Preparation of Simulated Waste Solutions for Solvent Extraction Testing

by

R. A. Peterson

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

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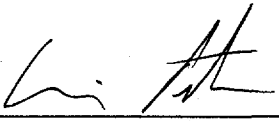
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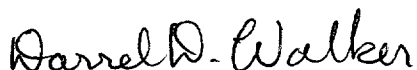
Preparation of Simulated Waste Solutions for Solvent Extraction Testing

Author

R.A. Peterson, Waste Processing Technology   5/2/00

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R.A. Peterson, Waste Processing Technology   Date

Technical Review

Darrel D. Walker   5/2/00

_____
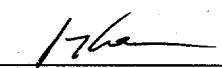
D.D. Walker, Waste Processing Technology   Date

Approvals

5/2/00

_____

S. D. Fink, Manager   Date
Waste Processing Technology

5/4/0.

_____

J.T. Carter, Manager   Date
High Level Waste

5/6/00

_____

W.L. Tamosaitis. FinkManager   Date
Waste Processing Technology

SUMMARY

Personnel will need to routinely prepare 0.5 to 10 L batches of salt solutions simulating Savannah River Site (SRS) soluble waste for solvent extraction testing. This report describes the compositions and preparation methods.

DISCUSSION

The simulant compositions vary by waste type (e.g., average, high hydroxide, and high nitrate) and by total sodium ion concentration (typically 3 to 7 molar Na^+). The waste types represent the average and extreme compositions expected in the feed stream sent to the salt decontamination process.[1-2] As such, they do not represent the extremes in composition of liquid waste currently in the SRS tank farms. Some blending is expected prior to transfer to the salt decontamination process. The average solution represents a blend of all soluble waste in the tank farm. The nominal sodium ion concentration is 5.6 molar for the feed to the solvent extraction option for salt disposition.

Table I lists the concentrations of 14 major components. The soluble salt values were derived from the average salt concentration as specified by Dimenna et al.[3] These average values were produced by analysis of the High Level waste Characterization And Tracking System (HLCATS), the chemical composition database of the Tank Farms. Speedup™ was used to produce feed compositions for the various options. In doing this, an average feed vector was developed based on the data found in HLCATS. This vector is the best estimate to date of an average feed solution for the various processes. The average feed vector produced a total soluble Na+ concentration of 6.29 M. The numbers in the table are the values presented in Tables 2.3-5 through 2.3-7 of the reference 3 adjusted to the new CSEX flowsheet Na^+ concentration of 5.6 M.

Appendix A lists the amounts and identities of chemicals used to prepare 1-L batches at 5.6 M Na^+. Small batches of simulants are prepared from reagent or similar purity chemicals.

When high purity chemicals are used in the preparation, typically less than 0.5 grams of solids fail to dissolve per liter of solution. Larger amounts of insoluble solids could be obtained if lower purity chemicals are used in the preparation. For most applications, the solutions are filtered if solids remain after final dilution. The solutions should be cooled to room temperature and aged for at least 24 hours before filtering.

Aluminum nitrate $[Al(NO_3)_3 \cdot 9H_2O]$ is the usual source of aluminate ion. Use of aluminum nitrate requires addition of extra sodium hydroxide and less sodium nitrate based on the following stoichiometry.

$$Al(NO_3)_3 + 4\,NaOH = NaAlO_2 + 3\,NaNO_3 + 2H_2O$$
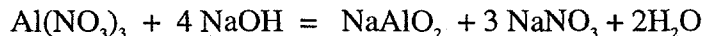
TABLE I. Composition of Simulated Waste Solutions

Component	Average (M)
Na^+	5.6
K^+	0.015
Cs^+	0.00014
OH^-	2.06
NO_3^-	2.03
NO_2^-	0.50
AlO_2^-	0.28
CO_3^{2-}	0.15
SO_4^{2-}	0.14
Cl^-	0.024
F^-	0.028
PO_4^{3-}	0.007
$C_2O_4^{2-}$	0.008
SiO_3^{2-}	0.03
MoO_4^{2-}	0.00007
NH_3	0.001

Aluminum nitrate yields an acidic solution in water and can react with sodium nitrite to form NO_2 gas. Thus, the preferred order of addition is to dissolve sodium hydroxide first, followed by aluminum nitrate. Sodium nitrite is added only after the aluminum nitrate is completely dissolved in excess sodium hydroxide.

If disodium hydrogen phosphate is used instead of trisodium phosphate, additional sodium hydroxide should be added to neutralize the acidic hydrogen.

Appendix B contains an example of instructions for the preparation of a 1-L batch of salt solution (components listed in Appendix A).   Salt solutions in volumes ≤2 L are usually prepared in volumetric glassware so that the amount of water required need not be measured. However, the densities of the salt solution has been measured and the required mass of water can be calculated. The density (g/mL) at 22 °C is calculated from the total sodium ion concentration (molar) by the following equation.[4]Note that this density correlation was developed for a slightly different composition of salts. The actual density of the as made salt solution may be slightly different.

Average: $d \text{ (g/mL)} = 1.009 + 0.04454[Na^+] \text{ (M)}$

Trace metals will also be added to the simulant. The metals may cause additional degradation of the solvent system and as such should be included in all simulant testing.

Table II contains the concentrations of the metals needed. Appendix C lists the amounts and identities of chemicals used to prepare 1-L batches of each waste type at 5.6 M Na⁺. These chemicals are added from prepared concentrated stock solutions.

Table II
Soluble Metals

Component	Concentration (mg/L)
Copper	1.44
Chromium	75
Ruthenium	0.82
Palladium	0.41
Rhodium	0.21
Iron	1.44
Zinc	8
Tin	2.4
Mercury	0.05
Lead	2.1
Silver	0.01

The values for the soluble metals are based on data obtained for Tank 48H during the analysis of the tetraphenylborate decomposition that occurred in late 1995 and early 1996 at ITP startup.[5] With the exception of chromium, all of the values in Table II are higher (3-10X) than would be predicted by the HLCATS database.[3] However, since these values are well documented and occurred in plant processing, they have been chosen for the simulant composition. They are not bounding but represent values that could be expected over the life of the plant.

Table III provides a list of organic components that will also be added to the salt solution.

Table III
Organic Components

Component	Concentration (mg/L)
tri-n-Butyl Phosphate (TBP)	0.5
di-n-Butyl Phosphate (DBP)	25
mono-n-Butyl Phosphate (MBP)	25
n-Butanol	2
Formate	1500
tri-Methylamine	10

The primary constituents of the organics in the waste tanks are byproducts of the hydrolysis of TBP. The solubility of TBP has been shown to be approximately 1.1 mg/L

under alkaline condtions.[6] The DBP, MBP and n-butanol are very soluble in salt solutions. The values presented in Table III are estimates based on prior results[7], Many trace organics are not dilineated. Most of the resin organics processed into the Tank Farm appear in very small quantities and should be pursued separately, but not included in the simulant to be employed for all tests. .

REFERENCES

1. P. L. Rutland et al., "Bases, Assumptions, and Results of the Flowsheet Calculations for the Initial Eighteen Salt Disposition Alternatives", WSRC-RP-98-00166, 25 June 1998.

2. D. D. Walker, "Modeling of Crystalline Silicotitanate Ion Exchange Columns," WSRC-TR-98-00343, Rev.0, October 2, 1998.

3. R. A. Dimenna, et al., "Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives," WSRC-RP-99-00006, Rev. 0, 9/30/99

4 D. D. Walker and G. K. Georgeton, "Viscosity and Density of Simulated Salt Solutions," WSRC-RP-89-1088, October 19, 1989.

5. D. D. Walker, et al., "Decomposition of Tetraphenylborate in Tank 48H (U)", WSRC-TR-96-0113, May 10, 1996.)

6. R. F. Swingle, "Evaluation of the Solubility of Tributyl Phosphate in ITP Salt Solutions", WSRC-RP-93-1397, December 13, 1993.

7. WSRC-TR-00091, Tank 39 Acceptance of Canyon Waste, Draft in preparation

Appendix A. Average Salt Solution (1-L batch)

Component	Source	Molecular Weight (g/mole)	Target Concentration (molar)	Amount Required (g)
K^+	KNO_3	101.1	0.015	1.517
Cs^+	$CsCl$	168.37	0.00014	0.024
OH^-	$NaOH$	40.00	2.06	127.48
NO_3^-	$NaNO_3$	84.99	2.03	99.85
NO_2^-	$NaNO_2$	69.00	0.50	34.50
AlO_2^-	$Al(NO_3)_3 \cdot 9H_2O$	375.14	0.28	105.04
CO_3^{2-}	$Na_2CO_3 \cdot H_2O$	124.01	0.15	18.6
SO_4^{2-}	Na_2SO_4	142.04	0.14	19.89
Cl^-	$NaCl$	58.44	0.024	1.403
F^-	NaF	41.99	0.028	1.176
PO_4^{3-}	$Na_2HPO_4 \cdot 7H_2O$	268.09	0.007	1.877
$C_2O_4^{2-}$	$Na_2C_2O_4$	134.00	0.02	2.680
SiO_3^{2-}	$Na_2SiO_3 \cdot 9H_2O$	284.2	0.03	8.526
MoO_4^{2-}	$Na_2MoO_4 \cdot 2H_2O$	241.95	0.00007	0.017
NH_3	NH_4NO_3	80	0.001	0.080
Water				835.8
			Total weight:	1258.

Appendix B
Instructions for Preparation of Salt Solution

Note: Appendix A contains a listing the chemicals required for this simulant. The following information should be recorded for each species: operator name, date, balance identification, manufacturers and lot numbers for each chemical).

1. Locate and label a clean, dry, 1-L volumetric flask. Weigh it empty and dry.
   The vessels shall be washed and thoroughly rinsed to remove all traces of contaminants (e.g., oils, surfactants, etc.).

   Do not use a glass vessel so as to avoid leaching of elements from the glass by the highly alkaline solution.

   If a large quantity of simulant is being prepared use a mixer of a size suitable for the preparation task. Loosely cover the mixing vessel with plastic, that is taped to the outside of the mixing vessel and that will allow condensed water vapor to collect near the center of the plastic cover and return to the mixing vessel.

2. Weigh the NaOH into the flask. Add _____ g of water and dissolve the NaOH before continuing.
   Caution: Dissolving NaOH will heat the solution. If the solution becomes too hot to handle safely, cool it before proceeding.

   Note: If the solution is not prepared in a volumetric flask (e.g., if the water is added by weight rather than by filling to the line on the flask), keep the container closed as much as possible when the solution is hot to avoid evaporation of water. If using volumetric glassware, reserve a portion of the water for the final addition in step 6.

3. Add the aluminum nitrate to the flask and mix to dissolve.

   Caution: Do not add sodium nitrite prior to dissolving the aluminum nitrate in excess NaOH. Poisonous red fumes of NO_2 could form.

4. Add the remaining chemicals.
   The additional chemicals should be added slowly and with continuous mixing. For the addition of F^-, PO_4^{3-}, $C_2O_4^{2-}$, and SiO_3^{2-} premix each reagent (NaF, $Na_2HPO_4 \cdot 7H_2O$, $Na_2C_2O_4$, and $Na_2SiO_3 \cdot 9H_2O$) as individual solutions in a small quantity of water to totally dissolve them prior to adding to the above salt solution. Add the $Na_2SiO_3 \cdot 9H_2O$ solution very slowly with good mixing to avoid local precipitation. Add the other solutions slowly with thorough mixing.

   Use NH_4NO_3 to provide the required amount of ammonia. Extreme caution should be employed when adding the ammonium nitrate. Poisonous and flammable ammonia gas may evolve from solution upon addition

Add the soluble metal components in the following order:
   a.   Cr
   b.   Sn
   c.   Hg
   d.   Cu
   e.   Rh/Pd/Ag/Ru
   f.   Zn/Pb/Fe

The reason for this suggestion is to minimize the possibility of irreversible sorption of metals on the more insoluble metal hydroxides that may be present in the solution. Some of these metals may precipitate and the simulant will need to be filtered after it is allowed to come to equilibrium. After filtration, the simulant must be analyzed to confirm the concentrations of soluble metals.

5. Mix to dissolve (1-2 hours).

6. Allow the solution to cool to room temperature.

    Note: If using volumetric glassware, fill to the line with water after cooling.

7. Reweigh the solution and compare to the expected weight. If the weights differ significantly, investigate for a missing component or error in weighing.

8. Allow the solution to age at least 24 hours.

    Note: The solution should equilibrate long enough after preparation to avoid concerns from slow precipitation. For volumes as large as 10 L, 24 hours generally provides adequate equilibration time. The best practice will include a second hold period and a second filtration.

9. Filter the solution through any convenient filter (medium frit sintered glass is acceptable).
10.
11. Submit a sample of the filtered simulant for QA analysis of composition.

Appendix C.

Table II. Metal Concentrations

	Compound	Molec. wt (g/mole)	Metal wt. (g/mole)	Stock Soln. vol (mL)	Solvent	Quantity of salt used (g)	Stock Metal Conc. (mg/L)	Nominal Conc. (mg/L)	Volume to Add for 1 L Test (mL)
Cu	$Cu(SO_4) \cdot 5H_2O$	249.68	63.546	100	Water	1.10	2806	1.4	0.5
Cr	Na_2CrO_4	161.97	51.9961	100	0.1 M NaOH	23.3639	75088	75	1.0
Zn/Pb/Fe	$Zn(NO_3)_2 \cdot 6H_2O$	297.47	64.39	100	0.1 M HNO_3	3.6422	8017	8.0	1.0
	$Pb(NO_3)_2$	331.2	207.2			0.3352	2100	2.1	
	$Fe(NO_3)_3 \cdot 9H_2O$	404.0	55.847			1.0421	1442	1.44	
Sn	$SnCl_2 \cdot 2H_2O$	225.63	118.71	100	0.1 M HNO_3	0.4563	2403	2.4	1.0
Hg	$Hg(NO_3)_2 \cdot H_2O$	342.61	200.59	100	0.1 M HNO_3	0.0854	500.7	0.05	0.1
Rh/Pd/Ag/Ru	$Rh(NO_3)_3$		4.93%	100	0.1 M HNO3	4.2609	2106	0.21	0.1
	$Pd(NO_3)_2$		15.27%			2.6872	4109	0.41	
	$AgNO_3$	169.87	107.868			0.0157	100	0.01	
	$RuCl_3 \cdot xH_2O$		41.74%			1.9645	8210	0.82	

CC: J.T. Carter, 704-3N   L.M. Nelson, 773-43A
H.D. Harmon, 704-3N R.A. Peterson, 773-A
H.H. Elder, 704-S   K.J. Rueter, 704-3N
S.D. Fink, 773-A   P.L. Rutland, 704-196N
F.F. Fondeur, 773-A P.C. Suggs, 704-196N
J.R. Fowler, 704-3N W.L. Tamosaitis, 773-A
G.A. Taylor, 704-196N R.A. Jacobs, 704-3N
R.T. Jones, 704-3N D.D. Walker, 773-A
D.T. Hobbs, 773-A M.G. Schwenker, 703-46A
J.M. Reynolds, 704-196N J.W. McCullough, 704-3N
STI, 703-43A   LWPG Files, c/o Cathy Canada, 773-A