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Chemistry of Application of Calcination/Dissolution to the Hanford Tank Waste Inventory

C. H. Delegard
T. D. Elcan
B. E. Hey

Date Published
May 1994

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

**Westinghouse
Hanford Company**

P.O. Box 1970
Richland, Washington 99352

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

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			ID Number (include revision, volume, etc.) WHC-EP-0766		
			List attachments. none		
			Date Release Required 27 May 1994		
Title Chemistry of Application of Calcination/Dissolution to the Hanford Tank Waste Inventory				Unclassified Category UC-601	
				Impact Level 4	
New or novel (patentable) subject matter? ☒ No ☐ Yes If "Yes", has disclosure been submitted by WHC or other company? ☐ No ☐ Yes Disclosure No(s).			Information received from others in confidence, such as proprietary data, trade secrets, and/or inventions? ☒ No ☐ Yes (Identify)		
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Title of Conference or Meeting			Group or Society Sponsoring		
Date(s) of Conference or Meeting		City/State		Will proceedings be published? ☐ Yes ☐ No Will material be handed out? ☐ Yes ☐ No	
Title of Journal					
CHECKLIST FOR SIGNATORIES					
Review Required per WHC-CM-3-4		Yes No Reviewer - Signature Indicates Approval Name (printed) Signature Date			
Classification/Unclassified Controlled Nuclear Information		☐ Yes ☒ No			
Patent - General Counsel		☐ Yes ☒ No			
Legal - General Counsel		☐ Yes ☒ No			
Applied Technology/Export Controlled Information or International Program		☐ Yes ☒ No			
WHC Program/Project		☒ Yes ☐ No K. A. Gasper <i>KAGasper</i> 5/23/94			
Communications		☐ Yes ☐ No			
RL Program/Project		☒ Yes ☐ No P. E. Lamont <i>P.E. Lamont</i> 5/31/94			
Publication Services		☒ Yes ☐ No G. O. Gesell <i>per telecom w/KMB</i> 5/31/94			
Other Program/Project		☐ Yes ☒ No			
Information conforms to all applicable requirements. The above information is certified to be correct.					
References Available to Intended Audience		Yes No ☒ Yes ☐ No			
Transmit to DOE-HQ/Office of Scientific and Technical Information		☒ Yes ☐ No			
Author/Requestor (Printed/Signature) C. H. Delegard <i>[Signature]</i>		Date 19 May 1994			
Intended Audience ☐ Internal ☐ Sponsor ☒ External					
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Date Cancelled			Date Disapproved		

Document Title: Chemistry of Application of Calcination/Dissolution to
the Hanford Tank Waste Inventory

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CHEMISTRY OF APPLICATION
OF CALCINATION/DISSOLUTION
TO THE HANFORD TANK WASTE INVENTORY

C. H. Delegard
T. D. Elcan
B. E. Hey

ABSTRACT

Approximately 330,000 metric tons of sodium-rich radioactive waste originating from separation of plutonium from irradiated uranium fuel are stored in underground tanks at the U.S. Department of Energy (DOE) Hanford Site in Washington State. Fractionation of the waste into low-level waste (LLW) and high-level waste (HLW) streams is envisioned via partial water dissolution and limited radionuclide extraction operations. Under optimum conditions, LLW would contain most of the chemical bulk while HLW would contain virtually all of the transuranic and fission product activity. The fractionation will be followed by production of durable waste forms (e.g., glass) for separate long-term storage of LLW and HLW fractions. Under this fractionation scheme, the water-insoluble solids, including insoluble radionuclides plus soluble radionuclides separated from the LLW fraction, will go to the HLW fraction.

Calcination at around 850 °C, followed by water dissolution, has been proposed as an alternative initial treatment of Hanford Site waste to improve waste dissolution and the envisioned LLW/HLW split. Results of literature and laboratory studies are reported on the application of calcination/dissolution (C/D) to the fractionation of the Hanford Site tank waste inventory. Both simulated and genuine Hanford Site waste materials were used in the lab tests.

The evaluation confirmed that C/D processing reduced the amount of several components from the waste. Organic carbon was converted to carbonate while nitrate and nitrite were converted to hydroxide ion and oxygen offgases. The evaluation also showed that calcination of the high-sodium, high-nitrate, alkaline waste achieved oxidizing and chemically aggressive conditions similar to classical, analytical fusions. Using C/D processing of simulated and genuine Hanford Site waste, solubilizations of formerly insoluble aluminum and chromium phases were demonstrated. The benefits of (C/D) processing, as based on these test results, are as follows:

- Destruction of organic components--up to 97%*
- Destruction of nitrate and nitrite--90 to 99.5%*
- Solubilization of nonradioactive aluminum and chromium--80 to 99% aluminum, 95 to >99% chromium.*

The C/D dissolutions of aluminum and chromium allow redistribution of these waste components from the HLW to the LLW fraction. This is envisioned to be a significant advantage because immobilization and disposal of HLW is expected to be considerably more expensive on a unit basis than that of LLW.

Comparisons of simple water-washing with C/D processing of genuine Hanford Site waste are also reported based on material (radionuclide and chemical) distributions to solution and solid residue phases. Depending on the waste source, aluminum dissolution by water wash was about 0.1 to 5% while chromium dissolution was about 2%. The lab results show that C/D processing yielded superior dissolution of aluminum and chromium sludges compared to simple water dissolution.

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LIST OF TERMS

CC	complexant concentrate
C/D	calcination/dissolution
DOE	U.S. Department of Energy
DSP	desilication product
DST	double shell tank
EDTA	ethylenediaminetetraacetate
FY	fiscal year
GEA	gamma energy analyses
HEDTA	N-2-hydroxyethylethylenediaminetriacetate
HLW	high-level waste
HWVP	Hanford Waste Vitrification Plant
LLW	low-level waste
PFP	Plutonium Finishing Plant
REDOX	reduction oxidation
SST	single-shell tank
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic
WHC	Westinghouse Hanford Company
WSTC	Westinghouse Science and Technology Center
XRD	X-ray diffraction

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LIST OF COMPOUNDS

Al	aluminum
Al(NO ₃) ₃	aluminum nitrate
Al(OH) ₃	aluminum hydroxide; gibbsite; hydrargillite; bayerite
Al(OH) ₄ ⁻	aluminate ion
AlOOH	böhmite; didspore
AlPO ₄	aluminum phosphate
Al ₂ O ₃	alumina; corundum
Am(OH) ₃	americium hydroxide
AmCO ₃ OH	americium hydroxide carbonate
Bi	bismuth
Bi(OH) ₆ ⁻	bismuthate anion
BiPO ₄	bismuth phosphate
Ca(OH) ₂	calcium hydroxide
Ca ₅ (PO ₄) ₃ OH	hydroxyapatite
CH ₃ CO ₂ ⁻	acetate
Cl ⁻	chloride
Cl ₂	chlorine
CO ₂	carbon dioxide
CO ₃ ²⁻	carbonate
Cr	chromium
CrO ₄ ²⁻	chromate
Cr(OH) ₃	chromium hydroxide
F ⁻	fluoride
Fe	iron
Fe ₂ O ₃	hematite; ferric oxide
Fe(CN) ₆ ⁴⁻	ferrocyanide
FeCO ₃	siderite
FeO ₄ ²⁻	ferrate ion
Fe(OH) ₃	ferric hydroxide
FeOOH	gothite
H ₂ O	water
KOH	potassium hydroxide
N ₂	elemental nitrogen
NaCl	sodium chloride

LIST OF COMPOUNDS (continued)

$\text{Na}_2\text{C}_2\text{O}_4$	sodium oxalate
Na_2CO_3	sodium carbonate
Na_3PO_4	sodium phosphate; trisodium phosphate
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	sodium phosphate dodecahydrate
$\text{NaAlCO}_3(\text{OH})_2$	dawsonite
$\text{NaAl}(\text{OH})_4; \text{NaAlO}_2$	sodium aluminate
$\text{NaC}_2\text{H}_3\text{O}_2$	sodium acetate
$\text{Na}_2\text{C}_2\text{O}_4$	sodium oxalate
NaF	sodium fluoride
NaFeO_2	sodium ferric oxide
NaNO_2	sodium nitrite
NaNO_3	sodium nitrate
NaOH	sodium hydroxide
Na_2SiO_3	sodium silicate
Na_2SO_4	sodium sulfate
$\text{Ni}(\text{OH})_2$	nickel hydroxide
NO_2^-	nitrite
NO_3^-	nitrate
NO_x	oxides of nitrogen
O_2	oxygen
OH^-	hydroxide
Pb	lead
RuO_4	ruthenium tetroxide
Si	silicon
SiO_2	silica; quartz
SO_4^{2-}	sulfate
ThO_2	thorium oxide
TiO_2	titania; anatase; rutile
UO_2	uraninite
$\text{UO}_2(\text{OH})_2$	uranyl hydroxide
ZrO_2	zirconia

1.0 INTRODUCTION

Calcination/dissolution (C/D) has been proposed as a method to treat Hanford Site tank waste to destroy organic, ferrocyanide, and nitrate and nitrite salts and thus, reduce the chemical quantity of waste material (Colby 1993). Chemistry development of this technology, via laboratory and literature studies, is being conducted to support an investigation of C/D as an initial pretreatment processing option, as well as a possible alternative waste treatment option in other waste processing scenarios. This report summarizes the results of chemical literature reviews and laboratory studies of C/D conducted in fiscal year (FY) 1993.

In the calcination step of the C/D approach to waste pretreatment, the waste solutions, salt cakes, and sludges comprising the waste will be heated to decompose the inorganic anions nitrite (NO_2^-) and nitrate (NO_3^-), organic waste components, (e.g., ethylenediaminetetraacetate [EDTA], N-2-hydroxyethylethylenediaminetriacetate [HEDTA], tributyl phosphate and degradation products of the source organics) and inorganic fuel-rich waste components (e.g., ferrocyanides). At high temperatures, a fluid, molten salt based on sodium hydroxide (NaOH) is produced in which NaOH acts as a solvent capable of metathesizing, demineralizing, and dissolving residual waste constituents.

The calcination step is followed by (partial) dissolution in water of the resulting NaOH melt. The dissolution step will produce water-soluble and -insoluble streams. The water-soluble stream, containing fission products (e.g., cesium-137 [^{137}Cs] and technetium-99 [^{99}Tc]) and the sodium salts (primarily NaOH), may be treated further to remove radionuclides and other hazardous materials before being processed to an engineered low-level waste (LLW) form.

The water-insoluble stream is expected to contain the long-lived transuranic (TRU) isotopes (e.g., neptunium-237 [^{237}Np], plutonium-239,-240 [$^{239,240}\text{Pu}$] and americium-241 [^{241}Am]) and insoluble fission products (e.g., strontium-90 [^{90}Sr]), as well as nonradioactive aluminosilicates and the multivalent metal oxides, hydroxides, and phosphates. The water-insoluble stream may be fed to high-level waste (HLW) (e.g., the vitrification plant). The residue may also undergo further treatments to isolate hazardous chemical or radioactive components still present in the residue before consignment to HLW treatment.

The attraction of C/D processing lies in its ability to eliminate significant chemical components from the waste inventory, and thus, the necessity to process or immobilize those components to produce an engineered final waste form (e.g., glass). The C/D processing also stabilizes the waste if intermediate storage is required before final (glass) disposition. The components eliminated by C/D are organic species (with their risks of chemical instability and implication as vectors for radionuclide migration for intermediate storage) and the nitrite and nitrate anions (with their high leachability and bulk for intermediate storage and their attendant gas-generation problems in glass processing).

By using the sodium hydroxide present in the waste, as well as the hydroxide produced by calcination of nitrite and nitrate, C/D can also solubilize aluminum-bearing compounds present in the tanked waste. The dissolved aluminum materials then may be immobilized in the LLW fraction rather than in the HLW fraction. Similarly, oxidation of sparingly soluble chromium hydroxide $[\text{Cr}(\text{OH})_3]$ present in the waste to form soluble chromate effects a redistribution of chromium from the HLW to the LLW fraction. Thus, reducing the quantity of HLW.

This paper summarizes and presents the current state of knowledge of the overall chemical and radionuclide inventory of the Hanford Site waste in light of its potential processing via C/D. The evaluation is based on both literature and laboratory studies (using both simulated and genuine Hanford Site waste materials) to describe the chemical behavior of the waste as it undergoes the separate calcination and dissolution treatments.

2.0 CHEMICAL AND RADIONUCLIDE INVENTORY OF HANFORD SITE WASTE

The inventory of Hanford Site waste is contained in 149 single-shell tanks (SST) and 28 double-shell tanks (DST). Estimates and projections of the quantity of chemical constituents present in these tanks are based on the quantity of materials processed through the various plutonium separation, plutonium and uranium recovery, and waste management operations conducted during the 50 years of Hanford Site chemical processing operations. Estimates also are based on limited sampling and analysis of the stored waste materials.

The inventories of chemical constituents present in both the SST and DST have been published by Boomer et al. (1993). The data from these separate projections have been combined and are presented in Table 2-1. The summary data for the Hanford Site tanked waste (obtained by summing the SST and DST data) are presented graphically in Figure 2-1.

Though the listing in Table 2-1 presents a large number of chemical elements and species, it is not inclusive and omits, for example, many fission product elements and species present as trace impurities in the bulk chemicals used in the Hanford Site operations. Nevertheless, the inventory data show that the Hanford Site waste can be considered, in large part, to be an alkaline aqueous mixture of water-soluble sodium salts (hydroxide, aluminate, nitrate, nitrite, carbonate, phosphate). In fact, water (45.3 mole%) and sodium and the accompanying soluble anions (48.8 mole%) dominate the waste chemical inventory.

Many of the remaining multivalent metallic constituents will exist as hydroxides, hydrated oxides, aluminosilicates, phosphates, or other poorly-soluble species. Notwithstanding the soluble sodium aluminate, poorly-soluble materials include significant aluminum present in the waste as aluminum hydroxide (gibbsite and bayerite) and oxyhydroxide (böhmite), as well as the transition and lanthanide metal oxides/hydroxides. These water-insoluble constituents still represent a formidable quantity of material for long-term immobilization because they will contain the long-lived TRU radioisotopes of plutonium, americium, and neptunium and be relegated to the HLW fraction.

Because TRU elements require immobilization in a durable and expensive waste form, such as glass in canisters, the presence of tramp nonradioactive materials strongly increases the quantity of material requiring immobilization in the HLW repository. The sensitivity of the "canister count" to the presence of nonradioactive, poorly-soluble materials has recently been described (Swanson 1993).

In addition, the waste inventory presented in Table 2-1 and depicted in Figure 2-1 is not distributed uniformly in the 177 Hanford Site waste tanks. For example, 400 metric tons of diatomaceous earth representing about 170 metric tons of silicon were deposited for use as a liquid sorbent in six waste tanks (Tanks 241-BX-102, -SX-113, -TX-116, -TX-117, -TY-106 and -U-104). These 170 tons compare with the 504 tons of silicon present in all Hanford Site waste.

Table 2-1. Chemical Constituent Inventory of SST, DST, and Waste Total.
Derived from Boomer et al. (1993).

Component	SST (kg)	DST (kg)	Waste sum (kg)	Formula weight (g)	SST (mol)	DST (mol)	Waste sum (mol)	Mole fraction
Ag	--	4.41e+02	4.41e+02	107.87	--	4.09e+03	4.09e+03	3.40e-07
Al	2.44e+06	2.04e+06	4.48e+06	26.98	9.04e+07	7.56e+07	1.66e+08	1.38e-02
As	--	8.41e+02	8.41e+02	74.92	--	1.12e+04	1.12e+04	9.35e-07
B	--	2.55e+03	2.55e+03	10.81	--	2.36e+05	2.36e+05	1.96e-05
Ba	6.07e+02	1.73e+03	2.34e+03	137.34	4.42e+03	1.26e+04	1.70e+04	1.42e-06
Be	--	9.95e+00	9.95e+00	9.01	--	1.10e+03	1.10e+03	9.20e-08
Bi	2.61e+05	--	2.61e+05	208.98	1.25e+06	--	1.25e+06	1.04e-04
Ce	1.28e+05	1.59e+04	1.44e+05	40.08	3.19e+06	3.97e+05	3.59e+06	2.99e-04
Cd	3.84e+03	6.71e+03	1.06e+04	112.40	3.42e+04	5.97e+04	9.39e+04	7.82e-06
Co	2.35e+05	--	2.35e+05	140.12	1.68e+06	--	1.68e+06	1.40e-04
Cr	--	8.14e+02	8.14e+02	58.93	--	1.38e+04	1.38e+04	1.15e-06
Cr	9.59e+04	6.51e+04	1.61e+05	52.00	1.84e+06	1.25e+06	3.10e+06	2.58e-04
Cu	--	1.23e+03	1.23e+03	63.55	--	1.94e+04	1.94e+04	1.61e-06
Fe	6.27e+05	1.02e+05	7.29e+05	55.85	1.12e+07	1.83e+06	1.31e+07	1.09e-03
Hg	9.00e+02	2.53e+02	1.15e+03	200.59	4.49e+03	1.26e+03	5.75e+03	4.79e-07
K	5.99e+04	1.09e+06	1.15e+06	39.10	1.53e+06	2.79e+07	2.94e+07	2.45e-03
La	1.88e+03	--	1.88e+03	138.91	1.35e+04	--	1.35e+04	1.13e-06
Mg	--	5.33e+03	5.33e+03	24.31	--	2.19e+05	2.19e+05	1.83e-05
Mn	1.20e+05	1.40e+04	1.34e+05	54.94	2.18e+06	2.55e+05	2.44e+06	2.03e-04
Mo	--	8.15e+03	8.15e+03	95.94	--	8.49e+04	8.49e+04	7.07e-06
Na	5.17e+07	1.57e+07	6.74e+07	22.99	2.25e+09	6.83e+08	2.93e+09	2.44e-01
Ni	1.78e+05	1.05e+04	1.89e+05	58.70	3.03e+06	1.79e+05	3.21e+06	2.67e-04
Pb	4.36e+05	3.43e+03	4.39e+05	207.19	2.10e+06	1.66e+04	2.12e+06	1.77e-04
Rare Earths	--	1.16e+04	1.16e+04	142.00	--	8.17e+04	8.17e+04	6.80e-06
Rh	--	4.42e+02	4.42e+02	102.91	--	4.30e+03	4.30e+03	3.58e-07
Ru	--	5.53e+02	5.53e+02	101.07	--	5.47e+03	5.47e+03	4.56e-07
Si	4.46e+05	5.82e+04	5.04e+05	28.09	1.59e+07	2.07e+06	1.79e+07	1.49e-03
Sn	5.37e+00	--	5.37e+00	118.69	4.52e+01	--	4.52e+01	3.77e-09
Sr	3.60e+04	--	3.60e+04	87.62	4.11e+05	--	4.11e+05	3.42e-05
Tb	--	8.26e+02	8.26e+02	232.04	--	3.56e+03	3.56e+03	2.96e-07
Ti	--	4.45e+02	4.45e+02	47.90	--	9.29e+03	9.29e+03	7.74e-07
U	--	3.83e+04	3.83e+04	238.03	--	1.61e+05	1.61e+05	1.34e-05
W	6.02e+02	--	6.02e+02	183.85	3.27e+03	--	3.27e+03	2.73e-07
Zn	--	2.26e+03	2.26e+03	65.37	--	3.46e+04	3.46e+04	2.88e-06
Zr	2.47e+05	3.13e+05	5.60e+05	91.22	2.70e+06	3.43e+06	6.13e+06	5.11e-04
Cl	4.00e+04	3.94e+05	4.34e+05	35.45	1.13e+06	1.11e+07	1.22e+07	1.02e-03
CO ₃ ²⁻	1.61e+06	1.07e+06	2.68e+06	60.00	2.68e+07	1.78e+07	4.47e+07	3.72e-03
F	8.05e+05	2.93e+05	1.10e+06	19.00	4.24e+07	1.54e+07	5.78e+07	4.81e-03
Fe(CN) ₆ ³⁻	3.22e+05	1.23e+03	3.23e+05	211.95	1.52e+06	5.80e+03	1.53e+06	1.27e-04
NO ₃ ⁻	4.80e+06	4.77e+06	9.57e+06	46.01	1.04e+08	1.04e+08	2.08e+08	1.73e-02
NO ₃ ⁻	9.67e+07	1.26e+07	1.09e+08	62.00	1.56e+09	2.03e+08	1.76e+09	1.47e-01
OH ⁻	9.14e+06	9.77e+06	1.89e+07	17.00	5.38e+08	5.75e+08	1.11e+09	9.26e-02
PO ₄ ³⁻	8.74e+06	2.13e+05	8.95e+06	94.97	9.20e+07	2.24e+06	9.43e+07	7.85e-03
SO ₄ ²⁻	1.65e+06	3.56e+05	2.01e+06	96.06	1.72e+07	3.71e+06	2.09e+07	1.74e-03
TOC	2.00e+05	5.99e+05	7.99e+05	12.01	1.67e+07	4.99e+07	6.65e+07	5.54e-03
H ₂ O	4.48e+07	5.33e+07	9.81e+07	18.02	2.49e+09	2.96e+09	5.44e+09	4.53e-01
Sum	2.26e+08	1.03e+08	3.29e+08	--	7.27e+09	4.74e+09	1.20e+10	1.00e+00

Figure 2-1. Molar Chemical Inventory of Hanford Site Waste.
Derived from Boomer et al. (1993).

The waste composition found in a particular tank is subject to the plutonium separation process producing the waste, as well as any ensuing waste volume reduction and processing schemes enacted on the tank's contents. Tank-to-tank transfers of supernatant solution and waste blending also contribute to confounding simple prediction of the contents of any particular tank. A number of waste types have been identified based on the waste generation history.

2.1 WASTE TYPES AND COMPOSITIONS

Efforts are underway to characterize the waste materials present in the Hanford Site waste tanks (especially the SST). In nearly all cases, however, data are limited and estimated waste compositions, based on process flowsheet information, tank transfer records, and projected compound solubilities, must be used. To investigate the C/D approach to waste processing, several waste types were selected as an initial basis for study. In addition to the overall Hanford Site waste composition presented in Table 2-1, the following waste types are proposed as models in C/D study.

- Complexant concentrate (Tank 241-SY-101).
- REDOX sludge.
- Bismuth Phosphate Process first and second cycle waste.
- Sodium nitrate salt cake.
- Plutonium Finishing Plant (PFP) waste.

The five waste types listed above do not represent all possible waste types present. Rather, they will encompass the bulk of the Hanford Site waste (hence, the sodium nitrate salt cake and the Bismuth Phosphate Process waste) and identify certain waste types suspected of being particularly challenging to the C/D approach (REDOX sludge, PFP waste) and of current concern (complexant concentrate [CC], such as that present in Tank 241-SY-101). The following sections present the compositions of the five selected waste types.

2.1.1 Complexant Concentrate

Complexant concentrate waste contains a high concentration of organic complexants (e.g., EDTA, HEDTA, citrate, glycolate) from B Plant strontium removal processing and the organic degradation products resulting from degradation of the source organics. One tank containing CC waste is 241-SY-101 (101-SY).

The contents of Hanford Site Tank 101-SY have undergone the most extensive characterization efforts of any waste source on the Site. Results of characterization of samples taken following the Windows C and E gas release events in May and December 1991, respectively, have been published (Herting 1992; Herting et al. 1992). On a whole-tank basis, these two sets of analytical data show virtually identical chemical compositions. The composition determined from the Window E sampling is the basis of one CC formulation given in Table 2-2.

Also shown for comparison in Table 2-2 is the CC waste composition published by Boomer et al. (1993). The data were derived from core and

Table 2-2. Compositions of Complexant Concentrate Waste.

Component	Composition 101-SY (wt%) (Herting et al. 1992)	Composition CC waste (wt%) (Boomer et al. 1993)
Al	3.2	4.4
Ca	0.023	0.028
Cr	0.41	0.092
Fe	0.028	0.10
K	0.326	0.11
Na	20.7	16.3
Ni	0.015	0.021
Zn	0.002	0.004
Cl ⁻	0.79	0.40
F ⁻	0.03	0.14
NO ₂ ⁻	10.5	3.0
NO ₃ ⁻	11.7	15.0
PO ₄ ³⁻	0.64	0.39
SO ₄ ²⁻	0.40	0.48
CO ₃ ²⁻	3.15	2.74
OH ⁻	2.47	9.0
NH ₃	0.19	--
TOC	1.53	1.6
H ₂ O	35.5	45.9

bottle-on-string samples. Comparison of the compositions show the 101-SY to contain relatively more sodium and less water than the CC waste described by Boomer et al. (1993). For most components, however, the concentrations are roughly comparable. Given the importance of 101-SY to resolve tank safety issues, the 101-SY Window E formulation is proposed for use as the CC model composition.

2.1.2 REDOX Sludge

REDOX sludge originated from plutonium and uranium separation operations based on the methyl isobutyl ketone solvent extraction process used at the REDOX plant. REDOX sludge is characterized by high concentrations of aluminum. Aluminum ion was used as a salting agent in the solvent extraction process and was also present in high concentrations from cladding dissolution. The composition of a water-washed and calcined REDOX sludge is given in

Table 2-3 (Kupfer 1981). The composition of REDOX sludge taken from Tank 241-S-104 (104-S) sampled for SST characterization is given in Table 2-4.

Table 2-3. Composition of Water-Washed Calcined REDOX Sludge (Kupfer 1981).

Component	Composition (wt%)
Al_2O_3	63.4
Fe_2O_3	8.0
SiO_2	7.9
MnO_2	1.8
Cr_2O_3	4.1
CaO	2.7
U_3O_8	0.5
Na_2SO_4	0.75
Na_2O	10.8

Table 2-4. Composition of REDOX Sludge from 104-S.

Component	Composition (wt%)
Al	11.9
Ca	0.056
Cr	0.26
Fe	0.19
K	0.11
Mn	0.12
Na	11.6
Ni	0.52
Si	0.12
U	0.73
Cl^-	0.31
NO_2^-	1.98
NO_3^-	20.4
PO_4^{3-}	0.11
SO_4^{2-}	0.24
CO_3^{2-}	2.28
TOC	0.13
H_2O	34.8
pH	13.3

Not surprisingly, the 104-S Tank sample analysis shows relatively more sodium (and associated anions) and less aluminum, iron, and silicon than the water-washed and calcined sludge formulation. Because of the additional sodium, the 104-S appears to be mixed with salt cake, but is judged to be a better model for REDOX sludge because it reflects an "as-retrieved" composition.

2.1.3 Bismuth Phosphate Process First and Second Cycle Waste

The Bismuth Phosphate Process was the first plutonium extraction process used at the Hanford Site. In this process, plutonium was separated from fission products and uranium by coprecipitation with bismuth phosphate (BiPO_4) produced by mixing bismuth nitrate and sodium phosphate solutions. To achieve further plutonium purification, similar coprecipitation steps took place, followed by lanthanum fluoride coprecipitation and finally separation as a pure plutonium compound. In comparison with the later REDOX and PUREX Processes, the coprecipitation steps of the Bismuth Phosphate Process generated relatively large quantities of waste per ton of fuel processed.

The composition of water-washed and calcined sludge from the composite first and second cycle waste of the Bismuth Phosphate Process is presented in Table 2-5 (Kupfer 1981). Compositions of Bismuth Phosphate Process waste sampled and analyzed from Tanks 241-BX-107, -T-104, and -T-111 (107-BX, 104-T, and 111-T) during SST characterization are given in Table 2-6. Also presented in Table 2-6 is a dry equal-weight composite waste composition based on the three tank analyses and hypothetical phases.

Table 2-5. Composition of Washed and Calcined First and Second Cycle Bismuth Phosphate Process Waste Blend (Kupfer 1981).

Component	Composition (wt%)
BiPO_4	37.6
Cr_2O_3	2.6
Fe_2O_3	23.7
Na_2O	17.8
SiO_2	15.3
NaF	2.2
Na_2SO_4	0.8

The resulting projected Bismuth Phosphate Process first and second cycle composite waste varies more in the sodium salts, contains a higher variety of components (e.g., aluminum hydroxide, nickel hydroxide, and uranyl hydroxide; $\text{Al}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$ and $\text{UO}_2(\text{OH})_2$ respectively), and contains relatively less bismuth phosphate and silica than the washed/calcined formulation given in Table 2-5. Because the composite formulation given in Table 2-6 better reflects the "as-retrieved" waste, it is recommended as the model Bismuth Phosphate first and second cycle waste.

Table 2-6. Composition of Bismuth Phosphate Process Wastes from Tanks 107-BX, 104-T and 111-T and a Hypothetical Dry Composite.

Component	Composition (wt%)			Hypothetical phase	Composite (wt%)
	107-BX (first C)	T-104 (first C)	T-111 (second C)		
Al	1.20	1.73	0.064	Al(OH) ₃	7.7
Bi	2.06	1.77	2.09	BiPO ₄	8.3
Ca	0.031	0.061	0.28	Ca(OH) ₂	0.7
Cr	0.084	0.081	0.19	Cr(OH) ₃	0.7
Fe	0.94	0.99	2.05	Fe(OH) ₃	23.6
K	0.011	0.11	0.11	KNO ₃	0.7
Mn	0.005	0.006	0.64	MnO ₂	3.5
Na	10.0	6.17	3.98	--	--
Ni	0.20	0.88	0.58	Ni(OH) ₂	2.8
Si	0.60	0.63	0.60	SiO ₂	3.8
U	0.20	0.087	0.22	UO ₂ (OH) ₂	0.64
Cl ⁻	0.12	0.066	0.047	NaCl	0.1
F ⁻	0.84	0.88	0.31	NaF	4.1
NO ₂ ⁻	0.92	0.40	0.095	NaNO ₂	1.7
NO ₃ ⁻	15.0	5.62	4.43	NaNO ₃	29.4
PO ₄ ³⁻	1.50	1.66	1.64	Na ₃ PO ₄	8.2
SO ₄ ²⁻	1.42	0.39	0.37	Na ₂ SO ₄	2.0
CO ₃ ²⁻	0.58	0.15	0.20	Na ₂ CO ₃	1.4
TOC	0.055	0.062	0.35	TOC	0.5
H ₂ O	56.4	70.4	74.6	--	--
pH	9.68	10.0	10.2	--	--

2.1.4 Sodium Nitrate Salt Cake

Nitric acid was the medium selected for uranium fuels dissolution and subsequent plutonium and uranium extraction at the Hanford Site. Making the nitric acid-bearing waste alkaline with sodium hydroxide allowed the waste to be stored in mild steel tanks. The sodium nitrate resulting from neutralization is the primary component in Hanford Site salt cake waste. Sodium nitrite (NaNO₂), generated radiolytically and intentionally added to the tanked waste to inhibit corrosion of the mild steel tank liner, is also found in the salt cake. Other less-soluble sodium salts, such as trisodium phosphate and sodium carbonate, may be found in salt cake.

In addition, aqueous liquors held interstitially by capillary forces in the salt cake contribute to the salt cake composition by their contained

dissolved sodium salts. Because of the presence of other salts and the salt-bearing interstitial liquor, sodium nitrate salt cake contains a number of components in addition to sodium nitrate.

A SST salt cake simulant composition has been proposed by Elmore et al. (1992) and is given in Table 2-7. Hanford Site salt cake compositions, originating from a variety of plant sources, were proposed by Kupfer (1981) and are also given in Table 2-7. Except for the lower sodium nitrate concentration (and the resulting higher concentrations of the other components), the Elmore formulation is an approximate average of the four plant-sourced formulations presented by Kupfer, and therefore, is proposed as a single model (sodium nitrate) salt cake formulation.

Table 2-7. Compositions of Sodium Nitrate Salt Cakes.

Component	Composition (wt%) (Kupfer 1981)				Composite composition (wt%) (Elmore et al. 1992)
	REDOX	PUREX & B Plant	BiPO ₄	Uranium recovery	
NaNO ₃	92	89	88	88	75.2
NaNO ₂	3	5	3	3	4.8
Na ₂ SO ₄	--	1	--	1	2.4
Na ₂ CO ₃	1	2	1	1	4.3
NaAlO ₂	2	1	1	1	4.3
Na ₃ PO ₄	--	--	5	5	4.6
NaOH	2	2	2	2	4.4

2.1.5 PFP Waste

Waste originating from plutonium scrap recovery operations at the PFP contains relatively high concentrations of chromium and aluminum in addition to the usual sodium salts. Aluminum ion, introduced as aluminum nitrate [Al(NO₃)₃], was used to enhance salting strength in plutonium-bearing solutions undergoing solvent extraction at the PFP. Aluminum ion was also used to complex corrosive fluoride ion introduced to effect plutonium oxide dissolution during scrap recovery. The formulation of PFP waste given in Table 2-8 is based on that presented by Boomer et al. (1993).

2.1.6 Radionuclide Concentrations in the Waste Types

The concentrations of the radionuclides ⁹⁰Sr, ¹³⁷Cs, ⁹⁹Tc, ²³⁷Np, ^{239,240}Pu and ²⁴¹Am, as well as total uranium found or estimated in the five proposed waste types, are given in Table 2-9. The radionuclide and uranium concentrations help explain the relative severity of radioactive loading of the various waste types; they also aid in formulating credible Hanford Site waste simulants using nonradioactive surrogates for the relevant radionuclides.

Table 2-8. Composition of PFP Waste (Boomer et al. 1993).

Component	Composition (wt%)	Dry composition (wt%)
Al	3.3	5.5
Ca	0.5	0.8
Cd	0.1	0.1
Cr	1.8	3.0
Cu	0.1	0.2
Fe	1.8	3.0
K	0.4	0.6
Mg	0.1	0.2
Mn	0.7	1.1
Na	11.8	19.7
Pb	0.1	0.2
RareEarths	0.1	0.2
Ru	0.4	0.7
Si	0.2	0.3
U	0.2	0.3
Cl ⁻	0.4	0.8
CO ₃ ²⁻	3.0	5.0
F ⁻	0.5	0.8
NO ₂ ⁻	3.0	5.1
NO ₃ ⁻	15.9	26.5
OH ⁻	9.8	16.4
PO ₄ ³⁻	4.6	7.6
SO ₄ ²⁻	0.8	1.3
H ₂ O	40.1	0

The radionuclide concentrations for CC (using 101-SV as the model) and the PFP waste were derived from data presented in Herting et al. (1992) and Boomer et al. (1993), respectively. The radionuclide concentrations for the REDOX sludge and Bismuth Phosphate Process Hanford Site waste types were derived from previously unpublished analyses of core samples. The sodium nitrate salt cake radionuclide concentrations are based on the expected high distributions of the actinides (U, Np, Pu, and Am) to the sludge and the ⁹⁰Sr, ¹³⁷Cs, and ⁹⁹Tc contamination of the salt cake caused by entrainment of interstitial liquor.

In the absence of organic complexing agents, ⁹⁰Sr will be primarily in the insoluble sludge phase. Complexing agents, such as EDTA and HEDTA, are particularly effective in solubilizing strontium (Delegard et al. 1984). Both ⁹⁹Tc and ¹³⁷Cs will be in the solution phase. Some fraction of the cesium may

Table 2-9. Radionuclide and Uranium Concentrations in Hanford Site Waste Types.

Waste type	Concentrations						
	⁹⁰ Sr (μ Ci/g)	¹³⁷ Cs (μ Ci/g)	⁹⁹ Tc (μ Ci/g)	U (μ g/g)	²³⁷ Np (μ Ci/g)	^{239,240} Pu (μ Ci/g)	²⁴¹ Am (μ Ci/g)
Complexant concentrate (101-SY)	21	350	0.30	63	< 0.01	0.0067	0.11
REDOX sludge (104-S)	320	64	0.026	730	0.015	0.16	0.12
Bismuth Phosphate 1 st and 2 nd cycle (107-BX, 104-T and 111-T mix)	20	11	0.037	540	0.104	0.38	0.13
Sodium nitrate salt cake (estimate)	20	100	0.30	small	small	small	small
PPF	340	710	0.55	1900	—	29	46
NOTE: To convert from μ Ci/g to μ g element/g, multiply the tabulated figures by:	0.0216 (assumes 3 μ gSr per μ g ⁹⁰ Sr)	0.0231 (assumes 2 μ gCs per μ g ¹³⁷ Cs)	59 (all Tc present as ⁹⁹ Tc)	—	1420 (all Np present as ²³⁷ Np)	15.3 (assumes 93% ²³⁹ Pu and 7% ²⁴⁰ Pu)	0.291 (all Am present as ²⁴¹ Am)

be precipitated as a ferrocyanide double salt in waste originating from the Bismuth Phosphate Process. Technetium is probably present as the highly-soluble pertechnetate anion (TcO_4^-) in the oxidizing Hanford Site waste materials (Vida 1989).

The Hanford Site waste contains three principal TRU elements: plutonium, americium, and neptunium. Of the three TRU elements, plutonium is present in the highest chemical and activity (Curie) concentration in the waste. It is generally accepted, though not proven, that the plutonium is present in the alkaline ($\text{pH} > 14$) waste primarily as hydrated plutonium dioxide (PuO_2) and is probably associated or coprecipitated with ferric (hydr)oxide. The solubility of hydrated PuO_2 in simulated Hanford Site waste is low, but increases with increasing NaOH concentration. The dissolved species found in simulated waste is a Pu(V) hydroxide complex (Delegard 1987).

The americium most likely is present as americium hydroxide [$\text{Am}(\text{OH})_3$], or possibly americium hydroxide carbonate (AmCO_3OH), in the waste and, in the absence of organic complexing agents, has low solubility (Delegard et al. 1984). Neptunium, though present in the Hanford Site waste, has a long half-life and may not appreciably contribute to the TRU (activity) burden. Based on solubility studies of simulated waste, neptunium is probably present in the aqueous phase (Delegard et al. 1984).

2.2 HANFORD SITE WASTE SIMULANTS

Simulants of Hanford Site waste have been used for numerous laboratory and pilot studies to avoid the radiological risks attendant with using genuine, highly radioactive Hanford Site waste. Several simulant recipes have been proposed for various Hanford Site waste types. The following simulants are presented for possible use in C/D laboratory studies.

2.2.1 Kupfer's Sludge and Salt Cake Simulants

Recipes for simulated Hanford Site waste sludges (REDOX, PUREX, Bismuth Phosphate first and second cycle, Bismuth Phosphate third cycle, and Uranium Recovery) and salt cakes (REDOX, PUREX, and B Plant, Bismuth Phosphate and Uranium Recovery) were proposed by Kupfer (1981). The REDOX and Bismuth Phosphate first and second cycle sludge compositions are presented in Tables 2-3 and 2-5, respectively. The salt cake compositions are presented in Table 2-7.

The sludge recipes were designed for use as genuine waste surrogates to prepare and test ceramic or glass waste forms. The recipes, though prepared in aqueous suspensions, involve salt washing and drying steps, and are formulated to produce dry, salt-free powders. As such, the sludge recipes are not good simulants, by themselves, for calcination testing. Kupfer (1981) recommended mechanical blending of the dried salt cake with the appropriate selected dried sludge if more realistic intermixed salt cake/sludge simulants were desired.

2.2.2 Elmore et al. SST Waste Simulant

A recipe for SST waste was proposed by Elmore et al. (1992) using separate salt cake and sludge formulations. The recipe simulates the mechanical, physical, and chemical characteristics of SST waste.

To produce the desired simulant, the sludge fraction is left in an aqueous slurry and blended with the simulant salt cake in ratios selected to achieve the desired composition. The blended sludge and salt cake is then digested at 105 °C to simulate and accelerate the thermal and radiolytic effects of long-term aging. For example, 5-day digestion of a 55/45 blend of sludge and salt cake resulted in the crystallization of a sodium aluminosilicate previously observed in genuine waste of similar composition, but not observed in the undigested simulant waste. Digestion also helped produce a particle size distribution more closely matching the particle size distribution observed in the genuine waste sample.

The recipe of Elmore et al. (1992) contains metals (zirconium, silver, magnesium, cerium) not found in the Kupfer (1981) formulations. Organics (EDTA, citric acid) are also included in the Elmore recipe, but not in Kupfer. Kupfer's recipe for Uranium Recovery sludge, however, contains ferrocyanide. Neither Kupfer (1981) nor Elmore et al. (1992) included chloride in their recipes. Because of the digestion step and the extensive list of components, the Elmore et al. (1992) recipe may provide a better simulant of genuine waste for the C/D studies than any of the Kupfer (1981) recipes.

2.2.3 Hohl's CC Waste (101-SY) Simulant

To conduct studies on the cyclic gas venting observed in Tank 101-SY, a number of simulated 101-SY formulations have been proposed and described. A recent recipe, based on the normalized composition of the 101-SY waste as analyzed following the Window E gas release event in December 1991 (Herting et al. 1992), was presented by Hohl (1993). The recipe proposed by Hohl (1993) is a 3:1, by volume, water:waste dilution of a full-strength 101-SY simulant proposed by Delegard (1993).

These 101-SY formulations contain the most extensive list of constituents published of any 101-SY recipe. Speciation of organics present in the 101-SY waste is incomplete, however (Herting et al. 1992). Therefore, the Hohl (1993) recipe allows selection of organic constituents (e.g., EDTA and HEDTA) to be added as desired to reach the 1.53 wt% total organic carbon (TOC) required for the 101-SY Window E composition.

2.2.4 Proposed Comprehensive Hanford Site Waste Simulant

Using the Hanford Site waste chemical constituent listing in Table 2-1 as a guideline, a comprehensive Hanford Site waste simulant recipe is proposed. The recipe, given in Appendix A, includes the most prevalent 27 chemical components (i.e., all chemical components present >0.000018 mole fraction). This simulant encompasses 0.999966 mole fraction of the nominal waste inventory.

Again, because organics are thought to undergo decomposition and are not well speciated, selection of organics to represent the 0.55 mole% TOC in the comprehensive waste simulant is arbitrary. For the purposes of C/D research, acetate (CH_3CO_2^-) represents the TOC in the comprehensive waste simulant.

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3.0 CALCINATION CHEMISTRY

The calcination step of the C/D process involves the thermal and oxidative degradation of targeted waste species: organics, ferrocyanides, and the nitrite and nitrate ions. Based on known chemistry, reaction products from degradation may be predicted and a calcined waste inventory projected. The chemistry of sodium hydroxide fusions exploited in chemical analyses of minerals guides the anticipated behavior of metallic components (e.g., aluminum, iron, chromium, manganese) during calcination of the NaOH-rich waste. The chemistry of TRU elements in alkali melts has been reported in the technical literature and has been reviewed.

3.1 CHEMICAL DECOMPOSITIONS VIA CALCINATION

In addition to the reduced volume and bulk occasioned by water evaporation during calcination, thermal and oxidative degradation of other chemical species will yield substantial reduction of the bulk waste quantity. The primary chemical constituents undergoing decomposition by calcination are nitrate, nitrite, the organics, and ferrocyanide.

3.1.1 Nitrate and Nitrite Decomposition

Sodium nitrate and nitrite (NaNO_3 and NaNO_2 , respectively), when present as pure compounds, decompose at 300 to 400 °C to produce N_2 or NO_x and oxygen (O_2) gases. Thermal analyses of simulated and genuine waste show, however, that decomposition of the nitrate and nitrite salts occurs slowly at 600 to 800 °C (Colby et al. 1994). Related crucible-scale calcination tests of NaNO_3 showed that significant volatilization of sample material occurred when calcination temperatures were raised from 930 to 950 °C. Calcination at 850 °C for 4 hours left about 28% of the original NaNO_3 as NaNO_x (Burger et al. 1973).

Thermodynamic predictions, as well as experimental data gathered during pilot-scale plasma torch-heated calcination tests, showed negligible NO_x in the offgas during 850 °C experiments using simulated 101-SY waste compositions (Colby et al. 1994). Nearly complete (95%) destruction of nitrate and nitrite was found in these tests. Residence time of the melt at temperature in the plasma test was on the order of an hour, however. Based on the plasma torch experiments, plasma calcination of nitrate and nitrite salts in genuine waste is expected to produce nonscrubbable and benign offgases of N_2 and O_2 . However, the slow rate of nitrate and nitrite salt decomposition may require either higher calcination temperatures or a significant residence time to achieve adequate nitrate and nitrite destruction.

The residue remaining from thermal decomposition of sodium nitrate and nitrite in the presence of water is an equimolar quantity of sodium hydroxide. The following reactions describe the calcination of sodium nitrate and sodium nitrite:

Some formation of sodium peroxide (Na_2O_2) is also expected (Bock 1979) and has been postulated (Burger et al. 1973) via absorption of evolved or atmospheric oxygen by the molten sodium hydroxide.

3.1.2 Organic and Ferrocyanide Decomposition

The organics, in the presence of oxidizing agents such as atmospheric oxygen, nitrite or nitrate, are expected to decompose rapidly at temperatures above about 200 to 300 °C to produce gaseous carbon dioxide (CO_2), water (H_2O), and, in the case of organics containing nitrogen species, gaseous nitrogen products. The CO_2 produced by oxidation of the organics, in turn, will be captured and scrubbed in the sodium hydroxide-bearing waste to form sodium carbonate (Na_2CO_3) and water in a type of acid-base reaction.

The stoichiometry of the organic oxidation reactions (i.e., the ratio of moles of oxidant and hydroxide required versus moles of organic carbon converted to carbonate) depends on the particular organic species being oxidized. This is because organic carbon can exist in formal oxidation states ranging from -4 (nonoxygenated hydrocarbons) to +3 (the highly-oxygenated species oxalate). The more chemically reduced, lower oxidation state, organic species require more oxidant to be converted to carbon dioxide or carbonate. The oxygen oxidant (supplied either by atmospheric oxygen in the calcination or, equivalently, by thermolysis of nitrate/nitrite) is converted to oxide (O^{2-}) oxygen that is hydrolyzed to the hydroxide ion (OH^-) in the calcine melt.

Thus, oxidation of organic carbon to carbonate consumes hydroxide while the accompanying reduction of oxygen produces hydroxide. The net amount of hydroxide consumed depends on the oxidation state of the organic carbon. The oxidations of sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$, average carbon oxidation state of 0) and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, average carbon oxidation state of +3), both two-carbon organic species present in Hanford Site waste, illustrate the effect of carbon oxidation state on stoichiometry:

Because of thermal, chemical, and radiolytic degradation of source organics, the residual organic species present in most of the Hanford Site waste are unknown. Thus, the amount of hydroxide required in the oxidation reactions is also unknown. It is anticipated that the average oxidation state of organic carbon in waste lies somewhere between acetate and oxalate. Using

the reactions above as a guide, it is estimated that in calcination, about 1.25 moles of hydroxide will be consumed per mole of organic carbon oxidized.

Calcination of ferrocyanides $[\text{Fe}(\text{CN})_6]^{4-}$ should leave iron oxides/hydroxides and carbonate in the melt residue, with nitrogen being released as gaseous oxides of nitrogen (i.e., NO_x such as NO_2 and NO) or, more likely, elemental nitrogen (N_2). The following reaction presents a plausible expression of the oxidative decomposition of ferrocyanide:

In the oxidation of ferrocyanide, 1.33 moles of hydroxide are consumed per mole of carbon.

3.2 COMPOSITION OF CALCINED HANFORD SITE WASTE

Using the initial inventory given in Table 2-1, the molar inventory of chemical species present in the Hanford Site waste following calcination may be projected based on the expected decomposition reactions. The resulting projected calcined waste inventory is presented in Table 3-1. It is useful to think of the individual waste components forming the named hypothetical compounds as shown in Table 3-1.

Table 3-1. Hanford Site Waste Inventory Following Calcination.

Component	After calcination (moles)			Hypo. comp.	Waste inv. (moles)	Mole fraction
	SST	DST	Sum			
Al	9.04e+07	7.56e+07	1.66e+08	$\text{Al}(\text{OH})_3$	1.66e+08	5.53e-02
Fe	1.27e+07	1.83e+06	1.46e+07	$\text{Fe}(\text{OH})_3$	1.46e+07	4.87e-03
K	1.53e+06	2.79e+07	2.94e+07	KOH	2.94e+07	9.80e-03
Na	2.25e+09	6.83e+08	2.93e+09	NaOH	2.45e+09	8.17e-01
Si	1.59e+07	2.07e+06	1.79e+07	SiO_2	1.79e+07	5.97e-03
Cl^-	1.13e+06	1.11e+07	1.22e+07	NaCl	1.22e+07	4.07e-03
CO_3^{2-}	4.35e+07	6.77e+07	1.11e+08	Na_2CO_3	1.11e+08	3.70e-02
F^-	4.24e+07	1.54e+07	5.78e+07	NaF	5.78e+07	1.93e-02
OH^-	2.19e+09	7.92e+08	2.98e+09	--	--	--
PO_4^{3-}	9.20e+07	2.24e+06	9.43e+07	Na_3PO_4	9.43e+07	3.14e-02
SO_4^{2-}	1.72e+07	3.71e+06	2.09e+07	Na_2SO_4	2.09e+07	6.96e-03
Others	1.80e+07	6.49e+06	2.50e+07	Others	2.50e+07	8.33e-03
Sum	4.75e+09	1.68e+09	6.43e+09	Sum	3.00e+09	1.00e+00

The itemized breakdown in Table 3-1 includes only those components present in the calcined waste at greater than 10^6 moles. Together, these 11 components comprise more than 99% of the calcined inventory. The inventory is clearly dominated by NaOH (2.45×10^9 moles or about 82 mole% of the total waste inventory of 3.00×10^9 moles). Aluminum and iron ion neutralization by

NaOH to form the corresponding hydroxide compounds has been considered in determining the amount of NaOH remaining.

After NaOH, the most prevalent hypothetical components on a mole basis are, in decreasing order, aluminum hydroxide [$\text{Al}(\text{OH})_3$; about 5.5 mole%]; (Na_2CO_3 ; about 3.7 mole%); and trisodium phosphate (Na_3PO_4 ; about 3.1 mole%). The remaining hypothetical components are, in descending order, sodium fluoride, potassium hydroxide, sodium sulfate, silicon dioxide, ferric hydroxide, and sodium chloride [NaF , KOH , Na_2SO_4 , SiO_2 , $\text{Fe}(\text{OH})_3$ and NaCl , respectively]. These six compounds represent about 5.1 mole% of the inventory. The balance of the waste (including zirconium, calcium, nickel, chromium, manganese) accounts for <1 mole% of the total inventory.

3.3 SODIUM HYDROXIDE FUSION

Molten sodium hydroxide is a highly aggressive and oxidizing fluxing agent with widespread application in chemical analysis of minerals and refractories (Bock 1979; Doležal et al. 1968). Therefore, the NaOH originating in the waste and produced from nitrite and nitrate decomposition is expected to be effective in breaking down the iron-, silicon-, and aluminum-rich sludges present in waste, as well as in dissolving and melting with the residual nonvolatile sodium salts (e.g., sodium sulfate [Na_2SO_4], sodium phosphate [Na_3PO_4], or sodium carbonate [Na_2CO_3]).

Significantly, NaOH fusions are widely used to dissolve bauxite ores for aluminum analyses (Bock 1979; Doležal et al. 1968). Bauxite is a generic term applied to aluminum-bearing ores which may contain either or both the aluminum hydroxide gibbsite [$\gamma\text{-Al}(\text{OH})_3$, also called hydrargillite] and the aluminum oxyhydroxide böhmite ($\gamma\text{-AlOOH}$). Both gibbsite and böhmite have been observed in X-ray diffractograms of genuine waste (Jones et al. 1992). Producing water-soluble sodium aluminate (NaAlO_2) from calcination of aluminum hydroxide with NaOH is the subject of a patent (Davies 1939). Sodium aluminate can be produced by the 800 °C calcination of refractory alumina (Al_2O_3) with NaOH (D'Ans and Löffler 1930). Thus, calcination of aluminum hydroxide/oxyhydroxide-bearing waste sludges with NaOH is expected to produce water-soluble sodium aluminate salts.

The reaction of other metal oxides with molten NaOH at 600 to 900 °C has been studied by D'Ans and Löffler (1930). Nonstoichiometric sodium-metal double oxides were produced for silica (SiO_2) and titania (TiO_2). Ceria (CeO_2) and zirconia (ZrO_2) starting materials produced stoichiometric sodium-metal double oxides (Na_2CeO_3 and Na_2ZrO_3 , respectively). No reaction was observed for mixtures of thorium (ThO_2), magnesia (MgO), or zinc oxide (ZnO) though ZnO was easily soluble in the molten NaOH.

To enhance the fluidity and reactivity of the melt (the melting point of NaOH is 320 °C), temperatures ranging from 400 to 850 °C are recommended in NaOH fusions in analytical chemistry. Although higher temperatures favor the effectiveness of NaOH as a fluxing agent and enhance the rate of nitrate, nitrite, and organic carbon decomposition, the resulting increased aggressiveness of molten NaOH at higher temperatures, directed at the

container materials, exacts its toll on the crucibles used in chemical analyses. Higher temperatures also result in volatilization of NaOH.

3.3.1 Container Materials for NaOH Melts

Container (crucible) materials used in analytical chemistry for NaOH fusions include gold, silver, and nickel. Zirconium crucibles also have been used in alkaline fusions (Dolezal et al. 1968). Platinum is acceptable if reducing conditions are maintained (Bock 1979). However, reducing conditions are not possible with calcined waste because of the presence of nitrate and nitrite salts in the waste and the possible use of air as the heat-transfer medium. Thus, platinum is unsatisfactory because of oxidative attack by the NaOH. Refractory crucible materials suggested for NaOH fusion service include thoria (ThO_2) and zirconia (ZrO_2) (Bock 1979) and alumina (Al_2O_3) (Dolezal et al. 1968). Porcelain is unsatisfactory (Bock 1979).

Destruction of a magnesium oxide (MgO) crucible during calcination tests of NaNO_3 conducted at temperatures up to 950 °C was described by Burger et al. (1973). In the same report, alumina crucibles suffered almost 2 g of weight loss during calcination of 18 to 25 g samples of sodium nitrate and nitrite at 850 °C for 4 hours.

The technical literature has revealed information regarding the handling of molten sodium hydroxide on an industrial basis. To evaluate suitable materials of construction to contain fused alkali hydroxide coolants for possible use in nuclear power plants, a set of screening tests was conducted on 30 elemental metals and 62 alloys (Craighead et al. 1951). The studies were run under reducing (pure hydrogen and 90% nitrogen--10% hydrogen) or nonoxidizing (argon, nitrogen) atmospheres using molten NaOH at 1000 and 1500 °F (538 and 816 °C). Though nickel was the most corrosion-resistant of the metals tested, the report concluded, "None of these container materials for sodium hydroxide look to be really satisfactory for service at 1500 °F."

A subsequent investigation by the same group (Craighead et al. 1952) studied nickel further, as well as a number of ceramic materials. Alumina (Al_2O_3 , including sapphire) and lime-stabilized (i.e., cubic) zirconia were the more resistant refractories, while sodium aluminate (NaAlO_2) in the NaOH melt inhibited nickel corrosion. Borides, carbides, and nitrides did not perform well. Oxides of calcium, magnesium, copper, titanium, and zinc were also unsatisfactory. In both studies, nickel was corroded by dissolution from high-temperature regions and deposition at lower-temperature regions. Results of further tests on nickel and nickel alloys are summarized by Mallett and Stang (1960).

A more recent investigation explored the corrosion resistance of various materials of construction to molten sodium hydroxide, as well as molten mixed carbonates and chlorides, for possible application as heat storage media (Coyle et al. 1984). In these screening experiments, only one coupon (specimen) was tested for each of the 16 metal alloys (including pure nickel, 304 and 316 stainless steels and a variety of Fe/Ni/Cr alloys) and 8 ceramic materials (including 99.8% Al_2O_3 , yttria-stabilized ZrO_2 , and ceramics high in oxides of Al, Cr, and Zr). The test coupons were completely submerged in the 900 °C molten salts under an air atmosphere.

After 3.5 days' exposure to molten sodium hydroxide, 7 of the 16 metals had disintegrated. Included in the failed metals were the stainless steels. All the surviving metals cracked. General corrosion, calculated by weight loss of the surviving metals, averaged 0.6 cm/year. Nickel, one of the surviving metals, showed only slight cracking. However, no particular trend could be discerned correlating alloy composition (e.g., high nickel or low chromium) to corrosion resistance.

Three days' exposure to molten sodium hydroxide destroyed five of the eight ceramics. Two of the three surviving ceramics were 99+% Al_2O_3 ; the third was a mixed composition containing 60 wt% Al_2O_3 plus oxides of Cr, Mg, Fe, and Si. The general corrosion rate of the surviving ceramics was about 2.5 cm/year. Corrosion of high-alumina ceramics ranged from 2.3 to 5.8 cm/year in tests conducted for 200 hours in 800 °C molten NaOH (Grantham and Ferry 1976).

Industrial manufacture of caustic soda (NaOH) requires dehydration of concentrated liquors and subsequent handling of molten sodium hydroxide to produce pellet and flake forms of this chemical commodity. In the first half of this century, industrial vessels handling molten sodium hydroxide up to 500 °C were constructed of cast iron (Hou 1969). Modern facilities use nickel or Inconel¹ to handle concentrated and molten anhydrous sodium hydroxide at temperatures up to 480 °C (Austin 1984).

Significantly, the heat-transfer fluid sometimes used to produce anhydrous sodium hydroxide in nickel vessels is a molten potassium nitrate, sodium nitrite, and sodium nitrate eutectic mixture. The eutectic, a mixture of oxidizing salts, apparently does not present corrosion problems for nickel. However, sodium chlorate (NaClO_3), a common oxidizing impurity found in sodium hydroxide produced by the electrolysis of brine, is highly corrosive in the presence of sodium hydroxide and must first be removed by chemical reduction (usually with sugar) before sodium hydroxide can be concentrated in nickel vessels (Kirk-Othmer 1978; Kirk-Othmer 1992a).

Sodium peroxide, an oxidizing component suspected to be present in molten sodium hydroxide, may be the active corrosive agent in molten sodium hydroxide (Bock 1979). Sodium peroxide is prepared in furnaces by oxidation of sodium oxide at 250 to 400 °C. The materials of construction for the synthesis are graphite-coated nickel alloy reactors equipped with zirconium stirrers. Molten sodium peroxide reportedly attacks steel, nickel, platinum, and porcelain crucibles; zirconium crucibles are recommended for analytical work (Kirk-Othmer 1982).

Thus, no materials that can withstand long-term exposure to molten at 850 °C NaOH were identified in the literature. Equipment design likely will be forced to some type of "cold skull" configuration in which the materials will only be exposed to frozen (i.e., <320 °C) NaOH. With this design, the frozen waste would act as its own container and the engineered container would be cold jacketed to produce the "cold skull" fused calcine liner. With lower

¹Inconel is a high-nickel alloy and is a trademark of the International Nickel Company, INCO, of Huntington, West Virginia.

temperatures imposed by cold jacketing, nickel and nickel-based alloys may perform satisfactorily in a NaOH environment (Craighead et al. 1952).

3.3.2 Sodium Hydroxide Volatility

Sodium hydroxide has significant volatility at higher temperatures; the boiling point is 1390 °C. Loss of NaOH from the calcine melt by volatilization and gas stripping by heat-transfer gas streams and decomposition offgases would effectively "dry out" the desired melt and eliminate the solvating effect of NaOH on the remaining waste components. A balance in choice of temperature between the solvation effected by NaOH, the desired destruction of the organics, and the nitrate and nitrite salts, and NaOH volatility must be sought in C/D process design. Based on these considerations (Colby et al. 1994) and some preliminary tests at the Westinghouse Science and Technology Center (WSTC), an operating temperature range of 850 to 900 °C for the plasma-heated calcination step is indicated; it was selected in pilot testing and as the reference design temperature.

In practice, however, some volatilization of NaOH will occur and can be tolerated because fume scrubbing of calciner offgases will be required for radiological control. Return of scrubbed NaOH to the sluice water (perhaps after removal of volatilized ^{137}Cs) and reintroduction to the calciner could then be performed.

3.3.3 Flux Requirements for Calcination

To take advantage of the solvating effect of molten NaOH, a sufficient quantity of NaOH flux is required. In analytical chemistry applications, weight ratios of NaOH to mineral to be dissolved range down to 2.5:1 (i.e., NaOH represents at least 70 wt% of the melt). Usually, however, this ratio is higher (Bock 1979).

The weight ratio of NaOH to the total weights of the balance of material in a composite Hanford Site waste calcine is about 2:1. However, the non-NaOH materials include other potential fluxing agents or fusible salts. Chief among these are sodium carbonate (Na_2CO_3). Sodium carbonate represents almost 8 wt% of the calcine and, like NaOH, is a fluxing agent (melting point 853 °C) used in analytical chemistry. Combining sodium carbonate with NaOH provides, in general, a more effective fluxing agent (Bock 1979). Including Na_2CO_3 with NaOH, a flux:mineral weight ratio of 3:1 exists in the calcined waste.

Trisodium phosphate (Na_3PO_4) is about 10 wt% of the calcined waste. Combined with NaOH, it may form low-melting mixtures (Schroeder et al. 1937), but by itself melts at 1512 °C. Few data on the melting of NaOH- Na_3PO_4 mixtures are found in the literature.

As discussed in Section 2.1, the waste is present in various waste types with a range of compositions. Not all waste types by themselves have, or will produce, sufficient NaOH and other fusible salt to achieve a flowable and thoroughly fused melt. For example, the REDOX sludge sampled from Tank 104-S and described in Table 2-4 contains only 29 wt% NaOH on a calcined basis. A further 10 weight percent Na_2CO_3 is available to flux this waste. Without

more fluxing agent, calcination of this waste, containing almost 69 wt% $\text{Al}(\text{OH})_3$, would ultimately yield nearly insoluble alumina (Al_2O_3). Fortunately, other waste, such as sodium nitrate salt cake (see Table 2-7) are rich in salts (NaNO_3 and NaNO_2) that form NaOH on calcination that can be blended with waste such as REDOX sludge to achieve successful fusions. Therefore, to maximize fluxing action, the quantities of NaOH, Na_2CO_3 , and Na_3PO_4 available in any waste calcine produced by the C/D process must be carefully assessed. The conversion of nitrate and nitrite to hydroxide is important in providing flux to calcination.

3.3.4 Oxidizing Chemistry of Molten NaOH

The highly oxidizing power of molten NaOH in the presence of atmospheric oxygen is exploited in fusions in analytical chemistry. Sodium peroxide (Na_2O_2) formed by heating NaOH in the presence of atmospheric oxygen may be responsible for this oxidizing effect (Bock 1979). The oxidative properties of molten NaOH in analytical fusions are further abetted by adding nitrate and nitrite salts. Thermal decomposition of NaNO_3 in melts with NaOH produces oxygen gas; this reaction helps achieve oxidation of reduced species [e.g., sulfides, ferrous iron (II) compounds, reduced chromium compounds] present in minerals. Fusions with sodium nitrite (NaNO_2) are also used to achieve oxidizing conditions (Bock 1979). Because NaNO_3 and NaNO_2 are present in high concentrations in virtually all Hanford Site waste, calcination is expected to produce highly oxidizing melts.

The oxidizing power of molten NaOH, especially in the presence of atmospheric oxygen and nitrate/nitrite-generated oxygen, is expected to drive elements having multiple oxidation states, at least to some extent, to their higher, if not highest, oxidation states (Doležal et al. 1968). Most important for the C/D process is oxidation of organic carbon to carbon dioxide, which will be captured in the alkaline melt as carbonate.

Fusion of metal compounds in alkali hydroxides, carbonates and nitrates, sometimes with oxygen or air purged through the melt, are common inorganic chemistry and industrial methods to prepare salts of metals in their higher oxidation states. Thus, chromium (III) hydroxide [$\text{Cr}(\text{OH})_3$] (which is present in the Hanford Site waste) can be oxidized to chromate (CrO_4^{2-}), manganese dioxide (MnO_2) to manganate (MnO_4^{2-}), iron hydroxide [$\text{Fe}(\text{OH})_3$] to ferrate (FeO_4^{2-}), nickel hydroxide [$\text{Ni}(\text{OH})_2$] to nickelate (NiO_2^-), bismuth hydroxide [$\text{Bi}(\text{OH})_3$] to bismuthate [$\text{Bi}(\text{OH})_6^-$] and cerium (III) to cerium (IV) during calcination (chromium and manganese, Kirk-Othmer [1981]; iron and nickel, Levason and McAuliffe [1974]; bismuth and cerium, Cotton and Wilkinson [1988]).

For the oxidizable metal oxides of iron (Fe_2O_3) and chromium (Cr_2O_3), fusion with NaOH at 800 to 900 °C in the presence of oxygen gives the ferrate and chromate double salts (Na_2FeO_4 and Na_2CrO_4 , respectively [D'Ans and Löffler 1930]). In these reactions, both metals oxidized from their (III) to their (VI) oxidation states. The reaction to form chromate was complete, but the reaction to form ferrate was incomplete (about 13% ferrate in the presence of air and 22% in the presence of pure oxygen). Reaction of Fe_2O_3 and Cr_2O_3 with NaOH in the presence of nitrogen gave no oxidation in forming the double salts $\text{Na}_2\text{Fe}_2\text{O}_4$ and $\text{Na}_2\text{Cr}_2\text{O}_4$.

Finally, oxidation may lead to loss of chemical elements from the alkaline melt by volatilization of the oxidized species. For example, chloride (Cl^-) may be oxidized and lost from the melt by volatilization as chlorine gas, while ruthenium has been shown to volatilize (perhaps as ruthenium tetroxide, RuO_4) from potassium nitrate-hydroxide melts at 400 °C (Bock 1979). Volatilization of technetium as the oxide Tc_2O_7 is predicted based on its boiling point of 311 °C; the potassium salt KTcO_4 boils at about 1000 °C (Vida 1989). The boiling point of the sodium pertechnetate (NaTcO_4) salt was not found in the technical literature.

3.3.5 Neptunium, Plutonium, and Americium Oxide Oxidation in NaOH Melts

The technical literature shows that ternary sodium actinide oxides in elevated actinide oxidation states can be prepared by fusing actinide dioxides (e.g., NpO_2 , PuO_2 , and AmO_2) in sodium oxide, peroxide, hydroxide, or carbonate (Keller 1972; Keller 1973). By varying reaction conditions, such as temperature, the presence of oxygen and use of the oxidant sodium peroxide (which can be formed by the interaction of moist air with molten NaOH [Bock 1979]), a variety of ternary oxides may be formed (Katz et al. 1986).

Ternary plutonium oxides with plutonium in the (V) state (e.g., Na_3PuO_4), the (VI) state (e.g., $\alpha\text{-Na}_4\text{PuO}_5$, $\beta\text{-Na}_4\text{PuO}_5$, and Na_6PuO_6), and the (VII) state (e.g., Na_5PuO_6 , though the evidence for this is indirect) are prepared under conditions similar to those postulated for calcination. In contrast, the only known Pu(IV) ternary oxide (Li_8PuO_6) is prepared under vacuum (i.e., in the absence of oxygen gas), and ternary Pu(III) oxides are unknown (Katz et al. 1986). Thus, treating PuO_2 with excess molten NaOH will likely produce oxidized $[\text{Pu}(\geq\text{V})]$ plutonates dispersed in a NaOH flux.

Analogous ternary americium oxides can be produced in the (V) state, Na_3AmO_4 , and in the (VI) state, $\alpha\text{-Na}_4\text{AmO}_5$ and Na_6AmO_6 . The compound Na_2AmO_3 , with americium in the (IV) state, can be produced under nitrogen atmosphere (Keller 1967). No reports of Am(III) or Am(VII) ternary oxides with sodium were found in the literature. Though americium shows tendencies to have lower oxidation states in ternary oxides than plutonium, oxidized $\text{Am}(\geq\text{V})$ species are expected in NaOH fluxes.

While only one ternary neptunium (V) oxide is known (Na_3NpO_4), at least five ternary Np(VI) oxides exist: $\text{Na}_2\text{Np}_2\text{O}_7$, $\alpha\text{-Na}_2\text{NpO}_4$, $\beta\text{-Na}_2\text{NpO}_4$, $\alpha\text{-Na}_4\text{NpO}_5$, $\beta\text{-Na}_4\text{NpO}_5$, and Na_6NpO_6 (Keller 1972 and Keller 1973). No reports of sodium neptunium (III), (IV), or (VII) oxides were found in the literature. Like plutonium, neptunium will probably form (V) and (VI) valent sodium double salts in molten NaOH.

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4.0 DISSOLUTION CHEMISTRY

Following the calcination step, the NaOH-rich melt will be partially dissolved and digested in water. The optimum conditions for dissolution, such as water:solid ratio, temperature, and time of digestion, are not yet determined. These conditions may vary according to the composition of the melt, the surface area:volume ratio of the calcined material fed to the dissolver, the precipitation and crystal growth of insoluble phases in the NaOH aqueous solution, and perhaps the chemical valence adjustment (e.g., reduction) of highly-oxidized metal species produced during calcination. Understanding the behaviors of the TRU elements during the dissolution step, especially their distributions to soluble and insoluble phases, is key to achieving the desired TRU/non-TRU split.

4.1 SOLUBILITIES OF THE PRIMARY HANFORD SITE WASTE CONSTITUENTS IN SODIUM HYDROXIDE SOLUTION

Examination of the overall composition of the calcined waste (see Table 3-1) shows that the inventory is dominated by NaOH. After NaOH, $\text{Al}(\text{OH})_3$, Na_3PO_4 , and Na_2CO_3 are the leading constituents of the calcine. These four components represent 95 mole% of the calcined waste. Therefore, the solubilities of the sodium salts of phosphate and carbonate and of aluminum species in sodium hydroxide solution are important in determining the dissolution characteristics of calcined waste.

The technical literature of Na_3PO_4 and Na_2CO_3 solubilities in NaOH aqueous solutions are summarized and reviewed by Linke (1965). The solubilities of gibbsite ($\gamma\text{-Al}(\text{OH})_3$) and sodium aluminate [$\text{NaAl}(\text{OH})_4$] in NaOH solution are important to the aluminum industry and have been studied extensively (Chaplygina et al. 1974; Wefers 1967). Figures 4-1, 4-2, and 4-3, derived from the cited studies, present the solubilities of Na_3PO_4 (mostly as the dodecahydrate), Na_2CO_3 (as the mono-, hepta- and decahydrates), and gibbsite/sodium aluminate in sodium hydroxide solution as functions of solution composition and temperature.

4.1.1 Na_3PO_4 and Na_2CO_3 Solubilities in NaOH Solution

The solubilities of Na_3PO_4 and Na_2CO_3 in NaOH solution are functions of the concentration of NaOH and of temperature. The effects of these variables on salt solubility must be considered in C/D processing and process design.

As shown in Figure 4-1, the solubility of Na_3PO_4 is highly temperature dependent and increases about five-fold in going from 25 to 100 °C. This is because the hydrated crystalline dodecahydrate species $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, when heated, essentially melts in its own water of hydration. Thus, to minimize the quantity of waste residue remaining after dissolution, incentive exists to perform the dissolution of phosphate-bearing calcines at the highest temperature possible.

Figure 4-1. Trisodium Phosphate Solubility in Sodium Hydroxide Solution. Line Corresponds to $\text{OH}^-/\text{PO}_4^{3-} = 6$ Mole Ratio. Derived from Linke (1965).

On the other hand, as shown in Figure 4-2, Na_2CO_3 solubility is practically temperature invariant above 15 wt% NaOH (corresponding to about 5M NaOH). Below 15 wt% NaOH , increasing temperature to about 30 °C favors Na_2CO_3 dissolution; further temperature increase has little effect on Na_2CO_3 solubility.

Both Figures 4-1 and 4-2 show that increasing NaOH concentration decreases the solubility of the respective salt. This is a manifestation of the "common ion effect" by which sodium ion from NaOH , in common with the sodium in the salt, drives down the salts' (Na_3PO_4 and Na_2CO_3) solubilities.

Ignoring other considerations (e.g., other components in the waste calcine, resulting solution viscosity, solution requirements for subsequent processing, speed of dissolution), optimum dissolution occurs when the quantity of water necessary to effect complete dissolution is minimized. For Na_3PO_4 at 100 °C dissolution, the optimum occurs at essentially 0% NaOH where about 50 wt% of the saturated solution is Na_3PO_4 (and 50% is water from the associated 12 waters of hydration of the trisodium phosphate dodecahydrate). By this measure of optimum dissolution, a high Na_3PO_4 waste, if it did exist, might be better processed separately from NaOH and its calcination sources (NaNO_3 and NaNO_2) to minimize waste volume. For Na_2CO_3 dissolution, the optimum is less distinct and total dissolved solute (NaOH plus Na_2CO_3) of 25 to 30 wt% is attainable in the range 0 to 20 wt% NaOH .

Figure 4-2. Sodium Carbonate Solubility in Sodium Hydroxide Solution. Line Corresponds to $\text{OH}^-/\text{CO}_3^{2-} = 6$ Mole Ratio. Derived from Linke (1965).

In the entire calcined Hanford Site waste inventory, the mole ratios of hydroxide/phosphate ($\text{OH}^-/\text{PO}_4^{3-}$) and hydroxide/carbonate ($\text{OH}^-/\text{CO}_3^{2-}$) are about 26 and 22, respectively (see Table 3-1). In practice, much lower ratios are expected for certain waste types. In the case of Na_3PO_4 , for example, the composite Bismuth Phosphate Process first and second cycle waste described in Table 2-6 would produce a hydroxide/phosphate ratio of 2 in the projected calcined waste.

Shown in Figures 4-1 and 4-2 are lines at hydroxide/phosphate and hydroxide/carbonate mole ratios of 6. These ratios, which correspond to about 20 wt% NaOH (~7M NaOH) at saturation in the respective sodium salt, are proposed to represent nominal phosphate- and carbonate-rich calcined waste dissolutions.

4.1.2 Gibbsite and Sodium Aluminate Solubilities in NaOH Solution

After NaOH , the most common hypothetical component of the calcined waste (at 5.5 mole%) is $\text{Al}(\text{OH})_3$. Besides the soluble sodium aluminate present in Hanford Site waste as double shell slurry, double shell slurry feed, or in other waste liquors (Boomer et al. 1993), much of the aluminum is present in the existing waste sludge as poorly soluble gibbsite and böhmite solid phases. Both gibbsite and böhmite have been observed in waste sludges (Jones et al. 1992).

The NaOH fusion occasioned by calcination of Hanford Site waste is expected to flux the solid aluminum phases by production of sodium aluminate salt. The ensuing water dissolution of the NaOH -rich calcine should

solubilize the aluminum to produce sodium aluminate solution. Thus, aluminum phases that might have otherwise been sent to HLW vitrification may be dissolved and immobilized as less-costly LLW glass. This potential redistribution of waste is a substantial incentive to pursue C/D technology.

Extensive study of phase solubility in the system $\text{Al}(\text{OH})_3\text{-NaOH-H}_2\text{O}$ has been undertaken by the aluminum industry and is reported in the technical literature. The solubility phase diagram of this system is shown in Figure 4-3.

Figure 4-3. Aluminum Species Solubility in Sodium Hydroxide Solution. Lines at $\text{Na}/\text{Al} = 2$ and 6 Mole Ratios. Solid Phases are $\text{Al}(\text{OH})_3$, at Left, and $\text{NaAl}(\text{OH})_4 \cdot 2.5\text{H}_2\text{O}$, at Right (Chaplygina et al. 1974; Wefers 1967).

The solubility curve for $\text{Al}(\text{OH})_3\text{-NaOH-H}_2\text{O}$ has a markedly different shape than those shown by Na_3PO_4 and Na_2CO_3 in NaOH solution. The concentration of aluminum in saturated solutions of varying NaOH concentration initially increases with increased NaOH concentration. Beginning at about 25 to 30 wt% NaOH , however, the aluminum saturation concentration decreases with increasing NaOH . Thus, the solubility phase diagram has the shape of a pointed hat with the solution region being the area "under the hat."

This two-part solubility behavior is caused by the presence of two solubility-controlling solid phases. In the left (low NaOH concentration) part of the phase diagram, $\gamma\text{-Al}(\text{OH})_3$ (i.e., gibbsite) is being dissolved by NaOH to produce dissolved sodium aluminate. As NaOH concentration increases, however, the common ion effect due to sodium takes over and crystalline sodium aluminate hydrate $[\text{NaAl}(\text{OH})_4 \cdot 2.5\text{H}_2\text{O}]$ precipitates. The right side of the curve (high NaOH concentration) describes the solubility of the sodium aluminate hydrate.

Like the cases for Na_3PO_4 and Na_2CO_3 in NaOH , increasing temperature in the $\text{Al}(\text{OH})_3\text{-NaOH}$ system also increases the solubilities of the solid phases. A substantial enhancement of solubility is found at the high-concentration

(i.e., 30 to 40 wt% NaOH) portion of the phase diagram in going from 95 to 135 °C. Increased solubility of gibbsite is also observed in solutions that contain added sodium salts such as carbonate, sulfate, chloride and fluoride (CO_3^{2-} , SO_4^{2-} , Cl^- , and F^- , respectively) (Hudson 1987). Similarly, enhanced solubility of gibbsite at lower sodium hydroxide concentrations in the presence of sodium salts of nitrate, nitrite, sulfate, and carbonate in simulated Hanford Site waste has been reported (Barney 1976).

Note also, however, the seemingly anomalous result that aqueous isothermal dilution of a well-behaved sodium aluminate/hydroxide solution could lead to the precipitation of gibbsite. For example, consider a 50 °C solution that is 25 wt% at both NaOH and $\text{Al}(\text{OH})_3$. As shown in Figure 4-3, this solution has a sodium:aluminum mole ratio of 2 (see line marked $\text{Na}/\text{Al} = 2$). By simple dilution to 15 wt% in both species (followed by proceeding down the $\text{Na}/\text{Al} = 2$ line as shown by the arrow), the solution becomes 2½-times oversaturated with respect to $\text{Al}(\text{OH})_3$ [i.e., the saturation concentration data point at 15 wt% NaOH is 6 wt% $\text{Al}(\text{OH})_3$]. This behavior is exploited in the precipitation of gibbsite from bauxite leach liquors during Bayer processing (Wefers and Misra 1987). Because of this behavior, solution concentrations must be monitored carefully during dissolution of high-aluminum calcines so that precipitation of gibbsite does not occur.

Precipitation of gibbsite by dilution of aluminate liquors with water is also plausible in the course of Hanford Site waste retrieval operations. Water will be used to dissolve sodium salts, decrease waste viscosity, and increase waste mobility (pumpability) during retrieval. According to the gibbsite solubility behavior in simulated Hanford Site waste (Barney 1976) as well as in the $\text{Al}(\text{OH})_3$ -NaOH system, gibbsite precipitation can occur by dilution of certain waste liquors and slurries concentrated in aluminate.

4.1.3 Dissolution of Aluminum Values from Bauxite

Because of the similarity of the chemical conditions of dissolution of Hanford Site waste calcine and the NaOH dissolution of bauxite, it is worthwhile to review the extensive experience of the aluminum industry as practiced in the Bayer process. The Bayer process for producing alumina (Al_2O_3) from bauxitic ores relies on the selective dissolution and precipitation of aluminum phases in NaOH solution and the subsequent calcination of purified $\text{Al}(\text{OH})_3$ to produce alumina. Gibbsite and böhmite are the two major aluminum-bearing minerals of interest in bauxite ore. Some bauxitic ores also contain the more refractory form of AlOOH , the mineral diaspore (α - AlOOH). Besides gibbsite and böhmite, tramp minerals such as hematite (Fe_2O_3), goëthite (FeOOH), siderite (FeCO_3), the titania (TiO_2) phases anatase and rutile, quartz (SiO_2) and clay (e.g., kaolinite, montmorillonite, and halloysite) also occur in bauxite (Kirk-Othmer 1992b).

In the Bayer process, crushed bauxite ores are leached in concentrated NaOH solution (200 to 300 g NaOH/L corresponding to 5 to 7.5M) at 150 to 300 °C (Misra 1986). Steam-heated pressurized autoclaves are used to achieve the high temperatures required. The primary aluminum-bearing ores are dissolved by the action of the hot NaOH by the following reactions:

Other than gibbsite, böhmite, and didspore, minerals present in the bauxite are generally not dissolved by NaOH. These undissolved minerals are separated from the "green" or "pregnant" liquor by cycloning, followed by settling and cloth or sand filtration (Kirk-Othmer 1992b). The undissolved residue is known archaically as "red mud" and more recently as bauxite residue. Disposal of this residue poses a major environmental problem for the aluminum industry because of the high pH of its associated liquid. The residue will form a vitreous bond when calcined at about 1200 °C (Hudson 1987). Thus, formation of C/D residue into calcined "brick" waste forms may be possible. Economic use of Bayer process residues to recover contained metals and minerals has been studied with limited success (EPA 1976).

Though most nonaluminum hydroxide minerals are insoluble in NaOH solution, dissolution of reactive silica by the hot and concentrated NaOH during bauxite digestion occurs to form soluble sodium silicate (Na_2SiO_3). One source of reactive silica is the clay kaolinite (kaolinite has the idealized formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The sodium silicate produced from dissolution of reactive silica can then react with dissolved sodium aluminate to form sodium aluminosilicate precipitate ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$), according to the following reaction sequence:

This reaction sequence, called desilication in the aluminum industry, is exploited to remove unwanted silica from the green liquor. The resulting sodium aluminosilicate is called the desilication product (DSP). The DSP reaction causes a loss of aluminum from solution equal, on a mole basis, to the amount of reactive silica. As shown in the above sequence, the DSP reaction also consumes NaOH by formation of the sodium aluminosilicate. Because silica is not desired in the aluminate solution for Bayer processing, reaction conditions (high temperatures and solution holding times) are maintained to drive the DSP reaction toward completion (Kirk-Othmer 1992b).

The DSP compound represents a series of zeolites based on aluminosilicate frameworks. The frameworks can incorporate various sodium salts such as carbonate, sulfate, chloride, hydroxide and aluminate. In the presence of excess aluminate (as is always true in the Bayer process), this reaction acts as a dissolved silica scavenger and reduces silicon solution concentration, under plant conditions, to about 0.3 g/L. In the presence of calcium ion, the DSP becomes the aluminosilicate cancrinite [$3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2) \cdot 2\text{CaCO}_3$]. With cancrinite, the dissolved silicon concentrations fall below 0.01 g/L (Hudson 1987).

The experience of the aluminum industry in the Bayer process, with respect to the DSP precipitation, implies that silicon and aluminum present in the C/D-processed Hanford Site waste will react on a 1:1 mole basis to form sodium aluminosilicates of low solubility. Furthermore, the sodium aluminosilicates will carry sodium salts. Unless otherwise dissolved or segregated, these sodium aluminosilicate residues and their contained salts will report to the vitrified HLW fraction.

It is important that high-silicon waste, such as the diatomaceous earth deposits present in six Hanford Site waste tanks, be processed separately from aluminum-bearing waste during C/D operations so that maximum aluminum and silicon dissolution can be effected. As shown in Table 2-1, silicon is present in the Hanford Site waste at about 10 mole% of the level found for aluminum.

The Bayer process experience with respect to plant design, phase separation and filtration technology, materials of construction, conditions of temperature, and residence time for DSP crystallization and growth, can also be profitably exploited for C/D plant design. The aspects of the chemical engineering of the Bayer process are given by Hudson (1987).

4.2 DISSOLUTION OF OXIDIZABLE CHEMICAL COMPONENTS OF THE CALCINED WASTE

Elements with multiple oxidation states will be oxidized to their higher, if not highest, oxidation states by calcination in NaOH. Some elements (e.g., chlorine, Cl_2 , and ruthenium as RuO_4) may be lost from the melt by volatilization and subsequently be scrubbed in the off-gas system. The transition metals iron, chromium, and manganese are expected to be oxidized in the melt to the (VI) oxidation state and form soluble oxyanions of the formula MeO_4^{2-} ; nickel would form the soluble oxyanion NiO_2^- [or $\text{Ni}(\text{OH})_4^-$]. Soluble bismuthate anion $[\text{Bi}(\text{OH})_6^-]$ and insoluble cerium (IV) oxide or hydrous oxide would also form.

On contact with alkaline solution during dissolution, many of these species are sufficiently oxidizing to oxidize hydroxide to oxygen gas and, in turn, be reduced. The following standard reduction potentials (in volts) for basic (pH = 14) solutions illustrate plausible reduction half-reactions for these metallic species and the corresponding hydroxide-oxygen couple potential (Bratsch 1989):

$\text{CrO}_4^{2-} / \text{Cr}(\text{OH})_3$ (fresh pt)	-0.12
$\text{MnO}_4^{2-} / \text{MnO}_2$ (pt)	(0.51)
$\text{FeO}_4^{2-} / \text{Fe}(\text{OH})_3$ (pt)	(0.71)
$\text{Ni}(\text{OH})_4^- / \text{Ni}(\text{OH})_2$ (pt)	(0.7)
$\text{Bi}(\text{OH})_6^- / \text{Bi}(\text{OH})_3$ (pt)	(0.7)
CeO_2 (pt) / $\text{Ce}(\text{OH})_3$ (pt)	(0.5)
O_2 / OH^-	0.411

pt = Noncrystalline precipitate.

() = Estimated value.

The above half reactions show that, except for chromate, all the listed oxidized metals are thermodynamically powerful enough oxidants to liberate oxygen from hydroxide. Oxidation of water by nickelate has been observed.

However, manganate ion reportedly is stable in alkaline solution (Cotton and Wilkinson 1988). Cerium (IV) oxide, with its low solubility, would probably remain oxidized.

Most likely, given the irreversibility of oxygen electrode couples and the resulting high overpotential for oxygen formation (Latimer 1952), only slow reduction of ferrate and bismuthate in the NaOH solution would occur. Thus, ferrate and bismuthate could act as soluble oxidizing redox (reduction/oxidation) buffers in the NaOH solutions.

The anticipated formation and stability of soluble chromate via C/D oxidation and dissolution of $\text{Cr}(\text{OH})_3$ from the Hanford Site waste sludge is significant. Chromium has been identified as a principal driver of the "canister count" resulting from Hanford Waste Vitrification Plant (HWVP) feed specifications (Swanson 1993). According to Swanson 1993, the Hanford Site waste inventory of chromium, by itself, requires 80,000 canisters to incorporate into glass. The aluminum in HLW, in comparison, requires 50,000 canisters, while sodium requires 1,000,000 canisters. These three elements, all expected to be readily solubilized by C/D and thus be fed to less-expensive LLW engineered waste forms if separated from TRU, are leading Hanford Site waste contributors to the HWVP "canister count."

4.3 INSOLUBLE RESIDUES REMAINING FOLLOWING DISSOLUTION

Water-insoluble residues will remain following the C/D treatment of the Hanford Site waste. As discussed in Section 4.1.3, sodium aluminosilicate phases, such as the zeolites and cancrinites found in bauxite residues from Bayer process desilication, are expected in the C/D residue if both aluminum and silicon are present in the Hanford Site waste feed.

Transition metal oxides and hydroxides from the Hanford Site waste sludge that do not undergo oxidation or that do oxidize but subsequently are reduced during the dissolution step (i.e., iron, zirconium, nickel, manganese), would reprecipitate as oxides and hydroxides. The lanthanides (e.g., cerium, lanthanum) would also precipitate as oxides/hydroxides. Bismuth phosphate (BiPO_4), identified in waste sludge samples by x-ray diffraction spectrometry (Jones et al. 1992), would be expected, like other phosphate minerals, to metathesize during $\text{NaOH}/\text{Na}_2\text{CO}_3$ fusion and the bismuth, if not oxidized to form soluble bismuthate, reprecipitate as the $\text{Bi}(\text{III})$ hydroxide or hydroxycarbonate (Doležal et al. 1968). Lead (Pb) is expected to oxidize in the NaOH fusion to $\text{Pb}(\text{IV})$. Whether lead (IV) precipitates or dissolves as the $\text{Pb}(\text{OH})_6^{2-}$ ion is not known.

Salts of the alkali metals (sodium and potassium), with the exception of those present in tectosilicate(s) (e.g., zeolite, cancrinite) will dissolve. Phosphate and sulfate are significant contributors to the "canister count" (Swanson 1993). According to Swanson 1993, phosphate immobilization requires 400,000 canisters while sulfate immobilization requires 200,000 canisters. It is anticipated that the majority of phosphate and sulfate will be readily soluble as their respective sodium salts. However, alkaline earth precipitates of phosphates and sulfates are only sparingly soluble. The alkaline earths (present in the Hanford Site waste principally as calcium,

strontium and magnesium) would be expected to precipitate as phosphates, sulfates, or possibly carbonates.

Uranium and thorium will not change oxidation states [(VI) and (IV), respectively] during C/D processing. Thorium hydrous oxide, which has a solubility of about 10^{-9} M (about 0.000002 g/L) at pH = 14 (Ryan and Rai 1987), will probably remain undissolved and will possibly be coprecipitated with a macroconstituent such as $\text{Fe}(\text{OH})_3$. The solubility of uranium in alkaline simulated Savannah River Site waste (with composition at about 1M NaOH, 2M NaNO_3 , 1M NaNO_2 , 0.2M $\text{NaAl}(\text{OH})_4$, 0.2M Na_2CO_3 , and 0.2M Na_2SO_4) was found to range from 1 to 10 mg/L (Hobbs et al. 1993). Thus, uranium will probably dissolve to some extent, especially in solutions of higher carbonate solution concentrations.

4.4 NEPTUNIUM, PLUTONIUM, AND AMERICIUM BEHAVIOR IN DISSOLUTION OF CALCINED WASTE

Ternary sodium actinide oxides, in which the actinides neptunium, plutonium, and americium are in oxidation states ranging from (V) to possibly (VII), are expected to form during Hanford Site waste calcination. The solubilities of the oxidized actinides in the alkaline solution, resulting from the ensuing dissolution step, may be sufficiently high that the solutions themselves will not be solubility-limited to non-TRU waste levels (non-TRU waste is <100 nCi/g corresponding to about 0.17 g ^{237}Np /L, 0.001 g $^{239,240}\text{Pu}$ /L, or 0.000035 g ^{241}Am /L). Furthermore, the redox buffering capacity of species such as manganate, ferrate, and bismuthate could maintain oxidizing conditions in the NaOH solution at about 0.5 volts, and thus, stabilize the oxidized actinide dissolved species.

Relatively low solubilities of hydrated plutonium (IV) oxide ($\text{PuO}_2 \cdot x\text{H}_2\text{O}$) in alkaline simulated Hanford Site waste solution (e.g., ~ 0.002g/L in 7M NaOH and 0.00012g/L at 3M NaOH) have been observed at intermediate electrode potentials of about 0 to 0.1 volts. The dissolved species was identified as Pu(V). As would be expected when the dissolved and solid phases are in different oxidation states, the plutonium solubility was sensitive to redox potential (Delegard 1987). In this case, a more oxidizing system, such as that furnished by ferrate, would increase dissolution by stabilizing the dissolved Pu(V) species.

The solubility of Pu(VI) hydroxide in NaOH is at least 1 g/L (Delegard 1987). Dissolutions of the ternary sodium plutonium (VI) oxides have been studied in water and dilute NaOH. In those studies, plutonium solution concentrations ranged from 0.2 to 2 g/L (Keller et al. 1965). At least 20 g/L concentrations of Pu(VII) in highly alkaline solution have been observed (Peretrukhin and Spitsyn 1982). The solubility data for oxidized plutonium, therefore, show solution concentrations that exceed the TRU limit.

Like plutonium, the solubility of oxidized Am is not expected to limit Am solution concentrations to less than TRU waste levels. The TRU waste constraint becomes more restrictive by the higher specific activity of ^{241}Am than that of the plutonium isotopes. The stability of the oxidized [$\geq$ (V)] Am species are, however, lower than those of the corresponding plutonium oxidation states in the alkaline solution (Peretrukhin and Spitsyn 1982). In

the absence of organic complexants, the solubility of the Am(III) phase precipitating in synthetic Hanford Site waste is less than the TRU waste limit (Delegard et al. 1984).

The stabilities of oxidized [$\geq(V)$] neptunium species are higher than those of the corresponding plutonium species (Peretrukhin and Spitsyn 1982). However, ^{237}Np has a low specific activity. The maximum solubility of the neptunium species precipitating in synthetic Hanford Site waste was about 0.2 g/L or approximately 100 nCi/mL (Delegard and Gallagher 1983). Thus, neptunium in the dissolved state may be solubility-limited to about the TRU threshold.

Therefore, dissolution of actinide values from waste sludges during C/D processing is probable. Actinide dissolutions, if found to occur, will require additional processing to implement C/D technology.

5.0 EXPERIMENTAL MATERIALS AND METHODS

Laboratory-scale calcination and aqueous dissolution experiments were conducted using both simulated and genuine Hanford Site waste materials. Some experiments with simulants were performed using compositions having few components to isolate the behavior of selected components. Other experiments were conducted using more comprehensive Hanford Site waste simulants. Finally, experiments using blended and unblended genuine Hanford Site waste materials were performed. Investigations of the compatibility of candidate materials of construction to molten sodium hydroxide were also conducted.

The materials, apparatus, and methods used to perform the experimentation are described in this section.

5.1 APPARATUS AND PROCEDURES

The technique and apparatus that will achieve full-scale Hanford Site waste calcination have not yet been selected. However, the heating required for waste calcination likely will not occur through a vessel wall. In earlier pilot calcination tests, simulant waste material adhesion to vessel walls occurred because of the formation of sticky and viscous high-sodium melts.

To overcome the poor heat transfer and material handling problems associated with through-the-wall heating, air plasma mediated calcination was selected for recent pilot testing. Two pilot tests (November 1992 and November 1993) were conducted at the WSTC. In the WSTC tests, simulated Tank 241-SY-101 (101-SY) waste slurry was injected into high-speed superheated air. A turbulent and rapid (ms) heating of the simulant waste to about 1500 °C was achieved by that method. The waste was then rapidly cooled (in the time range of 10 to 50 ms) by adiabatic expansion to reach ~850 °C in the calciner crucible where waste residence times were on the order of fractions of an hour to hours (Gass et al. 1993 in Colby et al. 1994).

Muffle furnace heating of material in crucibles achieved the 850 °C calcination temperature in the present lab tests. The crucible-in-furnace laboratory apparatus, however, models neither the rapid heating nor the turbulent mixing of the pilot calciner used at the WSTC, nor will it likely model any other selected full-scale calcination method for short (<1 minute) residence times at temperature. Muffle furnace heating of waste materials in crucibles was adopted because of its simplicity and the availability of the equipment. Results from the laboratory calcination tests are expected to give reliable calcination data for calcination time scales above about one minute (i.e., the time required for the crucible and contents to achieve the 850 °C calcination temperature in the preheated muffle furnace).

In most experiments using simulated waste and all experiments with genuine waste, several hours of laboratory oven preheating (at 120 to 130 °C) of the materials to be calcined were performed. The preheating step drove off solution water and allowed direct introduction of the dried waste materials into the heated furnace without risk of boil-over of the crucible contents. The preheating step, by driving off water, also reduced times required for the

waste to reach 850 °C calcination temperatures. Calcination times (time in the furnace) ranged from 1 to 42 minutes.

The calcination tests generally used crucibles constructed of corundum (also known as alumina, Al_2O_3). Experiments with simulants used 50-milliliter (mL) capacity, flat-bottomed conical crucibles; experiments with genuine waste used 100-mL capacity, high-form (curved-wall) crucibles.

Aqueous dissolutions were conducted directly in the crucibles with hot plate heating about 10 minutes after the crucibles had been removed from the furnace. The slurries then were transferred from the crucibles to 15- or 50-mL capacity centrifuge tubes by polyethylene transfer pipets. The slurries were centrifuged to produce a clear supernate. The supernatant solution was decanted and analyzed. For most experiments, the residual solids were water washed, air dried (at 60 to 100 °C) and analyzed.

Materials performance tests generally were conducted by heating 15 g of sodium hydroxide in crucibles constructed of the materials to be tested. Survey of the technical literature showed promising candidate materials were alumina (Al_2O_3), zirconia (ZrO_2), and unalloyed (commercially pure) nickel. Observations of corrosion attack were noted by visual checks and determination of material weight loss. Initial material performance studies showed that the zirconia and nickel crucibles were inferior to alumina. Therefore, further tests of corrosion rates as functions of temperature were performed for alumina.

5.2 MATERIALS

Materials used during the experiments included both simulated and genuine waste. Crucibles fabricated from alumina, zirconia, and nickel were used for the materials performance tests.

5.2.1 Simulated Waste

The simulated waste used during the experiments were prepared from reagent materials and distilled water. However, the sodium aluminate [$\text{NaAl}(\text{OH})_4$] used in the simulant preparations was technical grade.

Two Hanford Site waste simulant formulations were prepared: a simulant based on the composition of the contents of 101-SY and a composite based on the total Hanford Site waste inventory. The 101-SY recipe (Delegard 1993) was based on the composition found from samples taken during the December 1991 Window E (Herting et al. 1992). The composite Hanford Site waste formulation is presented in Appendix A.

Simplified waste materials were also prepared. The simplified waste formulations are presented in Table 5-1. The simplified waste formulations were based on two systems:

- 0.75 mole fraction sodium hydroxide (NaOH) with varying concentrations of aluminum hydroxide [$\text{Al}(\text{OH})_3$], silica (SiO_2), and ferric oxide (Fe_2O_3)

- 0.75 mole fraction sodium hydroxide with varying concentrations of aluminum hydroxide, sodium carbonate (Na_2CO_3), and trisodium phosphate (Na_3PO_4).

Table 5-1. Simplified Waste Formulations.

Expt.	Mole fraction					
	NaOH	$\text{Al}(\text{OH})_3$	SiO_2	$\text{FeO}_{1.5}$	Na_3PO_4	Na_2CO_3
1A	0.75	0.25	--	--	--	--
2A	0.75	--	0.25	--	--	--
3A	0.75	--	--	0.25	--	--
4A	0.75	0.125	0.125	--	--	--
5A	0.75	0.125	--	0.125	--	--
6A	0.75	--	0.125	0.125	--	--
7A	0.75	0.125	0.0625	0.0625	--	--
8A	0.75	0.0625	0.125	0.0625	--	--
9A	0.75	0.0625	0.0625	0.125	--	--
1B	0.75	0.25	--	--	--	--
2B	0.75	--	--	--	0.25	--
3B	0.75	--	--	--	--	0.25
4B	0.75	0.125	--	--	0.125	--
5B	0.75	0.125	--	--	--	0.125
6B	0.75	--	--	--	0.125	0.125
7B	0.75	0.125	--	--	0.0625	0.0625
8B	0.75	0.0625	--	--	0.125	0.0625
9B	0.75	0.0625	--	--	0.0625	0.125

The primary objectives of performing the first set of experiments were to investigate the possible formation of aluminosilicates during the dissolution step and to determine the disposition of iron during C/D processing. Of particular interest in the second set of experiments was determining the possible formation and subsequent dissolution of aluminum phosphate (AlPO_4) and dawsonite [$\text{NaAlCO}_3(\text{OH})_2$] from waste components.

Further C/D tests of simplified waste formulations were conducted to investigate the disposition of phosphate in the presence of calcium, aluminate, silica, and carbonate in sodium hydroxide. The tests helped determine the precipitation of calcium with phosphate. Formation of insoluble phosphate phases [e.g., apatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$] would increase the volume of high-level glass because of the high dilution of phosphate required to formulate an acceptable glass waste form. The experiments helped determine if

calcium would preferentially form an aluminate, silicate, aluminosilicate, or carbonate phase and thus leave phosphate as the relatively soluble trisodium phosphate. Two formulations were prepared:

- 0.75 mole fraction sodium hydroxide with equal molar concentrations of trisodium phosphate, calcium hydroxide $[\text{Ca}(\text{OH})_2]$, aluminum hydroxide, and silica
- 0.75 mole fraction sodium hydroxide with equal molar concentrations of trisodium phosphate, calcium hydroxide, aluminum hydroxide, and sodium carbonate (Na_2CO_3) .

The successful alkaline fusion of Hanford Site waste depends on the extent of conversion of sodium nitrate (NaNO_3) and sodium nitrite (NaNO_2) to sodium hydroxide (NaOH). A set of experiments, therefore, was performed to determine the extent of nitrate conversion to hydroxide. The experiments were conducted using 50 mole% reagent aluminum hydroxide. The aluminum hydroxide served as a sink for the initial and product sodium hydroxide. Gibbsite, $\gamma\text{-Al}(\text{OH})_3$, was the aluminum hydroxide phase used in these experiments and is the aluminum-bearing solid phase most commonly found in Hanford Site waste.

Sodium nitrate and sodium hydroxide, in mole ratios ranging from 0 to 1, comprised the remaining 50 mole% of the experimental mixtures. The varying nitrate:hydroxide ratios helped determine the effect, if any, sodium hydroxide had on sodium nitrate thermal stability. The solubilization of the aluminum hydroxide caused by formation of soluble sodium aluminate thus served as evidence of the extent of nitrate conversion to hydroxide. The aluminum hydroxide solubilization also served as a practical demonstration of a major objective of C/D processing.

5.2.2 Genuine Waste

Samples of genuine waste were used to test C/D. Samples were taken from Tanks 241-SY-101, 241-S-104, and 241-BX-107 (101-SY, 104-S, and 107-BX, respectively) representing, respectively, CC, REDOX sludge, and Bismuth Phosphate Process first and second cycle waste. The 101-SY sample material used was a composite prepared from samples collected following the Window C (May 1991) and Window E gas release events. The 104-S and 107-BX samples were collected during the SST characterization efforts. The chemical and radionuclide compositions of the waste samples used for the C/D tests are presented in Table 5-2.

Calcination/dissolution tests of blended genuine waste were also conducted. Approximately equal-weight blends of 104-S with 101-SY and 107-BX with 101-SY were prepared. These tests simulated the blending expected to be necessary to achieve successful alkaline fusion for waste containing relatively little NaOH or sodium hydroxide-producing components (i.e., NaNO_3 , and NaNO_2). Waste low in sodium hydroxide, sodium nitrate, and sodium nitrite have correspondingly higher concentrations of aluminum, phosphate, transition metals (e.g., iron, chromium), and bismuth. For the present tests, waste requiring extra fluxing agents were the 104-S and 107-BX materials.

Table 5-2. Compositions of Genuine Hanford Site Waste.

Component	Concentration (wt%)		
	CC (101-SY) (Herting et al. 1992)	REDOX (104-S)	Bismuth Phosphate Process (107-BX)
Al	3.2	11.9	1.20
Bi	—	0.003	2.06
Ca	0.023	0.056	0.31
Cr	0.41	0.26	0.084
Fe	0.028	0.19	0.94
K	0.326	0.11	0.011
Mn	—	0.12	0.005
Na	20.7	11.6	10.0
Ni	0.015	0.52	0.20
Si	—	0.12	0.60
U	0.0063	0.73	0.20
Zn	0.002	0.005	0.006
Cl ⁻	0.79	0.31	0.12
F ⁻	0.03	0.011	0.84
NO ₂ ⁻	10.5	1.98	0.92
NO ₃ ⁻	11.7	20.4	15.0
PO ₄ ³⁻	0.64	0.11	1.50
SO ₄ ²⁻	0.40	0.24	1.42
CO ₃ ²⁻	3.15	2.28	0.58
OH ⁻	2.47	0.2	—
TOC	1.53	0.13	0.055
H ₂ O	35.5	34.8	56.4
pH	—	13.3	9.68
Radionuclide	Concentration (μCi/g)		
⁹⁰ Sr	21	320	10
⁹⁹ Tc	0.21	0.026	0.038
¹³⁷ Cs	350	64	13
²³⁷ Np	0.000028	0.015	0.020
^{239,240} Pu	0.0067	0.16	0.044
²⁴¹ Am	0.11	0.12	0.075

Simple water dissolutions of noncalcined waste were also performed. Comparing the results of the simple water dissolution with the C/D results helped identify the benefits of C/D processing.

5.2.3 Crucibles

Crucible materials were tested for compatibility with the molten alkaline sodium hydroxide melts. In addition to the alumina crucibles used for most tests, zirconia and nickel crucibles were tested. The 50-mL capacity alumina (99.8 wt% Al_2O_3) crucibles were offered by Coors Ceramicon Designs Limited of Golden, Colorado. The 100-mL capacity, high-form alumina crucibles were also obtained from Coors.

Fully-(yttria)stabilized, 50-mL conical zirconia crucibles, from Coors Ceramicon, and 40-mL cylindrical stabilized zirconia crucibles (containing approximately 5 wt% calcia, CaO), from Alfa/Johnson Matthey, Ward Hill, Massachusetts, were obtained. The commercially-pure nickel (99% minimum nickel; maximum 0.25% copper, 0.40% iron, 0.35% magnesium, 0.15% carbon, 0.35% silicon, and 0.01% sulfur/weight basis) crucibles (100-mL capacity) were obtained from VWR Scientific. The nickel crucible manufacturer was Dual Manufacturing Company, Chicago, Illinois.

5.3 ANALYSES

Chemical and radionuclide concentrations were determined during the performance of these experiments. In addition, crystallographic (X-ray diffraction) analyses identified crystalline solid phases present in feed and product materials from C/D. All analyses were conducted by the Analytical Operations of the 222-S laboratory of the Westinghouse Hanford Company (WHC).

Metal concentrations (e.g., aluminum, sodium, phosphorus, sulfur, chromium, iron, silicon, calcium, nickel, manganese, potassium, bismuth) were determined by inductively coupled plasma (ICP) spectrometry. Inorganic anion analyses (e.g., for fluoride, chloride, nitrite, nitrate, phosphate and sulfate) were provided by an ion chromatography method.

Hydroxide concentrations were determined by standard titration. Carbonate (inorganic carbon) was determined by collecting carbon dioxide expelled from acidified sample aliquots and titrating the resulting carbonic acid. Organic carbon concentrations were determined by collecting carbon dioxide from pyrolyzed sample aliquots and a similar coulometric titration. A spectrophotometric technique was used for chromium (VI) (i.e., chromate) concentration determinations.

Radionuclide analyses included gamma energy analyses (GEA) to quantify gamma-emitting nuclides such as ^{137}Cs and ^{154}Eu (europium-154). Strontium-90 (^{90}Sr) and ^{99}Tc were determined by solvent extraction and counting techniques. Separate solvent extraction techniques helped determine concentrations of ^{237}Np , $^{239,240}\text{Pu}$, and ^{241}Am (the respective neptunium, plutonium, and americium isotopes). Uranium was quantified chemically by a time-resolved laser fluorescence method.

6.0 RESULTS AND DISCUSSION

Laboratory investigations were conducted to determine container material resistance to molten sodium hydroxide and to determine the chemical behaviors of Hanford Site waste to calcination and water dissolution processing. Chemical distributions (material balances) and rates of reaction were studied for simulated waste. Chemical and radionuclide material balances then were determined for genuine Hanford Site radioactive tanked waste processed, on a lab scale, by calcination and water dissolution.

6.1 MATERIAL PERFORMANCE

Review of the technical literature showed molten sodium hydroxide in air or oxygen to be an extremely corrosive and oxidizing solvent. The chemical aggressiveness of molten oxidizing sodium hydroxide will be obtained during calcination of Hanford Site radioactive tanked waste because sodium hydroxide is present in the waste. Sodium hydroxide also forms via thermal decomposition of sodium nitrate and nitrite waste components.

The aggressiveness of molten sodium hydroxide is key to the success of calcination in metathesizing refractory mineral phases, such as böhmite (AlOOH) and cancrinite ($\text{NaAlSiO}_4 \cdot x\text{H}_2\text{O} \cdot y\text{NaNO}_3$), present in the waste. The calciner material itself, however, must resist attack by sodium hydroxide. Crucibles constructed of a suitably resistant material were also required to perform the laboratory studies.

The technical literature showed alumina, zirconia, and nickel to be most likely to resist attack by molten oxidizing sodium hydroxide. Therefore, scoping tests of material performance were conducted using alumina, zirconia, and nickel crucibles. The scoping tests showed the zirconia and nickel materials performed relatively poorly compared with alumina. Data are presented in Appendix B.

6.1.1 Zirconia

Zirconia crucibles from two manufacturers were tested. The zirconia crucibles from Alfa failed upon introduction to the furnace by fracturing via thermal shock. Subsequent corrosion tests using shards of the broken zirconia crucible immersed in molten sodium hydroxide (held in an alumina crucible) showed rapid intergranular attack and high weight loss (about 2.5 wt% in 5 minutes). The shard itself, initially hard and dense, had become chalky after exposure to molten sodium hydroxide.

Zirconia crucibles from Ceramicon were also tested. Like the zirconia crucibles from Alfa, these crucibles failed by cracking. The inability of the zirconia crucibles to tolerate the thermal shock of direct introduction to a preheated furnace eliminated them from consideration for use in the present lab tests. Further tests of the Ceramicon zirconia crucibles were conducted to determine resistance to molten sodium hydroxide.

Subsequent attack of Ceramicon zirconia crucibles by molten sodium hydroxide was manifest by severe exfoliation (spallation, blistering, and scaling). The zirconia used in both the Alfa and Coors crucibles contain blends of agents (typically calcia or magnesia, Austin 1984, as well as yttria) to stabilize the cubic phase of zirconia. It is postulated, based on the composition of the crucibles and the mode of attack, that the respective intergranular and exfoliation failures were because of the action of molten NaOH on the stabilizing agents. Further tests of zirconia were not performed.

6.1.2 Nickel and Alumina

The corrosion behaviors of nickel and alumina crucibles in molten sodium hydroxide, as functions of temperature, are presented in Figure 6-1. Alumina performance was clearly superior to that of nickel. In short-term tests, alumina linear corrosion rates were about 30 cm/y at 750 °C, 70 cm/y at 875 °C, and 90 cm/y at 1000 °C. Nickel linear corrosion rates were at least two-times higher, based on weight losses, at 875 and 1000 °C. Nickel also showed marked preferential attack at the air-liquid (NaOH) interface. Unlike zirconia, neither nickel nor alumina fractured during testing.

Figure 6-1. Corrosion Behavior of Alumina and Nickel Crucibles in Molten Sodium Hydroxide.

Based on the corrosion scoping tests with alumina, zirconia, and nickel, alumina crucibles were selected for the laboratory calcination studies. Alumina performance was not ideal, however, and the corrosion rates may be unacceptably large for process equipment exposed directly to high-temperature molten sodium hydroxide. Alumina also may not have the strength and mechanical flexibility required for long-term (multiyear) performance.

Further corrosion studies must be conducted to select an acceptable material for calciner construction. Proper equipment design to avoid direct exposure of the vessel to molten sodium hydroxide probably will be required.

The alumina corrosion results are indicative, however, of the tremendous solvating power of molten sodium hydroxide. The linear corrosion rate of alumina at 875 °C (about 70 cm/y) corresponds to the dissolution of a 50 μ m-diameter alumina particle in 20 minutes. Aluminum hydroxide and oxyhydroxide particles in Hanford Site waste will be smaller than this diameter and substantially easier to corrode than high-fired alumina refractory.

6.2 C/D OF SIMPLIFIED WASTE COMPOSITIONS

To determine the behaviors and interactions of the principal chemical components of Hanford Site waste (aluminum hydroxide, silica, iron oxide, sodium carbonate, and trisodium phosphate in sodium hydroxide), C/D tests were conducted using simplified waste compositions. Two separate sets of tests were conducted. Both sets used compositions based on 75 mole% sodium hydroxide (sodium hydroxide represents about 82 mole% of the projected calcined Hanford Site waste inventory). Concentrations of the other materials comprised the remaining 25 mole%. The simplified waste compositions tested are given in Table 5-1.

In the first set, varying concentration combinations of aluminum hydroxide [Al(OH)₃], ferric oxide (Fe₂O₃), and silica (SiO₂) were used. The second set used varying concentration combinations of aluminum hydroxide, trisodium phosphate (Na₃PO₄), and sodium carbonate (Na₂CO₃). With sodium hydroxide, these three components represent about 95 mole% of the calcined Hanford Site waste inventory.

A single test was conducted to identify the preferred insoluble phase(s) formed from C/D of 75 mole% sodium hydroxide with equimolar (6.25 mole%) amounts of aluminum hydroxide, silica, trisodium phosphate, and calcium hydroxide [Ca(OH)₂]. A test similar to the above test was conducted in which sodium carbonate (Na₂CO₃) replaced silica. The concentrations of the remaining chemicals were otherwise identical. These experiments helped determine if calcium would react with aluminate, silicate, aluminosilicate, or carbonate preferentially over phosphate.

Finally, a set of experiments were run to test the thermal conversion of nitrate to hydroxide. The formation of the nitrite as an intermediate in the thermal decomposition of nitrate to hydroxide was also studied. Initial compositions were 50 mole% aluminum hydroxide with sodium nitrate and sodium hydroxide, in varying ratios, comprising the remaining 50 mole%. The experimental data for C/D of simplified waste are presented in Appendix C.

6.2.1 Al(OH)₃-SiO₂-Fe₂O₃ in NaOH

Calcinations for this set of experiments were performed at 750 °C for 30 minutes. The test matrices are presented in Table 5-1. Two sequential dissolutions in water (to produce, at completion, about 6.5M sodium) were

performed on the calcined material and the solutions analyzed. The washed and dried residues were analyzed by X-ray diffraction (XRD) to identify residual insoluble phases.

Results of the dissolution and XRD analyses are presented in Table 6-1. Several observations were made from the results. As shown in experiment 1A, the calcination time and temperature conditions were inadequate to convert the aluminum hydroxide reagent (found to be gibbsite by XRD) completely to soluble sodium aluminate. Likewise, not all silica was converted to soluble sodium silicate.

Table 6-1. Calcination/Dissolution of Various Sodium Hydroxide, Aluminum Hydroxide, Silica, and Ferric Oxide Mixtures.

Expt.	Mole ratio Na/Al/Si/Fe	Fraction dissolved				Insoluble solid phases formed (PDF ^a number)
		Na	Al	Si	Fe	
1A	12/4/0/0	1.0	0.9	--	--	Gibbsite (7-324) Bayerite (15-136)
2A	12/0/4/0	1.0	--	0.7	--	Opal (38-448)
3A	12/0/0/4	0.8	--	--	0.0003	Unknown X
4A	12/2/2/0	0.9	0.15	0.17	--	Zeolite A (38-323)
5A	12/2/0/2	0.9	1.0	--	0.0006	Unknown X
6A	12/0/2/2	0.8	--	0.7	0.03	Unknown X
7A	12/2/1/1	0.9	0.7	0.12	0.004	Zeolite A (38-323)
8A	12/1/2/1	0.9	0.22	0.21	0.01	Zeolite A (38-323)
9A	12/1/1/2	0.8	0.36	0.17	0.007	Unknown X Zeolite A (38-323)

^aPDF = Powder diffraction file.

Several new insoluble phases formed. Whenever both aluminum hydroxide and silica were present, a sodium aluminosilicate (zeolite A) formed. Whenever ferric oxide was present, an unidentified crystalline phase (called unknown X in Table 6-1) formed. Based on the sodium solution analyses, the unidentified crystalline phase contained sodium. The unidentified phase did not have the diffraction pattern of sodium ferric oxide (NaFeO_2). Significantly, ferric oxide was not identified in the diffraction pattern indicating metathesis of the original ferric oxide occurred. A duplicate experiment 3A, however, did produce sodium ferric oxide (PDF number 30-1196) in addition to the unidentified phase but again, no ferric oxide.

As shown in Table 6-1, little iron was dissolved by these C/D conditions. However, the solutions from all experiments having ferric oxide were an intense blue-violet color indicating hexavalent iron [Fe(VI) as the FeO_4^{2-} ion]. According to D'Ans and Löffler (1930), the presence of hexavalent iron showed that even without oxidizers in the melt, highly oxidizing conditions (apparently from atmospheric oxygen) are still attainable in molten sodium hydroxide.

6.2.2 $\text{Al}(\text{OH})_3\text{-Na}_3\text{PO}_4\text{-Na}_2\text{CO}_3$ in NaOH

Calcinations for this set of experiments were conducted at 850 °C for 10 minutes. The test composition matrices are given in Table 5-1. Two sequential water dissolutions were conducted: the first sufficient to produce about 6.7M NaOH and the second sufficient to produce a net (combined) concentration of 4.4M NaOH.

After the second water contact, experiments 4B, 5B, 6B, and 8B still had solid residue present. The residue from experiment 4B was identified as $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (sodium phosphate dodecahydrate), experiment 5B had Na_2CO_3 (PDF number 37-451), and experiment 6B had a high temperature form of Na_3PO_4 (PDF number 31-1323). The residue from experiment 8B was Na_2CO_3 and $\text{Na}_3\text{P}_3\text{O}_{10}$ (PDF numbers 19-1130 and 11-652, respectively). All these residues are readily soluble with additional water digestion. The limited solubilities of sodium carbonate and sodium phosphate in the presence of sodium hydroxide (caused by the common ion effect of sodium as discussed in the introductory sections of this report) are not altered by calcination.

The experimental results show that water-insoluble phases do not form in the calcination of sodium hydroxide, carbonate, phosphate, and aluminum hydroxide mixtures. These four components comprise about 95 mole% of the calcined Hanford Site waste inventory. The results also demonstrated that water-insoluble aluminum hydroxide could be dissolved by sodium hydroxide fusion followed by water dissolution in the presence of trisodium phosphate and carbonate. In contrast to the 750 °C experiment (test 1A), no $\text{Al}(\text{OH})_3$ insoluble residue remained in test 1B (conducted at 850 °C). Gibbsite, $\gamma\text{-Al}(\text{OH})_3$, (which is present in genuine Hanford Site waste) was the aluminum hydroxide phase used in these experiments.

Aluminum phosphate has been postulated as a phase forming from calcination of waste materials containing aluminum and phosphate. Aluminum phosphate, high-melting, and sparingly soluble in water is, however, soluble in acid or alkali. Though aluminum phosphate may have formed during calcination in the present experiments, total dissolution of the calcine nevertheless occurred, probably because of aluminum ion hydrolysis by the excess sodium hydroxide.

Aluminum phosphate would, however, be expected to be insoluble if the calcine were pH neutral. Calcination/dissolution processing of certain Hanford Site waste types could potentially produce such calcines. For example, Bismuth Phosphate Process wastes, which are closer to pH neutrality and contain significant aluminum and phosphate concentrations, may present this problem if the waste contained insufficient hydroxide-forming nitrate and nitrite. Similarly, aluminum phosphate might also be obtained if waste were first water washed before calcination because washing would remove not only hydroxide, but also soluble nitrate and nitrite salts necessary to produce the sodium hydroxide flux during calcination.

6.2.3 $\text{Al}(\text{OH})_3\text{-SiO}_2\text{-Na}_3\text{PO}_4\text{-Ca}(\text{OH})_2$ in NaOH

Duplicate experiments were run using equimolar amounts of aluminum hydroxide, silica, trisodium phosphate, and calcium hydroxide (0.0625 mole fraction each) in sodium hydroxide. The mixtures were preheated in an oven overnight at 120 °C to remove hydrate water from the trisodium phosphate and calcium hydroxide. Fusions were conducted at 850 °C for 20 minutes. The calcined products were contacted with water and the water-insoluble residues washed, dried, and weighed before XRD analysis.

XRD analyses showed that a hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$, PDF number 34-10] and a sodalite mineral (a sodium aluminosilicate, PDF number 31-1272) formed. The results indicate that calcium reacts preferentially with phosphate (over possible reaction with silica and aluminate) to make an insoluble residue phase (hydroxyapatite) that will report to the HLW fraction and thus increase the final vitrified HLW volume. Hydrothermal experiments of Barrer and Marshall (1965) confirm the stability of hydroxyapatite in reactions of the system $\text{NaOH-Ca}(\text{OH})_2\text{-Na}_3\text{PO}_4\text{-Al}(\text{OH})_3\text{-SiO}_2$.

6.2.4 $\text{Al}(\text{OH})_3\text{-Na}_2\text{CO}_3\text{-Na}_3\text{PO}_4\text{-Ca}(\text{OH})_2$ in NaOH

Duplicate experiments were conducted using equimolar quantities of aluminum hydroxide, sodium carbonate, trisodium phosphate, and calcium hydroxide (0.0625 moles fraction each) and 0.75 mole fraction sodium hydroxide. The mixtures were dried overnight in a 120 °C oven; fusions at 850 °C for 20 minutes followed. The calcined materials were partially dissolved in water and the residual water-insoluble materials washed and dried for XRD analyses.

The XRD analyses identified only calcium phosphate carbonate hydroxide [$\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2$, PDF number 19-272, a carbonate-substituted apatite structure] in the insoluble residue. Though carbonate appears in the residue, phosphate is still precipitated by calcium in this salt. The calcium:phosphate mole ratio, however, doubles from 1.67 to 3.33 in forming the carbonate-apatite instead of the hydroxyapatite formed in the absence of carbonate. This means that carbonate partially displaces phosphate from the insoluble residue phase.

By precipitating with calcium and forming the carbonate-apatite, carbonate decreases the quantity of calcium available to precipitate phosphate. Results from these experiments, therefore, suggest that carbonate may be an effective reagent to help "win" calcium away from phosphate. The carbonate may serve to solubilize phosphate in the presence of alkaline earth elements (e.g., calcium, magnesium, strontium) and thus deliver phosphate to the water-soluble LLW fraction.

6.2.5 $\text{Al}(\text{OH})_3$ in NaOH- NaNO_3

A series of six experiments were conducted to determine the behavior of nitrate in calcination with aluminum hydroxide and sodium hydroxide. For all experiments, 50 mole% aluminum hydroxide was present. Over the six experiments, the remaining 50 mole% ranged from pure sodium hydroxide to pure

sodium nitrate. Overnight drying of the experimental mixtures was performed at 120 °C to drive off water. The mixtures were then calcined at 850 °C for 20 minutes and dissolved to yield 1M total sodium solutions. The solutions were analyzed for sodium, aluminum, nitrate, nitrite, and hydroxide concentrations.

Experimental results summarized in Figure 6-2 show the fraction of sodium remaining after C/D processing, the fraction of aluminum dissolved, the fraction of nitrate remaining, and the fraction of initial nitrate converted to nitrite as functions of initial sodium nitrate to sodium hydroxide ($\text{NaNO}_3/\text{NaOH}$) ratio. The amount of sodium remaining is about 0.88 and is relatively constant with varying $\text{NaNO}_3:\text{NaOH}$ ratio. The sodium loss was likely because of volatilization of sodium hydroxide (boiling point 1390 °C).

Figure 6-2. Calcination of Mixtures of Sodium Nitrate, Sodium Hydroxide, and Aluminum Hydroxide.

The aluminum reporting to the solution phase is also independent of the $\text{NaNO}_3:\text{NaOH}$ ratio. The invariant amount of aluminum dissolved by C/D processing irrespective of $\text{NaNO}_3/\text{NaOH}$ ratio demonstrates that sodium nitrate effectively behaved like sodium hydroxide in dissolving aluminum hydroxide (to make sodium aluminate). The fraction of aluminum dissolved was about 0.27 of the initial aluminum introduced as aluminum hydroxide.

The fraction of the original sodium nitrate remaining, following calcination, decreased with increasing sodium nitrate fraction in the initial mixture. This may have happened because aluminum hydroxide reacted more rapidly with sodium nitrate than it did with sodium hydroxide.

As will be shown in kinetics tests with Hanford Site waste simulants, sodium nitrite is an intermediate in the thermal decomposition of sodium nitrate to form sodium hydroxide. The amount of sodium nitrite found in the calcine ranged from about 0.05 to 0.2 of the initial sodium nitrate molar quantity. No particular trend in sodium nitrite fraction could be discerned from the data.

6.3 CALCINATION KINETICS TESTS

Conversion of organic carbon to inorganic carbon and conversion of nitrate and nitrite to hydroxide are essential aspects of the C/D process. The kinetics of these decomposition reactions determine the time required for the waste melt to be held at the calcination temperature. Calcination kinetics tests were conducted by heating Hanford Site waste simulants at 850 °C for time periods varying from 0 (i.e., simple water dissolution) to 42 minutes. Two waste simulants were used in the kinetics tests: the simulated 101-SY waste and the composite Hanford Site waste simulant. To minimize the thermal inertia caused by the water contained in the simulant waste, overnight preheating and drying at about 120 °C was conducted for each experiment.

Calcination accomplishes several chemical transformations. Calcination can destroy organic species and convert the organic carbon to inorganic carbon (carbonate; CO_3^{2-}). Calcination can also convert nitrate and nitrite salts to the corresponding hydroxide salts. Finally, calcination can oxidize and metathesize inorganic species, thus affecting water solubilities. Observations of these chemical transformations were made to understand the kinetics of the C/D process. Data of the calcination kinetic tests are summarized in Appendix D.

6.3.1 Calcination Kinetics of the 101-SY Simulant

The C/D processing of simulated 101-SY waste was studied as a function of calcination time (0 to 30 minutes) at 850 °C. Dissolutions were conducted to produce final solutions about 3 to 6M in sodium ion concentration.

Figure 6-3 illustrates the rapid destruction of TOC and subsequent quantitative conversion to total inorganic carbon (TIC) observed in these tests. In one to three minutes' calcination time, TOC destruction was essentially complete.

The behaviors of nitrate (NO_3^-), nitrite (NO_2^-), and hydroxide (OH^-) during calcination are shown in Figure 6-4. A rapid initial decrease in hydroxide concentration was found because of the absorption, by the alkaline melt, of CO_2 evolved from oxidation of the TOC to form CO_3^{2-} :

Nitrate concentration decreased with time to about 95% destruction at 20 minutes' calcination; continued heating resulted in little further conversion of nitrate. Nitrite concentration appeared to increase slightly before decreasing below detection level after about 20 minutes at 850 °C.

Figure 6-3. TOC Conversion to TIC by Calcination of Simulated 101-SY Waste.

The behaviors of aluminum, chromium, and iron in the C/D of simulated 101-SY are presented in Figure 6-5. The rapid initial consumption of hydroxide by carbon dioxide absorption was reflected in the decreased solubility of aluminum, according to the following equilibrium:

Subsequently, after 5 to 10 minutes when nitrate and nitrite decomposition produced more hydroxide, the aluminum redissolved.

Chromium, initially present as the slightly-soluble chromium (III) hydroxide $[\text{Cr(OH)}_3]$, was entirely converted to the soluble chromate (CrO_4^{2-}) after a one minute calcination:

Iron solubility also increased with calcination time, but no visual evidence was found for oxidative dissolution to give the intensely blue-colored ferrate ion (FeO_4^{2-}).

6.3.2 Calcination Kinetics of the Hanford Site Waste Composite Simulant

The Hanford Site waste composite simulant was prepared using acetate (CH_3CO_2^-) as the surrogate organic species. Calcination times ranged from

Figure 6-4. Behavior of Nitrate, Nitrite, and Hydroxide in C/D of Simulated 101-SY Waste.

0 to 42 minutes. The aqueous dissolution step resulted in solutions of about 4 to 6M sodium concentration.

As was the case for C/D of the 101-SY simulant, rapid quantitative conversion of TOC to TIC was observed in the C/D of the Hanford Site waste composite simulant (Figure 6-6). Organic oxidation was essentially complete after about 3 minutes' calcination.

The kinetic behaviors of nitrate, nitrite, and hydroxide during C/D observed in simulated 101-SY waste were repeated in the Hanford Site waste composite simulant. The initial increase in nitrite concentration caused by nitrate decomposition is more evident in the case of the Hanford Site waste composite formulation:

The thermal decomposition of nitrate to form nitrite has been observed in experiments with nitrate melts (Kerridge 1972). As was the case for the 101-SY simulant, nitrite decomposition was about 99.9% complete after about 20 minutes. Similarly, nitrate decomposition reached about 95% at 20 minutes' calcination, but did not exceed about 98% after 30 to 40 minutes' heating.

Hydroxide concentration decreased during the initial 5 to 7 minutes of calcination probably because of neutralization of evolved carbon dioxide to form carbonate. Hydroxide concentration then increased above the feed concentration as nitrate and nitrite decomposition continued. The behaviors

Figure 6-5. Behaviors of Aluminum (Al), Chromium (Cr), and Iron (Fe) in the C/D of Simulated 101-SY Waste.

of nitrate, nitrite and hydroxide during calcination given in Figure 6-7 indicate little was gained by calcination in excess of about 20 minutes.

The solubility behaviors of elements in the Hanford Site waste composite simulant as a function of calcination time, are presented in Figures 6-8, 6-9, and 6-10. The solubility behaviors of aluminum, chromium, and iron (Figure 6-8) may be compared to those observed for the 101-SY waste simulant. Chromium was converted to soluble chromate after one minute's calcination. In contrast, aluminum, present initially as the aluminate ion in the waste simulant, was not affected in solubility by calcination. Though iron solubility did not exceed a few percent of its total concentration, the intense blue solution coloration because of formation of Fe(VI) was noted.

The behaviors of silicon and lead are similar: both increase in solubility with calcination time and are completely soluble by about 10 minutes' calcination. Bismuth is like iron and only reaches a few percent dissolution.

The behaviors of the elements manganese, zirconium, phosphorus, sulfur, potassium, and strontium are examined in Figure 6-9. Sulfur and potassium were completely soluble, while zirconium solubility was only a few percent. Strontium and manganese had solubilities of less than 1%.

Figure 6-6. Conversion of TOC to TIC in the C/D of Hanford Site Waste Composite Simulant.

Phosphorus solubility varied erratically from about 20 to 100% as calcination time varied. The erratic behavior of phosphorus (shown by separate ion chromatographic analyses to be present in solution as phosphate) may have been related to the limited solubility of (Na_3PO_4) in solutions containing significant sodium concentrations.

The solubilities of calcium, fluorine, and chlorine are presented in Figure 6-10. Chlorine (present as chloride) was completely soluble at all calcination times. Fluorine (present as fluoride) was 50 to 80% dissolved. The solubility behavior of phosphate and fluoride were similar and may be related to the formation of a sodium fluoride/phosphate mixed salt as discussed in Section 6.4.2.5. Calcium behaved like its chemical analog strontium and was soluble to less than 1%.

The chemical behaviors of the various elements and species are summarized in Table 6-2 for 20-minute calcination time. These observations, where appropriate, are common to both the simulated 101-SY waste and the Hanford Site waste composite simulant. Judging by analyses of the dissolved calcine, most reactions were at or near completion after 20 minutes' calcination. Therefore, 20 minutes was selected as the calcination time to be used in subsequent C/D tests with genuine waste materials.

Figure 6-7. Behaviors of Nitrate, Nitrite, and Hydroxide During C/D of Hanford Site Waste Composite Simulant.

Table 6-2. Calcination/Dissolution Behavior of Chemical Components in Hanford Site Waste Composite Simulant.

Component	Amount destroyed
TOC	95%
NO_3^-	90%
NO_2^-	99.9%
Component	Amount dissolved
Al, Cl, Cr, K, Na, Pb, S, Si	~100%
F, P	10 to 100%
Bi, Fe, Zr	1 to 10%
Ca, Mn, Sr	Less than 1%

Figure 6-8. Behaviors of Aluminum (Al), Iron (Fe), Chromium (Cr), Bismuth (Bi), Lead (Pb), and Silicon (Si) During C/D of Hanford Site Waste Composite Simulant.

6.4 CALCINATION/DISSOLUTION OF GENUINE HANFORD SITE WASTES

The C/D of genuine Hanford Site waste and blends of Hanford Site wastes were conducted and the chemical and radionuclide distributions compared with the distributions found for simple water dissolution. Materials from three Hanford Site waste tanks were investigated: 101-SY, 107-BX, and 104-S. Waste blends were prepared using 107-BX/101-SY and 104-S/101-SY materials.

These material combinations were selected for blending because the 107-BX and 104-S materials are relatively poor in sodium salts (hydroxide, nitrate, and nitrite) required to make fluxing agent (sodium hydroxide) for the calcination reactions (see Table 5-2 for waste compositions). The 101-SY, relatively rich in sodium hydroxide, nitrate, and nitrite was blended with the 107-BX and 104-S waste to provide additional fluxing sodium hydroxide.

Three sets of tests were performed corresponding to the three waste types. The test matrix is presented in Table 6-3. The test matrix shows the types of experiments performed: simple water dissolution of waste, C/D of the waste, and C/D of the waste/101-SY blend. The behaviors of the three waste types in simple water dissolution and C/D are described in the following sections. Data of the C/D tests conducted with genuine waste are given in Appendix E.

Figure 6-9. Behaviors of Manganese (Mn), Zirconium (Zr), Phosphorus (P), Sulfur (S), Potassium (K), and Strontium (Sr) During C/D of Hanford Site Waste Composite Simulant.

Table 6-3. Experiments Performed Using Genuine Hanford Site Waste.

Waste material	Number of experiments		
	Simple water dissolution	C/D of waste	C/D of waste blend (wt. waste/wt. 101-SY)
101-SY	1	2	--
107-BX	1	2	1 (4.12 g/2.93 g)
104-S	1	2	2 (3.11 g/3.71 g) (5.36 g/6.91 g)

Figure 6-10. Behaviors of Calcium (Ca), Fluorine (F), and Chlorine (Cl) During C/D of Hanford Site Waste Composite Simulant.

6.4.1 Behavior of Genuine 101-SY Waste

The behavior of genuine 101-SY waste to C/D processing was monitored by the changes in concentrations of chemical components destroyed (nitrate, nitrite, TOC), formed (TIC), or formed and consumed (hydroxide) as compared to the simple water dissolution. These chemical transformations had been shown to occur in the kinetics tests performed using simulated waste. The weight percents of insoluble residue remaining after simple water dissolution and C/D processing were also compared. In the same way, the distributions of elements and radionuclides to residue and solution in simple water dissolution and C/D were determined.

6.4.1.1 Carbon. The transformation of TOC to TIC by C/D processing of genuine 101-SY waste is shown in Figure 6-11. The material balance of total carbon shows TOC reported entirely to the melt as carbonate and was not lost to offgases in the calcination step.

6.4.1.2 Nitrite, Nitrate, and Hydroxide. The concentrations of nitrite, nitrate, and hydroxide in the water dissolution and C/D of genuine 101-SY waste are compared in Figure 6-12. The concentrations expressed are with respect to the initial weight of the 101-SY waste used. Decompositions of nitrite and nitrate were only 40 to 50% during C/D, however, suggesting calcination time or temperature were insufficient.

Figure 6-11. TOC Conversion to TIC by Calcination of Genuine 101-SY Waste.

In these first C/D tests conducted with genuine waste, radiological protection measures led to the furnace door being open for longer times with a significant drop (to about 750 °C) in the furnace temperature. Changes in technique in later tests overcame this difficulty, allowed more rapid introduction of the waste to the furnace, and resulted in more thorough calcination.

6.4.1.3 Metals. The disposition of the metals (including phosphorus and sulfur) to the solution and insoluble residue phases in the simple water dissolution and C/D of genuine 101-SY waste are presented in Figure 6-13. The data in Figure 6-13 are given with respect to the initial weight of the 101-SY waste.

Comparing of the water dissolution and C/D plots in Figure 6-13 identifies the effects calcination had on changing the solubilities of certain elements. The greatest effect is manifest for chromium. Simple water dissolution succeeded in dissolving about 5% of the chromium; after C/D, more than 99.9% of the chromium dissolved. Uranium distribution to the solution phase increased from 0.2% to about 90% by calcination. Slight improvement in sodium, aluminum, silicon, phosphorus, and sulfur solubilities also occurred because of calcination.

Iron solubility did not change. However, some iron dissolution was observed by a blue-green supernatant solution color immediately upon dissolution of the calcine. After about 12 hours the supernatant solution

Figure 6-12. Behavior of Nitrite, Nitrate, and Hydroxide in the C/D of Genuine 101-SY Waste.

color had become yellow and a fine layer of orange-colored precipitate had formed. These observations give evidence for the production of the deep blue FeO_4^{2-} from oxidation of iron in the waste material. With time, the ferrate chemically reduced to form sparingly soluble and orange-colored ferric hydroxide $[\text{Fe}(\text{OH})_3]$ precipitate.

Strontium solubility decreased from 30 to 10% and calcium solubility decreased from about 60 to 20% by the calcination step. The decrease in strontium and calcium solubility is probably because of loss of the organic complexing agents.

6.4.1.4 Radionuclides. The distributions of the radionuclides ^{90}Sr , ^{99}Tc , ^{137}Cs , ^{237}Np , $^{239,240}\text{Pu}$, and ^{241}Am to the solution and insoluble residue phases are presented in Figure 6-14. Data in Figure 6-14 are given in activities (μCi or nCi) with respect to the initial weights of the 101-SY waste. The "less than" (<) symbols appearing above certain of the bar values for ^{237}Np and $^{239,240}\text{Pu}$ show the concentrations were below the analytical threshold at that indicated level. For this reason, conclusions regarding the behaviors of neptunium and plutonium cannot be made.

Data in Figure 6-14 show some enhancement of ^{99}Tc solubility (from about 60 to >99%) occurred because of calcination. Cesium-137 solubility (90 to 99%) was improved slightly by calcination. The decrease in ^{90}Sr solubility (30 to 10% after calcination) was identical to the chemical strontium solubility behavior noted in the previous section. Americium-241 solubility decreased from about 90% to about 3% by calcination. The decreases in

Figure 6-13. Distribution of Metal Elements, Phosphorus, and Sulfur to the Residue and Solution Phases for Water Dissolution and C/D Processing of Genuine 101-SY Waste.

solubility behavior noted in the previous section. Americium-241 solubility decreased from about 90% to about 3% by calcination. The decreases in strontium and americium solubility were probably because of the loss of solubilizing organic complexing agents via calcination.

Figure 6-14. Distribution of Radionuclides to the Residue and Solution Phases by Water Dissolution and C/D Processing of Genuine 101-SY Waste.

6.4.1.5 Residue Quantities and Compositions. The amount of residue (in wt% with respect to initial weight of waste) remaining after water dissolution and C/D of genuine 101-SY waste were 6 and 0.02%, respectively.

The quantities, compositions, and solid phases of the insoluble residues remaining after water dissolution and C/D processing of genuine 101-SY are presented in Table 6-4.

Table 6-4. Compositions of Residues from Treatment of Genuine 101-SY Waste.

Component	Concentration (wt%)	
	Water dissolution	C/D
Al	3.9	5
Ca	0.087	14
Cr	6.2	0.2
Fe	0.46	24
Na	24	4
P	0.26	4
S	0.12	0.06
Si	0.25	5
U	0.42	0.8
Radionuclide	Concentration ($\mu\text{Ci/g}$)	
^{90}Sr	290	90000
^{99}Tc	0.49	0.1
^{137}Cs	310	3500
^{237}Np	<0.03	0.02
$^{239,240}\text{Pu}$	0.00020	<12
^{241}Am	0.0018	360
Solid phases		
Phase (PDF number)	$\text{Na}_2\text{C}_2\text{O}_4$ (20-1149) sodium oxalate, NaNO_3 (6-392) sodium nitrate, NaNO_2 (7-271), sodium nitrite	insufficient sample
Wt% residue		
	6.2	0.022

The XRD analyses of the solid residue remaining from water dissolution of 101-SY waste found sodium oxalate, nitrate and nitrite present. The nitrate and nitrite salts indicate the dissolution of water-soluble components was not complete. Sodium oxalate, however, has relatively low solubility.

The solids are also about 15 times enriched in chromium and iron compared with the composition of the intact 101-SY material. Aside from the excess water-soluble sodium salt and the undetermined amount of sodium oxalate, the principal component of the water-dissolution residue was chromium.

Because of insufficient amount of sample, no XRD analyses were possible on the residue from C/D processing of 101-SY. Chemical analyses showed the residue to be primarily iron (24 wt%) and calcium (14 wt%). Also found were sodium, aluminum, and silicon in approximately a 1:1:1 mole ratio suggesting the presence of a sodium aluminosilicate. Finally, about 4 wt% phosphorus, corresponding to 12 wt% phosphate, was found in the residue. The most striking differences in comparing the residues of the water dissolution and C/D processing are the 300-fold residue weight reduction and the virtually complete elimination of chromium from the residue by way of C/D treatment.

6.4.2 Behavior of Genuine 107-BX Waste

The behavior of genuine 107-BX waste to C/D processing was compared with the behavior following simple water dissolution of the 107-BX waste and the behavior following C/D of 107-BX and 101-SY waste blends. Again, behaviors were compared based on the changes in chemical concentrations of TOC, TIC, nitrate, nitrite, and hydroxide, as well as the distributions of the metals identified through ICP analyses and the distributions of the radionuclides. Finally, residue weights and X-ray identification of phases present in the residues were compared.

6.4.2.1 Carbon. Because the 107-BX waste contains TOC and TIC near the analytical detection limits, the redistributions of the carbon in the water dissolution and C/D processing experiments were difficult to discern. However, introduction of significant TOC and TIC occurred by blending the 107-BX waste with 101-SY waste. The blend was subjected to C/D processing. The C/D of the 107-BX/101-SY blend showed the expected high conversion of TOC to TIC. The distributions of organic and inorganic carbon in the 107-BX waste experiments are given in Figure 6-15.

6.4.2.2 Nitrate, Nitrite, and Hydroxide. The concentrations of nitrite, nitrate, and hydroxide in the water dissolution and C/D of genuine 107-BX and the C/D of 107-BX/101-SY blend are compared in Figure 6-16. Data in Figure 6-16 are given in wt% with respect to the initial weight of waste (107-BX or 107-BX/101-SY blend) used. The decomposition of nitrite and nitrate was at least 99.5% complete in the C/D of the 107-BX waste; for the blend, about 90% destruction was achieved for both nitrate and nitrite.

In spite of the large quantity of nitrite and nitrate decomposed, only a small increase in hydroxide concentration was observed. The initial hydroxide concentration of the 107-BX waste was negligible (pH = 9.7). The hydroxide produced by nitrate and nitrite decomposition evidently was consumed by metathesis and hydrolysis of metal ions, such as aluminum and bismuth, as shown in the analysis of the metals' distribution.

6.4.2.3 Metals. The disposition of the metals, including phosphorus and sulfur, to the solution and insoluble residue phases for the experiments with genuine 107-BX waste, are presented in Figure 6-17. Data in Figure 6-17 are

Figure 6-15. Distribution of TOC and TIC in Experiments With 107-BX Waste and 107-BX/101-SY Waste Blend.

given in weight fraction with respect to the initial weight of waste (107-BX or 107-BX/101-SY blend) used.

The distributions of 12 elements are presented in Figure 6-17 (sodium, aluminum, silicon, iron, chromium, manganese, bismuth, zirconium, phosphorus, sulfur, strontium, and uranium). Of these twelve, only two, sodium and sulfur, were primarily in the solution phase following simple water dissolution.

Following C/D processing of the 107-BX waste, chromium (90% dissolved) and phosphorus (80% dissolved) joined sodium and sulfur as being primarily in the solution phase. As shown by solution analyses, chromium again dissolved by oxidation to the soluble chromate ion. Phosphorus probably dissolved by hydroxide metathesis of insoluble metal phosphates (e.g., bismuth). Silicon was more soluble with C/D processing (about 20%) than with simple water dissolution (about 1%). Aluminum solubility also increased from about 0.1% to about 20% following C/D. However, insufficient excess hydroxide was generated by calcination of the nitrate present in the 107-BX waste to convert all aluminum to aluminate ion $[Al(OH)_4^-]$.

Blending 101-SY waste with 107-BX waste supplied the sodium nitrate, nitrite, and hydroxide whose calcination would yield the hydroxide required to dissolve more aluminum. About 80% aluminum dissolution was achieved in the

Figure 6-16. Behavior of Nitrite, Nitrate, and Hydroxide in the C/D of Genuine 107-BX Waste.

107-BX/101-SY blend as opposed to 20% dissolution in the C/D of unblended 107-BX.

Chromium dissolution also increased to 95% from about 90% and manganese solubility increased to 60 from 2% because of blending. As shown by solution analysis for hexavalent chromium, chromium increased solubility by oxidative dissolution; it is likely that manganese solubility increased by the same mechanism to form the manganate ion. Iron solubility was about 0.1% and was not appreciably affected by calcination or blending. Though visual evidence for ferrate ion was found in the blue coloration of the product solution from C/D of the blend, conversion of iron (III) hydroxide precipitate to the soluble ferrate ion apparently was not extensive.

Phosphorus (present as phosphate) solubility apparently decreased because of blending. As will be described in Section 6.4.2.5, phosphate was found in the residue as a moderately soluble sodium fluorophosphate salt that would have been easily dissolved with further washing.

In summary, iron, bismuth, zirconium, strontium, and uranium reported predominantly to the residue for all experiments with 107-BX waste. Calcination, and blending (with 101-SY waste) followed by calcination, increased the solubilities of aluminum, silicon, chromium and manganese. Calcination increased phosphorus solubility, apparently by metathesis of

insoluble phosphates, but the excess sodium supplied by blending with 101-SY resulted in the precipitation of a moderately soluble salt.

6.4.2.4 Radionuclides. The distribution of the strontium, technetium, cesium, neptunium, plutonium, and americium radionuclides to the soluble and residue phases are presented in Figure 6-18. Data are given in activities with respect to the initial weights of the 107-BX waste or 107-BX/101-SY waste blend used in the experiments. The "less than" (<) symbol above most of the neptunium bar values show that analytical limits were reached for these analyses and indicate conclusions cannot be made for the distribution of neptunium.

Consistent with the behavior observed for chemical strontium, ^{90}Sr favored the residue phase (90 to 99.9%) in all experiments. The data for ^{99}Tc show the expected distribution of technetium to the solution phase for the water dissolution and C/D blend experiments. However, ^{99}Tc unexpectedly is found primarily (80%) in the residue for the C/D of the unblended 107-BX waste. This result is suspect, however, because residue amount is two to three times higher than the amount of technetium thought to be present in the original 107-BX waste.

About 85% of ^{137}Cs reported to the residue phase in the water dissolution experiment. This result suggests the possible presence of a cesium precipitating agent (e.g., a ferrocyanide) in the 107-BX waste. Following C/D processing of the 107-BX waste, about 90% of ^{137}Cs was found in the solution. For the experiment with the blended waste, cesium distribution was about 70% to the solution phase. The cesium may have been partially carried to the residue by the phosphate salt.

The distribution behavior of ^{241}Am was primarily to the residue phases in all experiments. The americium behavior is analogous with that of bismuth, another trivalent metal, and could model the behavior of the lanthanides. No evidence of enhanced solubility of americium, as would be caused by formation of oxidized americium (V) or (VI) species, was found.

However, some increase in $^{239,240}\text{Pu}$ solubility was found by C/D of the 107-BX/101-SY blend. Plutonium solubility increased from about 1% for the water wash and C/D experiments with 107-BX waste to about 15% for the C/D of the waste blend. The enhanced solubility of plutonium may be explained by the oxidative dissolution of the insoluble plutonium species (e.g., $\text{PuO}_2 \cdot x\text{H}_2\text{O}$) to form an anionic Pu(V) or Pu(VI) species. The behavior of plutonium may be compared with the behavior of manganese in the same experiments.

6.4.2.5 Residue Quantities and Compositions. The amount of residue remaining after water dissolution of 107-BX waste was 28 wt% (compared to the original waste weight). The amount remaining after C/D processing of the 107-BX waste was about 18 wt% while the amount of residue from C/D processing of the 107-BX/101-SY blend was about 12 wt%. The quantities, compositions, and solid phases (identified by XRD) in the insoluble residues are presented in Table 6-5.

Figure 6-17. Distribution of Metal Elements, Phosphorus, and Sulfur, to the Residue and Solution Phases in Experiments With Genuine 107-BX Waste and 107-BX/101-SY Waste Blend.

Figure 6-18. Distribution of the Radionuclides to the Residue and Solution Phases by Water Dissolution and C/D of Genuine 107-BX Waste and by C/D of a 107-BX/101-SY Waste Blend.

Simple Water Dissolution of 107-BX

C/D of 107-BX

C/D of Blend 107-BX/101-SY

Table 6-5. Compositions of Residues From Treatment of Genuine 107-BX Waste.

Component	Concentration (wt%)		
	Water dissolution	C/D	C/D blend
Al	7.4	8.6	4.2
Bi	2.8	9.5	17
Ca	0.16	0.31	0.22
Cr	0.15	0.057	0.068
Fe	2.7	6.5	7.8
Mn	0.029	0.092	0.014
Na	15	15	19
P	8.1	2.2	5.0
Pb	0.011	0.035	0.076
S	0.22	0.070	0.078
Si	1.4	1.8	2.1
Sr	0.038	0.070	0.098
U	0.81	1.1	1.2
Zr	0.024	0.066	0.096
Radionuclide	Concentration ($\mu\text{Ci/g}$)		
⁹⁰ Sr	25	42	150
⁹⁹ Tc	0.018	0.64	0.057
¹³⁷ Cs	82	9.2	38
²³⁷ Np	<0.017	<0.042	<0.010
^{239,240} Pu	0.24	0.59	0.46
²⁴¹ Am	0.032	0.080	0.57
Solid phases			
Phase (PDF number)	Fe ₂ O ₃ (33-664) hematite UO ₂ uraninite	Fe ₂ O ₃ (33-664) hematite UO ₂ uraninite	2(Na ₃ PO ₄)·NaF·19H ₂ O (25-1311) sodium fluoro- phosphate
Wt% residue			
	28.1	17.8	12.3

The XRD analyses of the solid residue remaining from both from water dissolution and C/D processing of the 107-BX waste found hematite (Fe₂O₃) and uraninite (UO₂). Though the residues from the C/D of the blended 107-BX/101-SY waste also contained significant iron concentrations, hematite was not found in the XRD. The absence of hematite or other crystalline iron phase in the blend residue resulted from converting hematite to an amorphous hydroxide following the C/D processing and resulting metathesis.

The presence of hematite in the 107-BX water dissolution and C/D residue probably occurred by hydrothermal recrystallization, in the 40 years since the waste has been in the tank, of initially amorphous ferric hydroxide. The uraninite could be a residue from incomplete dissolution of the uranium metal fuel and subsequent oxidation to uraninite in the waste. Alternatively, the uraninite could have originated from in-tank chemical reduction of a hexavalent uranium phase (e.g., uranium trioxide, UO_3). Both explanations for the presence of uraninite are speculative. The presence of a reduced uranium [i.e., U(IV)] phase in the nitrate-laden 107-BX waste is not expected and indicates chemically reducing, or at least nonoxidizing, conditions exist in Tank 107-BX. The diffraction pattern also may be assigned to the isomorphous thorium oxide (ThO_2).

The only phase identified in the residue from C/D of the 107-BX/101-SY blend was the sodium fluoride/sodium phosphate double salt, sodium fluorophosphate [$2(\text{Na}_3\text{PO}_4) \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$]. This is a moderately soluble salt that should dissolve with additional water. The water solubility, at 25 °C, of the double salt is reported to be about 4.9 g per 100 g of water (Mason and Ashcraft 1939).

As shown in Table 6-5, sodium was the primary component of all residues. Because most sodium salts are water soluble, this result suggests that continued washing would further reduce the bulk of the residue, particularly the sodium fluorophosphate salt found in the C/D blend residue. The partition of the elements bismuth, iron, strontium, uranium, and zirconium to the residue phase was not affected by C/D processing. Aluminum, chromium, manganese, and sulfur, in contrast, were successfully leached from the waste by both unblended and blended (with 101-SY waste) C/D processing as compared with simple water dissolution.

The residue remaining after C/D processing of the unblended and blended waste contained primarily sodium, bismuth, aluminum, iron, and phosphorus. The presence of significant aluminum in the residue and the relatively low fraction of free hydroxide in the C/D blend (about 0.2 wt%; see Figure 6-16) suggests calcination of the 107-BX waste with higher proportions of "fluxing agent" (i.e., material furnishing more sodium hydroxide during calcination such as 101-SY waste) might have succeeded in dissolving more aluminum.

6.4.3 Behavior of Genuine 104-S Waste

The response of genuine 104-S waste to C/D processing was compared with the behavior following simple water dissolution of the 104-S waste and the behavior of 104-S/101-SY blends to C/D processing. The various processing procedures were compared based on the changes in chemical concentrations of TOC, TIC, nitrate, nitrite, and hydroxide, as well as the distributions of metals and radionuclides. The residue weights and the crystalline phases found by XRD were also compared.

6.4.3.1 Carbon. Like the case for the 107-BX waste, the 104-S waste contained little TOC and TIC. Because of the low concentrations of carbon, redistribution of the TOC to the TIC fraction by C/D of the 104-S waste was not evident. However, C/D processing of the 104-S/101-SY waste blend showed

the expected conversion of TOC to TIC. The distributions of TOC and TIC in the experiments with 104-S waste are shown in Figure 6-19.

Figure 6-19. Distribution of TOC and TIC in Experiments With Genuine 104-S Waste and 104-S/101-SY Waste Blend.

6.4.3.2 Nitrate, Nitrite, and Hydroxide. The concentrations of nitrate, nitrite, and hydroxide in the water dissolution and C/D processing of 104-S waste and the C/D of the 104-S/101-SY blend are compared in Figure 6-20. The data in Figure 6-20 are given in wt% with respect to the initial weight of the waste. The decomposition of nitrate and nitrite combined was >99% in the C/D of the 104-S waste. The nitrite decomposition in the C/D of the blend was >99%; nitrate decomposition was about 80%.

6.4.3.3 Metals

The distribution of metals, phosphorus, and sulfur to the solution and solid phases for the experiments with genuine 104-S waste are presented in Figure 6-21. The data again are given with respect to the initial weights of waste used.

Figure 6-20. Behavior of Nitrite, Nitrate, and Hydroxide in the C/D of Genuine 104-S Waste.

The distributions of 11 elements (Na, Al, Si, Fe, Cr, Mn, Zr, P, S, Ca, and U) are given in Figure 6-21. In the simple water dissolution, about half of the sodium, chromium, and sulfur were found in the solution phase. The other elements were predominantly in the residue. With C/D processing, the distribution of sodium, chromium, and sulfur to the solution phase increased to about 95% each. The aluminum and silicon solubilities also increased with about half reporting to the solution phase. In fact, the solubilities of all 11 elements increased by C/D processing.

Blending the 104-S waste with about equal weight quantities of 101-SY waste was performed for two experiments (Table 6-3). Performing C/D processing on the blends resulted in markedly increased dissolutions of aluminum (to 99%) and chromium (to >99%). Increases in solubility for silicon (to about 80%) and manganese (to about 50%) were also noted. The solubilities of the other elements were not affected by the blending step. As was the case for C/D of the 101-SY and the 107-BX/101-SY blend, the supernatant solutions from C/D of the 104-S/101-SY blends were blue, indicating the presence of ferrate ion (hexavalent iron). The increased solubility of manganese [presumably by oxidation of manganese (IV) hydrated oxide to produce soluble manganate or permanganate ions] and the presence of ferrate again indicate the highly oxidizing conditions reached with C/D, especially when employed with blending.

Figure 6-21. Distribution of Metal Elements, Phosphorus, and Sulfur to the Residue and Solution Phases in Experiments With Genuine 104-S Waste and 104-S/101-SY Waste Blend.

Sodium, aluminum, silicon, chromium, phosphorus, and sulfur reported primarily to the solution phase after blending and C/D processing. The elements iron, zirconium, calcium, and uranium reported to the residue, while the manganese was about evenly distributed to the solution and residue phases.

6.4.3.4 Radionuclides. The distributions of the radionuclides of strontium, technetium, cesium, neptunium, plutonium, and americium to the solution and residue phases are presented in Figure 6-22. Again, the data are given in activities with respect to the initial weights of the 104-S waste or the 104-S/101-SY waste blend used in the experiments. "Less than" (<) symbols appear above single technetium and neptunium values showing the analytical limits were reached at the indicated level for the particular radionuclide.

Strontium remained with the residue (98 to >99.99%) in all experiments. Calcination (and blending) appeared to have increased technetium dissolution with about 98% of the technetium reporting to the solution phase following C/D of the 104-S/101-SY blend. Cesium favored the solution phase in all experiments.

In spite of incomplete data, neptunium solubility appears to be slightly increased by blending and C/D. Nevertheless, most of the neptunium (90 to 95%) reported in the residue. Similarly, from about 98 to >99.9% of the americium reported to the residue. Plutonium solubility, however, clearly increased with C/D processing and blending. In the simple water wash, about 0.2% of the plutonium dissolved. Performing C/D processing on the 104-S waste increased plutonium solubility to about 3%. With blending and C/D processing, plutonium solubility increased to about 40%.

As was the case for the experiments with 107-BX waste, the increase in plutonium solubility via blending and C/D processing might be explained by the oxidation of sparingly soluble Pu(IV) hydrated oxide to more-soluble anionic Pu(V) or Pu(VI) species. Neptunium would be expected to show behavior similar to plutonium though oxidation should occur more readily. However, the 100-fold lower activity of neptunium in the waste compared with americium and plutonium may have made this expected behavior difficult to detect. Americium solubility was not appreciably increased by blending or C/D processing. This finding shows that the possible oxidation of americium to more-soluble Am(V) or Am(VI) was not extensive.

6.4.3.5 Residue Quantities and Compositions. The quantity of air-dried residue remaining after water wash of the 104-S waste was 57% as compared to the original waste weight. The residue weight following C/D of the 104-S waste was about 13% of the original waste weight, while the residue weight remaining from C/D processing of the 104-S/101-SY blend was about 1.1%. The quantities, compositions, and crystalline solid phases in the insoluble residues are presented in Table 6-6.

The XRD analyses of the residues remaining from water washing and C/D processing of both the unblended and blended 104-S waste show only the aluminum hydroxide phases gibbsite and bayerite [γ -Al(OH)₃ and α -Al(OH)₃, respectively] to be present. Analyses, by XRD, of separate unprocessed samples showed böhmite (γ -AlOOH) also may be found in 104-S waste. Clearly,

Figure 6-22. Distribution of the Radionuclides to the Residue and Solution Phases by Water Dissolution and C/D of Genuine 104-S Waste and by C/D of 104-S/101-SY Waste Blends.

Simple Water Dissolution of 104-S

C/D of 104-S

C/D of Blend 104-S/101-SY

Table 6-6. Compositions of Residues from Treatment of Genuine 104-S Waste.

Component	Concentration (wt%)		
	Water dissolution	C/D	C/D blend
Al	17	24	4.1
Ca	0.15	0.24	1.5
Cr	0.25	0.040	0.092
Fe	0.22	1.7	7.7
Mn	0.16	1.2	2.6
Na	13	3.3	9.1
P	0.007	0.016	0.35
S	0.053	0.005	0.027
Si	0.18	0.40	0.82
Sr	0.052	0.38	0.82
U	1.5	4.1	17
Zr	0.010	0.050	0.18
Radionuclide	Concentration ($\mu\text{Ci/g}$)		
^{90}Sr	44	3300	10,800
^{99}Tc	0.027	<4	0.19
^{137}Cs	6.8	20	92
^{237}Np	0.014	0.013	0.066
$^{239,240}\text{Pu}$	0.37	1.4	5.9
^{241}Am	0.17	1.2	8.0
Solid phases			
Phase (PDF number)	$\gamma\text{-Al}(\text{OH})_3$ (29-41) gibbsite $\alpha\text{-Al}(\text{OH})_3$ (15-136) bayerite	$\alpha\text{-Al}(\text{OH})_3$ (15-136) bayerite	$\gamma\text{-Al}(\text{OH})_3$ (12-460) gibbsite $\alpha\text{-Al}(\text{OH})_3$ (15-136) bayerite
Wt% residue			
	57.1	13.2	1.1

the dominant insoluble phases in the 104-S waste are hydroxides and oxyhydroxides of aluminum. The application of C/D and C/D with blending solubilizes these aluminum phases as shown by the sharply reduced residue weights following the successive treatments.

Increasing concentrations of the elements calcium, iron, manganese, phosphorus, silicon, strontium, uranium, and zirconium appear in the residues as the processing proceeds from simple water wash to C/D to blending plus C/D. Conversely, concentrations of aluminum, chromium, sodium, and sulfur generally decrease as processing becomes more extensive. The residue remaining after blending and C/D processing is primarily iron, sodium, and uranium. The residue composition suggests that sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$) may comprise part of the solid phase. However, no XRD evidence for this compound was found.

Carbonate leaching of the 104-S C/D residue may be successful in solubilizing the uranium and thus separating the uranium from the remainder of the residue. Carbonate leaching is used to perform *in situ* and heap solution mining of alkaline and oxidized uranium (i.e., ores containing hexavalent uranium minerals). The resulting uranium bis- and triscarbonate species [$\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, respectively] are dissolved leaving the remaining ore minerals in the solid phase (Benedict et al. 1981).

Ammonium carbonate [$(\text{NH}_4)_2\text{CO}_3$] is one such salt used for carbonate leaching. Ammonium carbonate is volatile and could therefore be evaporated from the leach liquor, recycled, and not contribute to the waste volume. Investigation of carbonate leaching of uranium-bearing residues from C/D processing is planned for future tests.

7.0 SUMMARY AND CONCLUSIONS

This report reviewed the technical literature related to Hanford Site waste composition. With the Hanford Site waste composition in mind, the chemistry technical literature applicable to proposed C/D processing of the waste was surveyed. Experimental investigation of the C/D process was then conducted using simulated and genuine Hanford Site waste.

7.1 THE HANFORD SITE WASTE INVENTORY

The published chemical inventories of the SST and DST were combined to arrive at a total Hanford Site waste inventory. Five process-origin waste types were defined as prototypes for C/D study and their compositions described. A composite waste, based on the total waste inventory, was also described. Existing Hanford Site waste simulant recipes were reviewed and a new simulant recipe, based on the Hanford Site waste composite formulation, was proposed.

7.2 LITERATURE SURVEY OF CALCINATION/DISSOLUTION CHEMISTRY

The overall composition of calcined waste was projected and showed sodium hydroxide, at 82 mole%, to be the dominant component. The hypothetical phases of aluminum hydroxide, trisodium phosphate, and sodium carbonate account for another 12 mole% of inventory. With the high fraction of sodium hydroxide in the projected calcine, the well-known chemistry of analytical fusions was explored to predict calcination performance.

Analytical fusion literature showed molten sodium hydroxide to be a highly aggressive and oxidizing solvent. The oxidizing properties are enhanced by the presence of sodium nitrate and nitrite salts. The technical literature, surveyed to identify materials of construction to hold sodium hydroxide melts, found no material that could resist long-term exposure at the anticipated 850 °C calcination temperature. Flux requirements for analytical fusions suggest that proper waste blending will be necessary to achieve efficient waste component dissolution in both the molten calcine and the subsequent aqueous dissolution.

The oxidizing conditions achieved in the molten sodium hydroxide will most likely drive many transition metals (such as iron, chromium, manganese, and nickel), as well as bismuth and cerium, to their higher oxidation states. The actinides of neptunium, plutonium, and americium are expected to be oxidized to (V), or greater, oxidation states and form ternary oxides with sodium.

The dissolution of the primary chemical components of the calcined waste was surveyed. Examination of trisodium phosphate and sodium carbonate solubilities in sodium hydroxide solution showed the temperatures and solution compositions required to minimize dissolution volumes. The dissolution of sodium aluminate and aluminum hydroxide dissolution in sodium hydroxide was examined in light of processing experience in the aluminum industry and the special case of aqueous dilution during retrieval operations that may result in the precipitation of aluminum hydroxide. The formation of sodium

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aluminosilicate solids of low solubility from calcined silicon- and aluminum-bearing waste was predicted based on aluminum industry experience.

The residue remaining following dissolution was predicted to contain sodium aluminosilicates, transition and lanthanide metal oxides and hydroxides and alkaline earth sulfates, phosphates, or carbonates. Thorium is expected to remain in the solid residue, but uranium will dissolve to some extent.

Dissolution of oxidized transition metals and bismuth from the Hanford Site waste calcine will impose highly oxidizing conditions in the sodium hydroxide solution. Chromium is expected to remain as soluble chromate ion and be removed from the insoluble fraction of the Hanford Site waste. In this oxidizing aqueous medium, the transuranic actinides (neptunium, plutonium, and americium), if oxidized to the (V), or higher oxidation state, are expected to report to the solution phase.

7.3 EXPERIMENTS WITH SIMULATED AND GENUINE HANFORD SITE WASTE

Experiments with simulated Hanford Site waste confirmed the highly-oxidizing and corrosive conditions available in the molten sodium hydroxide. Materials of construction investigated for laboratory calcination (fusion) experiments showed alumina to be most resistant, of the materials tested, to attack by molten sodium hydroxide. Evidence of highly oxidizing conditions available in the NaOH melt was shown in the rapid conversion of chromium (III) hydroxide to chromate and the formation of iron (VI) species from iron (III) oxide.

Experiments with simplified waste compositions confirmed the solubility characteristics of sodium aluminate, carbonate, and phosphate. Formation of slightly soluble sodium aluminosilicates occurred in the C/D processing of materials containing silica and aluminum hydroxide. The formation of slightly soluble calcium hydroxyphosphate (apatite) was also observed in C/D processing of simulated waste containing calcium ion and phosphate. The release of phosphate from precipitation by calcium was observed if carbonate was included in simulated waste formulations having calcium ion and phosphate.

Calcination kinetics tests were conducted using waste simulating the contents of Tank 101-STY and a hypothetical composite waste based on the entire Hanford Site waste tank inventory. The tests confirmed nitrate decomposed thermally, through nitrite, and that nitrite, in turn, was rapidly decomposed to form hydroxide. About 20 minutes of calcination at 850 °C were required to effect 90% nitrate decomposition. Organic carbon and chromium (III) hydroxide oxidation occurred within 1 to 3 minutes. Calcination beyond about 20 minutes' time had little effect on other elements' behaviors.

Calcination and dissolution of simulants destroyed 90% or more of the contained TOC, nitrate, and nitrite. The TOC converted quantitatively to TIC (carbonate). Aluminum, chlorine, chromium, potassium, sodium, lead, sulfur, and silicon dissolved entirely while the alkaline earths, bismuth, and the transition metals, other than chromium, (iron, zirconium, manganese) remained in the insoluble residue.

Calcination and dissolution tests with genuine waste materials obtained from Tanks 107-BX, 104-S, and 101-STY generally confirmed the behaviors of the principal chemical components observed in tests with simulants. The C/D tests with genuine waste were conducted in parallel with simple water dissolution of the same waste materials, and the results of the two waste treatments were compared.

The tests demonstrated that redistribution of aluminum and chromium from solid phases to the solution phase (i.e., from the HLW to the LLW stream) could be effected via C/D processing. Therefore, sharp reductions in the amount of insoluble residue remaining after the C/D treatments were noted when compared with residues remaining following simple water washing. A sodium fluoride-sodium phosphate double salt was also observed in the C/D residue from 107-BX waste. This salt, however, has moderate water solubility (similar to trisodium phosphate). Manganese tended to become more soluble with C/D processing. Like the case for chromium, the distribution of manganese to the solution phase was attributed to oxidative dissolution by conversion from an insoluble oxide or hydroxide to a soluble anion (in this case, manganate or permanganate) in a higher oxidation state.

The distribution of six radioelements were measured: technetium, strontium, cesium, neptunium, plutonium, and americium. For most experiments (whether water-wash or C/D), cesium and technetium reported to the solution phase, while strontium and americium, except in the case of water-washed waste containing significant organic carbon, reported to the solid phase. Neptunium concentrations were near analytical detection limits making observation of neptunium's distribution difficult. Plutonium tended to become more soluble with C/D processing. The plutonium behavior thus followed the behavior of manganese and chromium, and it appeared that oxidative dissolution of plutonium (IV) hydrated oxide occurred.

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8.0 REFERENCES

- Austin, G. T., 1984, *Shreve's Chemical Process Industries*, 5th Edition, p. 165 and pp. 237-238, McGraw-Hill, New York, New York.
- Barney, G. S., 1976, *Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes at Hanford*, ARH-ST-133, Atlantic Richfield Hanford Company, Richland, Washington.
- Barrer, R. M. and D. J. Marshall, 1965, "Chemistry of Soil Minerals, Part I, Hydrothermal Crystallization of Some Alkaline Al_2O_3 - SiO_2 - P_2O_5 Compositions," *J. Chem. Soc.*, pp. 6616-6621.
- Benedict, M., T. H. Pigford, and H. W. Levi, 1981, *Nuclear Chemical Engineering*, 2nd Edition, McGraw-Hill, New York, New York, pp. 236-241.
- Bock, R., 1979, *A Handbook of Decomposition Methods in Analytical Chemistry*, International Textbook Company, Glasgow, Scotland.
- Boomer, K. D., S. K. Baker, A. L. Boldt, J. D. Galbraith, J. S. Garfield, C. E. Goldberg, B. A. Higley, L. J. Johnson, M. J. Kupfer, R. M. Marusich, R. J. Parazin, A. N. Praga, G. W. Reddick, J. A. Reddick, E. J. Slaathaug, L. M. Swanson, T. L. Waldo, and C. E. Worcester, 1993, *Tank Waste Technical Options Report*, Appendix D, "Tank Waste Radionuclide and Chemical Compositions," WHC-EP-0616, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Bratsch, S. G., 1989, "Standard Electrode Potentials and Temperature Coefficients in Water at 298.15K," *J. Phys. Chem. Ref. Data*, Vol. 18(1), pp. 1-21.
- Burger, L. L., J. L. Ryan, J. L. Swanson, and L. A. Bray, 1973, *Salt Waste Volume Reduction by Sodium Removal*, BNWL-B-293, Battelle Pacific Northwest Laboratories, Richland, Washington.
- Chaplygina, N. M., L. S. Itkina, and E. V. Petrova, 1974, "Solubility and Solid Phases of the $\text{Al}(\text{OH})_3$ - NaOH - H_2O and $\text{Al}(\text{OH})_3$ - KOH - H_2O Systems at 50 °C," *Russian Journal of Inorganic Chemistry*, Vol. 19(5), pp. 762-766.
- Colby, S. A., C. H. Delegard, J. D. McCormack, S. V. Dighe, and D. F. McLaughlin, 1994, *Calcination/Dissolution Engineering White Paper for Input to the Initial Pretreatment Module Oxidation Process Evaluation*, WHC-SP-1065, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Colby, S. A., 1993, *Three Candidate Treatment Technologies for Remediating Hanford Site Watch-List Tanks*, WHC-SA-1825-FP, Westinghouse Hanford Company, Richland, Washington.
- Cotton, F. A. and G. Wilkinson, 1988, *Advanced Inorganic Chemistry*, 5th Edition, John Wiley & Sons, Inc., New York, New York, pp. 430 and 708.

- Coyle, R. T., R. W. Burrows, R. M. Goggin, and T. M. Thomas, 1984, *Exploratory Corrosion Tests on Materials and Fluids for Advanced High-Temperature Molten Salt Storage*, SERI/TR-255-2199, Solar Energy Research Institute, Golden, Colorado.
- Craighead, C. M., L. A. Smith, and R. I. Jaffee, 1951, *Screening Tests on Metals and Alloys in Contact with Sodium Hydroxide at 1000 and 1500F*, BMI-706, Battelle Memorial Institute, Columbus, Ohio.
- Craighead, C. M., L. A. Smith, E. C. Phillips, and R. I. Jaffee, 1952, *Continued Studies of Corrosion by Fused Caustic*, AECD-3704, Battelle Memorial Institute, Columbus, Ohio.
- D'Ans, J. and J. Löffler, 1930, "Metalloxyde und Ätznatron," *Chemische Berichte*, Vol. 63, pp. 1446-1455.
- Davies, R. L., 1939, "Process of Making Sodium Aluminate," U.S. Patent No. 2,159,843, Official Gazette, p. 1124.
- Delegard, C. H., 1993, *Test Plan for Ozone Oxidation of 241-SY-101 Waste Materials*, WHC-SD-WM-TP-145, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Delegard, C. H., 1987, "Solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in Alkaline Hanford High-Level Waste Solution," *Radiochimica Acta*, Vol. 41(1), pp. 11-21.
- Delegard, C. H., G. S. Barney, and S. A. Gallagher, 1984, "Effects of Hanford High-Level Waste Components on the Solubility and Sorption of Cobalt, Strontium, Neptunium, Plutonium, and Americium" in *Geochemical Behavior of Disposed Radioactive Waste*, G. S. Barney, J. D. Navratil and W. W. Schulz (eds.), American Chemical Society, Washington, D.C.
- Delegard, C. H. and S. A. Gallagher, 1983, *Effects of Hanford High-Level Waste Components on the Solubility of Cobalt, Strontium, Neptunium, Plutonium, and Americium*, RHO-RE-ST-3P, Rockwell Hanford Operations, Richland, Washington.
- Doležal, J., P. Povondra and Z. Šulcek, 1968, *Decomposition Techniques in Inorganic Analysis*, New York American Elsevier Publishing Co., Inc., New York, New York. See also Šulcek, Z., P. Povondra and J. Doležal, 1977, "Decomposition Procedures in Inorganic Analysis," *CRC Critical Reviews in Analytical Chemistry*, Vol. 7, pp. 255-323.
- Elmore, M. R., N. G. Colton, and E. O. Jones, 1992, *Development of Simulated Tank Wastes for the U.S. Department of Energy's Underground Storage Tank Integrated Demonstration*, PNL-SA-20912, Pacific Northwest Laboratory, Richland, Washington.
- EPA, 1976, *An Assessment of Technology for Possible Utilization of Bayer Process Muds*, EPA Report 600/276-301, Environmental Protection Agency, Washington, D.C.

- Grantham, L. F. and P. B. Ferry, 1976, "Corrosion in Alkali Metal Carbonate-Based Melts," in *Proceedings of the International Symposium on Molten Salts*, J. P. Pemsler, J. Braunstein, K. Nobe, D. R. Morris, and N. E. Richards (eds.), The Electrochemical Society, Inc., Princeton, New Jersey.
- Herting, D. L., 1992, *Laboratory Characterization of Samples Taken in May 1991 from Hanford Waste Tank 241-SY-101*, WHC-SD-WM-DTR-024, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Herting, D. L., D. B. Bechtold, B. E. Hey, B. D. Keele, L. Jensen, and T. L. Welsh, 1992, *Laboratory Characterization of Samples Taken in December 1991 (Window E) from Hanford Waste Tank 241-SY-101*, WHC-SD-DTR-026, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Hobbs, D. T., T. B. Edwards, and S. D. Fleischman, 1993, *Solubility of Plutonium and Uranium in Alkaline Salt Solutions (U)*, WSRC-TR-93-056, Westinghouse Savannah River Company, Aiken, South Carolina.
- Hohl, T. M., 1993, *Synthetic Waste Formulations for Representing Hanford Waste*, WHC-SD-WM-TI-549, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Hou, T.-P., 1969, *Manufacture of Soda, with Special Reference to the Ammonia Process*, Hafner Publishing Company, New York, New York, pp. 292-300.
- Hudson, L. K., 1987, "Alumina Production," in *Production of Aluminium and Alumina*, A. R. Burkin (ed.), *Critical Reports on Applied Chemistry*, Vol. 20, John Wiley & Sons, Inc., Chichester, England.
- Jones, E. O., N. G. Colton, G. R. Bloom, G. S. Barney, S. A. Colby, and R. G. Cowan, 1992, *Pretreatment Process Testing of Hanford Tank Waste for the U.S. Department of Energy's Underground Storage Tank Integrated Demonstration*, PNL-SA-20941, Pacific Northwest Laboratory, Richland Washington.
- Katz, J. J., G. T. Seaborg, and L. R. Morss (eds.), 1986, *The Chemistry of the Actinide Elements*, 2nd Edition, Chapman and Hall, London, pp. 711-714.
- Keller, C., 1973, *Comprehensive Inorganic Chemistry*, Vol. 5, "Actinides, Master Index," Pergamon Press, Oxford, pp. 252-269.
- Keller, C., 1972, "Lanthanide and Actinide Mixed-Oxide Systems with Alkali and Alkaline Earth Metals," in *MTP International Review of Science, Inorganic Chemistry Series One*, Vol. 7, Lanthanides and Actinides, K. W. Bagnall (ed.), Butterworths, London.
- Keller, C., 1967, "The Solid-State Chemistry of Americium Oxides," in *Lanthanide/Actinide Chemistry*, Advances in Chemistry Series 71, P. R. Fields, and T. Moeller (eds.), American Chemical Society, Washington, D.C.

- Keller, C., L. Koch, and K. H. Walter, 1965, "Die Reaktion der Oxide der Transurane mit Alkalioxiden - I, Ternäre Oxide der Sechswertigen Transurane mit Lithium und Natrium," *Journal of Inorganic and Nuclear Chemistry*, Vol. 27, pp. 1205-1223.
- Kerridge, D. H., 1972, "Chemistry of Molten Nitrates and Nitrites," in *MTP International Review of Science, Inorganic Chemistry Series One*, Vol. 2, Main Group Elements Groups V and VI, C. C. Addison and D. B. Sowerby (eds.), Butterworths, London.
- Kirk-Othmer, 1992a, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Edition, Vol. 1, "Alkali and Chlorine Products", John Wiley & Sons, Inc., New York, New York, p. 1011.
- Kirk-Othmer, 1992b, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Edition, Vol. 2, "Aluminum Compounds," John Wiley & Sons, Inc., New York, New York, pp. 252-330.
- Kirk-Othmer, 1982, *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 17, "Peroxides and Peroxy Compounds, Inorganic," John Wiley & Sons, Inc., New York, New York, pp. 2-3.
- Kirk-Othmer, 1981, *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 6, "Chromium Compounds," pp. 92-93 and Vol. 13, "Manganese Compounds," John Wiley & Sons, Inc., New York, New York, pp. 870-871.
- Kirk-Othmer, 1978, *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 1, "Alkali and Chlorine Products," John Wiley & Sons, Inc., New York, New York, pp. 858-859.
- Kupfer, M. J., 1981, *Preparation of Nonradioactive Substitutes for Radioactive Wastes*, DOE/ET/41900-8, Rockwell Hanford Operations, Richland, Washington.
- Latimer, W. M., 1952, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd Edition, Prentice-Hall, Inc., New York, New York.
- Levason, W. and C. A. McAuliffe, 1974, "Higher Oxidation State Chemistry of Iron, Cobalt and Nickel," in *Coordination Chemistry Reviews*, Vol. 12, p. 151-184.
- Linke, W. F., 1965, *Solubilities of Inorganic and Metal-Organic Compounds*, 4th Edition, American Chemical Society, Washington, D.C.
- Mallett, M. W., and J. H. Stang, 1960, Chapter 46, "Hydrides and Hydroxides," Vol. 1, "Materials," *Reactor Handbook*, 2nd Edition, C. R. Tipton Jr. (ed.), Interscience Publishers Inc., New York, New York.
- Mason, C. W. and E. B. Ashcraft, 1939, "Trisodium Phosphate - Sodium Fluoride, Phase Studies, and Analytical Methods," in *Industrial and Engineering Chemistry*, Vol. 31, pp. 768-774.

- Misra, C., 1986, *Industrial Alumina Chemicals*, American Chemical Society, Washington D.C.
- Peretrukhin, V. F. and V. I. Spitsyn, 1982, "Electrochemical Determination of the Oxidation Potentials and the Thermodynamic Stability of the Valence States of the Transuranium Elements in Aqueous Alkaline Media," in *Bulletin of the Academy of Sciences USSR, Division of Chemical Sciences*, Vol. 4, pp. 826-831.
- Ryan, J. L., and D. Rai, 1987, "Thorium(IV) Hydrous Oxide Solubility," *Inorganic Chemistry*, Vol. 26, pp. 4140-4142.
- Schroeder, W. C., A. A. Berk, and A. Gabriel, 1937, "Solubility Equilibria of Sodium Sulfate at Temperatures from 150 to 350 °C III Effect of Sodium Hydroxide and Sodium Phosphate," in *Journal of the American Chemical Society*, Vol. 59, pp. 1783-1790.
- Swanson, J. L., 1993, *Clean Option: An Alternative Strategy for Hanford Tank Waste Remediation*, PNL-8388, Vol. 2, Pacific Northwest Laboratory, Richland, Washington.
- Vida, J., 1989, *Zum chemischen Verhalten des Technetiums bei der Behandlung des hochradioaktiven Abfalls*, KfK 4642, Kernforschungszentrum Karlsruhe, Karlsruhe, Germany.
- Wefers, K. and C. Misra, 1987, "Oxides and Hydroxides of Aluminum," Alcoa Technical Paper No. 19, revised, Aluminum Company of America, Alcoa Center, Pennsylvania.
- Wefers, K., 1967, "Zur chemischen Technologie des Bauxitaufschlusses, Teil 1: Das System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$," *Metall*, Vol. 21(5), pp. 422-431, and in supporting data tables for this article obtained through Alcoa.

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9.0 ACKNOWLEDGEMENTS

The authors acknowledge the skilled and detailed assistance of Wayne Edmonson in the design and performance of the laboratory experiments reported in this study.

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APPENDIX A

**FORMULATION AND PROCEDURE FOR COMPREHENSIVE HANFORD SITE
HIGH-LEVEL WASTE SIMULANT**

B. E. HEY TO C. H. DELEGARD

WHC-EP-0766

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**Westinghouse
Hanford Company****Internal
Memo**

From: Process Chemistry Laboratory 12110-PCL93-046
Phone: 3-2529 T6-09
Date: June 7, 1993
Subject: FORMULATION AND PROCEDURE FOR COMPREHENSIVE HANFORD HIGH-LEVEL
WASTE SIMULANT

To: C. H. Delegard T6-09

cc: D. R. Bratzel L5-31
S. A. Colby L5-31
G. E. Culley N1-21
T. M. Hohl S4-25
J. R. Jewett T6-09
R. C. Knight L6-38
J. P. Slougher T6-07
BEH File/LB

- References:
- (1) Internal Memo, C. H. Delegard and B. E. Hey to G. E. Culley, "Compositions of Tanked Hanford High-Level Waste Types" dated March 31, 1993.
 - (2) Boomer, K. D., 1993, "Tank Waste Technology Options Report," WHC-EP-0616, Rev. 0 (Draft), Westinghouse Hanford Company, Richland, Washington.
 - (3) Internal Memo, J. S. Garfield to J. N. Appel, "TWRS Systems Engineering Study Double Shell Tank Waste Inventories," Rev. 1, dated September 18, 1992.

An advantage of a calcination/dissolution (C/D) high-level waste (HLW) remediation process is that this process is suitable to a broad range of tank wastes on the Hanford site. There are, however, a few waste tanks which contain abnormally high concentrations of certain chemical species. It is difficult to say how well C/D methods would work on those tanks with radically different chemical inventories. At the same time, the number of possible waste component interactions are impossible to test individually under C/D conditions. A first approach to identifying problem interactions would be to test C/D on a comprehensive Hanford HLW composite simulant containing all major HLW components. Such a formulation was prepared for this purpose. This letter describes the formulation and procedure for making this HLW simulant.

The comprehensive Hanford HLW simulant consists of the 27 most abundant chemical species (on a mole basis) listed in the HLW column in Table 1 of Reference 1. This waste material is therefore a mixture of the 27 most abundant chemicals found in the inventory of chemical constituents present in both the single shell (Reference 2) and double shell (Reference 3) underground waste storage tanks.

C. H. Delegard
Page 2
June 7, 1993

12110-PCL93-046

Reference 1, however, listed the chemical constituents in units of mole fraction and did not make any effort to indicate the phase or chemical nature of the chemical constituents. In order to make a formulation which contained the 27 chemical constituents in the correct proportions it was necessary to convert the chemical constituents into the most probable chemical compounds which would make up the Hanford HLW. This conversion process turned out to be an exercise in analytical mass and charge balancing and acid-base chemistry. It was discovered that the mole fraction values reported in Reference 1 resulted in an excess of cationic species in the formulation. Since sodium cation is the most plentiful cationic species in the comprehensive Hanford HLW, the concentration of sodium in the simulant is less by 7.58 g/kg than reported in Reference 1.

Attachment 1 contains a table which lists the chemical constituents in the comprehensive Hanford HLW simulant. The table also lists the most probable chemical compounds present and the chemical compounds which were actually used to make the comprehensive Hanford HLW simulant. The cation/anion imbalance is reflected in the value for Na listed under "Chemical Species" in the table. Values in the column headed with "Mole Fraction" refer to the moles of a chemical constituent per one unit measure of the comprehensive Hanford HLW. Values in columns headed as "g/kg(soln)" refer to the amount in grams of a particular chemical species or compound per a 1000 gram sample of either the actual HLW or HLW simulant.

Attachment 2 describes the procedure which was actually used to prepare the comprehensive Hanford HLW simulant.

If you have any questions please call me at 373-2529.

B. E. Hey, Advanced Scientist
Process Chemistry Laboratory

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Attachments (2)

Table 1. Comprehensive Hanford HLW and HLW Simulant Chemical Constituents.

COMPREHENSIVE HANFORD HLW THEORETICAL CHEMICAL INVENTORY				COMPREHENSIVE HANFORD HLW SIMULANT		
Chemical Constituent		Chemical Species		Chemical Compound		
Analyte	Mole Fraction	Compound	g/kg(soln)	Reagent	Formula Wt	g/kg(soln)
H ₂ O	4.53e-01	H ₂ O	2.97e+02	H ₂ O	18.0152	1.96e+02
Na	2.44e-01	†(Na ⁺)	-7.58e+00	Na ⁺	22.98977	0.00E+00
NO ₃ (-)	1.47e-01	NaNO ₃	4.47e+02	NaNO ₃	84.99467	4.06e+02
OH(-)	9.26e-02	NaOH	4.17e+01	NaOH	39.99707	5.63e+01
NO ₂ (-)	1.73e-02	NaNO ₂	4.34e+01	NaNO ₂	68.99527	4.49e+01
Al	1.38e-02	NaAl(OH) ₄	5.93e+01	NaAl(OH) ₄	118.00051	6.12e+01
PO ₄ (3-)	7.85e-03	Na ₃ PO ₄	4.68e+01	Na ₃ PO ₄ ·12H ₂ O	380.12307	1.12e+02
*TOC	5.54e-03	Na Acetate	8.27e+00	NaAc·3H ₂ O	50.024735	9.76e+00
F(-)	4.81e-03	NaF	7.35e+00	NaF	41.988173	7.60e+00
CO ₃ (2-)	3.72e-03	Na ₂ CO ₃	1.43e+01	Na ₂ CO ₃ ·H ₂ O	124.00394	1.74e+01
K	2.45e-03	KNO ₃	9.01e+00	KNO ₃	101.1032	7.39e+00
SO ₄ (2-)	1.74e-03	Na ₂ SO ₄	8.99e+00	Na ₂ SO ₄ ·10H ₂ O	322.18914	2.11e+01
Si	1.49e-03	Na ₂ SiO ₃	6.62e+00	Na ₂ SiO ₃ ·9H ₂ O	284.20004	1.59e+01
Fe	1.09e-03	Fe(OH) ₃	4.24e+00	Fe(NO ₃) ₃ ·9H ₂ O	403.9985	1.66e+01
Cl(-)	1.02e-03	NaCl	2.17e+00	NaCl	58.44277	2.24e+00
Zr	5.11e-04	Zr(OH) ₄	2.96e+00	Zr(NO ₃) ₄	339.2396	6.52e+00
Ca	2.99e-04	Ca(OH) ₂	8.06e-01	Ca(NO ₃) ₂ ·4H ₂ O	176.1506	1.98e+00
Ni	2.67e-04	Ni(OH) ₂	9.01e-01	Ni(NO ₃) ₂ ·6H ₂ O	290.801	2.92e+00
Cr	2.58e-04	Cr(OH) ₃	9.67e-01	Cr(NO ₃) ₃ ·9H ₂ O	400.1475	3.88e+00
Mn	2.03e-04	Mn(OH) ₂	6.57e-01	Mn(NO ₃) ₂ 50%	178.9478	1.37e+00
Pb	1.77e-04	Pb(OH) ₂	1.55e+00	Pb(Ac) ₂ ·3H ₂ O	325.289	2.17e+00
Ce	1.40e-04	Ce(OH) ₃	9.74e-01	Ce(NO ₃) ₃ ·6H ₂ O	434.2259	2.29e+00
Fe(CN) ₆ (4-)	1.27e-04	Na ₄ FeCN ₆	1.19e+00	K ₄ FeCN ₆ ·3H ₂ O	368.3464	1.76e+00
Bi	1.04e-04	Bi(OH) ₃	9.84e-01	Bi(NO ₃) ₃ ·5H ₂ O	485.0711	1.90e+00
Sr	3.42e-05	Sr(NO ₃) ₂	2.63e-01	Sr(NO ₃) ₂	211.6298	2.72e-01
B	1.96e-05	Na ₂ B ₄ O ₇	3.59e-02	Na ₂ B ₄ O ₇ ·10H ₂ O	95.341835	7.03e-02
Mg	1.83e-05	Mg(OH) ₂	3.88e-02	Mg(NO ₃) ₂ ·6H ₂ O	256.406	1.76e-01
Totals	0.9995815		1000			1000

* TOC: total organic carbon (Acetate used in this formulation)

† Measure of cation/anion imbalance.

PREPARATION OF THE COMPREHENSIVE HANFORD HLW SIMULANT.

1. Tare weight a 2000 mL beaker w/large stirbar and add to it approximately 50 mLs H_2O . Stir gently.
2. Starting with $Mg(NO_3)_2 \cdot 6H_2O$, in reverse order add all the chemicals through $Na_3PO_4 \cdot 12H_2O$. Rinse the weigh boat after each addition with a few mLs of H_2O and add the rinsate to the beaker as well.
3. After step 2, the beaker should contain approximately 340 mLs of brown murky liquid with undissolved solids. Gently heat the beaker to about $40^\circ C$. Continue stirring.
4. Add $NaAl(OH)_4$ and let dissolve.
5. Turn heat off and add $NaOH$. Let dissolve.
6. Add $NaNO_3$ and let dissolve.
7. Add $NaNO_2$ and let dissolve.
8. Heat beaker to $50-60^\circ C$. Maintain stirring and heat for two hours.
9. Remove from heat and let sit for two days (covered) without stirring.
10. Reweigh beaker.
11. Carefully and without agitation remove as much clear supernatant liquid as possible. Weigh the supernatant liquid.
12. Heat the liquid to boiling and let boil until the weight loss is enough to render a total net weight of the beaker and supernatant liquid of 1000g.
13. Recombine the boiled-down supernatant to the contents in the beaker. Stir gently for two hours.

APPENDIX B

MATERIAL PERFORMANCE TEST RESULTS

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APPENDIX C

C/D OF SIMULATED WASTE COMPOSITIONS

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C/D of NaOH/Al(OH)₃/SiO₂/Fe₂O₃ mixtures; data recorded pp. 8-11 & 16 in WHC-N-656 1
 Makeup of melt experiments, run at 750C for 30 minutes.

Expt	Tare	NaOH	Weights (g)			AfterWt	CrAfterWt	CrWtLoss	Moles				SumMoles	NaOH	Mole Ratio			NaOH Volatilized(%)	
			Al(OH) ₃	SiO ₂	Fe ₂ O ₃				NaOH	Al(OH) ₃	SiO ₂	Fe ₂ O ₃			Al(OH) ₃	SiO ₂	Fe ₂ O ₃	Mole Lost	Fr. Lost
1A	40.905	49.694	62.230				40.862	0.043	0.2197	0.1607			0.3805	0.578	0.422	0.000	0.000		
2A	42.493	53.098		63.906			42.443	0.050	0.2651		0.1043		0.3694	0.718	0.000	0.282	0.000		
3A	41.185	50.719			63.481		41.161	0.024	0.2384			0.1598	0.3962	0.599	0.000	0.000	0.401		
1	40.841	50.400	58.675			53.354	40.691	0.150	0.2390	0.0804			0.3194	0.748	0.252	0.000	0.000	0.083	0.3474
2	42.401	52.025		56.857		53.984	42.349	0.052	0.2406		0.0804		0.3210	0.750	0.000	0.250	0.000	0.072	0.3008
3	41.158	50.799			57.211	56.279	41.090	0.068	0.2410			0.0803	0.3213	0.750	0.000	0.000	0.250	0.023	0.0867
4	36.713	46.270	51.865	48.747		48.799	36.615	0.098	0.2389	0.0400	0.0412		0.3201	0.746	0.125	0.129	0.000	0.077	0.3208
5	40.691	53.572	56.701		43.885	54.545	40.552	0.139	0.2422	0.0401			0.3223	0.751	0.124	0.000	0.124	0.054	0.2226
6	42.349	57.771		44.810	48.019	55.915	42.268	0.083	0.2438		0.0410	0.0402	0.3250	0.750	0.000	0.126	0.124	0.048	0.1903
7	41.090	57.134	47.417	42.300	43.899	54.560	40.977	0.113	0.2429	0.0451	0.0201	0.0200	0.3282	0.740	0.137	0.061	0.061	0.064	0.2649
8	36.618	51.796	42.180	39.034	40.628	49.163	36.489	0.129	0.2404	0.0199	0.0402	0.0199	0.3205	0.750	0.062	0.125	0.062	0.066	0.2738
9	40.552	56.304	46.586	41.786	44.998	54.374	40.429	0.123	0.2430	0.0204	0.0202	0.0405	0.3240	0.750	0.063	0.062	0.125	0.048	0.1986
								AvWtLoss	0.106										
								StdWtLoss	0.031										

Dissolution analyses. 1st dilution using 15 mL for expts. 1A-3A; 18 mL for expts. 1-9. 2nd dilution using 15 mL and 18 mL additional, respectively.

Desolution analyses. 1st dilution using 15 mL for expts. 1A-3A; 18 mL for expts. 1-9. 2nd dilution using 15 mL and 18 mL additional, respectively.																			
Expt	Density		Concentration of 1st Dil (ug/mL)				Concentration of 2nd Dil (ug/mL)				Fraction Dissolved - 1st Dil				Fraction Dissolved - 2nd Dil				Vol + Dis Na
	1st Dil	2nd Dil	Na	Al	Si	Fe	Na	Al	Si	Fe	Na	Al	Si	Fe	Na	Al	Si	Fe	
1A	1.39	1.27	845	517	1.11	0.0446	603	390	0.841	0.0301	0.5018	0.3577	0.3824		0.7162	0.5398			
2A	1.41	1.30	989	3.86	383	0.0203	640	2.57	272	<0.02	0.4867			0.0001	0.6300		0.5573	0.0001	
3A	1.11	1.15	676	0.278	0.654	0.388	408	0.3	0.496	0.138	0.3701				0.4467	0.8804		1.137611	
1	1.40	1.26	981	348	0.3	0.0303	603	221	0.686	0.0253	0.6428	0.6774			0.7902		0.6662	1.124503	
2	1.42	1.27	1010	4.06	335	<0.02	633	3.38	209	<0.02	0.6573		0.5339		0.8239			0.0003	
3	1.19	1.12	916	6.22	0.482	0.625	510	3.46	0.386	0.185	0.5951			0.0005	0.6826		0.6632	0.984029	
4	1.19	1.16	641	20.4	38.6	<0.02	506	18.9	26.6	<0.02	0.4201	0.0799	0.1200		0.6632	0.1481	0.1654	0.0006	
5	1.31	1.26	744	152	0.575	0.287	600	126	0.666	0.198	0.4810	0.5934		0.0005	0.7759	0.9637		0.996436	
6	1.36	1.21	901	3.97	184	9.54	520	2.37	107	9.11	0.5787		0.5758	0.0153	0.6679		0.6697	0.0292	
7	1.35	1.19	965	184	28.9	3.38	539	94.7	9.79	0.647	0.6220	0.6389	0.1839	0.0109	0.6948	0.6576	0.1246	0.0042	
8	1.27	1.18	902	29.6	67.7	4.58	502	13.9	33.4	2.18	0.5875	0.2327	0.2158	0.0148	0.6539	0.2185	0.2129	0.0141	
9	1.22	1.17	529	26.5	16.9	3.44	484	23.7	13.6	2.21	0.3409	0.2038	0.1072	0.0055	0.6239	0.3646	0.1726	0.0070	

Expt	Al:Si:Fe	SolidPhase	PDF number
1A	4:0:0	insufficient sample	
2A	0:4:0	opal, Na silicate(Na ₂ Si ₂ O ₅)	38-448,22-1397
3A	0:0:4	unknownA & NaFeO ₂	&30-1196
1	4:0:0	gibbsite, bayerite(Al(OH) ₃)	7-324,15-136
2	0:4:0	opal(SiO ₂ .H ₂ O)	38-448
3	0:0:4	unknownA	
4	2:2:0	NaAlSiPO ₄ .H ₂ O	38-323
5	2:0:2	unknownA	
6	0:2:2	unknownA (less cryst)	
7	2:1:1	NaAlSiPO ₄ .H ₂ O	38-323
8	1:2:1	NaAlSiPO ₄ .H ₂ O	38-323
9	1:1:2	unknownA&NaAlSiPO ₄	&38-323

C-1

WHC-EP-0766

C/D experiments for the system NaOH/Al(OH)₃/Na₃PO₄/Na₂CO₃; recorded on pp. 18 & 20 of WHC-N-656 1
 Makeup of melt experiments, run at 850C for 30 minutes.

Makeup of melt experiments, run at 850C for 30 minutes.																	
Expt	Tare	NaOH	Weights (g)			AfterWt	CrAfterWt	CrWtLoss	Moles				SumMoles	NaOH	Mole Ratio		
			Al(OH)3	Na3PO4	Na2CO3				NaOH	Al(OH)3	Na3PO4	Na2CO3			Al(OH)3	Na3PO4	Na2CO3
1	40.313	49.889	56.114			52.530	40.185	0.128	0.2394	0.0798			0.3192	0.750	0.250	0.000	0.000
2	42.146	51.779		82.183		65.057	42.101	0.045	0.2408		0.0800		0.3208	0.751	0.000	0.249	0.000
3	36.044	45.670			55.588	54.033	36.021	0.023	0.2407			0.0800	0.3207	0.751	0.000	0.000	0.249
4	40.189	49.776	52.933	68.183		58.002	40.165	0.024	0.2397	0.0405	0.0401		0.3203	0.748	0.126	0.125	0.000
5	42.101	51.713	54.833		59.787	56.880	42.015	0.086	0.2403	0.0400		0.0400	0.3203	0.750	0.125	0.000	0.125
6	38.021	45.684		60.908	65.865	56.392	35.911	0.110	0.2416		0.0401	0.0400	0.3216	0.751	0.000	0.125	0.124
7	40.162	49.759	52.872	60.477	62.972	56.500	40.054	0.108	0.2399	0.0399	0.0200	0.0201	0.3200	0.750	0.125	0.063	0.063
8	42.007	51.643	53.213	68.412	70.905	61.080	41.817	0.190	0.2409	0.0201	0.0400	0.0201	0.3211	0.750	0.063	0.125	0.063
9	37.561	47.207	48.777	56.390	61.359	55.647	37.527	0.034	0.2412	0.0201	0.0200	0.0401	0.3214	0.750	0.063	0.062	0.125
								AvWtLoss	0.083								
								StDWtLoss	0.054								

Dissolution analyses. First dilution using 36 mL (g) H₂O. Second dilution using 18 mL H₂O plus weighed amount of first dilution slurry.

dissolution analyses. First dilution using 36 mL (g) H2O. Second dilution using 18 mL H2O plus weighed amount of												
			Concentration of 1st Dil (ug/mL)					Concentration of 2nd Dil (ug/mL)				
Expt	WtS&H2O	WtSubSam	Na	OH	Al	PO4	CO3	Na	OH	Al	PO4	CO3
1	47.941		133000	65.45	49200	6.13		40300	18.87	83.2	6160	
2	58.911	5.828										
3	54.012		186000	99620	165	<3.85		36300	14790	4810	5280	
4	53.640	5.519										
5	49.686		177000	78710	26100	<7.7		39300	17340	74.6	4470	
6	56.031	5.476						29200	14399	4060	2420	
7	51.410	5.200						40500	18020	2950	4890	
8	54.937	5.529						38400	18190	2470	2780	
9	53.976	5.430										
			Fraction Dissolved - 1st Dil					Fraction Dissolved - 2nd Dil				
	Expt		Na	OH	Al	PO4	CO3	Na	OH	Al	PO4	CO3
	1		0.8699	0.0006	0.8226			0.8476	0.0011		0.5781	
	2											0.0000
	3		0.7270	0.8762			0.0000	0.9803	0.8110	0.9846	0.9498	
	4											
	5		0.8655	0.6933	0.9374		0.0000	0.9108	0.9932		0.8480	0.0000
	6							0.8489	0.8023	0.8574	0.8880	0.0000
	7							1.0038	1.0051	1.2414	0.9023	0.0000
	8							1.0013	1.0139	1.0399	1.0246	0.0000
	9											

C-2

WHC-EP-0766

WHC-EP-0766

Aluminum Hydroxide:Sodium Hydroxide:Sodium Nitrate
From notebook RHO-RE-NB-247, pp. 58 & 59

SAMPLE	Lab ID#	cruc wt	Al(OH)3g	NaOH g	NaNO3g	cruc w/sam	Al(OH)3mol	NaOH mol	NaNO3mol	beg moles Na
TE26A	J1256	45.795	3.903	2.003	0.000	51.700	0.05004	0.05008	0.00000	0.05008 0/1.0
TE27A	J1257	46.125	3.894	1.602	0.900	52.521	0.04992	0.04005	0.01059	0.05064 0.2/0.8
TE28	J1207	50.299	3.870	1.283	1.703	57.135	0.04982	0.03158	0.02004	0.05161 0.4/0.6
TE29	J1208	45.943	3.926	0.894	2.644	53.407	0.05033	0.02235	0.03111	0.05346 0.6/0.4
TE30	J1209	47.020	3.881	0.408	3.493	54.802	0.04976	0.01020	0.04109	0.05129 0.8/0.2
average	1210/1211	47.622	3.915	0.000	4.261	55.793	0.05019	0.00000	0.05013	0.05013 1.0/0
TE31A	J1211	49.769	3.924	0.000	4.287	57.980	0.05031	0.00000	0.05044	0.05044
TE31	J1210	45.474	3.906	0.000	4.235	53.605	0.05008	0.00000	0.04982	0.04982

SAMPLE	Lab ID#	sam.w/H2O	Water added	Air Oven	difoven	Air Furn	loss furn.	begin-furn	tare wt. cent	cent&samp	wt samp
TE26A	J1256	51.700	0.000	51.700	0.000	49.712	1.988	1.988	14.365	68.265	53.900
TE27A	J1257	62.265	9.744	52.251	0.270	50.508	1.743	2.013	14.140	67.893	53.753
TE28	J1207	67.553	10.418	56.216	0.919	54.827	1.389	2.308	14.358	68.007	53.849
TE29	J1208	63.568	10.161	52.221	1.186	50.690	1.531	2.717	14.430	68.322	53.892
TE30	J1209	64.793	9.991	54.127	0.875	51.234	2.893	3.568	14.180	67.666	53.486
average	1210/1211	63.480	5.500	56.199	-0.407	51.820	4.379	3.972	14.328	67.781	53.453
TE31A	J1211	63.370	5.390	58.800	-0.820	54.061	4.739	3.919	14.240	67.699	53.459
TE31	J1210	63.589	5.609	53.598	0.007	49.579	4.019	4.026	14.416	67.863	53.447

SAMPLE	Lab ID#	super.mL	wet sam.wt.(g)	cent.prod.(g)	dry prod.(g)	fin.crc.wt.(g)	cruc. lost (g)
TE26A	J1256	48	5.900	14.891	0.526	45.793	0.002
TE27A	J1257	47	6.753	17.101	2.961	46.113	0.012
TE28	J1207	47	6.649	17.091	2.733	50.275	0.024
TE29	J1208	47	6.892	17.157	2.727	45.922	0.021
TE30	J1209	47	6.486	17.306	3.126	47.004	0.016
average	1210/1211	47	6.453	16.918	2.590	47.612	0.009
TE31A	J1211	47	6.459	16.209	1.969	49.761	0.008
TE31	J1210	47	6.447	17.626	3.210	45.483	0.011

SAMPLE	Lab ID#	OH (uG/mL)	NO2 (uG/mL)	NO3 (uG/mL)	SO4 (uG/mL)	Na (ug/mL)	Al (ug/mL)
TE26A	J1256	7020	<11	<11	23.5	21400	6170
TE27A	J1257	7790	575	5220	<11	19800	8150
TE28	J1207	9210	537	4620	<11	22000	8940
TE29	J1208	9530	264	5880	28.5	22800	9540
TE30	J1209	11900	150	1990	32.4	21600	6310
average	1210/1211	9135	508.5	2138.5	16.75	21000	7975
TE31A	J1211	6570	671	3400	<11	21600	10300
TE31	J1210	11700	346	877	33.5	20400	5650

SAMPLE	Lab ID#	Al dissolved g	Al dissolved moles	NO3 remain g	NO3 remain moles	NO3 lost g	NO2 formed moles	end OH moles	OH formed moles	NaNO3 moles
TE26A	J1256	0.29510	0.01093	0.00000	0.00000	0.00000	0.00000	0.01982	-0.01932	0.00000
TE27A	J1257	0.37670	0.01395	0.24534	0.00396	0.41113	0.00044	0.02154	-0.00456	0.01059
TE28	J1207	0.46747	0.01509	0.21714	0.00350	1.02505	0.00041	0.02546	0.00898	0.02004
TE29	J1208	0.43726	0.01619	0.27636	0.00446	1.65220	0.00020	0.02635	0.02019	0.03111
TE30	J1209	0.28810	0.01067	0.09353	0.00151	2.45431	0.00011	0.03290	0.03337	0.04109
average	1210/1211	0.36980	0.01370	0.10051	0.00162	3.00751	0.00039	0.02526	0.03895	0.05013
TE31A	J1211	0.47986	0.01777	0.15980	0.00258	2.96719	0.00051	0.01816	0.03594	0.05044
TE31	J1210	0.25973	0.00962	0.04122	0.00066	3.04784	0.00026	0.03235	0.04197	0.04982

SAMPLE	Lab ID#	rat Al:NO3	Frac NO3	rat NO3:NO2	Na dis.(g)	Na dis.(mol)	Fr.NO3Dec moles	OH form + NO3 remain	Lost NaOH
TE26A	J1256	0.00000		0.00000	1.02720	0.04466		-0.01932	0.01932
TE27A	J1257	1.31766	0.37373	0.04117	0.93060	0.04046	-0.43078	-0.00017	0.01076
TE28	J1207	0.75325	0.17480	0.02032	1.03400	0.04496	0.44819	0.01289	0.00715
TE29	J1208	0.52064	0.14330	0.00643	1.07160	0.04659	0.64916	0.02485	0.00626
TE30	J1209	0.25966	0.03671	0.00277	1.01520	0.04414	0.81205	0.03499	0.00610
average	J1211J1210	0.27322	0.03234	0.00769	0.98700	0.04291	0.77742	0.04096	0.00917
TE31A	J1211	0.35239	0.05110	0.01009	1.01520	0.04414	0.71253	0.03902	0.01141
TE31	J1210	0.19307	0.01334	0.00526	0.95880	0.04189	0.84230	0.04289	0.00693

SAMPLE	Lab ID#	frt. Al dissol	frt. Na dissol	NO2/NO3
TE26A	J1256	0.21843	0.89186	
TE27A	J1257	0.27946	0.79902	0.11015
TE28	J1207	0.30417	0.87106	0.11623
TE29	J1208	0.32175	0.87158	0.04490
TE30	J1209	0.21445	0.86051	0.07538
average	J1211J1210	0.27287	0.85005	0.23776
TE31A	J1211	0.35328	0.87516	0.19735
TE31	J1210	0.19209	0.83669	0.39453

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APPENDIX D

CALCINATION KINETICS TESTS

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C/D of 101-SY simulant		From WHC-N-656 1, pp. 46-47; RHO-RE-NB-247, pp. 33-34.															
Sample	Time	Cue #	WNCrueBA	WNCrueSYN	W1128C	W1128C	W1128C	W1128C	W1128C	W1128C	W1128C	W1128C	W1128C	W1128C	W1128C	W1128C	W1128C
C-151.J1012	0	1	11.726	16.570	50.256	50.072	11.726	28.553	16.284	47.227	0.000	0.000	0.000	0.000	0.000	0.000	0.000
A3TE1.J1112	1	A3	47.227	52.118	51.394	51.214	6.157	16.374	48.583	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
A4TE2.J1113	3	A4	48.583	53.092	50.597	50.853	14.336	23.291	56.814	0.008	0.008	0.004	0.004	0.004	0.004	0.004	0.004
C-145.R4083	5	A1	56.822	61.868	50.904	49.764	14.446	23.789	47.302	0.038	0.038	0.020	0.020	0.020	0.020	0.020	0.020
C-146.R4084	10	A3	47.340	52.353	50.904	49.764	14.446	23.789	47.302	0.038	0.038	0.020	0.020	0.020	0.020	0.020	0.020
C-147.R4085	23	A4	48.770	53.827	50.985	50.985	14.241	23.745	48.721	0.049	0.049	0.026	0.026	0.026	0.026	0.026	0.026
C-148.R4086	30	A6	55.806	60.869	59.530	57.975	14.207	22.795	55.757	0.049	0.049	0.026	0.026	0.026	0.026	0.026	0.026
Sample	Time	NetWt	F100s128	F100s550	W150s128	W150s550	W150s128	W150s550	W150s128	W150s550	W150s128	W150s550	W150s128	W150s550	W150s128	W150s550	W150s128
C-151.J1012	0	4.844	0.381	0.418	2.845	10.084	11.777	0.051	0.000	14.65	1.15	1.28	1.28	1.28	1.28	1.28	1.28
A3TE1.J1112	1	4.891	0.377	0.417	2.821	10.217	6.468	0.311	0.000	7.90	1.31	1.31	1.31	1.31	1.31	1.31	1.31
A4TE2.J1113	3	4.499	0.232	0.399	3.031	8.955	0.012	0.000	0.012	7.00	1.33	1.33	1.33	1.33	1.33	1.33	1.33
C-145.R4083	5	5.046	0.289	0.516	2.424	9.343	0.075	0.075	0.075	7.00	1.36	1.36	1.36	1.36	1.36	1.36	1.36
C-146.R4084	10	5.013	0.270	0.562	2.215	8.504	0.075	0.075	0.075	7.00	1.23	1.23	1.23	1.23	1.23	1.23	1.23
C-147.R4085	23	5.057	0.264	0.572	2.169	8.588	0.075	0.075	0.075	7.00	1.23	1.23	1.23	1.23	1.23	1.23	1.23
C-148.R4086	30	5.063	0.264	0.572	2.169	8.588	0.075	0.075	0.075	7.00	1.23	1.23	1.23	1.23	1.23	1.23	1.23
Sample	Time	NO2	NO3	OH	TOC	TIC	Na	Al	Si	Fe	Cr	Cr(VI)	P	S	PO4 as P	SO4 as S	K
C-151.J1012	0	34200	37300	8230	5050	2270	61600	9840	30.7	0.414	27.5	8.17	573	394	730	690	1040
A3TE1.J1112	1	74700	23700	6410	1010	11400	101000	2570	34.5	0.569	1720	2720	1160	578	1790	970	1500
A4TE2.J1113	3	52200	22300	4890	240	10300	85500	2530	23.4	0.569	1720	2720	961	516	1040	970	1250
C-145.R4083	5	69000	56900	6490	424	15400	144000	12200	16.7	2.79	2550	2840	1080	789	1690	1530	2270
C-146.R4084	10	3850	23300	21800	190	13200	113000	19100	21.4	2.79	2010	2320	858	602	1460	1000	1710
C-147.R4085	23	41	2330	33200	280	15400	123000	21600	20.9	7.77	2120	2680	974	619	1520	1430	1800
C-148.R4086	30	41	1990	38200	358	15800	135000	24100	25.1	9.28	2410	2770	963	714	1050	1090	2050
Sample	Time	NO2	NO3	OH	TOC	TIC	Na	Al	Si	Fe	Cr	Cr(VI)	P	S	PO4 as P	SO4 as S	K
C-151.J1012	0	10.50	11.70	2.47	1.53	0.63	20.70	3.20	0.0028	0.00000	0.008	0.002	0.17350	0.133	0.213	0.133	0.326
A3TE1.J1112	1	10.34	11.28	2.49	1.6	1.84	18.63	2.98	0.00557	0.00007	0.317	0.439	0.18736	0.08946	0.28912	0.15688	0.31453
A4TE2.J1113	3	12.07	3.83	1.04	0.16	1.94	16.31	0.42	0.00406	0.00010	0.298	0.251	0.16661	0.08946	0.18031	0.16817	0.21671
C-145.R4083	5	9.05	3.87	0.85	0.04	1.79	14.82	0.44	0.00286	0.00000	0.375	0.504	0.18812	0.14002	0.24883	0.22537	0.40285
C-146.R4084	10	10.16	8.57	0.95	0.06	2.27	25.56	2.08	0.00399	0.00052	0.375	0.432	0.15991	0.11220	0.22585	0.15469	0.31870
C-147.R4085	23	0.60	3.60	3.57	0.03	2.40	23.12	3.55	0.00383	0.00146	0.388	0.504	0.18305	0.11633	0.23710	0.22306	0.33829
C-148.R4086	30	0.01	0.28	5.38	0.05	2.22	22.90	3.58	0.00426	0.00157	0.409	0.470	0.16335	0.12111	0.14783	0.15346	0.34773
Sample	Time	NO2	NO3	OH	TOC	TIC	Na	Al	Si	Fe	Cr	Cr(VI)	P	S	PO4 as P	SO4 as S	K
C-151.J1012	0	10.50	11.70	2.47	1.53	0.63	20.70	3.20	0.0028	0.00000	0.008	0.002	0.17350	0.133	0.213	0.133	0.326
A3TE1.J1112	1	10.34	11.28	2.49	1.6	1.84	18.63	2.98	0.00557	0.00007	0.317	0.439	0.18736	0.08946	0.28912	0.15688	0.31453
A4TE2.J1113	3	12.07	3.83	1.04	0.16	1.94	16.31	0.42	0.00406	0.00010	0.298	0.251	0.16661	0.08946	0.18031	0.16817	0.21671
C-145.R4083	5	9.05	3.87	0.85	0.04	1.79	14.82	0.44	0.00286	0.00000	0.375	0.504	0.18812	0.14002	0.24883	0.22537	0.40285
C-146.R4084	10	10.16	8.57	0.95	0.06	2.27	25.56	2.08	0.00399	0.00052	0.375	0.432	0.15991	0.11220	0.22585	0.15469	0.31870
C-147.R4085	23	0.60	3.60	3.57	0.03	2.40	23.12	3.55	0.00383	0.00146	0.388	0.504	0.18305	0.11633	0.23710	0.22306	0.33829
C-148.R4086	30	0.01	0.28	5.38	0.05	2.22	22.90	3.58	0.00426	0.00157	0.409	0.470	0.16335	0.12111	0.14783	0.15346	0.34773
Sample	Time	NO2	NO3	OH	TOC	TIC	Na	Al	Si	Fe	Cr	Cr(VI)	P	S	PO4 as P	SO4 as S	K
C-151.J1012	0	10.50	11.70	2.47	1.53	0.63	20.70	3.20	0.0028	0.00000	0.008	0.002	0.17350	0.133	0.213	0.133	0.326
A3TE1.J1112	1	10.34	11.28	2.49	1.6	1.84	18.63	2.98	0.00557	0.00007	0.317	0.439	0.18736	0.08946	0.28912	0.15688	0.31453
A4TE2.J1113	3	12.07	3.83	1.04	0.16	1.94	16.31	0.42	0.00406	0.00010	0.298	0.251	0.16661	0.08946	0.18031	0.16817	0.21671
C-145.R4083	5	9.05	3.87	0.85	0.04	1.79	14.82	0.44	0.00286	0.00000	0.375	0.504	0.18812	0.14002	0.24883	0.22537	0.40285
C-146.R4084	10	10.16	8.57	0.95	0.06	2.27	25.56	2.08	0.00399	0.00052	0.375	0.432	0.15991	0.11220	0.22585	0.15469	0.31870
C-147.R4085	23	0.60	3.60	3.57	0.03	2.40	23.12	3.55	0.00383	0.00146	0.388	0.504	0.18305	0.11633	0.23710	0.22306	0.33829
C-148.R4086	30	0.01	0.28	5.38	0.05	2.22	22.90	3.58	0.00426	0.00157	0.409	0.470	0.16335	0.12111	0.14783	0.15346	0.34773
Sample	Time	NO2	NO3	OH	TOC	TIC	Na	Al	Si	Fe	Cr	Cr(VI)	P	S	PO4 as P	SO4 as S	K
C-151.J1012	0	10.50	11.70	2.47	1.53	0.63	20.70	3.20	0.0028	0.00000	0.008	0.002	0.17350	0.133	0.213	0.133	0.326
A3TE1.J1112	1	10.34	11.28	2.49	1.6	1.84	18.63	2.98	0.00557	0.00007	0.317	0.439	0.18736	0.08946	0.28912	0.15688	0.31453
A4TE2.J1113	3	12.07	3.83	1.04	0.16	1.94	16.31	0.42	0.00406	0.00010	0.298	0.251	0.16661	0.08946	0.18031	0.16817	0.21671
C-145.R4083	5	9.05	3.87	0.85	0.04	1.79	14.82	0.44	0.00286	0.00000	0.375	0.504	0.18812	0.14002	0.24883	0.22537	0.40285
C-146.R4084	10	10.16	8.57	0.95	0.06	2.27	25.56	2.08	0.00399	0.00052	0.375	0.432	0.15991	0.11220	0.22585	0.15469	0.31870
C-147.R4085	23	0.60	3.60	3.57	0.03	2.40	23.12	3.55	0.00383	0.00146	0.388	0.504	0.18305	0.11633	0.23710	0.22306	0.33829
C-148.R4086	30	0.01	0.28	5.38	0.05	2.22	22.90	3.58	0.00426	0.00157	0.409	0.470	0.16335	0.12111	0.14783	0.15346	0.34773
Sample	Time	NO2	NO3	OH	TOC	TIC	Na	Al	Si	Fe	Cr	Cr(VI)	P	S	PO4 as P	SO4 as S	K
C-151.J1012	0	10.50	11.70	2.47	1.53	0.63	20.70	3.20	0.0028	0.00000	0.008	0.002	0.17350	0.133	0.213	0.133	0.326
A3TE1.J1112	1	10.34	11.28	2.49	1.6	1.84	18.63	2.98	0.00557	0.00007	0.317	0.439	0.18736	0.08946	0.28912	0.15688	0.31453
A4TE2.J1113	3	12.07	3.83	1.04	0.16	1.94	16.31	0.42	0.00406	0.00010	0.298	0.251	0.16661	0.08946	0.18031	0.16817	0.21671
C-145.R4083	5	9.05	3.87	0.85	0.04	1.79	14.82	0.44	0.00286	0.00000	0.375	0.504	0.18812	0.14002	0.24883	0.22537	0.40285
C-146.R4084	10	10.16	8.57	0.95	0.06	2.27	25.56	2.08	0.00399	0.00052	0.375	0.432	0.15991	0.11220	0.22585	0.15469	0.31870
C-147.R4085	23	0.60	3.60	3.57	0.03	2.40	23.12	3.55	0.00383	0.00146	0.388	0.504	0.18305	0.11633	0.23710	0.22306	0.33829
C-148.R4086	30	0.01	0.28	5.38	0.05	2.22	22.90	3.58	0.00426	0.00157	0.409	0.470	0.16335	0.12111	0.14783	0.15346	0.34773
Sample	Time	NO2	NO3	OH	TOC	TIC	Na	Al	Si	Fe	Cr	Cr(VI)	P	S	PO4 as P	SO4 as S	K
C-151.J1012	0	10.50	11.70	2.47	1.53	0.63	20.70	3.20	0.0028	0.00000	0.008	0.002	0.17350	0.133	0.213	0.133	0.326
A3TE1.J1112	1	10.34	11.28	2.49	1.6	1.8											

WHC-EP-0766

APPENDIX E

C/D OF GENUINE HANFORD WASTE

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From WHC-A-008 1; pp. 23, 54 & 62

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