INEEL/EXT-01-01259

Characterization and Dissolution Kinetics Testing of Radioactive H-3 Calcine

T. G. Garn
T. A. Batcheller

September 2001

Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC

INEEL/EXT-01-01259

Characterization and Dissolution Kinetics Testing of Radioactive H-3 Calcine

T. G. Garn
T. A. Batcheller

September 2001

Idaho National Engineering and Environmental Laboratory
Idaho Falls, Idaho 83415

Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-99ID13727

SUMMARY

Characterization and dissolution kinetics testing were performed with Idaho radioactive H-3 calcine. Calcine dissolution is the key front-end unit operation for the Separations Alternative identified in the Idaho High Level Waste Draft EIS. The impact of the extent of dissolution on the feasibility of Separations must be clearly quantified.

Analytical fusion and SEM EDS elemental analyses were performed on the H-3 calcine. An estimation of the compounds in H-3 was made using these fusion results and based on previous thermodynamic modeling of calcine. The overall wt% for this estimation was within 8% of that determined from the analytical fusion and SEM results. Dissolution and kinetics testing experiments were performed. The calcine acid consumption coefficient was determined — **b** = 49.6 grams of H-3 dissolved per mol of acid consumed. Kinetics testing was performed at 60, 75, and 95ºC. Nearly complete dissolution of the H-3 calcine was achieved. Small liquid samples were drawn during the dissolution to determine the conversion kinetics of the elements in the calcine (based on the fusion data). The estimation of compounds in H-3 (based on the previous thermodynamic modeling) was used to back-calculate mass conversion from the elemental conversion kinetics data. Overall it was demonstrated that this approach is a reasonably valid technique for back-calculating mass conversion during dissolution. This is especially useful for handling kinetics testing with actual calcine—where attempting to obtain mass conversion data remotely at the early stages of dissolution (where it is noted that most of the dissolution occurs) is virtually impossible—and would require significant amounts of actual calcine. These kinetics results did reflect the trend that calcine conversion was accelerated with an increase in temperature. A reasonable Arrhenius analysis was not possible based on the limited kinetics results. The data also indicated that the alumina compounds in the H-3 were limiting the dissolution rate. Particle size distribution (PSD) analysis was desired, but was not performed due to the unavailability of the laser diffraction PSD analyzer.

ACKNOWLEDGMENTS

The authors wish to take this opportunity to thank Dr. R. S. Herbst and Mr. Arlin L. Olson for their expert review and input. Alan Olaveson is greatly appreciated for his tremendous effort in the preparation and performance of the fusion methods and dissolution experiments at RAL. Alan's unsurpassed remote manipulator skills enabled the non-routine kinetics dissolution testing to be completed without incident. Also, Dean Peterman for directing the fusion work at RAL. Thanks to Mr. Gary Gregston (INTEC Glass Shop) for providing dissolver fabrication services. The authors also wish to acknowledge the INTEC analytical department for their accurate and expeditious sample result analyses and reporting. Without the work ethic and dedication of these employees, this work would never have been accomplished.

CONTENTS

FIGURES

TABLES

Characterization and Dissolution Kinetics Testing of Radioactive H-3 Calcine

1. BACKGROUND AND INTRODUCTION

In 1995, a settlement agreement was reached between the State of Idaho and the U.S. Department of Energy. Sections of the agreement mandated treatment of high level radioactive calcine waste currently stored at the Idaho Nuclear Technology and Engineering Center (INTEC) at the Idaho National Engineering and Environmental Laboratory (INEEL). Treatment includes processing the calcine for transport to a national repository by the year 2035.

Radioactive calcine is the product of solidifying radioactive raffinates originating from nuclear fuel reprocessing activities previously conducted at INTEC. The calcination process converted liquid raffinates into granular solid material for volume reduction and safer interim storage. Numerous types of fuels were reprocessed at INTEC, resulting in a variety of calcine compositions. The calcine is stored in stainless steel bins encased in cylindrical concrete vaults known as Calcined Solids Storage Facilities (CSSFs). The CSSF structures are commonly referred to as binsets. There are seven binsets constructed at INTEC with six presently storing calcine. The current volume (August 2001) of calcine stored at INTEC is 4386 m^3.

Calcine dissolution is the key front-end unit operation of several separations' treatment options under consideration as documented in the Draft Environmental Impact Statement[1]. To support the investigation of proposed treatment alternatives, dissolved calcine solutions are used as feedstock for solid/liquid separations, ion exchange, and solvent extraction experiments performed in the INTEC Remote Analytical Laboratory (RAL). An understanding of the kinetics of calcine dissolution is required to design calcine dissolution equipment.

Nearing the end of calciner campaign H-3, the H-3 calcine bed material was sampled directly during calcination process operations in July 1993. Only bed material may be sampled during calciner operations. Note that the H-3 campaign resulted in calcination of the remaining volume of reprocessing raffinates. Six canisters filled with approximately 1kg samples each of H-3 calcine were stored in the Fluorinel Dissolution Process (FDP) waste loadout box at the INTEC New Waste Calcining Facility (NWCF). Approximately 150 grams of calcine from canister #5 was removed and sent to RAL and used for this experimental testing. This material represents the calcination product from a blend of a highly radioactive fluorinel reprocessing raffinate solution with a less radioactive Sodium Bearing Waste (SBW) solution resulting from solvent wash and equipment decontamination activities. The blend consisted of a six parts WM-188 (fluorinel) to one part WM-185 (sodium) volume ratio[2].

The bulk of the H-3 calcine sample was dissolved to provide a feedstock solution for solvent extraction testing. Dissolution kinetics testing was performed using the remaining material. This report documents the characterization and dissolution kinetics testing performed using the H-3 calcine.

2. EXPERIMENTAL

2.1 H-3 Characterization

Prior to performing kinetics testing, a detailed compositional analysis was completed for H-3 calcine. Three fusion methods performed in duplicate were used to determine solid elemental compositions. These methods use lithium tetraborate, sodium hydroxide, or sodium carbonate, dependent on which analyte is desired. Lithium tetraborate fusion is used for most metals and radioactive elements. Sodium hydroxide fusion is used for I-129, Tc-99, lithium, boron, fluoride, nitrate and sulfate. Sodium carbonate fusion is used for chloride and phosphate. Fusion analysis begins by mixing a measured mass of sample with the fusion fluxing compound at a 1:10 ratio, heating at high temperature in a furnace to form the flux melt, redissolving the melt in an appropriate solvent, and submitting the solvent matrix for typical liquid phase analyte analyses. These results provide the bulk of the composition information on the solid material.

Oxygen content in calcine is significant. Since oxygen can not be determined from the fusion methods, an RJ Lee Instruments® model Scanning Electron Microscope (SEM) was utilized to obtain an elemental analysis using energy dispersive spectrometry (EDS), which included oxygen. SEM photomicrographs were also utilized to provide morphological information of calcine particles.

X-Ray Diffraction (XRD) analysis requires an amount of material that greatly exceeds permissible radiological limits; therefore XRD analysis of H-3 calcine was not obtainable.

2.2 H-3 Dissolution Testing

Run H-3 radioactive calcine dissolution experiments were conducted in the Remote Analytical Laboratory (RAL) hot cell facility, which provides radiation shielding necessary to handle radioactive material remotely with manipulators. Using manipulators, RAL analysts assembled the dissolution setup using standard equipment. A typical dissolution experimental setup is shown in Figure 1. The standard equipment setup consists of a 1-liter glass dissolver, bimetallic thermometer, stirrer/hotplate, and reflux condenser. The dissolver was placed on a stirrer/hotplate with a reflux condenser inserted in the top of the dissolver allowing cooling water to reflux the acid vapors exiting the system.

The generic dissolution procedure consisted of adding a measured volume of nitric acid to the dissolver, heating to desired temperature, adding the measured mass of calcine, and observation of the dissolution for a set amount of time. At the end of the desired dissolution time, the solution was allowed to cool and any undissolved solids (UDS) were allowed to settle prior to filtering the solution. The filtered solution was transferred into an appropriately labeled bottle for use in solvent extraction testing.

Two sets of dissolution tests were performed: batch dissolutions to provide a liquid feed for the solvent extraction testing, and dissolution kinetics testing.

Figure 1. Remote dissolution equipment setup.

2.2.1 Dissolutions for solvent extraction testing

Three dissolution tests were performed to provide feed for the solvent extraction testing. All tests were performed at boiling temperature (using a reflux condenser) and a calcine to acid ratio of 1 gram/10 mLs 3M nitric acid for 1 hour. The dissolved solution was poured through a 0.45 µm pore size filter unit. The filtered solution was then recovered and used in the solvent extraction testing. The undissolved solids (UDS) from the first test were thoroughly water rinsed and then propanol washed three times (UDS resulting from the final two dissolutions were discarded). The washed UDS were allowed to air dry for a number of days before obtaining a final weight. The wt% calcine mass dissolved was determined using the following equation.

$$wt\%dissolution = \left[1 - \frac{UDS\ wt}{Initial\ Calcine\ wt}\right] * 100\%$$

2.2.2 Dissolution kinetics studies

Kinetics dissolution testing was performed on the remaining mass of H-3 calcine. Particle size distribution (PSD) measurements during dissolution of H-3 calcine were desired for coupling dissolving particle sizes to the chemical kinetics data. Due to technical difficulties, the laser diffraction PSD analyzer at the RAL was not available for this activity.

The dissolver setup in Figure 1 was used for the kinetics testing. Three dissolution kinetics tests were performed under similar conditions; 1 gram calcine to 300 milliliters of 3M nitric acid with a dissolution time up to 6 hours. Tests were performed at 60°, 75°, and 95°C. This testing was greatly hampered by the loss of a substantial amount of the material during attempts to transfer this calcine for this testing via the pneumatic transfer system from the NWCF to the RAL. The 60°and 95°C tests used a slightly lower calcine to acid ratio, because of the small mass of calcine remaining from previous dissolutions. Their ratios were 0.316 grams and 0.318 grams to 120mLs acid respectively.

Dissolution tests were initiated by measuring and adding the required volume of 3M nitric acid to the dissolver. Calcine was then weighed using the in-cell balance, which has a precision of ±1mg. The nitric acid was heated to the desired temperature as was indicated on the readout of the bimetallic thermometer. The weighed calcine was added to the heated nitric acid when the desired temperature stabilized. The sampling sequence was started immediately thereafter.

Sampling equipment was constructed outside the hot cell prior to performing the sampling sequence for each dissolution testing. The construction consisted of duct taping 10mL Luer-Lok™ syringes with attached 0.45µm Acrodisk® filters to 15mL polyethylene sample bottle openings (to direct filtered solution into sample bottle). The constructed sample devices were placed in and held upright by a tube sample tray and transferred into the cell. The plungers were removed from each syringe and placed next to the sample tray. A 1-5mL Oxford® pipetter was used to extract 1mL aliquots from the dissolving solution, which were directly pipetted into a sampling device (the pipetter and syringe filter are shown in Figure 1). The dissolved mixture was immediately filtered through the Acrodisk® filter using the plunger and captured in the 15mL sample bottle. Liquid samples were pulled from the solution as each dissolution progressed. Five samples were extracted within the first hour of each test; the sixth taken at one hour for each test; the seventh taken at 6 hours for the 75°C test and at 3 hours for the 60°and 95°C tests; and the eighth taken at 6 hours for the 60°and 95°C tests. The sampling matrix for this testing is presented in Table 1.

Table 1. Sampling sequence for the kinetic dissolution testing.

TEST	Sample #	1	2	3	4	5	6	7	8
60° C	**Time (min)**	4	7	10	20	30	60	180	370
	Temp.(C)	56.9	58.2	59.5	59.6	56.6	61.2	58.5	62.5
75° C	**Time (min)**	2	5	10	20	30	60	360	N/A
	Temp. (C)	72.3	74.5	76.0	73.2	75.6	75.4	74.2	N/A
95° C	**Time (min)**	3	5	10	20	30	60	153	360
	Temp. (C)	85.0	88.5	95.0	95.5	96.3	93.3	97.3	99.5

Most temperature values in the sampling sequence table indicate the inability to maintain the solution at the target temperature during sampling efforts. Every time the dissolver solution was exposed to the cell ambient temperature by opening the dissolver sampling port, the temperature of the solution would immediately decrease. To combat temperature fluctuations, the temperature would be increased to allow for cooling during sampling efforts.

The liquid samples were submitted and analyzed for the metals that comprise the majority of the composition of the H-3 calcine. The results were used to determine elemental conversion (based on the fusion results) with respect to time. The elemental conversion was then used to estimate compound and mass conversion.

After samples had been drawn, the remaining dissolved solutions were poured into tared 0.45µm Cole-Parmer filter units to determine weight percent calcine dissolved. The undissolved solids (UDS) were allowed to air-dry before re-weighing the filter units containing UDS.

3. RESULTS AND DISCUSSION

3.1 H-3 Characterization Results

A detailed composition of the H-3 calcine was determined. The analytical composition results for the duplicate fusion methods performed on the H-3 calcine are presented in Table 2.

Table 2. Analytical fusion results for H-3 calcine.

	Sample Labels	
ANALYTE	**0CK69**	**0CK70**
METALS (WT%)		
ALUMINUM	1.03E+01	9.32E+00
ANTIMONY	ND	2.74E-02
ARSENIC	ND	ND
BARIUM	1.63E-02	1.97E-02
BERYLLIUM	ND	ND
BORON	7.01E-01	7.17E-01
CADMIUM	3.88E+00	3.96E+00
CALCIUM	2.59E+01	2.61E+01
CERIUM	ND	ND
CESIUM	<0.05	<0.05
CHROMIUM	1.06E-01	1.50E-01
COBALT	ND	ND
GADOLINIUM	ND	ND
IRON	3.68E-01	6.23E-01
LITHIUM	ND	ND
MAGNESIUM	4.47E-01	5.24E-01
MANGANESE	8.83E-02	8.99E-02
MERCURY	<1.04E-02	<1.19E-02
MOLYBDENUM	ND	ND
NICKEL	7.01E-02	9.64E-02
NIOBIUM	1.38E-01	1.33E-01
PALLADIUM	ND	ND
PHOSPHOROUS	3.87E-01	ND
POTASSIUM	6.61E-01	6.84E-01
RUTHENIUM	ND	ND
SELENIUM	ND	ND
SILICON	9.24E-01	2.49E-01
SODIUM	2.72E+00	2.88E+00
STRONTIUM	3.55E-02	3.18E-02
SULFUR	1.43E+00	1.49E+00
THALLIUM	ND	ND
TIN	1.05E-01	1.21E-01
TITANIUM	ND	3.29E-02
URANIUM	ND	ND
VANADIUM	ND	ND
ZINC	1.63E-02	3.94E-02
ZIRCONIUM	7.95E+00	6.68E+00

	Sample Labels	
ANALYTE	**0CK69**	**0CK70**
RADIOACTIVE CONSTITUENTS (dps/gm)		
AM241	3.46E+04 +- 3.8E+03	3.33E+04 +- 3.7E+03
CO60	2.25E+05 +- 1.2E+04	2.35E+05 +- 1.3E+04
CS134	2.34E+05 +- 2.0E+04	2.84E+05 +- 1.5E+04
CS137	8.08E+07 +- 2.3E+06	8.73E+07 +- 3.3E+06
EU154	6.38E+05 +- 5.8E+04	6.95E+05 +- 5.7E+04
EU155	2.80E+05 +- 3.5E+04	ND
I129	<2.136E+04	<3.555E+04
NB94	2.95E+04 +- 4.2E+03	1.64E+04 +- 1.5E+03
PU238	1.33E+06 +- 1.2E+05	1.22E+06 +- 1.1E+05
PU239	2.44E+04 +- 3.0E+03	1.40E+04 +- 1.8E+03
TC99	1.31E+06 +- 1.38E+04 pCi/g	4.01E+06 +- 1.42E+04 pCi/g
TOTAL SR	7.55E+07 +- 5.7E+06	7.46E+07 +- 5.5E+06
U234	1.17E+04+-2.54E+03	2.36E+03+-6.68E+02
U235	8.35E+01+-1.33E+02	5.25E+01+-8.47E+01
U236	ND	5.11E+01+-8.22E+01
U238	ND	4.17E+01+-6.77E+01
ANIONS (mg/gm)		
CHLORIDE	8.09E-02	5.30E-01
FLUORIDE	7.77E+01	9.12E+01
NITRATE	6.67E+01	6.82E+01
PHOSPHATE	ND	ND
SULFATE	5.68E+01	6.87E+01

ND= Analyte not detected or below detection limit. Less than values indicate result is at or below analytical detection
Log# 0011061 NaOH fusion; Log#0011062 $Li_2B_4O_7$ fusion; Log#0012182 Na_2CO_3 fusion.

The major components of H-3 calcine include calcium, aluminum, zirconium, sodium and cadmium. Near the end of the H-3 campaign, excess calcium nitrate was added to chemically combine all fluoride, chloride, sulfate, and phosphate in the aqueous feed stream to the calciner[2]. Aluminum nitrate was added to prevent bed agglomeration during calcination. Zirconium was present in the fluorinel reprocessing raffinate solution. Sodium was present in the SBW portion of the feed and cadmium resulting from additions made during zirconium fuel dissolution activities for neutron poison. The remainder of the elements resulted from the SBW and reprocessing raffinates, or a combination of the two. The total of the fusion analyzed elements is approximately 60 wt%. The remaining wt% was assumed to be oxygen obviously due to the oxides formed during calcination. Oxygen can not be analyzed using the fusion methods.

Limited oxygen compositions were determined using the SEM EDS elemental analysis method. Two analyses were performed, each at a separate location on the H-3 sample prep. The elemental results are presented in Table 3.

Table 3. SEM EDS results for H-3 calcine.

Location 1 Log#0105172

Element	Wt. Pct.	At. Pct.	Std. Dev.	MDL
O	41.53	60.26	1.02	0.09
F	5.93	7.25	1.01	0.4
Na	12.45	12.57	0.78	0.32
Mg ?	1.11	1.06	0.45	1.03
Al	14.81	12.75	0.84	0.29
P ?	0	0	0	0.6
K	3.06	1.82	0.94	0.42
Ca ?	0	0	0	0.56
Fe ?	0.65	0.27	0.29	1.21
Zr	8.32	2.12	0.58	0.37
Mo ?	3.25	0.79	0.97	0.73
Cd ?	0.75	0.16	0.33	1.31
Total	100			

Location 2

Element	Wt. Pct.	At. Pct.	Std. Dev.	MDL
O	34.39	60.52	1.08	0.14
F ?	0.52	0.77	0.21	1.84
Na	7.94	9.72	0.86	0.54
Mg ?	1.85	2.14	0.61	0.97
Al	14.94	15.59	0.78	0.35
P ?	0	0	0	0.67
K ?	0.33	0.24	0.13	1.81
Ca ?	0	0	0	0.68
Cr ?	0.35	0.19	0.14	1.71
Fe ?	0.26	0.13	0.11	2.5
Zr	8.42	2.6	0.76	0.45
Mo	23.44	6.88	0.99	0.35
Cd ?	1.25	0.31	0.44	1.45
Total	100			

The SEM elemental analysis was used primarily to obtain an oxygen wt% result. Note that numerous elemental results in Table 3 are coupled with a question mark. This nomenclature indicates the normalized results are approaching or below the minimum detection limit (MDL) values which are shown in the table for these analytes.

The element with the highest wt% from the fusion data using the ICP method in Table 2 is calcium at 26 wt%, however as seen in Table 3, the method reports zero wt% for calcium. This discrepancy demonstrated the inaccuracy of the EDS method for the non-oxygen elemental analyses. Communications with the analytical analyst confirmed that the ICP method is a more accurate method than the SEM EDS for determining metals composition[3].

The photomicrographs from the SEM analyses performed on the H-3 calcine are presented in Figure 2; the composition spectra are also shown.

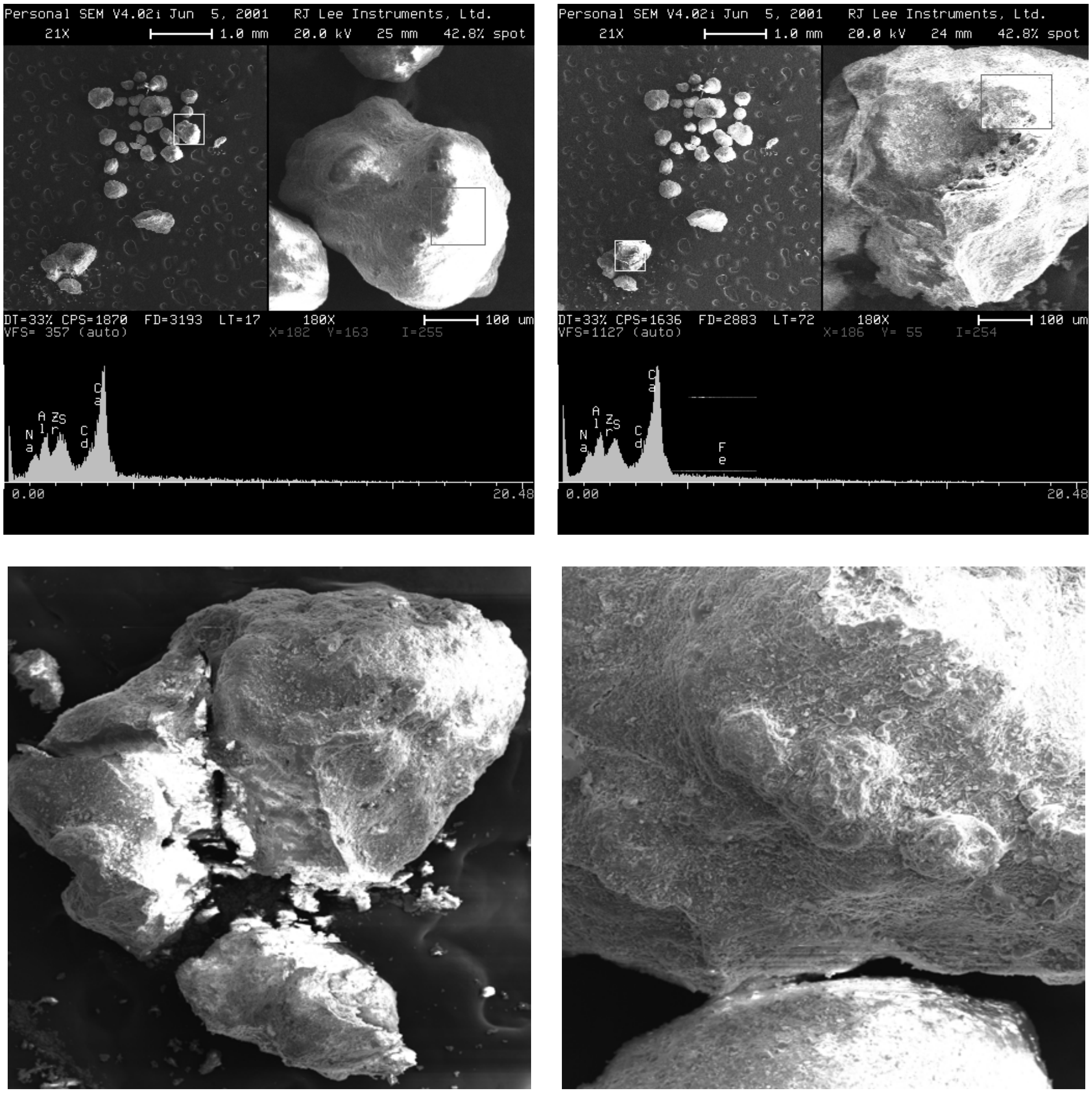

Figure 2. SEM photomicrographs of H-3 calcine particles.

The calcium, aluminum, zirconium, sodium, and cadmium amounts shown in the composition spectra, reveals excellent agreement with the fusion wt% results. The element with the highest wt% in the calcine is calcium; aluminum and zirconium follow at nearly equal wt%, and sodium and cadmium are the lowest wt% of the SEM elemental spectra and are also nearly equal wt%. The photomicrographs do not show substantial porosity in H-3 calcine.

3.1.1 Estimate of compounds in H-3 calcine

Chemical compound composition of the H-3 calcine was estimated using the fusion results (average of Table 2 fusion values was used), and based on the logic presented in Reference 4. The estimated compound wt%, the order of compound formation, and the calculated oxygen wt% are presented in Table 4.

Table 4. H-3 compound formation with final weight percent sum.

Compound	Formula weight	wt%	Specie tracking
$NaNO_3$	84.99	6.828762	1.06 wt% NO_3 remaining
KNO_3	101.11	1.147767	
CaF_2	78.10	17.36697	All F^- consumed
Na_3AlF_6	210.00	No F^-	
KF	58.10	No F^-	
K_2SO_4	174.27	0.51033	all K used, 6.0 wt% SO_4 remains
Na_2SO_4	142.10	2.940852	all Na used, 4.01 wt% SO_4 remains
$CaSO_4$	136.20	5.683267	all SO_4 used, 15.42 wt% Ca remains
$CdSO_4$	208.50	No SO_4^{2-}	
KCl	74.56	No K	
NaCl	58.50	No Na	
$CaCl_2$	111.10	0.047726	all Cl^- used, 15.4 wt% Ca remains
$NaAlO_2$	82.00	No Na	Oxygen concentration calculated from oxygen containing compounds = 29.57 weight percent.
Na_2O	62.00	No Na	
$KAlO_2$	98.10	No K	
K_2O	94.20	No K	
Al_2O_3	102.00	18.51637	
CaO	56.10	21.54464	
CdO	128.40	4.479681	
ZrO_2	123.20	9.879005	
B_2O_3	69.60	2.287778	
Fe_2O_3	159.60	0.708713	
Cr_2O_3	152.00	0.186864	
BaO	153.30	0.020121	
MgO	40.30	0.805247	
MnO_2	86.90	0.141006	
NiO	74.70	0.105942	
Nb_2O_5	265.81	0.193717	
SiO_2	60.10	1.254546	
SrO	103.60	0.039792	
SnO_2	150.70	0.142933	
ZnO	81.40	0.034704	
	Total sum wt%	94.87	

The spreadsheet used to determine the overall wt% of the H-3 calcine from the averaged fusion and averaged oxygen analytical SEM results is presented in the Appendix A, Table 11. The overall wt% result shows a 102.8 total wt% for the H-3 analytically determined calcine wt%; this is approximately an 8% relative difference from that of the 94.9% compound estimation value. This 8% discrepancy is due to the difference in the 37.9 wt% oxygen from the SEM results and the 29.6 wt% oxygen from the compound estimation results. To obtain an independent and more accurate estimation of compounds in the calcine, thermodynamic modeling of the calcination process, based on the liquid feed chemistry is recommended[5]. This approach was taken in the characterization and dissolution kinetics work with the non-radioactive RSH-1 alumina-type pilot plant calcine[6].

3.2 Dissolution and Kinetics Testing Results

3.2.1 Dissolutions for solvent extraction testing results

A total of 114 grams of H-3 calcine was dissolved in 2.9M nitric acid at a ratio of 1gram calcine to 10mLs acid. The calcine/acid slurry was heated to boiling with constant reflux for 60 minutes. Under these conditions 95.8 wt. % of the calcine mass was dissolved. Titration of the final dissolved solution indicated the acid concentration to be 0.99M. The calcine acid consumption coefficient, **b**, was calculated to be 49.6 grams of H-3 calcine dissolved per mol of acid consumed.

3.2.2 Dissolution kinetics testing results

Weight percent dissolved determinations indicated greater than 99% of the calcine was dissolved after 6 hours in each of the three kinetics tests. Weight percent dissolved at 75°C was calculated to be 99.1%. The 60°and the 95°C tests' UDS measurements indicated no detectable UDS (within analytical in-cell balance precision) were filtered from the solutions with the filter units. UDS removed with the 1mL sample aliquots taken from the solutions during testing were considered as negligible. Visual observation of the used syringe filters and the filter units used for filtering final dissolved solutions indicated complete dissolution. Between 7 and 8mLs were taken from the solutions for sampling purposes, resulting in a maximum net loss of 7% volume (8mLs/120mLs for 60°and 95°C tests) leaving a 93% remaining volume of filterable solution for UDS measurements. However in this reporting, volume reductions were also assumed negligible (i.e. volume corrections were not used in calculations).

Elemental analytical results for all liquid samples taken during the three kinetics dissolution tests is presented in Tables 12, 13, and 14 in Appendix A. Elemental conversion was calculated from these results and the averaged fusion data from Table 11 using the following equation:

$$X_{element} = \frac{element_{conc.} \times acid\ volume}{calcine_{initial} \times \frac{wt\%_{element}}{100\%}}$$

where:

$X_{element}$ = calculated elemental conversion

$element_{conc.}$ = analytical result in µg/mL from Tables 12, 13 and 14.

acid volume = volume of nitric acid added for dissolution

$calcine_{initial}$ = mass of calcine added to dissolution

$wt\%_{element}$ = averaged fusion result from Table 11

The calculated elemental conversion results are presented in Table 5, Table 6, and Table 7. Except for aluminum and sulfur, the results indicated 100% elemental conversion (i.e. conversion = 1.0) was reached within the first 10 minutes of dissolution at the three temperatures. Aluminum was 100% dissolved after 3 hours at 95°C but was not completely dissolved at 60 or 75°C while sulfur did not reach 100% conversion at any of the three temperatures.

Table 5. Elemental conversions at 60°C.

Sample Time	4 min	7 min	10 min	20 min	30 min	60 min	180 min	370 min
Aluminum	0.821	0.851	0.848	0.853	0.856	0.867	0.898	0.932
Boron	1.016	1.023	1.065	1.046	1.069	1.024	1.104	1.095
Cadmium	1.053	0.969	1.144	1.170	1.148	1.129	1.159	1.018
Calcium	0.953	0.928	1.131	1.165	1.156	1.064	1.137	1.041
Sulfur	0.748	0.649	1.109	1.074	1.079	1.134	1.134	1.005
Zirconium	0.974	0.942	1.065	1.105	1.080	1.092	1.095	1.025
Sodium	0.978	1.004	0.976	1.004	1.011	1.001	0.967	0.965
Potassium	1.052	0.950	0.950	1.012	0.989	1.001	0.961	1.069

Table 6. Elemental conversions at 75°C.

Sample Time	2 min	5 min	10 min	20 min	30 min	60 min	360 min
Aluminum	0.790	0.851	0.878	0.868	0.881	0.904	0.961
Boron	1.030	1.028	1.073	1.069	1.076	1.089	1.132
Cadmium	1.025	1.082	1.029	1.080	1.036	1.036	1.060
Calcium	0.986	1.071	1.017	1.067	1.051	1.065	0.966
Sulfur	0.856	0.874	0.771	0.845	0.837	0.851	0.805
Zirconium	0.967	1.020	0.993	1.020	1.013	1.018	1.022
Sodium	0.985	0.993	0.995	1.004	0.978	0.993	1.020
Potassium	0.939	0.939	0.953	0.975	0.930	0.921	0.930

Table 7. Elemental conversions at 95°C.

Sample Time	3 min	5 min	10 min	20 min	30 min	60 min	153 min	360 min
Aluminum	0.872	0.877	0.909	0.930	0.945	0.971	1.016	1.047
Boron	1.072	1.095	1.102	1.122	1.121	1.139	1.185	1.344
Cadmium	1.059	1.106	1.043	1.092	1.095	1.105	1.131	1.168
Calcium	1.093	1.079	1.082	1.113	1.093	1.110	1.099	1.227
Sulfur	0.869	0.885	0.773	0.912	0.891	0.902	0.864	0.968
Zirconium	1.012	1.024	1.031	1.034	1.016	1.052	1.024	1.076
Sodium	1.074	1.059	1.070	1.054	1.039	1.120	1.102	1.216
Potassium	0.997	1.008	0.980	0.986	0.963	1.025	1.048	1.177

3.2.3 Back-calculation of mass conversion

Compound conversion was back-calculated at each temperature and sample time using the following equation:

$$X_{compound} = \left[X_{elemental} \times compound\ wt\%\right]$$

where:

$X_{compound}$ = compound conversion at time T

$X_{elemental}$ = conversion of related element at time T

Compound wt% = estimated compound wt% from Table 4.

These compound conversions were summed to obtain a compound wt% dissolved at each sample time. Due to resource constraints, analysis of all elements (all corresponding fusion elements) were not requested on the liquid phase samples. A normalized estimated mass conversion for each temperature and sample time was calculated using the following equation:

$$X_{mass} = \frac{\sum wt\%}{\sum initialwt\%}$$

where:

X_{mass} = estimated mass conversion at time T

Σ wt% = sum of compound wt%'s at time T

Σ initial wt% = sum of initial total compound wt %'s from Table 4 (91.23 wt%)

The compound conversion data and the normalized mass conversions at each temperature and sample time are presented in Table 8, Table 9, and Table 10.

These estimated mass conversions were used to generate an Arrhenius plot. A reasonable Arrhenius analysis was not attained with these limited kinetics results.

Table 8. Compound conversion at 60°C with time.

Initial compound wt% = 91.23

Sample Time	$NaNO_3$	KNO_3	CaF_2	K_2SO_4	Na_2SO_4	$CaSO_4$	$CaCl_2$	Al_2O_3	CaO	CdO	ZrO_2	B_2O_3	Total Sum	Normalized conversion
4 min	6.68	1.21	16.55	0.54	2.88	5.41	0.05	15.21	20.53	4.72	9.62	2.32	85.70	0.94
7 min	6.86	1.09	16.11	0.48	2.95	5.27	0.04	15.76	19.99	4.34	9.31	2.34	84.56	0.93
10 min	6.66	1.09	19.65	0.48	2.87	6.43	0.05	15.70	24.37	5.13	10.52	2.44	95.39	1.05
20 min	6.86	1.16	20.23	0.52	2.95	6.62	0.06	15.80	25.10	5.24	10.92	2.39	97.85	1.07
30 min	6.90	1.14	20.08	0.50	2.97	6.57	0.06	15.85	24.91	5.14	10.67	2.45	97.24	1.07
60 min	6.84	1.15	18.47	0.51	2.94	6.05	0.05	16.06	22.92	5.06	10.79	2.34	93.17	1.02
180 min	6.61	1.10	19.74	0.49	2.84	6.46	0.05	16.62	24.49	5.19	10.81	2.53	96.94	1.06
360 min	6.59	1.23	18.07	0.55	2.84	5.91	0.05	17.25	22.42	4.56	10.13	2.50	92.09	1.01

Table 9. Compound conversion at 75°C with time.

initial compound wt% = 91.23

Sample Time	$NaNO_3$	KNO_3	CaF_2	K_2SO_4	Na_2SO_4	$CaSO_4$	$CaCl_2$	Al_2O_3	CaO	CdO	ZrO_2	B_2O_3	Total Sum	Normalized conversion
2 min	6.72	1.08	17.13	0.48	2.90	5.61	0.05	14.62	21.25	4.59	9.56	2.36	86.33	0.95
5 min	6.78	1.08	18.60	0.48	2.92	6.09	0.05	15.76	23.07	4.85	10.08	2.35	92.10	1.01
10 min	6.80	1.09	17.66	0.49	2.93	5.78	0.05	16.26	21.91	4.61	9.81	2.45	89.84	0.98
20 min	6.86	1.12	18.54	0.50	2.95	6.07	0.05	16.08	23.00	4.84	10.07	2.45	92.51	1.01
30 min	6.68	1.07	18.25	0.47	2.88	5.97	0.05	16.32	22.63	4.64	10.01	2.46	91.43	1.00
60 min	6.78	1.06	18.49	0.47	2.92	6.05	0.05	16.73	22.94	4.64	10.06	2.49	92.68	1.02
360 min	6.97	1.07	16.78	0.47	3.00	5.49	0.05	17.79	20.81	4.75	10.10	2.59	89.86	0.98

Table 10. Compound conversion at 95°C with time.

initial compound wt% = 91.23

Sample Time	$NaNO_3$	KNO_3	CaF_2	K_2SO_4	Na_2SO_4	$CaSO_4$	$CaCl_2$	Al_2O_3	CaO	CdO	ZrO_2	B_2O_3	Total Sum	Normalized conversion
3 min	7.33	1.14	18.99	0.51	3.16	6.21	0.05	16.14	23.55	4.74	9.62	2.45	93.91	1.03
5 min	7.23	1.16	18.74	0.51	3.12	6.13	0.05	16.24	23.25	4.96	9.31	2.50	93.21	1.02
10 min	7.31	1.12	18.79	0.50	3.15	6.15	0.05	16.83	23.31	4.67	10.52	2.52	94.92	1.04
20 min	7.20	1.13	19.34	0.50	3.10	6.33	0.05	17.21	23.99	4.89	10.92	2.57	97.23	1.07
30 min	7.10	1.11	18.99	0.49	3.06	6.21	0.05	17.50	23.55	4.90	10.67	2.56	96.19	1.05
60 min	7.65	1.18	19.28	0.52	3.29	6.31	0.05	17.98	23.91	4.95	10.79	2.60	98.51	1.08
153 min	7.53	1.20	19.08	0.53	3.24	6.24	0.05	18.82	23.67	5.07	10.81	2.71	98.96	1.08
360 min	8.30	1.35	21.31	0.60	3.57	6.97	0.06	19.39	26.43	5.23	10.13	3.07	106.42	1.17

It was demonstrated that this is a reasonably valid technique for back-calculating mass conversion during dissolution. This is especially useful for handling kinetics testing with actual calcine—where attempting to obtain mass conversion data remotely at the early stages of dissolution (where it is noted that most of the dissolution occurs[6,7]) is virtually impossible—and would require a significant amount of calcine.

For this testing, it was anticipated that some detectable undissolved calcine mass would remain at the end-point of these tests, so that a comparison between the experimentally determined mass conversion and the back-calculated mass conversion could be made. Because of the small calcine mass available for these dissolutions (due to the substantial loss of material during the transfer attempts, as mentioned previously), this comparison could not be made with this test data. To alleviate this shortcoming in the future, a larger calcine to acid volume will be used.

These limited kinetics results did reflect the trend that calcine conversion was accelerated with an increase in temperature. The data also indicated that the alumina compounds were limiting the dissolution rate. The alumina phase in the calcine was not determined. The larger calcine to acid volume should provide better defined kinetics data for the validation of the technique developed here. From the final conversion results, it is likely that alumina compounds existed as predominately soluble phases.

4. CONCLUSIONS

The conclusions based on the results of this characterization and dissolution kinetics with radioactive H-3 calcine work follow:

1. Analytical fusion methods and SEM EDS elemental analyses were performed on the H-3 calcine. An estimation of the compounds in H-3 was made based on previous thermodynamic modeling. The overall wt% for this estimation was within 8% of that determined from the analytical fusion and SEM results.

2. Dissolution and kinetics testing experiments were performed:

   - The calcine acid consumption coefficient was determined — **b** = 49.6 grams of H-3 dissolved per mole of acid consumed.

   - Kinetics testing was performed at 60, 75, and 95ºC. Complete dissolution of the H-3 calcine was achieved. Small liquid samples were drawn during the dissolution to determine the conversion kinetics of the elements in the calcine (based on the fusion data). The estimation of compounds in H-3 (based on previous thermodynamic modeling) was used to back-calculate mass conversion from the elemental conversion kinetics data. Overall it was demonstrated that this approach is a reasonably valid technique for back-calculating mass conversion during dissolution. This is especially useful for handling kinetics testing with actual calcine—where attempting to obtain mass conversion data remotely at the early stages of dissolution (where it is noted that most of the dissolution occurs) is virtually impossible—and would require significant amounts of actual calcine.

   - These kinetics results did reflect the trend that calcine conversion was accelerated with an increase in temperature. A reasonable Arrhenius analysis was not possible based on the limited kinetics results.

   - The data also indicated that the alumina compound in the H-3 was limiting the dissolution rate. The compound phase in the calcine could not be determined.

   - From the final conversion results, it is likely that alumina compounds existed as predominately soluble phases.

   - Particle size distribution (PSD) analysis was desired but was not performed due to the unavailability of the laser diffraction PSD analyzer.

5. REFERENCES

1. U.S. Department of Energy, “Idaho High-Level Waste and Facilities Disposition Draft Environmental Impact Statement”, DOE/EIS-0287D, December 1999.

2. B. J. Newby, B. H. O’Brien, “Summary of Waste Calcination at the Idaho Nuclear Technology and Engineering Center”, INEEL/EXT-2000-01206, October 2000.

3. B. R. Boyle, Idaho National Engineering and Environmental Laboratory, personal communication.

4. B. H. O’Brien, “Estimation of Alkali Metal Mole Percent and Weight of Calcined Solids for ICPP Calcine”, INEL-95/0184, March 1995.

5. B. H. O’Brien, Idaho National Engineering and Environmental Laboratory, personnel communication.

6. T. A Batcheller, “Dissolution Kinetics of Alumina Calcine”, INEEL/EXT-01-01225, September 2001 (to be published).

7. T. A Batcheller, “Dissolution Kinetics of Zirconia Calcine”, INEEL/EXT-99-0566, June 1999.

Appendix A

Table 11. Elemental wt% H-3 calcine using fusion and SEM EDS results.

	atomic wt.(g/mol)	**avg wt% (g/100 g calcine)**
ALUMINUM	27	9.802785
ANTIMONY	121.8	BDL
ARSENIC	74.9	BDL
BARIUM	137.3	0.0180211
BERYLLIUM	9	BDL
BORON	10.8	0.71
CADMIUM	112.4	3.921465
CALCIUM	40.1	26.00935
CERIUM	140.1	BDL
CESIUM	132.9	BDL
CHROMIUM	52	0.1278545
COBALT	58.9	BDL
GADOLINIUM	157.3	BDL
IRON	55.8	0.495566
LITHIUM	6.9	BDL
MAGNESIUM	24.3	0.485546
MANGANESE	54.9	0.08908215
MERCURY	200.6	BDL
MOLYBDENUM	95.9	BDL
NICKEL	58.7	0.0832502
NIOBIUM	92.9	0.135407
OXYGEN	16	N/A
PALLADIUM	106.4	BDL
PHOSPHOROUS	31	BDL
POTASSIUM	39.1	0.6725
RUTHENIUM	101.1	BDL
SELENIUM	79	BDL
SILICON	28.1	0.586568
SODIUM	23	2.8
STRONTIUM	87.6	0.0336469
SULFUR	32.1	1.46005
THALLIUM	204.4	BDL
TIN	118.7	0.112582
TITANIUM	47.9	BDL
URANIUM	238	BDL
VANADIUM	50.9	BDL
ZINC	65.4	0.0278829
ZIRCONIUM	91.2	7.31303
FLUORIDE	19	8.45E+00
N	-	1.53E+00
CHLORIDE	35.5	3.05E-02
PHOSPHATE	95	BDL
	Total wt% w/o O_2	64.89
OXYGEN SEM EDS	16	37.95
	Total wt%	102.84

Table 12. Analytical results for 60°C kinetics test.

Log# 0106263	Sample Labels								
Element	**60-1**	**60-2**	**60-3**	**60-4**	**60-5**	**60-6**	**60-7**	**60-8**	
Aluminum	2.11E+02	2.19E+02	2.18E+02	2.20E+02	2.20E+02	2.23E+02	2.31E+02	2.40E+02	ug/mL
Boron	1.89E+01	1.91E+01	1.98E+01	1.95E+01	1.99E+01	1.91E+01	2.06E+01	2.04E+01	
Cadmium	1.08E+02	9.98E+01	1.18E+02	1.20E+02	1.18E+02	1.16E+02	1.19E+02	1.05E+02	
Calcium	6.50E+02	6.33E+02	7.72E+02	7.95E+02	7.89E+02	7.26E+02	7.76E+02	7.10E+02	
Sulfur	2.86E+01	2.48E+01	4.24E+01	4.10E+01	4.12E+01	4.33E+01	4.33E+01	3.84E+01	
Zirconium	1.87E+02	1.81E+02	2.04E+02	2.12E+02	2.07E+02	2.10E+02	2.10E+02	1.97E+02	
Sodium	7.19E+01	7.38E+01	7.17E+01	7.38E+01	7.43E+01	7.36E+01	7.11E+01	7.09E+01	
Potassium	1.85E+01	1.67E+01	1.67E+01	1.78E+01	1.74E+01	1.76E+01	1.69E+01	1.88E+01	

Table 13. Analytical results for 75°C kinetics test.

Log# 0106263	Sample Labels							
Element	**75-1**	**75-2**	**75-3**	**75-4**	**75-5**	**75-6**	**75-7**	
Aluminum	2.59E+02	2.79E+02	2.87E+02	2.84E+02	2.88E+02	2.96E+02	3.15E+02	ug/mL
Boron	2.44E+01	2.44E+01	2.54E+01	2.53E+01	2.55E+01	2.58E+01	2.68E+01	
Cadmium	1.34E+02	1.42E+02	1.35E+02	1.41E+02	1.36E+02	1.36E+02	1.39E+02	
Calcium	8.55E+02	9.29E+02	8.82E+02	9.26E+02	9.11E+02	9.24E+02	8.38E+02	
Sulfur	4.16E+01	4.24E+01	3.74E+01	4.10E+01	4.06E+01	4.13E+01	3.91E+01	
Zirconium	2.36E+02	2.49E+02	2.42E+02	2.49E+02	2.47E+02	2.48E+02	2.49E+02	
Sodium	9.20E+02	9.28E+01	9.30E+01	9.38E+01	9.14E+01	9.28E+01	9.53E+01	
Potassium	4.20E+01	2.10E+01	2.13E+01	2.18E+01	2.08E+01	2.06E+01	2.08E+01	

Table 14. Analytical results for 95°C kinetics test.

Log# 0106263	Sample Labels								
Element	**95-1**	**95-2**	**95-3**	**95-4**	**95-5**	**95-6**	**95-7**	**95-8**	
Aluminum	2.27E+02	2.28E+02	2.36E+02	2.42E+02	2.46E+02	2.52E+02	2.64E+02	2.72E+02	ug/mL
Boron	2.02E+01	2.06E+01	2.07E+01	2.11E+01	2.11E+01	2.14E+01	2.23E+01	2.53E+01	
Cadmium	1.10E+02	1.15E+02	1.08E+02	1.13E+02	1.14E+02	1.15E+02	1.17E+02	1.21E+02	
Calcium	7.53E+02	7.44E+02	7.45E+02	7.67E+02	7.53E+02	7.65E+02	7.57E+02	8.45E+02	
Sulfur	3.35E+01	3.41E+01	2.98E+01	3.52E+01	3.44E+01	3.48E+01	3.33E+01	3.73E+01	
Zirconium	1.96E+02	1.99E+02	2.00E+02	2.00E+02	1.97E+02	2.04E+02	1.98E+02	2.09E+02	
Sodium	7.97E+01	7.86E+01	7.94E+01	7.82E+01	7.71E+01	8.31E+01	8.18E+01	9.02E+01	
Potassium	1.77E+01	1.79E+01	1.74E+01	1.75E+01	1.71E+01	1.82E+01	1.86E+01	2.09E+01	