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Development of Hazardous Sludge Simulants for Enhanced Chemical Cleaning Tests

Russell E. Eibling

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Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

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REVIEWS AND APPROVALS

AUTHORS:

R. E. Eibling, Engineering Process Development Date

TECHNICAL REVIEW:

C. J. Martino, Advanced Characterization & Process Date

APPROVAL:

A. B. Barnes, Manager Date
Engineering Process Development

F. M. Pennebaker, Manager Date
Advanced Characterization & Process

S. L. Marra, Manager Date
Environmental & Chemical Process Technology Research Programs

R. H. Spires, Project Manager Date
Closure Projects, Savannah River Remediation

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EXECUTIVE SUMMARY

Savannah River Remediation has requested the Savannah River National Laboratory to develop and produce three new sludge simulants that are resistant to oxalic acid dissolution and contain RCRA hazardous metals for use in additional planned Enhanced Chemical Cleaning process tests. The results of the simulant development are:

- The development and production of lab-scale quantities of the Purex, HM and Blend simulants has been completed.
- The hazardous metals in the new simulants are mercury, silver, barium, cadmium, chromium and lead with the mercury present at HM waste levels in all three simulants.
- The resistance of the three simulants to oxalic acid is similar to or more resistant than actual radioactive waste in prior lab and plant tests.
- The minimum amount of one weight percent oxalic acid required to adjust the pH of the three new simulants was determined to be from 12 to 16.4 times the volume of decanted simulant.
- At the minimum acid quantity, the simulant pH will tend to drift above pH 2 due to the slow reaction kinetics of the acid reactive sludge solids. Addition of more acid over time will be required to maintain a pH below 2.
- Sufficient quantities of each simulant were prepared for use in corrosion testing as requested by SRR.

Any additional improvement in the simulant properties with respect to actual waste using the approach applied to the current simulants will require more detailed information about the specific compounds present in actual radioactive sludge. Such information may provide alternative choices for the mineral phases that could be used in the production of simulants to represent the sludge heels in high level waste tanks to be closed.

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LIST OF ABBREVIATIONS

AOP	Advanced Oxidative Process
DI	Deionized
ECC	Enhanced Chemical Cleaning
ICPES	Inductively Coupled Plasma Emission Spectrophotometer
ISFET	Ion Sensitive Field Effect Transistor
RCRA	Resource Conservation and Recovery Act
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation

1.0 Introduction

An Enhanced Chemical Cleaning (ECC) process is being developed by Savannah River Remediation (SRR) to aid in Savannah River Site (SRS) High-Level Waste (HLW) tank closure. After bulk waste removal, the ECC process can be used to dissolve and remove much of the remaining sludge from HLW tanks. The ECC process uses dilute oxalic acid (1 wt %) with in-line pH monitoring and control. The resulting oxalate is decomposed through hydroxylation using an Advanced Oxidation Process (AOP). Minimizing the amount of oxalic acid used for dissolution and the subsequent oxidative destruction of oxalic acid will minimize the potential for downstream impacts. Initial efficacy tests by AREVA demonstrated that previous tank heel simulants could be dissolved using dilute oxalic acid. The oxalate could be decomposed by an AOP that utilized ozone and ultraviolet (UV) light, and the resultant metal oxides and hydroxides could be separated out of the process.[1]

Additional testing of the AOP process by AREVA is required by SRR to evaluate the impact of undissolved sludge solids and redox active metals on the proposed process. Prior tests used a Purex simulant that dissolved too easily and did not include hazardous metals. A technical task request from SRR asked SRNL to develop and produce three sludge simulants that were more resistant to oxalic acid dissolution and contained the hazardous (as defined by RCRA) metals.[2] The simulants to be developed were a Purex simulant, a HM Simulant and a blend simulant. This report describes the development of the simulants, acid dissolution tests, production of the simulants to support corrosion tests and documents the final recipes for the simulants.

2.0 Experimental Procedure

2.1 Purex Simulant Basis and Preparation

Sludge simulants can be produced by precipitation in the same manner in which the bulk of the SRS sludge was originally generated or by addition of oxides, hydroxides or typical waste species. The ECC Purex hazardous sludge simulant was prepared in the same manner as previous SRS simulants with modifications to improve resistance to acid dissolution. The simulant preparation process consists of the following steps:

1. Generation of hydrated manganese dioxide by reacting manganous nitrate with potassium permanganate at 40 °C while mixing.
2. Addition of the following transition and lanthanide metal nitrates while maintaining mixing to allow dissolution of the salts: Ferric nitrate, nickel nitrate, cerium nitrate, lanthanum nitrate, silver nitrate and cadmium nitrate.
3. Precipitation of the transition and lanthanide metals with sodium hydroxide by raising the pH to 10.
4. Washing the excess sodium nitrate from the precipitated solids using inhibited wash water (0.001 molar in sodium hydroxide and 0.001 molar in sodium nitrite) until the nitrate concentration is less than one gram per liter.
5. Thermally aging the precipitated solids by heating to 95 °C while mixing for a period of 24 hours.
6. Addition of the final insoluble solids and soluble salts to match the desired sludge basis composition.

To improve the acid dissolution resistance of the final sludge simulant a portion of the iron and aluminum were added as specific oxides (hematite and alumina).

The compositional basis of the Purex sludge simulant was derived from the same basis used for the simulant in prior acid cleaning tests (Tank 8F sludge) to provide both a link and a contrast to the prior simulant. The ECC hazardous Purex sludge simulant uses the same basis[3] as the previously tested simulant modified by results from an analysis of a sample[4] of Tank 8F. The hazardous metals were added at the level observed for Purex waste except for mercury which was added at the same level as observed in the HM sludge basis as requested by SRR. The analytical basis for the Purex simulant is show in Table 2-1.

Table 2-1. Purex Hazardous ECC Sludge Simulant Basis

Analyte	wt % Total Solids	grams/Liter
Ag	0.0154	0.03
Al	8.22	15.79
Ba	0.22	0.423
Ca	1.938	3.72
Cd	0.0062	0.012
Ce	0.22	0.42
Cl^-	0.9	1.73
CO_3^{-2}	4.103	7.88
Cr	0.22	0.422
Cu	0.12	0.23
F^-	0.0086	0.017
Fe	22.27	42.77
Hg	1.01	1.94
I^-	0.022	0.042
K	0.03	0.058
La	0.13	0.25
Li	0.0627	0.12
Mg	0.11	0.21
Mn	2.5	4.8
Na	6.594	12.66
Ni	2.55	4.9
NO_2^-	5.19	9.97
NO_3^-	1.167	2.24
OH^-	1.29	2.48
Pb	0.09	0.17
PO_4^{-3}	0.141	0.27
Si	0.7	1.34
SO_4^{-2}	0.763	1.47

Analyte	wt % Total Solids	grams/Liter
Sr	0.077	0.15
Zn	0.24	0.46
Zr	0.44	0.85
Wt % Total Solids	16.70	
Density, grams/mL	1.15	

The complete recipe for the ECC Purex hazardous sludge simulant is given in Appendix A.

2.2 HM Simulant Basis and Preparation

The HM sludge simulant was based on recent samples obtained for actual Tank 12H sludge[5,6] that were collected prior to transfer to Tank 51H for aluminum dissolution. The starting basis for the simulant is show in Table 2-2. This simulant preparation was designed to minimize the need for washing during production of the simulant. Therefore, the soluble species (hydroxide, nitrate, nitrite, chloride, sulfate, phosphate) were adjusted to represent a partial wash of the sludge since the actual sludge samples represented unwashed sludge. The concentrations for the hazardous metals in the HM simulant were set to the same level as in the Purex simulant by request of SRR.

Table 2-2. HM Hazardous ECC Sludge Simulant Basis

Analyte	wt % Total Solids	grams/Liter
Ag	0.006	0.032
Al (soluble)	0.71	3.72
Al (insoluble)	9.1	47.67
B	0.009	0.047
Ba	0.085	0.446
$C_2O_4^{-2}$	0.042	0.22
Ca	0.22	1.15
Cd	0.0024	0.013
Ce	0.021	0.11
Cl^-	0.06	0.31
CO_3^{-2}	9.51	49.8
Cr	0.086	0.45
Cu	0.01	0.052
F^-	0.02	0.11
Fe	1	5.24
Hg	0.39	2.04
K	0.045	0.24
La	0.011	0.06
Li	0.025	0.13
Mg	0.21	1.1

Analyte	**wt % Total Solids**	**grams/Liter**
Mn	0.98	5.11
Mo	0.005	0.024
Na	10.8	56.6
Nd	0.005	0.03
Ni	0.12	0.63
NO_2^-	1.1	5.73
NO_3^-	6.15	32.23
OH^-	0.35	1.84
Pb	0.04	0.18
PO_4^{-3}	0.02	0.1
Si	0.04	0.21
SO_4^{-2}	0.33	1.73
Sr	0.0069	0.036
Ti	0.0029	0.02
Zn	0.014	0.073
Zr	0.044	0.23
Wt% Solids	38.8	
Density, g/mL	1.35	

The steps in producing the HM hazardous sludge simulant are:

1. Generation of hydrated manganese dioxide by reacting manganous nitrate with potassium permanganate at 40 °C while mixing.
2. Addition of the following transition metal nitrates, lanthanide nitrates and soluble salts while maintaining mixing to allow dissolution of the salts: ferric nitrate, ferric oxide, nickel nitrate, zirconyl nitrate, cerium nitrate, lanthanum nitrate, barium nitrate, cupric nitrate, magnesium nitrate, lead nitrate, zinc nitrate, silver nitrate, neodymium nitrate, cadmium nitrate, chromium nitrate, boric acid, sodium fluoride, sodium chloride, sodium sulfate sodium phosphate, and potassium molybdate.
3. Precipitation of the transition and lanthanide metals with sodium hydroxide by raising the pH to 10.
4. Add sodium aluminate and sodium metasilicate to allow the potential generation of aluminosilicates.
5. Thermally aging the precipitated solids by heating to 95 °C while mixing for a period of 24 hours.
6. Add the acid-reactive salts (sodium oxalate, sodium carbonate and sodium nitrite) to allow conversion of some more soluble oxides in to lower soluble carbonates and oxalates,
7. Add the final insoluble compounds (aluminum oxide, aluminum hydroxide and titanium dioxide) other than mercury to the simulant.
8. Finally add mercuric nitrate plus additional sodium hydroxide and lithium hydroxide to generate mercuric oxide dispersed in the simulant.

After completion of the initial test simulants, SRR requested that an additional washing step be performed on the HM simulant to further reduce the hydroxide content of the simulant. Therefore, a decant of supernate, followed by a single stage of wash/decant/dilution was added between steps 7 and 8 to minimize mercury losses and also the volume of hazardous wash water for disposal. The final complete HM simulant recipe is shown in Appendix B.

2.3 Blend Simulant Basis and Preparation

The Blend simulant represents an equal volume blend of Purex sludge and HM sludge. The basis for the simulant was obtained by combining the concentration of the nonhazardous, insoluble species from both simulants and dividing by two. The hazardous species were set to be equivalent to the level in both simulants. The basis for the Blend simulant is shown in Table 2-3. The simulant preparation method is the same as the HM simulant listed above. The recipe for the simulant is listed in Appendix C.

Table 2-3. Blend (Purex+HM) Hazardous ECC Sludge Simulant Basis

Analyte	wt % Total Solids	grams/Liter
Ag	0.009	0.03
Al (soluble)	1.704	5.71
Al (insoluble)	11.226	37.606
B	0.014	0.047
Ba	0.129	0.432
$C_2O_4^{-2}$	0.088	0.294
Ca	1.14	3.82
Cd	0.004	0.012
Ce	0.033	0.11
Cl^-	1.17	3.92
CO_3^{-2}	11.9	39.85
Cr	0.13	0.44
Cu	0.068	0.23
F^-	0.049	0.17
Fe	11.92	39.92
Hg	0.6	2.01
K	0.07	0.24
La	0.017	0.058
Li	0.037	0.125
Mg	0.22	0.74
Mn	1.48	4.95
Mo	0.0001	0.024
Na	24.53	82.17

Analyte	**wt % Total Solids**	**grams/Liter**
Nd	0.008	0.028
Ni	1.37	4.59
NO_2^-	2.305	7.72
NO_3^-	2.95	9.89
OH^-	0.74	2.48
Pb	0.053	0.18
PO_4^{-3}	0.22	0.72
Si	0.7	2.35
SO_4^{-2}	0.79	2.66
Sr	0.077	0.26
Ti	0.005	0.015
Zn	0.13	0.44
Zr	0.25	0.85
Wt% Total Solids	26.8	
Density, g/mL	1.25	

2.4 Physical and Chemical Analysis Methods

The weight percent solids were determined using a Mettler Toledo HR73P Halogen Moisture Analyzer. The HR73P is programmed to heat the sample to 105 °C and monitor the mass of the sample until the change in mass is less than or equal to 1 mg over a period of 130 seconds. The advantage of this method is that weight percent solids analysis can be performed in less than 20 minutes while a complete analysis of total solids in the sludge and dissolved solids in the supernate can take less than an hour. The homogenous sample (slurry or liquid) is placed on a glass fiber pad and the pad placed in the HR73P. The HR73P weighs the sample. The initial mass of the sample is the total mass (m_{tt}). The sample is then heated by the infrared radiation from a Halogen lamp to 105 °C (controlled by a thermocouple) to drive off all the water (assuming mass loss is only from water) and the resulting remaining mass is the total solids (m_{ts}) in the sample. The weight percent (wt %) total solids (TS) of the sludge was determined using equation [1].

$$wt\,\%_{ts} = \frac{m_{ts}}{m_{tt}} \times 100\,\% \qquad [1.]$$

A sample of the slurry is centrifuged (at 4332 gravities) to obtain the supernate. The resulting supernate is then processed through a 0.45 μm filter. A sample of the filtered supernate is then placed on a glass fiber pad, placed in the HR73P, and weighed. The mass of sample used is the total mass of the supernate (m_{st}). The sample is then heated by the Halogen lamp to 105 °C to drive off all the water and the resulting remaining mass is the total dissolved solids (m_{ds}) in the supernate. The weight percent of total dissolved solids (DS) in the supernate is determined using equation [2]. This analysis assumes that all the solids in the resulting supernate are dissolved.

$$wt\%_{ds} = \frac{m_{ds}}{m_{st}} \times 100\% \qquad [2.]$$

The weight percent of insoluble solids (IS) and soluble solids (SS) of the slurry are then calculated by the following conservation of mass relationships, equations [3] and [4] respectively.

$$wt\%_{is} = \frac{wt\%_{ts} - wt\%_{ds}}{100\% - wt\%_{ds}} \times 100\% \qquad [3.]$$

$$wt\%_{ss} = wt\%_{ts} - wt\%_{is} \qquad [4.]$$

Density was determined using an Anton Paar DMA 4500 density meter. The density meter determines the density of a sample by measuring the resonant frequency of a sample-filled U tube at a specified temperature. Additional confirmation of simulant density was obtained by filling a tared 10 mL Class A volumetric flask to the mark and weighing the flask on an analytical balance on an as needed basis.

2.5 Acid Dissolution Testing

The resistance of each of the simulants to acid dissolution was tested using one weight percent oxalic acid (0.11 molar), or 0.11 molar nitric acid, or 0.11 molar sulfuric acid. To minimize the impact of the base on the supernate phase, each simulant was centrifuged and the supernate decanted from the sludge solids. The solid phase was mixed by stirring with a spatula and then 0.5 gram portions of the solid were added to labeled, tared 60 mL polypropylene wide mouth vials. In addition, a 0.5 gram portion of the ferric oxide and a 0.5 gram portion of the aluminum oxide were also prepared to test the reagent oxide resistance to acid dissolution. Next, 50 gram portions of one of the three acids were added to the vials (100:1 acid:sludge ratio). The vials were then placed in a New Brunswick C24 Incubator Shaker and shaken at 120 rpm while maintaining the temperature at 25 °C. The dissolution test duration was seven days after which a portion of the supernate was filtered through a 0.2 micron filter and submitted for analysis by ICPES for Al, Fe, Ca, Mg, Mn, Ni and Pb. A separate portion of each simulant was prepared in a similar manner and the solids analyzed for the initial content for each of the same elements. After the tests were completed, the pH of each of the test vessels were verified to be below pH 2 by measuring the pH with an IQ Scientific Instruments IQ150 pH meter and an Ion Sensitive Field Effect Transistor (ISFET) pH probe. Calibration of the meter was performed using buffers at pH 4, 7 and 10 buffers.

2.6 Simulant Titrations

A portion of each of the three simulants was titrated with 1 wt % oxalic acid to determine the minimum volume ratio of acid to add to a settled portion of the sludge simulant to produce a pH less than 2 to support corrosion testing and SRR planned tests. A 200 mL portion of the sludge simulant was allowed to settle for 24 hours so that the settled volume is 40 % or less of the total. One hundred mL of supernate was removed and the remaining portions of the simulant mixed and transferred to a glass beaker (500 to 1000 mL) for titration. A magnetic stir bar is added and the beaker placed on a Torrey Pines Scientific HS40 digital stirring hotplate. A platinum RTD temperature probe is inserted in the slurry and the target temperature of the slurry set to 40 °C. An ISFET pH probe is inserted and the pH measured with a pH meter. Calibration of the meter was performed using buffers at pH 4, 7 and 10 buffers. Periodically, the probe is cleaned to prevent adhering sludge particles from interfering with the sensor operation. Mixing is started and once the temperature reaches the target, periodic additions of oxalic acid are made. Due to the slow kinetics of solids dissolution, each addition of acid and measurement of pH takes 5 to 20 minutes for the pH reading to stabilize.

3.0 Results and Discussion

3.1 Simulant Results

The goal of the ECC hazardous simulant development program was to produce sludge simulants that have resistance to acid dissolution similar to that observed with actual sludge retrieved from the tank farm. The normal approach to produce an SRS sludge simulant is to precipitate the iron, manganese and nickel in the same manner that the original waste was generated. Next Gibbsite ($Al(OH)_3$) and sometimes Boehmite (AlOOH, if available) is added along with the remaining metals as oxides, carbonates phosphates and sulfates. Alternatively, the Al plus the trace metals will also be added as nitrate salts and then precipitated with sodium hydroxide. The freshly precipitated metal hydroxides tend to be gelatinous, amorphous solids with fluid properties that include the presence of yield stress when settled to a low percent insoluble solids bed. Actual sludge while also partially amorphous also has higher amount of oxides based on x-ray analysis. Previous simulant development for Hanford demonstrated that thermal treatment of a precipitated sludge can lead to the conversion of some of the amorphous hydroxides to oxides[7]. Another approach is to replace a portion of the Fe and Al with specific oxides to increase the crystalline nature of the sludge and to modify the sludge simulant dissolution properties. Therefore, both thermal treatment and oxide replacement were used in formulating the ECC hazardous sludge simulants. The ferric oxide to be used as a portion of the iron species is the < 5 micron, $\geq$99% Fe_2O_3 obtained from Sigma Aldrich. The small particle size was chosen to minimize the potential for separation from the precipitated sludge solids. The Al species added were either $Al(OH)_3$ or Al_2O_3.

The ECC Purex hazardous sludge simulant was prepared as described in section 2.1 using a composition that had 38% of the iron added as ferric nitrate and 68% of the iron added as the ferric oxide. The aluminum in the Purex simulant was mostly added as $Al(OH)_3$ (90%) and Al_2O_3 as the remaining 10%. This produced a simulant that settles very quickly which quickly changes a sample from homogenous to heterogeneous. Such a transition prevents the accurate measurement of rheology by rotational methods from being performed. Therefore, rheology measurements were not made. The physical properties of the simulant are listed in Table 3-1.

Table 3-1. Physical Properties of Purex ECC Sludge Simulant

Property	Result
Density, g/mL	1.119
Wt % Total Solids	13.55
Wt% Soluble Solids	3.05
Wt% Insoluble Solids	10.5
pH	12.32

The rapid settling of the Purex sludge allows easy concentration to higher insoluble solids loadings just by settling and decanting the supernate. The final measured composition of the sludge simulant is shown in Table 3-2. The ratio to Fe column was included since the ease of concentrating the insoluble portion by settling and decanting will modify the total concentration and the percent of total solids values while the ratio of the insoluble species remains constant. A portion of the initial simulant was thermally aged at both 70 and 95 °C to determine if the dissolution tests could identify differences between the aging conditions.

Table 3-2. Purex Hazardous ECC Sludge Simulant Composition

Species	Purex Conc. mg/L	Purex wt % Solids	Ratio to Fe	% of Planned
Ag	52	0.03	0.001	211.5
Al	10105	6.64	0.286	77.4
Ba	338	0.22	0.010	96.6
Ca	3310	2.18	0.094	107.5
Cd	<22	<0.010	<0.0006	<216
Ce	340	0.22	0.010	97.3
Cr	350	0.23	0.010	100.1
Cu	173	0.11	0.005	90.5
Fe	35383	23.25	1.000	100.0
K	189	0.12	0.005	396.9
La	205	0.13	0.006	99.1
Li	179	0.12	0.005	179.9
Mg	155	0.10	0.004	88.8
Mn	4568	3.00	0.129	115.0
Na	13718	9.01	0.388	130.9
Ni	4025	2.65	0.114	99.4
P	63	0.04	0.002	86.8
Pb	142	0.09	0.004	99.2
S	469	0.31	0.013	115.9
Si	1307	0.86	0.037	117.5
Sr	118	0.08	0.003	96.2
Zn	412	0.27	0.012	108.0
Zr	612	0.40	0.017	87.5
Hg	1757	1.16	0.050	109.5
F^-	<112	<0.08	NA	NA
Cl^-	1673	1.10	NA	NA
NO_2^-	10183	6.69	NA	NA
NO_3^-	2965	1.95	NA	NA

The ECC HM hazardous sludge simulant was prepared as described in section 2.2 using a composition that had 100% of the iron added as the ferric oxide. The aluminum was added mostly as the aluminum oxide (90%) to represent the aluminum that may be difficult to leach form HM sludges. The remainder was added as $Al(OH)_3$. The addition of aluminum was made after the thermal aging treatment was completed to prevent caustic dissolution of the insoluble aluminum. Aging was performed only at 95 °C. As in the Purex simulant, the use of the oxides produced a sludge which rapidly settles, therefore, the rheology of the simulant was not measured. The physical properties of the final HM simulant are listed in Table 3-3.

Table 3-3. Physical Properties of HM ECC Sludge Simulant

Property	Result
Density, g/mL	1.148
Wt % Total Solids	17.2
Wt% Soluble Solids	2.00
Wt% Insoluble Solids	15.2
pH	12.54

The HM simulant was initially formulated to not require any wash steps to allow quicker production of the simulant. When the initial batches of simulant were completed, SRR requested that a washing step be added to minimize the amount of soluble base present in the simulant. As this initial HM product was planned for use in corrosion testing, the washing step was applied after all of the chemical additions had been made. Therefore, a reanalysis of the final simulant composition was made and the results are shown for the initial and final product in Table 3-4. The additional wash consisted of a decant of measured amount of the clear supernate (64% of the total batch) followed by an addition of distilled water of equal volume. The simulant was mixed and allowed to settle. The supernate was again decanted and the volume of decanted supernate determined. A final addition of distilled water was made based upon the volume of the final decant liquid. This wash and two decants removed a substantial amount of soluble solids which is illustrated by the drop in sodium and in the anions and also be in shift the composition of the total solids shown in Table 3-4. The HM simulant recipe describes the steps involved in the wash in Appendix B. Note that in the final version of the recipe, the addition of mercury is made after the additional washing is complete to prevent losses of soluble mercury and to minimize the generation of waste water containing mercury.

Table 3-4. HM Hazardous ECC Sludge Simulant Composition

Species	Initial Conc. mg/L	Initial wt % Solids	Final Conc. mg/L	Final wt % Solids	Final Ratio to Fe	% of Planned
Ag	50	0.02	<172	<0.100	<0.032	NA
Al	55303	18.10	71935	36.42	11.65	118.7
Ba	476	0.16	506	0.26	0.08	96.3
Ca	1146	0.38	1318	0.77	0.24	111.2
Cd	<31	<0.010	<23	<0.010	<0.003	NA
Ce	122	0.04	135	0.07	0.02	103.8
Cr	483	0.16	140	0.07	0.02	26.4
Cu	64	0.02	102	0.05	0.02	165.0
Fe	5775	1.89	6176	3.13	1.00	100.0
K	1801	0.59	290	0.15	0.05	104.7
La	64	0.02	67	0.03	0.01	99.0
Li	<310	<0.100	153	0.08	0.02	101.1
Mg	1203	0.39	1193	0.60	0.19	92.0
Mn	5744	1.88	6435	3.26	1.04	106.8
Mo	<31	<0.010	<23	<0.010	<0.003	NA
Na	56005	18.33	8532	4.32	1.38	12.8

Species	Initial Conc. mg/L	Initial wt % Solids	Final Conc. mg/L	Final wt % Solids	Final Ratio to Fe	% of Planned
Nd	44	0.01	47	0.02	0.01	143.9
Ni	657	0.22	626	0.32	0.10	84.4
P	30	0.01	25	0.01	0.004	63.8
Pb	187	0.06	<172	<0.100	<0.)32	NA
S	607	0.20	79	0.04	0.01	11.6
Si	363	0.12	302	0.15	0.05	122.3
Sr	<31	<0.010	35	0.02	0.01	81.8
Ti	<31	<0.010	<23	<0.010	<0.003	NA
Zn	72	0.02	79	0.04	0.01	91.3
Zr	236	0.08	253	0.13	0.04	93.1
Hg	2455	0.80	3221	1.63	0.52	133.8
F-	<124	<0.04	<100	<0.06	NA	NA
Cl-	405	0.13	<100	<0.06	NA	NA
NO_2^-	6643	2.17	695	0.40	NA	NA
NO_3^-	35069	11.48	3730	2.17	NA	NA

The ECC Blend hazardous sludge simulant was prepared in exactly the same manner as the of the HM simulant including the late addition of a washing stage. Due to a batching error additional ferric oxide was added to the simulant used in dissolution testing and for corrosion tests. However, the final composition is still valid as representing a blend of both Purex and HM sludges. The iron in the produced Blend simulant, whose composition is given in Table 3-6, was the only addition that did not match the basis given in section 2.3. Therefore, the iron was added as 81 % oxide and 19 percent precipitated. The physical properties of the Blend simulant produced are shown in Table 3-5.

Table 3-5. Physical Properties of Blend ECC Sludge Simulant

Property	Result
Density, g/mL	1.215
Wt % Total Solids	23.0
Wt% Soluble Solids	3.3
Wt% Insoluble Solids	19.7
pH	13.07

The recipe in Appendix C is the final version for the Blend simulant that will match the original compositional target for the blend.

Table 3-6. Blend Hazardous ECC Sludge Simulant Composition

Species	Initial Conc. mg/L	Initial wt % Solids	Final Conc. mg/L	Final wt % Solids	Final Ratio to Fe	% of Planned
Ag	<40	<0.01	<182	<0.1	<0.004	NA
Al	40081	9.56	47331	16.95	0.71	110.5
Ba	412	0.10	374	0.13	0.01	87.5
Ca	3773	0.90	2569	1.41	0.06	104.2
Cd	<40	<0.010	<24	<0.01	<0.0004	NA

Species	Initial Conc. mg/L	Initial wt % Solids	Final Conc. mg/L	Final wt % Solids	Final Ratio to Fe	% of Planned
Ce	116	0.03	120	0.04	0.00	110.5
Cr	438	0.10	376	0.13	0.01	87.2
Cu	245	0.06	281	0.10	0.00	124.9
Fe	66452	15.85	66353	23.76	1.00	100.0
K	1914	0.46	433	0.15	0.01	185.9
La	61	0.01	55	0.02	0.00	97.0
Li	<400	<0.100	122	0.04	0.00	98.8
Mg	749	0.18	642	0.23	0.01	88.3
Mn	5622	1.34	5667	2.03	0.09	115.7
Mo	<40	<0.010	<24	<0.01	<0.0004	NA
Na	60813	14.51	13543	4.85	0.20	16.7
Nd	45	0.01	43	0.02	0.00	158.4
Ni	4635	1.11	3493	1.25	0.05	76.9
P	217	0.05	140	0.05	0.002	60.1
Pb	182	0.04	<182	<0.1	<0.004	NA
S	944	0.23	224	0.08	0.00	25.4
Si	1539	0.37	1408	0.50	0.02	60.6
Sr	239	0.06	271	0.10	0.00	106.2
Ti	<40	<0.010	<24	<0.01	<0.0004	NA
Zn	463	0.11	437	0.16	0.01	100.6
Zr	803	0.19	634	0.23	0.01	75.2
Hg	2246	0.53	2368	0.85	0.04	119.1
F-	<130	<0.04	<121	<0.04	NA	NA
Cl-	4121	0.98	791	0.28	NA	NA
NO_2^-	8262	1.97	1603	0.57	NA	NA
NO_3^-	82034	19.57	15059	5.39	NA	NA

3.2 Acid Dissolution Results

Acid dissolution test were performed with four different sludge simulants. The first two simulants were Purex simulants prepared using either a 70 °C thermal aging step or a 95 °C thermal aging step. The final two simulants were the HM and Blend simulants which were both thermally aged at 95 °C. The acids tested were 0.11 molar oxalic, nitric and sulfuric acids and the acids were added at a 100:1 mass to mass of sludge solids ratio. For comparison to the later described titration ratio measurements this is probably in the range of 100 to 200 on a volume to volume basis. Additionally samples of the ferric oxide (< 5 micron ≥99%, Sigma Aldrich) and aluminum oxide were also tested for the degree of dissolution. The tests were run at 25 °C for seven days under continuous agitation as described in section 2.5. A portion of the supernate was then removed and analyzed for the soluble metal content and compared to the metal content placed in the dissolution vials. The pH of the dissolution supernates was measured after the testing was complete and the pH of the oxalic acid test mixtures averaged 1.58 compared to an initial pH of 1.64. The nitric acid test mixtures averaged a pH of 1.44 compared to an initial pH of 1.41 and the sulfuric acid test mixtures averaged a pH of 1.44 compared to an initial pH of 1.43.

Results from the simulant testing are compared below to actual waste testing performed in the shielded cells[8] and in actual cleaning tests on Tanks 5F[9] and 6F[10].

Dissolution results for iron for the new simulants shown in Table 3-7 are considerably better than for the previous simulant which showed nearly complete dissolution for iron with oxalic acid at dissolution temperatures as low as 25 °C.[11] The amount of ferric oxide to use in the Purex and Blend simulants was based on earlier estimates of actual waste dissolution results and seem to reflect on the values measured in this test. The extremely low dissolution result for the HM simulant may be a consequence of the small amount of iron relative to the amount of other solids present leading to mass transfer issues.

Table 3-7. Acid Dissolution Results for Iron

Iron	Purex 70 °C	Purex 95 ºC	HM	Blended	Fe_2O_3	SRNL Tank 5F	Tank 5F	Tank 6F
Oxalic Acid, % dissolved	50.4 ± 5.3	47.7 ± 3.1	10.4 ± 0.3	72.8 ± 1.5	40.1	62	21	69
Nitric Acid, % dissolved	25.0 ± 0.1	6.8 ± 0.7	<0.04	21.9 ± 0.2	0.17	NA	NA	NA
Sulfuric Acid, % dissolved	28.3 ± 0.8	16.5 ± 0.1	0.94 ± 0.04	22.7 ± 0.3	3.8	NA	NA	NA
Dissolution Temp,°C	25	25	25	25	25	50	40	40
% Fe as Fe_2O_3	68	68	100	81	NA	NA	NA	NA
Precipitated Fe, %	32	32	0	19	NA	NA	NA	NA
Heat Treat Temp, °C	70	95	95	95	NA	NA	NA	NA
Washed before Heat	Yes	Yes	No	No	NA	NA	NA	NA

The aluminum dissolution results shown in Table 3-8 demonstrate that the three simulants as formulated and produced are very resistant to dilute acid dissolution, whether by oxalic acid or by either nitric or sulfuric acid. While these simulants may be excessively conservative toward aluminum they insure that some insoluble particles will remain for evaluating impacts on the ECC process.

Table 3-8. Acid Dissolution Results for Aluminum

Aluminum	Purex 70 °C	Purex 95 ºC	HM	Blended	Al_2O_3	SRNL Tank 5F	Tank 5F	Tank 6F
Oxalic Acid, % dissolved	4.9 ± 0.3	3.6 ± 0.4	4.04 ± 0.04	13.1 ± 0.2	0.03	84	81	85
Nitric Acid, % dissolved	2.4 ± 0.04	1.1 ± 0.03	3.9 ± 0.05	13.4 ± 0.5	0.03	NA	NA	NA

Aluminum	**Purex 70 °C**	**Purex 95 ºC**	**HM**	**Blended**	**Al_2O_3**	**SRNL Tank 5F**	**Tank 5F**	**Tank 6F**
Sulfuric Acid, % dissolved	5.0 ± 0.2	4.32 ± 0.06	4.07 ± 0.07	13.6 ± 0.2	0.04	NA	NA	NA
Dissolution Temp,°C	25	25	25	25	25	50	40	40
% Al_2O_3 in recipe	10	10	100	90	NA	NA	NA	NA
% $Al(OH)_3$ in recipe	90	90	0	10	NA	NA	NA	NA
Heat Treat Temp, °C	70	95	95	95	NA	NA	NA	NA
Washed before Heat	Yes	Yes	No	No	NA	NA	NA	NA

The manganese results for the Purex simulant are in line with previous simulant results and with the actual waste tests using Purex sludges (Tanks 5F and 6F) as shown in Table 3-9. Since both simulants produce the hydrated MnO_2 by the same generation step, agreement was expected. However, the higher degree of dissolution observed in the HM and Blend simulants may be indicating that applying a thermal aging step with higher levels of hydroxide and higher ionic strength could be impacting the acid resistance of the Mn in the sludge. Both the HM and Blend simulants are not washed before applying the 95 °C aging step. Future simulant development should consider testing what other species may be affected caustic strength during processes designed to accelerate the aging of a simulated sludge.

Table 3-9. Acid Dissolution Results for Manganese

Manganese	**Purex 70 °C**	**Purex 95 ºC**	**HM**	**Blended**	**SRNL Tank 5F**	**Tank 5F**	**Tank 6F**
Oxalic Acid, % dissolved	46.9 ± 1.6	31.9 ± 0.6	90 ± 2	86 ± 33	40	40	47
Nitric Acid, % dissolved	85 ± 1	42.8 ± 0.8	29.7 ± 0.6	58.8 ± 2.2	NA	NA	NA
Sulfuric Acid, % dissolved	88 ± 3	48.1 ± 0.6	30.9 ± 0.4	60 ± 8	NA	NA	NA
Dissolution Temp,°C	25	25	25	25	50	40	40
Heat Treat Temp, °C	70	95	95	95	NA	NA	NA
Washed before Heat	Yes	Yes	No	No	NA	NA	NA

The nickel dissolution results are shown in Table 3-10 and are in agreement with actual waste tests except for the HM simulant. The primary difference between the HM simulant and the other simulants is the very low level of nickel present in the HM simulant. Since the low dissolution is assumed to be due to the formation of an insoluble nickel oxalate, the result for the HM simulant may be related to the solubility limit for nickel. Nickel in the HM simulant is factor of five lower in concentration than in the Blend simulant.

Table 3-10. Acid Dissolution Results for Nickel

Nickel	Purex 70 °C	Purex 95 ºC	HM	Blended	SRNL Tank 5F	Tank 5F	Tank 6F
Oxalic Acid, % dissolved	2.7 ± 0.2	1.8 ± 0.9	84 ± 8	10.4 ± 1.3	0.1	0.6	1.7
Nitric Acid, % dissolved	93 ± 1	22 ± 3	95.4 ± 1.5	138 ± 4	NA	NA	NA
Sulfuric Acid, % dissolved	101 ± 3	51.5 ± 0.8	97.2 ± 0.9	132 ± 2	NA	NA	NA
Dissolution Temp,°C	25	25	25	25	50	40	40
Heat Treat Temp, °C	70	95	95	95	NA	NA	NA
Washed before Heat	Yes	Yes	No	No	NA	NA	NA

Calcium and lead dissolution results are shown in Table 3-11 and Table 3-12. The primary difference between the Purex simulant and the HM and Blend simulants is that all of the calcium is added as calcium compounds in the Purex simulant while either all or some of the calcium in the other simulants is added as calcium nitrate and precipitated with hydroxide. This difference may explain the solubility differences between these tests.

Table 3-11. Acid Dissolution Results for Calcium

Calcium	Purex 70 °C	Purex 95 ºC	HM	Blended	Tank 5F	Tank 6F
Oxalic Acid, % dissolved	26.8 ± 1.0	25.6 ± 0.5	64.7 ± 3.7	66.7 ± 2.2	92	91
Nitric Acid, % dissolved	88 ± 6	86 ± 17	111 ± 2	139 ± 14	NA	NA
Sulfuric Acid, % dissolved	87 ± 6	85.2 ± 0.9	115 ± 2	131 ± 15	NA	NA
Dissolution Temp,°C	25	25	25	25	40	40
Heat Treat Temp, °C	70	95	95	95	NA	NA
Washed before Heat	Yes	Yes	No	No	NA	NA

Table 3-12. Acid Dissolution Results for Lead

Lead	**Purex 70 °C**	**Purex 95 ºC**	**HM**	**Blended**
Oxalic Acid, % dissolved	26 ± 8	26 ± 4	31 ± 4	38 ± 5
Nitric Acid, % dissolved	101 ± 3	57 ± 5	33.6 ± 1.8	33 ± 39
Sulfuric Acid, % dissolved	13.2 ± 2.6	7.3 ± 0.7	6.7 ± 0.5	24 ± 11
Heat Treat Temp, °C	70	95	95	95
Washed before Heat	Yes	Yes	No	No

3.3 Oxalic Acid Titrations

The ECC process involves adding sufficient 1 wt % oxalic acid to the residual sludge to obtain a pH less than 2. As part of the simulant development process, SRR requested that the amount of oxalic acid required to perform the pH adjustment be determined. The current plans for processing the sludge simulant include allowing the simulant to settle and decanting supernate to minimize the amount of acid to reach the pH adjustment target value. For the titration tests to be performed, enough supernate must remain with the settled solids to allow easy transfer from the settling vessel to the titration vessel. Therefore, the process used for preparing the titration sample was to weigh out a known mass of simulant into four 50 mL centrifuge tubes and concentrate the solids at a low centrifuge speed (500 rpm) for five minutes and remove about half the total volume as clear supernate. The amount of concentrated sludge solids remaining is weighed and transferred to a titration beaker for the titration. The nominal volume of concentrated simulant titrated was about 100 mL for the Purex and HM simulants and about 114 mL for the Blend simulant.

The titration curves for each of the three simulants are shown in Figure 3-1, Figure 3-2 and Figure 3-3. A typical acid-base titration curve is a smooth curve with one or more breaks in the curve since acid-base reactions for soluble species are usually fast. The potential breaks in the titration curve would be due to hydroxide and carbonate between pH 10 and 6 and then nitrite below 6. Gas generation presumably due to CO_2 generation was observed in all three titrations. For sludge slurries, however, portions of the acid-reactive species are insoluble and the kinetics of dissolution/reaction can be slow and will impact the resulting measurements of pH. As a result, any break in the process due to having to stop for an evening or other reason (fouled pH probe, etc.) will allow the pH to drift higher until the entire insoluble base is reacted. These periods produce the vertical jumps which exist in the three pH curves displayed below. The Blend simulant titration shows a number of vertical breaks due to the pH drifting to higher pH values when checked the next day. The vertical line on all three figures indicates when the titrated sample had to be split into two separate portions due to the volume at that point exceeding the titration vessel size. The total volume of oxalic acid added to a specific simulant can be determined by summing the volume at the largest volume for each curve minus twice the batch split volume. For example, for the Purex simulant the calculation is Initial Portion volume (950 mL) plus First Portion volume (1100 mL) plus Second Portion volume (1025 mL) minus 2 times the Initial Portion. Therefore, the Purex titration volume is 1175 mL.

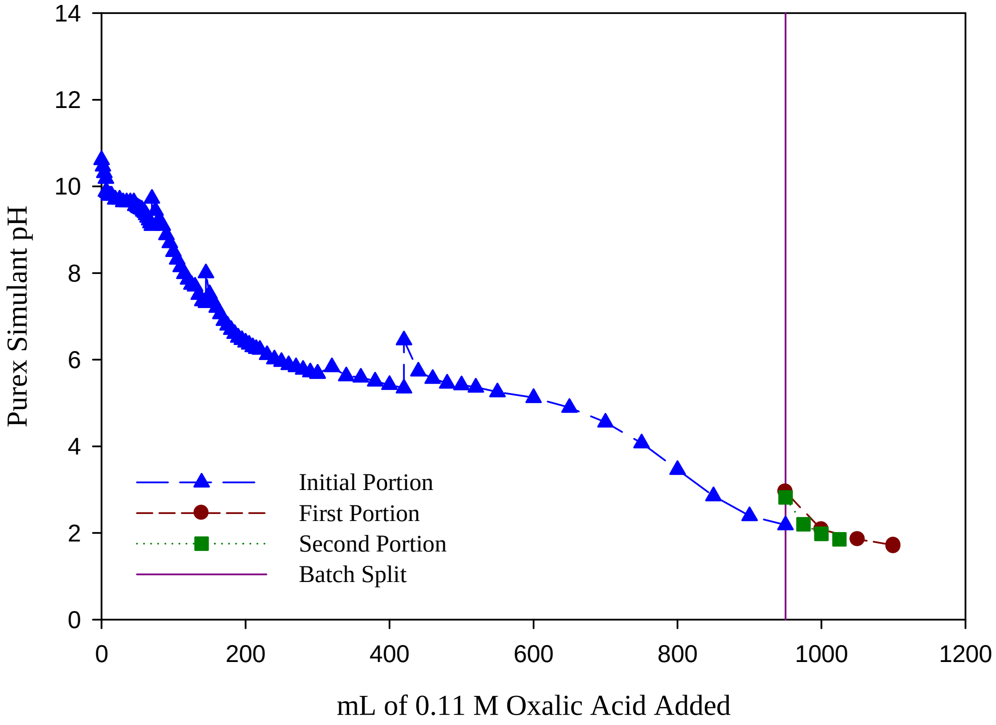

Figure 3-1. Titration of ECC Purex Sludge Simulant

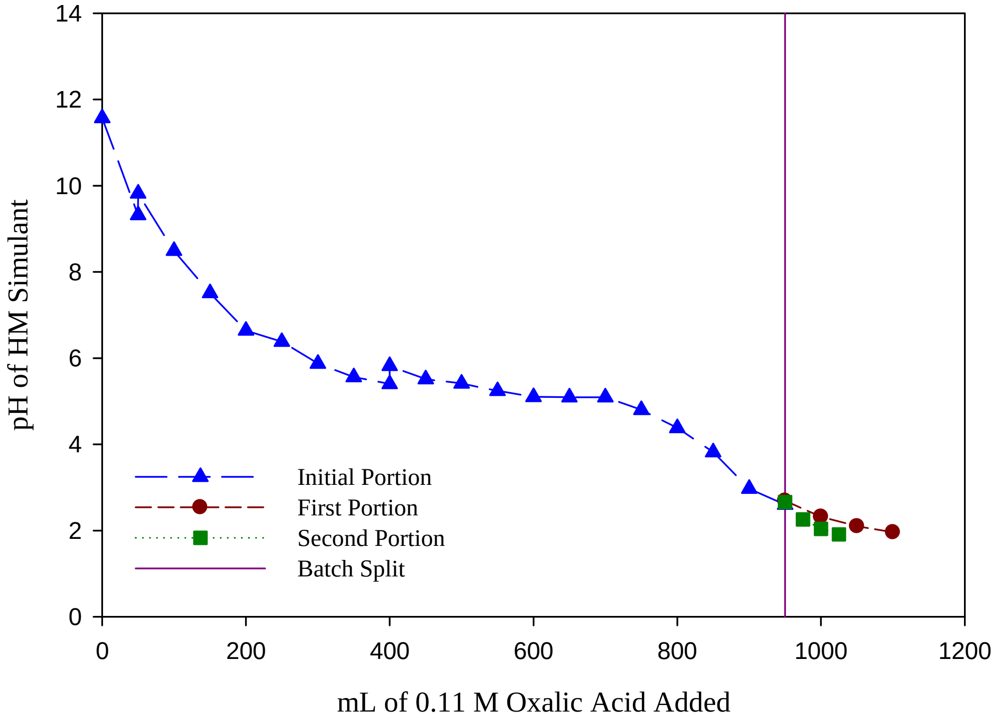

Figure 3-2. Titration of ECC HM Sludge Simulant

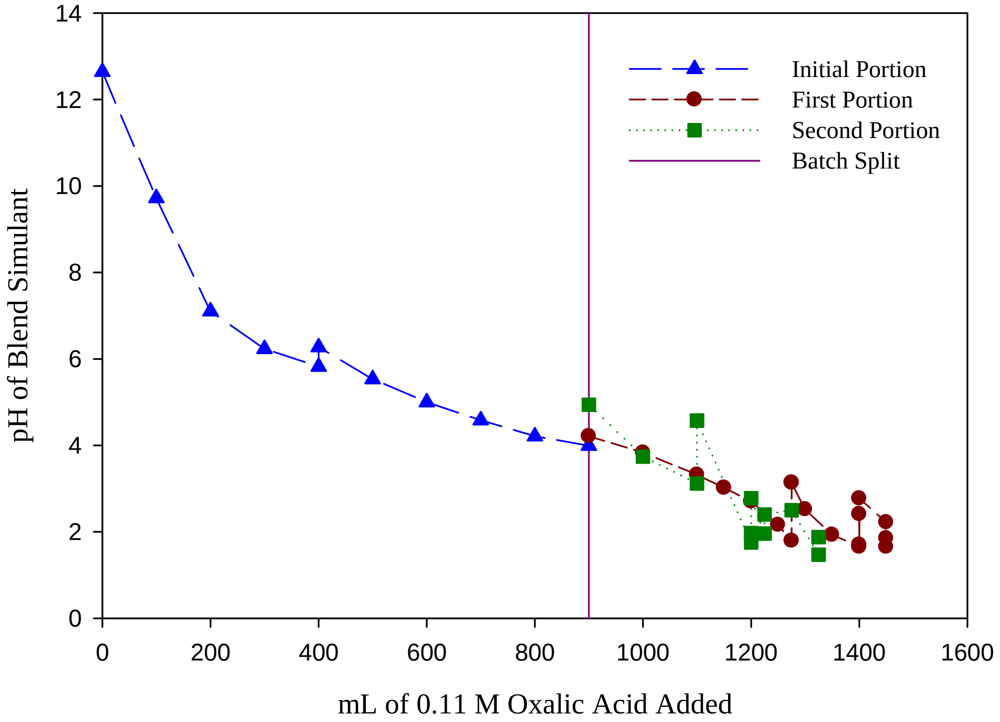

Figure 3-3. Titration of ECC Blend Sludge Simulant

The titration results for all three simulants are summarized in Table 3-13. These results should be considered to be the minimum amount of one weight percent oxalic acid required to achieve a pH of less than 2 as a function of the degree to which the solids were settled and the amount of residual supernate left with the solids. The Blend simulant, for example, had a higher volume of solids potentially containing more supernate with more acid-reactive capacity which would impact the amount of acid required.

Table 3-13. Summary of Simulant Titration Results

Simulant	Simulant Vol., mL	Conc Sludge Vol., mL	Titration Volume, mL	Ratio Titrant/Sludge
Purex	196	98	1175	12.0
HM	197	97	1175	12.1
Blend	197	114	1875	16.4

The drift observed in pH as a function of time is especially apparent in the titration curve for the Blend simulant, Figure 3-3. The titration for that simulant was performed over an 8 day period with all of the data for the initial day covering the initial portion, the first portion out to 1275 mL and the second portion out to 1100 mL. The remaining data was collected on day two, day three and day eight. To further highlight the issue of stability of the final pH measurement after additional time, additional measurements were made more than two weeks after completion of the titrations and the data is shown in Table 3-14.

Table 3-14. Stability of pH for Acid Adjusted Simulants

Simulant	Final Titration pH	Later pH	Days between pH measurements
Purex	1.78	2.34	34
HM	1.85	1.89	29
Blend	1.85	2.97	20

The acid-adjusted HM simulant appears to be at equilibrium while the Purex and Blend simulants continue to drift to higher pH levels. Both the Purex and Blend simulants added some of the metals as specific solids such as calcium carbonate, calcium phosphate and calcium sulfate whose slow dissolution probably impacts the achievement of an equilibrium pH while the HM simulant uses metal nitrates and sodium salts and relies totally on precipitation end equilibrium to generate the final solids of the simulant. Storage vessel composition can also impact pH if the vessel is composed of and acid-reactive solid such as carbon steel. All of the titration products were transferred from the glass beakers to polypropylene bottles so the pH shifts observed must be due to the solids present within the simulants.

4.0 Conclusions

Savannah River Remediation has requested the Savannah River National Laboratory to develop and produce three new sludge simulants that are resistant to oxalic acid dissolution and contain RCRA hazardous metals for use in additional planned Enhanced Chemical Cleaning process tests. The results of the simulant development are:

- The development and production of lab-scale quantities of the Purex, HM and Blend simulants has been completed.
- The hazardous metals in the new simulants are mercury, silver, barium, cadmium, chromium and lead with the mercury present at HM waste levels in all three simulants.
- The resistance of the three simulants to oxalic acid is similar to or more resistant than actual radioactive waste in prior lab and plant tests.
- The minimum amount of one weight percent oxalic acid required to adjust the pH of the three new simulants was determined to be from 12 to 16.4 times the volume of decanted simulant.
- At the minimum acid quantity, the simulant pH will tend to drift above pH 2 due to the slow reaction kinetics of the acid reactive sludge solids. Addition of more acid over time will be required to maintain a pH below 2.
- Sufficient quantities of each simulant were prepared for use in corrosion testing as requested by SRR.

Any additional improvement in the simulant properties with respect to actual waste using the approach applied to the current simulants will require more detailed information about the specific compounds present in actual radioactive sludge. Such information may provide alternative choices for the mineral phases that could be used in the production of simulants to represent the sludge heels in high level waste tanks to be closed.

5.0 References

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Appendix A: ECC Purex Hazardous Sludge Simulant Recipe

ECC Purex Hazardous Sludge Simulant Recipe

Development of the ECC hazardous Purex simulant used reagent grade chemicals and a specific oxide of known particle size. The specific metal oxide is ferric oxide, <5 micron, >99% purity, purchased from Sigma-Aldrich. Substitutions for this ferric oxide should not be made without additional studies. However, technical grade chemicals may be sufficient for replacing the reagent grade chemicals when producing larger scale quantities of the simulant. These technical grade chemicals should be at least 97 % pure. Care in choosing the technical grade chemicals are necessary to prevent the trace contaminants in the technical grade from swamping the intended concentration of minor waste species.

Many of the salts used in the simulant include waters of hydration and the specific form to be used is shown in the recipe. Care must be taken in storing and using some of these compounds due to their tendency to readily absorb water. Using a salt, which has obviously absorbed excess water, will lead to missing the target value for that compound. When necessary, a solution of the compound can be used. However, the water additions shown in the recipe will have to be appropriately reduced to account for the water in the solution of the compound.

The recipe is formulated below based on production of a one liter quantity of simulant with properties as stated in the body of the report. Larger volumes can be prepared by scaling the chemicals, liquids and vessels in the recipe as needed

ECC Hazardous Purex Sludge Simulant Preparation

Goal: Volume of Purex Simulant to be produced **1,000.0 mL**

PART I: Hydrated Manganese Dioxide, MnO_2, Preparation

Add the following to separate vessels: ($KMnO_4$ solution will then be fed to the $Mn(NO_3)_2$ vessel, both at 40 °C).

Compounds	Formula	Mass Needed, grams
Potassium Permanganate	$KMnO_4$	5.52
Water	H_2O	100.00

Manganese Nitrate Solution	$Mn(NO_3)_2$, 50 Wt % solution	20.94
Water	H_2O	100.00

Add the $KMnO_4$ solution to the mixed $Mn(NO_3)_2$ vessel at: 0.8 mL/minute while mixing.

Mix thoroughly. The addition will produce fine black solids which will remain suspended while being agitated.

PART II: Metals Precipitation, Sludge Washing and Thermal Aging

Next add remaining metal nitrates.

Addition of Metals

Compounds	Formula	Mass Needed, grams
Ferric Nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	99.01
Ferric Oxide	Fe_2O_3 <5 micron	41.58
Nickel Nitrate	$Ni(NO_3)_2 \cdot 6H_2O$	24.27
Cerium Nitrate	$Ce(NO_3)_3 \cdot 6H_2O$	1.31
Lanthanum Nitrate	$La(NO_3)_3 \cdot 6H_2O$	0.78
Silver Nitrate	$AgNO_3$	0.047
Cadmium Nitrate	$Cd(NO_3)_2 \cdot 4H_2O$	0.033
Water	H_2O	126.30

Mix until all of the nitrates are dissolved.

Standardize a pH electrode with pH 4, 7 and 10 buffers.

Place the pH electrode in the precipitation vessel with the metal nitrates and measure and record the pH.

pH

With the nitrate solution agitating, very slowly add 50 wt % NaOH at 0.8 mL/minute until the pH reaches 10.

Mass of 50 wt % NaOH required will be greater than 80.70 grams
Record mass of 50 wt % NaOH used grams

During the precipitation, monitor the temperature and control the addition to keep the temperature below 50 °C.

pH

Continue mixing for 1 Hour and then recheck pH.

pH

Allow the slurry to settle overnight or over a weekend.

Decant the supernate from the settled sludge.

Sludge Washing/Settling

The sludge at this point needs to be washed to remove the excessively high levels of NO_3^- in the current supernate (NO_3^- ~ 1.1 Molar).

Wash the Settled sludge by batch dilution and gravity settling using 0.001 M $NaOH/NaNO_2$ wash solutions.
Use a large vessel so that the wash volume is 3X the settled sludge volume (this minimizes the number of washes).
The washing will require at three or more washing stages.

Prepare batches of 0.001 M NaOH + 0.001 M $NaNO_2$ Wash Solution by adding:

Compounds	Grams needed/Liter
Sodium Hydroxide	0.04
Sodium Nitrite	0.07
Water	1000

Mix to dissolve to dissolve the salts.

Wash the settled solids with a 0.001 M NaOH + 0.001 M $NaNO_2$ Wash Solution until the supernate is less than 1000 mg/L Nitrate.

Thermal Aging the Washed Sludge

Transfer the sludge slurry to a 2 to 4 Liter reaction kettle with lid, temperature control and condenser to minimize loss of water. Heat the kettle to 95 C for a total of 24 hours while continuously mixing with an overhead mixer.

PART III: Remaining Compounds Addition

After cooling make the final compounds addition while continuing to mix.

Final Compounds Addition

Compounds	Formula	Mass Needed, grams
Mercuric Nitrate Monohydrate	$Hg(NO_3)_2{\cdot}H_2O$	3.31
Sodium Hydroxide	NaOH, 50 wt %	13.20
Alumina	Al_2O_3	2.98
Aluminum Hydroxide	$Al(OH)_3$	41.07
Barium Sulfate	$BaSO_4$	0.72
Calcium Carbonate	$CaCO_3$	8.25
Calcium Phosphate	$Ca_{10}(OH)_2(PO_4)_6$	0.38
Calcium Sulfate	$CaSO_4$	0.91
Chromium Oxide	Cr_2O_3	0.62
Copper Oxide	CuO	0.29
Lithium Hydroxide, Monohydrate	$LiOH{\cdot}H_2O$	0.73
Potassium Nitrate	KNO_3	0.15
Magnesium Oxide	MgO	0.35
Sodium Carbonate	Na_2CO_3	5.00
Sodium Sulfate	Na_2SO_4	1.10
Sodium Phosphate	$Na_3PO_4{\cdot}12H_2O$	0.23
Sodium Fluoride	NaF	0.04
Sodium Chloride	NaCl	2.85
Sodium Iodide	NaI	0.05
Sodium Nitrite	$NaNO_2$	14.95
Sodium Nitrate	$NaNO_3$	1.30
Lead Sulfate	$PbSO_4$	0.25

Compounds	**Formula**	**Mass Needed, grams**
Silica	SiO_2	2.88
Strontium Carbonate	$SrCO_3$	0.25
Zinc Oxide	ZnO	0.57
Zirconium Dioxide	ZrO_2	1.14

Mix the sludge mixture thoroughly for 2 hours then sample and measure density and solids content.

Appendix B: ECC HM Hazardous Sludge Simulant Recipe

ECC Hazardous HM Sludge Simulant Recipe

Development of the ECC hazardous HM simulant used reagent grade chemicals and a specific oxide of known particle size. The specific metal oxide is ferric oxide, <5 micron, >99% purchased from Sigma-Aldrich. Substitutions for this ferric oxide should not be made without additional studies. However, technical grade chemicals may be sufficient for replacing the reagent grade chemicals when producing larger scale quantities of the simulant. These technical grade chemicals should be at least 97 % pure. Care in choosing the technical grade chemicals are necessary to prevent the trace contaminants in the technical grade from swamping the intended concentration of minor waste species.

Many of the salts used in the simulant include waters of hydration and the specific form to be used is shown in the recipe. Care must be taken in storing and using some of these compounds due to their tendency to readily absorb water. Using a salt, which has obviously absorbed excess water, will lead to missing the target value for that compound. When necessary, a solution of the compound can be used. However, the water additions shown in the recipe will have to be appropriately reduced to account for the water in the solution of the compound.

The recipe is formulated below based on production of a one liter quantity of simulant with properties as stated in the body of the report. Larger volumes can be prepared by scaling the chemicals, liquids and vessels in the recipe as needed

ECC Hazardous HM Sludge Simulant Preparation

Goal: Volume of HM Simulant to be produced **1,000.0 mL**

PART I: Hydrated Manganese Dioxide, MnO_2, Preparation

Add the following to separate vessels: ($KMnO_4$ solution will then be fed to the $Mn(NO_3)_2$ vessel, both at 40°C).

Compounds	Formula	Mass Needed, grams
Potassium Permanganate	$KMnO_4$	5.88
Water	H_2O	100.00

Manganese Nitrate Solution	$Mn(NO_3)_2$, 50 Wt % solution	20.97
Water	H_2O	100.00

Add the $KMnO_4$ solution to the mixed $Mn(NO_3)_2$ vessel at: 0.83 mL/minute while mixing.

Mix thoroughly. The addition will produce fine black solids which will remain suspended while being agitated.

PART II: Metals Precipitation + Heat Treatment

Add to the vessel containing the Part I solution plus MnO_2 precipitate:

DI Water	H_2O	150.00 grams

Then add the following compounds to the vessel (100 g DI water is available for rinsing as indicated at the end of the table):

Compounds	**Formula**	**Mass Needed, grams**
Ferric Nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	0.000
Ferric Oxide	Fe_2O_3 <5 micron	7.489
Nickel Nitrate	$Ni(NO_3)_2 \cdot 6H_2O$	3.115
Zirconyl nitrate	$ZrO(NO_3)_2 \cdot xH_2O$, x~6	0.857
Cerium nitrate	$Ce(NO_3)_3 \cdot 6H_2O$	0.341
Lanthanum nitrate	$La(NO_3)_3 \cdot 6H_2O$	0.180
Barium Nitrate	$Ba(NO_3)_2$	0.848
Calcium Nitrate	$Ca(NO_3)_2 \cdot 4H_2O$	6.790
Cupric Nitrate	$Cu(NO_3)_2 \cdot 2.5H_2O$	0.192
Magnesium Nitrate	$Mg(NO_3)_2 \cdot 6H_2O$	11.604
Lead Nitrate	$Pb(NO_3)_2$	0.293
Zinc Nitrate	$Zn(NO_3)_2 \cdot 6H_2O$	0.334
Silver Nitrate	$AgNO_3$	0.050
Neodymium Nitrate	$Nd(NO_3)_3 \cdot 6H_2O$	0.084
Cadmium Nitrate	$Cd(NO_3)_2 \cdot 4H_2O$	0.035
Strontium Nitrate	$Sr(NO_3)_2$	0.087
Chromium Nitrate	$Cr(NO_3)_3 \cdot 9H_2O$	3.457
Sodium Nitrate	$NaNO_3$	14.423
Boric Acid	H_3BO_3	0.270
Sodium Fluoride	NaF	0.238
Sodium Chloride	NaCl	0.517
Sodium Sulfate	Na_2SO_4	2.561
Sodium Phosphate	$Na_3PO_4 \cdot 12H_2O$	0.403
Potassium Molybdate	K_2MoO_4	0.060
Rinse Water	H_2O	100.00

All the compounds should completely dissolve.

Standardize a pH electrode with pH 4, 7 and 10 buffers.

Place the pH electrode in the precipitation vessel with the metal nitrates and measure the pH.

pH

With the nitrate solution agitating, slowly add 28.78 grams of NaOH (50 wt %)
grams of NaOH (50 wt %) actually added.
Planned Addition Rate 0.75 mL/min for batch precipitation. Approximate Feed time will be 38.4 minutes.
Note that the pH after addition will be >13.

pH

Continue mixing for 30 minutes and then recheck pH.

pH

Add the following species to allow generation of aluminosilicates during heat treatment.

Compounds	Formula	Mass Needed, grams
Sodium Aluminate	$NaAlO_2$	11.30
Sodium Metasilicate	$Na_2SiO_3 \cdot 9H_2O$	2.1202
Rinse Water	H_2O	25.00

Heat Treatment Process

Transfer the slurry to a 2 to 4 Liter reaction kettle with lid, temperature control and condenser to minimize loss of water. Heat the kettle to 95 C for a total of 24 hours while continuously mixing with an overhead mixer.

PART III: Remaining Salts Addition

Next add while mixing

Compounds	Formula	Mass Needed, grams
Sodium Oxalate	$Na_2C_2O_4$	0.33
Sodium Carbonate	Na_2CO_3	87.98
Sodium Nitrite	$NaNO_2$	8.59
Rinse Water	H_2O	50.00

Thoroughly mix the slurry for at least 30 minutes to insure good mixing and complete dissolution of the added salts.

Check pH of the slurry.

pH

PART IV: Base-Reactive Insoluble Solids Addition

Add the final insoluble compounds listed below to the simulated sludge while maintaining complete mixing.

Final Insoluble Compounds Addition

Compounds	Formula	Mass Needed, grams
Alumina	Al_2O_3	90.08
Aluminum Hydroxide	$Al(OH)_3$	0.00
Titanium dioxide	TiO_2	0.025
Rinse & Final Water	H_2O	264.26

Mix thoroughly for 30 minutes.

Allow the slurry to settle for at least one night.

The settled sludge volume should be about 30 % of the total volume.

Decant the clear supernate to remove between 50 and 60% of the original volume without removing any insoluble sludge solids.

Measure either the decanted supernate volume or the decanted supernate mass and density and calculate the volume.

Decanted Supernate Volume ☐ mL

Now add the same volume of DI water to the simulant.

DI Water Added ☐ mL

Mix the slurry for one hour and allow settling overnight.

The settled sludge volume should again be about 30 % of the total volume.

Decant the clear first wash supernate to remove between 50 and 60% of the original volume without removing and insoluble sludge solids.

Measure either the decanted first wash supernate volume or the decanted first wash supernate mass and density and calculate the volume.

Decanted first wash Volume ☐ mL

Now add the same volume of DI water to the simulant.

DI Water Added ☐ mL

Mix the diluted sludge simulant for one hour then proceed to Part V: Final Additions.

Part V: Final Additions

Add the following compounds while mixing.

Compounds	Formula	Mass Needed, grams
Mercuric Nitrate Monohydrate	$Hg(NO_3)_2 \cdot H_2O$	3.49
Sodium Hydroxide	NaOH, 50 wt %	1.63
Lithium Hydroxide, Monohydrate	$LiOH \cdot H_2O$	0.78
Rinse Water	H_2O	50.00

Mix the final simulant for one hour and then collect a sample and measure the solids content (Total, Insoluble Soluble) and the simulant density.

Appendix C: ECC Blend Hazardous Sludge Simulant Recipe

ECC Blend (Purex+HM) Hazardous Sludge Simulant Recipe

Development of the ECC hazardous Blend simulant used reagent grade chemicals and a specific oxide of known particle size. The specific metal oxide is ferric oxide, <5 micron, >99% purchased from Sigma-Aldrich. Substitutions for this ferric oxide should not be made without additional studies. However, technical grade chemicals may be sufficient for replacing the reagent grade chemicals when producing larger scale quantities of the simulant. These technical grade chemicals should be at least 97 % pure. Care in choosing the technical grade chemicals are necessary to prevent the trace contaminants in the technical grade from swamping the intended concentration of minor waste species.

Many of the salts used in the simulant include waters of hydration and the specific form to be used is shown in the recipe. Care must be taken in storing and using some of these compounds due to their tendency to readily absorb water. Using a salt, which has obviously absorbed excess water, will lead to missing the target value for that compound. When necessary, a solution of the compound can be used. However, the water additions shown in the recipe will have to be appropriately reduced to account for the water in the solution of the compound.

The recipe is formulated below based on production of a one liter quantity of simulant with properties as stated in the body of the report. Larger volumes can be prepared by scaling the chemicals, liquids and vessels in the recipe as needed

ECC Hazardous Blend Sludge Simulant Preparation

Goal: Volume of Blend Simulant to be produced **1,000.0 mL**

PART I: Hydrated Manganese Dioxide, MnO_2, Preparation

Add the following to separate vessels: ($KMnO_4$ solution will then be fed to the $Mn(NO_3)_2$ vessel, both at 40°C).

Compounds	Formula	Mass Needed, grams
Potassium Permanganate	$KMnO_4$	5.70
Water	H_2O	75

Manganese Nitrate Solution	$Mn(NO_3)_2$, 50 Wt % solution	21.59
Water	H_2O	50.0

Add the $KMnO_4$ solution to the mixed $Mn(NO_3)_2$ vessel at: 0.83 mL/minute while mixing.

Mix thoroughly. The addition will produce fine black solids which will remain suspended while being agitated.

PART II: Metals Precipitation + Heat Treatment

Next add the following compounds to the vessel (75 grams DI water is available for rinsing as indicated at the end of the table):

Compounds	**Formula**	**Mass Needed, grams**
Ferric Nitrate	$Fe(NO_3)_3{\cdot}9H_2O$	92.41
Ferric Oxide	Fe_2O_3 <5 micron	38.81
Nickel Nitrate	$Ni(NO_3)_2{\cdot}6H_2O$	22.72
Cerium Nitrate	$Ce(NO_3)_3.6H_2O$	0.34
Lanthanum Nitrate	$La(NO_3)_3.6H_2O$	0.18
Neodymium nitrate	$Nd(NO_3)_3.6H_2O$	0.08
Silver Nitrate	$AgNO_3$	0.05
Calcium Nitrate	$Ca(NO_3)_2{\cdot}4H_2O$	22.52
Cadmium Nitrate	$Cd(NO_3)_2{\cdot}4H_2O$	0.03
Copper Nitrate	$Cu(NO_3)_2{\cdot}2.5H_2O$	0.83
Potassium Nitrate	KNO_3	0.56
Magnesium Nitrate	$Mg(NO_3)_2{\cdot}6H_2O$	7.75
Strontium nitrate	$Sr(NO_3)_2$	0.62
Zinc Nitrate	$Zn(NO_3)_2{\cdot}6H_2O$	2.00
Sodium Sulfate	Na_2SO_4	3.81
Sodium Phosphate	$Na_3PO_4.12H_2O$	2.90
Sodium Fluoride	NaF	0.36
Sodium Chloride	NaCl	6.46
Sodium Nitrate	$NaNO_3$	0.00
Boric Acid	H_3BO_3	0.27
Potassium Molybdate	K_2MoO_4	0.06
Water	H_2O	75.00

Mix until all of the nitrates are dissolved.

Standardize a pH electrode with pH 4, 7 and 10 buffers.

Place the pH electrode in the precipitation vessel with the metal nitrates and measure and record the pH.

pH

With the nitrate solution agitating, very slowly add 50 wt % NaOH at 0.7 mL/minute until the pH reaches 10.

Mass of 50 wt % NaOH required may be greater than 101.90 grams
Record mass of 50 wt % NaOH used grams

During the precipitation, monitor the temperature and control the addition to keep the temperature below 50 °C.

pH

Continue mixing for 1 Hour and then recheck pH.

pH

Add the following species to allow generation of aluminosilicates during heat treatment.

Compounds	Formula	Mass Needed, grams
Sodium Aluminate	$NaAlO_2$	17.35
Sodium Metasilicate	$Na_2SiO_3 \cdot 5H_2O$	17.71
Water	H_2O	75.00

Heat Treatment Process

Transfer the slurry to a 2 to 4 Liter reaction kettle with lid, temperature control and condenser to minimize loss of water. Heat the kettle to 95 C for a total of 24 hours while continuously mixing with an overhead mixer.

PART III: Base Reactive Compounds Addition

Next add while mixing.

Compounds	Formula	Mass Needed, grams
Alumina	Al_2O_3	63.95
Aluminum Hydroxide	$Al(OH)_3$	10.87
Barium Sulfate	$BaSO_4$	0.73
Chromium Oxide	Cr_2O_3	0.64
Sodium Oxalate	$Na_2C_2O_4$	0.45
Sodium Carbonate	Na_2CO_3	41.94
Sodium Nitrite	$NaNO_2$	11.58
Lead Sulfate	$PbSO_4$	0.26
Titanium Oxide	TiO_2	0.03
Zirconium Dioxide	ZrO_2	1.15
Water	H_2O	408.92

Mix thoroughly for 30 minutes.

Allow the slurry to settle for at least one night.

The settled sludge volume should be about 30-40 % of the total volume.

Decant the clear supernate to remove between 50 and 60% of the original volume without removing any insoluble sludge solids.

Measure either the decanted supernate volume or the decanted supernate mass and density and calculate the volume.

Decanted Supernate Volume ☐ mL

Now add the same volume of DI water to the simulant.

DI Water Added ☐ mL

Mix the slurry for one hour and allow settling overnight.

The settled sludge volume should again be about 30-40 % of the total volume.

Decant the clear first wash supernate to remove between 50 and 60% of the original volume without removing and insoluble sludge solids.

Measure either the decanted first wash supernate volume or the decanted first wash supernate mass and density and calculate the volume.

Decanted first wash Volume mL

Now add the same volume of DI water to the simulant.

DI Water Added mL

Mix the diluted sludge simulant for one hour then proceed to Part V: Final Additions.

Part IV: Final Additions

Add the following compounds while mixing.

Compounds	Formula	Mass Needed, grams
Mercuric Nitrate Monohydrate	$Hg(NO_3)_2 \cdot H_2O$	3.43
Sodium Hydroxide, 50 wt %	NaOH, 50 wt%	13.27
Lithium Hydroxide Monohydrate	$LiOH.H_2O$	0.76
Water	H_2O	50.0

Mix the final simulant for one hour and then collect a sample and measure the solids content (Total, Insoluble, and Soluble) and the simulant density.

Distribution:

A. B. Barnes, 999-W
D. A. Crowley, 773-43A
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
A. M. Murray, 773-A
F. M. Pennebaker, 773-42A
J. H. Scogin, 773-A
W. R. Wilmarth, 773-A
C. J. Martino, 773-42A
M. S. Hay, 773-42A
W. D. King, 773-42A
M. R. Poirier, 773-42A
M. R. Williams, 786-5A
N. R. Davis, 704-26F
R. H. Spires, 704-26F
E. T. Ketusky, 704-70F
T. M. Punch, 704-71F
G. D. Thaxton, 704-70F
T. H. Huff, 704-71F
J. R. Vitale, 704-70F
C. B. Sudduth, 704-71F
K. J. Bumpus, 730-2B