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CRUCIBLE TESTING OF TANK 48H RADIOACTIVE WASTE SAMPLE USING FLUIDIZED BED STEAM REFORMING (FBSR) TECHNOLOGY FOR ORGANIC DESTRUCTION

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EXECUTIVE SUMMARY

The purpose of crucible scale testing with actual radioactive Tank 48H material was to duplicate the test results that had been previously performed on simulant Tank 48H material. The earlier crucible scale testing using simulants was successful in demonstrating that bench scale crucible tests produce results that are indicative of actual Fluidized Bed Steam Reforming (FBSR) pilot scale tests. Thus, comparison of the results using radioactive Tank 48H feed to those reported earlier with simulants would then provide proof that the radioactive tank waste behaves in a similar manner to the simulant. Demonstration of similar behavior for the actual radioactive Tank 48H slurry to the simulant is important as a preliminary or preparation step for the more complex bench-scale steam reformer unit that is planned for radioactive application in the Savannah River National Laboratory(SRNL) Shielded Cells Facility (SCF) later in 2008.

The goals of this crucible-scale testing were to show 99% destruction of tetraphenylborate and to demonstrate that the final solid product produced is sodium carbonate. Testing protocol was repeated using the specifications of earlier simulant crucible scale testing, that is sealed high purity alumina crucibles containing a pre-carbonated and evaporated Tank 48H material. Sealing of the crucibles was accomplished by using an inorganic ‘nepheline’ sealant. The sealed crucibles were heat-treated at 650ºC under constant argon flow to inert the system. Final product REDOX measurements were performed to establish the REDuction/OXidation (REDOX) state of known amounts of added iron species in the final product. These REDOX measurements confirm the processing conditions (pyrolysis occurring at low oxygen fugacity) of the sealed crucible environment which is the environment actually achieved in the fluidized bed steam reformer process. Solid product dissolution in water was used to measure soluble cations and anions, and to investigate insoluble fractions of the product solids. Radioanalytical measurements were performed on the Tank 48H feed material and on the dissolved products in order to estimate retention of Cs-137 in the process.

All aspects of prior crucible scale testing with simulant Tank 48H slurry were demonstrated to be repeatable with the actual radioactive feed. Tetraphenylborate destruction was shown to be >99% and the final solid product is sodium carbonate crystalline material. Less than 10 wt% of the final solid products are insoluble components comprised of Fe/Ni/Cr/Mn containing sludge components and Ti from monosodium titanate present in Tank 48H. REDOX measurements on the radioactive solid products indicate a reducing atmosphere with extremely low oxygen fugacity – evidence that the sealed crucible tests performed in the presence of a reductant (sugar) under constant argon purge were successful in duplicating the pyrolysis reactions occurring with the Tank 48H feed. Soluble anion measurements confirm that using sugar as reductant at 1X stochiometry was successful in destroying nitrate/nitrite in the Tank 48H feed. Radioanalytical measurements indicate that ~ 75% of the starting Cs-137 is retained in the solid product. No attempts were made to analyze/measure other potential Cs-137 in the process, i.e., as possible volatile components on the inner surface of the alumina crucible/lid or as offgas escaping the sealed crucible.

The collective results from these crucible scale tests on radioactive material are in good agreement with simulant testing. Crucible scale processing has been shown to duplicate the complex reactions of an actual fluidized bed steam reformer. Thus this current testing should provide a high degree of confidence that upcoming bench-scale steam reforming with radioactive Tank 48H slurry will be successful in tetraphenylborate destruction and production of sodium carbonate product.

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LIST OF ACRONYMS

AD	Analytical Development
dpm	Disintegrations per minute
EA	Environmental Assessment
EMF	Electromotive force
FBSR	Fluidized Bed Steam Reformer
HRI	Hazen Research Inc.
HPLC	High-Performance Liquid Chromatography
ITP	In-Tank Processing
LWO	Liquid Waste Operations
MST	Monosodium titanate
NaTPB	Sodium tetraphenylborate
PBA	Phenylboronic acid
ppb	parts per billion
ppm	parts per million
PS&E	Process Science and Engineering
PSAL	Process Science Analytical Laboratory
REDOX	REDuction/OXidation
RSD	Relative standard deviation
SCF	Shielded Cells Facility
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TPB	Tetraphenylborate
TT&QAP	Task Technical and Quality Assurance Plan
TTR	Task Technical Request
XRD	X-ray diffraction
3PB	Triphenylboron
2PB	Diphenylboronic acid

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1.0 INTRODUCTION AND BACKGROUND

Liquid Waste Operations (LWO) personnel at the Savannah River Site (SRS) issued a Task Technical Request (TTR) for crucible-scale testing of radioactive Tank 48H samples related to Fluidized Bed Steam Reformer (FBSR) technology using the carbonate flowsheet (Aponte 2008). Previous proof-of-concept testing with simulant Tank 48H material had involved crucible-scale investigations in 2003 (Jantzen 2004), and pilot-scale runs in both 2003 (Soelberg et al. 2004) and 2006 (THOR 2007). Since the 2003 crucible-scale tests with simulant Tank 48H material were successful in duplicating the complex reactions in the FBSR process, LWO personnel sought to repeat some of these tests using optimized conditions with actual radioactive Tank 48H material. These crucible-scale tests using radioactive Tank 48H would serve as preliminary confirmation of the FBSR process, as a larger ‘bench-scale’ FBSR unit was being developed for application in the Savannah River National Laboratory (SRNL) Shielded Cells Facility (SCF) for real waste testing (Ferrara 2008).

Details of the processing history of Tank 48H involving use of sodium tetraphenylborate (NaTPB) and the In-Tank Processing (ITP) have been previously described in detail (Jantzen 2004). FBSR testing using Tank 48H simulants in the 2003 and 2006 timeframe resulted from a 2001 review that recommended a thermal treatment method (FBSR) for further investigation (Adams et al. 2002). The FBSR operation, flowsheet and chemistries have also been reviewed in detail (see Section 2.0 of Jantzen 2004).

Process Science and Engineering (PS&E) personnel at the SRNL issued a Task Technical and Quality Assurance Plan (TT&QAP) (Crawford 2007) and an Analytical Study Plan (Crawford 2008) to address the testing criteria and objectives for the current crucible-scale work. The purposes of the current study were to demonstrate the following objectives with actual radioactive Tank 48H material:

- Design and fabricate a crucible test using radioactive Tank 48H material that emulates the FBSR process conditions and chemistry based on Tank 48H crucible-scale simulant tests runs using the carbonate flowsheet
- Perform up to three crucible tests with both simulant and radioactive Tank 48H material
- Characterize product chemistries to include 1) phenylborates (to show > 99% destruction of starting TPB), 2) crystalline components and 3) REDuction/OXidation (REDOX)
- Dissolution testing of products to qualitatively and quantitatively determine soluble (cations and anions) and insoluble (crystalline solids) components
- Upon discussions with the LWO customer after issuance of the TTR and TTQAP, it was also decided to investigate retention of the radio-cesium (Cs-137) in the crucible-scale process by performing gamma-counting on the process feed slurry and the dissolved product solutions

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2.0 EXPERIMENTAL

2.1 SIMULANTS

Simulants of the Tank 48H slurries were obtained from excess feed from the 2006 pilot-scale testing from Hazen Research, Inc. (HRI) facility in Golden, CO. **Table 2-1** shows the characterization data (obtained from Analysis Results Tables 4-8 and 4-9 from THOR 2007).

Table 2-1 Simulant Characterization Data (THOR 2007)

Tank 48H Simulant			
Component	**(mg/L)**	**Component**	**(mg/L)**
Al	1918	Ru	<1
B	573	S	122
Ba	0.68	Si	116
Ca	90.3	Sn	16.8
Cd	<1	Sr	16.6
Ce	3.47	Ti	650
Cr	37.1	Zn	4.84
Cu	4.48	Zr	<1
Fe	144	F	<92
K	2983	Cl	136
La	1.06	NO_2	19877
Mg	1.07	NO_3	11637
Mn	30.5	SO_4	185
Mo	7.33	PO_4	357
Na	73182	wt% Total solids*	17.45 (17.3 – 17.6)
Ni	10.4	wt% Insoluble solids*	1.68 (1.55 – 1.81)
P	170	wt% Soluble solids*	15.8 (15.8 – 15.8)
Pb	17.9	pH	14
Pd	2.11	Density (g/mL)	1.09
Rh	6.68		

Table 4-8 and 4-9 from THOR 2007
* wt% values shown as the average and as (range) of the 2 different analytical data sets shown in Table 4-8 from THOR 2007.

Radioactive Tank 48H samples were obtained from a 3.5 L composite located in the SCF. Table 2-2 shows characterization data for the radioactive sample that was obtained and analyzed in 2005 (Fondeur et al. 2005).

Table 2-2 Radioactive Tank 48H Data from Fondeur et al. 2005

Tank 48H Radioactive			
Component	**(mg/L)**	**Component**	**(mg/L)**
Al	2014	Ru	<1.2
B	867	S	378
Ba	<0.1	Si	125
Ca	43	Sn	<77*
Cd	<1*	Sr	9
Ce	<35*	Ti	<1**
Cr	70	Zn	5
Cu	4	Zr	<2*
Fe	169	F	14
K	2310	Cl	170
La	<13*	NO_2	23531
Mg	19	NO_3	14118
Mn	6	SO_4	320
Mo	<0.1	PO_4	424
Na	74980	wt% Total solids	20.19
Ni	<10*	wt% Insoluble solids	3.05
P	129	wt% Soluble solids	17.14
Pb	<196*	pH	14
Pd	NR	Density (g/mL)	1.165
Rh	<0.7		

NR = not reported
* filtrate values
** Ti as monosodium titanate (MST = $NaTi_2O_5H$) reported as 0.15 wt%

2.2 TEST PARAMETERS

Test parameters used in this study were determined from recommended parameters from the crucible-scale proof-of-concept work with simulants (Jantzen 2004). These test parameters were detailed in that report (Executive Summary of Jantzen 2004) as heat treatment at 650ºC for 3-48 hours at 1X stoichiometric sugar to make Na_2CO_3 product. All of the processing steps previously demonstrated with simulants were followed. The Tank 48H material was batched into stainless steel beakers and carbonated with dry ice to convert the NaOH to Na_2CO_3 until a pH of ~ 9.5 was reached. Prior to carbonation, a calculated mass of iron as the oxidized ferric(+3) salt ($Fe(NO_3)_3 \cdot 9H_20$) was added to target ~ 5 wt% Fe_2O_3 in the final calculated sodium carbonate product as a REDOX indicator. Sucrose was added as a reductant at a 1X stoichiometric level based on the nitrate (from the slurry and that added from the iron nitrate chemical) and nitrite content of the starting Tank 48H material.

Justification for use of sucrose as the reductant in these tests was addressed in a pre-testing memo from C. M. Jantzen to LWO personnel (Jantzen 2007). The carbonated slurries were oven-dried at 60ºC to a peanut butter or 'paste' consistency per procedure ITS-00052, Rev. 0 (ITS procedure 2003). **Table 2-3** shows the process details of the two batches of feed material for both the simulant and radioactive samples. Slurries were stirred with a large spatula intermittently during drying steps in order to keep the samples homogeneous. These data indicate that for all slurries batched in this manner, the post-carbonated slurries had pHs of ~ 9.3 and about 60 – 67% mass (water) loss was obtained in going from the original slurry to the final paste samples. All pHs measured in this testing used a Piccolo ATC pH Meter/HI 1280 Amplified Electrode probe (Hanna Instruments, Van Nuys, CA).

Table 2-3 Test Parameters for Processing Simulant and Radioactive Samples

	Slurry Mass (g)	$Fe(NO_3)_3 \cdot 9H_2O$	Sucrose	Post-Carbonation pH	Final Paste Mass (g)	wt% Mass Loss
Simulant Batch 1	298.81	5.59	7.00	9.2	109.42	63.38
Simulant Batch 2	291.26	5.455	7.02	9.2	95.76	67.12
Radioactive Batch 1	299.73	6.91	6.78	9.4	104.6	65.10
Radioactive Batch 2	87.66	2.153	1.98	9.4	35.66	59.32

The peanut butter/paste dried samples from the various batches were aliquoted/sub-sampled into high purity (99.999%) 100-mL alumina (Al_2O_3) crucibles. Crucibles were sealed with nepheline ($NaAlSiO_4$) gel using fitted high purity alumina crucible tops. The nepheline gel is an inorganic coating referred to as 'S-Prime Mod' (ZYP Coatings, Inc., Oak Ridge, TN). **Table 2-4** shows general component data for the gel. Sealing of the crucibles and lids generally started with a thin layer of gel around the top of the crucible, followed by another gel layer on the inside bevel of the lid. The lid was then carefully fixed on top of the crucible and the seal layer was inspected to verify complete coverage of the lid/crucible interface. Finally another thin layer of gel was applied to the outer surface lid/crucible interface. This method of sealing the crucibles was initially performed by hand on several practice vessels, then the sealing steps were demonstrated via remote handling using the SCF manipulator devices. A 'C-clamp' device was used to mount the final heat-treated, sealed crucibles so that the tops could be cracked for eventual sample removal. Each crucible lid was lightly 'scored' with a diamond blade saw prior to use so that the lid would preferentially crack into four separate pieces instead of shattering into many different sized pieces.

Table 2-4 General Component Data for Nepheline Sealant Material

Component	CAS Number	% by Weight
Sodium Potassium Aluminum Silicate	37244-96-5	46
Water	7732-18-5	35
Chromia Titania Frit	68186-90-3	5
Aluminum Oxide	1344-28-1	6
Potassium Hydroxide	1310-68-3	5
Amorphous Silica	7631-86-9	3

Sealed crucibles were pre-heated in a drying oven at 60ºC for ~ 1 hour, prior to heat-treatment in a Barnstead Thermolyne Model 1400 benchtop muffle furnace. High purity argon gas (99.99%) was used as inerting gas flow during all furnace heat treatments. Argon gas flow was maintained at 15 scfm (~ 7 L/min). The Thermolyne furnace used for remote testing in the SCF was previously used in simulant testing. It was modified by inserting a quartz insert into the back of the chamber allowing constant argon purge. This furnace has a nominal 5"x 5"x7" chamber, or about 3L volume. The modified furnace temperature readout was checked against an M&TE calibrated thermocouple to verify temperature accuracy for the heat treatments using a furnace functional check procedure (ITS-0096 2006). Figure 2-1 shows the M&TE thermocouple temperature plotted vs. the furnace readout temperature in the range of 100 to 700ºC. These data indicate excellent agreement of the furnace temperature readout vs. the M&TE thermocouple values.

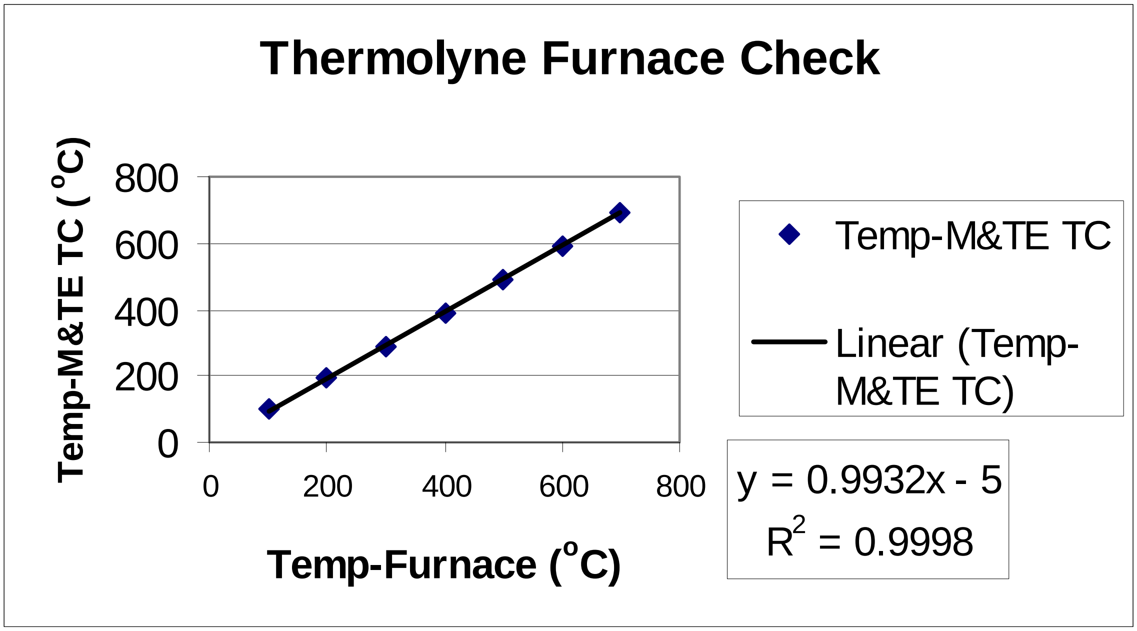

Figure 2-1 Furnace Check Thermocouple Data

After heat-treating the sealed crucibles at 650ºC for at least 3 hours, final product samples were obtained from the cooled alumina crucibles after the sealed lids were removed. Care was taken to minimize any sealant material from dropping down into the crucible filled with product. The sodium carbonate crystalline phase products were observed to be ‘friable’ in that relatively little force/pressure/grinding was required to reduce the solids/chunks down to powder-sized solids. Each crucible product sample was well-mixed/homogenized using a steel spatula and collected into a separate glass jar for sample storage.

2.3 SAMPLE ANALYSES

Gram-portions of the solids were submitted for powder X-ray diffraction (XRD) analyses. Phenylborate analyses were performed by using 0.4 g to 0.8 g portions of the solid product extracted with 2 mL of acetonitrile. The organic phase extracts were analyzed by High-Performance Liquid Chromatography (HPLC) for tetraphenylborate, triphenylboron, diphenylboronic acid, phenlyborate, phenol and biphenyl. A developmental investigation to establish these extraction ratios was completed on simulant samples prior to this testing (White 2008). Established minimum detection limits for the HPLC method and the various phenlyborates are given in Table 2-5. (ADS-1601 1998)

Table 2-5 Established Minimum Detection Limits for the HPLC Method

Component	Minimum Detection Limit (ppb)
NaTPB	223
Triphenylboron (3PB)	482
Diphenylboronic acid (2PB)	103
Phenylboronic acid (1PB)	397
Phenol	784

Quantitation limits are typically ~ 5X higher than minimal detection limits. Using a nominal minimum quantitation limit of ~ 1,400 ppb (1.4 ppm) and an overall 70% extraction efficiency, the minimum quantitation limit for 4PB from extraction of the FBSR solids can be calculated as,

1.4 mg TPB/L x (0.002 L extract / 0.4 g product) x (1000 g/kg) x (1/0.7) = 10 mg TPB/kg product

By increasing the solid to liquid extraction ratio, e.g., 0.8 g product to 2 mL acetonitrile, one can lower the nominal minimum quantitation limit to 5 mg TPB/kg product. Previous crucible scale testing with Tank 48H simulants attained this 5 mg/kg quantitation limit in HPLC analyses for 4PB, 3PB and 2PB (Jantzen 2004). HPLC analysis results for the more recent pilot-scale Hazen samples were reported as < 50 mg/kg for 4PB and < 100 mg/kg for all other phenlyborates, phenol and biphenyl (THOR 2007).

REDOX measurements on the final product solids were performed via ITS-0042, Rev. 0 (2004) that was developed from the work of Bauman (1992). This method involves dissolution of the solid using sulfuric/hydrofluoric acid containing ammonium metavanadate. Boric acid is added to destroy any iron-fluoride complexes and a pH 5 buffered ferrozine reagent is added to form a colored complex with ferrozine. This solution absorbance is determined to give the Fe^{2+} content. Addition of excess ascorbic acid converts all Fe^{3+} to Fe^{2+} and forms more ferrozine complex. This final solution absorbance gives total Fe. Subtraction of the initial absorbance reading (Fe^{2+}) from the latter absorbance reading (total iron) gives the calculated Fe^{3+}. This method is routinely used in the PS&E Process Science Analytical Laboratory (PSAL) using a HP8452A Diode Array spectrophotometer. The method was repeated via remote handling in the SCF for radioactive sample REDOX determination by using a portable EPP-2000 StellarNet UV-visible diode array spectrometer and optical fibers (Lascola 2008). A REDOX reference standard Environmental Assessment (EA) glass was measured in each experimental setup (Jantzen et al. 1993).

Solid product samples were dissolved in deionized ASTM-I water at a ratio of 1 g product to 100 mL water, or 10 g/L in the manner of previous analyses for the pilot-scale samples (THOR 2007). The dissolved samples were well-mixed and allowed to stand overnight. Filtration was then performed using a 0.5 micron disposable filter unit and slight vacuum. The filtrates were analyzed for soluble cations and anions. Dried filter solids were weighed and carefully scraped off the filters for submission to XRD for crystalline characterization.

The feed slurry and dissolved product samples were analyzed by gamma spectroscopy using an in-cell counting method. Each 3-mL sample was counted for 3 minutes. Standards and blanks were analyzed in parallel. For comparison, a separate portion of the dissolved product samples were removed from the SCF and analyzed by Analytical Development personnel in a contained gamma spectroscopy counting facility. In order to estimate the volume reduction in processing the radioactive Tank 48H slurry through the carbonate flowsheet crucible scale testing, the bulk loose-packed product density of the solids was measured. These measurements used 5-mL graduated glass cylinders. The powdered solids were added to the cylinder with gentle tapping to prevent any observable voids in the 5-mL column. Each 5-mL product mass was measured in triplicate.

3.0 RESULTS AND DISCUSSION

3.1 TEST MATRIX

The test matrix for simulant and radioactive samples is shown in **Table 3-1**. Five simulant products were obtained from the two starting slurry batches. Initial attempts to heat-treat the sealed crucibles by slow ramp of increasing temperature in the furnace were unsuccessful due to likely pressurization of the crucible lid due to steam generation. Simulants 1-3 all resulted in the lid displacement during heatup with some small amount of sample displaced from inside the crucibles. Simulant samples 4 and 5 used the method of initial heating of the sealed crucible at 60ºC in a drying oven, followed by direct placement into a furnace that was preheated to 650ºC. This method resulted in sealed crucibles throughout the heat treatment. Appendix A shows digital photos of the various simulant product crucibles and the various solid products. Simulant 1 product appeared noticeably darker in color than the other products.

The radioactive products 1-4 were processed with similar steps of preheating for 1 hour at 60ºC, followed by direct placement into the 650ºC furnace. The first three radioactive products (Rad 1-3) were all prepared from the 1st batch of carbonated/dried radioactive Tank 48H slurry. This testing took place over a 3-week period. The wt% mass loss on heat-treatment data indicates that the starting paste could have dried out some over the three weeks since less mass was lost in going from radioactive sample 1 through 3 from radioactive slurry batch 1. A final radioactive sample 4 was produced as a single sample from radioactive slurry batch 2. It should be noted that similar wt% mass losses are observed for the two successful (sealed) simulant 4 & 5 products, the initial radioactive 1 product, and the final radioactive 4 product. These data indicate that these 4 product samples had similar consistency, i.e., wt% mass loss values in the range of 49 to 55 wt% of the peanut butter/paste-like material that was initially sealed inside the crucibles. By comparison, Simulants 1-3 showed higher mass loss on heat treatment (in the range of 58 – 71 wt%) indicating possibly too much moisture present in the starting pastes. These measured mass losses for Simulants 1-3 could also have been compromised by some of the material that was lost from the crucible during heat treatment. Conversely, radioactive samples 2 and 3 show significantly lower mass loss on heat treatment indicating that the starting paste samples were ‘drier’ than radioactive samples 1 and 4.

Table 3-1 Test Matrix for Simulant and Radioactive Tests

Test	Paste Mass (g)	Product Mass (g)	wt% Mass Loss	Process Date	Comments
Sim 1 (Batch 1)	53.29	15.038	71.78	1/24/08	Heat ramp 50ºC to 650ºC in 4 hrs, 650ºC for 3 hours
Sim 2 (Batch 1)	29.58	12.42	58.01	1/25/08	Heat ramp 50ºC to 650ºC in 4 hrs, 650ºC for 3 hours
Sim 3 (Batch 1)	25.68	10	61.06	1/28/2008 & 1/29/08	Day 1:Heat ramp 50ºC to 300ºC in 6 hrs; Day 2:Heat ramp 50ºC to 650ºC in 5 hrs, 650ºC for 3 hours
Sim 4 (Batch 2)	20.52	9.85	52.00	1/29/08	Pre-heat 60ºC 1 hr; Heat treat 650ºC 3 hr & 25 min
Sim 5 (Batch 2)	24.24	11.88	50.99	1/30/08	Pre-heat 60ºC 1 hr; Heat treat 650ºC 3 hr & 25 min
Rad 1 (Batch 1)	20.26	10.31	49.11	2/13/2008	Pre-heat 60ºC 1 hr; Heat treat 650ºC 3 hr & 10 min
Rad 2 (Batch 1)	25.86	16.61	35.77	2/20/2008	Pre-heat 60ºC 1 hr; Heat treat 650ºC 3 hr & 10 min
Rad 3 (Batch 1)	35.23	23.5	33.30	2/26/2008	Pre-heat 60ºC 1 hr; Heat treat 650ºC 3 hr & 20 min
Rad 4 (Batch 2)	21.36	9.58	55.15	3/13/2008	Pre-heat 60ºC 1 hr; Heat treat 650ºC 6 hr & 25 min

3.2 CRYSTALLINE PHASES OF PRODUCTS

All XRD data for the simulant and radioactive products, as well as the insoluble filter solids are shown in Appendix B and C. **Table 3-2** summarizes the major and minor crystalline phases identified by XRD. The expected $Na_2CO_3 \cdot H_2O$ and Na_2CO_3 phases are the major phases observed for the products. Trace levels of $Na_2C_2O_4$ and sodium aluminosilicates $Na_{1.95}(Al_{1.95}Si_{0.05}O_4)$ and $Na_{14.88}Al_{15.26}Si_{32.74}O_{96}$ were also identified in radioactive products 3 and 4. Presence of sodium oxalate in the product sample is questionable due to its reported pure-phase melting point of 250-270 ºC. A possible explanation for the Na/Al/Si species in radioactive product 4 is trace contamination of the dried gel material used to seal the crucibles. This minor amount of Na/Al/Si species could also derive from 1) these cation species present in the Tank 48H material, i.e., these cations in the ratio of Na ~70,000 ppm) : Al (~2000 ppm) : Si (~100 ppm) (Fondeur et al. 2005), or 2) these cations present in minor sludge components in Tank 48H.

The bottom part of **Table 3-2** shows data for the insoluble solids obtained from dissolving 3-gram portions of the solid product in 300 mL of water. The far column indicates that the total insoluble solids for the simulants were in the range of 7 to 13 wt%, and 6-9 wt% for the radioactive insoluble products. The major phases identified in the insoluble solids are Fe/Ni/Cr/Mn containing crystals. These elements could derive from minor insoluble sludge components in the Tank 48H material (simulant and radioactive). Additionally, iron was added as REDOX indicator in all of these tests. A variety of minor phases are identified in the insoluble solids - $Na_3H(CO_3)_2(H_2O)_2$ and metal oxides/hydroxides of Al, Si, Mn. A minor titania-containing phase is present in radioactive sample 3. This minor phase component could derive from the monosodium titanate that is known to be present in Tank 48H material. It should be noted that the presence of a Ti-phase, as well as many other minor phases associated with the insoluble solids has been observed in the previous Hazen pilot-scale studies (THOR 2007).

3.3 TETRAPHENYLBORATE DESTRUCTION IN PRODUCTS

One of the main analytical characterization goals of this work was to demonstrate > 99% destruction of the tetraphenylborate in the starting Tank 48H feed slurry. HPLC data for the simulant and radioactive samples are shown in **Table 3-3**. Comparison of the analyzed tetraphenylborate in the simulant products to target and measured values for the simulant feed (from the Hazen pilot report - THOR 2007) indicates > 99% destruction was obtained in these 3-hour heat treatments. In the second part of **Table 3-3** (Radioactive Samples), similar comparisons of radioactive Tank 48H product organics to the starting tetraphenlyborate feed values obtained from Fondeur et al. (2005) also show >99% destruction.

The first set of radioactive HPLC data was performed at 0.4 g product extracted with 2 mL acetonitrile. The last four radioactive product HPLC data sets used 0.8 g product extracted with 2 mL acetonitrile. This enabled a reported minimum quantitation limit of < 5 mg/Kg. In the first set of product analyses, only radioactive product sample 3 showed measurable 57 mg/Kg tetraphenylborate. In the second set of product analyses using higher amounts of product (0.8 g vs. 0.4g), radioactive product samples 1, 2 and 3 showed measurable tetraphenlyborate in the range of 25 – 126 mg/Kg. However, radioactive product sample 4 that was heat treated for > 6 hours contained no quantifiable TPB in the product extract in both analyses sets. It should be noted as shown in Table 3-3, that even though TPB was detected in some of the radioactive product samples, all the tests show > 99% destruction of the starting TPB. Optimization of residence time in static crucibles designed to mimic dynamic conditions, i.e., ‘bed turnover’, in the FBSR is difficult as discussed in Jantzen (2004). It is likely that the longer residence times in crucible-scale testing like 8-24 hours are more prototypic of the actual fluidized bed steam reforming process. For instance, it has been calculated that the Hazen pilot FBSR testing experienced denitration and mineralization reformer (DMR) bed turnover of approximately 24 hours (Section 6.2.3 of THOR 2007).

Table 3-2 XRD Major and Minor Phases

Product Characterization			
Test Sequence	Major Phases Identified by X-Ray Diffraction	Minor Phases Identified by X-Ray Diffraction	
Sim 1 Product	$Na_2CO_3 \cdot H_2O$, Na_2CO_3	NONE	
Sim 2 Product	$Na_2CO_3 \cdot H_2O$, Na_2CO_3	NONE	
Sim 3 Product	$Na_2CO_3 \cdot H_2O$, Na_2CO_3	NONE	
Sim 4 Product	$Na_2CO_3 \cdot H_2O$, Na_2CO_3	NONE	
Sim 5 Product	$Na_2CO_3 \cdot H_2O$, Na_2CO_3	NONE	
Rad 1 Product	Na_2CO_3	NONE	
Rad 2 Product	Na_2CO_3	NONE	
Rad 3 Product	Na_2CO_3	$Na_2C_2O_4$	
Rad 4 Product	Na_2CO_3	$Na_{1.95}(Al_{1.95}Si_{0.05}O_4)$, $Na_{14.88}Al_{15.26}Si_{32.74}O_{96}$	
Insoluble Filter Product Characterization	**(Major Phases)**	**(Minor Phases)**	**Weight % of Total Product**
Sim 1 Filter Product	FeNi, NiCrFe	$Na_3H(CO_3)_2(H_2O)_2$, $Al(OH)_3$	7.3
Sim 3 Filter Product	$MnFe_2O_4$	$Na_3H(CO_3)_2(H_2O)_2$, SiO_2 , Al_2O_3	13.0
Sim 5 Filter Product	$MnFe_2O_4$	$Na_3H(CO_3)_2(H_2O)_2$, Mn_3O_4 , $Al(OH)_3$	11.0
Rad 1 Filter Product	$Fe^{+2}Fe_2^{+3}O_4$	$K(Na,K)_3Al_4Si_4O_{16}$, $Na(AlSi_3O_8)$, $K(Si_3Al)O_8$, $KAlSiO_4$, $Na_{14.88}Al_{15.26}Si_{32.74}O_{96}$	9.5
Rad 2 Filter Product	$Fe^{+2}Fe_2^{+3}O_4$	$Na(AlSi_3O_8)$, $Na_{14.88}Al_{15.26}Si_{32.74}O_{96}$, Mn_3O_4	8.8
Rad 3 Filter Product	$Fe^{+2}Fe_2^{+3}O_4$	Mn_3O_4, $NaFeTiO_4$, $Na_8(AlSiO_4)_6(NO_3)_2$	7.9
Rad 4 Filter Product	$Fe^{+2}Fe_2^{+3}O_4$	$HNa_3(CO_3)_2(H_2O)_2$, $Na_{14.4}Al_{15.26}Si_{32.74}O_{96}(H_2O)_{1.76}$	6.1

Table 3-3 Organics Measured in Simulant and Radioactive Products

		TPB anion		**Percent Destruction***		**3PB**	**2PB**	**PBA**	**Phenol**	**Biphenyl**
Sample	**Sample ID**	**mg/kg**		**Vs. analyzed**	**Vs. target**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Simulant Samples										
Sim Feed	3-246211	41000		NA	NA	<500	<500	<10	<10	10
Sim Feed	3-246212	30000		NA	NA	<500	<500	<10	<10	25
Sim Prod 1	3-246205	<10	>	99.945	99.985	<10	<10	<10	<10	<10
Sim Prod 2	3-246206	<10	>	99.945	99.985	<10	<10	<10	<10	<10
Sim Prod 3	3-246207	<10	>	99.945	99.985	<10	<10	<10	<10	<10
Sim Prod 4	3-246208	<10	>	99.945	99.985	<10	<10	<10	<10	<10
Sim Prod 5	3-246209	<10	>	99.945	99.985	<10	<10	<10	<10	<10
Radioactive Samples										
Rad Feed	3-247907	19300		NA	NA	<500	<500	98	597	1468
Rad Feed	3-247908	21900		NA	NA	<500	<500	39	102	224
Rad Prod 1	3-247902	<10	>	99.959	-	<10	<10	<10	<10	<10
Rad Prod 2	3-247903	<10	>	99.959	-	<10	<10	<10	<10	<10
Rad Prod 3	3-247904	57		99.767	-	<10	<10	<10	<10	<10
Rad Prod 4	3-247905	<10	>	99.959	-	<10	<10	<10	<10	<10
Rad Prod 1	3-247902	126		99.485	-	<10	<10	<10	<10	<10
Rad Prod 2	3-247903	34		99.861	-	<10	<10	<10	<10	<10
Rad Prod 3	3-247904	25		99.898	-	<10	<10	<10	<10	<10
Rad Prod 4	3-247905	<5	>	99.980	-	<10	<10	<10	<10	<10

* Percent destruction for simulants based on analyzed NaTPB (68,000 mg/Kg) or recipe target of 18,073 mg/Kg); Percent destruction for radioactive samples based on NaTPB of 21,000 mg/L and 1.165 g/mL slurry density.

-Also note that Sim Prod 1-5 and Rad Prod 1-3 all used ~3-hour residence times (see Comments column of Table 3-1); Rad Prod 4 used ~ 6.5-hour residence time (see Comments column of Table 3-1).

3.4 PRODUCT SOLUBILITY AND SOLUBLE CATIONS AND ANIONS

Solid product samples from the simulant and radioactive tests were dissolved in high purity ASTM-1 water at 3 grams to 300 mL ratio, or 10 g/L. As indicated in the Hazen pilot testing report, this dissolution ratio is well below the maximum solubility of sodium carbonate in water (400 g/L). After mixing and standing overnight, the resulting solutions were filtered and the filtrates were analyzed for cations and anions. These data are shown in **Table 3-4** and **Table 3-5**. The soluble cations are present at similar ratios as they are in the starting Tank 48H slurry. Sodium, potassium and aluminum are the main soluble cations present at > 1 wt%, along with lower levels of B, Ca, P, S and Si. For both the simulant and radioactive filtrates the sodium cation comprises 92% of the total detected cations. The pH values of these solutions are consistent with dissolution of sodium carbonate in water, i.e., the pK_a of HCO_3^-/CO_3^{2-} is 10.3 at 25ºC.

Soluble anion data for the simulants indicate that only phosphate and sulfate are present. The values shown in **Table 3-5** are calculated from the elemental P and S data from cation analyses because of interferences obtained in the simulant ion chromatography data. Nitrite anion analysis was also inconclusive due to interference. These issues with phosphate, sulfate and nitrite anion detection in the simulant solutions likely derive from the relatively large amount of carbonate present in the filtrates. The IC instrumentation used for simulant filtrate analyses does not have any carbonate trap/suppression system. Nitrate data for the simulant filtrates at less than detectable levels (< 10 mg/L) indicates complete destruction during processing. Soluble anion data for the radioactive filtrates showed detectable levels of Cl^- and SO_4^{2-}. Nondetectable levels of nitrite and nitrate indicate complete destruction of the starting nitrite/nitrate present in the Tank 48H slurry (23,000 and 14,000 mg/L, respectively).

3.5 REDOX MEASUREMENTS

REDOX data for the simulant tests in this study were varied. The initial simulants became unsealed during testing. The last two simulants remained sealed. **Table 3-6** shows the REDOX absorbance values for these samples. Since the REDOX values were obtained for these simulant samples after the actual radioactive sample preparation and testing had started, no efforts were made to further investigate these data. Previous sealed crucible testing with Tank 48H simulants using the carbonate flowsheet produced heat-treated products having Fe^{2+}/Fe_{total} values in the range of 0.4 to 0.9 indicating very low oxygen fugacity levels during processing (see discussion on radioactive sample REDOX values).

Table 3-4 Soluble Cations

	Rad Avg. (Rad. 1-4)	Sim Avg. (Sim 1,3,5)
	wt%	wt%
Al	1.07	1.11
B	0.45	0.13
Ca	0.01	0.01
Fe	<0.01	<0.01
K	1.19	1.89
Na	34.93	40.27
P	0.11	0.13
S	<0.16	0.12
Si	0.04	0.05
Sum	37.95	43.71
Na / Sum	0.92	0.92
pH	10.4	~ 11

Table 3-5 Soluble Anions

		F	Cl	NO_2	NO_3	PO_4*	SO_4*	C_2O_4	HCO_2
	Sample ID	*(mg/L)*	*(mg/L)*	*(mg/L)*	*(mg/L)*	*(mg/L)*	*(mg/L)*	*(mg/L)*	*(mg/L)*
Simulant Filtrates									
Sim 1 (A)	08-0771	<10	<10	Interference*	<10	46	34	<10	<10
Sim 1 (B)	08-0771	<10	<10	Interference*	<10	40	38	<10	<10
Sim 3 (A)	08-0772	<10	<10	Interference*	<10	41	35	<10	<10
Sim 3 (B)	08-0772	<10	<10	Interference*	<10	40	36	<10	<10
Sim 5 (A)	08-0773	<10	<10	Interference*	<10	41	38	<10	<10
Sim 5 (B)	08-0773	<10	<10	Interference*	<10	40	37	<10	<10
Radioactive Filtrates									
Rad 1	101726	<10	73	<10	<10	<10 (36)**	53 (<48)**	<10	<10
Rad 2	101727	<10	72	<10	<10	<10 (36)	52 (<48)	<10	<10
Rad 3	101728	<10	73	<10	<10	<10 (33)	53 (<48)	<10	<10
Rad 4	101729	<10	73	<10	<10	<10 (33)	46 (<48)	<10	<10

* Phosphate and sulfate values for simulants calculated from P and S cation data.

* Phosphate and sulfate values for radioactive samples in parenthesis calculated from P and S cation data.

Table 3-6 REDOX Values for Simulant Products

Sample	Lab ID	$Fe^{(2+)}$	$Fe^{(3+)}$	Fe(total)	$Fe^{(2+)}$ / $Fe^{(3+)}$	$Fe^{(2+)}$ / Fe(total)
EA		0.038	0.144	0.182	0.264	0.209
Batch 2, Simulant 4	**08-0140**	<0.010	0.100	0.100	All Fe $^{3+}$	
		<0.010	0.105	0.105	All Fe $^{3+}$	
Batch 2, Simulant 5	**08-0141**	<0.010	0.094	0.094	All Fe $^{3+}$	
		<0.010	0.088	0.088	All Fe ^{3}+	

In order to measure the REDOX of the radioactive sample products the method was developed using a remote stage connected by fiber optic cables. **Table 3-7** shows various Environmental Assessment (EA) REDOX standard glass values determined throughout the development/ checkout phases of the remote method. These data are important in establishing that the remote REDOX measurements are consistent with the established PSAL method. The overall average EA value in these trials is very close to the two multi-sample averages referenced in Jantzen et al. (1993) i.e., the remotely performed REDOX EA average for Fe^{2+}/Fe^{3+} of 0.27 +/- 0.2 compared to the reference range of 0.22 to 0.23.

Table 3-7 REDOX Values for Environmental Assessment Glass

Trial	$A(Fe^{2+})$	$A(Fe_{total})$	Fe^{2+}/Fe_{total}	Fe^{2+}/Fe^{3+} *
2/27/2008	0.038	0.18	0.209	0.264
3/4/2008	0.083	0.388	0.214	0.272
	0.085	0.394	0.216	0.275
	0.085	0.395	0.216	0.275
3/19/2008	0.116	0.53	0.225	0.284
3/25/2008	0.06	0.34	0.179	0.217
3/26/2008	0.106	0.50	0.214	0.272
	0.112	0.48	0.232	0.302
Average (6)			0.213	0.270
Standard Deviation			0.016	0.024

*Fe^{2+}/Fe^{3+} reference value = 0.22 to 0.23 (Jantzen et al. 1993)

REDOX values for the radioactive products are shown in **Table 3-8**. The first 3 values for samples derived from Batch 1 show similar levels of Fe^{2+}/Fe^{3+} in the range of 0.1 to 0.2. Radioactive sample 4 shows a markedly higher Fe^{2+}/Fe^{3+} value of 0.6 indicating that more iron was in the +2 reduced state compared to the first 3 radioactive sample products. All of these radioactive sample REDOX values can be compared to previous crucible and pilot scale Tank 48H testing using the electromotive force (EMF) series plot presented previously in the Jantzen memo (2007). Figure 3-1 shows the plot relating measured REDOX as log (Fe^{2+}/Fe^{3+}), or log R, to the oxygen fugacity levels shown as (-) log (oxygen fugacity). As discussed in SRNL-PSE-2007-00252, the red lines in this plot are the range of log (Fe^{2+}/Fe^{3+}) values obtained in previous simulant Tank 48H crucible scale studies (Jantzen 2004) and the blue dashed lines are log (Fe^{2+}/Fe^{3+}) values determined in previous Hazen pilot scale testing (THOR 2007).

Table 3-8 REDOX Values for Radioactive Products

Sample	A(Fe^{2+})	A(Fe_{total})	Fe^{2+}/Fe_{total}	Fe^{2+}/Fe^{3+}	Log(Fe^{2+}/Fe^{3+})
Rad 1 (Batch 1)	**0.019**	**0.118**	0.161	0.192	-0.717
Rad 2 (Batch 1)	**0.017**	**0.187**	0.091	0.100	-1.000
Rad 3 (Batch 1)	**0.024**	**0.130**	0.185	0.226	-0.646
Rad 4 (Batch 2)	**0.041**	**0.107**	0.383	0.621	-0.207

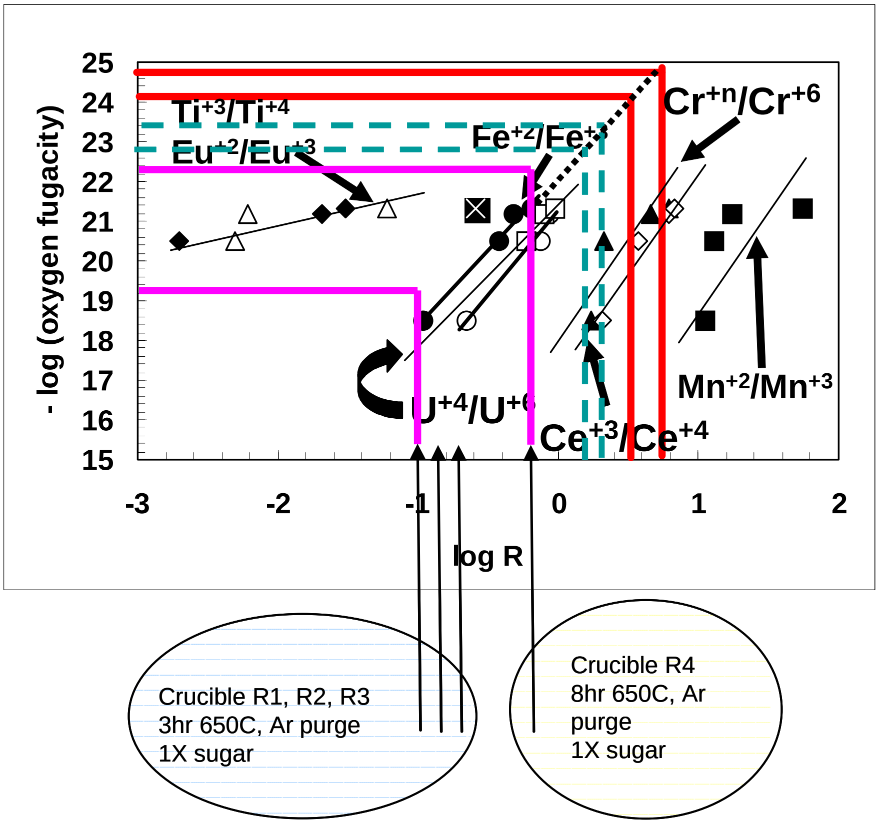

Figure 3-1 Plot of Oxygen Fugacity (-log(oxygen fugacity) vs. Log (Fe^{2+}/Fe^{3+})

3.6 GAMMA SPECTROSCOPY FOR ESTIMATING FATE OF RADIO-CESIUM

Radioactive Cs-137/Ba-137m was measured in the Tank 48H feed slurry and in all of the dissolved product solutions. The 'in-cell' gamma spectroscopy instrument was used for all feed samples and on duplicate dissolved product samples. Separate dissolved product samples were also removed from the SCF for counting in the AD contained gamma spectroscopy instrument. **Table 3-9** shows the feed data and the product data (samples 'A' and 'B') from the in-cell counting. The product samples counted outside of the SCF are labeled as 'C' samples. All data are in units of disintegrations per minute (dpm) per mL of volume counted. The in-cell system shows larger uncertainty values of ~ 10% vs. the more precise method using the contained instrument with uncertainty of ~ 1%. Replicate counting of the feed slurries gave very good precision with the average value of 9.17E+08 dpm/mL and 1.19 % relative standard deviation (RSD). The average value for all of the product data is 3.69E+07 with %RSD of 9.6%.

Table 3-9 Gamma Spectroscopy Data for Feed and Products

Sample	I.D. Number	Cs-137 (dpm/mL)	Uncertainty		
Feed Data					
Feed 1A	300248879	9.04E+08	10.60%	**Feed**	**dpm/mL**
Feed 2A	300248880	9.28E+08	10.50%	**Avg.**	**9.17E+08**
Feed 1B	300248879	9.13E+08	10.60%	**St. Dev.**	**1.09E+07**
Feed 2B	300248880	9.24E+08	10.50%	**%RSD**	**1.19**
Product Data					
Prod1A	300248881	3.52E+07	11.10%		
Prod1B	300248882	3.59E+07	11.10%		
Prod1C	300248883	3.64E+07	1.07%		
Prod2A	300248884	3.91E+07	11.00%		
Prod2B	300248885	4.00E+07	11.00%		
Prod2C	300248886	4.01E+07	1.22%		
Prod3A	300248887	3.23E+07	11.20%		
Prod3B	300248888	3.19E+07	11.20%		
Prod3C	300248889	3.28E+07	1.22%	**Product**	**dpm/mL**
Prod4A	300248890	3.86E+07	11.00%	**Avg.**	**3.69E+07**
Prod4B	300248891	3.75E+07	11.10%	**St. Dev.**	**3.55E+06**
Prod4C	300248892	4.35E+07	1.22%	**%RSD**	**9.61**

The measured cesium levels in the Tank 48H feed slurry and final products can be compared to access the fate of cesium during the sealed crucible Tank 48H processing. If one takes the starting slurry on a 1-L basis and calculates the total dpm expected from 1 Liter, we get:

1 Liter x 9.17E+08 dpm/mL x 1000 mL/L = <u>9.17E+11 dpm in 1 Liter of feed</u>

Next, if we assume that all the major cations in the Tank 48H slurry (Na, Al and K) go to produce their respective anhydrous metal carbonate salts, one can compute the total grams of metal carbonate salts that would derive from treatment of 1 liter of slurry. These calculations are detailed in **Table 3-10** giving a calculated total metal carbonate mass of 172.747 g Na_2CO_3 + 4.084 g K_2CO_3 + 8.732 $Al_2(CO_3)_2$ = <u>185.56 g of metal carbonate solids</u>. About 1.04 wt% of insoluble solids (sludge and MST) are in the Tank 48H radioactive sample. These would contribute 1,000 mL x 1.165 g/mL x (1.04/100) = <u>12.116 g insolubles (non-TPB)</u>. Now if we assume that all of the cesium from the original 1 liter of slurry remains with the dry solid product (metal carbonates and insoluble sludge/MST = total of 197.68 g), then the expected cesium counts for the products would be 9.17E+11 dpm / 197.68 g solid = <u>4.64E+09 dpm/g dry solid product</u>. Since the gamma spectroscopy was performed on 1g/100mL dilutions of the dry solid product, we would expect these solutions to have measured values of 4.64E+09 dpm/g x (1g/100mL) = <u>4.64 E+07 dpm/mL dissolved product</u>. Comparison of the overall average from the four dissolved radioactive products to this target value gives;

Measured (3.69E+07 dpm/mL) / Target (4.64E+07 dpm/mL) = <u>0.80 (assuming anhydrous natrite)</u>

The above calculation assumes no hydrated metal carbonate species. However previous **Table 3-2** XRD data indicates that some partially hydrated sodium carbonate solids are present. These various hydrated forms of sodium carbonate have also been identified in the Hazen pilot-scale tests (THOR 2007). These hydrated forms (thermonatrite and trona) are also shown in **Table 3-10** in bold italics. If one repeats the above calculations and assumes that all the sodium carbonate is about 33% of each sodium carbonate form (natrite, thermonatrite and trona), then comparison of measured Cs vs. target gives;

Measured (3.69E+07 dpm/mL) / Target (3.99E+07 dpm/mL) = <u>0.92 (assuming 1/3rd natrite, trona and thermonatrite)</u>

If one uses the hydrated forms of sodium carbonate as the assumed solid products, the calculations above indicate that measured/target are in the range of 91% – 110% for $Na_2CO_3 \cdot H_2O$ (thermonatrite) and $Na_3H(CO_3)_2 \cdot 2H_2O$ (trona), respectively. The XRD method is a qualitative method so there is now way to determine from these tests the exact quantitative distribution of the various sodium carbonate phases in the products. We conclude that these cesium mass balance calculations based on radiochemical measurements and the assumed various sodium carbonate hydrated/anhydrous phases (in the range of 91% to 110%) approach 100% closure given the 10% uncertainty in the actual radiochemical measurements that were performed in the shielded cells facility.

It should be noted that no attempts were made in this study to collect/measure/rinse/strip any residual radio-cesium that could have accumulated on the inside of the crucible/lid, e.g., due to potential volatility during the 650ºC processing. Regarding cesium volatility in the carbonate matrix, we note that the melting point of pure Cs_2CO_3 is 610ºC is significantly lower than melting points for other pure alkali metal carbonates (Na_2CO_3 m.p. = 851ºC, K_2CO_3 m.p. = 891ºC, no information located for aluminum carbonate m.p.).

Table 3-10 Calculation of Metal Carbonates from 1 Liter Processing

	Rad. Concentration (mg/L)	**Moles Metal / L**	**Moles Metal Carbonate / L**	**Grams Metal Carbonate / L**	**Metal Carbonate* Formula Wt.**
Na	74980	3.261	1.630	172.747	105.98 (Na_2CO_3)
Na	***74980***	***3.261***	***1.630***	***202.087***	***123.980 ($Na_2CO_3{\cdot}H_2O$)***
Na	***74980***	***3.261***	***1.087***	***245.553***	***225.970 ($Na_3H(CO_3)_2{\cdot}2H_2O$)***
K	2310	0.059	0.030	4.084	138.2 (K_2CO_3)
Al	2014	0.075	0.037	8.732	233.96 ($Al_2(CO_3)_3$)
				Total = 185.563	
Insolubles (non-TPB)				Total = 12.12	

*Na_2CO_3 (natrite)
*$Na_2CO_3{\cdot}H_2O$ (thermonatrite)
*$Na_3H(CO_3)_2{\cdot}2H_2O$ (trona)

3.7 VOLUME REDUCTION

The volume reduction on processing Tank 48H slurry with the crucible scale FBSR carbonate flowsheet can be estimated with measurement of the final dry solid product loose-packed or bulk density. **Table 3-11** shows the bulk density measurements that were performed in triplicate for each of the four radioactive products. These measurements used ~ 3.5 g powder portions added to a 5-mL graduated clear glass cylinder. As the powders were added into the cylinder, gentle tapping was used to assure that there were no visible voids or air-space gaps in the cylinder column. These data show that overall bulk density of the solids is 0.752 +/- 0.03 g/mL. Using a 1-Liter basis and the 181.98 g calculated metal carbonate dry solid product value, one calculates that 1 liter of Tank 48H slurry would produce (190.01 g / 0.752 g/mL) = 252 mL of dry solid product, or 0.252 L. This gives a ‘concentration factor’ of 1L slurry / 0.252L solid = 3.96. These data show that the dry solid product volume of 0.252 L is ~ 25% of the starting 1 L volume, or a 100-25 = 75% volume reduction is achieved. Similar conclusions were reached in the Hazen pilot scale testing where it was concluded that ~ 240,000 gal of Tank 48H slurry would produce ~ 50,000 gal of dry carbonate solids, or a volume reduction of ~ 80%.

Table 3-11 Bulk Density Measurements

Sample	Mass (g)	Volume (mL)	Density (g/mL)
Rad 1	3.599	5	0.7198
	3.58	5	0.716
	3.575	5	0.715
Rad 2	3.742	5	0.7484
	3.853	5	0.7706
	3.74	5	0.748
Rad 3	3.89	5	0.778
	4.023	5	0.8046
	3.948	5	0.7896
Rad 4	3.724	5	0.7448
	3.748	5	0.7496
	3.725	5	0.745
		Avg.	**0.752**
		St.dev.	**0.029**
		%RSD	**3.81**

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4.0 CONCLUSIONS

The purposes of the current study of organic destruction with formation of a primarily sodium carbonate solid product were fulfilled as documented by the following:

- The TPB was destroyed to > 99% for all simulant and radioactive crucible scale samples that used the precarbonation, evaporation, and 650ºC heat treatment for 3 to 6 hours in sealed alumina crucibles inside of an argon-purged furnace.
- Destruction of nitrate/nitrite was achieved using sugar additive as reductant at 1X stoichiometry.
- Sodium carbonate (Na_2CO_3) was the primary phase formed from all crucible scale simulant and radioactive Tank 48H processing. Insoluble solids XRD characterization indicates that various Fe/Ni/Cr/Mn phases are present. These crystalline phases are associated with the insoluble sludge components of Tank 48H slurry. The total insoluble fraction of the crucible scale solid products is 7 to 13 wt% for simulants, and 6-9 wt% for radioactive samples.
- REDOX measurements for the simulant products showed varied results with an initial product sample fully reduced and other product samples showing no indication of reduction. REDOX values for all radioactive products showed measureable amounts of reduction (Fe^{2+}). The REDOX values for radioactive products, expressed as Fe^{2+}/Fe^{3+}, are slightly lower than previous simulant crucible testing and simulant pilot tests using the carbonate flowsheet.
- Soluble cations in the dissolved simulant and radioactive products were as expected comprised of the main cations in the Tank 48H slurry, i.e., Na, Al and K. Soluble anion analyses confirmed destruction of nitrate/nitrite and show some detectable S and P as sulfate and phosphate.
- Detailed radioanalytical analyses of the Tank 48H feed slurry and all product samples indicate that ~ 80% of the starting Cs-137/Ba-137m is retained in the product solids assuming complete anhydrous Na_2CO_3 (natrite). However using other forms of sodium carbonate that have been observed in these and previous tests, i.e., thermonatrite and trona, calculations show a better Cs-137 mass balance. For instance assuming 1/3rd percentage of each phase (natrite, thermonatrite and trona), the measured vs. target Cs is about 92%. This value is within 100% closure given the ~ 10% uncertainty in the radiochemical measurements. No attempts were made to sample/analyze the inside of the process crucibles/lids for other sources of cesium, i.e., potentially volatilized cesium inside the sealed crucible surface.
- The measured bulk density of solid sodium carbonate products produced from radioactive Tank 48H processing in these tests support earlier simulant testing that indicates ~80% volume reduction occurs. This would result in the current Tank 48H volume going from nominally 240,000 gallons slurry down to ~ 50,000 gallons of dry bulk solid product.

- Finally, collective results from these crucible scale tests indicate that planned processing of actual radioactive Tank 48H slurry through the carbonate flowsheet using fluidized bed steam reformer technology will, to a high degree of confidence, produce results that are similar to recent pilot scale processing of simulant Tank 48H material.

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5.0 QUALITY ASSURANCE

All data reported in this study were developed under the quality assurance given in technical task plan SRNL-PSE-2007-00232 (Crawford 2007). The research program and task plan were developed to address SP-TTR-2007-00011, Rev. 0, Sept. 18, 2007 and Rev. 1, Jan. 2, 2008. The data are recorded in laboratory notebook WSRC-NB-2007-00174.

6.0 ACKNOWLEDGEMENTS

Many people contributed to the success of the crucible-scale Tank 48H FBSR testing program. The simulant testing was conducted with assistance and advice from S. T. Vissage, M. R. Williams and C. M. Jantzen. Their experience in the crucible-scale method helped to provide guidance in developing/translating the method using remote-handling for radioactive samples. The radioactive sample work was led by the team of SRNL Shielded Cells Facility technicians – P. U. Burkhalter and D. J. Wheeler served as lead technicians for the radioactive sample processing and analyses. Mr. J. G. Dobos of the SRNL Glassblowing and Apparatus Development Lab and R. W. Blessing of the SRNL Shielded Cells were very helpful in developing the sealed alumina crucible apparatus used in the shielded cells. Analytical procedures were successful for these tests due to the diligent efforts of D. R. Best and R. J. Lascola, Jr. (REDOX), T. L. White (HPLC) and A. R. Jurgensen and D. M. Missimer (XRD). Ms. C. C. Diprete coordinated the gamma spectroscopy analyses.

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7.0 REFERENCES

Adams, R. A. et al., (2002) “HLW Tank 48 Disposition Alternatives Identification – Phase I and II Summary Report”, U. S. DOE Report, WSRC-RP-2002-00154, Westinghouse Savannah River Co., Aiken, SC, July 2002.

ADS-1601, AD Procedure L16.1, ADS-1601, High Performance Liquid Chromatography (HPLC) Analysis of Aqueous Alkaline Solution for Sodium Tetraphenylborate, Triphenylborane, Diphenylborinic Acid, Phenolboric Acid, Phenol, and Biphenyl, 8/5/98.

Aponte, C. I., (2008) Technical Task Request, “Crucible testing of Tank 48H Real Waste Sample using FBSR Technology with Carbonate Flowsheet for Organic Destruction”, SP-TTR-2007-00011, Rev. 0, Sept. 18, 2007 & Rev. 1, Jan. 2, 2008.

Baumann, E. W., (1992) “Colorimetric Determination of Iron(II) and Iron(III) in Glass”, Analyst, 117, 913-916 (1992).

Crawford, C. L., (2007) Task Technical & QA Plan, “T48 Treatment Project – Crucible testing of Tank 48H Real Waste Sample Using FBSR Technology with Carbonate Flowsheet for Organic Destruction,” SRNL-PSE-2007-00232, Rev. 0, Nov. 12, 2007.

Crawford, C. L., (2008) Analytical Study Plan, “T48 Treatment Project – Crucible testing of Tank 48H Real Waste Sample Using FBSR Technology with Carbonate Flowsheet for Organic Destruction,” SRNL-PSE-2007-00259, Rev. 0, Feb. 8, 2008.

Ferrara, D. M.,(2008) Savannah River National Laboratory Tank 48H Benchtop Steam Reformer Consolidated Hazard Analysis (U), WSRC-TR-2007-00457, Rev. 1, March 2008.

Fondeur, F. F., D. P. Lambert and S. D. Fink, (2005) “Analysis of Tank 48H Sample – HTF-E-05-021,” WSRC-TR-2005-00358, Rev.0, Oct. 3, 2005.

ITS-0042, “Determining Fe2+/3+ and Fe+2/Fetotal Using UV VIS Spectrometer,” Procedure Manual L29, Procedure ITS-0042, Rev. 0, June 2, 2004.

ITS-0052, “Heat Treatment of Waste Slurries for REDOX (Fe+2/ΣFe) and Chemical Composition Measurement,” Procedure Manual L29, Procedure ITS-0052, Rev. 1, November 6, 2003.

ITS-0096, “Furnace Functional Check,” Procedure Manual L29, Procedure ITS-0096, Rev. 0, March 31, 2006.

Jantzen, C. M. et al., (1993) “Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material”, WSRC-TR-92-346, Rev. 1, June 1, 1993.

Jantzen, C. M., (2004) “Disposition of Tank 48H Organics by Fluidized Bed Steam Reforming (FBSR),” WSRC-TR-2003-00352, Rev. 1, March 29, 2004.

Jantzen, C. M., (2007) “Shielded Cell Facility (SCF) Crucible Studies with Tank 48 Waste,” SRNL-PSE-2007-00252, Nov. 19, 2007.

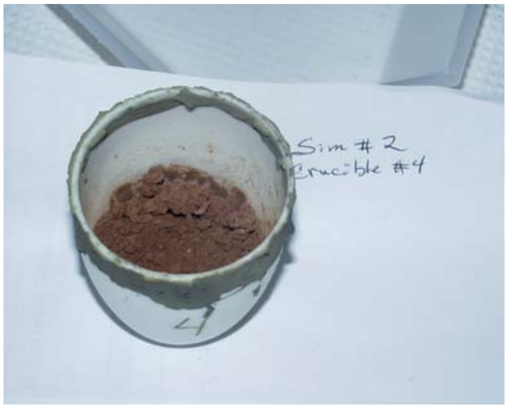
Lascola, R. J., (2008) “Fe Redox Measurements in the Shielded Cells by Absorbance Spectroscopy,” SRNL-ADD-2008-00089, Rev. 0, April 3, 2008.

Soelberg, N., D. Marshall, S. Bates, D. Siemer, “SRS Tank 48H Waste Steam Reforming Proof-of-Concept Test Results,” INEEL/EXT-03-01118, Rev. 1 (May 2004).

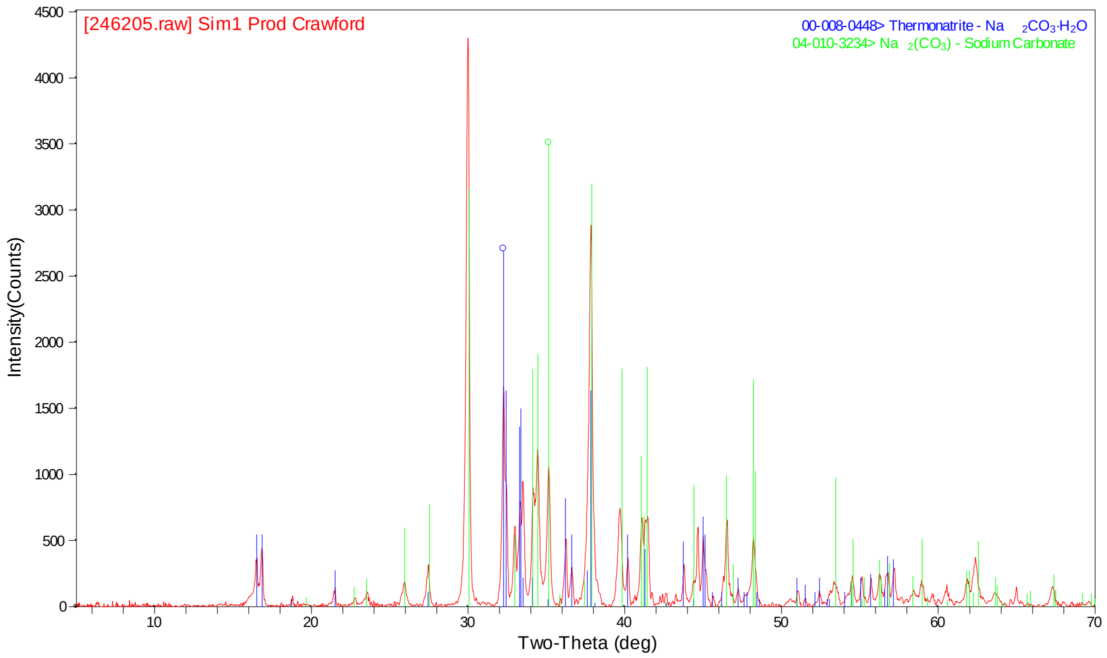
THOR (2007), Tank 48 Test Report, “Pilot Plant Reporting for Treating Tank 48H Simulants Carbonate Flowsheet”, Doc. No. 28927-WEC-RPT-00001, Rev. 2, Prepared for WSRC by THOR Treatment Technologies, LLC and Washington Group International, May 2007.

White, T. L., (2008) “Preparation for Analysis of fluidize bed Steam Reforming (FBSR) Product by High Performance Liquid Chromatography,” SRNL-ADD-2008-00121, Rev. 0, June 27, 2008.

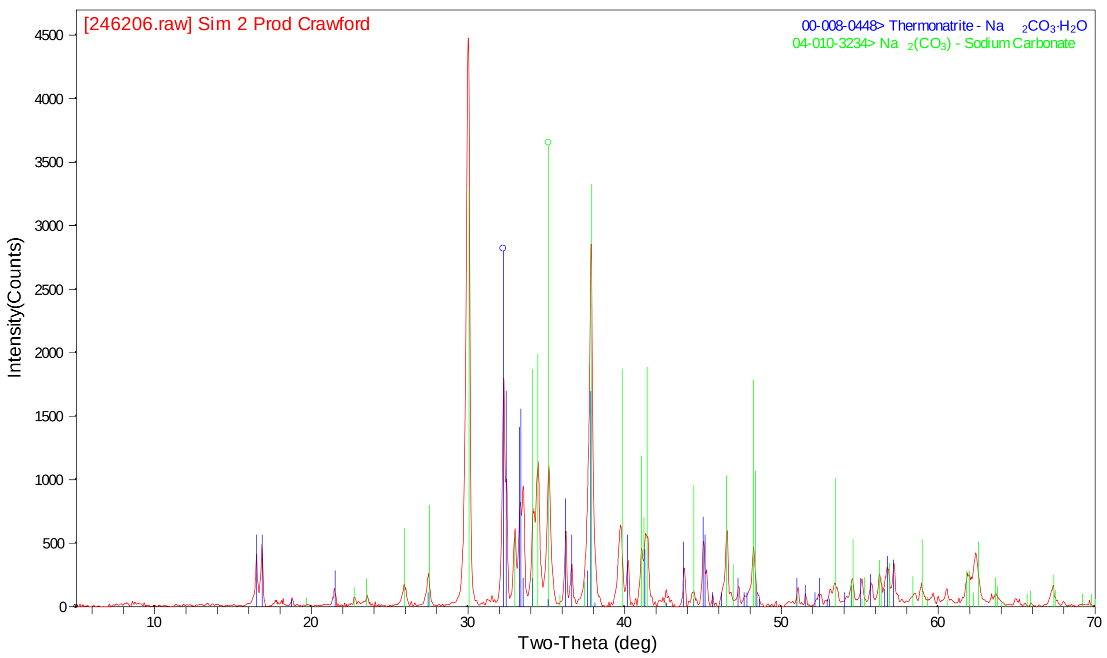
APPENDIX A. SIMULANT PRODUCTS

 Simulant 1 Final Product	 Simulant 2 Final Product
 Simulant 3 Final Product	 Simulant 4 Final Product
 Simulant 5 Final Product	 Simulant 4 Post Heat Treatment Showing Intact Lid/Seal

APPENDIX B. SIMULANT PRODUCT XRD



Simulant 1 Product XRD



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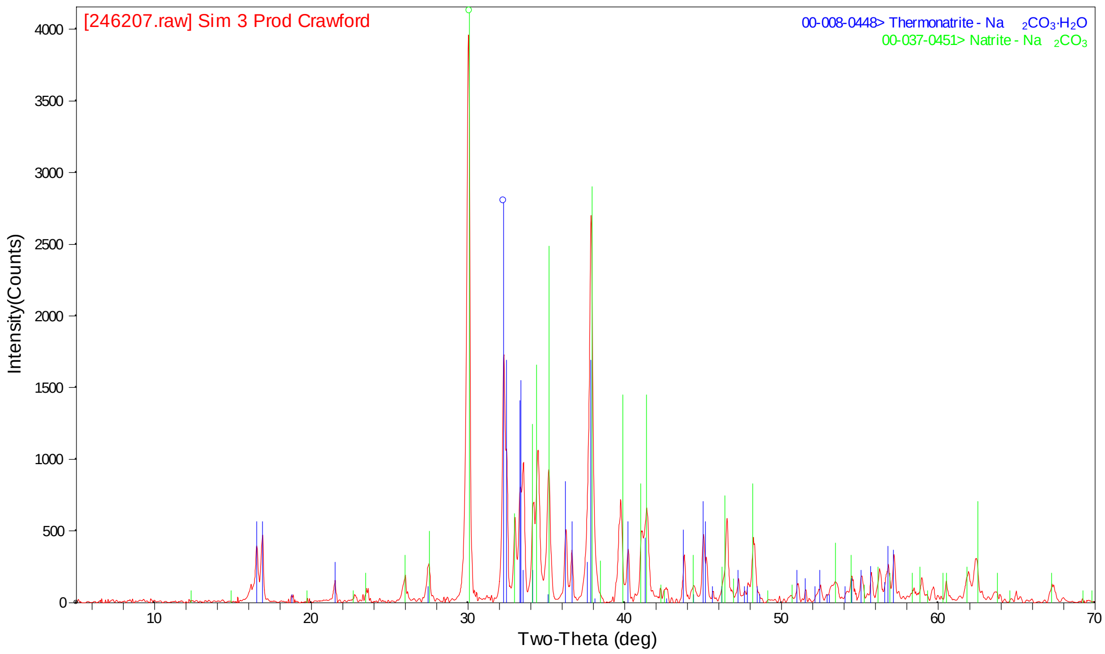

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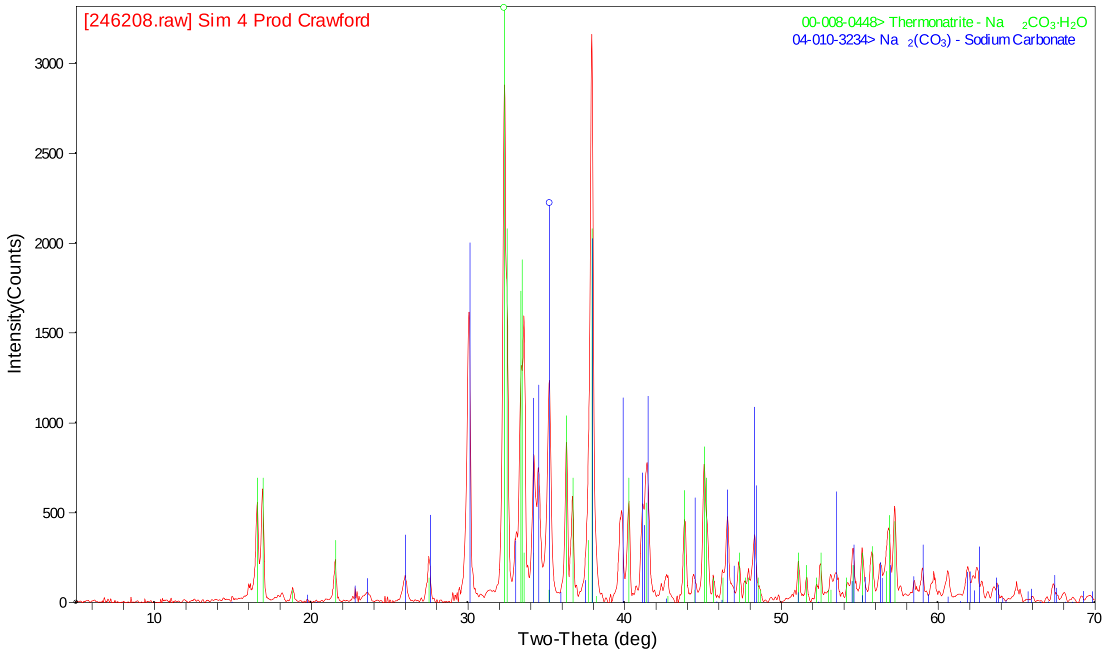
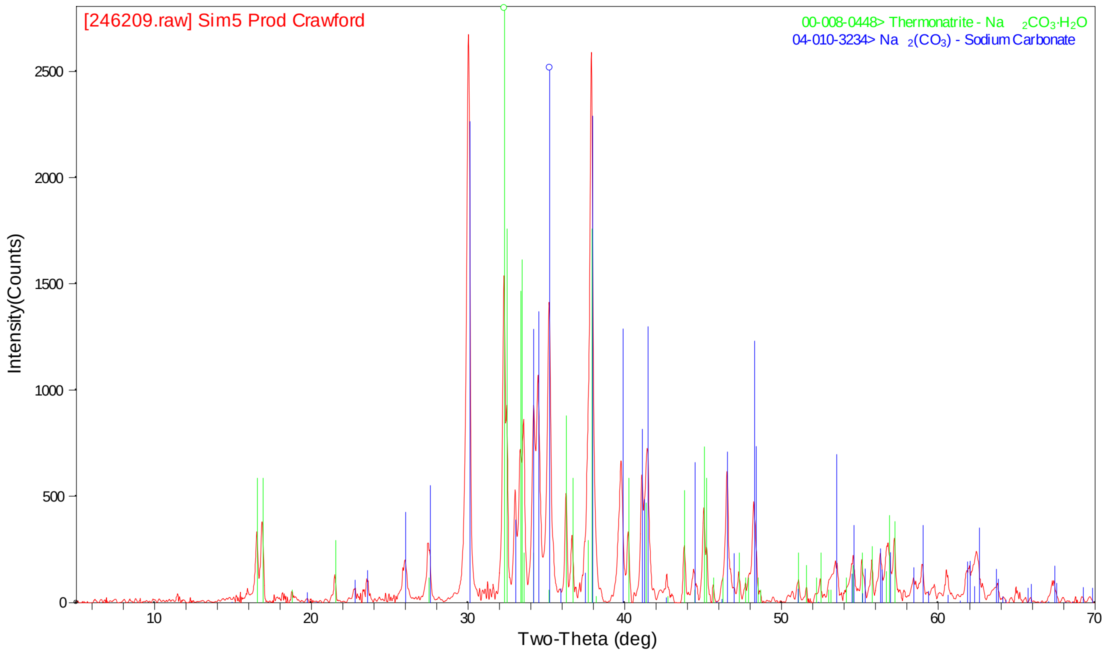
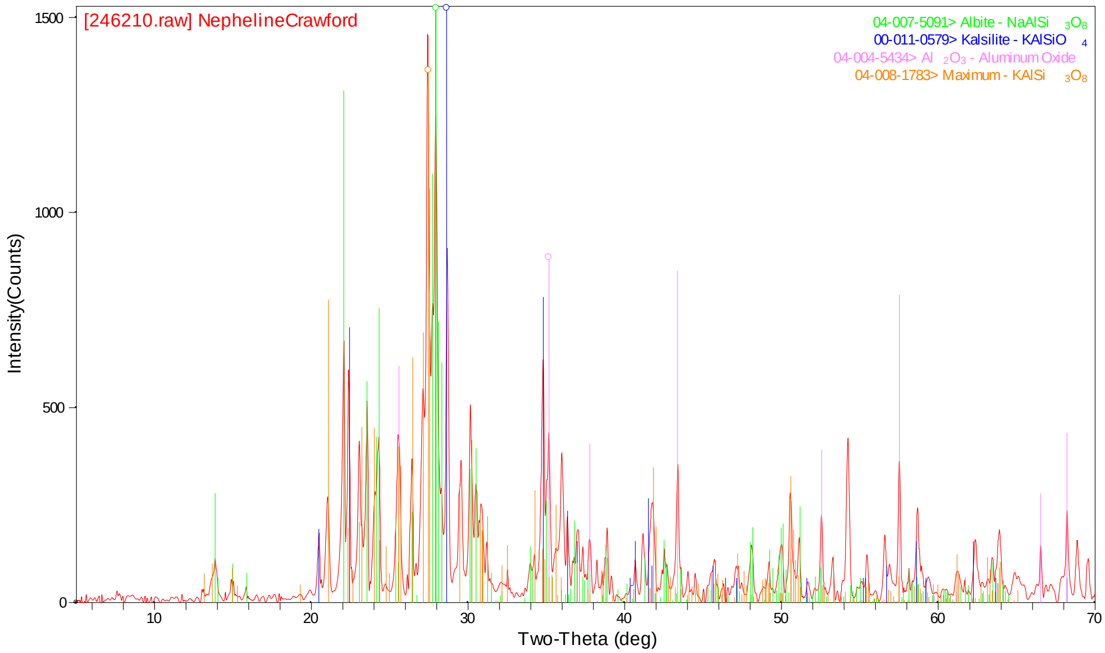


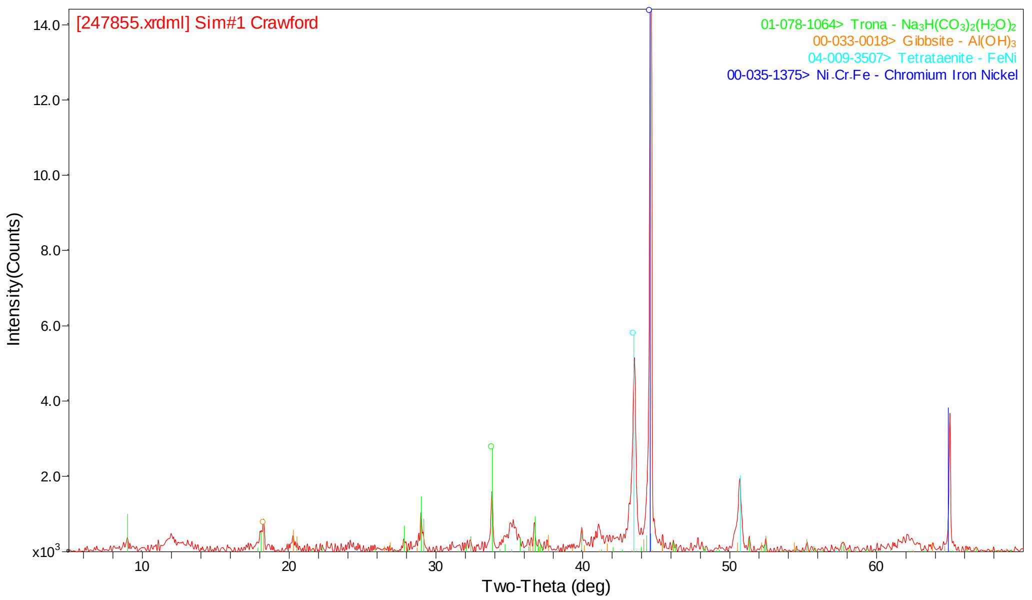
Simulant 4 Product XRD



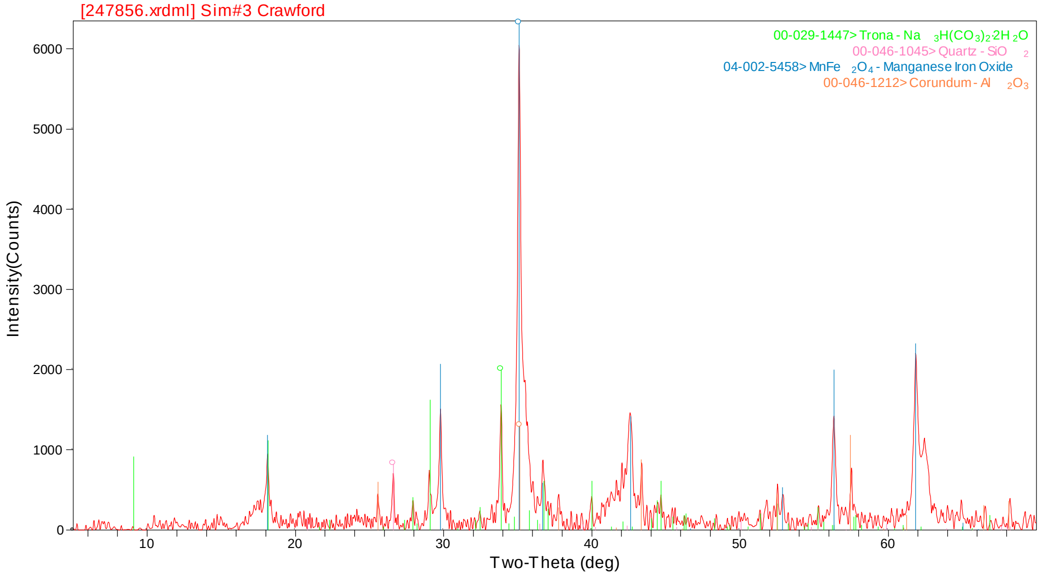
Simulant 5 Product XRD



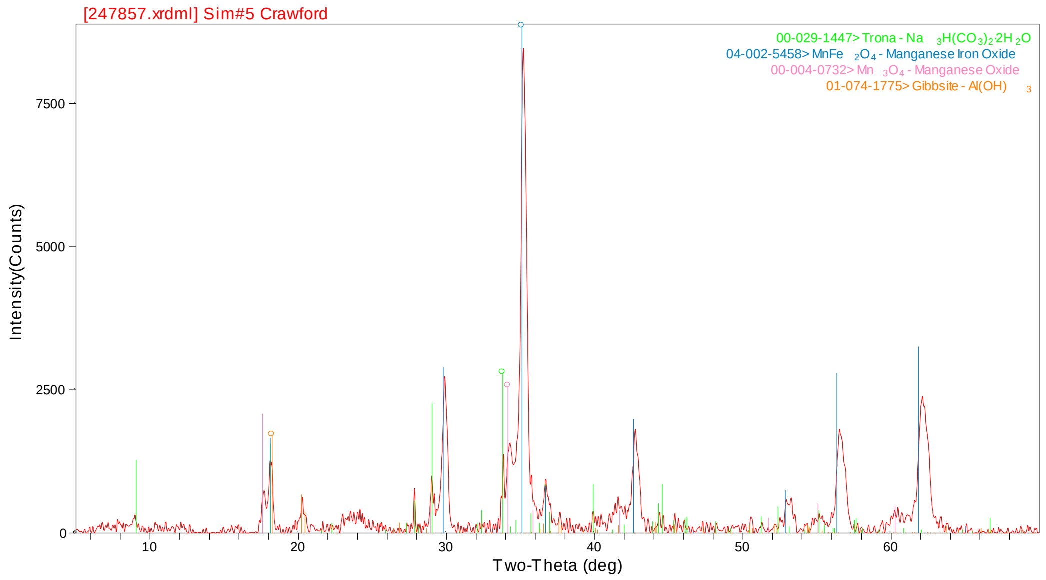
Nepheline Sealant Material After Heat Treatment XRD



Simulant 1 Insoluble Product XRD

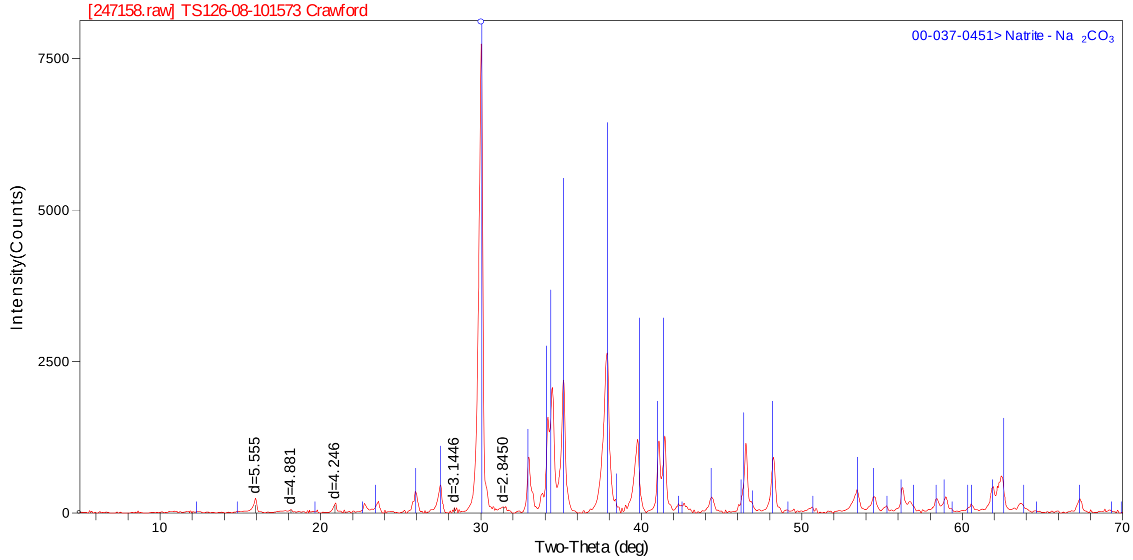


Simulant 3 Insoluble Product XRD

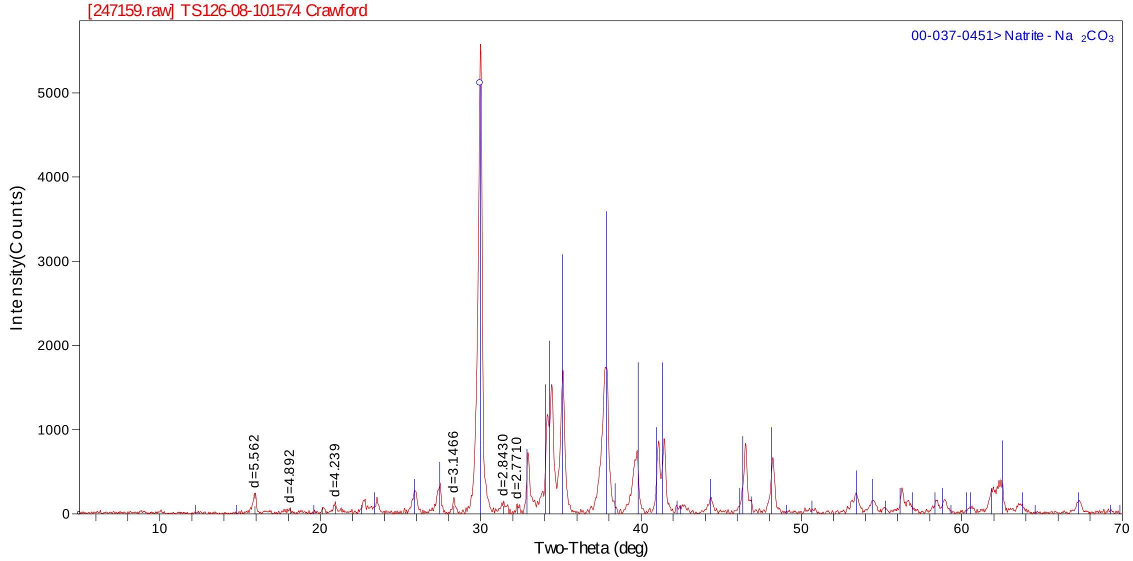


Simulant 5 Insoluble Product XRD

APPENDIX C. RADIOACTIVE PRODUCT XRD



Radioactive 1 Product XRD



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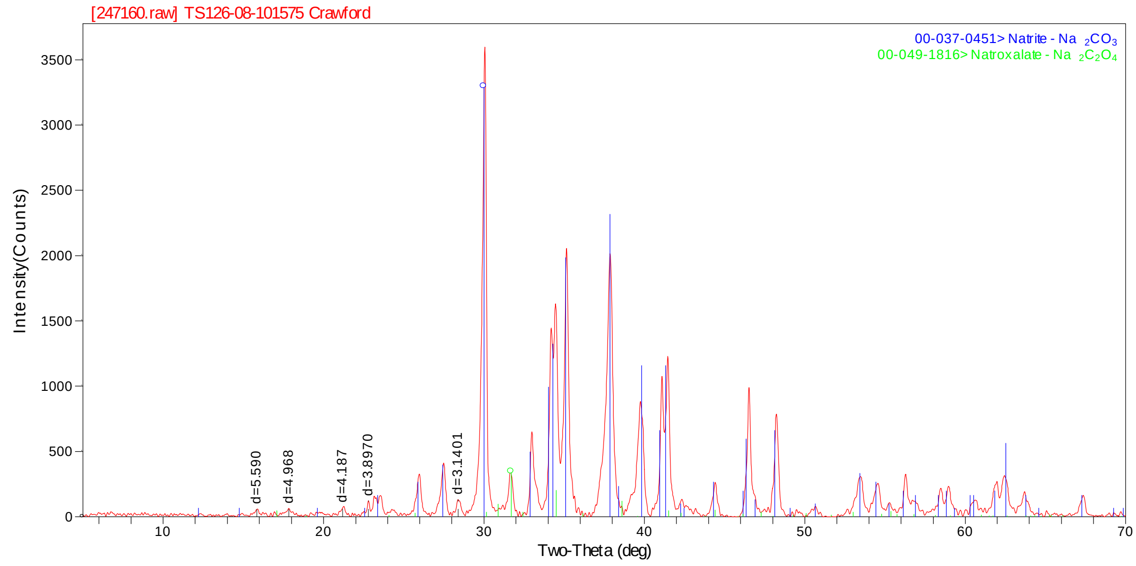
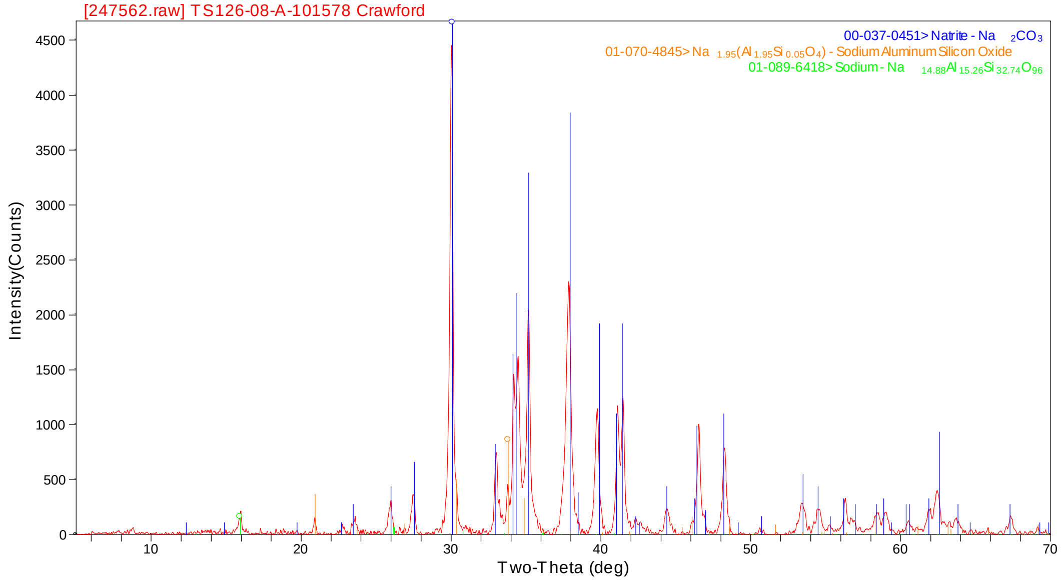
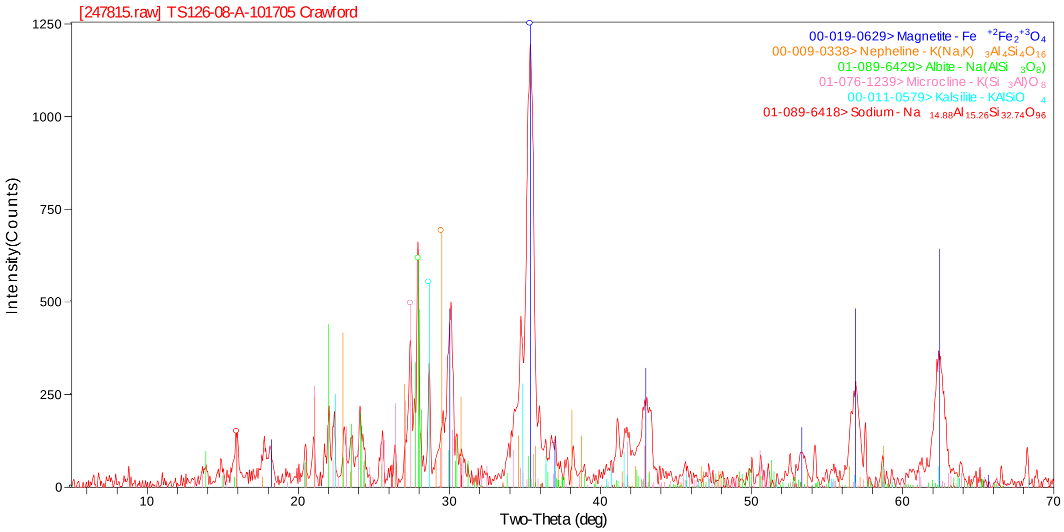


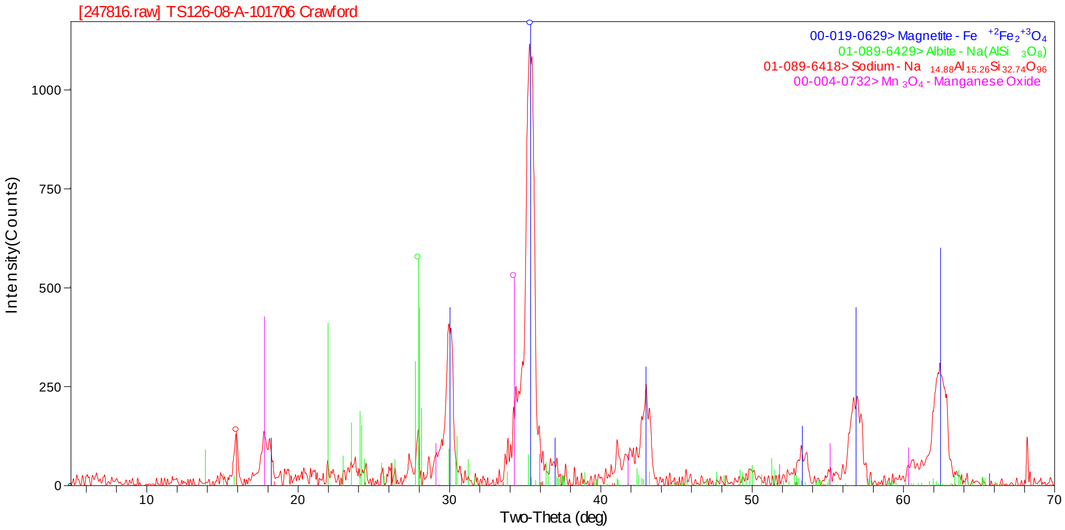
Radioactive 3 Product XRD



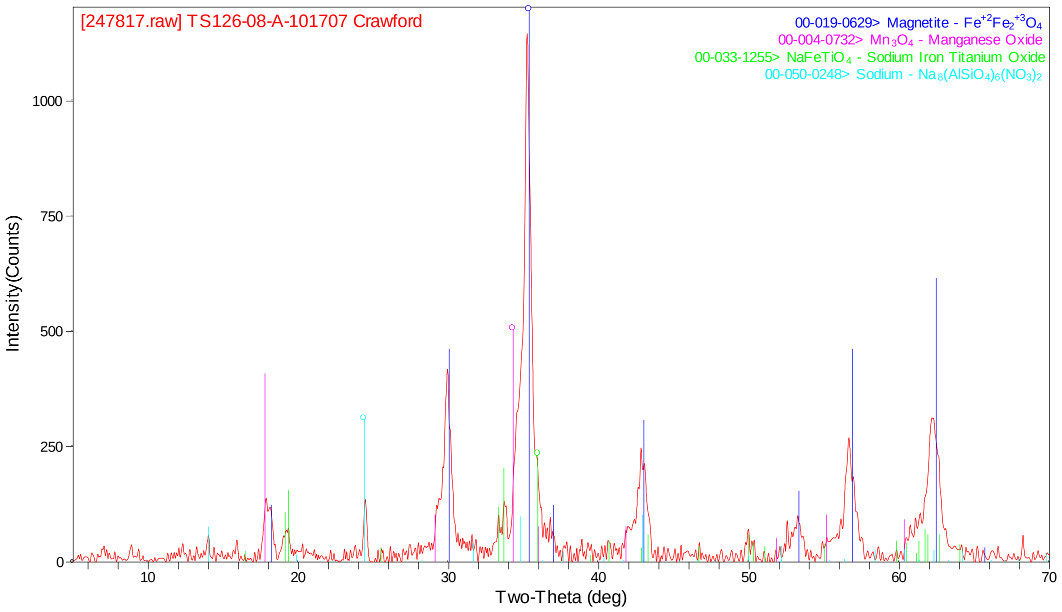
Radioactive 4 Product XRD



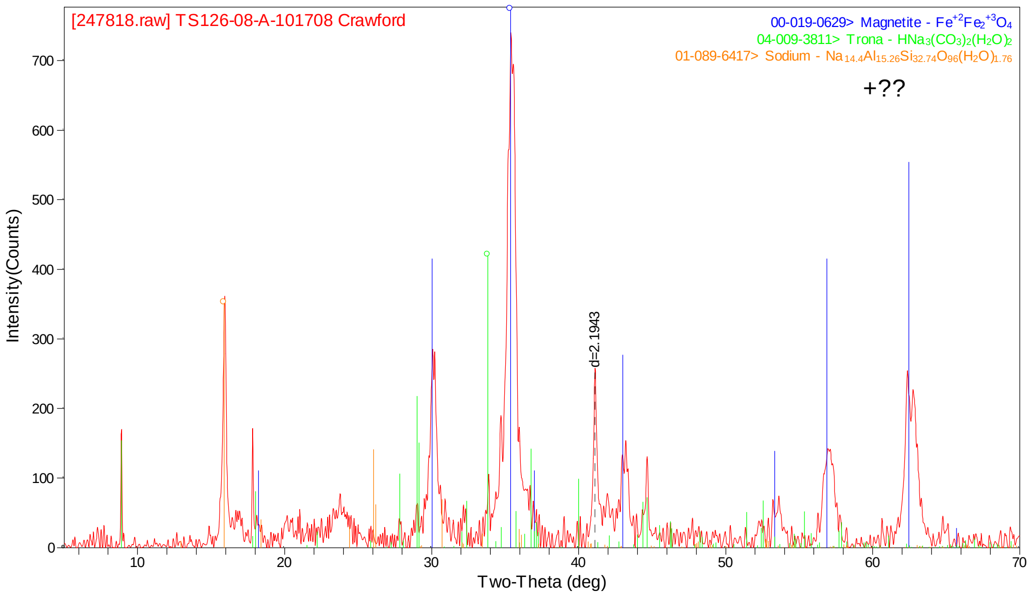
Radioactive 1 Insoluble Product XRD



Radioactive 2 Insoluble Product XRD



Radioactive 3 Insoluble Product XRD



Radioactive 4 Insoluble Product XRD

Distribution:

J. E. Marra, 773-A
J. C. Griffin, 773-A
A. B. Barnes, 999-W
D. A. Crowley, 999-W
C. C. Herman, 999-W
D. J. McCabe, 773-42A
C. M. Jantzen, 773-A
P. R. Burket, 773-42A
W. E. Daniel, 999-W
M. R. Williams, 786-5A
C. A. Nash, 773-42A
K. Adu-Wusu, 773-42A

S. D. Burke, 766-H
J. R. Lunn, 766-H
S. C. Shah, 766-H
M. J. Augeri, Jr., 766-H
C. I. Aponte, 766-H
D. L. McWhorter, 766-H
C. G. Lampley, 766-H
C. D. Hammond, 776-H