DEVELOPMENT OF A SUPERNATE SIMULANT FOR HANFORD TANK 241-AN-102 WASTE (U)

February 2003

Immobilization Technology Section
Savannah River Technology Center

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500

SRS
savannah river site

Key Words:
River Protection Project
Entrained Solids Simulant

Retention:
#Permanent#

Key WTP R&T References:
S141 – Simulant Development

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Russell E. Eibling, Building 999-W

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LIST OF ACRONYMS

cP	Centipoise (equivalent to milliPascal-seconds)
ED3A	Ethylenediaminetriacetic acid
EDTA	Ethylenediaminetetraacetic acid
GCMS	Gas Chromatograph – Mass spectrometer
HEDTA	N-(2-hydroxyethyl)ethylenediaminetriacetic acid
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectrometer
IDA	Iminodiacetic acid
IEC	Ion Exclusion Chromatography
MDL	Method Detection Limit
MSDS	Material Safety Data Sheet
NTA	Nitrilotriacetic acid
RPP-WTP	River Protection Project – Waste Treatment Plant
SRTC	Savannah River Technology Center
TFCOUP	Tank Farm Contractor Operation and Utilization Plan, Rev 3A
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
XRD	X-ray Diffraction analysis

1.0 SUMMARY OF TESTING

1.1 Objectives

Envelope C waste includes Hanford Tank 241-AN-102, which contains high levels of organic complexants and high levels of soluble aluminum. Supporting SRTC studies of RPP-WTP processes require the use of a simulant for AN-102 supernate. A simulant has been developed that contains the levels of soluble transition metals observed in tank AN-102. Development of the simulant was based on the most recent characterizations of AN-102 waste. Estimating the amount of gluconate ion present in the AN-102 supernate was necessary to produce the correct soluble metals concentrations. The simulant formulation is based on the nominal composition of Tank AN-102 supernate at 9.5 molar sodium and diluted to 6.5 molar sodium concentrations.

The primary uses for the simulant will be:

- Precipitation/Filtration studies (lab, bench and pilot-scale)
- LAW evaporation and antifoam studies.

Additional applications may be identified as the project proceeds.

1.2 Conduct of Testing

The development of the AN-102 simulant involved identifying an analytical basis for the waste composition. Charge balancing the basis composition requires using a method acceptable to the programs planning to use the simulant. Bench-scale experiments on metal solubility as a function of sodium gluconate concentration were conducted to establish a basis for the gluconate concentration. Additional tests were performed to determine the sequence of chemical addition to prevent unwanted reactions. The final step was measurement of the physical properties of the simulant for use in developing large batch recipes and for comparison with actual waste properties.

1.3 Results and Performance against Objectives

A formulation for a supernate simulant has been developed to represent waste from Hanford Tank 241-AN-102. The simulant is designed to reproduce the nominal chemical composition of the supernate at 9.5 molar sodium (undiluted) and when the supernate is diluted to 6.5 molar sodium concentration. The simulant also includes a formulation to represent the unwashed entrained solids expected in the undiluted supernate.

1.4 Quality Requirements

This work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRTC as identified in DOE IWO MOSRLE60. SRTC has provided matrices to WTP demonstrating compliance of the SRTC QA program with the requirements specified by WTP. Specific information regarding the compliance of the SRTC QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Subpart 2.7 is contained in these matrices.

The simulant development supports Sr/TRU precipitation/filtration, evaporation and ion exchange testing as specified in the following task plans:

- Task Technical and Quality Assurance Plan In Support of RPP-WTP Pilot-Scale Precipitation Testing.[1]
- Task Technical and Quality Assurance Plan for AN-102 Simulant Sr/TRU Precipitation and Ultrafiltration.[2]
- Evaluation of Post-Filtration Precipitation Mechanism.[3]
- Complexant Identification in Hanford Waste Simulant Sr/TRU Filtrate.[4]
- Task Technical and Quality Assurance Plan for – LAW Evaporation: Antifoam/Defoamer Testing for Low Activity Waste Solution.[5]

1.5 Issues

The development of the AN-102 simulant has not identified any issues for design or operation of the River Protection Project – Waste Treatment Plant (RPP-WTP)**.**

2.0 DISCUSSION

2.1 INTRODUCTION AND BACKGROUND

Research and testing of the proposed processes for RPP-WTP typically requires the use of waste simulants designed to duplicate the chemical and physical properties of the waste. The complexity of the specific simulant is a function of the specific waste and of the process to be tested. Envelope C wastes such as the supernate from Hanford tanks 241-AN-107 and 241-AN-102, are complex mixtures of metal ions, complexants and other anions. The Savannah River Technology Center has been asked to develop a simulant for the supernate from Tank 241-AN-102 based upon recent waste characterization results. The simulant development

supports Sr/TRU precipitation/filtration, evaporation and ion exchange testing previously cited in section 1.4.

2.2 SIMULANT DEVELOPMENT

2.2.1 Supernate Simulant

The supernate within tank 241-AN-102 is known as complex concentrate because it contains high levels of complexed metals. These organic complexing agents result in the supernate having the high Total Organic Carbon value reported in waste characterization reports. The difference between tank AN-102 supernate and the previously developed AN-107 simulant (also Envelope C) is that the AN-102 supernate has a relatively high hydroxide level and therefore a high soluble aluminate concentration instead of the very low hydroxide level observed in previous AN-107 waste samples. A successful supernate simulant for AN-102 must have sufficient complexing agents present to duplicate the soluble metal concentrations observed within the waste as well as a hydroxide concentration sufficient to support the required soluble aluminate. As previously mentioned, the AN-102 simulant will be used for testing the following processes: ion exchange, Sr/TRU precipitation, pilot-scale crossflow filtration and antifoam selection for evaporator operation.

The analytical basis for the simulant composition for most of the waste components comes from recent waste samples.[6-9] The final waste component, sodium gluconate, was reported as a less than value (<1000 mg/Liter) while process history indicates that sodium gluconate was used during Hanford B plant processing. Sodium gluconate was used as a sequestering agent to prevent metal precipitation during B plant processing. An essential materials document from the 1970's indicates the consumption of 10,000 pounds per year of sodium gluconate (Reference 18).

The sample analyses used in formulating the AN-102 simulant are listed in Table 1. The value shown for ethylenediaminetetraacetic acid (EDTA) for Reference 7 is based upon the sum of the maximum values observed for EDTA and for ethylenediaminetriacetic acid (ED3A). The concentration for cesium was based on summing the isotopic results from an analysis by inductively coupled plasma – mass spectrometry. The carbonate concentration was calculated from the TIC measurement.

Table 1 Recent Sample Analyses of AN-102 Supernate

	Reference 6 SRTC Sampled 8/98	Reference 7 Battelle, Sampled 8/2000	Reference 8 Hanford Sampled 2/98	Reference 9 Hanford Sampled 1994-1995	Average
Component	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**
Acetate	993	NM	NM	NM	993
Aluminum	14608	12300	15933	15100	14485
Ammonium	NM	152	132	NM	142
Boron	39	NM	43	NM	41

	Reference 6 SRTC Sampled 8/98	Reference 7 Battelle, Sampled 8/2000	Reference 8 Hanford Sampled 2/98	Reference 9 Hanford Sampled 1994-1995	Average
Component	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**
Cadmium	60	62	67	NM	63
Calcium	491	489	518	434	483
Carbonate	72944	54958	68281	65950	65533
Cesium	20	16	NM	NM	18
Chloride	3803	4800	4303	3810	4179
Chromium	252	215	300	297	266
Cobalt	4	NM	LT	NM	4
Copper	24	23	26	NM	24
Ethylenediaminetetraacetic acid	9221	2780	NM	NM	6001
Fluoride	2190	LT	1837	1860	1962
Formate	10760	8000	NM	NM	9380
Glycolate	13020	10500	NM	NM	11760
Hydroxide	22020	4300	2580	3610	8128
Iron	35	37	50	50.9	43
Lanthanum	14	16	LT	NM	15
Lead	182	186	185	NM	184
Manganese	17	17	26	39.1	25
Molybdenum	58	NM	55	NM	56
Neodymium	NM	32	NM	NM	32
n-(2-Hydroxyethyl)ethylenediaminetriacetic acid	7105	150	NM	NM	3628
Nickel	407	416	445	381	412
Nitrate	190132	221000	233667	225000	217450
Nitrite	82390	85400	92967	82600	85839
Oxalate	591	460	NM	NM	526
Phosphate	4975	5580	6080	4820	5364
Phosphorus	1900	1820	1803	1610	1783
Potassium	2190	1980	2373	3880	2606
Rubidium	NM	8.74	NM	NM	9
Silicon	12	235	LT	LT	124
Sodium	234500	184000	219000	240000	219375
Strontium	2.9	2.3	LT	NM	3
Sulfate	12910	16900	15533	13800	14786
Sulfur	NM	NM	5673	4750	5212
TIC	14600	11000	13667	13200	13117
TOC	27015	29300	24567	26200	26770
Tungsten	NM	NM	201	NM	201
Zinc	6	LT	LT	NM	6
Zirconium	17	8.2	10	NM	12
Additional Organics					
Nitrilotriacetic Acid	NM	260	NM	NM	260
Citric Acid	5965	4400	NM	NM	5183
Iminodiacetic Acid	3880	4500	NM	NM	4190
Succinic Acid	NM	36	NM	NM	36

NM = Not Measured, LT = Less than, NA = Not applicable

To provide a consistent basis for comparison, all of the samples were mathematically diluted to 6.5 molar Na based upon their specific sodium measurements. The result of the dilution is shown in Table 2.

Table 2 AN-102 Sample Results Diluted to 6.5 Molar Na Basis

	Reference 6	Reference 7	Reference 8	Reference 9	Average	Diluted Simulant Basis	Undiluted Simulant Basis
Component	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**
Acetate	633	NM	NM	NM	633	630	925
Aluminum	9309	9989	10872	9402	9893	10000	14682
Ammonium	NM	123	90	NM	107	120	176
Boron	25	NM	29	NM	27	30	44
Cadmium	38	50	46	NM	45	50	73
Calcium	313	397	353	270	333	400	587
Carbonate	46483	44634	46591	41063	44693	44714	65650
Cesium	13	13	NM	NM	13	13	19
Chloride	2423	3898	2936	2372	2908	3900	5726
Chromium	161	175	205	185	181	205	301
Cobalt	3	NM	LT	NM	3	3	4
Copper	15	19	18	NM	17	20	29
Ethylenediamine-tetraacetic acid	5876	2258	NM	NM	4067	2260	3318
Fluoride	1396	LT	1253	1158	1269	1400	2055
Formate	6857	6497	NM	NM	6677	6860	10072
Glycolate	8297	8527	NM	NM	8412	8530	12524
Hydroxide	14032	3492	1760	2248	5383	5500	8075
Iron	22	30	34	32	30	34	50
Lanthanum	9	13	LT	NM	11	13	19
Lead	116	151	126	NM	131	151	222
Manganese	11	14	18	24	17	24	35
Molybdenum	37	NM	37	NM	37	37	54
Neodymium	NM	26	NM	NM	26	26	38
n-(2-Hydroxyethyl)ethylenediaminetriacetic acid	4528	122	NM	NM	2325	300	440
Nickel	259	338	304	237	285	340	499
Nitrate	121160	179483	159441	140094	150045	160000	234913
Nitrite	52502	69357	63435	51430	59181	63000	92497
Oxalate	377	374	NM	NM	375	377	554
Phosphate	3170	4532	4149	3001	3713	4500	6607
Phosphorus	1211	1478	1230	1002	1230	1468	2155
Potassium	1396	1608	1619	2416	1760	1620	2378
Rubidium	NM	7	NM	NM	7	7	10
Silicon	8	191	LT	LT	99	8	12
Sodium	149434	149434	149434	149434	149434	149434	219400
Strontium	2	2	LT	NM	2	2	3
Sulfate	8227	13725	10599	8592	10286	10290	15108
Sulfur	NM	NM	3871	2958	3414	3434	5042
TIC	9304	8934	9325	8219	8945	8950	13140
TOC	17215	23796	16763	16313	18522	18522	27194

	Reference 6	Reference 7	Reference 8	Reference 9	Average	Diluted Simulant Basis	Undiluted Simulant Basis
Component	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**	**mg/Liter**
Tungsten	NM	NM	137	NM	137	137	201
Zinc	4	LT	LT	NM	4	4	6
Zirconium	11	7	7	NM	8	11	16
Additional Organics							
Nitrilotriacetic Acid	NM	211	NM	NM	211	211	310
Citric Acid	3801	3573	NM	NM	3687	3800	5579
Iminodiacetic Acid	2473	3655	NM	NM	3064	3655	5366
Succinic Acid	NM	29	NM	NM	29	29	43
Dilution Factor	0.637	0.812	0.682	0.623	NA	NA	1.468

NM = Not Measured, LT = Less than, NA = Not applicable

The basis for the simulant is shown in the columns labeled "Diluted Simulant Basis" and "Undiluted Simulant Basis". The value for sodium for the undiluted supernate is based on the average of all four of the sample analyses. The values used for the major waste components (greater than 500 mg/L) were selected to represent the most recent sample analyses (References 6, 7,and 8). For the minor waste components (<500 mg/L), the value used was the maximum observed over the four samples. The organic composition is based primarily on the latest sample analysis (Reference 7) as requested by the project, supplemented as needed from the other samples. The value shown from Reference 7 for Ethylenediaminetetraacetate (EDTA) concentration is the sum of the maximum values observed for EDTA and for ethylenediaminetriacetate (ED3A) concentrations. The value for N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) shown in Table 1 from Reference 7 was set to the method detection limit (MDL) since the complexant is expected to be present in the AN-102 supernate. To allow for some uncertainty and to reflect the preliminary status of the analytical method used, the basis value for HEDTA was set at twice the MDL. The organic compounds included in the tables is based on the commercially available compounds that are either complexing agents, organic degradation products that are complexing agents, known organic additives from Hanford processes, or major organic radiolysis products.

The analytical basis derived as explained above is listed in Table 3 and Table 4. Table 3 lists the inorganic composition undiluted (9.5 molar Na) and diluted (6.5 molar Na) used to create the simulant.

Table 3 Analytical Basis for Inorganic Composition of AN-102 Simulant

	Undiluted		Diluted to 6.5 M Na	
Component	**mg/Liter**	**Moles/Liter**	**mg/Liter**	**Moles/Liter**
Al	14682	0.544	10000	0.371
B	44	0.0041	30	0.00277
Cd	73	0.00065	50	0.00044
Ca	587	0.0146	400	0.00998
CO_3^{-2}	65650	1.09	44714	0.745
Co	4	0.000068	3	0.000046

	Undiluted		Diluted to 6.5 M Na	
Component	**mg/Liter**	**Moles/Liter**	**mg/Liter**	**Moles/Liter**
Cr	301	0.0058	205	0.0039
Cs	19	0.00014	13	0.000097
Cu	29	0.00046	20	0.00031
OH^-	8075	0.475	5500	0.323
Fe	50	0.000895	34	0.00061
K	2378	0.0608	1620	0.0414
La	19	0.00014	13	0.000093
Mn	35	0.00064	24	0.00043
Mo	54	0.00056	37	0.00038
Na	219400	9.543	149430	6.5
Nd	38	0.00026	26	0.00018
NH_3	176	0.0098	120	0.0066
Ni	499	0.0085	340	0.0058
Pb	222	0.001	151	0.00073
Rb	10	0.00012	7	0.00008
Si	12	0.00043	8	0.00029
Sr	3	0.000034	2	0.000023
W	201	0.0011	137	0.00075
Zn	6	0.000092	4	0.000063
Zr	16	0.00018	11	0.00012
Chloride	5726	0.16	3900	0.11
Fluoride	2055	0.108	1400	0.0737
Nitrate	234910	3.79	160000	2.58
Nitrite	92500	2.01	63000	1.37
Phosphate	6607	0.0696	4500	0.0474
Sulfate	15108	0.157	10290	0.107
TIC	13140	1.09	8950	0.745
TOC	27194	2.26	18522	1.54

The basis for the organic components is listed in Table 4 including the sodium gluconate value whose derivation is explained below.

Table 4 Organic Basis for the AN-102 Supernate Simulant

	Undiluted		Diluted to 6.5 M Na	
Component	**mg/Liter**	**Moles/Liter**	**mg/Liter**	**Moles/Liter**
Ethylenediaminetetraacetate (EDTA anion)[a]	3318	0.0115	2260	0.0078
n-(2-Hydroxyethyl)ethylenediaminetriacetate (HEDTA anion)	440	0.0016	300	0.00109
Oxalate	554	0.0063	377	0.0043
Glycolate	12524	0.167	8530	0.114
Citrate	5580	0.0295	3800	0.0201
Formate	10070	0.224	6860	0.152
Acetate	925	0.016	630	0.0107

	Undiluted		Diluted to 6.5 M Na	
Component	**mg/Liter**	**Moles/Liter**	**mg/Liter**	**Moles/Liter**
Nitrilotriacetate (NTA anion)	310	0.00165	211	0.00112
Succinate	43	0.00037	29	0.00025
Sodium Gluconate	1970	0.009	1342	0.0062
Iminodiacetate (IDA anion)	5366	0.0409	3655	0.0279
Glutaric Acid	78	0.0006	53	0.00041
Adipic Acid	294	0.002	200	0.0014
Suberic Acid	2167	0.0126	1476	0.0086
Azelaic Acid	1233	0.0066	840	0.0045

Ethylenediaminetetraacetate (EDTA) concentration is the sum of EDTA and of ethylenediaminetriacetate (ED3A) concentrations.

The final four organic acids were added to the simulant in order to produce a solution with some tendency to foam as observed with the actual AN-102 supernate. The concentrations the final four organic acids were based upon measurements of these compounds in tank AN-107 waste because quantitative analysis of these in a sample from tank AN-102 was not available when this report was issued.[10, 11] The concentrations for the rest of the organic components other than sodium gluconate were derived from the information in Table 1 and Table 2.

The basis for a concentration of sodium gluconate for the AN-102 simulant was determined by examining the transition metal solubility as a function of sodium gluconate concentration with all of the other complexing agents held constant. Test solutions were prepared that contained all of the measured waste components but with varying levels of sodium gluconate. After mixing for a minimum of 24 hours, the solutions were filtered through a 0.2-micron nylon filter and the filtrate submitted for analysis by inductively coupled plasma emission spectrophotometry (ICP-ES). This analysis technique is similar to photometric titrations where the absorbance or emission intensity is a linear function of the concentration of a light absorbing or emitting species. In this case, the metal ion is insoluble unless complexed. Therefore, if the solutions are filtered after adding the varying amounts of gluconate ion, then the measured increase in the soluble metal concentration will be directly related to the gluconate concentration. The expected result was that the concentration of soluble iron and other metals would be a linear function of the sodium gluconate concentration. A review of the data on the transition metals revealed that all of the soluble metal concentrations measured varied directly with the sodium gluconate concentration. Figures 1 through 5 show the linear relationship between sodium gluconate and several soluble metal species.

Figure 1 Soluble Lanthanum versus Sodium Gluconate

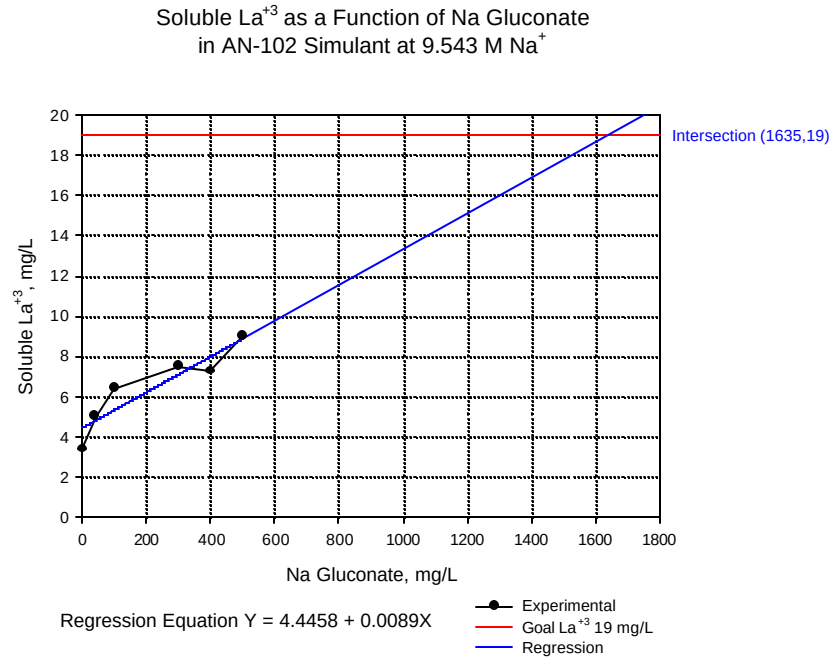


Figure 2 Soluble Iron versus Sodium Gluconate

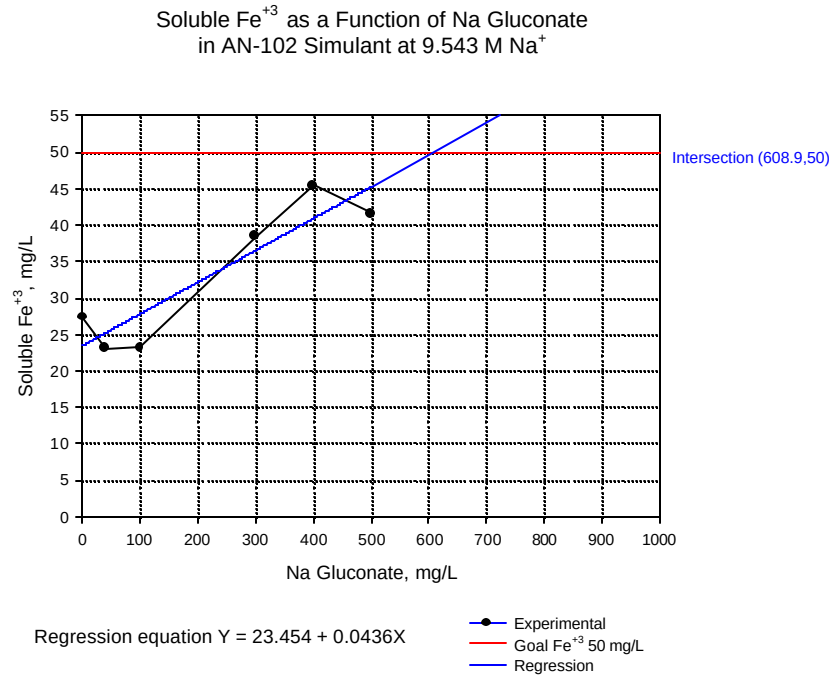


Figure 3 Soluble Neodymium versus Sodium Gluconate

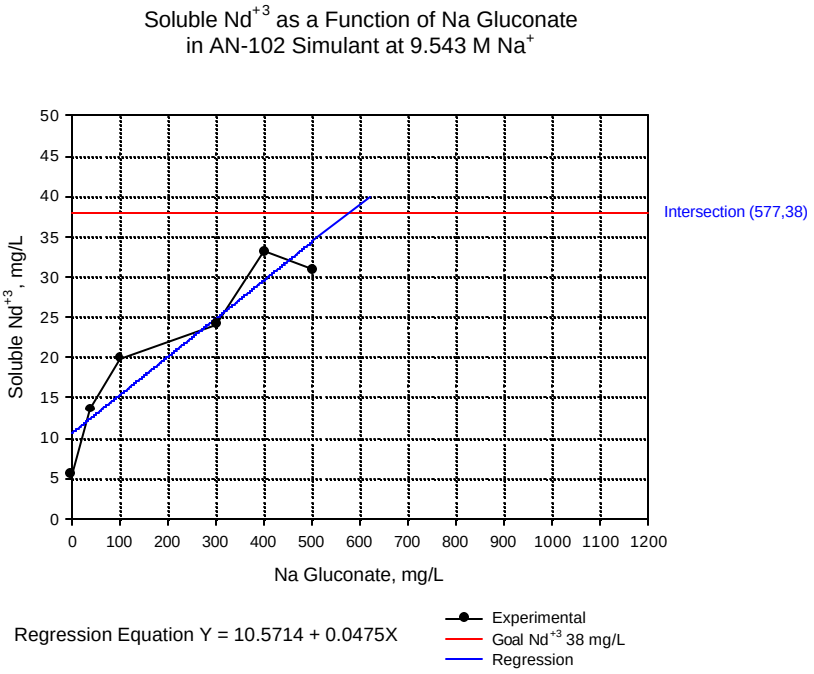


Figure 4 Soluble Lead versus Sodium Gluconate

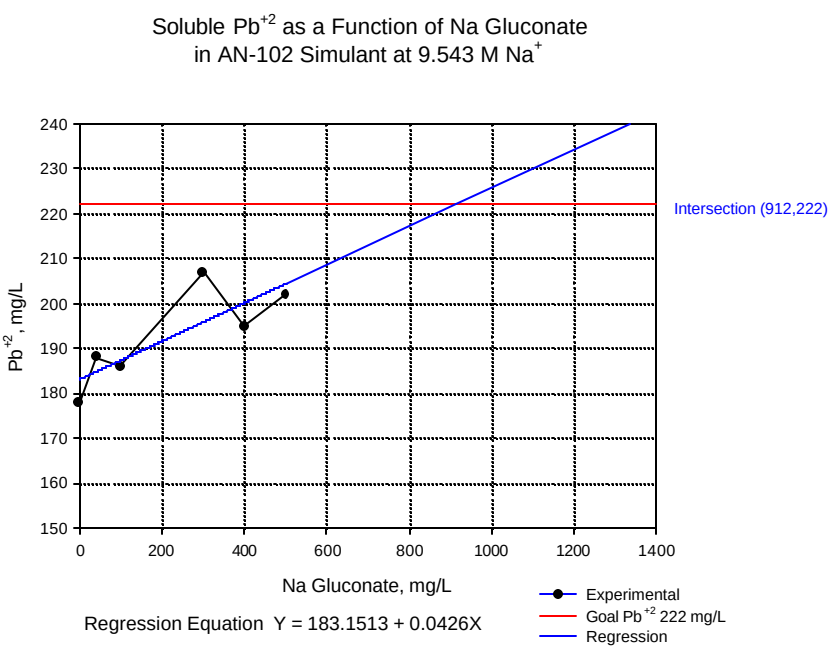
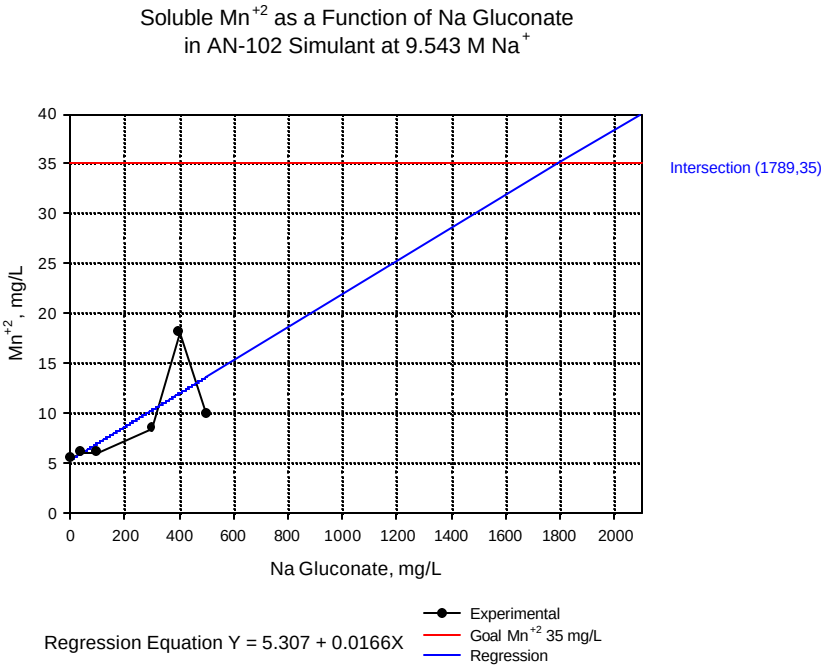


Figure 5 Soluble Manganese versus Sodium Gluconate



Each set of data was fitted to a straight line as shown on each figure in order to determine the intersection with the target concentration for that metal. The intersection represents the minimum amount of sodium gluconate necessary to achieve the specific metals soluble concentration observed in the actual waste analyses. Table 5 lists the results obtained for the metals in Figures 1 through 5 and for Ca.

Table 5 Calculated Sodium Gluconate Requirement for AN-102 Simulant at 9.5 Molar Na

Metal	***Required Na Gluconate Concentration, mg/L***
Nd	577
Fe	609
Pb	912
La	1635
Mn	1789
Ca	2692

A target concentration of sodium gluconate of 1970 mg/L was chosen as a basis for the undiluted simulant based upon the information shown in Table 5. This was derived from the amount required for manganese plus 10 percent to allow for some analytical variability. The

value based upon calcium was not used because it was expected that EDTA would complex the calcium when the other metals are sequestered by the gluconate ion.

The first step in converting the analytical values to compounds is to check the balance between negative and positively charged ions. The balance is calculated by multiplying the concentration of an ion in moles/Liter by the charge of the ion and then summing the negative and positive concentrations as shown in Table 6.

Table 6 Charge Balancing Calculations

Cations				Anions			
Species	Charge	Moles/Liter	Charge, moles/Liter	Species	Charge	Moles/Liter	Charge, moles/Liter
Ammonium	1	9.76E-03	9.76E-03	Acetate	-1	1.57E-02	-1.57E-02
Barium	2	0.00E+00	0.00E+00	Aluminum	-1	5.44E-01	-5.44E-01
Cadmium	2	6.49E-04	1.30E-03	Boron	-3	4.07E-03	-1.22E-02
Calcium	2	1.46E-02	2.93E-02	Carbonate	-2	1.09E+00	-2.19E+00
Cerium	3	0.00E+00	0.00E+00	Chloride	-1	1.62E-01	-1.62E-01
Cesium	1	1.43E-04	1.43E-04	Chromium	-2	5.79E-03	-1.16E-02
Cobalt	2	6.79E-05	1.36E-04	Ethylenediaminetetraacetate	-4	1.15E-02	-4.61E-02
Copper	2	4.56E-04	9.13E-04	Fluoride	-1	1.08E-01	-1.08E-01
Iron	3	8.95E-04	2.69E-03	Formate	-1	2.24E-01	-2.24E-01
Lanthanum	3	1.37E-04	4.10E-04	Glycolate	-1	1.67E-01	-1.67E-01
Lead	2	1.07E-03	2.14E-03	Hydroxide	-1	4.75E-01	-4.75E-01
Magnesium	1	0.00E+00	0.00E+00	Molybdenum	-2	5.63E-04	-1.13E-03
Manganese	2	6.37E-04	1.27E-03	n-Hydroxyethylenediaminetriacetate	-3	1.60E-03	-4.80E-03
Neodymium	3	2.63E-04	7.90E-04	Nitrate	-1	3.79E+00	-3.79E+00
Nickel	2	8.50E-03	1.70E-02	Nitrite	-1	2.01E+00	-2.01E+00
Potassium	1	6.08E-02	6.08E-02	Oxalate	-2	6.29E-03	-1.26E-02
Rubidium	1	1.17E-04	1.17E-04	Phosphate	-3	6.96E-02	-2.09E-01
Sodium	1	9.54E+00	9.54E+00	Silicon	-2	4.27E-04	-8.55E-04
Strontium	2	3.42E-05	6.85E-05	Sulfate	-2	1.57E-01	-3.15E-01
Zirconium	4	1.75E-04	7.02E-04	Tungsten	-2	1.09E-03	-2.19E-03
Sodium Gluconate	1	9.03E-03	9.03E-03	Zinc	-2	9.18E-05	-1.84E-04
				Nitrilotriacetate	-3	1.65E-03	-4.94E-03
				Citric Acid	-3	2.95E-02	-8.85E-02
				Iminodiacetate	-2	4.09E-02	-8.19E-02
				Succinic Acid	-2	3.70E-04	-7.41E-04
				Glutaric Acid	-2	6.00E-04	-1.20E-03
				Adipic Acid	-2	2.04E-03	-4.08E-03
				Azelaic Acid	-2	6.62E-03	-1.32E-02
				Suberic Acid	-2	1.26E-02	-2.52E-02
				Sodium Gluconate	-1	9.03E-03	-9.03E-03
Total Plus Charge			9.68	Total Minus Charge			-10.53

The charge balance based upon the information in Table 6 was 0.846 moles more anions than cations (balance is 92 %). Reducing the hydroxide concentration to achieve charge balance was not possible or desirable without disturbing the aluminum solubility. Charge balancing by adjusting the carbonate level was not recommended because the carbonate concentration is crucial to the Sr/TRU precipitation process. Another option for achieving the charge balance was to adjust either the nitrate or nitrite concentrations. However, the relative concentrations of nitrate to nitrite were assumed to control the redox of the supernate. Therefore, the concentrations of nitrate and nitrite anions for an undiluted AN-102 supernate were proportionately decreased by 0.846 moles/Liter (NO_3^- by 0.553 and NO_2^- by 0.293 moles/Liter). Table 7 gives the concentrations of nitrate and nitrite anions after revising to obtain a charge-balanced composition.

Table 7 Revised Nitrate and Nitrite Concentrations from Charge Balancing

	Undiluted		Diluted to 6.5 M Na	
Component	**mg/Liter**	**Moles/Liter**	**mg/Liter**	**Moles/Liter**
Nitrate	200640	3.24	136660	2.20
Nitrite	79006	1.72	53810	1.17

Based upon a volumetric preparation of the diluted 6.5 molar simulant, the density of the AN-102 simulant at 6.53 molar Na was 1.303 grams/mL at 298 K. The density for the undiluted AN-102 simulant (9.5 Molar Na) was 1.434 grams/mL at 298 K.

Table 8 and Table 9 list the formulation of the 6.5 molar and 9.5 molar sodium simulant. A variation on this formulation has also been used which uses the trisodium salt of HEDTA and, therefore, uses slightly less sodium hydroxide.

The organic compounds in the simulant account for 58 % of the measured TOC (total organic carbon) in the actual waste. Matching the measured TOC was not attempted because complete identification and quantitation of all organic compounds would be necessary to match the TOC. If the known or currently measured organic species were increased to match the TOC, then additional charge balance problems would arise because it is assumed that the remaining organic species are oxidized portions of the complexing agents (typically organic acids). These remaining organic species are produced by reactions between the complexing agents and the reactive intermediates ($OH^{\cdot}$ and O^-) produced by the radiolysis of water in the presence of hydroxide ion.

Table 8 AN-102 Supernate Simulant Formulation at 6.5 Molar Na

Compounds	Formula	Grams/Liter
Aluminum Nitrate	$Al(NO_3)_3 \bullet 9H_2O$	139.03
Boric Acid	H_3BO_3	0.17
Cadmium Nitrate	$Cd(NO_3)_2 \bullet 4H_2O$	0.14
Calcium Nitrate	$Ca(NO_3)_2 \bullet 4H_2O$	2.36
Cesium Nitrate	$CsNO_3$	0.019
Cobalt Nitrate	$Co(NO_3)_2 \bullet 6H_2O$	0.013
Copper Nitrate	$Cu(NO_3)_2 \bullet 2.5H_2O$	0.07

Compounds	Formula	Grams/Liter
Disodium EDTA	$C_{10}H_{14}N_2Na_2O_8 \bullet 2H_2O$	2.92
Ferric Nitrate	$Fe(NO_3)_3 \bullet 9H_2O$	0.25
HEDTA	$C_{10}H_{18}N_2O_7$	0.30
Lanthanum Nitrate	$La(NO_3)_3 \bullet 6H_2O$	0.04
Lead nitrate	$Pb(NO_3)_2$	0.24
Manganous Chloride	$MnCl_2 \bullet 4H_2O$	0.09
Neodymium Nitrate	$Nd(NO_3)_3 \bullet 6H_2O$	0.08
Nickel Nitrate	$Ni(NO_3)_2 \bullet 6H_2O$	1.68
Potassium Nitrate	KNO_3	4.11
Rubidium Nitrate	$RbNO_3$	0.01
Strontium Nitrate	$Sr(NO_3)_2$	0.005
Zinc Nitrate	$Zn(NO_3)_2 \bullet 6H_2O$	0.02
Zirconyl Nitrate	$ZrO(NO_3)_2 \bullet xH_2O$, x~1	0.03
Sodium Glycolate	$HOCH_2COONa$	11.14
Sodium Gluconate	$C_6H_{11}O_7Na$	1.34
Citric Acid	$C_6H_8O_7 \bullet H_2O$	4.22
Nitrilotriacetic Acid	$C_6H_9NO_6$	0.21
Iminodiacetic Acid	$C_4H_7NO_4$	3.71
Succinic Acid	$C_4H_6O_4$	0.03
Glutaric Acid	$C_5H_8O_4$	0.05
Adipic Acid	$C_6H_{10}O_4$	0.20
Suberic Acid	$C_8H_{14}O_4$	1.49
Azelaic Acid	$C_9H_{16}O_4$	0.85
Sodium Chloride	NaCl	6.38
Sodium Fluoride	NaF	3.09
Sodium Chromate	Na_2CrO_4	0.64
Sodium Sulfate	Na_2SO_4	15.22
Ammonium Acetate	NH_4CH_3COO	0.51
Potassium Molybdate	K_2MoO_4	0.09
Sodium Hydroxide	NaOH	79.31
Sodium Oxalate	$Na_2C_2O_4$	0.57
Sodium Acetate	$NaCH_3COO \bullet 3H_2O$	0.55
Sodium Formate	NaHCOO	10.36
Sodium Phosphate	$Na_3PO_4 \bullet 12H_2O$	18.01
Sodium Tungstate	$Na_2WO_4 \bullet 2H_2O$	0.25
Sodium Metasilicate	$Na_2SiO_3 \bullet 9H_2O$	0.08
Sodium Carbonate	Na_2CO_3	78.98
Sodium Nitrate	$NaNO_3$	87.85
Sodium Nitrite	$NaNO_2$	80.71
Water	H_2O	745.58

Table 9 AN-102 Supernate Simulant Formulation at 9.5 Molar Na

Compounds	Formula	Grams/Liter
Aluminum Nitrate	$Al(NO_3)_3 \bullet 9H_2O$	204.12
Boric Acid	H_3BO_3	0.25
Cadmium Nitrate	$Cd(NO_3)_2 \bullet 4H_2O$	0.20
Calcium Nitrate	$Ca(NO_3)_2 \bullet 4H_2O$	3.46
Cesium Nitrate	$CsNO_3$	0.028
Cobalt Nitrate	$Co(NO_3)_2 \bullet 6H_2O$	0.02
Copper Nitrate	$Cu(NO_3)_2 \bullet 2.5H_2O$	0.11
Disodium EDTA	$C_{10}H_{14}N_2Na_2O_8 \bullet 2H_2O$	4.29
Ferric Nitrate	$Fe(NO_3)_3 \bullet 9H_2O$	0.36
HEDTA	$C_{10}H_{18}N_2O_7$	0.44
Lanthanum Nitrate	$La(NO_3)_3 \bullet 6H_2O$	0.06
Lead nitrate	$Pb(NO_3)_2$	0.35

Compounds	Formula	Grams/Liter
Manganous Chloride	$MnCl_2 \bullet 4H_2O$	0.13
Neodymium Nitrate	$Nd(NO_3)_3 \bullet 6H_2O$	0.12
Nickel Nitrate	$Ni(NO_3)_2 \bullet 6H_2O$	2.47
Potassium Nitrate	KNO_3	6.03
Rubidium Nitrate	$RbNO_3$	0.02
Strontium Nitrate	$Sr(NO_3)_2$	0.007
Zinc Nitrate	$Zn(NO_3)_2 \bullet 6H_2O$	0.03
Zirconyl Nitrate	$ZrO(NO_3)_2 \bullet xH_2O$, x~1	0.04
Sodium Glycolate	$HOCH_2COONa$	16.36
Sodium Gluconate	$C_6H_{11}O_7Na$	1.97
Citric Acid	$C_6H_8O_7 \bullet H_2O$	6.20
Nitrilotriacetic Acid	$C_6H_9NO_6$	0.31
Iminodiacetic Acid	$C_4H_7NO_4$	5.45
Succinic Acid	$C_4H_6O_4$	0.04
Glutaric Acid	$C_5H_8O_4$	0.08
Adipic Acid	$C_6H_{10}O_4$	0.30
Suberic Acid	$C_8H_{14}O_4$	2.19
Azelaic Acid	$C_9H_{16}O_4$	1.25
Sodium Chloride	NaCl	9.36
Sodium Fluoride	NaF	4.54
Sodium Chromate	Na_2CrO_4	0.94
Sodium Sulfate	Na_2SO_4	22.34
Ammonium Acetate	NH_4CH_3COO	0.75
Potassium Molybdate	K_2MoO_4	0.13
Sodium Hydroxide	NaOH	116.44
Sodium Oxalate	$Na_2C_2O_4$	0.84
Sodium Acetate	$NaCH_3COO \bullet 3H_2O$	0.80
Sodium Formate	NaHCOO	15.22
Sodium Phosphate	$Na_3PO_4 \bullet 12H_2O$	26.44
Sodium Tungstate	$Na_2WO_4 \bullet 2H_2O$	0.36
Sodium Metasilicate	$Na_2SiO_3 \bullet 9H_2O$	0.12
Sodium Carbonate	Na_2CO_3	115.95
Sodium Nitrate	$NaNO_3$	128.98
Sodium Nitrite	$NaNO_2$	118.50
Water	H_2O	615.60

Table 8 and Table 9 do not specify the sequence of addition that was determined to produce an acceptable simulant. The procedure with the correct addition sequence used to produce one liter of the AN-102 supernate simulant at 6.5 molar Na is listed in Table 10.

Table 10 Procedure for One Liter of AN-102 Supernate Simulant at 6.5 Molar Na

Volume of Feed	**1000**	**mL**
To the Simulant Preparation Vessel Add	**Grams**	
Water	200	
Next add the following while maintaining good mixing		

Metal Compounds and Complexants	Formula	Mass Needed, grams
Aluminum Nitrate	$Al(NO_3)_3 \bullet 9H_2O$	139.03
Cadmium Nitrate	$Cd(NO_3)_2 \bullet 4H_2O$	0.14
Calcium Nitrate	$Ca(NO_3)_2 \bullet 4H_2O$	2.36
Cesium Nitrate	$CsNO_3$	0.019
Copper Nitrate	$Cu(NO_3)_2 \bullet 2.5H_2O$	0.07
Cobalt Nitrate	$Co(NO_3)_2 \bullet 6H_2O$	0.013

Ferric Nitrate	$Fe(NO_3)_3 \bullet 9H_2O$	0.25
Lanthanum Nitrate	$La(NO_3)_3 \bullet 6H_2O$	0.04
Lead nitrate	$Pb(NO_3)_2$	0.24
Manganous Chloride	$MnCl_2 \bullet 4H_2O$	0.09
Neodymium Nitrate	$Nd(NO_3)_3 \bullet 6H_2O$	0.08
Nickel Nitrate	$Ni(NO_3)_2 \bullet 6H_2O$	1.68
Potassium Nitrate	KNO_3	4.11
Rubidium Nitrate	$RbNO_3$	0.01
Strontium Nitrate	$Sr(NO_3)_2$	0.005
Zinc Nitrate	$Zn(NO_3)_2 \bullet 6H_2O$	0.02
Zirconyl Nitrate	$ZrO(NO_3)_2 \bullet xH_2O$, x~1	0.03
Disodium Ethylenediaminetetraacetate	$C_{10}H_{14}N_2Na_2O_8 \bullet 2H_2O$	2.92
n-(2-Hydroxyethyl)ethylenediaminetriacetic acid	$C_{10}H_{18}N_2O_7$	0.30
Sodium Gluconate	$C_6H_{11}O_7Na$	1.34
Citric Acid	$C_6H_8O_7 \bullet H_2O$	4.22
Nitrilotriacetic Acid	$C_6H_9NO_6$	0.21
Iminodiacetic Acid	$C_4H_7NO_4$	3.71
Succinic Acid	$C_4H_6O_4$	0.03
Glutaric Acid	$C_5H_8O_4$	0.05
Adipic Acid	$C_6H_{10}O_4$	0.20
Suberic Acid	$C_8H_{14}O_4$	1.49
Azelaic Acid	$C_9H_{16}O_4$	0.85
Boric acid	H_3BO_3	0.17
Ammonium Acetate	NH_4CH_3COO	0.51
Sodium Chloride	NaCl	6.38
Sodium Fluoride	NaF	3.09
Sodium Sulfate	Na_2SO_4	15.22
Potassium Molybdate	K_2MoO_4	0.09
Mix thoroughly. Then add the following while mixing.	**Formula**	**Mass Needed, grams**
Sodium Hydroxide	NaOH	79.31
Sodium Phosphate	$Na_3PO_4 \bullet 12H_2O$	18.01
Sodium Tungstate	$Na_2WO_4 \bullet 2H_2O$	0.25
Sodium Metasilicate	$Na_2SiO_3 \bullet 9H_2O$	0.08
Sodium Glycolate	$HOCH_2COONa$	11.14
Sodium formate	NaHCOO	10.36
Sodium Acetate	$NaCH_3COO \bullet 3H_2O$	0.55
Sodium Oxalate	$Na_2C_2O_4$	0.57
Water	H_2O	200
Mix thoroughly then Add	**Formula**	**Mass Needed, grams**
Sodium Chromate	Na_2CrO_4	0.64
Sodium Carbonate	Na_2CO_3	78.98
Mix thoroughly then Add	**Formula**	**Mass Needed, grams**
Sodium Nitrate	$NaNO_3$	87.85
Sodium Nitrite	$NaNO_2$	80.71
Water	H_2O	245.58
Mix thoroughly for 24 hours.		

The addition sequence used in Table 10 eliminates undesirable destruction of carbonate by the acidic compounds (acidic nitrates and acids) and prevents oxidation of the organic species by chromate. The analytical results for the AN-102 supernate simulant are described in the simulant validation section of this document.

2.2.2 Entrained Solids Simulant

The entrained solids in envelope C will experience the precipitation of strontium carbonate and manganese dioxide before being processed through a crossflow filter. Because the presence of the unwashed entrained solids may have an impact on the precipitation product, the entrained solids must represent the unwashed solids in the AN-102 supernate. The basis for the unwashed solids composition on a dried solids basis is shown in Table 11. The basis was derived from a recent AN-102 sample after removing the easily soluble nitrate, nitrite and chloride.[7] The TIC value was converted to carbonate before formulating compounds to represent the entrained solids.

Table 11 Basis for AN-102 Unwashed Entrained Solids

Component	*Micrograms/gram unwashed dried solids*
Al	113000
Ba	146
Ca	733
Ce	122
Cr	9000
F	20100
Fe	6050
La	122
Mn	1310
Na	319000
Nd	245
Ni	93
Oxalate	151000
Pb	728
Phosphate	43300
Si	341
Sulfate	35600
TIC	58400
W	979
Zn	116
Zr	221

The most significant species present in the unwashed solids were sodium, carbonate, oxalate, aluminum, phosphate, sulfate and fluoride. By definition, the entrained solids should be compounds of limited or low solubility. After reviewing various combinations of cations and anions based on the requirement of low or limited solubility, the formulation given in Table 12 was deemed the most reasonable composition while providing consistency with the associated waste solution. The compounds were also chosen based upon their industrial availability.

Table 12 Recipe for Unwashed AN-102 Entrained Solids Simulant

Recipe For AN-102 Solids	CAS #	Formula	grams/100 grams of entrained solids
Sodium Carbonate Monohydrate	5968-11-6	$Na_2CO_3 \bullet H_2O$	42.71
Sodium Oxalate	62-76-0	$Na_2C_2O_4$	16.10
Aluminum Oxide	1344-28-1	Al_2O_3	15.12
Sodium Phosphate Dodecahydrate	10101-89-0	$Na_3PO_4 \bullet 12H_2O$	12.28
Sodium Sulfate	7727-73-3	$Na_2SO_4 \bullet 10H_2O$	8.35
Sodium Fluoride	7681-49-4	NaF	3.15
Chromic Oxide	1308-38-9	Cr_2O_3	0.93
Ferric Hydroxide	1310-14-1	FeOOH	0.68
Manganese Dioxide	1313-13-9	MnO_2	0.15
Calcium Oxalate Monohydrate	5794-28-5	$CaC_2O_4 \bullet H_2O$	0.13
Calcium Tungstate	7790-75-2	$CaWO_4$	0.11
Lead Sulfate	7446-14-2	$PbSO_4$	0.08
Silica	7631-86-9	SiO_2	0.05
Neodymium Oxalate	28877-87-4	$Nd_2(C_2O_4)_3 \bullet 10H_20$	0.04
Barium Sulfate	7727-43-7	$BaSO_4$	0.02
Cerium Oxalate	15750-47-7	$Ce_2(C_2O_4)_3 \bullet 9H_20$	0.02
Lanthanum Oxalate	537-03-1	$La_2(C_2O_4)_3 \bullet 9H_20$	0.02
Zirconium Dioxide	1314-23-4	ZrO_2	0.02
Zinc Oxalate Dihydrate	4255-07-6	$ZnC_2O_4 \bullet 2H_2O$	0.02
Nickel Oxide	1313-99-1	NiO	0.01

Note: The weight percent entrained solids will be set by the task using the simulant.

Some of the compounds present in the largest amounts are expected to be dissolved during the Sr/TRU washing process.

Particle size information is not available for the entrained solids in actual AN-102 waste. Therefore, the basis used for the particle size of the entrained solids simulant was set to less than 325 mesh (smaller than 44 micron) based upon an agreement with the customer. The particle size of the entrained solids is expected to decline (become smaller) due to shearing

during the SR/TRU mixing/filtration and due to dissolution during washing. Entrained solids loading will be determined by the tests that utilize the simulant.

2.2.3 Simulant Validation

2.2.3.1 Chemical Composition Validation

The first step in validation of the simulant is to determine whether the simulant basis (Table 3) is consistent with other sources of information for this waste within the WTP project. Table 13 provides a comparison of the inorganic simulant basis to the batch LAW-4 (AN-102) in the TFCOUP Appendix D, Table D-2.[12]

Table 13 AN-102 Simulant Basis Compared to AN-102 Composition from Reference 12

Component	Reference 12 AN-102, Moles/Liter	AN-102 Simulant Basis, Moles/Liter	% of Reference 12 Value
Aluminum	5.40E-01	5.44E-01	101
Ammonium	7.09E-03	9.76E-03	138
Boron	3.47E-03	4.07E-03	117
Cadmium	5.15E-04	6.49E-04	126
Calcium	1.09E-02	1.46E-02	134
Carbonate	1.19E+00	1.09E+00	92
Cesium	8.88E-05	1.43E-04	161
Chloride	1.15E-01	1.62E-01	141
Chromium	5.53E-03	5.79E-03	105
Cobalt	1.84E-04	6.79E-05	37
Copper	3.59E-04	4.56E-04	127
Fluoride	9.49E-02	1.08E-01	114
Hydroxide	5.06E-01	4.75E-01	94
Iron	8.30E-04	8.95E-04	108
Lanthanum	8.88E-06	1.37E-04	1543
Lead	8.1E-04	1.07E-03	132
Manganese	5.37E-04	6.37E-04	119
Molybdenum	5.04E-04	5.63E-04	112
Neodymium	3.78E-04	2.63E-04	70
Nickel	6.52E-03	8.50E-03	130
Nitrate	3.79E+00	3.24E+00	85
Nitrite	1.95E+00	1.72E+00	88
Phosphate	5.68E-02	6.96E-02	123
Potassium	6.98E-02	6.08E-02	87
Silicon	2.30E-03	4.27E-04	19
Sodium	1.01E+01	9.54E+00	94

Component	Reference 12 AN-102, Moles/Liter	AN-102 Simulant Basis, Moles/Liter	% of Reference 12 Value
Strontium	6.48E-05	3.42E-05	53
Sulfate	1.82E-01	1.57E-01	86
TOC	2.17E+00	2.26E+00	104
Tungsten	1.00E-03	1.09E-03	109
Zinc	8.36E-05	9.18E-05	110
Zirconium	1.69E-04	1.75E-04	104

Most of the transition metals are at slightly higher concentrations in the simulant basis than those in the TFCOUP. For the major species, sodium and the anions, the value in TFCOUP is larger. Comparing the composition on an equivalent sodium basis would have had the anions matching better but also shifted the transition metals to a higher percentage of the TFCOUP.

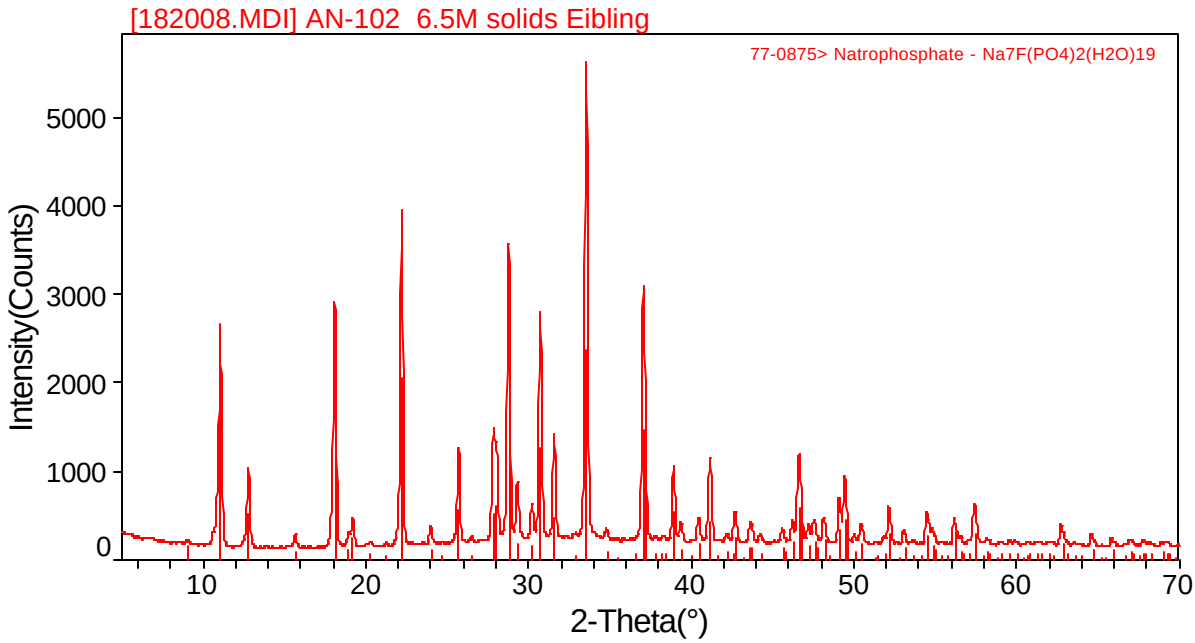
Test solutions of the undiluted simulant and diluted simulant were prepared using the general procedure shown in Table 10. After mixing for 24 hours the solution was filtered through a 0.45-micron nylon filter and the supernate submitted for analysis. The wet (unwashed) solids were collected from the filters and submitted for x-ray diffraction (XRD) to determine the major phases present. The amount of undissolved solids recovered from the undiluted simulant was estimated at less than one weight percent.

The undiluted simulant produced two different types of solids, which were analyzed separately. The first type of solid was white and denser than the other solids. The second solid was finer and had a yellow-white color. The XRD analysis of the white solids tentatively identified the solids as Thermonatrite ($Na_2CO_3 \bullet H_2O$) and Natrophosphate ($Na_7F(PO_4)_2(H_2O)_{19}$). The presence of sodium carbonate in the solids for the undiluted simulant implies that the solution is probably saturated in carbonate anion. Dilution of the simulant to the nominal starting conditions of the SR/TRU process should dissolve the sodium carbonate. The presence of the sodium carbonate solids matches the expected high level of carbonate (based on TIC) in the unwashed entrained solids shown in Table 11. The other compound detected is the double salt, sodium fluorophosphate, and may be the result of excessive fluoride levels. Analysis of fluoride by ion chromatography can produce high results due to interference from organic acids. The second type of solid found in the undiluted simulant was also analyzed by XRD. The tentatively identified compounds included the thermonatrite and the natrophosphate previously observed. Also identified were a second double salt, Kogarkoite (Na_3FSO_4) and Nitratine ($NaNO_3$). The sodium nitrate observed by the XRD is expected to be due to the interstitial liquid within the filtered solids layer. The impact of these solids on the supernate composition is that the supernate should be low in fluoride, phosphate, sulfate and carbonate.

Considerably fewer solids (estimated at less than 0.5 weight %) were obtained from the 6.5 molar simulant solution. The only compound detected by XRD was the fluorophosphate double salt, natrophosphate ($Na_7F(PO_4)_2(H_2O)_{19}$) as shown in Figure 6. The vertical lines in

Figure 6 indicate the positions where peaks are expected based upon the identified compound and the relative intensity of those peaks. The nearly perfect match with the identified compound indicates that practically no other insoluble solids were present. As expected, because the supernate was much more dilute, all of the carbonate was in solution.

Figure 6 Solids filtered from AN-102 simulant at 6.5 Molar Na



The analytical results for the filtered AN-102 supernate simulant listed in Table 14 and Table 15 were produced as previously described. The samples of the supernate were analyzed by inductively coupled plasma- emission spectroscopy (ICP-ES), ion chromatography (IC), ion exclusion chromatography (IEC), high performance liquid chromatography (HPLC), derivatization gas chromatography-mass spectrometry (GCMS), and total inorganic carbon/total organic carbon by persulfate oxidation (TIC/TOC).

Table 14 Analytical Results for the Undiluted AN-102 Simulant (9.5 Molar Na)

Sample ID	182000	182001	182002	Average	Target		
Component	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**% of Target**	**Method**
Al	14600	14700	14700	14667	14680	100	ICP-ES
B	40.3	41.8	41.9	41	44.0	94	ICP-ES
Ca	371	379	380	377	587	64	ICP-ES
Cd	68.1	70.1	68.8	69	73	95	ICP-ES
Co	3.6	4.4	3.5	4	4	96	ICP-ES
Cr	287	293	291	290	301	96	ICP-ES
Cu	30.3	30.2	30.3	30	29.0	104	ICP-ES
Fe	48.1	48.8	48.3	48	50.0	97	ICP-ES
K	2700	2670	2800	2723	2378	115	ICP-ES
La	14.9	14.6	14.8	15	19	78	ICP-ES
Mn	34.0	34.5	34.2	34	35.000	98	ICP-ES
Mo	49.3	53.0	50.6	51	54.0	94	ICP-ES
Na	211000	217000	219000	215667	219390	98	ICP-ES
Nd	40.0	39.1	39.9	40	38	104	ICP-ES
Ni	470	485	476	477	499	96	ICP-ES
P	697	720	699	705	2156	33	ICP-ES
Pb	191	208	199	199	222	90	ICP-ES
S	2870	2900	2900	2890	5033	57	ICP-ES
Si	18.1	19.4	18.4	19	12	155	ICP-ES
Sr	0.30	0.32	0.31	0.3	3	10	ICP-ES
W	204	202	186	197	201	98	ICP-ES
Zn	7.68	7.90	7.90	7.8	6	130	ICP-ES
Zr	4.80	4.80	4.70	4.77	16	30	ICP-ES
Acetate	1260	1300	1270	1277	925	138	IEC
Chloride	5280	5190	5170	5213	5726	91	IC
Citrate	3470	4000	1790	3087	5579	55	IEC
EDTA	1740	1830	1880	1817	3318	55	HPLC
Fluoride	1810	1830	1790	1810	2055	88	IC
Formate	10300	10200	10200	10233	10070	102	IC
Formate	17000	14800	13400	15067	10070	150	IEC
Glycolate	11600	8370	7930	9300	12520	74	IEC
HEDTA	73	71	75	73	440	17	HPLC
Iminodiacetic Acid	8630	3480	5180	5763	5580	103	GCMS
Nitrate	195000	189000	195000	193000	200640	96	IC
Nitrite	79400	73800	88600	80600	79000	102	IC
Oxalate	316	568	315	400	554	72	IC
Phosphate	2430	2680	2450	2520	6610	38	IC
Sulfate	8350	8300	10900	9183	15110	61	IC
Nitrilotriacetic Acid	249	132	208	196	310	63	GCMS
TIC	10600	10800	10600	10667	13140	81	TIC/TOC
TOC	15200	14800	15200	15067	16245	93	TIC/TOC
Total Carbon	25800	25600	25800	25733	29385	88	TIC/TOC

Table 15 Analytical Results for the AN-102 Simulant at 6.5 M Na

Sample ID	182003	182004	182005	Average	Target		
Component	mg/L	mg/L	mg/L	mg/L	mg/L	% of Target	Method
Al	9810	9850	9880	9847	10000	98	ICP-ES
B	31.9	31.7	31.5	32	30	106	ICP-ES
Ca	350	350	349	350	400	87	ICP-ES
Cd	47.6	47.4	47.6	48	50	95	ICP-ES
Cr	196	195	195	195	205	95	ICP-ES
Cu	25.1	25	25.1	25	20	125	ICP-ES
Fe	34.5	34.3	34.4	34	34	101	ICP-ES
K	2030	1960	2030	2007	1620	124	ICP-ES
La	13.3	13.3	13.5	13	13	103	ICP-ES
Mn	22.3	22.2	22.3	22	24	93	ICP-ES
Mo	44.3	43.9	43.6	44	37	119	ICP-ES
Na	152000	150000	149000	150333	149434	101	ICP-ES
Nd	23.6	23.7	24.5	24	26	92	ICP-ES
Ni	324	323	322	323	340	95	ICP-ES
P	661	655	656	657	1468	45	ICP-ES
Pb	141	139	138	139	151	92	ICP-ES
S	3520	3420	3420	3453	3430	101	ICP-ES
Si	11.2	11.4	11.2	11	8	141	ICP-ES
Sr	2.61	2.59	2.58	2.6	2	130	ICP-ES
W	139	135	138	137	137	100	ICP-ES
Zn	6	5.9	5.8	5.9	4	147	ICP-ES
Zr	1.5	1.5	1.5	1.5	11	14	ICP-ES
Acetate	791	814	808	804	630	128	IEC
Chloride	3710	3720	3670	3700	3900	95	IC
Citrate	1770	1790	1770	1777	3800	47	IEC
EDTA	1040	913	987	980	2260	43	HPLC
Fluoride	1930	1940	1890	1920	1400	137	IC
Formate	6830	6890	6850	6857	6860	100	IC
Formate	8640	15600	12400	12213	6860	178	IEC
Glycolate	5020	4730	4370	4707	8530	55	IEC
HEDTA	31	27	26	28	300	9	HPLC
Iminodiacetic Acid	3700	3830	3550	3693	3655	101	GCMS
Nitrate	126000	134000	133000	131000	136700	96	IC
Nitrilotriacetic Acid	224	208	205	212	211	101	GCMS
Nitrite	55600	60800	59200	58533	53800	109	IC
Oxalate	341	352	482	392	377	104	IC
Phosphate	2240	2250	2430	2307	4500	51	IC
Sulfate	12200	10200	10200	10867	10290	106	IC
TIC	7650	7580	7580	7603	8950	85	TIC/TOC
TOC	10150	10420	10120	10230	11065	92	TIC/TOC
Total Carbon	12800	18000	17700	16167	20015	81	TIC/TOC

In general, the agreement between the measured concentration and the planned concentration for the transition and lanthanide metals is very good. Agreement for the major anions, nitrate

and nitrite, is also very good. The supernate analysis for phosphorus and phosphate are fairly consistent and are low which is also consistent with the insoluble fluorophosphate species observed in the solids at both concentrations of simulant. The higher phosphate level measured in actual AN-102 supernate probably indicates that the actual fluoride level is lower than the level that has previously been reported. The fluoride analysis result, particularly in Table 15, demonstrates the presence of interfering components because fluoride should be low due to the precipitated fluorophosphate salt instead of high. Sulfate in the undiluted supernate is also low and confirms the precipitation of sulfate as the fluorosulfate salt. Other analyses showing evidence of interference are formate and carbonate by IEC and the interference is probably due to the complex nature of the AN-102 formulation (multitude of organic acids). The low result for HEDTA may be due to chemical degradation of the complexing agent as previously reported for caustic solutions.[14-16]

2.2.3.2 Physical Property Validation

2.2.3.2.1 Density

The density of the simulant was measured at several different sodium concentrations for comparison with actual AN-102 supernate densities. Table 16 compares the simulant density to the actual density at 25 ° C for diluted and undiluted supernate.

Table 16 Supernate Density at 25 Celsius

Simulant		Actual AN-102 Sample[6-8]	
Na, Moles/Liter	g/mL	Na, Moles/Liter	g/mL
6.5	1.30	6.4	1.33
9.54	1.43	Undiluted (8-10.4)	1.41-1.47

During development of a prior envelope C simulant, for tank AN-107 supernate, Equation (1) which related the sodium concentration (X, molarity) to the density (Y, gm/L) was empirically developed to allow predictions of densities for different sodium concentrations when the supernate is diluted:

$$Y^2 = 0.998 + 0.1054X \quad (1).^{17}$$

Equation (1) was tested to determine if it could also be applied to the AN-102. As shown in Table 17, Equation (1) can be used to predict the density of the simulant at a different sodium concentration.

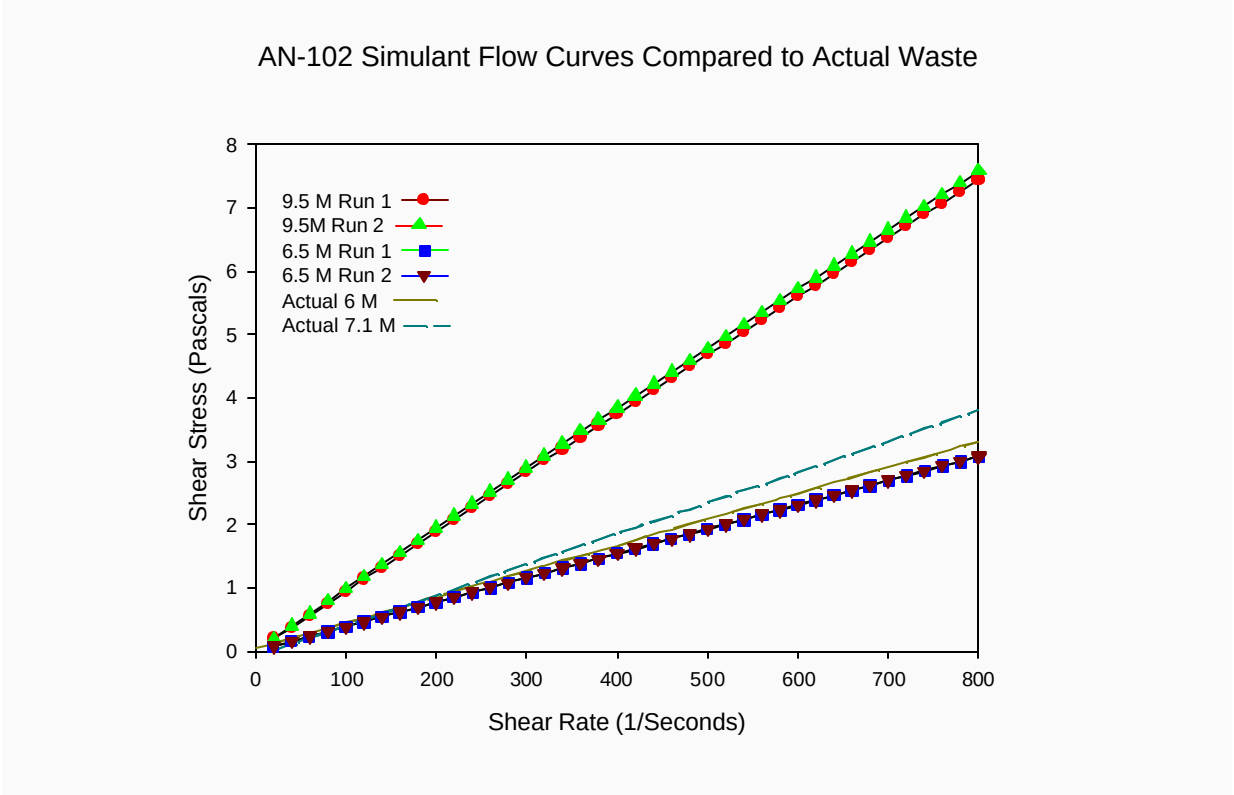
Table 17 Simulant Density Based on Empirical Equation

Simulant Na Concentration, Moles/Liter	Measured Density, g/mL	Predicted Density, g/mL
4.016	1.192	1.192
5.02	1.236	1.236
6.024	1.278	1.278
6.527	1.303	1.298
7.53	1.34	1.339
9.581	1.434	1.417

2.2.3.2.2 Rheology

The rheological properties of the diluted and undiluted supernate simulant were investigated using a Haake RS-150 rheometer. The samples were analyzed across the shear rate range of 0 to 800 1/seconds using the DG-41 (double gap) concentric cylindrical sensor at 25 ° C. Figure 7 shows comparisons of the flow curves for duplicate runs at 6.5 molar Na and 9.58 molar Na to the linear regression lines from actual waste sample runs.

Figure 7 AN-102 Supernate Simulant Flow Curve Compared to Actual Waste



The actual waste samples were pretreated AN-102 samples and were run on a Haake RV20/M5 rheometer with the NV double-gap concentric, cylindrical sensor at 25 ° C.[13] The flow curves for both simulants and for the actual waste samples show that the liquids are Newtonian. For a Newtonian liquid, the ratio of shear stress to shear rate is a constant, which is the viscosity of the liquid. A comparison of the viscosity of the simulant to the pretreated AN-102 waste sample is shown in Table 18.

Table 18 Viscosity of AN-102 Simulant and Actual AN-102 Supernate at 25 Celsius

Na, Moles/Liter	Simulant Viscosity milliPascal-sec	Actual AN-102 Viscosity[13] milliPascal-sec
5	NM	2.9±1
6	NM	4±1
6.5	3.8	NM
7	NM	5.1±1
9.54	9.4	NM

NM = Not Measured

The agreement between the actual waste and the simulant is very good after allowing for the error factor listed for the waste sample.

3.0 CONCLUSION/SUMMARY

A formulation for a supernate simulant has been developed to represent waste from Hanford Tank 241-AN-102. The simulant is designed to reproduce the chemical composition of the supernate at 9.5 molar sodium and after the supernate is diluted to a 6.5 molar sodium concentration. The simulant also includes a formulation to represent the unwashed entrained solids expected in the undiluted supernate.

4.0 REFERENCES

1. Williams, M. R. *Task Technical and Quality Assurance Plan In Support of RPP-WTP Pilot-Scale Precipitation Testing*. WSRC-TR-2000-00496, Rev 1, SRT-RPP-2000-00050, Rev. 1, Savannah River Site, Aiken SC 29808 (November 30, 2001).

2. Poirier, M. R. *Task Technical and Quality Assurance for AN-102 Simulant Sr/TRU Precipitation and Ultrafiltration***.** WSRC-TR-2001-Draft, SRT-RPP-2001-Draft, Rev 0, Savannah River Site, Aiken, SC 29808 (December 14,2001).

3. Bannochie, C., and C. Nash. *Evaluation of Post-Filtration Precipitation Mechanisms.* WSRC-TR-2001-00425, SRT-RPP-2001-00147, Rev 0, Savannah River Site, Aiken, SC 29808 (November 12, 2001).

4. Bannochie, C. *Complexant Identification in Hanford Waste Simulant Sr/TRU Filtrate.* WSRC-TR-2001-00608, SRT-RPP-2001-00238, Rev B, Savannah River Site, Aiken, SC 29808 (December 17, 2001).

5. Josephs, J. E. and T. B. Calloway, Jr. *Task Technical and Quality Assurance Plan for – LAW Evaporation: Antifoam/Defoamer Testing for Low Activity Waste Solution*. WSRC-RP-2001-00791, SRT-RPP-2001-00142 Revision 0, Savannah River Site, Aiken, SC 29808 (December 1, 2001).

6. Hay, M. S., Bronikowski, M. G., Hsu, C. W., and T. L. White. *Chemical Characterization of an Envelope C Sample from Hanford Tank 241-AN-102*. USDOE Report BNF-003-98-0250, Rev 0, Savannah River Site, Aiken, SC 29808 (July 31, 2000).

7. Urie, M. W., Fiskum, S. K., Campbell, J. A., Farmer, O. T., Greenwood, L. R., Hoppe, E. W., Mong, G. M., Soderquist, C. Z., Swoboda, R. G., Thomas, M. P., and J. J. Wagner. *Chemical Analysis and Physical Property Testing of 241-AN-102 Tank Waste--Supernatant and Centrifuged Solids*. PNWD-3173, WTP-RPT-020, Pacific Northwest National Laboratory, Richland, WA 99352 (July, 2002).

8. Esch, R. A. *Tank 241-AN-102 Low Activity Waste Envelope C Analytical Results for the Final Report*. HNF-SD-WM-DP-310, Rev 0, Waste Management Federal Services of Hanford, Inc for Fluor Daniel Hanford, Inc., Richland, WA, (1998).

9. Jo, J., Morris, B. J., and T. T. Tran. *Tank Characterization Report for Double-Shell Tank 241-AN-102*. WHC-SD-WM-ER-545, Rev 1, Westinghouse Hanford Company, Richland, WA 99352 (August 1996).

10. Lokken, R.O., Scheele, R. D., Strachan, D. M., and A. P. Toste. *Complex Concentrate Pretreatment FY 1986 Progress Report*. PNL-7687, Pacific Northwest Laboratory, Richland, WA 99352 (September 1986).

11. Toste, A. P., Lechner-Fish, T. J., Hendren, D. J., Scheele, R. D., and W. G. Richmond. "Analysis of Organics in Highly Radioactive Nuclear Wastes". *Journal of Radioanalytical and Nuclear Chemistry*, 123, p 149 (1988).

12. Kirkbride, R. A., Allen, G. K., Higley, B. A., Hohl, T. M., Lambert, S. L., Orme, R. M., Pace, D. E., Seidl, J. A., Wittman, R. S., Baldwin, J. H., Jo, J. and J. N. Strode. *Tank Farm Contractor Operation and Utilization Plan*. HNF-SD-WM-SP-012 REV 3A, Numatec Hanford Corporation and CH2MHILL Hanford Group, Inc., Richland, WA (September 2001).

13. Zamecnik, J. R., Crawford, C. L., and D. C. Koopman. *Large Scale Vitrification of 241-AN-102 (Envelope C) Sample*. WSRC-TR-2002-00093, Rev.0, SRT-RPP-2001-00190, Rev. 0, Savannah River Site, Aiken, SC 29808 (May 31, 2002).

14. Babad, H., Camaioni, D. M., Lilga, M. A., Samuels, W. D. and D. M. Strachan. *Tank Waste Chemistry – A New Understanding of Waste Aging*. WHC-SA-1694-FP, Westinghouse Hanford Company, Richland, WA (February 1993).

15. Toste, A. P. and T. J. Lechner-Fish. "Chemo-Degradation of Chelating and Complexing Agents in a Simulated, Mixed Nuclear Waste". *Proceedings of Waste Management'93*, Tucson, AZ, Vol. 13, pp. 237-244 (1993).

16. Babad, H. and D. M. Camaioni. "The Aging of Organic Chemicals in Hanford High-Level Wastes". *Proceedings of Waste Management '00*, Tucson, AZ, (2000).

17. Eibling, R. E. and C. Nash. *Hanford Waste Simulants Created to Support the Research and Development on the River Protection Project – Waste Treatment Plant*. WSRC-TR-2000-00338, Rev.0, SRT-RPP-2000-00017, Rev. 0, Savannah River Site, Aiken, SC 29808 (July 26, 2001).

18. *Final Environmental Statement, Waste Management Operations, Hanford Reservation, Richland, Washington. Volume 2.* ERDA—1538 (Vol.2), Richland. WA (December 01, 1975).

APPENDIX A: AN-102 SUPERNATE AND ENTRAINED SOLIDS SIMULANT PREPARATION PROCEDURE

1.0 SIMULANT DESIGNATION

The AN-102 supernate simulant replicates the chemical and physical properties of the Envelope C Hanford tank 241-AN-102 supernate diluted to 6.5 molar in sodium. The AN-102 entrained solids simulant is designed to represent the unwashed entrained solids present in the supernate from Hanford tank 241-AN-102. The supernate simulant and entrained solids simulant are intended for use in testing the Sr/TRU precipitation and filtration pretreatment processes. The simulant recipes were formulated based upon the actual tank waste analyses of diluted and undiluted AN-102 waste.

2.0 SIMULANT WASTE STREAM COMPOSITION AND UNIT OPERATION USAGE

2.1 CHARACTERIZATION DATA DESCRIPTION

The AN-102 supernate simulant was developed to replicate the chemical and physical properties of the actual AN-102 supernate diluted to 6.5 molar Na. The simulant metals and anionic constituents' concentrations are to agree with actual waste concentrations within ±10%, or within analytical error of the method as determined by inductively coupled plasma atomic emission spectrometry (ICPAES), inorganic ion chromatography (IC), gas chromatography-mass spectrometry (GCMS) and other organic characterization methods. Density is determined gravimetrically. Viscosity is determined as a function of temperature.

The AN-102 entrained solids simulant was developed to represent the types of compounds expected to be present in the unwashed solids entrained in the AN-102 supernate.

2.2 FLOWSHEET OPERATION FOR WHICH THE SIMULANT WAS DEVELOPED

The AN-102 supernate and entrained solids simulants are intended to support the Sr/TRU precipitation process, crossflow filtration process and waste feed evaporation pretreatment studies. The close match in rheological behavior of the supernate simulant and actual waste also makes it a good candidate as a rheological simulant.

3.0 ACTUAL SIMULANT PREPARATION PROCEDURE

3.1 CHEMICALS TO USE

Reagent-grade nonradioactive compounds were chosen to match the chemical composition of the AN-102 waste. Cost, chemical availability, and ease of scale up were considered in choosing which chemicals to use.

The metals are primarily added as the metal nitrates due to their high solubility and availability. Many of these salts contain waters of hydration and the specific form to be used is shown in Table A-1. 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 metal. When necessary, a solution of the metal nitrate can be used. However, the water additions shown in Table A-1 will have to be appropriately reduced to account for the water in the metal nitrate solution. Chromium, molybdenum and tungsten are added as the chromate, molybdate and tungstate salts matching the soluble properties of the measured species in the waste.

The complexing agents are generally added as the free acid form or as the sodium salt of the acid. Boric acid is used for boron because the expected form of boron in the waste is as the borate anion. The remainder of the anions are added as the sodium salt.

The entrained solids simulant was formulated with very low-solubility or limited-solubility compounds that are easily obtained. The recommended particle size for the solids is less than 44 micron (smaller than 325 mesh).

All radioactive components are deleted from both simulant compositions. Radioactive Cs was replaced with non-radioactive Cs, which was added at the total Cs concentration. Radioactive Sr was replaced with non-radioactive Sr, which was added at the total Sr concentration. No appropriate surrogate for U or the other transuranics was identified.

3.2 CHEMICAL ADDITION ORDER

The order of chemical addition to produce the supernate simulant is shown in Table A-1 and is based upon the following logical steps:

- Prepare solution of metal nitrates.
- Add acid-stable complexing agents and acid stable salts.
- Convert solution from acid to base by addition of sodium hydroxide and selected basic salts.
- Add base-stable salts and complexing agents.

These steps produce the desired complexes expected in the waste simulant while avoiding the acid-induced decomposition of carbonate or nitrite or oxidation-reduction reactions between reducing species such as formate, glycolate or oxalate and the transition metals.

The water used for the simulant should be deionized water to limit the addition of other uncontrolled species. The mass of water added in each step is based upon producing a simulant solution with a total Na concentration of 6.5 molar and a solution density of 1.303 g/mL at 25 ° C.

Table A- 1 Chemical Addition Order and Amounts for Producing One Liter of the AN-102 Supernate Simulant at 6.5 M Na

Volume of Feed	**1000**	**mL**
To the Simulant Preparation Vessel Add	**Grams**	
Water	200	
Next add the following while maintaining good mixing		

Metal Compounds and Complexants	**Formula**	**Mass Needed, grams**
Aluminum Nitrate	$Al(NO_3)_3 \bullet 9H_2O$	139.03
Cadmium Nitrate	$Cd(NO_3)_2 \bullet 4H_2O$	0.14
Calcium Nitrate	$Ca(NO_3)_2 \bullet 4H_2O$	2.36
Cesium Nitrate	$CsNO_3$	0.019
Copper Nitrate	$Cu(NO_3)_2 \bullet 2.5H_2O$	0.07
Cobalt Nitrate	$Co(NO_3)_2 \bullet 6H_2O$	0.013
Ferric Nitrate	$Fe(NO_3)_3 \bullet 9H_2O$	0.25
Lanthanum Nitrate	$La(NO_3)_3 \bullet 6H_2O$	0.04
Lead nitrate	$Pb(NO_3)_2$	0.24
Manganous Chloride	$MnCl_2 \bullet 4H_2O$	0.09
Neodymium Nitrate	$Nd(NO_3)_3 \bullet 6H_2O$	0.08
Nickel Nitrate	$Ni(NO_3)_2 \bullet 6H_2O$	1.68
Potassium Nitrate	KNO_3	4.11
Rubidium Nitrate	$RbNO_3$	0.01
Strontium Nitrate	$Sr(NO_3)_2$	0.005
Zinc Nitrate	$Zn(NO_3)_2 \bullet 6H_2O$	0.02
Zirconyl Nitrate	$ZrO(NO_3)_2 \bullet xH_2O$, x~1	0.03
Disodium Ethylenediaminetetraacetate	$C_{10}H_{14}N_2Na_2O_8 \bullet 2H_2O$	2.92
n-(2-Hydroxyethyl)ethylenediaminetriacetic acid	$C_{10}H_{18}N_2O_7$	0.30
Sodium Gluconate	$C_6H_{11}O_7Na$	1.34
Citric Acid	$C_6H_8O_7 \bullet H_2O$	4.22
Nitrilotriacetic Acid	$C_6H_9NO_6$	0.21
Iminodiacetic Acid	$C_4H_7NO_4$	3.71
Succinic Acid	$C_4H_6O_4$	0.03
Glutaric Acid	$C_5H_8O_4$	0.05
Adipic Acid	$C_6H_{10}O_4$	0.20
Suberic Acid	$C_8H_{14}O_4$	1.49
Azelaic Acid	$C_9H_{16}O_4$	0.85
Boric acid	H_3BO_3	0.17
Ammonium Acetate	NH_4CH_3COO	0.51
Sodium Chloride	NaCl	6.38
Sodium Fluoride	NaF	3.09
Sodium Sulfate	Na_2SO_4	15.22
Potassium Molybdate	K_2MoO_4	0.09

Mix thoroughly. Then add the following while mixing.	**Formula**	**Mass Needed, grams**
Sodium Hydroxide	NaOH	79.31
Sodium Phosphate	$Na_3PO_4 \bullet 12H_2O$	18.01
Sodium Tungstate	$Na_2WO_4 \bullet 2H_2O$	0.25
Sodium Metasilicate	$Na_2SiO_3 \bullet 9H_2O$	0.08
Sodium Glycolate	$HOCH_2COONa$	11.14
Sodium formate	NaHCOO	10.36
Sodium Acetate	$NaCH_3COO \bullet 3H_2O$	0.55
Sodium Oxalate	$Na_2C_2O_4$	0.57
Water	H_2O	200
Mix thoroughly then Add	**Formula**	**Mass Needed, grams**
Sodium Chromate	Na_2CrO_4	0.64
Sodium Carbonate	Na_2CO_3	78.98
Mix thoroughly then Add	**Formula**	**Mass Needed, grams**
Sodium Nitrate	$NaNO_3$	87.85
Sodium Nitrite	$NaNO_2$	80.71
Water	H_2O	245.58
Mix thoroughly for 24 hours.		

The order of addition for the chemicals needed to produce the entrained solids simulant is not an issue. Instead, the entrained solids simulant must be prepared by adding the compounds to a completed AN-102 supernate simulant. The compounds to add are shown in Table A-2 in terms of grams of each compound per 100 grams of entrained solids. The weight percent entrained solids loading should be specified by the specific task that will use the simulant.

Table A- 2 AN-102 Entrained Solids Simulant Formulation

Recipe For AN-102 Solids	CAS #	Formula	grams/100 grams of entrained solids
Sodium Carbonate Monohydrate	5968-11-6	$Na_2CO_3 \bullet H_2O$	42.71
Sodium Oxalate	62-76-0	$Na_2C_2O_4$	16.10
Aluminum Oxide	1344-28-1	Al_2O_3	15.12
Sodium Phosphate Dodecahydrate	10101-89-0	$Na_3PO_4 \bullet 12H_2O$	12.28
Sodium Sulfate	7727-73-3	$Na_2SO_4 \bullet 10H_2O$	8.35
Sodium Fluoride	7681-49-4	NaF	3.15
Chromic Oxide	1308-38-9	Cr_2O_3	0.93
Ferric Hydroxide	1310-14-1	FeOOH	0.68
Manganese Dioxide	1313-13-9	MnO_2	0.15
Calcium Oxalate Monohydrate	5794-28-5	$CaC_2O_4 \bullet H_2O$	0.13
Calcium Tungstate	7790-75-2	$CaWO_4$	0.11
Lead Sulfate	7446-14-2	$PbSO_4$	0.08
Silica	7631-86-9	SiO_2	0.05
Neodymium Oxalate	28877-87-4	$Nd_2(C_2O_4)_3 \bullet 10H_20$	0.04

Recipe For AN-102 Solids	CAS #	Formula	grams/100 grams of entrained solids
Barium Sulfate	7727-43-7	$BaSO_4$	0.02
Cerium Oxalate	15750-47-7	$Ce_2(C_2O_4)_3 \bullet 9H_20$	0.02
Lanthanum Oxalate	537-03-1	$La_2(C_2O_4)_3 \bullet 9H_20$	0.02
Zirconium Dioxide	1314-23-4	ZrO_2	0.02
Zinc Oxalate Dihydrate	4255-07-6	$ZnC_2O_4 \bullet 2H_2O$	0.02
Nickel Oxide	1313-99-1	NiO	0.01

3.3 PRECAUTIONS

- Material Safety Data Sheets (MSDS) should be reviewed for all of the compounds in the simulant formulation.
- Appropriate safety apparel (acid-resistant gloves, etc) should be worn when working with chemicals as specified in the MSDS.
- Addition of the transition metal nitrates to the initial solution will produce a very acidic solution.
- Addition of the NaOH results in significant heat generation. The NaOH can be added slowly allowing heat to dissipate, or the mixing container can be cooled by use of an external or internal cooling system (ice bath, cooling coils, etc).
- During the initial stages of sodium hydroxide addition, significant Al solids form. Mixing may become difficult at this point. The Al solids will return to solution when pH ~9 is exceeded.
- The carbonate salts are added after the NaOH to avoid carbonate decomposition.
- The sodium formate and sodium glycolate are added after the NaOH to prevent any redox reactions from occurring. The acid forms (formic acid and glycolic acid) are fairly strong reducing agents and can react with nitric acid and other possible oxidizers such as some of the transition metals.
- The sodium chromate is also added after the NaOH. In acid, the chromate converts to dichromate, which is a very strong oxidizer and can react with acetate, formate, glycolate, citrate, oxalate and other organic species in the simulant.
- Addition of sodium nitrite must be made after the addition of sodium hydroxide to avoid generation of NO_x vapors.

3.4 OTHER CONSIDERATIONS

The supernate simulant can be filtered through a 0.45 µm filter to remove the sodium fluorophosphate solids if the simulant is needed for some purpose other than the Sr/TRU process studies. However, if the simulant is for precipitation studies then prefiltering the simulant is unnecessary.

The simulant should be stored in a polyethylene container (or equivalent). Storage in glass may result in etching of the glass.

The shelf life for this simulant has not been fully evaluated. However, based on appearance of a film on the bottles after several months, the slow decomposition of the less stable complexes may be occurring.

4.0 KEY CHARACTERISTICS AND LIMITATIONS OF AN-102 SUPERNATE SIMULANT

4.1 KEY CHARACTERISTICS

The simulant composition is to match major, minor, and trace constituents of actual AN-102 waste diluted to 6.5 M Na. Of specific concern are the constituents that affect the Sr/TRU precipitation processing parameters. These constituents include the Na, Sr, OH^-, and CO_3^{-2} concentrations. Solution density and viscosity are also process-affecting (Townson, 2001).

4.2 LIMITATIONS

The simulant limitations are based primarily on chemical composition.

- Fluoride concentration may be excessive in the supernate simulant due to potential interferences in the fluoride measurements for Envelope C wastes.

- Envelope C wastes contain very high levels of organic carbon due to the presence of complexants and their decomposition products. Only about 50-55% of the TOC in the actual AN-102 is accounted for in the AN-102 simulant. The incomplete organic constituent reconstruction *may* have an effect on the minor and/or trace cation solubilities and behavior. In addition, application of the AN-102 simulant to LAW vitrification studies may require the careful selection of additional organic compounds to increase the TOC loading.

These uncertainties are not expected to cause significant performance variability for filtration processing activities.

5.0 VALIDATION OF THE SIMULANT

Validating simulants includes determining chemical composition, physical properties, rheological properties, and process performance (Townson 2001). The simulant chemical composition was evaluated from three independent measurements relative to four independent analyses of actual AN-102 tank waste supernate. Major, minor, and trace analyte compositions in the simulant were to match the actual waste composition to within ±10% or within the analytical uncertainty of the analysis method. Physical-property testing specifically included density, again in comparison to actual AN-102 tank supernate. The rheological properties were tested similarly to the AN-102 diluted-feed tank waste that was processed through the small-scale pretreatment unit operations.

5.1 CHEMICAL COMPOSITION

The measured concentrations of the major constituents for the supernate simulant (present at >0.1 molar) compared very well with the planned simulant composition. The major species, which included Na, Al, Cl, formate, NO_3^-, NO_2^-, and SO_4^{-2}, were within 10 percent of the target value and the carbonate was within 15 percent of the target value. The only major species that missed the target value was glycolate based upon an analytical result that may be problematic and needs more work. Hydroxide which was also present at >0.1 molar was not measured.

Most of the minor and trace species, present at less than 0.1 molar, also compared favorably with the target values. These minor and trace species that were within 10 % of target values included B, Cd, Cr, Fe, La, Mn, Nd, Ni, Pb, W, iminodiacetic acid, nitrilotriacetic acid, oxalate and total organic carbon. Minor and trace species that were within 25 % of target values included Ca, Cu, K and Mo. Analytical measurements of some of the complexing agents such as EDTA and HEDTA produce highly variable results and additional analytical measurement work is probably necessary. Two of the minor species, fluoride and phosphate, are definitely off of their target values and this is consistent with the production of an insoluble fluorophosphate salt, natrophosphate.

Undissolved solids (UDS) were formed as a by-product of the supernate simulant preparation. The solids were analyzed by XRD and were primarily sodium fluorophosphate, $Na_7F(PO_4)_2(H_2O)_{19}$, also known as natrophosphate. Simulant preparations at higher Na concentrations also produced additional insoluble compounds based upon XRD and these included sodium carbonate (thermonatrite ($Na_2CO_3 \bullet H_2O$)), sodium fluorosulfate (kogarkoite (Na_3FSO_4)), and sodium nitrate. After filtration, no additional solids were observed.

The entrained solids simulant composition was not analyzed for chemical composition due to the problems with sampling and characterization of very dilute insoluble solids systems. Instead, the composition is administratively controlled to insure that all additions are made to the supernate in the correct amounts. Verification that all of the compounds in the entrained solids have been added to the supernate simulant are required when producing an AN-102 entrained solids simulant.

5.2 CHARGE BALANCING

The anionic and cationic species present in the targeted AN-102 simulant composition was charge-balanced and a summary of the charges and the balance are shown in Table A- 3

Table A- 3 Charge Balance for AN-102 Supernate Simulant at 6.5 M Na

Cations				Anions			
Species	Charge	Moles/Liter	Charge, moles/Liter	Species	Charge	Moles/Liter	Charge, moles/Liter
Ammonium	1	6.65E-03	6.65E-03	Acetate	-1	1.07E-02	-1.07E-02
Barium	2	0.00E+00	0.00E+00	Aluminum	-1	3.71E-01	-3.71E-01
Cadmium	2	4.42E-04	8.85E-04	Boron	-3	2.77E-03	-8.32E-02
Calcium	2	9.98E-03	2.00E-02	Carbonate	-2	7.45E-01	-1.49E+00
Cerium	3	0.00E+00	0.00E+00	Chloride	-1	1.10E-01	-1.10E-01
Cesium	1	9.74E-05	9.74E-05	Chromium	-2	3.94E-03	-7.89E-03
Cobalt	2	4.62E-05	9.25E-05	Ethylenediaminetetraacetate	-4	7.84E-03	-3.14E-02
Copper	2	3.11E-04	6.22E-04	Fluoride	-1	7.37E-02	-7.37E-02
Iron	3	6.10E-04	1.83E-03	Formate	-1	1.52E-01	-1.52E-01
Lanthanum	3	9.32E-05	2.79E-04	Glycolate	-1	1.14E-01	-1.14E-01
Lead	2	7.30E-04	1.46E-03	Hydroxide	-1	3.23E-01	-3.23E-01
Magnesium	1	0.00E+00	0.00E+00	Molybdenum	-2	3.83E-04	-7.67E-04
Manganese	2	4.34E-04	8.68E-04	n-Hydroxyethylenediaminetriacetate	-3	1.09E-03	-3.27E-03
Neodymium	3	1.79E-04	5.38E-04	Nitrate	-1	2.20E+00	-2.20E+00
Nickel	2	5.79E-03	1.16E-02	Nitrite	-1	1.17E+00	-1.17E+00
Potassium	1	4.14E-02	4.14E-02	Oxalate	-2	4.29E-03	-8.57E-03
Rubidium	1	7.97E-05	7.97E-05	Phosphate	-3	4.74E-02	-1.42E-01
Sodium	1	6.50E+00	6.50E+00	Silicon	-2	2.91E-04	-5.82E-04
Strontium	2	2.33E-05	4.66E-05	Sulfate	-2	1.07E-01	-2.14E-01
Zirconium	4	1.19E-04	4.78E-04	Tungsten	-2	7.45E-04	-1.49E-03
Sodium Gluconate	0	6.15E-03	0.00E+00	Zinc	-2	6.25E-05	-1.25E-04
				Nitrilotriacetate	-3	1.12E-03	-3.37E-03
				Citric Acid	-3	2.01E-02	-6.03E-02
				Iminodiacetate	-2	2.79E-02	-5.58E-02
				Succinic Acid	-2	2.52E-04	-5.05E-04
				Glutaric Acid	-2	4.08E-04	-8.17E-04
				Adipic Acid	-2	1.39E-03	-2.78E-03
				Azelaic Acid	-2	4.51E-03	-9.02E-03
				Suberic Acid	-2	8.57E-03	-1.71E-02
				Sodium Gluconate	0	6.15E-03	0.00E+00
Total Plus Charge			6.59	Total Minus Charge			-6.58

Careful attention was given to the ionic form of each component added to the simulant as well as to simulant chemistry at the time the component was added. The addition sequence was designed to produce the expected chemical species in the simulant such as the complexes of the alkaline earth and transition metals with the organic complexants. Chromate was added after shifting the pH to basic conditions to maintain Cr in the +6 oxidation state. The organic species, which can act as acidic reductants, were added to the caustic solution as sodium salts to prevent unwanted oxidation state changes. Phosphorous is expected to be present in tank waste as phosphate and was thus added as phosphate.

Development of the entrained solids simulant focused on mass balance for the major species (especially for sodium) in determining the compounds to use in the simulant.

6.0 SIMULANT PROPERTIES COMPARED TO ACTUAL WASTE PROPERTIES

Good agreement was obtained with the actual waste supernate and supernate simulant densities. The measured density of the AN-102 diluted simulant at 6.5 Molar Na was 1.33 g/mL while the actual untreated AN-102 supernate diluted to 6.4 molar Na was 1.30g/mL.

The rheograms of the waste and the simulant indicate that the fluids are Newtonian in behavior since they are linear with the shear rate versus shear stress relationship passing through the origin. The viscosity of the AN-102 simulant was virtually identical to that of the pretreated (Sr/TRU processed and Cs and Tc removed) actual waste AN-102 diluted feed. The AN-102 actual waste and the simulant were both Newtonian fluids in rheological behaviors. The average viscosity of the actual AN-102 waste at 6.0 M Na and 25°C was 4.0±1.0 cP, and the average viscosity of the AN-102 simulant at 6.5 M Na was 3.5±0.1 cP. The difference in error bars was due to the difference in the instruments used to make the measurements. Based upon a comparison of their relative errors, there is no statistical difference between the viscosities of the simulant or the actual waste.

Comparison of the properties of the entrained solids simulant to actual entrained solids has not been performed due to the limited availability of actual AN-102 entrained solids in current samples.

Sr/TRU process testing with the AN-102 simulant to compare to the actual AN-102 waste performance is in progress.

7.0 SIMULANT DEVELOPMENT ORGANIZATION

The AN-102 diluted supernate and entrained solids simulants were developed at Westinghouse Savannah River Company, Savannah River Technology Center. The primary contact for the simulant development work is:

Russell Eibling
SRTC
Building 999-W, Room 335
Aiken, SC 29808
Phone: 803-819-8411
FAX: 803-819-8416
Email: russell.eibling@srs.gov

8.0 REFERENCES

Townson, PS. 2001. *Simulant Definition and Verification Methodology*, 24590-WTP-RPT-TE-01-003, Rev. 0, River Protection Project Waste Treatment Plant, Richland, WA.

Hay, M. S., Bronikowski, M. G., Hsu, C. W., and T. L. White. July 31, 2000. *Chemical Characterization of an Envelope C Sample from Hanford Tank 241-AN-102*. USDOE Report BNF-003-98-0250, Rev 0, Savannah River Site, Aiken, SC 29808.

Urie, M. W., Fiskum, S. K., Campbell, J. A., Farmer, O. T., Greenwood, L. R., Hoppe, E. W., Mong, G. M., Soderquist, C. Z., Swoboda, R. G., Thomas, M. P., and J. J. Wagner. July, 2002. *Chemical Analysis and Physical Property Testing of 241-AN-102 Tank Waste--Supernatant and Centrifuged Solids*. PNWD-3173, WTP-RPT-020, Pacific Northwest National Laboratory, Richland, WA 99352.

Esch, R. A. 1998. *Tank 241-AN-102 Low Activity Waste Envelope C Analytical Results for the Final Report*. HNF-SD-WM-DP-310, Rev 0, Waste Management Federal Services of Hanford, Inc for Fluor Daniel Hanford, Inc., Richland, WA, 99352.

Jo, J., Morris, B. J., and T. T. Tran. August 1996. *Tank Characterization Report for Double-Shell Tank 241-AN-102*. WHC-SD-WM-ER-545, Rev 1, Westinghouse Hanford Company, Richland, WA 99352.

Lokken, R.O., Scheele, R. D., Strachan, D. M., and A. P. Toste. September 1986. *Complex Concentrate Pretreatment FY 1986 Progress Report*. PNL-7687, Pacific Northwest Laboratory, Richland, WA 99352.

Toste, A. P., Lechner-Fish, T. J., Hendren, D. J., Scheele, R. D., and W. G. Richmond. "Analysis of Organics in Highly Radioactive Nuclear Wastes". *Journal of Radioanalytical and Nuclear Chemistry*, 123, p 149 (1988).