WSRC-TR-2002-00273, Rev. 0

SRT-RPP-2002-00143

Cesium Eluate Evaporation Solubility and Physical Property Behavior

June 11, 2002

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 ™

WSRC-TR-2002-00273, Rev. 0

SRT-RPP-2002-00143

KEYWORDS:
River Protection Project
Laboratory
Cesium
Eluate
Evaporation
Solubility
Physical Properties

RETENTION TIME:
0.1.1.1.1 Permanent

Cesium Eluate Evaporation Solubility and Physical Property Behavior

Authors: **R. A. Pierce, 773-A, SRTC, SRS**
T. B. Edwards, 773-42A, SRTC, SRS

Issue Date: **June 11, 2002**

Test Specification No. **24590-WTP-TSP-RT-01-009, Rev. 0**

Test Plan No. **WSRC-TR-2001-00508, Rev. 0**

Test Scoping Statement: **S-78**

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-96SR18500

SRS savannah river site ™

Completeness of Testing

This report describes the results of work and testing specified by 24590-WTP-TSP-RT-01-009, Rev. 0 and WSRC-TR-2001-00508, Rev. 0.. The performed work followed established quality assurance requirements and was conducted as authorized. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Results required by the test plan are reported. Also reported are any unusual or anomalous occurrences that are different from starting hypotheses. The test results and this report have been reviewed and verified.

ABSTRACT 7
1.0 INTRODUCTION 8
2.0 SUMMARY OF TESTING 8
3.0 EXPERIMENTAL DESCRIPTION 9
3.1 DENSITY DATA MATRIX 9
3.1.1 Sample Preparation *9*
3.1.2 Analysis Method: *11*
3.2 SOLID MATRIX PREPARATION 11
3.3 SOLUBILITY DETERMINATION AT 55°C 12
3.4 EFFECT OF ORGANIC COMPOUNDS ON SALT SOLUBILITY AT 55°C 13
3.5 SOLUBILITY DETERMINATION AT 20°C 13
3.6 INTERMEDIATE COMPOSITION IDENTIFICATION 14
4.0 DISCUSSION OF RESULTS 15
4.1 DENSITY DATA MATRIX 15
4.1.1 Graphical Treatment of the Data *18*
4.1.2 Statistical Treatment of the Data *20*
4.2 SOLUBILITY DATA 22
4.2.1 Individual Cation Solubility *22*
4.2.2 Multiple Cation Solubility *26*
4.2.3 Effect of Organic Compounds on Salt Solubility *34*
4.3 PHYSICAL PROPERTY DATA OF SATURATED SOLUTIONS 35
4.4 PHYSICAL PROPERTY DATA FOR INTERMEDIATE COMPOSITIONS 39
5.0 CONCLUSIONS 41
6.0 ISSUES & RECOMMENDATIONS 42

LIST OF FIGURES

FIGURE 3-1. SALT SOLUBILITY TEST UNIT 12
FIGURE 3-2. AZ-102 CALCULATED EVAPORATION WITH INTERMEDIATE COMPOSITIONS DEFINED 14
FIGURE 4-1. EFFECT OF ACID/SALT CONTENT ON DENSITY 18
FIGURE 4-2 . ALUMINUM AND ACID EFFECTS ON DENSITY 18
FIGURE 4-3. EFFECTS OF ALKALI METALS ON DENSITY 19
FIGURE 4-4. $NaNO_3$-HNO_3-H_2O DENSITY DATA 23
FIGURE 4-5. KNO_3-HNO_3-H_2O DENSITY DATA 24
FIGURE 4-6. $CsNO_3$-HNO_3-H_2O DENSITY DATA 24
FIGURE 4-7. ESTIMATED ALKALI NITRATE SOLUBILITY LIMITS 25
FIGURE 4-8. COMPARISON OF SRTC DATA WITH LITERATURE DATA 25
FIGURE 4-9. HEAT CAPACITY CORRELATION WITH DENSITY 36
FIGURE 4-10. HEAT CAPACITY CORRELATION WITH DISSOLVED SALT/ACID CONTENT 36
FIGURE 4-11. VISCOSITY AS A FUNCTION OF SALT/ACID CONCENTRATION 37
FIGURE 4-12. THERMAL CONDUCTIVITY AS A FUNCTION OF SALT/ACID CONCENTRATION 38
FIGURE 4-13. VISCOSITY TREND VS. TEMPERATURE 38
FIGURE 4-14. INTERMEDIATE COMPOSITION DENSITY BEHAVIOR 40
FIGURE 4-15. INTERMEDIATE COMPOSITE VISCOSITY BEHAVIOR 40
FIGURE 4-16. INTERMEDIATE COMPOSITION HEAT CAPACITY BEHAVIOR 40

LIST OF TABLES

TABLE 3-1. DENSITY DATA MATRIX 9
TABLE 3-2. SOLUBILITY COMPOUND MATRIX 12
TABLE 3-3. ORGANIC BEARING MATRIX COMPOSITIONS 13
TABLE 3-4. INTERMEDIATE COMPOSITION MAKE-UP 15
TABLE 4-1. SATURATION WEIGHT RATIOS AT 20-22^{O}C (DISSOLVED AT AND COOLED FROM 52-55^{O}C) 16
TABLE 4-2. SATURATION WEIGHT RATIOS AT 20-22^{O}C 17
TABLE 4-3. DENSITY PARAMETER ESTIMATES AND CALCULATIONS 21
TABLE 4-4. TERNARY SYSTEM DENSITY DATA 22
TABLE 4-5. SALT-HNO_3-H_2O APPROXIMATE SOLUBILITY LIMITS 22
TABLE 4-6. FEED RATIOS AND SOLIDS FORMED 28
TABLE 4-7. SATURATION WEIGHT RATIOS AT 52-55^{O}C 29
TABLE 4-8. PHYSICAL PROPERTIES OF SATURATED SOLUTIONS 30
TABLE 4-9. COMPARISON OF FEED COMPOSITIONS WITH SATURATED SOLUTIONS 31
TABLE 4-10. COMPARISON OF FEED COMPOSITIONS WITH SATURATED SOLUTIONS – EXCLUDING SODIUM 32
TABLE 4-11. SOLUBILITY PARAMETER ESTIMATES FOR 20-22^{O}C DATA 34
TABLE 4-12. SOLUBILITY IN THE PRESENCE OF ORGANIC COMPOUNDS –52-55^{0} C 35
TABLE 4-13. PHYSICAL PROPERTIES OF INTERMEDIATE SOLUTIONS 39

LIST OF ATTACHMENTS

ATTACHMENT 1 - DUPLICATE DENSITY MEASUREMENTS 43
ATTACHMENT 2 - MULTIPLE TEMPERATURE HEAT CAPACITY (IN CAL/G-^{O}C) DATA 44
ATTACHMENT 3 - MULTIPLE TEMPERATURE VISCOSITY DATA 45
ATTACHMENT 4 - MULTIPLE-TEMPERATURE HEAT CAPACITY (IN CAL/G-^{O}C) DATA FOR INTERMEDIATE COMPOUNDS 46

LIST OF ACRONYMS

AA	Atomic Absorption
IC	Ion Chromatography
ICPES	Inductively Coupled Plasma Emissions Spectroscopy
LAW	Low Activity Waste

RPP	River Protection Project
SRTC	Savannah River Technology Center
WTP	Waste Treatment Plant
XRD	X-ray Diffraction

ABSTRACT

The baseline flowsheet for low activity waste (LAW) in the Hanford River Protection Project (RPP) Waste Treatment Plant (WTP) includes pretreatment of supernatant by removing cesium using ion exchange. When the ion exchange column is loaded, the cesium will be eluted with a 0.5M nitric acid (HNO_3) solution to allow the column to be conditioned for re-use. The cesium eluate solution will then be concentrated in a vacuum evaporator to minimize storage volume and to recycle HNO_3.

A fundamental element of predicting evaporator product solubility is to collect data that will cover the evaporator behavior for a range of conditions up to and including precipitation. Of central importance is identifying the effect of varying feed components on overall solubility. A systematic plan was developed and carried out to collect the fundamental data necessary to predict solubility and physical property behavior for the RPP cesium eluate evaporator.

A large body of experimental data was collected at 20-22^{o}C and 52-55^{o}C for the cesium eluate evaporation system that will help confirm and supplement ongoing modeling activities. The results show that linear models do a very good job predicting solution density over a wide range of acid and dissolved salt concentrations with typical calculation errors on the order of 1-3%. The behavior of heat capacity, thermal conductivity, and viscosity as a linear function of dissolved salt and acid content show more scatter in the data.

Linear models using the 20-22^{o}C data do a good job of predicting solution solubility at room temperature over a calculated acid concentration range of 2.0 to 4.5 moles per liter. Linear models account for 84% of the variability in solubility as a function of changes in the individual component concentrations and yield typical calculation errors are on the order of 1-4%. Linear models developed with 52-55^{o}C data do not do a good job of predicting room temperature solubility behavior. The agreement between calculated and measured values is typically off by 10-20%. Analyses of precipitates from solubility testing show that sodium nitrate is always the dominant solid (>98%) and almost always the only detectable solid.

The effects of several organic compounds on solubility were tested; the selection of the organic compounds is discussed in an earlier report (WSRC-TR-2001-00594). The presence of oxalate, DBP, and EDTA all exhibited significant negative effects on salt solubility. The addition of 500 mg/L oxalate into a statistically designed salt matrix reduced the total amount of matrix dissolved by 50% for both 3M and 5M HNO_3. The presence of 500 mg/L EDTA reduced solubility of the same matrix by 24% in 3M HNO_3 and by 42% in 5M HNO_3. Similarly, DBP readily precipitates from solution when the same solid matrix is dissolved into the liquid. The presence of 350-700 mg/L DBP in the liquid into which the salt matrix is dissolved reduces solubility by more than 95% for both 3M and 5M HNO_3 experiments.

1.0 INTRODUCTION

The baseline flowsheet for low activity waste (LAW) in the Hanford River Protection Project (RPP) Waste Treatment Plant (WTP) includes pretreatment of supernatant by removing cesium using ion exchange. When the ion exchange column is loaded, the cesium will be eluted with a 0.5M nitric acid (HNO_3) solution to allow the column to be conditioned for re-use. The cesium eluate solution will then be concentrated in a vacuum evaporator to minimize storage volume and recycle HNO_3. To prevent the formation of solids during storage of the evaporator bottoms, criteria have been set for limiting the concentration of the evaporator product to 80% of saturation at 25°C.

A fundamental element of predicting evaporator product solubility is to collect data that can be used to estimate key operating parameters. The data must be able to predict evaporator behavior for a range of eluate concentrations that are evaporated to the point of precipitation. Parameters that were selected for modeling include solubility, density, viscosity, thermal conductivity, and heat capacity.

Of central importance is identifying the effect of varying feed components on overall solubility. The point of solubility defines the upper limit for eluate evaporation operations and liquid storage. The solubility point also defines those chemical compounds that have the greatest effects on physical properties. Third, solubility behavior identifies intermediate points where physical property data should be measured for the database. Physical property data (density, viscosity, thermal conductivity, and heat capacity) may be an integral part of tracking evaporator operations as they progress toward their end point. Once the data have been collected, statistical design software can develop mathematical equations that estimate solubility and other physical properties.

This report completes the activities of Section 3.2 of the Task Technical and Quality Assurance Plan for Evaluating the Evaporation Behavior of Cs Eluate (WSRC-TR-2001-00508). Section 3.2 of the TTQAP addresses Cs eluate simulant solubility and physical property determinations.

2.0 SUMMARY OF TESTING

A systematic plan was developed and carried out to collect the fundamental data necessary to predict solubility and physical property behavior for the RPP cesium eluate evaporator. The development of this body of data included:

- *Development of Fundamental Property Data*: Savannah River Technology Center (SRTC) personnel measured the density of a wide range of salt-acid solutions. A test matrix was developed that varied HNO_3 [4-8M], $NaNO_3$ [0-6M], KNO_3 [0-0.5M], $CsNO_3$ [0-0.5M], $Ca(NO_3)_2$ [0-0.5M], $Mg(NO_3)_2$ [0-0.5M], $Fe(NO_3)_3$ [0-0.5M], and $Al(NO_3)_3$ [0-0.5M]. Although other analytes exist in measurable quantities in the Hanford waste tanks, the compounds selected are the only ones present in the cesium eluate at high enough concentrations to affect liquid density measurably.[1]

- *Experimental Determination of Precipitation*: Precipitation of cesium eluate was approximated by measuring the solubility of component mixtures into approximately 3.0, 4.0, and 5.0M HNO_3 at the evaporator operating temperature (52-55°C) and at the storage temperature (20-22°C). A total of 15 component mixtures were identified for testing, including cesium eluate simulants based on the cesium eluate derived from ion exchange treatment of waste samples from Tanks AZ-102, AN-102, AN-103, AN-105, and AN-107. The other 10 compositions were determined from a statistically generated matrix.[2] One

[1] R. A. Pierce. Cesium Eluate Analytical Data Evaluation. WSRC-TR-2001-00594 (January 2002).
[2] Edwards, T. B., "A Statistically Designed Test Matrix for Studying Cesium Eluate Solubility (U)," SRT-SCS-2001-00060, dated December 4, 2001.

of the mixtures was also prepared with varying concentrations of oxalate, DBP (dibutylphosphate) and EDTA (ethylenediamine-tetraacetic acid) to assess the potential effect of organic components on solubility.

- *Measurement of Properties for Saturated Solutions*: Saturated solutions from the precipitation tests at 52-55^{o}C were filtered at room temperature (after settling overnight) and the filtrate was analyzed for acidity, cation concentrations (ICPES and AA), anion concentrations (IC), heat capacity, liquid density, thermal conductivity, and viscosity. Solids were analyzed by x-ray diffraction to determine the type of precipitate formed. Saturated solutions from the precipitation tests at 20-22^{o}C were analyzed for liquid density and viscosity; the solutions were allowed to settle, but were not filtered.

- *Simulant Physical Property Measurements*: Following the determination of the saturation conditions for the various simulants, intermediate concentration samples were prepared that represent process conditions during evaporation prior to saturation. Four cesium eluate simulants based on the cesium eluate derived from ion exchange treatment of waste samples (AZ-102, AN-102, AN-103 and AN-107) were evaluated at 20%, 40%, 60% and 80% of saturation. The physical properties of the solutions were analyzed for heat capacity, thermal conductivity, viscosity, and liquid density.

3.0 EXPERIMENTAL DESCRIPTION

3.1 DENSITY DATA MATRIX

3.1.1 Sample Preparation

A matrix of samples was prepared using the proportions listed in Table 3-1. All components were mixed together in a 25- cm^3 volumetric flask, and water was added until the total volume reached the mark. All solids were allowed to dissolve in the flask. As needed, additional water was added to compensate for the volume loss when the solids dissolved. Some samples were prepared with slightly more solids than could be dissolved and were analyzed without filtering because the analytical instrument is capable of handling small amounts of solids. The solids were allowed to settle and the liquid sample was withdrawn from the top. Saturated solutions are noted in Table 3-1 with a "*".

Table 3-1. Density Data Matrix

Bottle I.D.	HNO3 mol/L	NaNO3 mol/L	KNO3 mol/L	CsNO3 mol/L	Ca(NO3)2 mol/L	Mg(NO3)2 mol/L	Al(NO3)3 mol/L	Density at 20 C	Density at 55 C	Wt of dry solids per cm^3
A*	0	7.31	0	0	0	0	0	1.378	1.352	0.663
1	4.0	0	0	0	0	0	0	1.130	1.107	0.252
2	5.0	0	0	0	0	0	0	1.161	1.135	0.315
3	6.0	0	0	0	0	0	0	1.191	1.163	0.378
4	7.0	0	0	0	0	0	0	1.230	1.197	0.441
5	8.0	0	0	0	0	0	0	1.258	1.226	0.504
6	4.0	1.00	0	0	0	0	0	1.182	1.156	0.337
7	4.0	2.00	0	0	0	0	0	1.233	1.205	0.422
8	4.0	3.00	0	0	0	0	0	1.283	1.254	0.507
9	6.0	1.00	0	0	0	0	0	1.245	1.214	0.463
10	6.0	2.00	0	0	0	0	0	1.292	1.259	0.548
11*	6.0	2.27	0	0	0	0	0	1.305	1.272	0.574
12	8.0	1.00	0	0	0	0	0	1.299	1.262	0.589
13*	8.0	1.56	0	0	0	0	0	1.322	1.286	0.640
14	0	0	0.25	0	0	0	0	1.014	1.001	0.025
15	0	0	0.50	0	0	0	0	1.029	1.015	0.051
17	0	0	0	0.50	0	0	0	1.070	1.055	0.097
19	0	0	0	0	0.50	0	0	1.058	1.043	0.082
21	0	0	0	0	0	0.50	0	1.053	1.038	0.074

* Denotes Saturated Sample

Table 3-1. Density Data Matrix (cont'd)

Bottle I.D.	HNO3 mol/L	NaNO3 mol/L	KNO3 mol/L	CsNO3 mol/L	Ca(NO3)2 mol/L	Mg(NO3)2 mol/L	Al(NO3)3 mol/L	Density at 20 C	Density at 55 C	Wt of dry solids per cm^3
22	0	0	0	0	0	0	0.25	1.039	1.025	0.053
23	0	0	0	0	0	0	0.50	1.078	1.063	0.106
25	4.0	0	0.50	0	0	0	0	1.159	1.135	0.303
27	4.0	0	0	0.50	0	0	0	1.200	1.175	0.349
29	4.0	0	0	0	0.50	0	0	1.187	1.161	0.334
31	4.0	0	0	0	0	0.50	0	1.182	1.157	0.326
32	4.0	0	0	0	0	0	0.25	1.169	1.145	0.305
33	4.0	0	0	0	0	0	0.50	1.206	1.180	0.359
35	6.0	0	0.50	0	0	0	0	1.222	1.192	0.429
37	6.0	0	0	0.50	0	0	0	1.261	1.231	0.476
39	6.0	0	0	0	0.50	0	0	1.248	1.217	0.460
41	6.0	0	0	0	0	0.50	0	1.243	1.212	0.452
42	6.0	0	0	0	0	0	0.25	1.231	1.201	0.431
43	6.0	0	0	0	0	0	0.50	1.267	1.236	0.485
44	4.0	2.50	0.50	0	0	0	0	1.286	1.257	0.515
46	4.0	2.50	0	0.50	0	0	0	1.326	1.296	0.562
47	6.0	2.50	0.50	0	0	0	0	1.336	1.302	0.641
49	6.0	2.50	0	0.50	0	0	0	1.378	1.346	0.688
50	4.0	2.50	0	0	0.50	0	0	1.309	1.279	0.547
52	4.0	2.50	0	0	0	0	0.50	1.330	1.299	0.571
53	6.0	1.25	0	0	0.25	0	0	1.283	1.250	0.525
55	6.0	1.25	0	0	0	0	0.25	1.292	1.260	0.538
56	0	1.00	0	0	0	0	0	1.054	1.038	0.085
57	0	2.00	0	0	0	0	0	1.107	1.088	0.170
58	0	3.00	0	0	0	0	0	1.160	1.138	0.255
59	0	4.00	0	0	0	0	0	1.210	1.187	0.340
61	4.0	3.50	0	0	0	0	0	1.311	1.280	0.550
62	8.0	1.50	0	0	0	0	0	1.320	1.283	0.632
66	0	0	1.00	0	0	0	0	1.053		0.101
67	0	0	2.00	0	0	0	0	1.121		0.202
68	0	0	3.00	0	0	0	0	1.176		0.303
69	0	0	0	0.50	0	0	0	1.069		0.097
70	0	0	0	1.00	0	0	0	1.142		0.195
71*	0	0	0	1.16	0	0	0	1.164		0.226
72	4.0	0	0.33	0	0	0	0	1.150		0.286
73	4.0	0	0.67	0	0	0	0	1.169		0.319
74	4.0	0	1.00	0	0	0	0	1.187		0.353
75	4.0	0	0	0.25	0	0	0	1.165		0.301
76	4.0	0	0	0.50	0	0	0	1.201		0.349
77	4.0	0	0	0.75	0	0	0	1.235		0.398
78	6.0	0	0.33	0	0	0	0	1.211		0.412
79	6.0	0	0.67	0	0	0	0	1.231		0.445
80	6.0	0	1.00	0	0	0	0	1.247		0.479
81	6.0	0	0	0.25	0	0	0	1.234		0.427
82	6.0	0	0	0.50	0	0	0	1.267		0.476
83	6.0	0	0	0.75	0	0	0	1.302		0.524
84*	0	0	2.93	0	0	0	0	1.174		0.296

* Denotes Saturated Sample

Table 3-1. Density Data Matrix (cont'd)

Bottle I.D.	HNO3 mol/L	NaNO3 mol/L	KNO3 mol/L	CsNO3 mol/L	Ca(NO3)2 mol/L	Mg(NO3)2 mol/L	Al(NO3)3 mol/L	Density at 20 C	Density at 55 C	Wt of dry solids per cm^3
85*	4.0	0	1.43	0	0	0	0	1.213		0.397
86	4.0	0	0	0.80	0	0	0	1.243		0.408
87*	6.0	0	1.55	0	0	0	0	1.274		0.535
88*	6.0	0	0	1.09	0	0	0	1.349		0.591
89	4.0	0	1.40	0	0	0	0	1.208		0.394
90*	4.0	0	0	0.80	0	0	0	1.238		0.408
91	6.0	0	1.40	0	0	0	0	1.268		0.520
92	6.0	0	0	1.00	0	0	0	1.326		0.573
94	0.0	0	0	0	0	0	0.50	1.078		0.106
95	0.0	0	0	0	0	0	1.00	1.155		0.213
96	0.0	0	0	0	0	0	1.50	1.231		0.319
97	0.0	0	0	0	0	0	2.00	1.304		0.426
98	4.0	0	0	0	0	0	0.50	1.205		0.359
99	4.0	0	0	0	0	0	1.00	1.277		0.465
100	4.0	0	0	0	0	0	1.50	1.348		0.571
102	6.0	0	0	0	0	0	0.50	1.263		0.485
103	6.0	0	0	0	0	0	1.00	1.332		0.591
106	3.0	0	0.40	0	0	0	0	1.116		0.229
109	3.0	0	0	0.25	0	0	0	1.127		0.238
110	3.0	0	0	0.50	0	0	0	1.162		0.286
111	3.0	0	0	0.75	0	0	0	1.196		0.335
112	5.0	0	0.40	0	0	0	0	1.180		0.355
113	5.0	0	0.80	0	0	0	0	1.204		0.396
114	5.0	0	1.20	0	0	0	0	1.225		0.436
115	5.0	0	0	0.25	0	0	0	1.193		0.364
116	5.0	0	0	0.50	0	0	0	1.224		0.413
117	5.0	0	0	0.75	0	0	0	1.257		0.461
118*	3.0	0	1.83	0	0	0	0	1.194		0.374
119*	3.0	0	0	0.78	0	0	0	1.201		0.341
120*	5.0	0	1.60	0	0	0	0	1.249		0.477
121*	5.0	0	0	1.0	0	0	0	1.297		0.510

* Denotes Saturated Sample

3.1.2 Analysis Method:

The samples from the matrix were analyzed using an Anton-Paar DMA 4500 density meter. The density meter is accurate to 0.0001 g/cm^3. Prior to analyzing samples, the instrument calibration is verified using deionized water. Additional checks are performed using a 28 wt% $NaNO_3$ solution in water. The samples are injected into the instrument, the instrument adjusts the sample temperature to 20°C, and the sample is analyzed. Samples are periodically re-analyzed to confirm that the results can be duplicated. Some samples were analyzed at 55°C, and the data is presented in Table 3-1.

3.2 SOLID MATRIX PREPARATION

A matrix of solid samples was prepared using the proportions listed in Table 3-2. To evaluate the effect of the various salts on solubility, the ratio of salts in the matrix represent the approximate ratios of salts observed in cesium eluate from ion exchange tests using actual tank waste, as well as those ratios proposed as part of the statistically-designed matrix. The ratio of salts selected was based on an analysis of the

available cesium eluate data.[3] The salts are individually weighed on a calibrated balance and added to a sample bottle. When necessary, the salts are first ground using a mortar and pestle. After each component is added, the bottle shaken to distribute each component throughout the bottle. Because the concentrations of Cu, Mg and Zn in AZ-102 are sufficiently low to make it difficult to evenly distribute their solids throughout the matrix, Cu, Mg and Zn were omitted from the AZ-102 matrix for these tests. Although there is no way simple way to guarantee that the solids have been intimately mixed, visual inspection of the matrices and subsequent data indicate that adequate mixing of the solids has occurred.

Table 3-2. Solubility Compound Matrix

Salt (grams)	AZ-102	AN-102	AN-103	AN-107	AN-105		CNTR-A	CNTR-B
CsNO3	9.908	0.339	2.346	1.449	0.392		2.595	2.595
KNO3	3.883	2.049	2.605	1.846	2.309		2.018	2.018
NaNO3	84.340	54.170	54.804	74.429	69.608		52.612	52.612
Al(NO3)3-9H2O	0.787	36.882	11.469	9.159	25.721		24.607	24.607
Ca(NO3)2-4H2O	0.725	3.850	23.895	1.294	1.530		10.428	10.428
Cu(NO3)2-2.5H2O	0.000	1.088	0.410	1.273	0.071		0.695	0.695
Fe(NO3)3-9H2O	0.356	0.502	1.215	9.803	0.094		6.185	6.185
Mg(NO3)2-6H2O	0.000	0.941	1.919	0.580	0.274		0.601	0.601
Zn(NO3)2-6H2O	0.000	0.180	1.336	0.167	0.000		0.259	0.259
Salt (grams)	MTRX-1	MTRX-2	MTRX-3	MTRX-4	MTRX-5	MTRX-6	MTRX-7	MTRX-8
CsNO3	0.295	3.299	0.418	5.054	0.296	6.836	0.301	0.417
KNO3	0.867	1.187	1.229	0.990	2.607	4.018	2.650	3.676
NaNO3	37.285	50.892	75.014	42.593	37.257	57.418	40.772	63.910
Al(NO3)3-9H2O	41.948	3.830	3.966	47.920	42.056	4.321	42.746	3.953
Ca(NO3)2-4H2O	17.776	24.344	1.681	1.354	5.743	8.850	1.208	25.127
Cu(NO3)2-2.5H2O	0.492	0.672	0.991	0.563	0.492	0.758	0.538	0.844
Fe(NO3)3-9H2O	0.727	14.944	15.475	0.831	10.940	16.860	11.120	1.028
Mg(NO3)2-6H2O	0.426	0.581	0.856	0.486	0.425	0.656	0.466	0.730
Zn(NO3)2-6H2O	0.184	0.251	0.369	0.210	0.183	0.283	0.201	0.315

3.3 SOLUBILITY DETERMINATION AT 55°C

Figure 3-1. Salt Solubility Test Unit

A test vessel was set up on a hot plate/stirrer with temperature monitoring. A known volume and concentration of HNO_3 (3-5M) was added to the test vessel. The test vessel is designed with a chilled headspace to minimize acid or water evaporation. The vessel was sealed and the nitric acid was stirred and heated to 52-55°C at atmospheric pressure. Periodically, the vessel was opened, and solids from the mixed batches were incrementally added to the nitric acid and allowed to dissolve. The solubility limit was identified as that point when solids did not dissolve after 30 minutes in contact with the heated acid. The acid was then cooled to 25 +0/-5°C overnight and additional precipitates were allowed to form. This provides

[3] R. A. Pierce. Cesium Eluate Analytical Data Evaluation. WSRC-TR-2001-00594 (January 2002).

one approximation of the storage condition solubility and helps define the difference between solubility during evaporator operation and solution storage. The solids were filtered at room temperature and analyzed using x-ray diffraction (XRD). The liquid was analyzed for density, viscosity, heat capacity, thermal conductivity, metal content (ICPES), and free/total acid (autotitrator). For physical property measurements, the temperature of analysis is included later in the report.

3.4 EFFECT OF ORGANIC COMPOUNDS ON SALT SOLUBILITY AT 55°C

The solubility tests were repeated in the presence of oxalate, added as oxalic acid, and the complexant EDTA (ethylenediaminetetraacetic acid), added as Na_2-EDTA. The objective of the tests is to develop a qualitative understanding of how organic components might affect ionic solubility. The CNTR-A (Table 3-2) composition was used with the organic compounds because it represents a statistically centered composition for all of the solubility testing. The CNTR-A composition was mixed with oxalic acid to produce mixtures containing the equivalent of 100 mg/L, 200 mg/L, and 500 mg/L oxalate. The CNTR-A composition was also mixed with Na_2-EDTA to yield a mixture containing the equivalent of 500 mg/L EDTA. The salt weights for these test matrices are listed in Table 3-3.

Testing with DBP (dibutylphosphate) was conducted by adding DBP to the liquid prior to dissolving the CNTR-A solids. Three different liquid concentrations were evaluated, 175 mg/L, 350 mg/L, and 700 mg/L in both 3M HNO_3 (nominal) and 5M HNO_3 (nominal). The solubility was tested at 52-55°C by dissolving the CNTR-A solid matrix into the different liquids in the manner discussed in Section 3.3.

Table 3-3. Organic Bearing Matrix Compositions

MATRIX / Salt	CNTR-A	CNTR-A w/ 500 ppm oxalate	CNTR-A W/ 200 ppm oxalate	CNTR-A w/ 100 ppm oxalate	CNTR-A w/ 500 ppm EDTA
CsNO3	1.298	1.298	1.298	1.298	1.298
KNO3	1.009	1.009	1.009	1.009	1.009
NaNO3	26.306	26.306	26.306	26.306	26.306
Al(NO3)3-9H2O	12.304	12.304	12.304	12.304	12.304
Ca(NO3)2-4H2O	5.214	5.214	5.214	5.214	5.214
Cu(NO3)2-2.5H2O	0.347	0.347	0.347	0.347	0.347
Fe(NO3)3-9H2O	3.092	3.092	3.092	3.092	3.092
Mg(NO3)2-6H2O	0.300	0.300	0.300	0.300	0.300
Zn(NO3)2-6H2O	0.130	0.130	0.130	0.130	0.130
H2C2O4	0.000	7.740	3.095	1.548	0.000
Na2-EDTA	0.000	0.000	0.000	0.000	5.750

3.5 SOLUBILITY DETERMINATION AT 20°C

Experiments, similar to the solubility experiments conducted at 52-55°C, were performed at ambient temperature (approx. 20°C). A known volume and concentration of HNO_3 (3-5M) was added to the test vessel. The vessel was sealed and the HNO_3 was stirred at atmospheric pressure. Periodically, the vessel was opened, and solids from the mixed batches were incrementally added to the nitric acid and allowed to dissolve. The solubility limit was identified as that point when solids do not dissolve after 30 minutes in contact with the acid. This approximates the storage condition solubility. The solids were allowed to settle overnight and the liquid sample was withdrawn from the top. The filtrate was analyzed for density, viscosity, and heat capacity. The samples were analyzed without filtering because the analytical instruments were capable of handling small amounts of solids. The concentrations of metals and acid were determined by calculations based on weight of acid at the beginning of the test, the total amount of solid added during the test, and the final density of the solution at the end of the test.

3.6 INTERMEDIATE COMPOSITION IDENTIFICATION

With solubility at room temperature defined experimentally for each matrix from the above tests, it was possible to perform mass balance calculations to predict when solubility is reached during evaporation of each matrix. With the solubility point defined, it is also possible to define solution compositions that represent 20%, 40%, 60% and 80% of the solubility limit. These mass balance calculations were performed for cesium eluate solutions generated from the treatment of tanks wastes (AZ-102, AN-102, AN-103, and AN-107) assuming semi-batch operation, a constant acid concentration in the overheads, and a starting acid concentration of 7.25M.

Figure 3-2 shows a plot of the calculation conducted for AZ-102. The nominal acid concentration was used for defining solubility. With the point of precipitation at room temperature defined (in total grams salt/acid per cm^3) and the starting condition defined (in total grams acid per cm^3), percent solubility was defined as the appropriate percentage of the difference between start and precipitation in grams of solid per cm^3.

Dissolved Salt at X % of Storage Solubility = {(X/100) x [(grams salt and acid per cm^3 at ppt.) - (grams acid per cm^3 start)]} + {grams acid per cm^3 start}

With the intermediate compositions defined, solutions were prepared with the appropriate chemical make-up calculated. The chemical make-up of the intermediate solutions is defined in Table 3-4. Once prepared, the solutions were analyzed for density, viscosity, thermal conductivity, and heat capacity.

Figure 3-2. AZ-102 Calculated Evaporation with Intermediate Compositions Defined

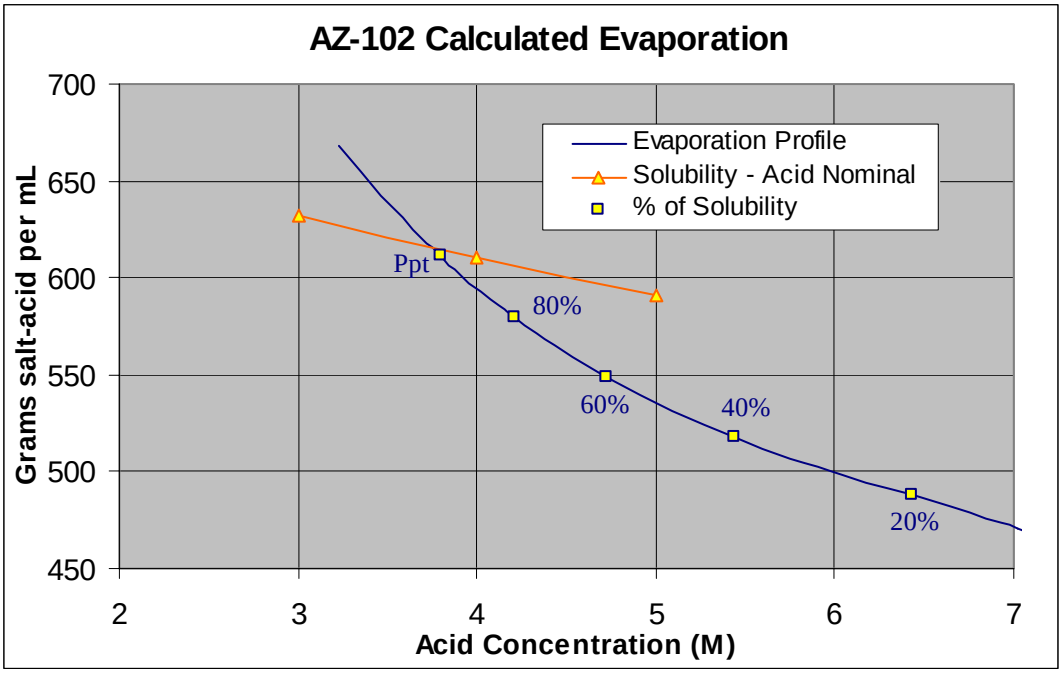


Table 3-4. Intermediate Composition Make-Up**

	AZ-102					AN-102			
	20%	40%	60%	80%		20%	40%	60%	80%
CsNO3 (g)	0.416	0.878	1.258	1.579		0.010	0.022	0.035	0.048
KNO3 (g)	0.162	0.342	0.489	0.614		0.058	0.132	0.208	0.284
NaNO3 (g)	3.513	7.417	10.630	13.336		1.534	3.495	5.505	7.516
Al(NO3)3-9H2O (g)	0.033	0.069	0.098	0.123		1.045	2.381	3.751	5.121
Ca(NO3)2-4H2O (g)	0.031	0.065	0.094	0.118		0.109	0.249	0.391	0.534
Cu(NO3)2-2.5H2O (g)	0.000	0.000	0.000	0.000		0.031	0.070	0.111	0.151
Fe(NO3)3-9H2O (g)	0.017	0.036	0.051	0.064		0.014	0.032	0.051	0.070
Mg(NO3)2-6H2O (g)	0.000	0.000	0.000	0.000		0.027	0.061	0.096	0.131
Zn(NO3)2-6H2O (g)	0.000	0.000	0.000	0.000		0.005	0.012	0.018	0.025
15.7M HNO3 (cm^3)	20.470	17.318	15.054	13.402		22.091	20.470	18.795	17.213
Total Volume (cm^3)	50.0	50.0	50.0	50.0		50.0	50.0	50.0	50.0
	AN-103					AN-107			
	20%	40%	60%	80%		20%	40%	60%	80%
CsNO3 (g)	0.170	0.332	0.435	0.533		0.206	0.258	0.303	0.341
KNO3 (g)	0.187	0.366	0.480	0.588		0.260	0.326	0.383	0.432
NaNO3 (g)	3.943	7.708	10.099	12.369		10.483	13.148	15.448	17.400
Al(NO3)3-9H2O (g)	0.826	1.614	2.115	2.590		1.271	1.594	1.873	2.110
Ca(NO3)2-4H2O (g)	1.720	3.362	4.406	5.396		0.180	0.225	0.265	0.298
Cu(NO3)2-2.5H2O (g)	0.029	0.058	0.075	0.092		0.178	0.224	0.263	0.296
Fe(NO3)3-9H2O (g)	0.087	0.171	0.224	0.274		1.389	1.742	2.046	2.305
Mg(NO3)2-6H2O (g)	0.138	0.270	0.354	0.433		0.096	0.121	0.142	0.160
Zn(NO3)2-6H2O (g)	0.096	0.188	0.246	0.302		0.028	0.035	0.041	0.046
15.7M HNO3 (cm^3)	18.795	14.932	12.933	11.320		11.609	9.750	8.411	7.429
Total Volume ($cm^{3)}$	50.0	50.0	50.0	50.0		50.0	50.0	50.0	50.0

** Note: Percentages indicated are percentages of solubility at approximately 20°C.

4.0 DISCUSSION OF RESULTS

4.1 DENSITY DATA MATRIX

The density data for all tests are listed in Table 3-1, Table 4-1, and Table 4-2. Also included in the tables is a calculation of weight of dry solids per cm^3 total liquid. Duplicate sample measurements (Attachment 1) show typical repeatability within +/- 0.0002 g/ cm^3. Analyses of water and 28.00 wt% $NaNO_3$ in water confirm the accuracy of the instrument calibration.

The collected density data show a strong linear relationship with total dissolved acid plus salt. A plot of the data from the sample matrix (Table 3-1) and solubility test data from Table 4-1and Table 4-2 are shown in Figure 4-1. This type of behavior is expected, but the agreement of the solubility data with the general trend lends credibility to the data. Aluminum is specifically indicated in Figure 4-1 because the data does not readily follow the trend of the rest of the data. An effort to examine the data in greater detail shows more specific effects and suggests that allowances in the calculations need to be made for acid and aluminum concentration. It is important to note that the data labeled 55°C in Figure 4-1 represents data where dissolution occurred at 55°C followed by cooling of the solutions to 20°C before density is measured. The reason for plotting as a function of acid plus salt content is discussed in Section 4.2.2.4.

Table 4-1. Saturation Weight Ratios at 20-22°C (Dissolved at and cooled from 52-55°C)

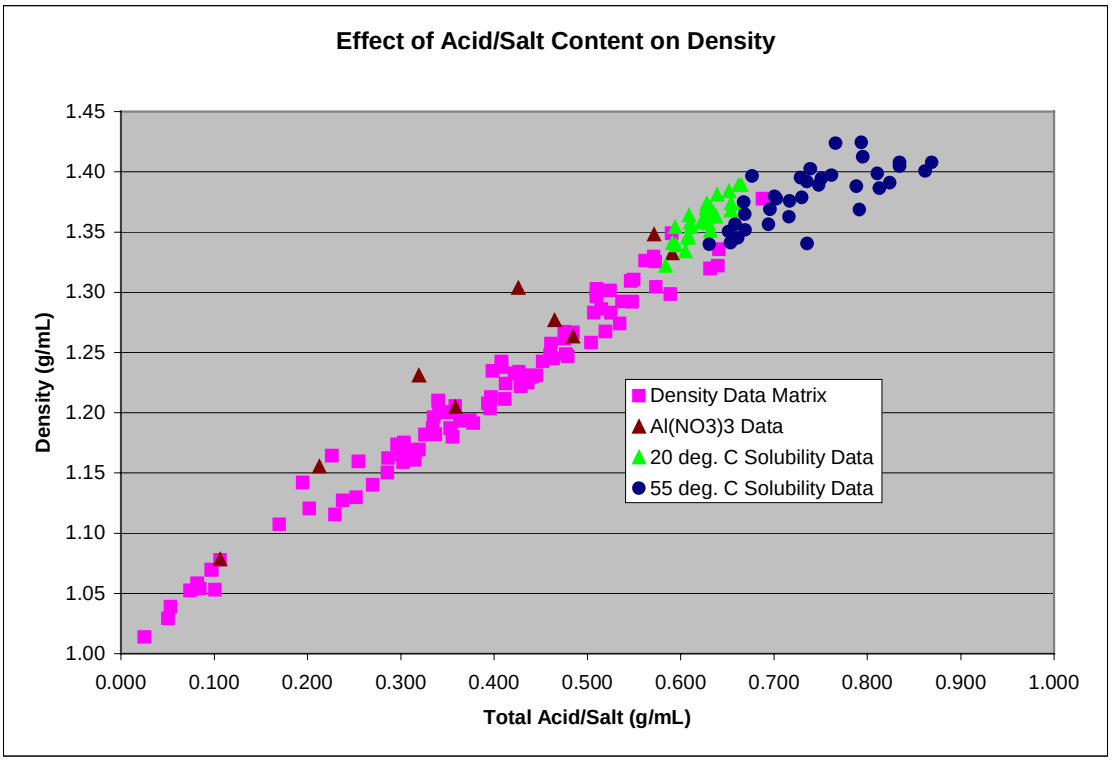
	Matrix	AZ-102		AN-102		AN-103		AN-107		AN-105		CNTR-A		CNTR-B			
Nominal	[HNO3]	3	5	3	5	3	5	3	5	3	5	3	5	3	5		
Anhydrous	Method																
Cs (mg/L)	AA	49477	36091	1951	1220	11409	10336	6575	5063	2163	1417	13083	11494	11806	11012		
K (mg/L)	ICP-ES	13000	10900	5950	6250	8780	8450	6980	5130	5270	4070	6680	5650	6575	5567		
Na (mg/L)	ICP-ES	119000	78900	67400	48200	79300	56100	81400	58600	73900	59000	63700	49900	66400	49400		
Al (mg/L)	ICP-ES	425	448	20700	19900	7450	6350	4200	3680	14800	10500	14600	11100	14300	11200		
Ca (mg/L)	ICP-ES	666	1290	5350	4700	38600	26600	1700	1170	2050	1500	13500	11500	16700	13700		
Cu (mg/L)	ICP-ES	0	0	2320	2160	911	983	2380	1880	159	112	1300	1120	1410	1150		
Fe (mg/L)	ICP-ES	450	462	549	591	1554	1191	9080	7370	86	74	6830	5390	6980	4950		
Mg (mg/L)	ICP-ES	0	0	693	669	2060	1240	338	345	149	202	612	254	424	403		
Zn (mg/L)	ICP-ES	0	0	292	407	3800	1350	300	110	0	0	377	291	353	293		
Density (g/cm^3)		1.380	1.365	1.369	1.369	1.413	1.392	1.350	1.341	1.357	1.341	1.394	1.379	1.389	1.376		
Free Acid (M), measured		2.08	4.1	2.19	3.95	2.34	3.84	2.43	4.09	2.45	5.37	2.16	3.73	2.12	3.62		
Total Acid (M), measured		2.33	4.53	4.76	6.43	3.38	4.96	3.71	5.44	4.4	5.48	4.29	5.56	4.22	5.48		
Grams salt/cm^3 liquid, calculated		0.70	0.67	0.77	0.79	0.80	0.74	0.65	0.65	0.69	0.67	0.75	0.73	0.76	0.73		
	Matrix	MTRX-1		MTRX-2		MTRX-3		MTRX-4		MTRX-5		MTRX-6		MTRX-7		MTRX-8	
Nominal	[HNO3]	3	5	3	5	3	5	3	5	3	5	3	5	3	5	3	5
ANHYDROUS																	
Cs (mg/L)	AA	1674	1536	18959	14502	1618	1731	25770	21484	1618	1674	33436	27538	1825	1731	1845	2299
K (mg/L)	ICP-ES	3030	2280	4240	3110	3220	2440	3200	2870	8680	7820	13500	10700	8650	7360	11300	11300
Na (mg/L)	ICP-ES	60500	39300	76800	50500	84600	60400	57400	43500	47500	43100	76600	58300	50700	40500	84300	63100
Al (mg/L)	ICP-ES	23900	23700	2677	1860	2181	1578	27900	22300	27500	21800	2445	2227	24500	21600	1943	1819
Ca (mg/L)	ICP-ES	23900	23900	36100	28800	1700	1620	1960	1530	8590	7350	12500	9910	1650	1470	33000	25500
Cu (mg/L)	ICP-ES	948	909	1510	1180	1730	1480	1050	860	1000	848	1680	1370	1080	969	1460	13900
Fe (mg/L)	ICP-ES	833	752	17400	14800	15200	11900	1030	746	12100	12500	20100	14300	12400	10200	1190	828
Mg (mg/L)	ICP-ES	340	296	473	358	603	485	289	371	385	303	543	339	335	362	664	307
Zn (mg/L)	ICP-ES	294	395	499	392	662	429	394	324	363	316	505	399	347	296	530	350
Density (g/cm^3)		1.399	1.408	1.425	1.402	1.357	1.340	1.405	1.388	1.408	1.401	1.424	1.395	1.391	1.386	1.397	1.378
Free Acid (M), measured		1.64	3.24	2.06	3.86	2.52	4.07	2.08	3.42	1.86	3.21	2.13	3.7	1.94	3.16	2.18	3.69
Total Acid (M), measured		4.46	6.15	3.46	5.07	3.72	5.07	5.36	6.31	5.68	6.64	3.68	5.04	5.58	6.59	2.66	4.3
Grams salt/cm^3 liquid, calculated		0.81	0.83	0.79	0.74	0.66	0.63	0.83	0.79	0.87	0.86	0.77	0.73	0.82	0.81	0.68	0.70

Table 4-2. Saturation Weight Ratios at 20-22°C

Matrix	AZ-102		AN-102		AN-103		AN-107		CTR-A		MTX-1		MTX-2	
Nominal [HNO3]	3	5	3	5	3	5	3	5	3	5	3	5	3	5
CsNO3 (g)	1.192	0.710	0.050	0.034	0.386	0.253	0.192	0.134	0.404	0.270	0.062	0.043	0.583	0.411
KNO3 (g)	0.467	0.278	0.304	0.206	0.428	0.281	0.244	0.171	0.314	0.210	0.182	0.126	0.210	0.148
NaNO3 (g)	10.146	6.047	8.044	5.444	9.010	5.913	9.847	6.900	8.192	5.472	7.825	5.412	8.996	6.344
Al(NO3)3 (g)	0.054	0.032	3.109	2.104	1.070	0.703	0.688	0.482	2.175	1.453	4.997	3.456	0.384	0.271
Ca(NO3)2 (g)	0.061	0.036	0.397	0.269	2.729	1.791	0.119	0.083	1.128	0.753	2.592	1.793	2.990	2.108
Cu(NO3)2 (g)	0.000	0.000	0.130	0.088	0.054	0.036	0.136	0.095	0.087	0.058	0.083	0.058	0.096	0.068
Fe(NO3)3 (g)	0.026	0.015	0.045	0.030	0.120	0.078	0.776	0.544	0.576	0.385	0.091	0.063	1.581	1.115
Mg(NO3)2 (g)	0.000	0.000	0.081	0.055	0.182	0.120	0.044	0.031	0.054	0.036	0.052	0.036	0.059	0.042
Zn(NO3)2 (g)	0.000	0.000	0.017	0.012	0.140	0.092	0.014	0.010	0.026	0.017	0.025	0.017	0.028	0.020
Water (g)	18.285	16.987	20.726	18.574	20.374	18.288	19.370	17.756	18.054	18.511	23.131	20.277	20.803	18.704
HNO3 (g)	3.728	6.264	4.030	6.601	4.030	6.601	3.728	6.264	4.030	6.601	4.030	6.601	4.030	6.601
Total (g)	33.958	30.370	36.934	33.416	38.524	34.156	35.158	32.470	35.040	33.766	43.070	37.881	39.760	35.831
Grams salt/cm^3 liquid, calculated	0.632	0.591	0.594	0.595	0.652	0.630	0.610	0.605	0.666	0.608	0.639	0.635	0.662	0.654
Density (g/cm^3)	1.370	1.341	1.354	1.339	1.384	1.357	1.358	1.334	1.374	1.345	1.381	1.366	1.389	1.368

Matrix	MTX-3		MTX-4		MTX-5		MTX-6		MTX-7		MTX-8			
Nominal HNO3	3	5	3	5	3	5	3	5	3	5	3	5		
CsNO3 (g)	0.057	0.036	0.947	0.640	0.060	0.042	1.148	0.762	0.055	0.038	0.067	0.045		
KNO3 (g)	0.166	0.105	0.186	0.125	0.533	0.367	0.675	0.448	0.487	0.336	0.588	0.393		
NaNO3 (g)	10.143	6.407	7.983	5.395	7.620	5.245	9.641	6.399	7.489	5.170	10.216	6.831		
Al(NO3)3 (g)	0.304	0.192	5.098	3.445	4.883	3.361	0.412	0.273	4.457	3.077	0.359	0.240		
Ca(NO3)2 (g)	0.158	0.100	0.176	0.119	0.816	0.562	1.032	0.685	0.154	0.106	2.791	1.866		
Cu(NO3)2 (g)	0.108	0.068	0.085	0.057	0.081	0.056	0.103	0.068	0.080	0.055	0.109	0.073		
Fe(NO3)3 (g)	1.252	0.791	0.093	0.063	1.339	0.922	1.694	1.125	1.223	0.844	0.098	0.066		
Mg(NO3)2 (g)	0.067	0.042	0.053	0.036	0.050	0.035	0.064	0.042	0.049	0.034	0.067	0.045		
Zn(NO3)2 (g)	0.032	0.020	0.025	0.017	0.024	0.016	0.030	0.020	0.023	0.016	0.032	0.021		
Water (g)	19.434	17.716	22.150	19.533	23.099	20.238	20.192	18.258	22.404	19.769	19.859	18.045		
HNO3 (g)	3.728	6.264	4.030	6.601	4.030	6.601	3.728	6.264	4.030	6.601	3.728	6.264		
Total (g)	35.449	31.741	40.826	36.032	42.536	37.444	38.718	34.344	40.452	36.046	37.913	33.889		
Grams salt/cm^3 liquid, calculated	0.608	0.584	0.627	0.622	0.628	0.626	0.665	0.638	0.609	0.611	0.654	0.632		
Density (g/cm^3)	1.347	1.322	1.370	1.358	1.374	1.362	1.389	1.363	1.364	1.354	1.374	1.351		

Figure 4-1. Effect of Acid/Salt Content on Density

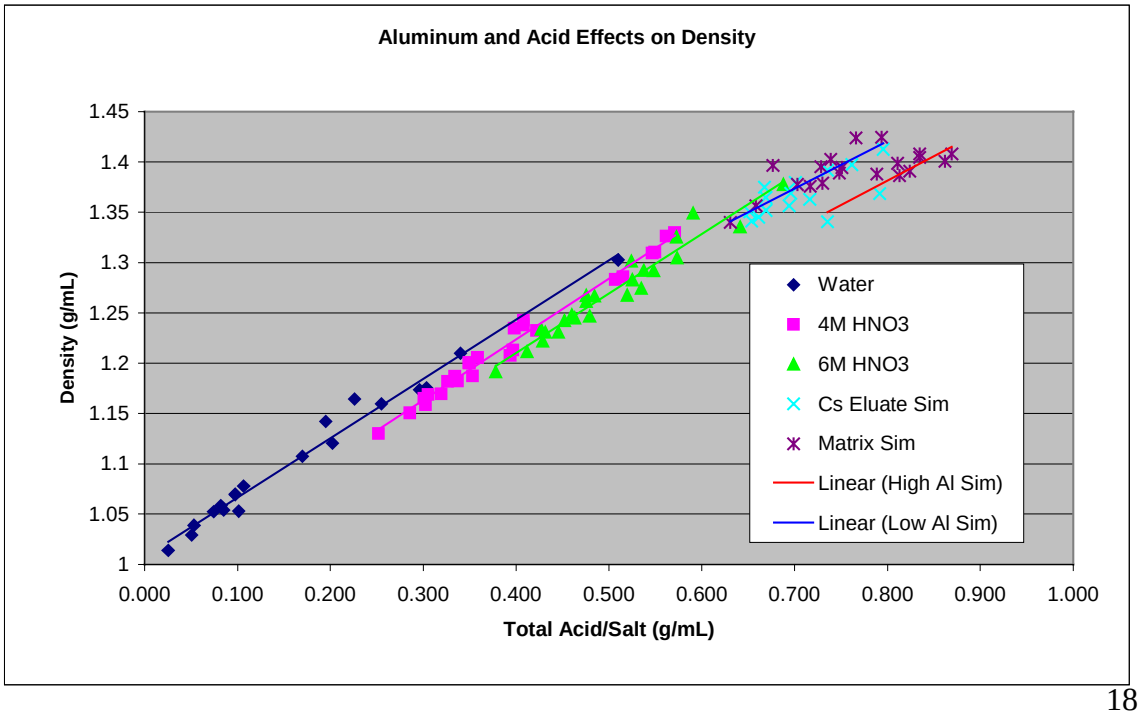


4.1.1 Graphical Treatment of the Data

4.1.1.1 Acid Effects:

A re-plot of the data from Figure 4-1 is shown in Figure 4-2. Data for 4M and 6M HNO_3 are plotted because much of the available data is at these concentrations. The data from Table 3-1 show a detectable effect of acid concentration with the linear regression lines being parallel, but not extensions of each other. This may be the result of the high charge density of H^+ relative to its mass relative to other cations.

Figure 4-2 . Aluminum and Acid Effects on Density



4.1.1.2 Aluminum Effects:

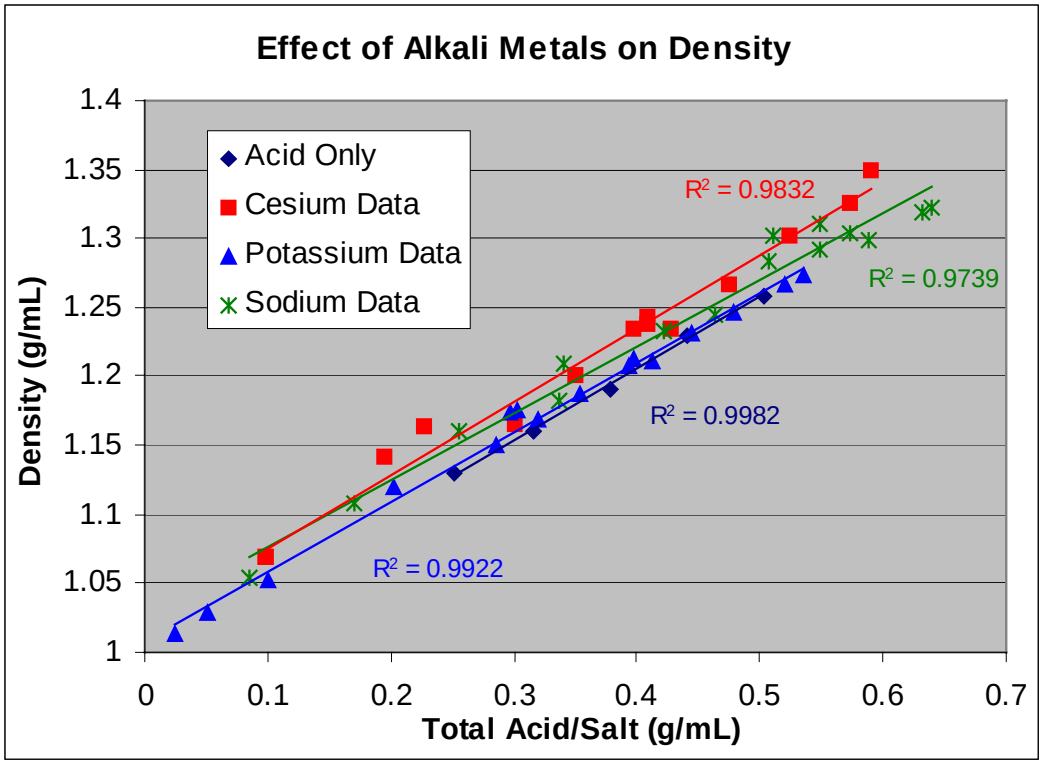
A closer look at the cesium eluate simulant data in Figure 4-2 at 55°C indicates a pronounced aluminum effect. While examining the data in Figure 4-1, it was observed that there were 10 data points noticeably below the linear regression line. Of the 10 points, eight of them represent all of the high aluminum tests for the matrix composition tests (the 3M and 5M acid tests for MTX-1, MTX-4, MTX-5, and MTX-7). The other two data points are cesium eluate simulant tests, both which have relatively high levels of aluminum (the 5M acid tests for AN-102 and AN-105).

It is unclear at this time why the other AN-102 points (at 3M and 4M acid) are not above the line. Separating the high aluminum simulation data points from the other simulation points yields two lines running parallel to those drawn using the data from Table 3-1. The difference between the high aluminum simulant points (red line) and the other simulant points (blue line) is noteworthy.

4.1.1.3 Alkali Cation Effects:

A similar treatment of the data can be made for the alkali metals. Figure 4-3 shows the comparative effects of acid, sodium, potassium and cesium. The acid and potassium data (R^2 = 0.9982 and 0.9922, respectively) exhibit strong linearity while the cesium and sodium data exhibit slightly more scatter (R^2 = 09832 and 0.9739, respectively. A preliminary explanation for the presence of the parallel lines in Figure 4-2 and Figure 4-3 is likely to involve ionic charge density as well as how tightly specific cations bind water and nitric acid. However, a specific understanding of the behavior is not clearly defined.

Figure 4-3. Effects of Alkali Metals on Density



4.1.1.4 Dissolution Temperature:
Figure 4-1 shows a distinct difference between the density levels for the 20°C data and the solubility tests at 55°C that were subsequently cooled to 20°C. The causes of this difference will be discussed in the section dealing directly with solubility data.

4.1.2 Statistical Treatment of the Data

When the cesium eluate simulant data were treated with the JMP statistical design software[4], the effects of the different cations became better quantified. Because of the number of data points available, only linear effects could be estimated.[5] Although determining a solution's solubility is a function of the total amount of salt added to a liquid, it is important to note that the use of linear parameter estimates in no way attempts to chemically describe the intricacies of how each component affects total density. Rather, parameter estimates provide a simple mathematical tool based on experimental data for estimating solubility using known quantities of salt and acid. The use of the equations should be limited to the range conditions in the experimental data.

Parameter estimates for each of the seven major variables can be multiplied with the cation mole percent values to obtain an estimated density.[6] The calculation to estimate density is performed in the following manner:

$$\text{Estimated Density} = \Sigma\,(\text{cation density parameter estimate})_i\,(\text{cation mole percent})_i$$

The parameter estimates, density calculations, and comparison with measured data are listed in Table 4-3 for the 52-55°C data. The 52-55°C data show good agreement for a linear model between calculated values and measured values with the worst value showing a 3.70% difference between the measured and calculated values. The average absolute percent difference for all simulant data points is 1.12%.

The parameter estimates from the 20-22°C data in Table 4-2 were also calculated and are in Table 4-3 for comparison. The values are similar to those calculated using the 52-55°C data. The two major components, sodium and hydronium ions, are almost identical for the two data sets. As a result, the density estimates for both parameter sets show good agreement. For comparison, the worst value shows a 2.97% difference between the measured and calculated values with an average absolute percent difference for all 20-22°C points of 0.98%

It should be noted that percent difference is calculated using water as the standard reference point because the calculations assume that the salts (including HNO_3) are dissolved into water.

$$\%\ \text{Difference} = [(\text{Calculated} - \text{Measured}) / (\text{Calculated} - \text{Water})] * 100$$

---

[4] SAS Institute, Inc., JMP® Statistics and Graphics Guide, Version 4, SAS Institute, Inc., Cary, NC, 2000.
[5] Edwards, T. B., "A Statistically Designed Test Matrix for Studying Cesium Eluate Solubility (U)," SRT-SCS-2001-00060, dated December 4, 2001.
[6] Edwards, T. B., "A Statistical Analysis of Results from the Cesium Eluate Solubility Study (U)," SRT-SCS-2002-00031 dated May 23, 2002.

Table 4-3. Density Parameter Estimates and Calculations

MOLE PERCENT CATION PARAMETER ESTIMATES FOR DENSITY																		
Cation	Al	Ca	Cs	Fe	K	Na	H+	Others										
52-55 deg. C	0.0160	0.0186	0.0249	0.0183	0.0200	0.0131	0.0133	0.0202										
20-22 deg. C	0.0150	0.0171	0.0219	0.0165	0.0169	0.0134	0.0130	0.0166										
MOLE PERCENT CATION (52-55 deg. C)																		
	AZ-102			AN-102			AN-103			AN-107			AN-105				CNTR-A	
	3	4	5	3	4	5	3	4	5	3	4	5	3	4	5		3	5
Cs	3.623	3.266	2.755	0.157	0.139	0.120	1.057	0.965	0.830	0.545	0.492	0.409	0.159	0.135	0.119		1.235	0.939
K	2.738	2.468	2.082	1.823	1.617	1.393	2.262	2.066	1.777	1.338	1.209	1.005	1.806	1.536	1.348		1.852	1.408
Na	70.722	63.751	53.775	57.322	50.864	43.817	56.622	51.714	44.469	64.142	57.972	48.191	64.754	55.065	48.332		57.423	43.649
Al	0.149	0.135	0.114	8.842	7.846	6.759	2.685	2.452	2.108	1.788	1.616	1.344	5.421	4.610	4.046		6.085	4.625
Ca	0.219	0.197	0.166	1.466	1.301	1.121	8.885	8.115	6.978	0.401	0.363	0.302	0.512	0.436	0.382		4.096	3.114
Fe	0.063	0.057	0.048	0.112	0.099	0.085	0.264	0.241	0.207	1.777	1.606	1.335	0.018	0.016	0.014		1.420	1.079
H	22.487	30.127	41.061	29.474	37.419	46.089	27.018	33.345	42.683	29.401	36.192	46.957	27.221	38.111	45.678		27.314	44.749
Others	0.000	0.000	0.000	0.805	0.714	0.615	1.206	1.102	0.947	0.608	0.549	0.456	0.109	0.093	0.081		0.575	0.437
Measured	1.380	1.375	1.365	1.369	1.363	1.369	1.413	1.397	1.392	1.350	1.352	1.341	1.357	1.345	1.341		1.394	1.379
Calculate	1.379	1.374	1.368	1.371	1.367	1.362	1.411	1.404	1.394	1.353	1.351	1.348	1.350	1.347	1.346		1.395	1.380
	MTRX-1		MTRX-2		MTRX-3		MTRX-4		MTRX-5		MTRX-6		MTRX-7		MTRX-8		CNTR-B	
	3	5	3	5	3	5	3	5	3	5	3	5	3	5	3	5	3	5
Cs	0.174	0.135	1.631	1.214	0.161	0.121	2.738	2.066	0.175	0.135	3.105	2.381	0.166	0.132	0.174	0.137	1.229	0.940
K	0.984	0.765	1.131	0.842	0.913	0.687	1.034	0.780	2.982	2.287	3.518	2.698	2.825	2.236	2.961	2.331	1.843	1.409
Na	50.349	39.164	57.696	42.946	66.269	49.867	52.913	39.925	50.698	38.878	59.810	45.863	51.698	40.930	61.234	48.219	57.151	43.679
Al	12.834	9.983	0.984	0.732	0.794	0.597	13.487	10.177	12.966	9.943	1.020	0.782	12.280	9.722	0.858	0.676	6.056	4.628
Ca	8.639	6.720	9.933	7.393	0.534	0.402	0.605	0.457	2.812	2.157	3.318	2.544	0.551	0.436	8.664	6.823	4.077	3.116
Fe	0.207	0.161	3.564	2.653	2.876	2.164	0.217	0.164	3.132	2.402	3.695	2.833	2.966	2.348	0.207	0.163	1.413	1.080
H	26.309	42.680	24.484	43.790	27.789	45.662	28.476	46.031	26.727	43.810	24.935	42.440	28.996	43.785	25.288	41.168	27.658	44.711
Others	0.504	0.392	0.578	0.430	0.664	0.500	0.530	0.400	0.508	0.389	0.599	0.459	0.518	0.410	0.613	0.483	0.572	0.438
Measured	1.399	1.408	1.425	1.402	1.357	1.340	1.405	1.388	1.408	1.401	1.424	1.395	1.391	1.386	1.397	1.378	1.389	1.376
Calculate	1.414	1.396	1.422	1.400	1.349	1.345	1.403	1.386	1.411	1.393	1.421	1.401	1.396	1.383	1.394	1.381	1.395	1.380

4.2 SOLUBILITY DATA

4.2.1 Individual Cation Solubility

Based on data in Table 3-1, it is possible to approximate the room-temperature solubility limits for certain salt-HNO_3-H_2O systems. In particular, the matrix targeted $NaNO_3$, KNO_3, and $CsNO_3$. Density plots as a function of $NaNO_3$, KNO_3, and $CsNO_3$ versus HNO_3 concentrations are shown in Figure 4-4, Figure 4-5 and Figure 4-6; the data is contained in Table 4-4. The linear plots for the unsaturated samples are then extrapolated to the saturation density (red points in each figure) and the corresponding salt molarity is read from the chart to approximate the solubility limits for each system. The approximated solubility limits based on the linear extrapolations are listed in Table 4-5.

Table 4-4. Ternary System Density Data (in g/cm^3)

Sodium Nitrate Solubility							
NaNO3 Conc (M)	In H2O	NaNO3 Conc (M)	On 4M HNO3	NaNO3 Conc (M)	In 6M HNO3	NaNO3 Conc (M)	In 8M HNO3
0.00	0.9983	0.00	1.1289	0.00	1.1981	0.00	1.2582
1.00	1.0540	1.00	1.1822	1.00	1.2450	1.00	1.2985
2.00	1.1074	2.00	1.2325	2.00	1.2920	1.50	1.3198
3.00	1.1595	3.00	1.2831				
4.00	1.2100						
6.00	1.3027						
Sat'd	1.3785	Sat'd	1.3105	Sat'd	1.3046	Sat'd	1.3221

Potassium Nitrate Solubility									
KNO3 Conc (M)	In H2O	KNO3 Conc (M)	In 3M HNO3	KNO3 Conc (M)	In 4M HNO3	KNO3 Conc (M)	In 5M HNO3	KNO3 Conc (M)	In 6M HNO3
0.00	0.9982	0.00	1.0930	0.00	1.1289	0.00	1.1560	0.00	1.1981
1.00	1.0593	0.40	1.1155	0.33	1.1504	0.40	1.1800	0.33	1.2114
2.00	1.1205	0.80	1.1402	0.67	1.1694	0.80	1.2036	0.67	1.2310
3.00	1.1755	1.20	1.1613	1.00	1.1873	1.20	1.2251	1.00	1.2468
		1.75	1.1938	1.40	1.2077			1.40	1.2675
Sat'd	1.1737	Sat'd	1.1984	Sat'd	1.2130	Sat'd	1.2488	Sat'd	1.2742

Cesium Nitrate Solubility									
CsNO3 Conc (M)	In H2O	CsNO3 Conc (M)	In 3M HNO3	CsNO3 Conc (M)	In 4M HNO3	CsNO3 Conc (M)	In 5M HNO3	CsNO3 Conc (M)	In 6M HNO3
0.00	0.9982	0.00	1.0930	0.00	1.1289	0.00	1.1599	0.00	1.1981
0.50	1.0693	0.25	1.1272	0.25	1.1650	0.25	1.1931	0.25	1.2339
1.00	1.1424	0.50	1.1624	0.50	1.2006	0.50	1.2242	0.50	1.2673
		0.75	1.1965	0.75	1.2346	0.75	1.2573	0.75	1.3015
								1.00	1.3255
Sat'd	1.1644	Sat'd	1.2006	Sat'd	1.2426	Sat'd	1.2965	Sat'd	1.3490

Table 4-5. Salt-HNO_3-H_2O Approximate Solubility Limits

HNO3 (M)	NaNO3 (M)	KNO3 (M)	CsNO3 (M)
0	7.31	2.93	1.16
3		1.83	0.78
4	3.52	1.43	0.80
5		1.60	1.00
6	2.27	1.55	1.09
8	1.56		

Some of the density data were developed as part of an effort to quantify the individual solubilities of $NaNO_3$, KNO_3, and $CsNO_3$ in HNO_3-H_2O experimentally. The approximated solubility information contained in Table 4-5 is plotted in Figure 4-7. When SRTC approximate sodium solubility data is plotted with literature data, excellent agreement is exhibited between the two data sets Figure 4-8. The behavior of cesium and potassium, in comparison to that of sodium, is different than what was expected. Typical predictions have the solubility of cesium and potassium gradually decreasing with acid concentration in a manner similar to that of sodium. However, while the absolute solubility values may have a few percent error associated with them, it should be noted that additional samples of the saturated cesium and potassium salts were prepared to confirm the observed behavior.

A first attempt to explain the observed behavior involves performing a curve fit to the sodium data and extrapolating that curve. The calculated curve, when extrapolated, shows sodium nitrate solubility passing through a minimum near 10M nitric acid. However, preliminary experimental work in 10M and 12M HNO_3 contradicts the mathematically extrapolated data for sodium nitrate.

Figure 4-4. $NaNO_3$-HNO_3-H_2O Density Data

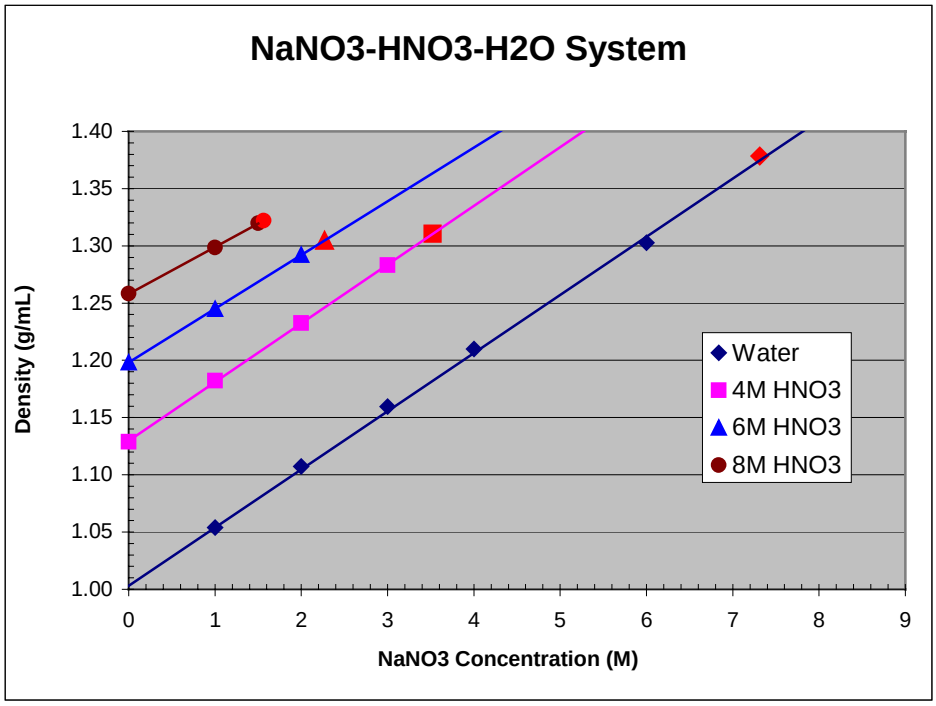


Figure 4-5. KNO_3-HNO_3-H_2O Density Data

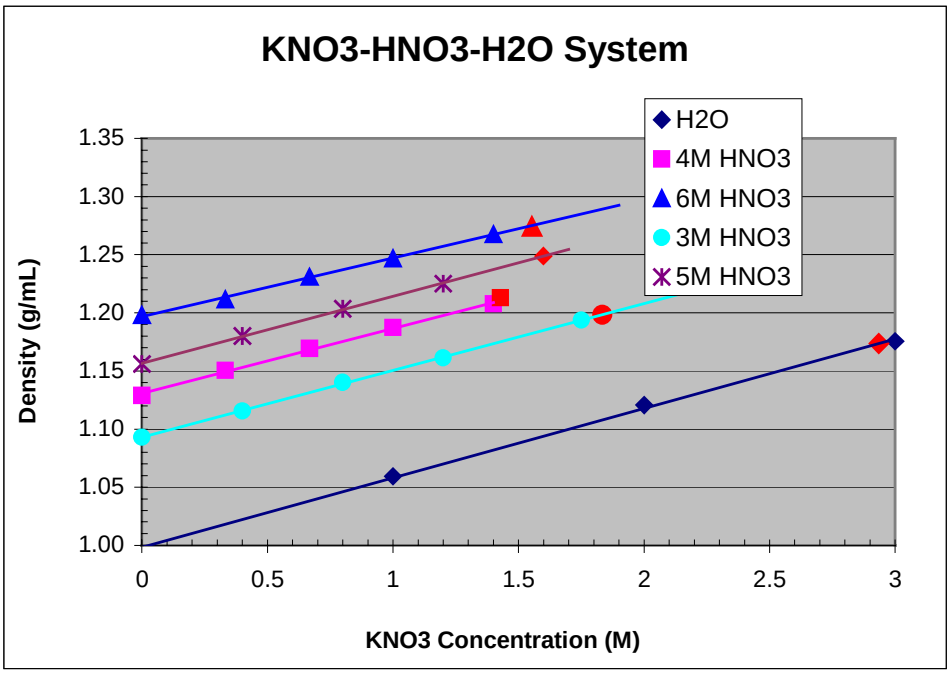


Figure 4-6. $CsNO_3$-HNO_3-H_2O Density Data

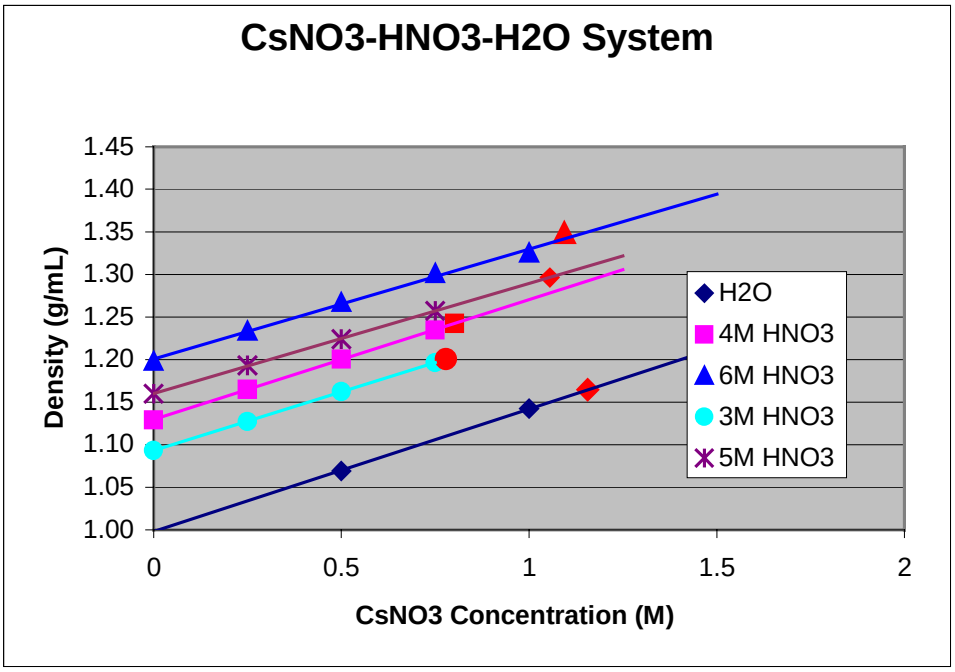


Figure 4-7. Estimated Alkali Nitrate Solubility Limits

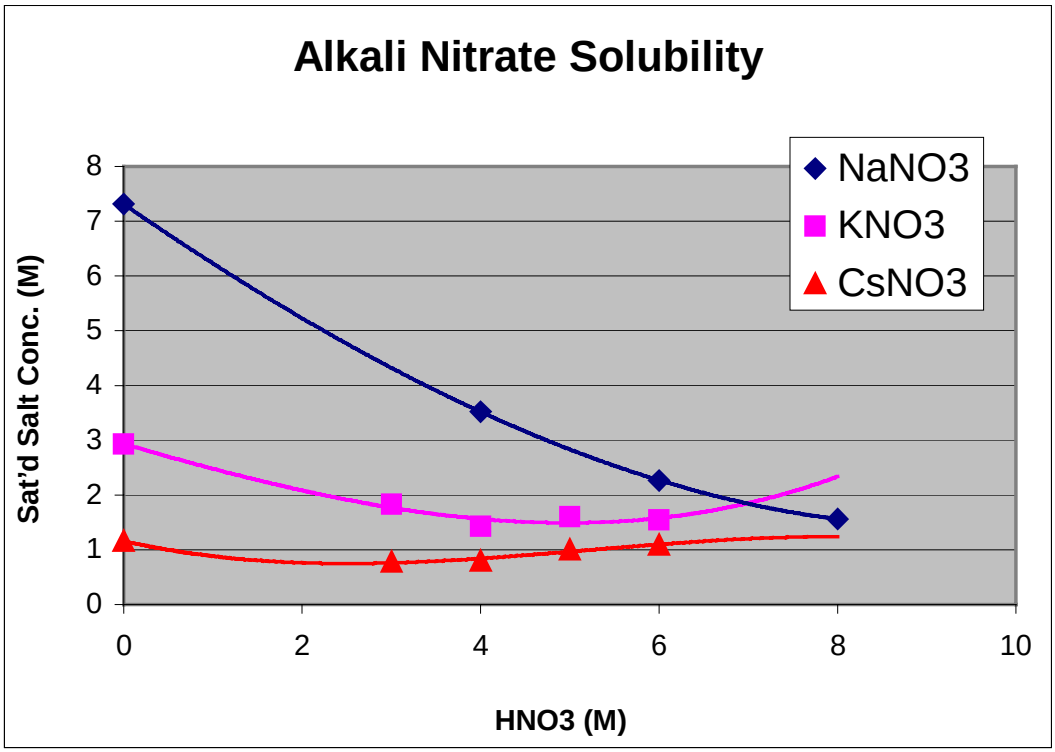
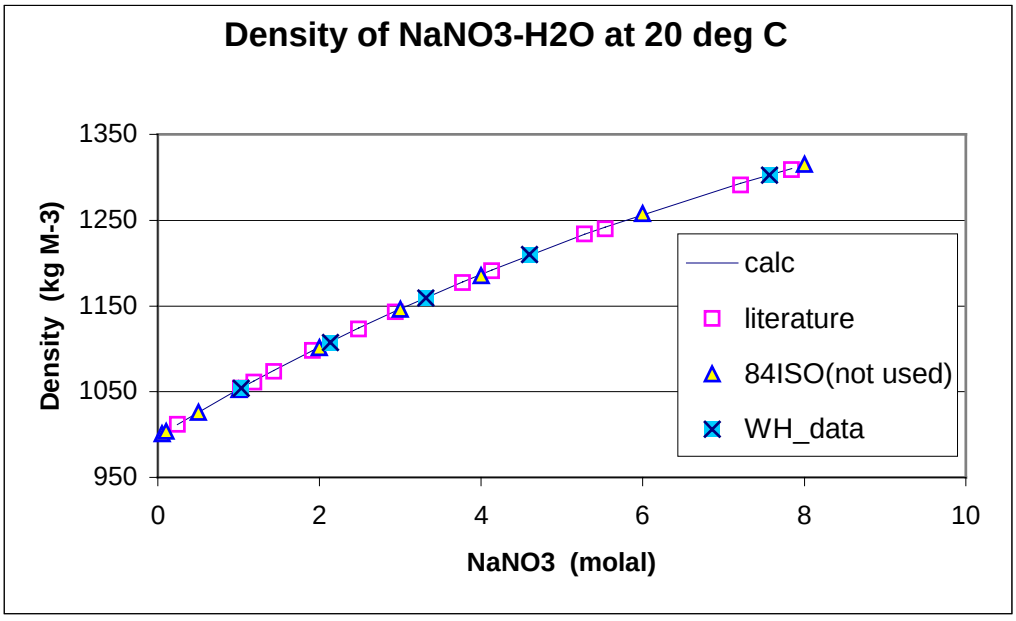


Figure 4-8. Comparison of SRTC Data with Literature Data



4.2.2 Multiple Cation Solubility

4.2.2.1 Solids Formation:
For each experiment at 52-55°C, a large amount of precipitation occurred when the solution saturated at 52-55°C was cooled to room temperature (20-22°C). Samples of the precipitate were analyzed using XRD. The types of solids identified for each matrix composition is shown in Table 4-6 along with the weight percent and mole percent ratios in the initial solid feed that was dissolved. The quantities of solids are broken into three categories: >10%, 1-2%, and <1%. The only precipitate appearing above 2% was sodium nitrate, and it was the dominant precipitate for all experiments. Trace amounts of precipitate were found in AN-103 (Cs), MTX-1 (Al), MTX-7 (Al). Approximately 1% cesium nitrate was identified in the AZ-102 precipitate.

4.2.2.2 Data Integrity:
The next area of discussion for the solubility data is the quality of the experimental method and the subsequent data. A review of the data indicates that the variability within the experimental method is acceptably low. Two identical center point compositions (CNTR-A and CNTR-B) were incorporated into the study to assess the experimental method. The available data for both samples (total dissolved solids, composition at 20°C, density, and heat capacity) exhibit excellent concurrence (see Table 4-1, Table 4-7and Table 4-8). Therefore, these data lend credibility to the method.

A separate examination of the data demonstrates the integrity of the analytical data. Apart from standards that have been analyzed containing known compositions of sodium, potassium, cesium, and HNO_3, a comparison of the soluble salt compositions with the starting composition also shows good agreement. Table 4-9 lists a comparison between the feed composition and the saturated salt composition for each matrix after the test solutions had been cooled from 55°C to 20°C. Table 4-9 clearly confirms that sodium nitrate was the dominant precipitate for each sample tested.

Table 4-10 reviews the data from Table 4-9 excluding the presence of sodium because the sodium percentage in solution has been reduced by precipitation during cooling. With the sodium removed from the feed composition and the sample analyses, the percentages of the other cations in the feed can be compared against the analyzed values. An examination of Table 4-10 shows that, in the absence of sodium nitrate, the analytical results have very good agreement with the feed composition. Therefore, it is possible to have confidence in quality of the cation data and the XRD results that show sodium nitrate as the dominant precipitate.

4.2.2.3 Soluble Solids Concentrations:
During the experiments at 52-55°C, the point of precipitation was readily identified. Furthermore, the total acid at the start of the test was measured, and the total amount of solids added to the system during the test was also measured. Assuming minimal liquid losses due to evaporation (because of the cooled vessel headspace) and uniform distribution of components within the solid matrix dissolved, the concentrations of salts in solution at the precipitation point can be calculated for each test. The data in Table 4-9 and Table 4-10 indicate that the assumption of uniform solid distribution within the solid matrix is valid.

The relative weights are listed in Table 4-7. Table 4-7 also lists a calculation of the total dissolved solids (acid plus salt) per total cm^3 water in the system (accounts for water in the HNO_3 at the start and water from hydrated salts added to system). Total dissolved solid as a function of system volume could not be reported for this set of tests because the density was not measured at 52-55°C.

After precipitation, the solutions were cooled to room temperature (20-22°C). The precipitates (discussed 4.2.2.1) were filtered and the filtrates were analyzed. Results from ICPES, AA, free acid, total acid, and density are listed in Table 4-1. Using the total acid value, Table 4-1 also includes a calculation of the total dissolved solids (acid plus salt) per total cm^3 in the system.

Because the dominant precipitate for the 52-55°C tests was $NaNO_3$, it was recognized that the measured solubility values at 20-22°C after precipitation might differ from values achieved by dissolving the salt

matrix into acid at 20-22°C instead of 52-55°C. Several 20-22°C tests were performed, the calculated solubility values were significantly lower than the values calculated from the solutions prepared at 52-55°C and cooled to 20-22°C.

Because of the difference in solubility, a complete set of solubility tests was run at 20-22°C. The average solubility for Table 4-2 of 0.626 grams of acid plus salt per cm^3 is much lower than the average value of 0.748 g/cm^3 for Table 4-1. A comparison of the average solution density values for each data set shows a smaller differential – 1.361 g/cm^3 for Table 4-2 versus 1.384 g/cm^3 for Table 4-1. The density shift is clearly depicted in Figure 4-1. It is worth noting that the apparent density shift caused by aluminum for the 52-55°C tests (red line in Figure 4-2) is not noticeable for the 20-22°C data (Figure 4-1).

The differences between Table 4-1 and Table 4-2 are not surprising when considering that a significant amount of sodium nitrate, which is the least soluble of the components in the matrices, precipitated out prior to the measurements taken for Table 4-1. The logical consequence of sodium nitrate precipitation (removal of a large amount of the least soluble component) is that the overall solubility of that particular solution will increase, thereby increasing the total salt dissolved per unit volume. As a result, it is reasonable that the solubility and density values of Table 4-1 are somewhat higher than the corresponding data in Table 4-2.

Table 4-6. Feed Ratios and Solids Formed

WEIGHT PERCENT															
	MTX-1	MTX-2	MTX-3	MTX-4	CTR-A	MTX-5	MTX-6	MTX-7	MTX-8	CTR-B	AN-103	AN-102	AZ-102	AN-107	AN-105
Al	17.77	1.18	1.18	17.77	8.24	17.77	1.18	17.76	1.18	8.24	3.62	13.75	0.18	2.65	8.05
Ca	17.77	17.77	1.18	1.18	8.24	5.73	5.73	1.18	17.72	8.24	17.60	3.37	0.40	0.88	1.15
Cs	1.18	9.68	1.18	17.77	8.24	1.18	17.77	1.18	1.18	8.24	7.08	1.23	21.13	4.07	1.25
Fe	0.59	8.89	8.84	0.59	3.98	8.89	8.89	8.88	0.59	3.98	0.74	0.36	0.18	5.55	0.10
K	1.97	1.97	1.96	1.97	3.63	5.92	5.92	5.92	5.91	3.63	4.43	4.09	4.73	2.91	3.95
Na	59.44	59.24	83.87	59.44	66.26	59.24	59.24	63.72	71.88	66.26	65.14	75.60	71.85	82.18	83.71
Cu	0.79	0.79	1.12	0.79	0.88	0.79	0.79	0.85	0.96	0.88	0.87	1.01	0.96	1.10	1.12
Mg	0.24	0.24	0.34	0.24	0.27	0.24	0.24	0.25	0.29	0.27	0.26	0.30	0.29	0.33	0.33
Zn	0.24	0.24	0.34	0.24	0.27	0.24	0.24	0.25	0.29	0.27	0.26	0.30	0.29	0.33	0.33
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Quantity of Nitrate Precipitate															
>10%	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na
1-2%													Cs		
<1%	Al							Al			Cs				
MOLE PERCENT															
	MTX-1	MTX-2	MTX-3	MTX-4	CTR-A	MTX-5	MTX-6	MTX-7	MTX-8	CTR-B	AN-103	AN-102	AZ-102	AN-107	AN-105
Al	17.42	1.30	1.10	18.86	8.37	17.70	1.36	17.29	1.15	8.37	3.71	12.63	0.19	2.50	7.25
Ca	11.72	13.15	0.74	0.85	5.64	3.84	4.42	0.78	11.60	5.64	12.16	2.09	0.29	0.56	0.70
Cs	0.24	2.16	0.22	3.83	1.70	0.24	4.14	0.23	0.23	1.70	1.47	0.23	4.60	0.78	0.23
Fe	0.28	4.72	3.98	0.30	1.95	4.27	4.92	4.18	0.28	1.95	0.37	0.16	0.09	2.53	0.04
K	1.34	1.50	1.26	1.45	2.55	4.07	4.69	3.98	3.96	2.55	3.14	2.59	3.50	1.89	2.45
Na	68.33	76.40	91.77	73.98	79.00	69.19	79.68	72.81	81.96	79.00	78.37	81.49	90.42	90.83	88.44
Cu	0.33	0.37	0.44	0.36	0.38	0.33	0.38	0.35	0.40	0.38	0.38	0.39	0.44	0.44	0.43
Mg	0.26	0.29	0.35	0.28	0.30	0.26	0.30	0.28	0.31	0.30	0.30	0.31	0.34	0.34	0.33
Zn	0.10	0.11	0.13	0.10	0.11	0.10	0.11	0.10	0.12	0.11	0.11	0.11	0.13	0.13	0.12
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Quantity of Nitrate Precipitate															
>10%	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na	Na
1-2%													Cs		
<1%	Al							Al			Cs				

Table 4-7. Saturation Weight Ratios at 52-55°C

Matrix	AZ-102		AN-102		AN-103		AN-107		AN-105		CNTR-A		CNTR-B	
Nominal [HNO3]	3	5	3	5	3	5	3	5	3	5	3	5	3	5
Salt, anhydrous														
CsNO3	1.858	1.300	0.064	0.050	0.472	0.376	0.224	0.168	0.071	0.050	0.546	0.406	0.537	0.406
KNO3	0.728	0.510	0.387	0.303	0.524	0.417	0.285	0.215	0.415	0.296	0.425	0.315	0.417	0.316
NaNO3	15.814	11.065	10.238	8.012	11.032	8.780	11.484	8.649	12.522	8.917	11.067	8.220	10.878	8.233
Al(NO3)3	0.084	0.059	3.957	3.097	1.311	1.043	0.802	0.604	2.627	1.870	2.938	2.182	2.888	2.186
Ca(NO3)2	0.094	0.066	0.506	0.396	3.342	2.660	0.139	0.104	0.191	0.136	1.524	1.132	1.498	1.134
Cu(NO3)2	0.000	0.000	0.166	0.130	0.066	0.053	0.158	0.119	0.010	0.007	0.118	0.088	0.116	0.088
Fe(NO3)3	0.040	0.028	0.057	0.044	0.146	0.116	0.905	0.682	0.010	0.007	0.779	0.578	0.765	0.579
Mg(NO3)2	0.000	0.000	0.103	0.080	0.223	0.178	0.052	0.039	0.029	0.020	0.073	0.054	0.072	0.054
Zn(NO3)2	0.000	0.000	0.022	0.017	0.171	0.136	0.016	0.012	0.000	0.000	0.035	0.026	0.034	0.026
Water	18.332	17.028	19.512	17.592	18.953	17.192	17.476	15.958	18.226	16.437	19.642	17.554	19.582	17.558
HNO3	3.728	6.264	3.903	6.248	3.903	6.248	3.903	6.248	3.903	6.248	3.903	6.248	3.903	6.248
Total	40.678	36.320	38.914	35.969	40.144	37.199	35.444	32.799	38.004	33.989	41.049	36.803	40.689	36.827
Grams salt/cm^3 H2O, calculated	1.22	1.13	0.99	1.04	1.12	1.16	1.03	1.06	1.09	1.07	1.09	1.10	1.08	1.10

Matrix	MTRX-1		MTRX-2		MTRX-3		MTRX-4		MTRX-5		MTRX-6		MTRX-7		MTRX-8	
Nominal [HNO3]	3	5	3	5	3	5	3	5	3	5	3	5	3	5	3	5
ANHYDROUS																
CsNO3	0.080	0.061	0.804	0.536	0.070	0.052	1.161	0.867	0.079	0.059	1.506	1.104	0.069	0.058	0.083	0.066
KNO3	0.234	0.180	0.289	0.193	0.206	0.154	0.227	0.170	0.699	0.523	0.885	0.649	0.610	0.512	0.734	0.578
NaNO3	10.074	7.733	12.405	8.265	12.576	9.370	9.782	7.309	9.986	7.478	12.649	9.272	9.386	7.878	12.769	10.049
Al(NO3)3	6.434	4.939	0.530	0.353	0.377	0.281	6.247	4.668	6.399	4.792	0.540	0.396	5.586	4.688	0.448	0.353
Ca(NO3)2	3.337	2.561	4.123	2.747	0.196	0.146	0.216	0.161	1.069	0.801	1.355	0.993	0.193	0.162	3.488	2.745
Cu(NO3)2	0.107	0.082	0.132	0.088	0.134	0.100	0.104	0.078	0.106	0.080	0.135	0.099	0.100	0.084	0.136	0.107
Fe(NO3)3	0.118	0.090	2.180	1.453	1.553	1.157	0.114	0.085	1.755	1.314	2.223	1.630	1.532	1.286	0.123	0.097
Mg(NO3)2	0.067	0.051	0.082	0.055	0.083	0.062	0.065	0.048	0.066	0.049	0.084	0.061	0.062	0.052	0.084	0.066
Zn(NO3)2	0.032	0.024	0.039	0.026	0.039	0.029	0.031	0.023	0.031	0.023	0.040	0.029	0.029	0.025	0.040	0.032
Water	22.649	19.949	19.902	17.457	18.640	17.020	21.130	18.681	22.723	19.882	19.724	17.796	21.564	19.508	19.183	17.512
HNO3	3.903	6.248	3.903	6.248	3.910	6.361	3.903	6.248	3.903	6.248	3.910	6.361	3.903	6.248	3.910	6.361
Total	47.034	41.919	44.389	37.418	37.785	34.733	42.980	38.340	46.816	41.251	43.050	38.389	43.034	40.500	41.000	37.965
Grams salt/cm^3 H2O, calculated	1.08	1.10	1.23	1.14	1.03	1.04	1.03	1.05	1.06	1.07	1.18	1.16	1.00	1.08	1.14	1.17

Table 4-8. Physical Properties of Saturated Solutions

Matrix	Starting [HNO3] (M)	Temp of Dissolution (deg C)	Density at 20 C (g/cm^3)	Heat Cap at 50 C (cal/g-C)	Viscosity at 50 C (cP)	Thermal Conductivity (W/m-C)	Conc. Dry Solids (g/cm^3)
AZ-102	3	52-55	1.380	0.667	1.38	0.463	0.701
AZ-102	4	52-55	1.375	0.657	1.28	0.450	0.668
AZ-102	5	52-55	1.365	0.670	1.27	0.464	0.669
AZ-102	3	20-22	1.370				0.632
AZ-102	5	20-22	1.341		1.28		0.591
AN-102	3	52-55	1.369	0.662	1.96	0.461	0.696
AN-102	4	52-55	1.363	0.667	1.66	0.458	0.716
AN-102	5	52-55	1.369	0.665	1.88	0.465	0.792
AN-102	3	20-22	1.354		1.75		0.594
AN-102	5	20-22	1.339		1.52		0.595
AN-103	3	52-55	1.413	0.651	2.10	0.477	0.795
AN-103	4	52-55	1.397	0.653	1.93	0.486	0.762
AN-103	5	52-55	1.392	0.620	1.66	0.450	0.735
AN-103	3	20-22	1.384		1.75		0.652
AN-103	5	20-22	1.357		1.51		0.630
AN-107	3	52-55	1.350	0.676	1.37	0.443	0.652
AN-107	4	52-55	1.352	0.684	1.41	0.449	0.669
AN-107	5	52-55	1.341	0.682	1.23	0.430	0.654
AN-107	3	20-22	1.358		1.54		0.610
AN-107	5	20-22	1.334		1.35		0.605
AN-105	3	52-55	1.357	0.674	1.56	0.483	0.694
AN-105	4	52-55	1.345	0.686	1.38	0.472	0.661
AN-105	5	52-55	1.341	0.686	1.46	0.473	0.735
CNTR-A	3	52-55	1.394	0.645	2.11	0.409	0.751
CNTR-A	5	52-55	1.379	0.666	1.70	0.465	0.730
CNTR-A	3	20-22	1.374		1.82		0.666
CNTR-A	5	20-22	1.345		1.49		0.608
CNTR-B	3	52-55	1.389	0.696	1.97		0.748
CNTR-B	5	52-55	1.376	0.660	1.80		0.717
MTX-1	3	52-55	1.399	0.699	2.44	0.468	0.811
MTX-1	5	52-55	1.408	0.648	2.21	0.465	0.835
MTX-2	3	52-55	1.425	0.639	2.04	0.465	0.794
MTX-2	5	52-55	1.402	0.658	1.64		0.739
MTX-3	3	52-55	1.357	0.689	1.43	0.494	0.658
MTX-3	5	52-55	1.340	0.685	1.27		0.631
MTX-4	3	52-55	1.405	0.659	2.18	0.467	0.835
MTX-4	5	52-55	1.388	0.662	1.74	0.495	0.789
MTX-5	3	52-55	1.408	0.656	2.87	0.489	0.869
MTX-5	5	52-55	1.401	0.659	2.41	0.479	0.862
MTX-6	3	52-55	1.424	0.657	1.86	0.496	0.766
MTX-6	5	52-55	1.395		1.66		0.728
MTX-7	3	52-55	1.391	0.689	2.51	0.448	0.824
MTX-7	5	52-55	1.386	0.636	2.24	0.443	0.813
MTX-8	3	52-55	1.397	0.618	1.73		0.677
MTX-8	5	52-55	1.378	0.718	1.62	0.547	0.703

Table 4-9. Comparison of Feed Compositions with Saturated Solutions

MOLE PERCENT COMPARISION - INCLUDING SODIUM																										
	AZ-102				AN-102				AN-103				AN-107				AN-105				CTR-A			CTR-B		
	Feed	PPT	PPT	PPT	Feed	PPT	PPT	PPT	Feed	PPT	PPT	PPT	Feed	PPT	PPT	PPT	Feed	PPT	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT
Nom. H+		3	4	5		3	4	5		3	4	5		3	4	5		3	4	5		3	5		3	5
Cs	4.67	6.29	6.85	6.73	0.23	0.36	0.40	0.29	1.47	1.66	1.92	2.08	0.78	1.18	1.08	1.24	0.23	0.41	0.33	0.34	1.70	2.41	2.68	1.70	2.08	2.54
K	3.53	5.62	5.35	6.90	2.59	3.73	3.83	5.00	3.14	4.33	5.44	5.78	1.89	4.27	3.61	4.29	2.45	3.39	3.33	3.34	2.55	4.18	4.48	2.55	3.95	4.37
Na	91.2	87.4	87.0	85.0	81.5	71.9	71.0	65.5	78.4	66.5	66.0	65.2	90.8	84.6	84.7	83.3	88.4	80.8	83.5	82.3	79.0	67.7	67.2	79.0	67.7	65.9
Al	0.19	0.27	0.28	0.41	12.6	18.8	19.7	23.1	3.71	5.33	4.82	6.29	2.50	3.72	4.15	4.46	7.25	13.8	11.5	12.5	8.37	13.2	12.8	8.37	12.4	12.7
Ca	0.28	0.28	0.34	0.80	2.09	3.27	3.21	3.67	12.2	18.6	19.1	17.7	0.56	1.01	0.90	0.95	0.70	1.29	1.04	1.20	5.64	8.23	8.89	5.64	9.78	10.5
Cu	0.00	0.00	0.00	0.00	0.39	0.90	0.88	1.06	0.38	0.28	0.32	0.41	0.44	0.90	0.86	0.97	0.43	0.06	0.05	0.06	0.38	0.50	0.55	0.38	0.52	0.56
Fe	0.08	0.14	0.20	0.20	0.16	0.24	0.23	0.33	0.37	0.54	0.49	0.57	2.53	3.89	4.21	4.31	0.04	0.04	0.05	0.04	1.95	2.99	2.99	1.95	2.93	2.72
Mg	0.00	0.00	0.00	0.00	0.31	0.70	0.62	0.86	0.30	1.64	1.22	1.36	0.34	0.33	0.34	0.46	0.33	0.15	0.16	0.27	0.30	0.62	0.32	0.30	0.41	0.51
Zn	0.00	0.00	0.00	0.00	0.11	0.11	0.09	0.19	0.11	1.12	0.76	0.55	0.13	0.11	0.12	0.05	0.12	0.00	0.00	0.00	0.11	0.14	0.14	0.11	0.13	0.14
	MTX-1			MTX-2			MTX-3			MTX-4			MTX-5			MTX-6			MTX-7			MTX-8				
	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT		
Nom. H+		3	5		3	5		3	5		3	5		3	5		3	5		3	5		3	5		
Cs	0.24	0.30	0.35	2.16	2.88	3.14	0.22	0.29	0.43	3.83	4.96	5.32	0.24	0.32	0.38	4.14	5.30	5.69	0.23	0.38	0.43	0.23	0.28	0.43		
K	1.34	1.82	1.77	1.50	2.19	2.29	1.26	1.95	2.04	1.45	2.09	2.42	4.07	5.86	6.00	4.69	7.27	7.51	3.98	6.07	6.24	3.96	5.85	7.22		
Na	68.3	61.9	51.8	76.4	67.4	63.2	91.8	87.0	85.7	74.0	63.9	62.2	69.2	54.5	56.2	79.7	70.2	69.6	72.8	60.4	58.4	82.0	74.2	68.5		
Al	17.4	20.8	26.6	1.30	2.00	1.98	1.10	1.91	1.91	18.9	26.5	27.2	17.7	26.9	24.2	1.36	1.91	2.27	17.3	24.9	26.5	1.15	1.46	1.68		
Ca	11.7	14.0	18.1	13.2	18.2	20.7	0.74	1.00	1.32	0.85	1.25	1.26	3.84	5.66	5.50	4.42	6.57	6.79	0.78	1.13	1.22	11.6	16.7	15.9		
Cu	0.33	0.35	0.43	0.37	0.48	0.53	0.44	0.64	0.76	0.36	0.42	0.45	0.33	0.42	0.40	0.38	0.56	0.59	0.35	0.47	0.51	0.40	0.46	5.46		
Fe	0.28	0.35	0.41	4.72	6.29	7.62	3.98	6.43	6.96	0.30	0.47	0.44	4.27	5.72	6.72	4.92	7.58	7.03	4.18	6.09	6.05	0.28	0.43	0.37		
Mg	0.26	0.33	0.37	0.29	0.39	0.42	0.35	0.59	0.65	0.28	0.30	0.50	0.26	0.42	0.37	0.30	0.47	0.38	0.28	0.38	0.49	0.31	0.55	0.32		
Zn	0.10	0.11	0.18	0.11	0.15	0.17	0.13	0.24	0.21	0.10	0.15	0.16	0.10	0.15	0.15	0.11	0.16	0.17	0.10	0.15	0.15	0.12	0.16	0.13		

Note: Feed indicates feed cation mole percent values. PPT indicates the post-precipitation cation mole percent values.

Table 4-10. Comparison of Feed Compositions with Saturated Solutions – Excluding Sodium

MOLE PERCENT COMPARISION - EXCLUDING SODIUM																											
	AZ-102				AN-102				AN-103				AN-107				AN-105				CTR-A				CTR-B		
	Feed	PPT	PPT	PPT	Feed	PPT	PPT	PPT	Feed	PPT	PPT	PPT	Feed	PPT	PPT	PPT	Feed	PPT	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT
Nom. H+		3	4	5		3	4	5		3	4	5		3	4	5		3	4	5		3	5		3	5
Cs	53.3	50.0	52.6	44.7	1.23	1.28	1.37	0.83	6.82	4.95	5.65	5.98	8.49	7.67	7.06	7.44	1.98	2.14	2.01	1.93	8.09	7.45	8.17	8.09	6.47	7.47
K	40.3	44.6	41.1	45.9	14.0	13.3	13.2	14.5	14.5	12.9	16.0	16.6	20.7	27.7	23.6	25.6	21.2	17.7	20.2	18.8	12.1	12.9	13.7	12.1	12.2	12.8
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	2.20	2.11	2.15	2.73	68.2	66.9	68.0	66.9	17.2	15.9	14.2	18.1	27.2	24.1	27.2	26.6	62.7	72.1	69.8	70.4	39.9	41.0	38.9	39.9	38.6	37.4
Ca	3.22	2.23	2.63	5.30	11.3	11.6	11.1	10.6	56.2	55.5	56.0	51.0	6.11	6.58	5.88	5.70	6.06	6.72	6.32	6.77	26.8	25.5	27.1	26.8	30.3	30.8
Cu	0.00	0.00	0.00	0.00	2.12	3.18	3.05	3.08	1.75	0.83	0.93	1.19	4.78	5.81	5.64	5.77	3.69	0.33	0.33	0.32	1.82	1.55	1.67	1.82	1.62	1.63
Fe	0.93	1.08	1.56	1.36	0.86	0.86	0.79	0.96	1.69	1.60	1.45	1.64	27.6	25.2	27.6	25.8	0.36	0.20	0.33	0.24	9.30	9.26	9.12	9.30	9.10	7.98
Mg	0.00	0.00	0.00	0.00	1.67	2.49	2.15	2.50	1.37	4.89	3.58	3.92	3.75	2.16	2.26	2.77	2.90	0.81	0.99	1.50	1.42	1.91	0.99	1.42	1.27	1.49
Zn	0.00	0.00	0.00	0.00	0.62	0.39	0.32	0.56	0.51	3.35	2.24	1.59	1.39	0.71	0.76	0.33	1.08	0.00	0.00	0.00	0.53	0.44	0.42	0.53	0.39	0.40
	MTX-1			MTX-2			MTX-3			MTX-4			MTX-5			MTX-6			MTX-7			MTX-8				
	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT	Feed	PPT	PPT		
Nom. H+		3	5		3	5		3	5		3	5		3	5		3	5		3	5		3	5		
Cs	0.74	0.78	0.73	9.15	8.84	8.52	2.71	2.21	2.98	14.7	13.7	14.1	0.78	0.71	0.86	20.4	17.8	18.7	0.86	0.95	1.04	1.29	1.09	1.37		
K	4.22	4.78	3.67	6.35	6.72	6.21	15.4	14.9	14.3	5.56	5.80	6.40	13.2	12.9	13.7	23.1	24.4	24.7	14.6	15.3	15.0	22.0	22.6	22.9		
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Al	55.0	54.7	55.2	5.52	6.15	5.38	13.4	14.6	13.4	72.5	73.3	72.1	57.4	59.2	55.4	6.68	6.40	7.45	63.6	63.0	63.7	6.37	5.64	5.34		
Ca	37.0	36.8	37.5	55.7	55.8	56.1	8.99	7.68	9.24	3.25	3.46	3.33	12.5	12.4	12.6	21.7	22.0	22.3	2.85	2.85	2.92	64.3	64.4	50.4		
Cu	1.04	0.92	0.90	1.56	1.47	1.45	5.38	4.93	5.33	1.37	1.17	1.18	1.08	0.91	0.91	1.89	1.87	1.95	1.29	1.18	1.21	2.19	1.80	17.3		
Fe	0.89	0.92	0.85	20.0	19.3	20.7	48.4	49.3	48.7	1.17	1.31	1.16	13.9	12.6	15.3	24.2	25.4	23.1	15.4	15.4	14.5	1.54	1.67	1.18		
Mg	0.82	0.86	0.77	1.23	1.21	1.15	4.22	4.49	4.56	1.08	0.84	1.33	0.85	0.92	0.85	1.48	1.58	1.26	1.01	0.96	1.19	1.72	2.14	1.00		
Zn	0.30	0.28	0.38	0.46	0.47	0.47	1.57	1.83	1.50	0.40	0.43	0.43	0.32	0.32	0.33	0.55	0.55	0.55	0.38	0.37	0.36	0.64	0.63	0.42		

Note: Feed indicates feed cation mole percent values. PPT indicates the post-precipitation cation mole percent values.

4.2.2.4 Statistical Analysis of Multiple Cation Solubility Data:

When the cesium eluate simulant data were analyzed with the JMP statistical design software, individual component effects become better quantified. The first data set analyzed was taken from the tests when dissolution occurred at 52-55°C and then the samples cooled to form precipitates. Because of the number of data points available, only linear effects could be estimated.

Parameter estimates were developed for each of the seven major variables as a function of cation mole percent. The combination of salt plus acid is used because, as shown in Section 4.2.1 and Figure 4-7, the presence of nitric acid reduces the solubility of sodium nitrate (the major component), in a near-linear manner. It is important to note that the use of linear parameter estimates in no way attempts to describe the intricacies of solubility theory in a way similar to a complex computer model. Rather, parameter estimates provide a simple mathematical tool based on experimental data for estimating solubility using known quantities of salt and acid. The use of the equations should be limited to the range conditions in the experimental data. The calculation provides an estimate of dissolved salt plus acid per cm^3 water.

When treating all 35 data points together, without discriminating against acid, linearity predicts about 81% of the variability. When the samples that are nominally 3M in HNO_3 are separated from those that are nominally 5M in HNO_3, the data show better linearity. For the 15 samples at 3M acid, linearity predicts 96% of the variability; at 5M acid, linearity predicts 98% of the variability. However, when these linear equations are applied to the tests involving dissolution at 20-22°C, the agreement between calculated and measured values is typically off by 10-20%. The reason for the disagreement is because the 20-22°C samples have higher acid (8-12 mol% higher) and lower sodium (5-8 mol%) concentrations. The cause of these differences was discussed in the previous section.

The data taken at 20-22°C should be more representative of the expected storage conditions because the evaporation process will be stopped at 80% of the room temperature solubility. When the 20-22°C solubility data were analyzed with the JMP statistical design software, the effects of the different cations became better quantified.[7] Because of the number of data points available, only linear effects could be estimated.[8] The parameter estimates, solubility calculations, and comparisons with measured data are listed in Table 4-11 for the 20-22°C data. Parameter estimates for each cation can be multiplied with the associated cation mole percent values and added together to obtain an estimated density.

$$\text{Estimated Solubility} = \Sigma\,(\text{cation solubility parameter estimate})_x\,(\text{cation mole percent})_x$$

The data show good agreement for a linear model between calculated values and measured values. According to the JMP software, a linear correlation can accurately account for 83.6% of the variability in the data. The worst value in Table 4-11 shows a 3.49% difference between the measured and calculated values. The average percent difference for all simulant data points is 0.97%. It should be noted that the software identified the 4.73% difference value for the CNTR-A, 3M HNO_3 sample as being a bad data point. As a result, it is not factored into the statistical conclusions drawn from the data in Table 4-11.

It is also important to clarify that the linear model for solubility is limited to a calculated acid range of approximately 2.0-4.5M. The performance of the linear model at lower acid concentrations is uncertain. However, as larger amounts of water become available at lower acid concentrations, it is expected that the solubility behavior for the specific matrices will begin to diverge.

[7] Edwards, T. B., "A Statistical Analysis of Results from the Cesium Eluate Solubility Study (U)," SRT-SCS-2002-00031 dated May 23, 2002.
[8] Edwards, T. B., "A Statistically Designed Test Matrix for Studying Cesium Eluate Solubility (U)," SRT-SCS-2001-00060, dated December 4, 2001.

Table 4-11. Solubility Parameter Estimates for 20-22°C Data

MOLE % PARAMETER ESTIMATES							
Al	Ca	Cs	Fe	H	K	Na	Others
0.00657	0.01215	0.01655	0.01046	0.00580	0.00957	0.00586	0.00454
Test Matrix	**3M HNO3 Measured**	**3M HNO3 Calculated.**	**Percent Difference.**	**5M HNO3 Measured**	**5M HNO3 Calculated.**	**Percent Difference.**	
AZ-102	0.632	0.629	0.53	0.591	0.611	3.49	
AN-102	0.594	0.605	1.86	0.595	0.597	0.38	
AN-103	0.652	0.656	0.62	0.630	0.631	0.18	
AN-107	0.610	0.605	0.75	0.605	0.598	1.16	
AN-105	0.599	0.598	0.24	0.591	0.592	0.15	
MTRX-1	0.639	0.648	1.34	0.635	0.627	1.21	
MTRX-2	0.662	0.675	1.91	0.654	0.647	1.08	
MTRX-3	0.608	0.604	0.66	0.584	0.596	2.05	
MTRX-4	0.627	0.627	0.09	0.622	0.612	1.57	
CNTR-A	0.666	0.634	4.73	0.608	0.616	1.43	
MTRX-5	0.628	0.633	0.82	0.626	0.616	1.50	
MTRX-6	0.665	0.663	0.22	0.638	0.637	0.12	
MTRX-7	0.609	0.618	1.62	0.611	0.606	0.88	
MTRX-8	0.654	0.649	0.80	0.632	0.628	0.56	
CNTR-B	0.633	0.636	0.46	0.622	0.618	0.58	

4.2.3 Effect of Organic Compounds on Salt Solubility

The presence of oxalate and EDTA both exhibited significant negative effects on salt solubility (Table 4-12). The effect of oxalate was the more pronounced of the two. The addition of 500 mg/L oxalate into the CNTR-A matrix reduced the total matrix dissolved per cm^3 of water by 50% for both 3M and 5M nitric acid. The presence of 500 mg/L EDTA reduced solubility by 24% in 3M HNO_3 and by 42% in 5M HNO_3. It should be noted that the units of dissolved matrix per cm^3 of water differ from other places where solubility is reported in grams per total volume. The necessary data are not available to report the solubility in grams per total volume.

While the effect of oxalate on solubility is greater than that of EDTA, the presence of oxalate may be less problematic from an operations perspective. When oxalate begins to precipitate from these solutions, only trace amounts of very fine solid form. Attempts to filter the sample and analyze it were unsuccessful because of the small amounts of precipitate even after the liquid had been allowed to cool from 52-55°C to room temperature. The solutions containing EDTA behaved in a manner similar to the other 52-55°C solubility tests. When the solutions were cooled, large amounts of precipitate formed. Analysis by XRD was unable to directly identify the compound that precipitated. However, the diffraction pattern was compared against the diffraction patterns of all other nitrate salts that might be present, and no matches were observed. Furthermore, since EDTA is one of only a few components in the solution that could create the amount of solids observed, it is expected that the solid is a derivative of EDTA.

Similarly, the presence of DBP greatly reduced solubility. In both 3M and 5M acid and a liquid concentration of 700 mg/L DBP, the addition of the first 1.4 grams CNTR-A solid immediately produced a precipitate. Without DBP present, 3M acid required 21.0 grams under similar conditions to yield a precipitate while 5M acid needed 15.6 grams (a greater than 95% reduction in solubility for both tests). When 3M and 5M acid had only 350 mg/L DBP, both solutions yielded a precipitate at the addition of the first 1.4 grams of CNTR-A solid. When the DBP concentration in the liquid was reduced to 175 mg/L, 3M acid precipitated after 2.1 grams of solid addition (90% reduction in solubility) while 5M acid precipitated after 6.1 grams of CNTR-A solid addition (61% reduction).

The data clearly show that some organic components, if present in the cesium eluate, can affect solubility. However, insufficient data exist to identify specific compounds that are present in the eluate in high enough concentrations to be of concern. The use of DBP, oxalate and EDTA represent three compounds with a reasonable probability of being in the eluate at measurable quantities. They also indicate that other organic species may have similar effects. As better organic data become available, additional solubility tests need to be performed using the appropriate organic compounds.

Table 4-12. Solubility in the Presence of Organic Compounds –52-55^0 C

	CNTR-A	CNTR-A w/ 500 ppm oxalate	CNTR-A w/ 200 ppm oxalate	CNTR-A w/ 100 ppm oxalate	CNTR-A w/ 500 ppm EDTA
Matrix Dissolved					
into 20 cm^3 of 3M	23.37	7.07	8.54	16.42	13.49
Nitric Acid (g)					
Matrix Dissolved (g)	1.09	0.54	0.60	0.96	0.83
per cm^3 of H_2O [3M]					
Matrix Dissolved					
into 20 cm^3 of 5M	17.36	5.17			6.67
Nitric Acid (g)					
Matrix Dissolved (g)	1.10	0.56			0.64
per cm^3 of H_2O [5M]					

4.3 PHYSICAL PROPERTY DATA OF SATURATED SOLUTIONS

Physical property data were collected on many of the saturated solutions generated at both 20-22^{o}C and 52-55^{o}C. The collected data include density at 20^{o}C, viscosity at 50^{o}C, and heat capacity from 30-80^{o}C, and thermal conductivity at 50^{o}C. Most samples were analyzed for viscosity at one temperature because if one low-temperature liquid-viscosity datum point is available, viscosity at other temperatures may be approximated.[9] Several viscosity samples were also analyzed at 20^{o}C and 77^{o}C to confirm the expected behavior. Much of these data are listed in Table 4-8. For simplicity, only the values for heat capacity and viscosity at 50^{o}C are included in the table. All of the thermal conductivity is shown in Attachment 2 and the multiple-temperature viscosity data is listed in Attachment 3. Thermal conductivity is determined from the heat capacity data measured over the range of temperatures.

A discussion of density response as a function of total dissolved salt plus acid was provided above. It is expected that dissolved salt and acid content would affect heat capacity in a manner similar to density. When heat capacity is plotted against density (Figure 4-9), the graph shows good linearity with two scattered points. A closer examination of Figure 4-9 indicates that the scatter is likely due to experimental error. For example, MTX-8 in 5M acid is well above the trend line while MTX-8 in 3M acid is well below the trend line. A second analysis of both MTX-8 samples confirmed the results. Other data listed in Figure 4-9 had exhibited significant scatter, but re-analysis brought those points in line with the expected behavior. With the omission of the MTX-8 data, the linear data fit yields an R^2 value of 0.724.

A comparable plot of heat capacity versus dissolved acid and salt concentration (Figure 4-10) exhibits more scatter than Figure 4-9. Without the MTX-8 data, the linear data fit produces an R^2 value of 0.610. While heat capacity shows good agreement with dissolved acid/salt content using a linear model, density provides a much more linear measure of acid/salt content.

[9] Perry R. H. and Green, D. W. Perry's Chemical Engineer's Handbook, Sixth Edition. McGraw-Hill Book Company (New York, NY), 1984, p. 3-281.

Figure 4-9. Heat Capacity Correlation with Density

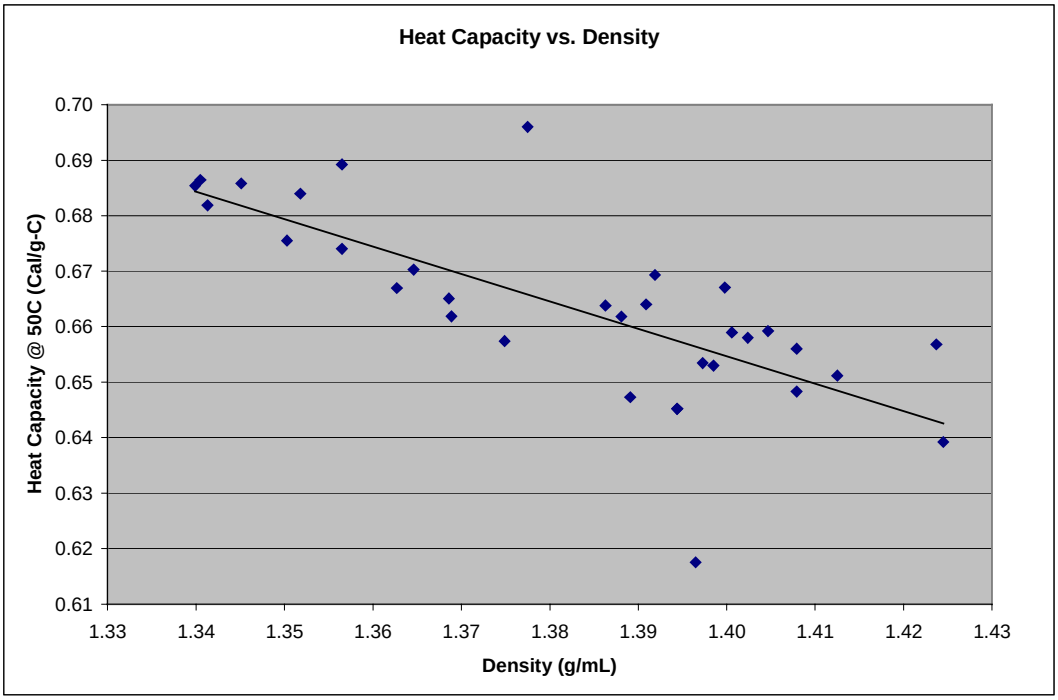


Figure 4-10. Heat Capacity Correlation with Dissolved Salt/Acid Content

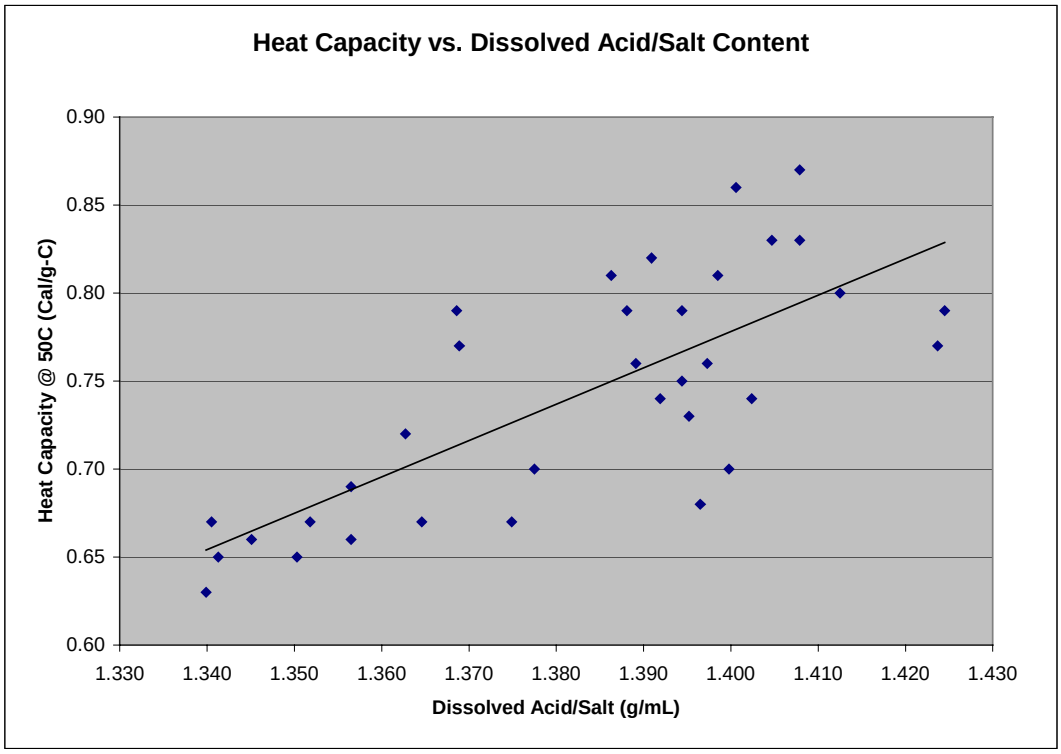
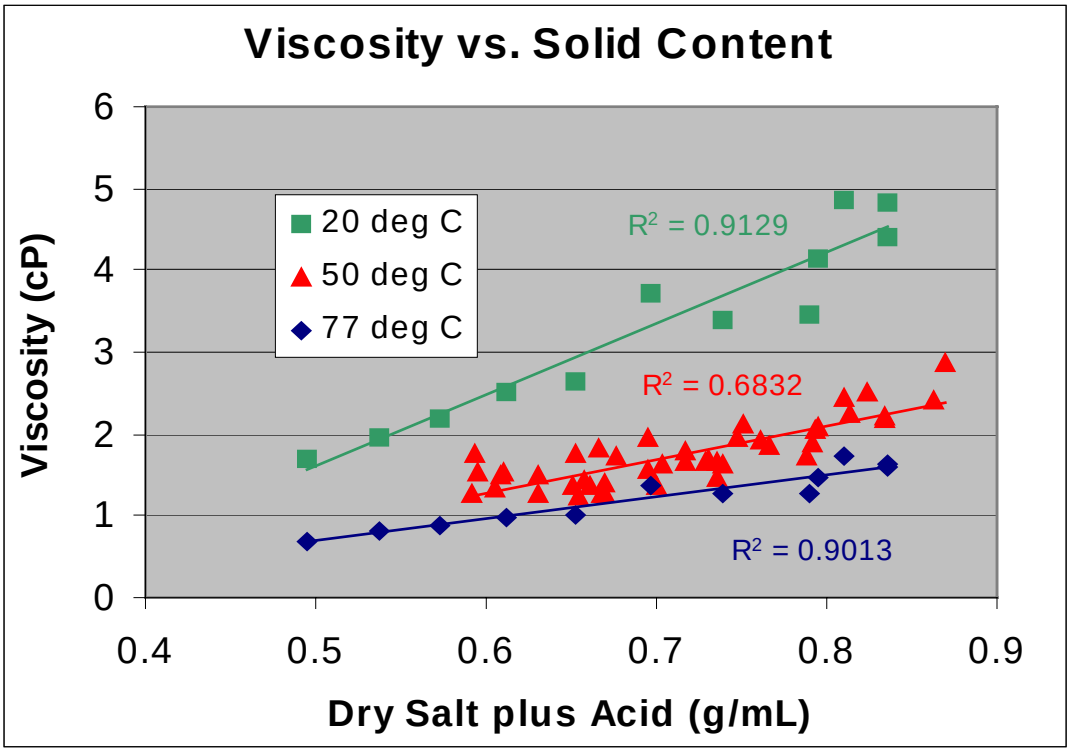


Figure 4-11. Viscosity as a Function of Salt/Acid Concentration



Similarly, thermal conductivity data in Table 4-8 were plotted as a function of acid/salt content. To that data were added intermediate concentration data of Table 4-13. The data are represented in Figure 4-12. The thermal conductivity for all of these saturated solutions are relatively constant with a fair amount of scatter. If the thermal conductivity of water at 50°C (k=0.645 W/m°C) is added to the plot, it seems reasonable to draw a line from water through the other data. However, apart from the data point for water, the data from Table 4-8 and Table 4-13 a linear fit of the data produces a different trendline.

Solution viscosity as a function of dissolved acid and salt follows a linear trend comparable to those of density and heat capacity (Figure 4-11). The smaller data sets at 20°C and 77°C exhibit much better agreement to linear models than the larger data set at 50°C. The reason for this result may be attributable to analytical method variability. The smaller data sets (20°C and 77°C) were submitted at one time and contained a sufficiently small number of samples to be analyzed in a single day. The larger data set (50°C) contains data from three separate sets of samples submitted at different times. Consequently, more variability can be expected in the 50°C data.

It is also worth noting that the measured viscosity of several samples as a function temperature shows good agreement with what was expected. Figure 4-13 depicts the relatively uniform behavior of samples with a range of viscosity values as a function of temperature. The shape of the curves in Figure 4-13 are consistent with the shape of the curve in Perry's Handbook.[5] The uniformity of the viscosity measurements as a function of temperature, and their agreement with what was expected from the literature, lends credibility to the quality of the viscosity data.

Figure 4-12. Thermal Conductivity as a Function of Salt/Acid Concentration

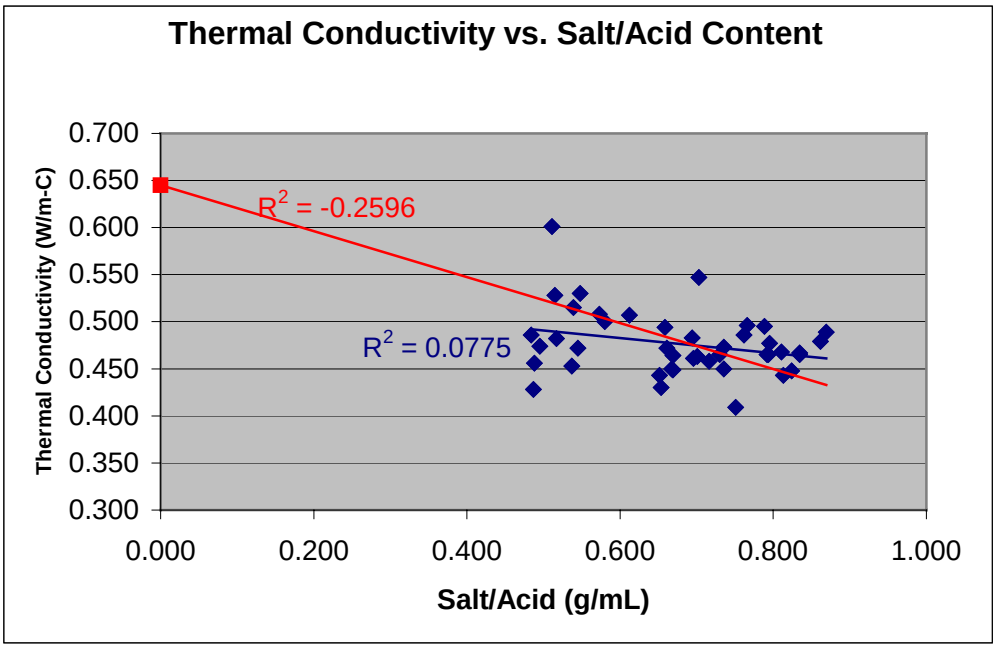
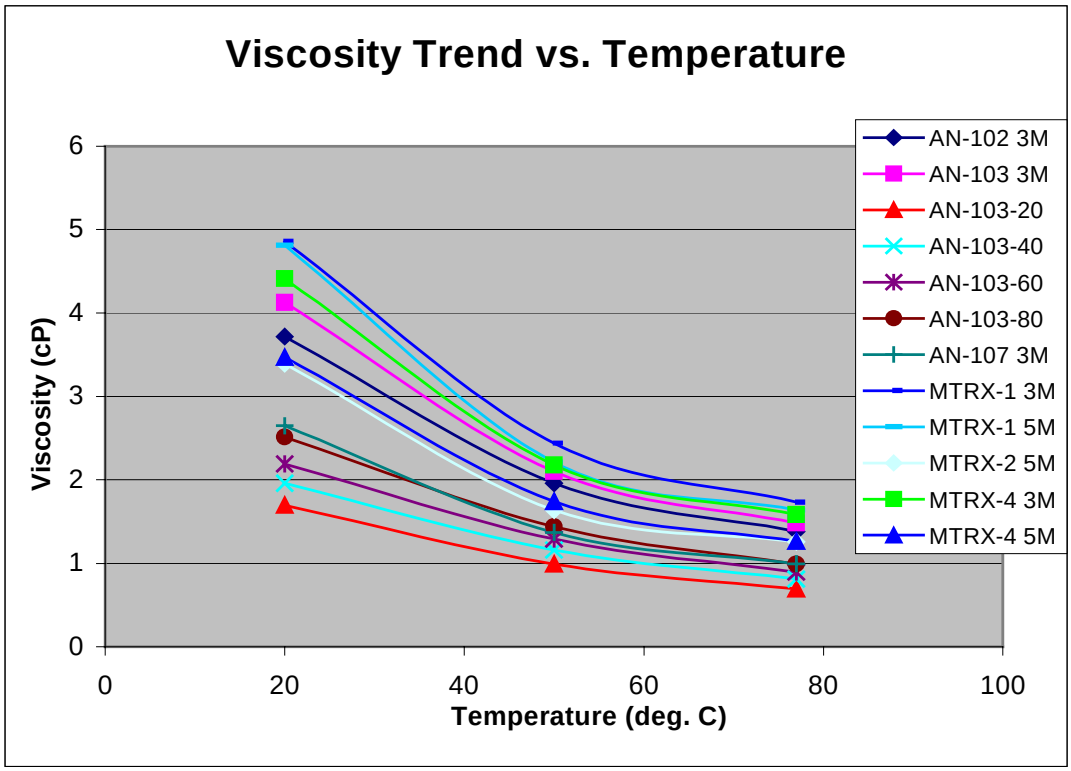


Figure 4-13. Viscosity Trend vs. Temperature



4.4 PHYSICAL PROPERTY DATA FOR INTERMEDIATE COMPOSITIONS

Physical property data were collected on all of the intermediate composition solutions prepared. The data collected include density at 20°C, viscosity at 50°C, thermal conductivity at 50°C, and heat capacity from 30-80°C. Much of these data are listed Table 4-13. For simplicity, only the values at 50°C are included for heat capacity and viscosity. Additional viscosity data is included in Attachment 3. Additional heat capacity data is included in Attachment 4. It should also be noted that a saturated sample for AN-107 (AN-107-100) has been created because the calculations show precipitation occurring at an acid concentration well outside the range of the experimental data.

Table 4-13. Physical Properties of Intermediate Solutions

	Nominal	Density	Heat Cap	Viscosity	Thermal	Conc. Dry
Matrix	[HNO3]	at 20 C	at 50 C	at 50 C	Conductivity	Solids
	(M)	(g/cm^3)	(cal/g-C)	(cP)	(W/m-C)	(g/cm^3)
AZ-102-20	6.4	1.251	0.506	0.93	0.456	0.488
AZ-102-40	5.4	1.277	0.668	1.00	0.482	0.517
AZ-102-60	4.7	1.302	0.719	1.10	0.530	0.548
AZ-102-80	4.2	1.324	0.692	1.13	0.500	0.580
AN-102-20	6.9	1.247	0.669	0.93	0.486	0.484
AN-102-40	6.4	1.269	0.707	1.04	0.601	0.511
AN-102-60	5.9	1.290	0.702	1.14	0.515	0.539
AN-102-80	5.4	1.311		1.25		0.568
AN-103-20	5.9	1.263	0.602	0.99	0.474	0.495
AN-103-40	4.7	1.299	0.674	1.16	0.453	0.537
AN-103-60	4.1	1.324		1.29		0.573
AN-103-80	3.6	1.352	0.6548	1.44	0.507	0.612
AN-107-20	3.6	1.274	0.663	1.07	0.428	0.487
AN-107-40	3.1	1.296	0.712	1.18	0.528	0.515
AN-107-60	2.6	1.316	0.677	1.26	0.472	0.545
AN-107-80	2.3	1.336	0.684	1.33	0.508	0.573
AN-107-100	2.0	1.360		1.50		0.612

The density data that have been collected exhibit linearity comparable to the data in Figure 4-2. Intermediate composition density data are plotted in Figure 4-14. The data for AZ-102, AN-102 and AN-103 fall essentially on the same line. The data for AN-107 is slightly below the other data sets. A review of the compositions (Table 3-4) indicates that the distinguishing characteristic of the AN-107 intermediate compositions is their relatively low acidity. It is unclear whether the low acidity is the cause of the divergence of the AN-107 data.

A plot of the intermediate composition viscosity data (Figure 4-15) shows behavior similar to that of Figure 4-14. The viscosity data clearly exhibit more scatter than the density data, but are still linear as a function of acid/salt content. A plot of heat capacity data as a function of acid/salt content shows a large amount of data scatter and no clear evidence of linear behavior (Figure 4-16). Based on the larger data sets taken on the saturated samples (Figure 4-9) which demonstrate a linear relationship between heat capacity and salt/acid content, the scatter of Figure 4-16 can likely be attributed to analytical variability. A discussion of thermal conductivity behavior as a function of acid/salt content for both saturated and intermediate composition solutions has already been given in Section 4.3.

Figure 4-14. Intermediate Composition Density Behavior

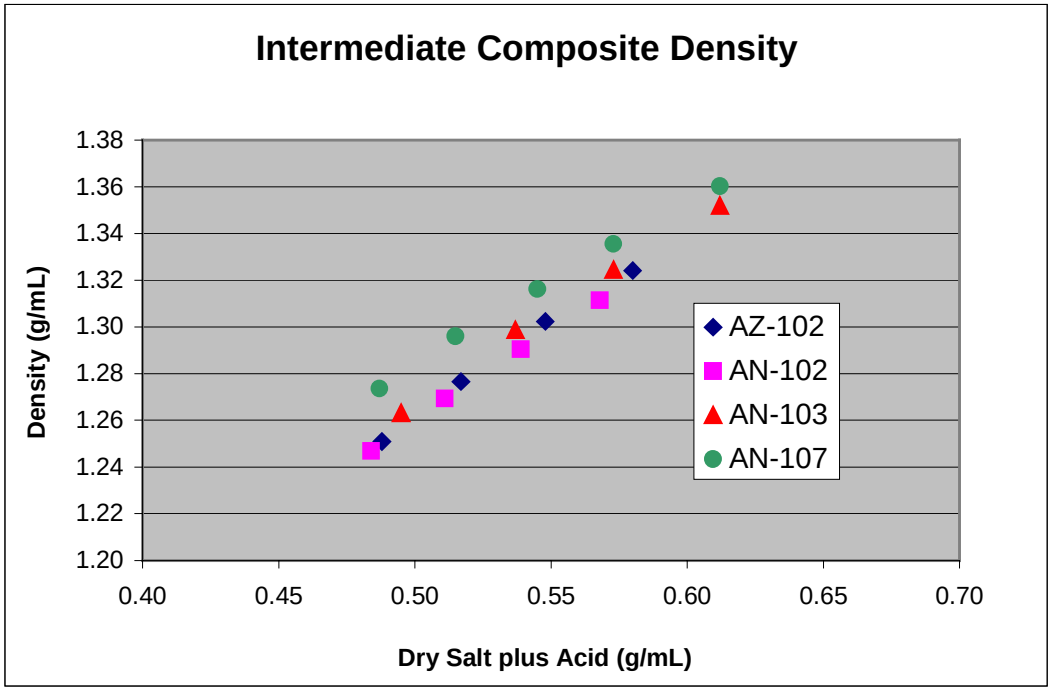


Figure 4-15. Intermediate Composite Viscosity Behavior

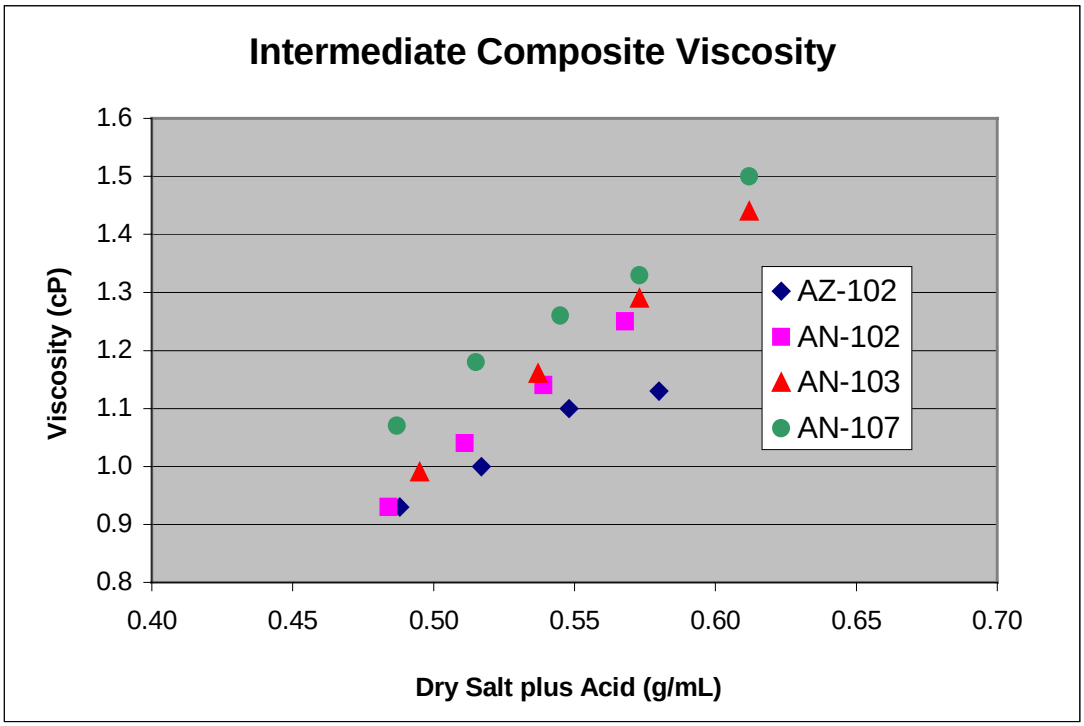
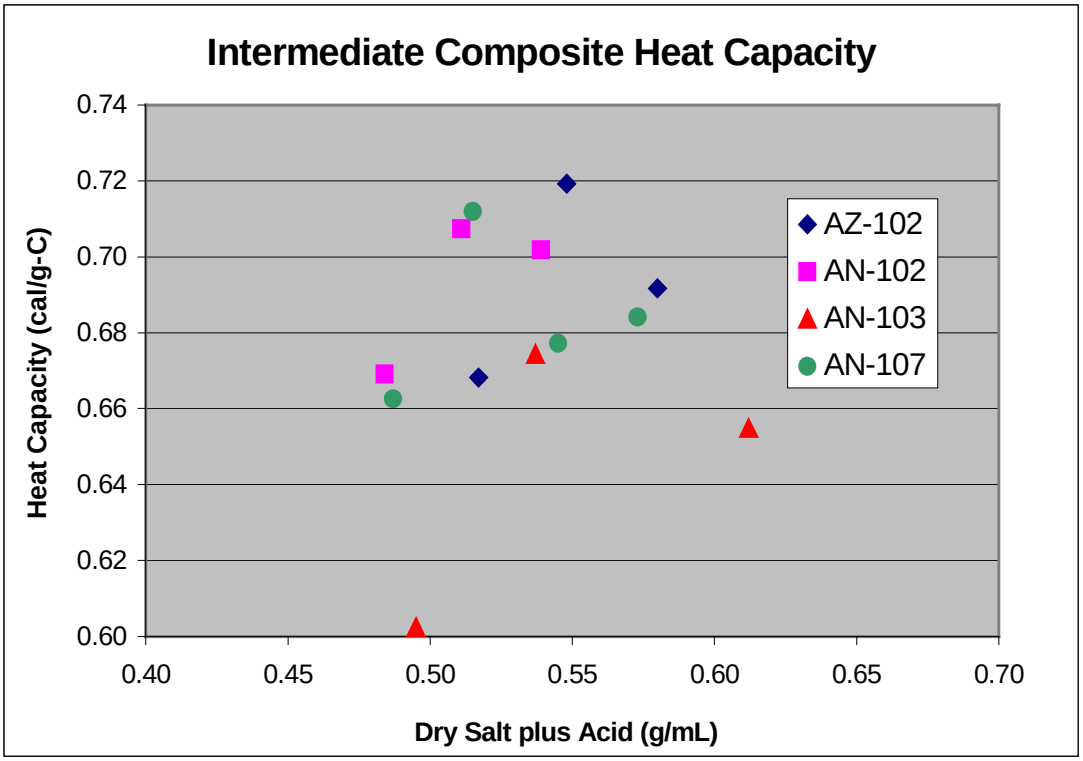


Figure 4-16. Intermediate Composition Heat Capacity Behavior



5.0 CONCLUSIONS

A large body of experimental data has been collected for the cesium eluate evaporation system. The data helps confirm and supplement ongoing modeling activities. Duplicate samples, repeat experiments, and correlations of the data suggest that the experimental methods are reliable. The results show that linear models do a very good job predicting solution density over a wide range of acid and dissolved salt concentrations. Typical calculation errors are on the order of 1-3%. The linear behavior of heat capacity and viscosity as a function of dissolved salt and acid content is clearly present from plots of the data, but attempts to produce an effective linear model will likely be limited by the accuracy of the analytical technique.

Linear models with the 20-22^{o}C data also do a good job of predicting solution solubility at room temperature over a calculated acid concentration range of 2.0 to 4.5 molar. Linear models account for 84% of the variability in solubility as a function of changes in the individual component concentrations. Typical calculation errors are on the order of 1-4%. The primary non-linear affect may be caused by difference in the way HNO_3 binds with H_2O at difference HNO_3 concentrations. Some indication of this behavior is seen in the solubilities of cesium and potassium in nitric acid as a function of acid concentration. The performance of the linear model at lower acid concentrations is uncertain. However, as larger amounts of water become available at lower acid concentrations, it is expected that the solubility behavior for the specific matrices will begin to diverge.

Linear models developed with 52-55^{o}C data do not do a good job of prediction room temperature solubility behavior. The agreement between calculated and measured values is typically off by 10-20%. The reason for the disagreement is because precipitation upon cooling causes the data from the 52-55^{o}C solubility tests to have much higher acid concentrations (8-12 mol% higher) and lower sodium concentrations (5-8 mol%). Analyses of the precipitates using XRD from the 52-55^{o}C solubility tests show that sodium nitrate is always the dominant solid (>98%) and almost always the only detectable solid.

The presence of DBP, oxalate and EDTA all exhibited significant negative effects on salt solubility. The effect of DBP was the most pronounced of the three. The presence of 350-700 mg/L DBP in the dissolution liquid reduced

the solubility of the CNTR-A solid matrix by more than 95% for both 3M and 5M HNO_3 experiments. The addition of 500 mg/L oxalate into the CNTR-A matrix reduced the total matrix dissolved per cm^3 of water by 50% for both 3M and 5M nitric acid. The presence of 500 mg/L EDTA reduced solubility of the same matrix by 24% in 3M HNO_3 and by 42% in 5M HNO_3.

6.0 ISSUES & RECOMMENDATIONS

The linear models developed for estimating density and solubility show promise as simple tools for predicting and controlling cesium eluate evaporator operation. Knowledge of the eluate concentrations being fed to the evaporator could be used to predict evaporation endpoint. The density estimates can then be used to determine when the endpoint is reached during actual operations. Testing with simulant eluates at SRTC will help evaluate the value of the two models.

The density data package is quite extensive and covers a wide range of component compositions. The solubility data package is much more limited to an acid concentration range of 2.0-4.5M. Based on data developed as part of other efforts, attempts to use the solubility model at lower acid concentrations may produce estimates with as much as 9% error near 1.0M for one matrix composition. Additional testing would be needed to use the model for 1.0-3.0M acid.

A significant unknown in the test program is the identity and concentration of organic compounds that might be contained in the cesium eluate. If present in quantities greater than 100 mg/L, certain organic compounds can have large negative effects on overall solubility. Not only will these greatly reduce the effectiveness of eluate evaporation, they will also invalidate the use of models based solely on ionic species. There is a great need to develop more conclusive organic data for the cesium eluate evaporation program if it is to generate a product that is of value to the RPP WTP. Once additional data is available that identifies and quantifies the presence of specific organic compounds, a decision can be made regarding additional solubility testing.

Another issue developed during testing related to the initial test objectives. An element of the program was to test the effect of varying salt components and concentrations on vapor pressure. However, the presence of acid in the samples caused a reaction with the metal parts in the vapor space of the vapor pressure instrument. The reaction released NOx and caused the instrument to give false readings. Attempts to measure vapor pressures by an alternate method were unsuccessful. Since this data was only intended to supplement the OLI calculations, the omission of the vapor pressure data is not considered to be a significant issue. Furthermore, vapor phase pressures will be measured during the actual evaporation of simulated cesium eluate generated during pilot plant experiments. The subsequent data will be extremely valuable in assessing the OLI model's ability to predict vapor pressure behavior.

Attachment 1 - Duplicate Density Measurements

Sample	1st Analysis	2nd Analysis	3rd Analysis
D.I. H2O	0.9983	0.9982	0.9982
28% NaNO3	1.2079	1.2080	1.2080
14	1.0139	1.0140	
22	1.0389	1.0389	
57	1.1074	1.1077	
32	1.1689	1.1691	
7	1.2325	1.2325	
50	1.3094	1.3088	
46	1.3262	1.3267	
35	1.2220	1.2221	
42	1.2310	1.2311	
53	1.2830	1.2831	
47	1.3356	1.3364	
12	1.2985	1.2984	
62	1.3198	1.3201	

Attachment 2 - Multiple Temperature Heat Capacity (in cal/g-^{o}C) Data

	MTX-1		MTX-2		MTX-3		MTX-4		MTX-5		MTX-6		MTX-7		MTX-8	
Temp Deg. C	3M HNO_3	5M HNO_3	3M HNO_3	5M HNO_3	3M HNO_3	5M HNO_3	3M HNO_3	5M HNO_3	3M HNO_3	5M HNO_3	3M HNO_3	5M HNO_3	3M HNO_3	5M HNO_3	3M HNO_3	5M HNO_3
30								0.632	0.632		0.632					
35	0.646	0.639	0.631	0.651	0.686	0.676	0.640	0.640	0.639	0.651	0.640		0.658	0.656	0.580	0.657
40	0.649	0.642	0.634	0.653	0.686	0.680	0.646	0.648	0.644	0.654	0.645		0.659	0.658	0.591	0.674
45	0.651	0.645	0.637	0.656	0.687	0.683	0.653	0.656	0.650	0.656	0.651		0.662	0.661	0.601	0.685
50	0.653	0.648	0.639	0.658	0.689	0.685	0.659	0.662	0.656	0.659	0.657		0.664	0.664	0.618	0.696
55	0.651	0.651	0.642	0.661	0.695	0.688	0.664	0.663	0.660	0.661	0.661		0.665	0.666	0.620	0.704
60	0.656	0.654	0.644	0.663	0.700	0.690	0.672	0.672	0.664	0.663	0.671		0.667	0.668	0.625	0.711
65	0.657	0.657	0.647	0.668	0.702	0.693	0.678	0.678	0.670	0.666	0.677		0.668	0.670	0.636	0.715
70	0.658	0.661	0.649	0.670	0.705	0.696	0.684	0.685	0.675	0.667	0.683		0.670	0.672	0.657	0.724
75	0.660	0.663	0.651	0.672	0.707	0.699	0.690	0.691	0.681	0.669	0.689		0.671	0.674	0.664	0.732
80	0.660	0.665	0.654	0.674	0.709	0.701	0.696	0.698	0.686	0.671	0.695		0.673	0.676	0.675	0.740
85		0.667		0.677		0.704			0.692							

	AZ-102			AN-102			AN-103			AN-107			AN-105			CTR-A		CTR-B	
Temp Deg. C	3M HNO_3	4M HNO_3	5M HNO_3	3M HNO_3	4M HNO_3	5M HNO_3	3M HNO_3	4M HNO_3	5M HNO_3	3M HNO_3	4M HNO_3	5M HNO_3	3M HNO_3	4M HNO_3	5M HNO_3	3M HNO_3	5M HNO_3	3M HNO_3	5M HNO_3
30									0.662							0.637			
35	0.665	0.646	0.661	0.657	0.656	0.658	0.647	0.648	0.664	0.671	0.677	0.673	0.668	0.679	0.668	0.638	0.658	0.654	0.653
40	0.666	0.650	0.665	0.659	0.661	0.660	0.648	0.650	0.665	0.673	0.680	0.676	0.670	0.681	0.673	0.645	0.661	0.654	0.655
45	0.665	0.654	0.668	0.661	0.664	0.663	0.650	0.651	0.667	0.674	0.682	0.679	0.672	0.683	0.679	0.644	0.663	0.651	0.658
50	0.667	0.657	0.670	0.662	0.667	0.665	0.651	0.653	0.669	0.676	0.684	0.682	0.674	0.686	0.686	0.645	0.666	0.647	0.660
55	0.667	0.661	0.673	0.664	0.669	0.667	0.653	0.655	0.671	0.677	0.685	0.685	0.676	0.688	0.699	0.649	0.668	0.643	0.662
60	0.668	0.665	0.676	0.665	0.671	0.669	0.653	0.657	0.673	0.680	0.687	0.687	0.677	0.690	0.706	0.654	0.671	0.639	0.665
65	0.669	0.668	0.678	0.667	0.674	0.671	0.655	0.658	0.675	0.682	0.689	0.691	0.679	0.693	0.716	0.661	0.673	0.636	0.667
70	0.669	0.672	0.681	0.668	0.676	0.674	0.656	0.660	0.676	0.683	0.691	0.693	0.680	0.694	0.724	0.665	0.675	0.637	0.670
75	0.670	0.676	0.684	0.669	0.678	0.676	0.657	0.662	0.678	0.685	0.692	0.697	0.682	0.695	0.732	0.666	0.677	0.646	0.673
80	0.671	0.679	0.687	0.671	0.680	0.679	0.658	0.661	0.679	0.686	0.694	0.700	0.683	0.696	0.740	0.669	0.679	0.664	0.674
85	0.672	0.683				0.681		0.662			0.695			0.698		0.673		0.669	

Note: Listed acid concentrations are nominal starting acid concentrations

Attachment 3 - Multiple Temperature Viscosity Data

Matrix	Viscosity at 20 C (cP)	Viscosity at 50 C (cP)	Viscosity at 77 C (cP)	Conc. Dry Solids (g/mL)
AN-102 3M	3.72	1.96	1.38	0.696
AN-103 3M	4.13	2.10	1.48	0.795
AN-103-20	1.70	0.99	0.69	0.495
AN-103-40	1.96	1.16	0.81	0.537
AN-103-60	2.19	1.29	0.89	0.573
AN-103-80	2.51	1.44	0.99	0.612
AN-107 3M	2.65	1.37	1.00	0.652
MTRX-1 3M	4.86	2.44	1.73	0.811
MTRX-1 5M	4.81	2.21	1.64	0.835
MTRX-2 5M	3.39	1.64	1.26	0.739
MTRX-4 3M	4.41	2.18	1.59	0.835
MTRX-4 5M	3.47	1.74	1.26	0.789

Attachment 4 - Multiple-Temperature Heat Capacity (in cal/g-^{o}C) Data for Intermediate Compounds

Temp deg. C	AZ-102-20	AZ-102-40	AZ-102-60	AZ-102-80	AN-102-20	AN-102-40	AN-102-60	AN-102-80
30	0.483	0.625	0.662	0.624		0.668	0.627	Not
35	0.516	0.665	0.694	0.664	0.621	0.692	0.676	Available
40	0.522	0.673	0.707	0.678		0.700	0.692	
45	0.516	0.672	0.714	0.686	0.655	0.704	0.698	
50	0.506	0.668	0.719	0.692		0.707	0.702	
55	0.494	0.663	0.724	0.697	0.683	0.710	0.705	
60	0.479	0.658	0.729	0.702		0.713	0.708	
65	0.457	0.653	0.735	0.707	0.711	0.716	0.711	
70	0.427	0.647	0.740	0.713		0.719	0.714	
75	0.389	0.642	0.746	0.719	0.739	0.723	0.718	
80	0.343	0.638	0.752	0.725		0.727	0.721	
85	0.287							

Temp deg. C	AN-103-20	AN-103-40	AN-103-60	AN-103-80	AN-107-20	AN-107-40	AN-107-60	AN-107-80
30	0.585	0.614	Not	0.628	0.554	0.645	0.581	0.624
35	0.607	0.654	Available	0.653	0.628	0.691	0.645	0.666
40	0.609	0.666		0.658	0.652	0.704	0.667	0.679
45	0.606	0.671		0.657	0.661	0.709	0.674	0.683
50	0.602	0.674		0.655	0.663	0.712	0.677	0.684
55	0.598	0.677		0.652	0.662	0.714	0.679	0.684
60	0.593	0.680		0.649	0.660	0.717	0.680	0.684
65	0.589	0.682		0.646	0.658	0.719	0.681	0.685
70	0.584	0.684		0.643	0.656	0.720	0.683	0.685
75	0.579	0.687		0.640	0.654	0.721	0.684	0.686
80	0.574	0.690		0.637	0.651	0.721	0.686	0.687
85					0.649			