohesive chips of dried sludge to the flux tended to break up the samples. While still in the flux (at 233° C for six days), the larger chips of dried sludge had already started breaking up (Fig 9, Top). When the salts in the fused mass were dissolved, only a powder was left (Fig. 9, Bottom). Sludge chemistry did not appear to be a significant factor in determining behavior. A final, possibly pertinent, observation is that when washed, samples of the heated sludge had a gritty feel, in contrast to the feel of spreading a smooth paste that was observed on unheated sludges. Thus, it appears that elevated temperatures may, in fact, play a role in producing particles that would be coarse enough to settle rapidly from solution, even though there seems to be no basis for assuming that they would comprise a rigid heel.

The main phase changes associated with this treatment were the breakdown of boehmite, ferrihydrite and (where present) bayerite, to produce a poorly crystallized spinel phase. Presumably the Ni, Mn and Cr present in the mixes were incorporated into this phase as well. A poorly crystalline hydrated akdalaite [(Al<sub>2</sub>O<sub>3</sub>)·4H<sub>2</sub>O] was also found in some samples, but it is probably a rehydration product formed as the samples were being washed prior to the X-ray diffraction study. The lack of cohesion of the heated sludges can be tied to the fact that spinel-group minerals typically form equi-dimensional grains. This is in contrast to the needle-like, or lath-like morphologies, that are usually required to get an interlocking framework of crystals, which is difficult to disaggregate. Finally, the cancrinite/sodalite zeolites survived the heat treatment unchanged.



**Fig. 9 - (top) Degraded chips of SRS PUREX sludge in a molten NaNO<sub>3</sub>-NaOH-NaNO<sub>2</sub> flux. (Bottom) Overall reduction in particle sizes in going from starting materials to the samples that have been washed free of soluble salts.**

To summarize, a variety of tests were performed on artificial sludge mixes which represent compositions likely to be encountered at Savannah River and Hanford. Across the board, no unique heel forming responses were observed that could be tied to sludge chemistry. Also, no process was identified that served to cement sludge particles together. Thus, none of the materials produced artificially met the criteria for

The same experimental setup was used to evaluate the heel-forming potential of each of these four materials. Between 0.8 and 0.9 grams of solid material was placed in a bottle with 28 grams of a tank fluid simulant referred to as DESSF-7. In fact, the supernates found in the tanks have a great range of chemistries. However, they are generally strongly caustic with significant levels of sodium nitrate, nitrite and often high aluminum concentrations. The DSSF-7 simulant combines all of these characteristics (Table 10). At the conclusion of the tests, samples were removed from the test bottles, washed free of the solution and dried at room temperature. Where solid clumps were observed, further characterization was carried out by scanning electron microscopy (SEM).

**Table 10 - DSSF-7 Concentration**

Component	Molar Concentration
Na	7.0
K	0.95
Al	0.72
SO <sub>4</sub> <sup>=</sup>	0.008
CO <sub>3</sub> <sup>=</sup>	0.15
NO <sub>2</sub> <sup>-</sup>	1.51
NO <sub>3</sub> <sup>-</sup>	3.52
PO <sub>4</sub> <sup>-3</sup>	0.014
OH <sup>-</sup>	4.63
OH <sup>-</sup> (Free)	1.75

### 5.2.1 Portland Cement

Of the “anomalous additions” Portland cement stands out by not being comprised principally of silica. The experimental results agreed with in-tank experience (Agnew, 1996), in that none of the samples had set to form a solid mass. Rather the balance of the charge was removed from the bottles as a fine powder; however, in this fine mass would usually be found several 0.3 - 3 mm grains of very solid material. In contrast, prior investigations into the behavior of Portland cement in the presence of such fluids (Westrich, et al., 1998), found that a normal slurry of cement and fluid did set to produce a coherent solid mass. The apparent contradiction can be resolved as follows. In fluids of this nature, it is likely that surface coatings of a prezeolitic material form quickly and prevent suspended particles from adhering to each other when they come in contact later. However, in densely packed clumps or low water:solid pastes, the hydration process still produces calcium aluminosilicate bridges between grains and a set is achieved. The solid grains in these experiments are probably clumps that existed in the original mix (left sample, Fig. 10). These probably formed as water diffused into the interior of the pellet, before a surface coating of zeolite formed in the surfaces of the individual grains comprising the pellets.

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**Fig. 10 - Portland cement in DSSF-7 for 31 days**

Scanning electron microphotographs of two large (well-solidified) pellets, one treated at 90° C and one at room temperature, show different surface textures. (Fig. 11). The bladed coating observed at room temperature is typical of the calcium aluminosilicate ("tobermorite") texture normally found on recently set Portland cements (Odler, 1998). At 90° C, this is replaced by a more eqigranular texture which matches more closely that of the sodalite/cancrinite zeolite observed as an alteration product of the other (predominantly silica) anomalous materials that were tested. EDS spectral results, however, still indicated an abundance of calcium, in addition to silicon and aluminum. A trace of phosphorous was also observed, probably because it was scavenged from the DSSF-7 (Table 10) by the abundant calcium in the cement. In an actual tank, it is reasonable to assume that the same clumping may have occurred, though the size of the residual hard pellets is likely to be somewhat larger.

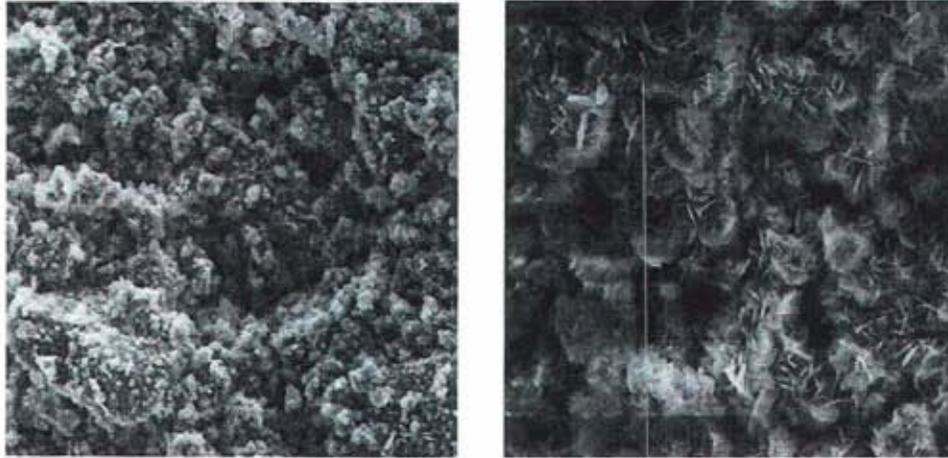


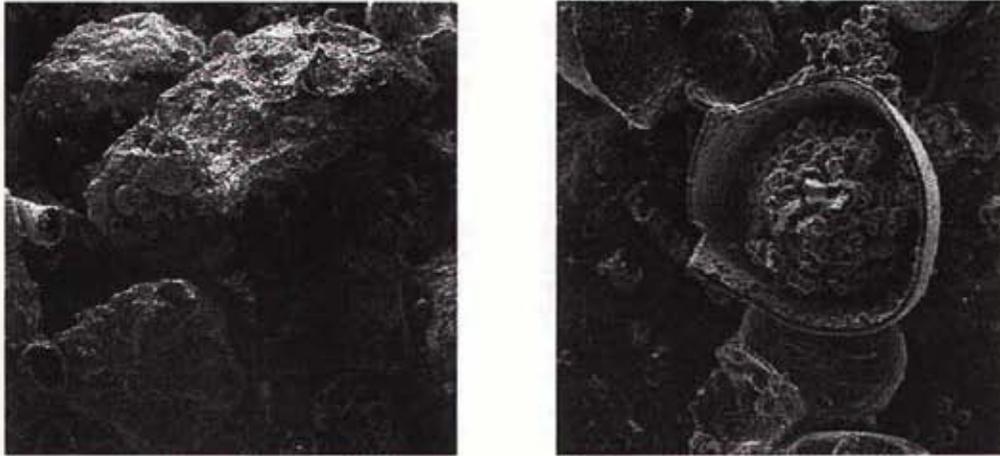
Fig. 11 - Scanning electron microphotographs of Portland cement grains in DSSF-7 at 90° C (left) and 25° C (right). Taken at 1500X, frame width is 92 microns

### 5.2.2 Zeolite "Resin"

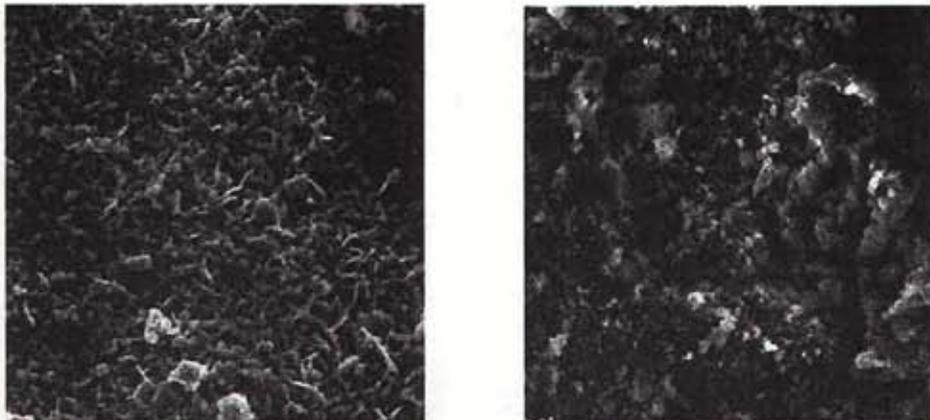
The results of zeolite "resin" treatment are of interest because of their direct bearing on simulating "heels" which are similar to those that have already been largely removed from Tank 19F at Savannah River. After 23 days of treatment at room temperature, the only (macroscopic) change was a rusty coloration. At 50° C, mild clumping is evident and at 90° C, most of the mass was cemented together prior to the disruption caused by removing the sample from the bottle. However, the clumps are not strongly cemented (Fig. 12). The two fragments in the lower-left of the 90° C sample, were broken because they were handled with a tweezers rather than the watercolor brush normally used to arrange the rather fragile samples on the filter papers. The white material that is particularly evident at high temperatures is the zeolite cement accumulating on the grain surfaces. It typically forms masses of rounded grains which occasionally appear to have nucleated around other zeolite grains that had precipitated earlier (Fig. 13). EDS spectra for these materials indicates essentially equal amounts of Al and Si, which is consistent with the X-ray diffraction results and show successively more in-growth of sodalite/cancrinite with increasing temperature. The 25° C experiment shows incipient growth of new zeolite on grain surfaces, but apparently, not enough to cause clumping of grains (Fig. 14). A lack of significant cohesion is also indicated for the "real thing" by the well-defined individual grains that were photographed from the actual Tank 19 "heel".



Fig. 12 - AW-500 Treated in DSSF-7 for 23 days



**Fig. 13 - (left) Sodalite/cancrinite growing on and cementing grains of AW-500 (IE-95) treated at 90° C. (right) Zeolite sphere that appears to have nucleated on previously grown granular zeolitic materials. Both materials give the same EDS spectra indicating that aluminum and silicon are present in nearly the same amounts.**



**Fig. 14 - (left) AW-500 (UOP-95) treated for 23 days in DSSF-7. (Right) Surface texture of starting material.**

### *5.2.3 Sand/Soil*

The response of sand to the treatment (Figure 15) was qualitatively similar to that of the zeolite, except that the extent of reaction was significantly less because of the larger grain size and lower reactivity of the phases in the sand (quartz, feldspar, basalt and metamorphic lithics). Significant adhesion was not observed in samples treated at either 25° C or 50° C, although a rusty coloration indicative of iron oxidation was observed. These results agree substantially with longer tests (82 days at 25°, 60°, and 90° C) performed using dune sand collected near Hanford (Nyman, et al., 2000). In these earlier tests at 90° C, both quartz and feldspar were completely missing from the sample, but basaltic fragments were relatively unaffected. Cancrinite/sodalite zeolite was the primary alteration product formed. At 60° C, only mild adhesion of grains was noted and again, at 25° C the grains did not adhere. Unpublished data from the same study (Table 11) documents the effects of DSSF-7 on different clays. In all, it is evident that over prolonged times, only a mild degree of cohesion should develop in sands and soils that were placed or blown into tanks.

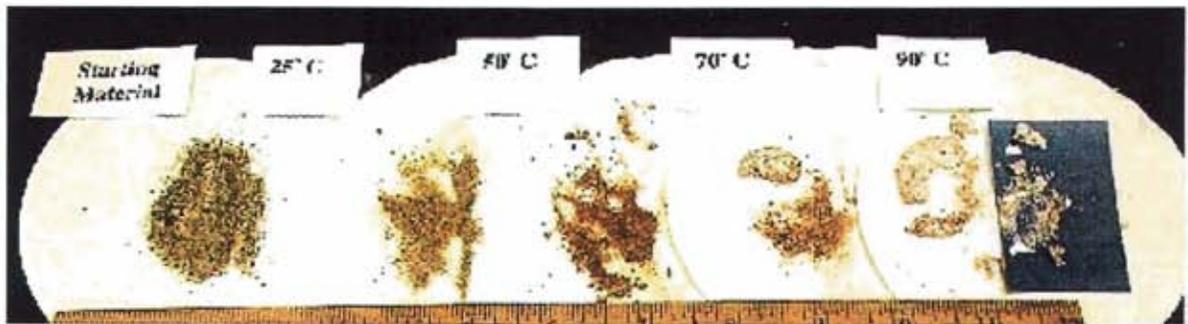


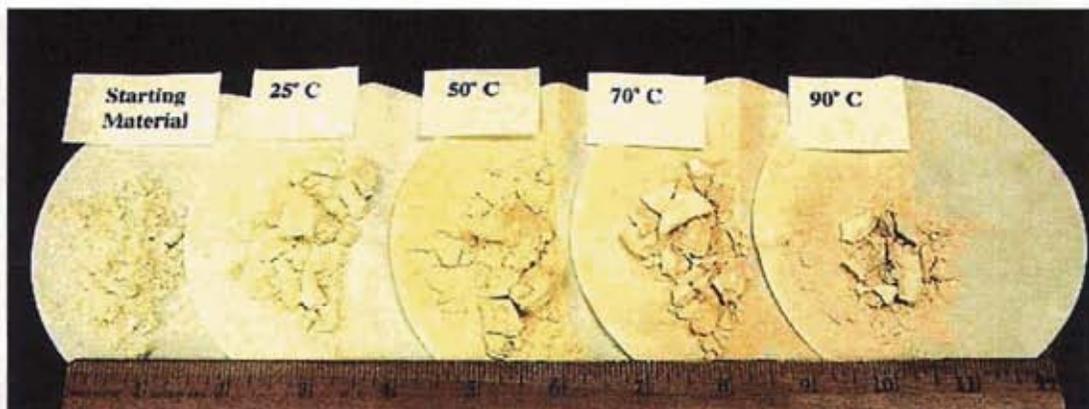
Fig. 15 - Sand treated with DSSF-7 for 31 days.

Table 11 - Alteration of Clays in DSSF-7 With Two Weeks Exposure

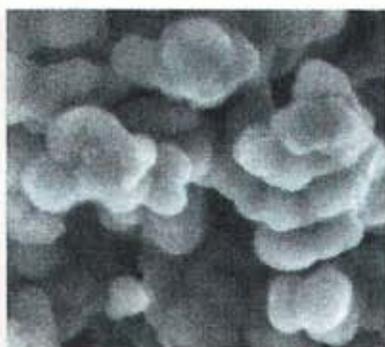
Clay	Reaction at 25° C	Reaction at 60° C	Reaction at 90° C
Smectite (Swy-1)	Totally zeolitized, all clay and quartz gone.	Partly zeolitized, quartz diminished and clay removed.	Totally zeolitized, all clay and quartz Gone.
Illite (Fithian)	No zeolite, both quartz and illite Remain.	No zeolite, both quartz and illite Remain.	Partly zeolitized, Some quartz and ill it remain
Kaolinite (KGa-1)	No zeolite, only kaolinite is detectable	Partly zeolitized, some kaolinite remains	Totally zeolitized, No kaolinite remains.

#### 5.2.4 Diatomaceous Earth

Finally, the behavior of diatomaceous earth is at the other end of the spectra from sand, as would be expected from the fact that it is comprised of exceedingly fine grains of a highly reactive silica. In all experiments, X-ray diffraction indicated essentially complete conversion to a sodalite/cancrinite zeolite. A marked difference, however, was observed with ascending temperature (Fig. 16). Removing the settled diatomaceous from the 25° C experiment, revealed a homogeneous paste with modest cohesiveness. It would not have survived the shaker test used to assess heel formation with sludges. At 50° C and higher, a distinct stratification is evident with a white layer between two light rust colored layers. When these samples were removed and dried, the rust colored material lost all cohesiveness, but the white layers retained enough integrity to snap when broken. It is likely that fragments of this material would survive the shaker test and a thick mass of such material could prove problematic during waste retrieval operations. SEM photographs of this material revealed that the cohesiveness arises from the individual grains having grown together (Fig. 17). This texture is similar to the intergranular growths observed on cemented AW-500 and sand samples at higher temperatures.



**Fig. 16 - Diatomaceous earth treated with DSSF-7 for 31 days**



**Fig. 17 - Diatomaceous Earth exposed to DSSF-7 for 31 days. (Right) From left to right 25 °C, 50 °C, 70 °C, 90 °C. (Left) SEM photograph taken at 5000X showing the interlocking zeolite grains which comprise the white layer in the high-temperature samples.**

## 6.0 Summary and Conclusions

The overall program objective is to develop chemically assisted methodologies for the removal of tank heels. To achieve this, two activities were carried out in FY-01: (a) a review of site records to document the occurrence of heels and identify which materials may be available at Site archives and (b) investigate ways of fabricating artificial heel materials so that promising removal technologies might be tested in a preliminary manner on non-radioactive samples.

During the Site investigations, it was found that the existence of heels depends on one's definition for such a material. If the criteria is a "hard", mechanically cohesive, accumulation of material, then verifiable instances are almost nonexistent. There is one record of an Fe-CO<sub>3</sub>-SO<sub>4</sub> heel of hard crust in tank A-105 (Hanford), which had to be softened with acid; however, that seems to be the only documented occurrence of a truly hard material. Other examples of heels appear to be made up of less stout stuff. The widely cited tank 19F zeolite "heel" at SRS, was essentially removed using a water jet after the mound was disrupted by merely placing a sluicing pump on top.

If, however, the definition of a "heel" is broadened to include semi-solid hydrated pastes or chunky masses, then "heels" do apparently occur with some frequency. Ample documentation was found for materials which might present problems if normal sluicing techniques were the only technology available for closing tanks. None of these materials appear to be tied to the thermal effects in the tanks and unfortunately, the records do not provide enough detail to account for their occurrence, or uniquely define their chemical compositions. The zeolite "heel" at Savannah River was reviewed in some detail. The modest adhesion clearly resulted from bringing a source of siliceous material in contact with the caustic, Al-rich supernates which resulted in formation of a cancrinite cement. The mass was not, however, strong enough to resist desegregation with a water jet.

The second "experimental" phase of the program was designed to develop artificial heels. Instead, this became, in essence, a study to define what was needed to produce something that could pass as a heel. A number of possibilities can be ruled out with regard to normal sludge materials: (a) settling, even with the aid of centrifuge, did not produce a cohesive material (b) drying, even in conjunction with great compaction, also failed to produce a surrogate heel once the sample was rewetted and (c) exposure to molten salt bath merely served to disaggregate the larger chips added initially to the crucibles. Conditions conducive to increasing the strength of sludges are those instances where the pore fluid is wicked out of the sludge, while the sludge is simultaneously compacted. Capillary force or osmotic gradients can effectively accomplish this in a matter of days. ***Although such materials did not possess intergranular cements which allowed them to withstand prolonged agitation, they were significantly more resilient than materials prepared during the other test procedures.***

Testing on the anomalous addition materials was also informative. It suggests that the diatomaceous earth is the material that is most likely to have reacted at room temperature to produce a cohesive mass of material. Zeolite "resin" grains proved to be the next most reactive, followed by sand grains. Thus, at most, the fate of sand accumulations in the tanks should be to produce a mass with the approximate cohesiveness of the zeolite heels in the Savannah River tanks. The tanks containing the diatomaceous earth at Hanford may be more problematic. Finally, although additions of Portland cement apparently will not produce a solid mass, it is likely that chunks or granules of highly cemented material will be encountered in a matrix of otherwise loose paste. These are relics from clumping in the initial mix, so the water required to initiate setting of the cement will have diffused into the clumps. Since mechanical mixing with the sludge is not involved, the radionuclide inventory of these pieces will be mostly constituents that partition into liquid supernate.

Excepting zeolitic heels, it is likely that if "heels" do exist, they will be mostly hydrated oxides of iron and aluminum, the primary components of "normal" sludges. Thus, developing technologies to chemically attack heels should focus on these two elements. Secondly, unless dissolving a heel in mass is proposed, the active agent will have to enter the heel through the pore fluid. Without using mechanical means (which would probably render chemical remediation redundant anyway), the time needed to accomplish

such an objective is governed by the diffusion rate into the pore spaces of the heel. For reference, water-saturated clay rich sediments have diffusion coefficients in the range of  $10^{-7}$  to  $10^{-6}$   $\text{cm}^2/\text{sec}$ , are appropriate. These values, then, could be applied to assessing the time required for a potential remediation technology to work, given various heel thickness.

With time, surfactants, radionuclide-specific complexing agents, or even agents able to generate a voluminous amount of (disruptive) gas, could diffuse into the pore spaces of a heel. Other technologies might focus on the pore fluid rather than the sludge. The basic plan would be to disengage the sludge in some manner from the tank. Freezing might cause an expansion coupled with forming a brittle material which would chip off the surfaces. Alternatively, simply drying should result in very large volume decreases and produce a granular material with little adhesion to the surfaces. Either an air current (vacuum cleaner) or water jet could then be used in final recovery. Possibly, combinations of processes could be used in a cyclic manner to achieve effects not obtainable in a single pass with a single technology.

To conclude, before proceeding with a program to develop chemically assisted heel removal technologies, it is first necessary to establish a clearer definition of the target (what really is a "heel"). Then, it will be possible to discuss how, or if, a proposed technology would produce the desired result. A key element in such a discussion should be whether the overall process could occur rapidly enough to be compatible with the overall tank decommissioning schedule. Within these confines, however, exist numerous possibilities, with the potential for moving beyond the brute force approach of completely dissolving a troublesome heel.

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## ***8.0 Appendix A:***

Hanford Tank Waste Heel Search Results:  
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### *8.1 Introduction*

This appendix provides the results of a survey conducted to identify the location and identity of potential heel materials from various Hanford Site databases. The focus of this report is on waste sample data, as seen in Sections 2 and 3. Section 4 briefly discusses heel observations made during past sluicing programs and Section 5 reviews some, (not all), of the work that has been done on solid phase identification.

For the present purposes, a “waste heel” can be defined as waste that

cannot be dissolved with volumes of water or caustics that are small enough to make dissolution a practical retrieval method; and

is so hard or heavy (large density and/or particle size) as to be impractical to retrieve by sluicing and

contains toxic or radiological constituents that are either mobile (present in interstitial liquid) or relatively easy to mobilize (sorbed onto insoluble solids such as zeolites).

Over decades of sluicing experience, heel material has been observed at the bottom of many Hanford waste tanks. In some cases, these heels were not removable using the sluicing methods that were employed at the time, and they may well constitute part of the residuum in tanks waiting decommissioning. However, potential heel material could also be located in the top or middle of tank waste, and would form a layer on the tank bottom only after the other, less obdurate, waste in a tank has been removed by one or another method.

In general, only the Hanford wastes with high contents of materials other than sodium salts (for example aluminum, silicon, and iron), are likely to produce heels. Some of the insoluble or poorly soluble phases observed in Hanford tank waste have been boehmite, gibbsite, aluminosilicates, amorphous iron hydroxide, apatite and forms of bismuth oxide, bismuth phosphate, and iron bismuth silicate hydroxide (Krumhansl 2000). Analyses have also been carried out with sludge simulants that were based on BiPO<sub>4</sub>, Redox, TBP, and PUREX waste streams (rather than on tank wastes). These studies (Krumhansl 2000) showed that phases in the simulant solids were similar to those in tank waste, though in some cases, crystallization was more developed in actual sludge than in simulants.

### *8.2 Desired Data and Sources of Data*

Data that identify and fully describe possible heel samples are required to fulfill the purpose of this report. Sample identification requires

using existing analytical data, observations and process historical records to decide which existing samples are likely to represent heel material and

establishing the sample identity (tank, sampling depth, sampling method and date, sample identification number).

The sample description includes the amount and appearance of the sample, the manner in which it was prepared, analytical data and (where available), other observations that are pertinent to waste properties and particle size. It will also be necessary to find out which of the samples remain in archive and could be re-analyzed and which were discarded or entirely consumed by previous analyses.

The Tank Waste Information Network System (TWINS) provides a great many data about Hanford tank waste samples. Most of these data come from the period after 1990, but a limited number of documents and records are available from earlier periods. (However, no samples pre-dating 1994 still exist in archive). Specifically, the useful data on TWINS include:

Sample analyses: tank and sample IDs, analyte concentrations, quality control (QC) footnotes, general analysis methods, and sample acquisition method.

Sample event descriptions: sample quantity and appearance (focusing on sample color, consistency, and wetness).

Core profiles: sample elevation, observations of the samples which were difficult or impossible to acquire because of waste resistance to the core-sampling drillstring and (for some tanks) estimates of the push-force required to drive the drillstring down through the waste.

Waste transfer spreadsheets: records of waste transfers and sluicing in each tank based in part on Anderson (1990).

Best Basis Inventories (BBIs): tank inventory of many of the pertinent analytes, including total tank inventory and volumes and inventories in different waste types within the tank.

Non-TWINS data include tabulation by Flanagan et al. (1994), of the maximum temperatures experienced in each tank as of 1993. Temperatures are important because higher waste temperatures are expected to have promoted crystallization and generated solid phases (such as boehmite) that could not have been formed at the present lower temperatures. The reference does not include peak temperatures for the 55,000-gallon tanks (the 200-series).

The videos that are taken of core sample extrusions, as standard practice, can also be useful: the extent to which the sample bends as it leaves the sampler can be used to roughly estimate the shear strength of the waste (Gauglitz and Aikin 1997). This report does not include any shear strength estimates; the method is mentioned for completeness and as a possibility for a later report.

### *8.3 Screening to Select Heel Samples*

With 177 tanks, a detailed examination of the analysis results for every tank sample was not possible. A screening of tanks and samples was performed to reduce the data examination effort to something that would fit within the accelerated project schedule.

The primary screening consideration was whether or not any of the waste in each tank had been exposed to high temperature, a condition that early in the survey was expected to lead to heel formation. For screening purposes, a temperature of 180 °F was used as the cut-off point; tanks whose lifetime maximum temperature was below that were removed from consideration. Next, the waste transfer spreadsheets on TWINS were consulted to determine how much of the waste that was present at the time the peak temperature occurred, was still present when later sampling was done. These spreadsheets provided the minimum waste volume that existed in each high-temperature tank after the date when the peak temperature was measured.

The core profiles were then reviewed to find out which core samples were taken from the waste that had been in the waste, which had reached high temperatures. In some of the high-temperature tanks, there were no samples deep enough to be in the erstwhile heated waste, or no samples at all, or none except liquid grab samples; however, many tanks have been successfully sampled from the heated waste. Table A-1 lists the high-temperature tanks and the samples available from each.<sup>(1)</sup> In general, samples taken before 1994 are no longer available, but are listed for completeness.

At this point, the average waste composition in each tank was reviewed. The first step was to gather the analyte inventories and total waste volumes given in the BBIs on TWINS and use these to calculate the average molar concentrations of each analyte of interest. The analytes of interest fell into the categories of sludge solid contributors (Al, Bi, Ca, Fe, PO<sub>4</sub>, Si, TIC) and toxic or radioactive constituents of concern, or their surrogates (Cr., Pb, <sup>79</sup>Se, <sup>99</sup>Tc, <sup>137</sup>Cs). In many cases, the waste in the tank had not been sampled, or samples had not been analyzed for all of the BBI constituents; the BBIs for these tanks are based in whole or in part, on the predictions of the Hanford Defined Waste (HDW) model or on other historical process knowledge. The samples in Table A-1 that are marked (with boldface) as having high concentrations of a sludge solid analyte are those whose measured concentrations were higher than the 90<sup>th</sup> percentile of the BBI-based average concentration distributions.

The core samples in Table A-1 are also marked (with italics) to show which ones required high downforce to obtain, indicating that the waste in this region was unusually hard. It should be noted that although low downforce can be safely interpreted as soft waste, high downforce is more ambiguous. High downforce could indicate a discarded object in the waste, or the presence of a hard, but more or less soluble salt, rather than the insoluble hard material required for a heel proper. In general, high downforce was at least as likely to be associated with salt-type compositions as with sludge and was as likely in low-temperature wastes as in those exposed to high temperature.

Table A-2 is a tabulation of samples which have been archived that were either from high temperature tanks and/or contained granular materials.

Table A-3 includes some notes about core samples that were unusually stiff (high shear strength) and samples which contained material that was described as "coarse", "granular", "gravel", or "rocks". A list of such samples that covers both low and high temperature tank wastes, is given in Tables A-1 and A-2. An overview of the observations in Table A-3 shows that these coarser materials were not exclusively associated either with sludge-type composition or with past high temperatures.

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<sup>1</sup> The core samples in the table were listed without being checked for contamination by the hydrostatic head fluid (HHF) used during core sampling. LiBr is added to HHF as a tracer, most often in 0.3 M concentration, so Br concentrations greater than 1000 µg/mL or µg/g in a sample indicate HHF contamination of several percent or more. HHF is not used in acquiring grab, auger, and finger-trap samples.

**Table A-1. Samples from Heated Waste in High-Temperature Tanks**

Tank	Maximum Temperature (°F)	Date of Temp.	Minimum Subsequent Waste Level (in)	Date of Level	Sample(s) Below Min. Subsequent Level	Sample Date(s)	Notes
A-101	399	5/61	2	1/76-7/76	<b>A101-2,3</b>	4/1/76	Residual sludge containing chunks; only <sup>137</sup> Cs, <sup>90</sup> Sr, Al, Fe, and Si were measured. High Al, Si.
A-102	420	8/61	0	7/63-10/63	n/a	n/a	
A-103	300	6/60	1	10/76-2/77	A103-5	12/10/76	Residual sludge; only <sup>137</sup> Cs and <sup>90</sup> Sr measured.
A-104	430	2/63	8	4/75 -->	A104-4	memo 2/12/76	Residual sludge; only <sup>137</sup> Cs and <sup>90</sup> Sr measured.
A-105	325	3/63	7	7/79 -->	n/a	n/a	
A-106	583	5/63	17	10/73 - 1/74	?	?	Some 1/5/88 samples, but no clues as to their elevation.
AX-101	260	6/71	1	9/76 - 11/76	226:15 AX101-3	2/23/98 memo 11/1/76	No sign of solids other than salt slurry in core. Sample referred to as liquid; only <sup>137</sup> Cs, <sup>90</sup> Sr, and Pu were measured.
AX-102	250	12/70	2	4/77 - 8/77	<b>AX102-6</b>  <b>95AUG006, 7</b>  <b>102AX-98-1, 2, 3</b>	memo 7/20/77  2/10/95 2/14/95 2/11/98	Sludge; only <sup>137</sup> Cs, <sup>90</sup> Sr, <sup>60</sup> Co, <sup>144</sup> Ce, <sup>154</sup> Eu, <sup>155</sup> Eu, <sup>125</sup> Sb, Pu, Si, and U were measured. High Si. These auger and finger-trap surface samples in 1995 and 1998 probably were not below the "minimum subsequent level" but might still be useful as representing a residuum. TIC was the only high analyte, but many analytes of interest were not measured.
AX-103	330	5/66	0	6/77 - 9/77	n/a	n/a	
AX-104	320	5/70	1	9/78 - 3/79	AX104-5  <b>97-AUG-001,2,3,4</b>	memo 6/15/78 11/13 - 11/21/97	Residual sludge; only <sup>137</sup> Cs, <sup>90</sup> Sr, and <sup>155</sup> Fu were measured. Auger samples showed high Fe and Ca and contained flakes and coarse particles.
BY-104 BY-104	237	1/21/75	128	9/85 -->	<b>BY104-6</b>  <b>Core 116</b> <b>Core 117</b>	memo 10/26/92 11/15/95 11/15/95	No clues as to the sample elevation(s).  High Al, Fe, TIC, and Ca, especially in core segments 116:7 and 116:8.
BY-105	180	1/21/75	66	3/76	  246:8,9  250:6,7,9B  251:5	7/23 - 9/9/98  7/23 - 9/9/98 7/23 - 9/9/98 7/23 - 9/9/98	108:2AR and 108:3 were above the "minimum subsequent level", but solids contained dark gravel-like chunks.  High Fe, Ca.  High TIC, Ca. Just above the "minimum subsequent level", but produced a downforce that prevented further sampling. BY-105 waste was topped with Portland cement in 1977.
BY-106	199	1/21/75	45	3/76	64:11,12,13  65:11,12,13	1/21/95  1/24/95	Samples 64:11 - 64:13 looked like hard, dry, crumbly white crystalline solids. Core 64 was not analyzed for most analytes of interest. The sludge portion of sample 65:13 contained high Fe, Ca.

Tank	Maximum Temperature (°F)	Date of Temp.	Minimum Subsequent Waste Level (in)	Date of Level	Sample(s) Below Min. Subsequent Level	Sample Date(s)	Notes
					121:10B	1/2/96	and PO <sub>4</sub> . It was impossible to penetrate <u>below</u> 121:10B, but the sample itself seems uninteresting.
BY-110	205	4/8/75	78	3/76	92:4,5,6,7 95:4,5,6,7 101:6A,7,8,9	7/13/95 8/2/95 8/29/95	High TIC. 6 contained yellow crystalline solids resembling crushed or shaved ice. High TIC. High TIC in 6A, 7, and 8; also high Ca in 8. 7 contained grainy sludge with small bits of solids dispersed in it. Larger solid chunks were found in samples above the minimum subsequent level. High Fe, Ca in 8 and 9; high TIC in 6 and 7. 7 and 8 contained hard gray-black granular solids.
BY-110					103:6,7,8,9 107:6,7,8,9	8/15/95 8/24/95	High Fe in 107:9; high TIC in 6 and 7; high Ca in 8 and 9. 7 contained hard brown chunky material in sludge. High Fe in 8; high Ca in 7,8.
					113:5,5A,6,7,8	10/28/95	
C-106	198	1992	21	10/99 -->	6C-96-10	2/23/96	Grab sample was at 29", just above the "minimum subsequent level". High Fe, Si, and TIC.
C-111	190	1964	14	4/85 -->	58:1 59:1 60:1 95AUG003 95AUG016	4/11/94 4/22/94 4/29/94 1/17/95 3/25/95	None of these core samples were analyzed for constituents of interest. 58:1 and 60:1 were described as clay-like. High in Al, Ca, and Fe. No analysis for other constituents of interest.
S-101	300	11/53	52	12/69	137:7,8,9 138:7,8,9 142:6,7,8	3/12/96 3/26/96 4/3/96	No analysis data for Core 137; however, it may have been archived. High Al. High Al.
S-104	300	7/53	57	12/69	42:4,5,6 43:4,5,6 44:4,5,6	7/30/92 7/31/92 8/2/92	
S-107	240	11/52	120	7/68 – 11/68	105:3,4,5,6,7,8 110:3,3A,4,5,6,7,8 111:3,4,5,6,7,8	9/19/95 9/25/95 10/2/95	High Al in 110:6 and 110:8; high PO <sub>4</sub> in 105:3, 110:7, and 111:4. Hard black chunks of solids were observed in 110:3.
S-108	195	1/13/82	163	1/96	n/a	n/a	
S-110	240	10/52	74	10/74–11/74	140:4C 240:7,8,9,10 241:5,6,7,8	5/9/96 5/26/98 6/3/98	140:4C was the last sample taken before the core was abandoned owing to high downforce. High Al in 240:9, 240:10, and 241:8; high TIC and Bi in 240:8.

Tank	Maximum Temperature (°F)	Date of Temp.	Minimum Subsequent Waste Level (in)	Date of Level	Sample(s) Below Min. Subsequent Level	Sample Date(s)	Notes
SX-101	320	11/57	141	1/75 - 2/75	Core 225 227:2,4,5,5A, 6,7,7A		High Al in 227:4, 227:5, and 227:7A. Highest downforce (2200 lb) was in 227:2.
SX-102	212	8/6/85	191	8/85	Core 243 Core 244	6/30/98 7/6/98	2000 lb downforce in 244:4.
SX-103	225	8/13/85	194	4/01	<b>Core 235</b> 239:1A,2,3,4, 5,6,7,8,9,9R1,10R 1,11R,12, 12A	4/28/98 5/5/98	2100 lb downforce in 235:6 and 235:6A. High Al in 235:12A and 239:12, high TIC in 235:3, 235:8, and 238:10R1. Large crystals seen in 239:1A.
SX-104	300	12/56	40	9/70	n/a	n/a	
SX-105	330	11/75	173	4/76 - 5/76	229:5,6,6R,7, 8,9,10,11,12, 12A,13 233:6,7,8,9,10, 10AR,11,12, 13A	3/3/98 5/15/98	High TIC in 229:8 and 11, high Fe in 229:13, high Al in 229:12A, 13. 1500 lb downforce in 233:6, high Al in 233:12, 13A.
SX-106	195	10/63	20	1/76 - 3/76	223:10 224:10,11	10/31/97 12/11/97	
SX-107	390	2/5/58	36	6/70	n/a	n/a	
SX-108	320	9/58	35	3/68, 10/74 -->	95-AUG-042 <b>95-AUG-043</b>	9/15/95 9/18/95	Both auger samples were dry and contained large gray chunks. High Fe in 95-AUG-043.
SX-109	295	9/62	26	6/69	n/a	n/a	
SX-110	310	5/66	16	6/67	n/a	n/a	
SX-111	320	11/65	35	6/68	n/a	n/a	
SX-112	315	3/62	33	6/69	n/a	n/a	
SX-113	255	7/58	0	3/58 - 10/62	n/a	n/a	SX-113 contains 32 tons of diatomaceous earth, added in 1972.
SX-114	335	8/58	9	12/63	n/a	n/a	
SX-115	260	9/60	7	4/65 -->	<b>SX115-3</b> 15SX-93-1,2,3	memo 4/22/75 3/13/98	Not all of the analytes of interest were measured. High Ca and Fe. None of the analytes of interest were measured in these fingertrap samples.
SY-101	260	1/91	n/a	n/a	n/a	n/a	SY-101 was diluted and pumped in 12/99 - 3/2000. The solids layer present in the waste before that time was largely soluble and could be dispersed by a mixer pump, so SY-101 samples do not appear to be good candidates for heel waste.
TX-105	238	1/52	0	2/57 - 4/57	n/a	n/a	
TX-117	191	???	n/a	n/a	n/a	n/a	Maximum temperature was called "suspect" in Flanagan, making it difficult to identify the minimum subsequent layer, and there were no samples.

Tank	Maximum Temperature (°F)	Date of Temp.	Minimum Subsequent Waste Level (in)	Date of Level	Sample(s) Below Min. Subsequent Level	Sample Date(s)	Notes
Sample IDs are in <b>bold</b> if they contain high analyte concentrations, and/or in <i>italics</i> if high downforce was required to take the sample.							

Table A-2 summarizes the availability (as of May 2001) of archived samples of interest and of the original core extrusion videos for those samples. The samples in the table included all of those with some variety of rocky or grainy consistency, plus those with an apparently smooth consistency that came from high-temperature layers. The ID numbers of the archive jars and the amounts of sample in them are given in the table. The label names of the core extrusion videotapes are also given.

**Table A-2.** Description of Samples of Interest

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
<b>A-101</b>					
1A-96-2	grab	1996	gray chunks possibly high T	#9768, 58 g	N/A
1A-96-3	grab	1996	gray chunks possibly high T high $C_2O_4^{2-}$	#9710, 79 g 1A-96-3, 62 g	N/A
<b>A-102</b>					
95AUG33	auger	1995	black pebbles possibly high T	N/A	N/A
96-AUG-003	auger	1996	pebbles possibly high T high $C_2O_4^{2-}$ , Cr, Mn, U	N/A	U-Farm Tape 7B
<b>AW-105</b>					
5AW-96-20	grab	1996	black and white chunks high La, U, Zr	#11472, 58	N/A
196:5-UH	core	1997	small black chunks high F, La, Mn, U, Zr	#12558, 58 g #12737, 80 g	AW-Farm Tape 3A

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
AX-102					
95AUG006	auger	1995	possibly high T high CO <sub>3</sub> <sup>-2</sup>	N/A	AX-Farm Tape 4
95AUG007	auger	1995	possibly high T high CO <sub>3</sub> <sup>-2</sup> , C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	N/A	AX-Farm Tape 4
102AX-98-1	finger- trap	1998	possibly high T high CO <sub>3</sub> <sup>-2</sup>	composite #14464, 62 g	N/A
102AX-98-2		1998	possibly high T high CO <sub>3</sub> <sup>-2</sup>		N/A
102AX-98-3		1998	possibly high T high CO <sub>3</sub> <sup>-2</sup>		N/A
AX-104					
97-AUG-001	auger	1997	coarse dark material high T high Fe	#11848, 42 g	AX-Farm Tapes 14 & 18
97-AUG-002	auger	1997	coarse dark material high T high Fe	#14068, 31 g	AX-Farm Tapes 14 & 18
97-AUG-003	auger	1997	clumps and flakes high T high Ca, Fe, La, Mn, Zr	salt (no sludge) #14013, 109 g	AX-Farm Tapes 14 & 18
AX-104 97-AUG-004	auger	1997	clumps and flakes high T high Ca, Fe, La, Mn, Zr	N/A	AX-Farm Tapes 14 & 18
AZ-101					
266:7	core	1999	white chunks	#15905, 171 g	AZ-Farm Tapes 2 & 3
269:16	core	1999	small rocks high Fe, La, Zr	#17505, 9 g (liquid only?)	AZ-Farm Tapes 2 & 3
B-101					
91:1-UH	core	1995	½" hard piece	#13159, 63 g	B-Farm Tape 6

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
				(unclear if this is UH or LH)	
B-103					
95AUG31	core	1995	black fiber-like crystals	N/A	B-Farm Tape 6
B-107					
217:1-LH	core	1997	salt chunks high F, SO <sub>4</sub> <sup>-2</sup>	#13175, 93 g #13177, 63 g Not sure which is LH	B-Farm Tapes 6B & 6C
BX-103					
86:1	core	1995	black grainy solids	#7183, 33 g #8426, 47 g	N/A
86:2	core	1995	black grainy solids	#15549, 33 g #7185, 42 g #13157, 31 g	N/A
87:1	core	1995	black grainy solids	#7193, 40 g #7195, 38 g #15895, 125 g	N/A
BX-106					
95-AUG-49	auger	1995	white pieces	#8976, 10 g	BX-Farm Tape 8
BX-108					
94AUG007	auger	1994	hard clay-like material	N/A	BX-Farm tape
BX-112					
118:3	core	1995	clay-like chunks high Bi, F	N/A	BX-Farm Tape 8
BY-104					
116:2	core	1995	high T high CO <sub>3</sub> <sup>-2</sup> , Cr, F, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup>	#8410, 20 g #8411, 69 g	BY-Farm Tape 2C
BY-104 116:3	core	1995	high T high CO <sub>3</sub> <sup>-2</sup> , Cr, SO <sub>4</sub> <sup>-2</sup>	#8757, 29 g #8758, 69 g #16938, 45 g	BY-Farm Tape 2C
116:4	core	1995	high T	#8759, 47 g	BY-Farm Tape

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
			high $\text{CO}_3^{-2}$ , $\text{C}_2\text{O}_4^{-2}$ , $\text{SO}_4^{-2}$	#8760, 40 g #8761, 46 g	2C
116:5	core	1995	high T high $\text{CO}_3^{-2}$ , Cr	#8762, 80 g #8763, 63 g #8764, 84 g #8765, 64 g	BY-Farm Tape 2C
116:6	core	1995	high T high $\text{CO}_3^{-2}$ , Cr, $\text{C}_2\text{O}_4^{-2}$	#8777, 65 g #8780, 74 g #8778, 62 g	BY-Farm Tape 2C
116:7	core	1995	high T high $\text{CO}_3^{-2}$ , Cr, $\text{C}_2\text{O}_4^{-2}$ , $\text{SO}_4^{-2}$ in subsegments A-C high Ca, Cr, Fe, U in subsegment D	#8770, 68 g	BY-Farm Tape 2C
116:8	core	1995	high T high Ca, Fe, U in subsegment A high Al, U in subsegment D	#8784, 85 g	BY-Farm Tape 2C
117:1	core	1995	high T	#8791, 7 g	BY-Farm Tape 2C
117:2	core	1995	high T high $\text{CO}_3^{-2}$ , Cr, F, $\text{C}_2\text{O}_4^{-2}$ , $\text{SO}_4^{-2}$	#8803, 13 g #8804, 112 g	BY-Farm Tape 2C
117:3	core	1995	high T	#8802, 61 g #8806, 127 g	BY-Farm Tape 2C
117:4	core	1995	high T	N/A	BY-Farm Tape 2C
117:5	core	1995	high T	#8808, 23 g #8810, 20 g	BY-Farm Tape 2C
BY-105					
108:2AR	core	1995	dark hard rocks	#8643, 79 g	BY-Farm Tapes 2B & 2C
108:3	core	1995	dark gravel	N/A	BY-Farm Tapes 2B & 2C
246:8	core	1998	high T high $\text{CO}_3^{-2}$ , Ca, F, $\text{SO}_4^{-2}$	#13599, 11 g	BY-Farm Tape 98

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
BY-105 246:9	core	1998	high T high Ca, Fe, U	#15012, 73 g	BY-Farm Tape 98
250:6	core	1998	high T	#14738, 63 g #15024, 49 g	BY-Farm Tape 98
250:7	core	1998	high T	#14965, 31 g	BY-Farm Tape 98
250:9B	core	1998	high T high CO <sub>3</sub> <sup>-2</sup> , Ca, U	#14991, 6 g (salt) #14992, 17 g (sludge)	BY-Farm Tape 98
251:5	core	1998	high push force high T	#14793, 99 g #15018, 137 g	BY-Farm Tape 98
BY-106					
64:11	core	1995	high T	#7042, 34 g	BY-Farm Tapes A, 2A, 2C, & 2D
64:12	core	1995	high T	#6381, 65 g	BY-Farm Tapes A, 2A, 2C, & 2D
64:13	core	1995	high T	#7048, 7 g	BY-Farm Tapes A, 2A, 2C, & 2D
65:11	core	1995	high T high Zr	N/A	BY-Farm Tapes A, 2A, 2C, & 2D
65:12	core	1995	high T	N/A	BY-Farm Tapes A, 2A, 2C, & 2D
65:13	core	1995	high T high Ca, Fe, F, PO <sub>4</sub> <sup>-3</sup>	#6403, 31 g (sludge) #13454, 16 g (salt)	BY-Farm Tapes A, 2A, 2C, & 2D

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
BY-110					
92:4	core	1995	high T high CO <sub>3</sub> <sup>-2</sup> , F, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup> , Zr	N/A	BY-Farm Tapes 2A, 2B & 2C
92:5	core	1995	high T high CO <sub>3</sub> <sup>-2</sup>	#7663, 18 g	BY-Farm Tapes 2A, 2B & 2C
92:6	core	1995	crushed ice appearance high T high Cr	#7666, 81 g #16520, 25 g	BY-Farm Tapes 2A, 2B & 2C
BY-110 92:7	core	1995	high T high Cr	#7668, 68 g #16510, 26 g	BY-Farm Tapes 2A, 2B & 2C
95:4	core	1995	very hard brown crystals high T high CO <sub>3</sub> <sup>-2</sup>	#7669, 17 g	BY-Farm Tapes 2A, 2B & 2C
95:5	core	1995	high T high CO <sub>3</sub> <sup>-2</sup>	#7673, 37 g #7675, 38 g	BY-Farm Tapes 2A, 2B & 2C
95:6	core	1995	high T	#7670, 29 g	BY-Farm Tapes 2A, 2B & 2C
95:7	core	1995	high T	N/A	BY-Farm Tapes 2A, 2B & 2C
101:3	core	1995	½" chunks high CO <sub>3</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup>	#7652, 15 g	BY-Farm Tapes 2A, 2B & 2C
101:6A	core	1995	high T high CO <sub>3</sub> <sup>-2</sup> , C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	#7711, 53 g	BY-Farm Tapes 2A, 2B & 2C
101:7	core	1995	small pieces high T high CO <sub>3</sub> <sup>-2</sup> , Cr, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup>	#7706, 45 g #7707, 30 g #7708, 41 g #7709, 23 g #7710, 71 g	BY-Farm Tapes 2A, 2B & 2C
101:8	core	1995	high T high CO <sub>3</sub> <sup>-2</sup> , Cr, SO <sub>4</sub> <sup>-2</sup> in subsegments A & B high Ca, U in subsegment C	#7965, 62 g #7966, 30 g #7967, 47 g #7968, 41 g	BY-Farm Tapes 2A, 2B & 2C
101:9	core	1995	high T	#7964, 68 g	BY-Farm Tapes

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
			high Ca, Fe, $\text{SO}_4^{-2}$ , U	#7969, 58 g #7970, 46 g #7971, 67 g	2A, 2B & 2C
103:6	core	1995	high T high $\text{CO}_3^{-2}$ , $\text{C}_2\text{O}_4^{-2}$ , $\text{SO}_4^{-2}$	#7468, 65 g #7469, 59 g #13519, 61 g	BY-Farm Tapes 2A, 2B & 2C
103:7-UH	core	1995	hard gray-black granular high T	#7471, 60 g	BY-Farm Tapes 2A, 2B & 2C
103:7-LH	core	1995	high T high $\text{CO}_3^{-2}$ , Cr, $\text{SO}_4^{-2}$	#7470, 45 g	BY-Farm Tapes 2A, 2B & 2C
BY-110 103:8-A	core	1995	hard gray-black granular high T high $\text{SO}_4^{-2}$	#7645, 68 g #13535, 40 g	BY-Farm Tapes 2A, 2B & 2C
103:8-B	core	1995	high T	#7646, 60 g #13461, 19 g	BY-Farm Tapes 2A, 2B & 2C
103:8-D	core	1995	high T high Ca, Fe, U	N/A	BY-Farm Tapes 2A, 2B & 2C
103:9	core	1995	high T high Ca, U in subsegments A & B high Ca, Fe, U in subsegment C high Ca, Fe, F, $\text{SO}_4^{-2}$ , U in subsegment D	#7649, 29 g #7650, 46 g	BY-Farm Tapes 2A, 2B & 2C
107:6	core	1995	high T high $\text{CO}_3^{-2}$ , Cr, $\text{SO}_4^{-2}$	#7697, 75 g #7698, 67 g #13528, 98 g	BY-Farm Tapes 2A, 2B & 2C
107:7	core	1995	hard chunks high T high $\text{CO}_3^{-2}$ , Cr, $\text{C}_2\text{O}_4^{-2}$ , F, $\text{SO}_4^{-2}$	#7701, 70 g #7702, 25 g #7703, 70 g #13489, 33 g	BY-Farm Tapes 2A, 2B & 2C
107:8	core	1995	high T high $\text{CO}_3^{-2}$ , Cr, $\text{SO}_4^{-2}$ in subsegment A high Ca, U in subsegment B	#7704, 73 g #7705, 9 g	BY-Farm Tapes 2A, 2B & 2C

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
107:9	core	1995	high T high Ca, Fe, U	#7712, 27 g #7713, 54 g #7714, 54 g #7715, 64 g	BY-Farm Tapes 2A, 2B & 2C
109:1	core	1995	gray-black sand high CO <sub>3</sub> <sup>-2</sup>	#7972, 41 g	BY-Farm Tapes 2A, 2B & 2C
113:4A	core	1995	hard brown granular high CO <sub>3</sub> <sup>-2</sup> , C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup>	#8662, 36 g	BY-Farm Tapes 2A, 2B & 2C
113:5	core	1995	high T high CO <sub>3</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup>	#8665, 25 g (sludge) #8666, 77 g (salt)	BY-Farm Tapes 2A, 2B & 2C
BY-110 113:5A	core	1995	high T	#8667, 101 g	BY-Farm Tapes 2A, 2B & 2C
113:6	core	1995	high T	#8668, 65 g #8669, 24 g #8670, 60 g #8671, 20 g	BY-Farm Tapes 2A, 2B & 2C
113:7	core	1995	high T high Ca, Cr in subsegment A high Ca, CO <sub>3</sub> <sup>-2</sup> , U in subsegment C high F, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup> in subsegment D	#8679, 31 g #8680, 37 g #8754, 55 g #8755, 58 g	BY-Farm Tapes 2A, 2B & 2C
113:8	core	1995	high T high Ca, Fe, F, SO <sub>4</sub> <sup>-2</sup> , U	#8485, 39 g #8486, 56 g #8487, 49 g #8488, 22 g	BY-Farm Tapes 2A, 2B & 2C
C-106					
6C-96-10	grab	1996	high T high CO <sub>3</sub> <sup>-2</sup> , Fe, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , Si	N/A	N/A
C-107					
69:5-UH	core	1995	firm white chunks	#6743, 46 g	C-Farm

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
				(not clear if this is UH)	Tape 1
C-108					
94AUG015	auger	1994	hard off-white chunks high Ca, PO <sub>4</sub> <sup>-3</sup> in composite from this sample	N/A	C-Farm Tape Auger15, Riser 4
C-111					
58:1	core	1994	high T clay-like	N/A	N/A
59:1	core	1994	high T	N/A	N/A
60:1	core	1994	high T clay-like	N/A	N/A
95AUG003	auger	1995	high T high Al, Ca, Fe	N/A	C-Farm Tape 1
95AUG016	auger	1995	high T	#13481, 45 g #13482, 70 g #13485, 46 g	C-Farm Tape 1
S-101					
137:7	core	1996	high T	#16902, 136 g #16911, 116 g	S-Farm Tapes B, 13A, & 13B
S-101 137:8	core	1996	high T	#10006, 52 g	S-Farm Tapes B, 13A, & 13B
137:9	core	1996	high T	#10007, 46 g #15581, 51 g #16664, 71 g	S-Farm Tapes B, 13A, & 13B
138:7	core	1996	high T high Al	#9899, 80 g #9898, 88 g #16953, 88 g #15899, 60 g #9517, 72 g	S-Farm Tapes B, 13A, & 13B
138:8	core	1996	high T high Al, Mn	#9564, 91 g #9815, 68 g	S-Farm Tapes B, 13A, & 13B
138:9	core	1996	high T high Al, Mn, U	#9900, 83 g #9901, 61 g	S-Farm Tapes B, 13A, & 13B

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
				#16914, 59 g	
142:6	core	1996	high T high Al, Cr	#9875, 83 g #9876, 61 g #16673, 43 g #16908, 91 g	S-Farm Tapes B, 13A, & 13B
142:7	core	1996	high T high Al	#9877, 84 g #9878, 79 g #16921, 95 g #16925, 97 g	S-Farm Tapes B, 13A, & 13B
142:8	core	1996	high T high Al, Mn, U	#9879, 59 g #9880, 74 g #14916, 122 g #15608, 21 g	S-Farm Tapes B, 13A, & 13B
S-107					
105:3	core	1995	high T high Cr, F, Mn, PO <sub>4</sub> <sup>-3</sup> in UH high F, Zr in LH	#7983, 65 g #7984, 52 g #13156, 15 g	S-Farm Tape 13
105:4	core	1995	high T high F, U, Zr	#7985, 64 g #7986, 65 g #11839, 95 g #13162, 74 g	S-Farm Tape 13
105:5	core	1995	high T high F, U, Zr	#7835A, 43 g #7836, 75 g #7987, 60 g #7988, 61 g	S-Farm Tape 13
105:6	core	1995	high T	#7989, 55 g #7990, 82 g	S-Farm Tape 13
S-107 105:7	core	1995	high T high U	#7991, 63 g #7992, 39 g	S-Farm Tape 13
105:8	core	1995	high T high U	#7993, 7 g #7995, 38 g #13075, 79 g	S-Farm Tape 13
110:3-UH	core	1995	hard black chunks	#8452, 39 g	S-Farm Tape 13

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
			high T high F, Mn, Zr	#13463, 86 g	
110:3-LH	core	1995	high T high Zr	#8456, 25 g #13161, 66 g	S-Farm Tape 13
110:3A	core	1995	high T high F, U, Zr	#13471, 100 g #13165, 58 g #8001, 53 g #8002, 49 g	S-Farm Tape 13
110:4	core	1995	high T high F, Zr in UH	#8006, 66 g #8007, 51 g #13520, 102 g	S-Farm Tape 13
110:5	core	1995	high T	#8008, 62 g #8011, 72 g #11842, 78 g #13167, 98 g	S-Farm Tape 13
110:6	core	1995	high T high Al in UH	#8009, 60 g #8010, 76 g #13450, 105 g	S-Farm Tape 13
110:7	core	1995	high T high $C_2O_4^{-2}$ , $PO_4^{-3}$ in UH	#8012, 55 g #9793, 129 g	S-Farm Tape 13
110:8	core	1995	high T high Al, U	#8017, 32 g #8018, 58 g	S-Farm Tape 13
111:3	core	1995	high T high F, Zr	#7743, 50 g #8021, 58 g #8022, 59 g #10309, 33 g	S-Farm Tape 13
111:4	core	1995	high T high F, $PO_4^{-3}$ , Zr	#8019, 72 g #8020, 73 g #13439, 81 g	S-Farm Tape 13
111:5	core	1995	high T high U, Zr	#8368, 81 g #8369, 112 g #13465, 75 g #13467, 31 g	S-Farm Tape 13
111:6	core	1995	high T	#8366, 103 g	S-Farm Tape 13

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
			high U in LH	#8367, 107 g	
111:7	core	1995	high T	#8370, 120 g #8371, 119 g	S-Farm Tape 13
S-107 111:8	core	1995	high T high Al, U	#8374, 30 g	S-Farm Tape 13
S-110					
140:4C	core	1996	high push force high T	#10202, 23 g	S-Farm Tape 13B
240:7	core	1998	high T	#14625, 34 g	S-Farm Tapes B & C
240:8	core	1998	high T high Bi, CO <sub>3</sub> <sup>-2</sup> , Cr, La, Mn, SO <sub>4</sub> <sup>-2</sup>	#14628, 5 g #15001, 66 g	S-Farm Tapes B & C
240:9	core	1998	high T high Al, U	#14972, 18 g	S-Farm Tapes B & C
240:10	core	1998	high T high Al	#14601, 57 g #14999, 55 g #14639, 13 g	S-Farm Tapes B & C
241:5	core	1998	high T	N/A	S-Farm Tapes B & C
241:6	core	1998	high T	N/A	S-Farm Tapes B & C
241:7	core	1998	high T high Al, U	#14727, 44 g #14730, 48 g #14558, 96 g #14632, 129 g	S-Farm Tapes B & C
241:8	core	1998	high T high Al, U	#14998, 32 g #15000, 70 g	S-Farm Tapes B & C
SX-101					
225:1	core	1998	high T high Cr	#13640, 27 g	SX-Farm Tapes 10 & 10A
225:2	core	1998	high T high Cr	#11845, 58 g #13650, 109 g	SX-Farm Tapes 10 & 10A

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
225:3	core	1998	high push force high T high Cr	N/A	SX-Farm Tapes 10 & 10A
225:3A	core	1998	high T high Cr	#13506, 46 g	SX-Farm Tapes 10 & 10A
225:4	core	1998	high T	#13652, 40 g	SX-Farm Tapes 10 & 10A
SX-101 225:5	core	1998	high T high Cr	#13667, 71 g	SX-Farm Tapes 10 & 10A
225:5R	core	1998	high T high Cr	N/A	SX-Farm Tapes 10 & 10A
225:6	core	1998	high T high Cr, Mn, U in UH	#13662, 74 g #14067, 116 g	SX-Farm Tapes 10 & 10A
225:7	core	1998	high T high Mn	#12924, 20 g	SX-Farm Tapes 10 & 10A
225:7A	core	1998	high T high Cr	#12931, 30 g #13657, 68 g	SX-Farm Tapes 10 & 10A
225:7B	core	1998	high T high Cr	#13653, 83 g #12930, 7 g	SX-Farm Tapes 10 & 10A
225:8	core	1998	high T high Cr	#13669, 14 g	SX-Farm Tapes 10 & 10A
227:2	core	1998	high push force high T high Cr, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	#13635, 51 g	SX-Farm Tapes 10 & 10A
227:4	core	1998	high T high Al, Cr	#14023, 29 g	SX-Farm Tapes 10 & 10A
227:5	core	1998	high push force high T high Al, Cr	#12963, 100 g #14001, 123 g	SX-Farm Tapes 10 & 10A
227:5A	core	1998	high T	#12957, 82 g #12973, 62 g #13999, 52 g #14000, 47 g #14006, 79 g	SX-Farm Tapes 10 & 10A

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
227:6	core	1998	high T	#14007, 85 g #14002, 49 g #14003, 34 g #14005, 79 g #14008, 93 g #13846, 25 g	SX-Farm Tapes 10 & 10A
227:7	core	1998	high T high Cr	#14009, 42 g #14004, 10 g	SX-Farm Tapes 10 & 10A
SX-101 227:7A	core	1998	high T high Al, Cr	#14030, 18 g	SX-Farm Tapes 10 & 10A
SX-102					
243:1	core	1998	high T	N/A	SX-Farm Tapes 20A, C
243:2	core	1998	high T high Cr	#12388, 21 g #14644, 110 g	SX-Farm Tapes 20A, C
243:3	core	1998	high T high Cr	#14974, 12 g	SX-Farm Tapes 20A, C
243:4	core	1998	high T	#14626, 83 g	SX-Farm Tapes 20A, C
243:5	core	1998	high T	N/A	SX-Farm Tapes 20A, C
243:6	core	1998	high T high Cr	#14588, 44 g #14648, 124 g	SX-Farm Tapes 20A, C
243:7	core	1998	high T	#14652, 47 g	SX-Farm Tapes 20A, C
243:8	core	1998	high T	N/A	SX-Farm Tapes 20A, C
243:9	core	1998	high T	#14642, 126 g	SX-Farm Tapes 20A, C
243:10	core	1998	high T	#14646, 79 g	SX-Farm Tapes 20A, C
244:2	core	1998	high T high Cr	#12390, 13 g #14651, 123 g	SX-Farm Tapes 20A, C

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
244:3	core	1998	high T high Cr	#14653, 57 g	SX-Farm Tapes 20A, C
244:4	core	1998	high push force high T high Cr, $C_2O_4^{-2}$	#14604, 98 g (sludge) #14967, 108 g (salt)	SX-Farm Tapes 20A, C
244:5	core	1998	high push force high T	N/A	SX-Farm Tapes 20A, C
244:6	core	1998	high T high Cr, $C_2O_4^{-2}$	#14966, 76 g	SX-Farm Tapes 20A, C
244:7	core	1998	high T high Cr	#13005, 10 g #14968, 2 g #14969, 120 g	SX-Farm Tapes 20A, C
244:8	core	1998	high T	#15030, 50 g	SX-Farm Tapes 20A, C
244:9	core	1998	high T high Cr	N/A	SX-Farm Tapes 20A, C
SX-102 244:10	core	1998	high T high Cr	#14612, 21 g	SX-Farm Tapes 20A, C
SX-103					
235:3	core	1998	high T high $CO_3^{-2}$ , Cr, $SO_4^{-2}$	N/A	SX-Farm Tapes 20, 20A
235:4	core	1998	high T	#13935, 40 g	SX-Farm Tapes 20, 20A
235:5	core	1998	high T	#13902, 60 g	SX-Farm Tapes 20, 20A
235:6	core	1998	high push force high T	#14569, 26 g #14463, 121 g	SX-Farm Tapes 20, 20A
235:6A	core	1998	high push force high T	#14224, 67 g	SX-Farm Tapes 20, 20A
235:7	core	1998	high T	#14466, 110 g	SX-Farm Tapes 20, 20A
235:8	core	1998	high T	#14467, 125 g	SX-Farm Tapes

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
			high CO <sub>3</sub> <sup>-2</sup> , Cr, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup>		20, 20A
235:9	core	1998	high T	#14950, 80 g	SX-Farm Tapes 20, 20A
235:9A	core	1998	high T	#14062, 14 g	SX-Farm Tapes 20, 20A
235:10	core	1998	high T	#14446, 12 g	SX-Farm Tapes 20, 20A
235:11	core	1998	high T high Al	#14468, 83 g	SX-Farm Tapes 20, 20A
235:12A	core	1998	high T high Al	#14444, 19 g	SX-Farm Tapes 20, 20A
239:1A	core	1998	high T	#14445, 8 g #14594, 241 g	SX-Farm Tapes 20, 20A
SX-103 239:2	core	1998	high T	N/A	SX-Farm Tapes 20, 20A
239:3	core	1998	high T	N/A	SX-Farm Tapes 20, 20A
239:4	core	1998	high T	N/A	SX-Farm Tapes 20, 20A
239:5	core	1998	high T high Cr, SO <sub>4</sub> <sup>-2</sup>	N/A	SX-Farm Tapes 20, 20A
239:6	core	1998	high T	N/A	SX-Farm Tapes 20, 20A
239:7	core	1998	high T	N/A	SX-Farm Tapes 20, 20A
239:8	core	1998	high T high Cr, SO <sub>4</sub> <sup>-2</sup>	#13595, 45 g	SX-Farm Tapes 20, 20A
239:9	core	1998	high T high Cr	#14589, 32 g	SX-Farm Tapes 20, 20A
239:9R1	core	1998	high T high Cr, SO <sub>4</sub> <sup>-2</sup>	#14577, 50 g	SX-Farm Tapes 20, 20A
239:10R1	core	1998	high T high CO <sub>3</sub> <sup>-2</sup>	N/A	SX-Farm Tapes 20, 20A

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
239:11R	core	1998	high T high Cr, Mn, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	#14605, 133 g #14607, 43 g	SX-Farm Tapes 20, 20A
239:12	core	1998	high T high Al, Cr	N/A	SX-Farm Tapes 20, 20A
239:12A	core	1998	high T	#14475, 30 g	SX-Farm Tapes 20, 20A
SX-105					
229:5	core	1998	high T	N/D	N/A
229:6	core	1998	high T	N/D	N/A
229:6R	core	1998	high T high Cr, SO <sub>4</sub> <sup>-2</sup>	N/D	N/A
SX-105 229:7	core	1998	high T	N/D	N/A
229:8	core	1998	high T high Cr, CO <sub>3</sub> <sup>-2</sup> , C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup>	N/D	N/A
229:9	core	1998	high T	N/D	N/A
229:10	core	1998	high T	N/D	N/A
229:11	core	1998	high T high Cr, CO <sub>3</sub> <sup>-2</sup> , C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup>	N/D	N/A
229:12	core	1998	high T high Cr, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	#13588, 69 g #14046, 94 g	N/A
229:12A	core	1998	high T high Al	#13558, 55 g #14052, 69 g	N/A
229:13	core	1998	high T high Al, Fe, Mn	#14263, 74 g #14261, 121 g #14054, 132 g #14055, 96 g	N/A
233:6	core	1998	high T high downforce	N/D	N/A
233:7	core	1998	high T	N/D	N/A
233:8	core	1998	high T	N/D	N/A
233:9	core	1998	high T	N/D	N/A
233:10	core	1998	high T	N/D	N/A
233:10AR	core	1998	high T	N/D	N/A

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
233:11	core	1998	high T	#14449, 13 g	N/A
233:12	core	1998	high T high Al	#14593, 92 g #14616, 24 g	N/A
233:13A	core	1998	high T high Al	N/A	N/A
SX-106					
223:10	core	1997	high T high Cr, C <sub>2</sub> O <sub>4</sub> <sup>-2</sup>	#13541, 100 g #13622, 121 g	SX-Farm tape
224:10	core	1997	high T	N/A	SX-Farm tape
224:11	core	1997	high T high Cr	#12918, 192 g #13648, 94 g #13649, 100 g	SX-Farm tape
SX-108					
95-AUG-042-UH	auger	1995	high T high Cr, Mn	N/A	SX-Farm Tape 10
95-AUG-042-LH	auger	1995	large gray chunks high T high Cr	N/A	SX-Farm Tape 10
SX-108 95-AUG-043-UH	auger	1995	large gray-black chunks high T high Cr, Fe, Mn, U	#7978, 55 g #8116, 7 g	SX-Farm Tape 10
95-AUG-043-LH	auger	1995	high T high Cr, Fe, Mn, U	#8115, 3 g	SX-Farm Tape 10
SX-115					
15SX-98-1	finger- trap	1998	clumps of black material high T	Composites: #14056, 28 g #14252, 25 g	N/A
15SX-98-2		1998	clumps of black material high T		N/A
15SX-98-3		1998	clumps of black material high T		N/A
SY-103					
62:3	core	1994	colorless chunks	N/A	N/A
62:4	core	1994	light-brown chunks	N/A	N/A

Tank/ Sample	Type	Year Taken	Notes	Archive Jars	Videotapes
62:5	core	1994	light-brown chunks	#7029, 7 g	N/A
62:6	core	1994	light-brown chunks	#7035, 3 g	N/A
62:7	core	1994	light-brown chunks	N/A	N/A
94AUG003	auger	1994	hard crumbly solids	N/A	N/A
T-105					
205:2	core	1997	gray and clear crystals high Al, F, Mn, PO <sub>4</sub> <sup>-3</sup> , U	#13046, 19 g #13057, 21 g	T-Farm Tape 17
207:1	core	1997	black gravel high Mn	#13054, 40 g	T-Farm Tape 17
U-101					
1U-96-1	grab	1996	pea gravel	#13241, 47 g	N/A
1U-96-2	grab	1996	pea gravel	#13240, 47 g	N/A
1U-96-3	grab	1996	½" gravel	#13242, 47 g	N/A
1U-96-4	grab	1996	sand	#13243, 47 g	N/A
<p>Samples taken before 1994 have been excluded as categorically unavailable. Samples from the 200-series tanks have also been excluded because those tanks contain little waste and the waste is not typical of what is found in the large tanks.</p> <p>UH is the "upper half" of a segment; LH is the "lower half".</p> <p>"N/A" is "not available"; "N/D" is "not determined".</p> <p>Sub-segments and half-segments are distinguished from each other only to the extent necessary to distinguish between those containing chunks or granules and those of relatively smooth or salt-like (i.e., soluble) appearance.</p>					

**Table A-3. Samples Observed to Contain Hard or Stiff Waste**

Tank	Sample	Date	Description
A-101	1A-96-2	4/3/96	Grab sample (taken from 101" elevation) was a clear yellow liquid containing approximately 50% solids. Solids were dirty white and crystalline in appearance with hard, dark gray chunks that had settled on the bottom of sample jar.
A-101	1A-96-3	4/3/96	Grab sample (taken from 13" elevation) was 95% solids. A dark gray, very wet, crystalline slurry, containing small chunks.
A-102	95AUG33	6/7/95	Auger collected 96.5 g of a gritty, paste-like material, which contained small black, chunky pebbles. Flutes 7-19 contained the majority of the sample. The black pebbles were archived.
A-102	'96-AUG-003	3/21/96	Auger collected 198.3 g of solid material from the bottom 26 flutes. The solids were brown, runny and wet with a texture resembling a wet sludge. The sludge contained pebble-like material throughout. The solids were sub-sampled into one jar.
AP-104	4AP-96-2C	1/23/96	Grab sample was 100 mLs of a clear homogeneous liquid, no turbidity. A large particle was observed at the bottom of the jar. Sample was collected in an amber jar so the color was undeterminable.
AW-105	196:5	5/9/97	Push-mode core sample contained no drainable liquid, but 19 inches of white solids with a texture resembling a wet sludge. Upper half contained small black chunks. Sub-sampled solids in half segments.
AW-105	5AW-96-20	8/20/96	~125 mL of grab sample, which was 92.6%, settled solids. The material was a non-homogeneous mixture consisting of somewhat even amounts of yellow and gray soft sludge swirled together with larger black and/or white chunks scattered throughout.
AX-104	97-AUG-001	11/13/97	Auger collected 96.8 g of solids from flutes 1-12 and the auger liner. The sample appeared to be a mixture of light brown, fine powder and darker, coarser material. Two small pieces of clear plastic or glass were found but not added to the sample jar.
AX-104	97-AUG-002	11/13/97	Auger collected 39.5 g of solids from flutes 1-11 and the auger liner. The sample was a mixture of light brown, fine powder and darker, coarser material.
AX-104	97-AUG-003	11/14/97	Auger collected 80.8 g of solids from flutes 1-18 and the auger liner. The sample was dark brown and varied from a fine powder to clumps of dried sludge and flakes of crystalline material.
AX-104	97-AUG-004	11/21/97	Auger collected 36.9 g of solids from flutes 1-6 and the auger liner. The sample varied in appearance from a fine powder to clumps of dried sludge and flakes of crystalline material. Some small plastics like pieces were added to the jar.
AZ-101	3:1	6/29/89	Push-mode core sample contained 2.5 g of drainable liquid. Extruded 173 g of solid material which was fluid and didn't maintain the cylindrical shape of the sampler after extrusion. One large chunk of material, which was shiny and non-magnetic, was segregated.

AZ-101	266:7	11/6/99	Drainable liquid from the push-mode core sample was clear and yellow in color. Two pea-sized chunks of white solids having a texture resembling a dry salt were observed. The solids were retained with the liquid.
AZ-101	269:16	11/19/99	The push-mode core sample drainable liquid was opaque and brown in color. Extruded 4 inches of brown solids with a texture resembling sludge slurry. There were 3 small rocks found which were cleaned and retained separately.
B-101	91:1	6/23/95	Core sample extruded 16 inches of smooth solids. The upper 12 inches was medium brown, the lower 4 inches was dark brown. A 1/2-inch piece of flat hard material was found in the upper segment.
B-103	95AUG31	5/24/95	Auger sample extruded approximately 4 inches (45 g) of damp gray-black crystals, which were shaped like short fibers from flutes 15 through 18 of the auger.
B-107	217:1	9/5/97	Push-mode core sample extruded 11 inches of solids. Upper half was brown, had a white paste center and a texture resembling wet sludge. The lower half was brown with salt chunks and a texture like wet salt.
B-201	27:2 – 27:5	7/3/91	No drainable liquid in push-mode core sample. Shiny black sludge. The top 1-inch of the segment flowed upon extrusion while the remainder was stiff. The sample contained a significant amount of moisture.
B-201	27:6 – 27:8	8/3/91	No drainable liquid in push-mode core sample. Stiff shiny black sludge that maintained its shape upon extrusion. The sample contained a significant amount of moisture.
B-202	24:5	6/26/91	Push-mode core sample contained no drainable liquid and was visually homogeneous throughout. The sample was black-brown in color, drier than segment above and extruded like thick paste.
B-202	25:8	7/18/91	Push-mode core sample contained no drainable liquid. The segment was filled with a thick, black homogeneous material. The consistency of the segment was drier than the upper segments; a paste that broke into cylindrical pieces when extruded.
BX-103	86:1	5/24/95	Drainable liquid from push-mode core sample was turbid and dark black in color. Extruded 4 inches of black, grainy, runny, very wet solids.
BX-103	86:2	5/26/95	Drainable liquid from push-mode core sample was turbid and black in color. Extruded 14 inches of black, wet, grainy solids. The interior of the sample contained a white, chalky material.
BX-103	87:1	5/30/95	Drainable liquid from push-mode core sample was turbid and black in color. Extruded 7 inches of shiny black, wet, grainy solids.
BX-106	95-AUG-49	12/15/95	Extruded black soft wet sludge material from the bottom 8 flutes of the auger. The auger sample also contained about 3 pieces of white material.
BX-108	94AUG007	7/22/94	No drainable liquid in the auger sample. Collected 8.25 g of hard brittle white crust material from flutes 1-3. Collected 10.35 g of hard brittle tan clay-like material from flutes 4 & 5. Collected 15.68 g of dry brittle light brown material from flutes 6-8.
BX-112	118:3	11/30/95	A medium brown material poured from the push-mode

			core sampler during extrusion. Two brown clay-like chunks were observed. 242.2 g of solid material and 45.3 mL of drainable liquid.
<b>BY-105</b>	108:2AR	8/30/95	Drainable liquid was cloudy and light brown in color. Extruded 5-6 inches of light and medium brown solids with a texture resembling salt cake. The solids contained a few dark hard chunks, which appeared to be rocks.
<b>BY-105</b>	108:3	8/30/95	Rotary-mode core sample extruded a small amount of gray-brown slushy material, which ranged from clear crystals to dark chunks that resembled gravel.
<b>BY-110</b>	92:6	7/13/95	Drainable liquid from the rotary-mode core sample was turbid and yellow-green in color. Extruded 9 inches of yellow, crystalline solids. Upper 6 inches resembled crushed ice while the lower 3 inches resembled shaved ice. Sub-sampled in half segments.
<b>BY-110</b>	95:4	8/2/95	Rotary-mode core sample extruded 2.5 inches of a crumbly, very hard, brown crystalline solid material.
<b>BY-110</b>	101:3	8/29/95	Rotary-mode core sample extruded 2 inches of dry, tan, powdery solid material that resembled sand. 4 large, hard chunks of material (0.5 inches in diameter) were also recovered.
<b>BY-110</b>	101:7	8/29/95	Rotary-mode core sample extruded 18 inches of dark gray-brown, grainy sludge. Slurry material with small, discrete pieces of solid dispensed throughout was also recovered.
<b>BY-110</b>	103:7	8/15/95	Rotary-mode core sample extruded 100 mL of a slurry liquid followed by 3 to 4 inches of gray-black solids designated as the lower half. A 6 inch gap followed the lower half. The upper half was 7 inches of gray-black, hard, granular, wet solids. Sub-sampled in half segments.
<b>BY-110</b>	103:8	8/15/95	Rotary-mode core sample extruded 19 inches of wet material; the upper 14-15 inches were gray-black, hard, granular solids. The bottom 4-5 inches appeared to be dark brown sludge.
<b>BY-110</b>	107:7	8/24/95	Rotary-mode core sample extruded 10 inches of slurry with brown, homogeneous solids consisting of sludge and hard, chunky material.
<b>BY-110</b>	109:1	9/13/95	Rotary-mode core sample extruded 3 inches of dry, crumbly, yellow and white sand-like particles intermixed with gray to black sand-like material.
<b>BY-110</b>	113:4A	10/28/95	Rotary-mode core sample extruded 16 inches. The first 2 inches were solids, followed by a 7 inch gap, and another 7 inches of solids. The solids were brown, granular, wet, hard and crystalline.
C-107	69:5	3/7/95	Push-mode core sample extruded 18 inches of light brown to tan sludge. The lower 9 inches showed some pitting but retained its shape. The upper 9 inches was wetter, didn't retain its shape and contained some firm white chunks of material. Sub-sampled solids in half segments.
C-108	94AUG015	12/12/94	Auger collected 295 g of moist, tan, paste-like solids with an off-white material embedded throughout. The off-white chunks were hard and could not be homogenized.
C-109	49:1	9/6/92	Push-mode core sample extruded 13 inches of light brown sludge with white streaks apparent throughout. Sample maintained its shape upon extrusion but contained a significant amount of moisture. A hard white chunk of

			solid material was observed in the sludge.
C-201	221:1, 221:4	9/23/97	Push-mode core sample collected a very dry, gray-black solid material with some white crystalline material dispersed throughout with a texture ranging from a fine powder to large chunks. Material exhibited magnetic properties.
C-201	221:1A	9/23/97	Push-mode core sample extruded one-half inch (4.05 g) of very dry gray-black sludge material with some white particles dispersed throughout. Sample consisted of a large hard chunk with powdery solids surrounding it.
S-107	110:3	9/25/95	Push-mode core sample extruded 425.9 g of solid material. The lower half was white/cream colored and covered with a gray-brown coat. The upper half had a tendency to flow in some portions, was black in color and contained hard chunks of solids. Sub-sampled into half segments.
SX-108	95-AUG-042	9/15/95	Auger collected 81.3 g of solids. Upper half portion was 30.8 g of very dry, powdery gray solids. Lower half portion was 50.5 g of material similar to the upper portion but also contained some large chunks of material. Sub-sampled in half segments.
SX-108	95-AUG-043	9/19/95	Auger collected a total of 144.1 g of solids. The upper portion was 135 g of dry, powdery gray-black solids containing some large chunks of material. The lower half was 9.1 g of a fine, gray powder.
SY-103	62:3	8/19/94	Push-mode core sample collected 262 mLs of a turbid medium brown drainable liquid. Collected 20 g of homogeneous, colorless chunky solid material resembling wet salt or crushed ice.
SY-103	62:4 – 62:7	8/19/94	Push-mode core sample collected >250 mLs of a turbid medium brown drainable liquid. Collected 20-40 g of homogeneous, light brown chunky solid material resembling "snow cone" ice.
SY-103	94AUG003	6/8/94	Auger collected approximately 11 g of white and gray solids from flutes 1-6. The sample appeared to be crumbly, inhomogeneous and had a hard crusty texture.
T-105	205:2	6/24/97	Push-mode core sample collected 35 mLs of opaque black drainable liquid. Extruded 3 inches of black sludge/slurry coating large pieces of very hard crystalline material. Some material was faceted clear crystals and the rest was darker gray and more cement-like.
T-105	207:1	6/24/97	Push-mode core sample collected 160 mls of an opaque black drainable liquid. Extruded 2 inches of black sludge slurry with very small gravel-like chunks mixed in resembling granular sludge slurry.
U-101	1U-96-1, 1U-96-2	5/30/96	Grab sample collected a clear yellow liquid containing large settled solid chunks the size of pea gravel and a small amount of fine precipitate.
U-101	1U-96-3	5/29/96	Grab sample collected a clear yellow liquid containing a few large settled solid chunks the size of 1/2 inch gravel and a small amount of fine precipitate.
U-101	1U-96-4	5/29/96	Grab sample collected a clear yellow liquid containing approximately 29% by volume of sand sized solids.
U-110	5:4	11/7/89	Push-mode core sample contained no drainable liquid. Extruded 16 inches light brown to black solids. The bottom 4 inches were very soft and runny, middle was

			firmer and top 5 inches were rubbery firm. Small hard chunks 1/8 inch in diameter throughout solids.
U-110	7:3	11/15/89	Push-mode core sample contained no drainable liquid. Extruded 6 inches dark brown solids. Granular texture throughout the sample with some hard "bits".
U-110	7:4	11/15/89	Push-mode core sample contained no drainable liquid. Extruded 7 inches of brown solids, which broke into 6 segments. Surface of bottom 2 inches was moist with the rest dry and very crumbly. Middle section had no cohesiveness. Hard chunks were found in the very dry crumbly part.
U-110	12:2	11/29/89	Push-mode core sample contained no drainable liquid. Extruded 4 inches of very dark brown solids, which broke into cohesive portions upon extrusion. One hard "chunk" (1/4 inch) in the sample.
U-110	13:4	11/30/89	Push-mode core sample contained no drainable liquid. Extruded 8 inches of dark brown solids, which were slightly soft and contained some hard "chunks".
U-110	14:1	12/3/89	Push-mode core sample contained no drainable liquid. Extruded 10 inches of white chalk like solid material.
U-110	14:4	12/3/89	Push-mode core sample contained no drainable liquid. Extruded 15 inches of brown solids, which were somewhat crumbly but moist throughout. Small hard solids found in the sample.
U-201	70:1	3/15/95	Push-mode core sample collected 35 g of drainable liquid. Collected 193 g of yellow solids containing large chunks of crystals and small black spots throughout. Sub-sampled solids in half segments.
U-201	70:2	3/15/95	Push-mode core sample collected 59 g of drainable liquid. Collected 259 g of solid material. The lower half contained large crystals and the upper 4-5 inches was yellow sludge and tended to melt on the sample tray. Sub-sampled solids in half segments.
U-201	73:1	3/17/95	Push-mode core sample collected 142 g of drainable liquid. Collected 17 g of yellow sludge mixed with large chunks of crystals. Sludge did not retain the shape of the sampler.
U-201	73:2	3/17/95	Push-mode core sample collected 117 g of drainable liquid. Collected 132 g solid material that did not retain the shape of the sampler. Large crystalline solids were extruded near the top of extrusion.
U-202	75:1	3/22/95	Push-mode core sample collected 155 g of yellow drainable liquid. Extruded 5 inches of light yellow, damp, creamy solids containing some black specks and large crystals. The first 3 inches of solids retained the shape of the sampler while the last 2 inches melted on the tray.
U-202	78:2	3/22/95	Push-mode core sample collected 19 g of yellow drainable liquid. Extruded 8 inches of light yellow solids with the first 4 inches being light yellow crystals and the last 4 inches being light yellow sludge. Subsampled solids in half segments.
U-203	79:1	3/31/95	Push-mode core sample collected 45 g of a yellow drainable liquid. Collected 105 g of solids, which consisted of yellow crystals with black specks dispersed throughout the crystals.

U-203	80:1	3/31/95	Push-mode core sample extruded 6 inches of solid material. The lower half segment consisted of 3 inches of yellow crystals. The upper half segment consisted of 3 inches of yellow sludge.
<b>Boldface</b> indicates high-temperature tanks (those listed in Table 1).			

#### 8.4 Relevant Sluicing History

This section summarizes past sluicing practice, with an eye to observations of heels. The major sluicing efforts at Hanford were programs carried out in the 1950s and 1960s, and the transfer of high-heat waste from tank C-106 to tank AY-102 in the late 1990s.

Rodenhizer (1987) described the effects of two sluicing programs. The first was carried out in forty-three tanks in the 241-B-, BX-, BY-, C-, T-, TX-, and U-tank farms between 1952 and 1957 to recover uranium from the Bismuth Phosphate Plant (BPP) waste in the tanks. The second sluicing program was carried out to various degrees of completeness in ten tanks in the A- and AX-tank farms between 1962 and 1978 to separate strontium and cesium from the bulk of the waste.

##### 8.4.1 Heavy Metal Waste

The solids in BPP waste were believed to be  $\text{SiO}_2$ ,  $\text{NaUO}_2\text{PO}_4$  (needle-like crystals thought to make up most of the soft sludge), and  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$  (a chalk-like dense agglomerate of imperfectly formed crystals thought to make up most of the "hard rock" or "hard pan" sludge). It is worth noting here that one 1995 core sample from the bottom of BX-103, core segment 86:2, contained a white chalky material. (BX-103 is not included in Table A-1 because records showed that the maximum measured waste temperature was only 99 °F.) The sodium uranyl phosphate was easily slurried, unlike the carbonate. The sodium uranyl carbonate solubility was found to decrease with temperature.

Uranium recovery sluicing was performed initially with supernatant, later with water as the sludge level in a tank decreased, and finally a steam jet was used to remove "virtually all of the remaining sludge in the tank" (the waste below the pumpable level). Water sluicing greatly improved the recovery of the sodium uranyl carbonate, compared to what was achieved with supernatant.

Rodenhizer (1987) describes the uranium recovery tanks as all being "essentially empty" when sluicing was ended, but does not define what that meant. These tanks were B-101 through B-103, BX-101 through BX-106, BY-101 through BY-106, BY-111, BY-112, C-101 through C-106, C-201 through C-204, T-101 through T-103, TX-101 through TX-108, and U-101 through U-109. Of these, only four tanks (BY-104 through BY-106 and TX-105) had peak temperatures above 180 °F. Except in the case of TX-105, whose peak temperature was in 1952, the peaks all occurred decades after the uranium recovery sluicing was complete.

##### 8.4.2 Strontium Recovery Sluicing

In many cases, hard heavy particles were found in the waste in the strontium recovery tanks. The available details were given by Rodenhizer (1987) and are summarized here.

The post-sluicing residual sludge in tank A-101 in 1976 was water-insoluble and contained coarse gray sand-like crystals combined with small reddish-brown particles and quarter-sized hard chunks. The particle density was 2.78 g/cc. X-ray analysis showed that  $\text{AlPO}_4$ ,  $\text{SiO}_2$  (alpha-quartz),  $\text{FeAl}_2\text{SiO}_5(\text{OH})_2$ ,  $\text{Al}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ , and  $\text{KAlSiO}_4$  were present.

Tank A-102 was sampled during a sluicing campaign in 1972. Sodium, manganese, and iron were found the major constituents, with 96 wt% of the particles falling in the 10 to 50  $\mu\text{m}$  ranges. Particles of similar size were found in Tank A-104 when partially sluiced in July 1974 (major constituents Al, Fe, Si, and Mn).

Samples were taken from all of the other strontium recovery tanks as well, but in general these were pre-sludging samples, or their relation to sludging was not clear. Aluminum, iron, silicon, and manganese appeared repeatedly in analyses, and these sludges were generally soft, red to dark brown, and less than 50  $\mu\text{m}$  in particles size. AX-103 sludge contained some larger particles, with 10 wt% having diameters greater than 100  $\mu\text{m}$ . However, considering the carbonate and phosphate content of this sludge the sample was probably taken before sludging and the large particles may have been soluble.

Partway through sludging A-105 a very hard crust was found, whose major constituents were Na, Fe,  $\text{CO}_3$ , and  $\text{SO}_4$ ; only nitric acid and inhibited sulfuric acid acted to soften this material. It was also observed that the heel in tank AX-102 was heavy and difficult to suspend.

The strontium recovery sludging technique was similar to that of uranium recovery except that no steam jet was used. The goal of the strontium recovery-sludging program was to reduce the waste level to a one to two inch heel. All six tanks in A-farm and all four tanks in AX-farm were sludged to some extent. Tanks A-101 through A-103, AX-101, and AX-102 were sludged to the one to two inch levels. The remaining tanks were not sludged so far down because they were found to be leaking (A-104 and A-105) or because the program ended before sludging operations were complete. All of the strontium recovery tanks were high-temperature tanks and are listed in Table A-1.

#### **8.4.3 C-106 Sludging**

In-tank videos show that gravel-like waste, including pieces a few inches across, was left behind in C-106 after the sludging campaign of November 1998 to October 1999. No samples of this waste heel have been taken to date.

#### **8.5 Phase Identification Studies**

Rapko and Lumetta (2000) gathered together phase information that had been collected at Los Alamos National Laboratory (LANL) and Pacific Northwest National Laboratory (PNNL) for a number of sludge waste samples. The samples were typically core sample composites rather than single core segments. Details of the analysis methods are given in the reference. Table A-4 contains a precis of the results given by Rapko and Lumetta (2000). The italicized phases are those that were seen only after caustic leaching, whether because they were formed by leaching or because they had previously been masked by higher-concentration leachable phases. Note that salt phases – for example, sodium nitrate and nitrite – may represent material from interstitial liquid that had dried out, rather than in-situ salt solids.

**Table A-4.** Phase Information for Hanford Sludge Waste Composites

Tank	Phases	Method
AN-104	aluminosilicate (am), $UO_2$ or $U_3O_7$	TEM
AW-105	$Al(OH)_3$ , aluminosilicate (c)	TEM/SEM/XRD
AZ-101	$NaNO_3$ , $NaNO_2$ , $Na_2CO_3(H_2O)$	SEM
AZ-102	$NaNO_3$ , $NaNO_2$ , $Na_2U_2O_7$	SEM
B-104	$Na(NO_3)(SO_4)(H_2O)$ (darapskite), $KMg_3(Si_3AlO) \cdot 10H_2O$ (phlogopite)	XRD
B-110	sodium aluminum silicate hydrate, $BiPO_4$ , $NaNO_3$	SEM/XRD
B-111	aluminosilicates (c), $Bi_{38}CrO_{60}$ , $Na_3PO_4$ , $Fe(OH)_3$ (am), $Bi_2O_3$ , $Fe_2Bi(SiO_4)_2(OH)$	TEM/SEM/XRD
B-202	$NaNO_3$ (natratine)	XRD
BX-103	$Al(OH)_3$ (gibbsite), $Na_2U_2O_7$	XRD
BX-105	$Al(OH)_3$ (gibbsite)	XRD
BX-107	$AlPO_4$ , $Al(OH)_3$ (am), aluminosilicates (c, am), $Bi/FePO_4$ , $Fe_2Bi(SiO_4)_2(OH)$ , $Bi_2O_3$	TEM/SEM/XRD
BX-109	$Al(OH)_3$ (nordstrandite), $NaNO_3$ (natratine), $Na_2U_2O_7$	XRD
BY-104	$(Al_2O_3)_x(H_2O)_y$ , aluminosilicates (am), $Ca_5(OH)(PO_4)_3$ , $Fe(Fe,Cr)_2O_4$ (donathite), $\beta-U_3O_8$ , $Ni_3O_2(OH)_4$ , $FeOOH$	TEM
BY-108	$Ca_xSr_{10-x}(PO_4)_6(OH)_2$ , $\beta-U_3O_8$ , $\gamma-Fe_2O_3$ (maghemite), $FeOOH$	TEM
BY-110	$CrOOH$ (grimaldite), $Ca_5(OH)(PO_4)_3$ , $\beta-U_3O_8$ , $Ni_3O_2(OH)_4$ , $\gamma-Fe_2O_3$ (maghemite)	TEM
C-105	$Al(OH)_3$ (gibbsite), $UO_3(H_2O)$ , $Na_2U_2O_7$	XRD
C-106	$Al(OH)_3$ (am), aluminosilicates (am), $FeOOH$ , $Ag_2O$ , $ZrO_2$	TEM
C-107	$(Al_2O_3)_x(H_2O)_y$ , aluminosilicates (am), $Pb_5(OH)(PO_4)_3$ , $Fe_3O_4$ (hematite), $FeOOH$ , $ZrO_2$	XRD, TEM
C-108	$Al(OH)_3$ (gibbsite), $Ca_3(PO_4)_2$ , $Ca_5F(PO_4)_3$ , $NaNO_3$ (natratine)	XRD
C-109	$Al(OH)_3$ (gibbsite), $AlOOH$ (boehmite), nickel aluminum oxide, $NaNO_3$ , $NaNO_2$ , $SiO_2$ , $Ni(OH)_2$ , $UO_3$	SEM/XRD
C-112	$Al(OH)_3$ (gibbsite), $NaNO_3$ , $NaNO_2$ , $SiO_2$ , $CaU_2O_7$ , $Na_2U_2O_7$	SEM/XRD
S-101	$AlOOH$ (boehmite), aluminosilicates (am), $AlOOH$ (diaspore), $Mn/FeOOH$	TEM/SEM/XRD
S-104	$AlOOH$ (boehmite), aluminosilicates (am), $\beta-U_3O_8$ , $NaNO_3$ (natratine), $UO_2 \cdot 2H_2O$ , $FeMnO_4$	TEM
S-107	$AlOOH$ (boehmite), aluminosilicates (am), $ZrO_2$ , $FeOOH$ , $UO_3$	TEM
S-111	$Al(OH)_3$ (bayerite), $AlOOH$ (boehmite), $FeCr_2O_4$ , $Mn_2CrO_4$ , $Mn_{1.5}Cr_{1.5}O_4$ , $UO_3$	TEM
SX-108	$AlOOH$ (boehmite), aluminosilicates (am), $Ca_3Al_2O_6$ , $(Al_2O_3)_x(H_2O)_y$ , $\beta-U_3O_8$ , $FeOOH$ , $(Mn,Fe)_3O_4$	TEM
SY-101	$NaAlO_2$ , $Al(OH)_3$ (am)	TEM/SEM/XRD
SY-103	$Al(OH)_3$ (am), $(Al_2O_3)_x(H_2O)_y$ (c), $Cr(OH)_3$ , $Fe/Mn$ oxide	TEM/SEM/XRD
T-104	$AlPO_4$ , $Al(OH)_3$ (am), aluminosilicates (c, am), $Bi_{24}Al_2O_{39}$ , $Bi_{38}CrO_{60}$ , chromium phosphate, $Na_2Fe_2Al(PO_4)_3$ , uranyl phosphate hydrate, $Fe_2Bi(SiO_4)_2(OH)$ , $Bi_2O_3$ , bismuth iron oxide silicate	TEM/SEM/XRD
T-107	$Al(OH)_3$ (gibbsite), aluminosilicates (c), $AlPO_4$ , $NaNO_3$ (natratine)	XRD
T-111	$Na_3PO_4$ , $La_4(P_2O_7)_3$ , $Ca_5(OH)(PO_4)_3$ , $Bi/FePO_4$ , $Fe(OH)_3$ (am), $Mn_2MnO_4$ , $Fe_2MnO_4$ (jacobsite), $FeOOH$ (goethite)	TEM/SEM/XRD

TY-104	NaNO <sub>3</sub> (natratine)	XRD
U-110	Al(OH) <sub>3</sub> (gibbsite), AlOOH (boehmite), NaNO <sub>3</sub>	SEM/XRD
(c) – crystalline (am) – amorphous  SEM – scanning electron microscopy and electron dispersive X-ray technique TEM – transmission electron microscopy and electron diffraction technique XRD – X-ray diffraction technique  <b>Boldface</b> indicates high-temperature tanks (those listed in Table 1). <i>Italics</i> indicate phases that appeared only after caustic leaching, either because they were formed by leaching or because they had previously been masked by higher-concentration leachable phases.		

### 8.6 References for Appendix A

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