Chemical Cleaning Dissolution Sludge Simulant Development

Russell E. Eibling

BACKGROUND

Earlier Chemical Cleaning Tests performed with Tank 8F (PUREX) Sludge Simulant

- **Simulant originally prepared for filtration studies**
- **Contained no RCRA hazardous metals**
- **Prepared by precipitating Fe, Ni, and Mn**
- **Remaining species added as carbonates or oxides**
- **Modified by mild thermal treatment**

Acid Dissolution of primary simulant species nearly complete

OBJECTIVE

Develop SRS sludge simulants to support additional chemical cleaning dissolution and corrosion tests that:

- **Are resistant to Acid dissolution similar to that of actual waste**
- **Contain RCRA hazardous metals**
- **Represent Purex, HM and Blend of sludge wastes**

Purex and HM Simulant Basis

Purex Sludge Simulant

Purex Sludge composition based on SRS Tank 8F composition used in previous filtration and dissolution studies to provide continuity with prior work

Trace species were included for the new simulant formulation

Mercury was added to the simulant basis at HM waste levels

HM Sludge Simulant

Composition based on 3 Liter sample retrieved from SRS Tank 12H in September 2008

Composition was adjusted to a lower soluble salts composition to represent the effect of sludge and supernate retrieval before cleaning

Trace species were included to make the simulant formulation as complete as possible

The RCRA metals were adjusted to the levels added in the Purex simulant for the purposes of the dissolution testing

Analyte	Purex, Wt % Total Solids	HM, Wt% Total Solids
Ag	0.0154	0.006
Al (soluble)	NB	0.71
Al (insoluble)	8.22	9.1
B	NB	0.009
Ba	0.22	0.085
$C_2O_4^{-2}$	NB	0.042
Ca	1.938	0.22
Cd	0.0062	0.0024
Ce	0.22	0.021
Cl^-	0.9	0.06
CO_3^{-2}	4.1	9.51
Cr	0.22	0.086
Cu	0.12	0.01
F^-	0.0086	0.02
Fe	22.27	1.0
Hg	1.01	0.39
I^-	0.022	NB
K	0.03	0.045
La	0.13	0.011
Li	0.0627	0.025
Mg	0.11	0.21
Mn	2.5	0.98
Mo	NB	0.005
Na	6.594	10.8
Nd	NB	0.005
Ni	2.55	0.12
NO_2^-	5.19	1.1
NO_3^-	1.167	6.15
OH^-	1.29	0.35
Pb	0.09	0.04
PO_4^{-3}	0.141	0.02
Si	0.07	0.04
SO_4^{-2}	0.763	0.33
Sr	0.077	0.0069
Ti	NB	0.0029
Zn	0.24	0.014
Zr	0.44	0.044

NB No Basis available for this species

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Simulant Development Approach

Substitute oxides for a portion of the primary metals

- **Previous simulants used $Fe(NO_3)_3$ and precipitated with NaOH**
- **Fe_2O_3 (< 5 micron) substituted for a portion of the Fe in the simulant Used Aldrich Fe_2O_3 < 5 micron, ≥ 99%**
- **Past simulants added $Al(OH)_3$ as the Al form**
- **Al_2O_3 < 10 micron substituted for a portion of the Al in the simulant**

Remaining metals added either as nitrates and precipitated or in some cases oxides or carbonates

Mercury added as Hg(NO3)2 and precipitated to form HgO

Prepared Purex and HM Simulant

Purex Simulant Preparation

- **MnO_2 generated by reaction**
- **Fe added as Ferric Nitrate (32%) and Ferric Oxide (68 %) to match real waste dissolution for Tank 5 sludge**
- **Precipitation used for Fe, Ni, Cd, Ag, Ce, and La**
- **Washing followed Precipitation**
- **Thermal Treatment (24 hours at 95 °C)**
- **Addition of remaining metals and salts similar to prior simulant except for Al and Pb**
- **Al added as $Al(OH)_3$ (90%) and Al_2O_3 (10%)**
- **Lead added as the sulfate**
- **Mercuric Nitrate added followed by sufficient NaOH to precipitate HgO**

HM Simulant Preparation

MnO_2 generated by reaction

Following metals added as nitrates then precipitated with NaOH: Ni, Zr, Ce, La, Ba, Ca, Cu, Mg, Pb, Zn, Ag, Nd, Cd, Sr, and Cr. Fe added as Fe_2O_3 (100%) prior to precipitation

Sodium Aluminate and Sodium Metasilicate added after precipitation

Thermal Treatment (24 hours at 95 °C)

A decant and a single stage of washing applied to reduce soluble salts

Mercuric Nitrate added followed by sufficient NaOH to precipitate HgO

Al added as Al_2O_3 (100%) at the end of processing

Species	Purex wt % Solids	Purex Ratio to Fe	Purex % of Planned	HM wt % Solids	HM Ratio to Fe	HM % of Planned
Ag	0.03	0.001	211.5	<0.100	<0.032	NA
Al	6.64	0.286	77.4	36.42	11.65	118.7
Ba	0.22	0.010	96.6	0.26	0.08	96.3
Ca	2.18	0.094	107.5	0.77	0.24	111.2
Cd	<0.010	<0.0006	<216	<0.010	<0.003	NA
Ce	0.22	0.010	97.3	0.07	0.02	103.8
Cr	0.23	0.010	100.1	0.07	0.02	26.4
Cu	0.11	0.005	90.5	0.05	0.02	165.0
Fe	23.25	1.000	100.0	3.13	1.00	100.0
K	0.12	0.005	396.9	0.15	0.05	104.7
La	0.13	0.006	99.1	0.03	0.01	99.0
Li	0.12	0.005	179.9	0.08	0.02	101.1
Mg	0.10	0.004	88.8	0.60	0.19	92.0
Mn	3.00	0.129	115.0	3.26	1.04	106.8
Mo	NA	NA	NA	<0.010	<0.003	NA
Na	9.01	0.388	130.9	4.32	1.38	12.8
Nd	NA	NA	NA	0.02	0.01	143.9
Ni	2.65	0.114	99.4	0.32	0.10	84.4
P	0.04	0.002	86.8	0.01	0.004	63.8
Pb	0.09	0.004	99.2	<0.100	<0.032	NA
S	0.31	0.013	115.9	0.04	0.01	11.6
Si	0.86	0.037	117.5	0.15	0.05	122.3
Sr	0.08	0.003	96.2	0.02	0.01	81.8
Ti	NA	NA	NA	<0.010	<0.003	NA
Zn	0.27	0.012	108.0	0.04	0.01	91.3
Zr	0.40	0.017	87.5	0.13	0.04	93.1
Hg	1.16	0.050	109.5	1.63	0.52	133.8
F^-	<0.08	NA	NA	<0.06	NA	NA
Cl^-	1.10	NA	NA	<0.06	NA	NA
NO_2^-	6.69	NA	NA	0.40	NA	NA
NO_3^-	1.95	NA	NA	2.17	NA	NA

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Acid Dissolution Test

Acid Dissolution Testing performed with

- 1 wt % Oxalic Acid (0.11 M)
- 0.11 M Nitric Acid
- 0.11 M Sulfuric Acid

Acid Addition based on 100 g Acid to 1 Gram centrifuged solids

Sludge solids were separated from the supernate by centrifuging and decanting the supernate

Damp sludge solids were mixed and then added by wt to sample vessels

Temperature maintained at 25 °C and limited mixing using a platform shaker

Samples were removed after 7 days and the supernates analyzed for soluble metals

Acid Dissolution Test Results

Iron	Purex	HM	Blended	Fe_2O_3	Shielded Cells Tank 5F	Tank 5F	Tank 6F
Oxalic Acid, % dissolved	47.7 ± 3.1	10.4 ± 0.3	72.8 ± 1.5	40.1	62	21	69
Nitric Acid, % dissolved	6.8 ± 0.7	<0.04	21.9 ± 0.2	0.17	NA	NA	NA
Sulfuric Acid, % dissolved	16.5 ± 0.1	0.94 ± 0.04	22.7 ± 0.3	3.8	NA	NA	NA
% Fe as Fe_2O_3	68	100	68	100	NA	NA	NA

Aluminum	Purex	HM	Blended	Al_2O_3	Shielded Cells Tank 5F	Tank 5F	Tank 6F
Oxalic Acid, % dissolved	3.6 ± 0.4	4.04 ± 0.04	13.1 ± 0.2	0.03	84	81	85
Nitric Acid, % dissolved	1.1 ± 0.03	3.9 ± 0.05	13.4 ± 0.5	0.03	NA	NA	NA
Sulfuric Acid, % dissolved	4.32 ± 0.06	4.07 ± 0.07	13.6 ± 0.2	0.04	NA	NA	NA
% Al as Al_2O_3	10	100	90	100	NA	NA	NA

Manganese	Purex	HM	Blended	Shielded Cells Tank 5F	Tank 5F	Tank 6F
Oxalic Acid, % dissolved	31.9 ± 0.6	90 ± 2	86 ± 33	40	40	47
Nitric Acid, % dissolved	42.8 ± 0.8	29.7 ± 0.6	58.8 ± 2.2	NA	NA	NA
Sulfuric Acid, % dissolved	48.1 ± 0.6	30.9 ± 0.4	60 ± 8	NA	NA	NA

Nickel	Purex	HM	Blended	Shielded Cells Tank 5F	Tank 5F	Tank 6F
Oxalic Acid, % dissolved	1.8 ± 0.9	84 ± 8	10.4 ± 1.3	0.1	0.6	1.7
Nitric Acid, % dissolved	22 ± 3	95.4 ± 1.5	138 ± 4	NA	NA	NA
Sulfuric Acid, % dissolved	51.5 ± 0.8	97.2 ± 0.9	132 ± 2	NA	NA	NA

Calcium	Purex	HM	Blended	Tank 5F	Tank 6F
Oxalic Acid, % dissolved	25.6 ± 0.5	64.7 ± 3.7	66.7 ± 2.2	92	91
Nitric Acid, % dissolved	86 ± 17	111 ± 2	139 ± 14	NA	NA
Sulfuric Acid, % dissolved	85.2 ± 0.9	115 ± 2	131 ± 15	NA	NA

Lead	Purex	HM	Blended
Oxalic Acid, % dissolved	26 ± 4	31 ± 4	38 ± 5
Nitric Acid, % dissolved	57 ± 5	33.6 ± 1.8	33 ± 39
Sulfuric Acid, % dissolved	7.3 ± 0.7	6.7 ± 0.5	24 ± 11

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