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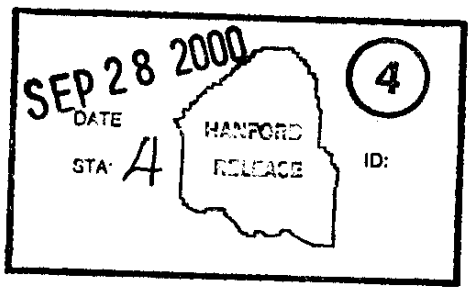

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ACRONYMS AND ABBREVIATIONS

103-AN	Tank 241-AN-103
AT	total alpha
BBI	Best Basis Inventory
ChgBal	charge balance (cation/anion ratio)
Ci	curie
cP	centipoise
CSol	centrifuged solids
g	gram
GEA	gamma energy analysis
hr	hour
IC	ion chromatography
ICP	inductively coupled plasma spectroscopy
ISL	interstitial liquid
MassAdd	total mass based on sum of components
MassBal	mass balance
MassCalc	total mass based on hotcell weight measurements
mL	milliliter
MT	metric ton (1000 kg)
n.a.	not available
PLM	polarized light microscopy
PSD	particle size distribution
s^{-1}	reciprocal seconds
SpG	specific gravity (or density)
SSol	settled solids
TCR	Tank Characterization Report
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic isotopes
Vol	volume
Wt	weight
WTC	whole-tank composite

1.0 INTRODUCTION AND EXECUTIVE SUMMARY

Tank 241-AN-103 (103-AN) has been identified as one of the first tanks to be retrieved for low activity waste pretreatment and immobilization (Kirkbride 2000). Retrieval of the tank waste will require dilution to dissolve solids. Laboratory tests are needed to determine the amount and type of dilution required for safe retrieval of the tank waste. The tests have been carried out according to a prescribed test plan (Jewett 1999). The test plan was based on requirements established by Process Development (Nguyen 1999).

The dilution parameters that were evaluated were volume percent dilution and temperature. All dilutions were made with water. Chemical concentrations in liquid and solid phases were measured so that the behavior of the samples could be understood in terms of which solids were dissolving (or not dissolving). Other measurements made in the laboratory include rheology (viscosity) and polarized light microscopy (PLM).

The main body of dilution tests was done on a series of eight samples at 45 °C, representing the retrieval scenario in which the supernatant liquid is pumped from the tank and dilution water is added to settled solids remaining in the tank. Dilution values ranged from 0% to 125% by volume, expressed as 100 times the volume of diluent (water) divided by the volume of settled solids being diluted.

To evaluate the effect of temperature on the dilution test results, comparison tests were done on two settled-solids samples at 25 °C and two at 65 °C, at dilutions ranging from 66% to 91% by volume.

Two dilution tests were done on whole-tank-composite samples, one at 0% dilution and one at 50% dilution, by volume. These samples represent the retrieval scenario in which mixer pumps are installed in the tank, and the entire tank contents are mixed before any dilution takes place. These tests were done at 45 °C.

Heating and cooling tests were done to determine whether the amount of solids in the waste would change if the waste were heated (by the mixer pump, for example) or cooled (during tank-to-tank transfer, for example). Liquid phase samples were heated from 25 to 65 °C and cooled from 65 to 25 °C, both at 0% and 20% dilution by volume. Solids formed on cooling in both diluted and undiluted samples, so additional tests were run at 40% and 60% dilution. No solids formed on cooling at the higher dilutions.

Viscosity measurements were made on several waste fractions over the 25 to 65 °C temperature range.

1.1 SUMMARY AND CONCLUSIONS

Tank 103-AN currently contains approximately 52% by volume supernatant liquid and 48% solids (settled solids plus crust, including retained gas) at roughly 38 °C (Jewett 1999). In the current study, the settled solids and crust are combined as settled solids because the mixing of the sample dislodges the gas from the crust, and the solids settle. Most of the dissolution tests were done at 45 °C because (a) dissolution tests on other tanks (241-AN-105, 241-AN-104, 241-AW-101) were done at 45 °C, and (b) some heating of the waste due to mixer pump operation is inevitable.

Whole-tank-composite (WTC) samples T1 through T4 in 500 mL jars contained 46-54% settled solids after 18 months of undisturbed settling at ambient temperature (approximately 25 °C). The laboratory test samples in 50 mL centrifuge cones had an average of 61.5% settled solids (including floating crust) after 5 days of undisturbed settling at 45 °C. These measurements suggest that the composite samples used for the laboratory tests are reasonably representative of the waste in the tank.

As with most other typical tank wastes, most of the settled solids layer is interstitial liquid; the actual solid phase ("true" solids) makes up a relatively small fraction. Based on the laboratory test results at 45 °C, the undiluted WTC samples contained 20-25% true solids by weight, and the settled solids contain approximately 33% true solids and 67% interstitial liquid. Although the settled solids contain more liquid than "true solids", the ratio of solid phase to liquid phase is much higher than in the other tanks that have been studied. Tanks AN-105, AN-104, and AW-101 averaged approximately 10% "true solids" in the settled solids, compared to 33% for AN-103.

The species that make up the true solids at 45 °C are as follows (with approximate weight percent of total solids): 54% $NaAl(OH)_4$, 22% $Na_2CO_3 \cdot H_2O$, 20% $NaNO_3$, 2% $Na_2C_2O_4$ (sodium oxalate), 1% Na-F-PO_4-SO_4 (combination of sodium fluoride, sodium phosphate, sodium sulfate, and various double salts), and <1% Other (oxides or hydrous oxides of Cr, Si, Ca, Fe, in order of abundance, plus several very minor metals). Sodium nitrite and chloride are not present in the solid phase, nor are any potassium salts.

At 40 volume percent dilution of the settled solids with water (40 mL water per 100 mL settled solids), nearly all of the aluminate and nitrate salts have dissolved, and the weight of true solids has fallen from 33 g to 7 g per 100 g undiluted settled solids. At 120 volume percent dilution, nearly all of the carbonate has also dissolved, and the weight of true solids is down to 1 g per 100 g. At this point the solids that remain are composed of almost 60% $Na_2C_2O_4$, 30% aluminum compounds (unspecified), and 10% Other (as defined above).

The fraction of the total sodium inventory in the tank that is retrievable in the supernatant liquid after gravity settling is approximately 43-48% at zero dilution. The retrievable fraction increases with dilution to approximately 95% retrievable at 125 volume percent dilution of the settled solids.

2.0 DESCRIPTION OF LABORATORY STUDIES

Most of the laboratory testing with actual tank 103-AN waste took place in the 1E-1 hotcell in the 222-S Laboratory. The procedures, volume/weight data, and observations are recorded in controlled laboratory notebook HNF-N-70-1, pages 80-123. The procedures are described in this section, and the raw data are shown in the following section (3.0).

2.1 PREPARATION OF WHOLE-TANK-COMPOSITE SAMPLES

The whole-tank-composite WTC samples were prepared in hotcell 11A-2 by personnel from the 222-S Laboratory Analytical Services organization. Instructions for preparation of the composite samples were provided in a Letter of Instruction from Lockheed Martin Hanford Corporation (see Appendix A in Jewett 1999).

To the extent possible, the hotcell operators used appropriate amounts (in proportion to respective amounts in the tank) of crust samples, drainable liquid samples, convective layer solids samples, and non-convective layer samples from tank 103-AN core samples (cores 166 and 167). The contents of each segment jar were mixed and transferred into four 500 mL WTC sample jars, dividing the contents of the segment jar evenly among the four WTC jars.

2.2 COOLING AND HEATING TESTS

WTC Jar T1 was stirred with a magnetic stirrer to homogenize the sample. Due to the thickness of the slurry, the large magnetic stirbar sat on top of the crust when it was added to the composite jar. It was necessary to heat the slurry to ~45 °C to initiate stirring. While the waste was stirring, 30 mL aliquots were removed from the WTC jar by drawing the waste into a 60 mL syringe with an orifice diameter of approximately 2 mm. The aliquots were dispensed from the syringe into tared 50 mL plastic screw-cap centrifuge cones labeled 3AN-1 through 3AN-4.

Cones 3AN-1 and 3AN-3 were placed in a metal heater block held at 65 °C (±3 °C). Cones 3AN-2 and 3AN-4 were placed in a rack held at ambient hotcell temperature (25 ±2 °C). Temperatures throughout the test were monitored with a thermocouple wire inserted through a hole in the cap of a 50 mL centrifuge cone containing water. The cone was kept in the same heater block as the samples undergoing the test.

Table 2-1. Tank 103-AN Core Samples Used in Composite Samples T1-T4
(page 1 of 2)

Core	Segment	Jar No.	Weight Used (grams)	Sample Description
166	1	11775	3[a]	Crust
167	1	11536	6[a]	
167	1	11785	11	
167	1	11786	13[a]	
167	2	11546	24	Drainable Liquid
166	3	11524	35[a]	
166	3	11413	3	
167	6	11525	38	
166	6	11537	30	
167	6	11569	36	
167	8	11534	23	
167	9	11560	39	
166	10	11528	30	
166	11	11539	30	
166	12	11558	28	
166	4	11616	5	Convective Layer Solids
167	5	11500	6	
167	6	11485	5	
167	7	11638	4	
166	7	11779	3	
167	9	11784	5	
166	9	11617	4	
166	10	11618	4	
166	11	11624	3	
166	12	11776	2	

[a] Composite jar T4 received significantly less weight than T1-T3 for these segments.

Table 2-1. Tank 103-AN Core Samples Used in Composite Samples T1-T4
(page 2 of 2)

Core	Segment	Jar No.	Weight Used (grams)	Sample Description
167	12U[b]	11503	14	Non-convective Layer
167	12L[b]	11502	14	
166	13U	11515	13[a]	
166	13L	11634	12	
167	14U	11504	14	
167	14L	11512	16	
166	15U	11508	12	
166	15L	11509	14	
166	15U	11396	11	
166	15L	11402	11	
167	15U	11790	17	
167	15L	11791	16	
167	15L	11527	6	
166	16U	11777	14	
166	16L	11778	13	
166	16U	11531	8[a]	
166	16L	11533	10	
166	17U	11510	11	
166	17L	11511	12	
167	17U	11622	16	
167	17L	11621	12	
166	18U	11635	14	
166	18L	11636	12	
166	18L	11553	8[a]	
166	19U	11781	12	
166	19L	11782	10	

[a] Composite jar T4 received significantly less weight than T1-T3 for these segments.
[b] U = upper half of segment; L = lower half of segment.

2.2.1 Cooling Test

After an equilibration period of approximately 90 hours at 65 °C, cones 3AN-1 and 3AN-3 were centrifuged in a heated centrifuge (approximately 65 °C). Volumes and weights of centrifuged solids and supernatant liquids were recorded. Supernatant liquids were decanted into clean cones labeled 3AN-1L and 3AN-3L. The liquid in cone 3AN-3L was diluted 20% by volume with warm (65 °C) water, and both cones (-1L and -3L) were returned to the heater block, where they remained overnight.

Beginning early the following morning (7:30 am), the temperature of the heater block was reduced slowly, about 5 °C per hour, while the liquid samples were observed for changes in appearance. Large crystals began to appear in cone 3AN-1L at 41 °C. The volume of crystals continued to grow steadily throughout the day. At 2:45 pm and 28 °C, there were roughly 4.5 mL of settled crystalline solids in the cone. At 8:30 am the next morning there were 7 mL of settled solids at 27 °C.

No solids formed in cone 3AN-3L by the time the samples had reached ambient temperature (28 °C) at 2:45 pm. Crystals had formed, though, by the following day, at which point the 22 mL sample contained approximately 1 mL of white crystalline solids. The solids from both cones were saved for examination by PLM.

The PLM analysis of the 3AN-1L solids (undiluted sample) showed that the solids were clearly dominated by $NaNO_3$ crystals (estimated 90% of solids). There were also some octahedral crystals of the fluoride phosphate double salt $Na_7F(PO_4)_2 \cdot 19H_2O$. In sample 3AN-3L, which was diluted 20% by volume, the same two phases were present, but the ratio of nitrate crystals to double salt crystals was closer to 50:50. Based on previous experience, it is likely that both samples contained about the same total amount of the fluoride phosphate double salt crystals, but the diluted sample contained much less sodium nitrate than the undiluted sample.

Because the 20%-diluted sample formed solids on cooling, the cooling test was repeated on liquid samples diluted 40% and 60% by volume (cones 3AN-5L and 3AN-6L, respectively). Neither cone formed any solids on cooling to 25 °C on the first day. Cone 3AN-5L contained a barely-visible trace of solids the following morning at 26 °C, but no attempt was made to identify the solids. No solids were present in cone 3AN-6L even after 5 days.

2.2.2 Heating Test

After an equilibration period of approximately 24 hours at ambient temperature, cones 3AN-2 and 3AN-4 were centrifuged. Volumes and weights of centrifuged solids and supernatant liquids were recorded. Supernatant liquids were decanted into clean

cones labeled 3AN-2L and 3AN-4L, which were placed in an ambient temperature heater block.

The liquid in cone 3AN-4L was diluted 20% by volume with ambient temperature water, and returned to the heater block. Cones 3AN-2L and 3AN-4L remained in the heater block overnight.

Beginning early the following morning (7:30 am), the temperature of the heater block was raised slowly, about 5 °C per hour, while the liquid samples were observed for changes in appearance. No solids formed in either cone by the time the samples had reached 63 °C at 2:30 pm. No solids had formed by 8:30 am the following morning, at which time the heater block was at 65 °C.

2.3 DILUTION TESTING, SETTLED SOLIDS SAMPLES, 45 °C

WTC Jar T1 or T2 was stirred with a magnetic stirrer to homogenize the sample. While the waste was stirring, 35-50 mL aliquots were transferred by the syringe method into tared 50 mL plastic centrifuge cones labeled 3AN-A through 3AN-H. Jar T1 was used for cones A-D. Jar T2 was used for cones E-H. All eight cones were placed in a heater block at 45 °C (±2 °C).

After the cones had been in the heater block for 6 days, the total sample volumes, settled solids volumes, and floating crust volumes were recorded. Cones E-H from Jar T2 had significantly more crust than cones A-D from Jar T1, implying that Jar T2 contained significantly more entrapped gas than Jar T1. That could be due to the prior mixing of Jar T1 for the heating and cooling tests.

The supernatant liquid was carefully decanted from each cone into a 250 mL jar labeled "103-AN Supernate" (see Section 2.3.1). The liquid was decanted by drawing off the liquid with a syringe to leave the floating crust in the cones. The settled solids, including the crust, were then diluted with warm water (45 °C) by the following volume percents:

cones A and B – 0% (no water added)
cones C and D – 39% and 40%, respectively
cones E and F – 71% and 76%, respectively
cones G and H – 118% and 125%, respectively

All eight cones were then mixed five times at thirty-minute intervals. The next day, all eight cones were mixed again three times at one hour intervals. For the next 7 days, the samples were allowed to settle undisturbed while the volume of settled solids was monitored and recorded.

After the settling period, all eight samples were centrifuged at 45 °C. The total sample volume and weight were determined for each cone. The supernatant liquid from

each cone was divided among three sub-samples: (1) one fraction poured into a 15 mL centrifuge cone to be kept in a 45 °C heater block for at least 30 days to monitor for possible precipitation of aluminum hydroxide; (2) one fraction into a sample vial for gravimetric percent water analysis; (3) the remainder into a sample vial for the following analyses:

IC (ion chromatography for anions)
ICP (inductively-coupled plasma spectroscopy for metals)
TIC/TOC (total inorganic carbon/total organic carbon)
OH^- (free hydroxide)
GEA (gamma energy analysis)
AT (total alpha)
^{90}Sr and ^{99}Tc

The cones were re-weighed to determine the weight of centrifuged solids remaining. The solids were then transferred to a sample vial (one vial for each cone) for the following analyses: TGA (thermogravimetric analysis for percent water); TIC/TOC; water digest for IC and OH^-; and acid digest for ICP, GEA, AT, ^{90}Sr, and ^{99}Tc.

To prevent precipitation of solids upon cooling from 45 °C to ambient temperature, the liquid samples for chemical analyses (liquid fraction #3 in the above list) were diluted with water. Dilutions were done by weight, and the density of the undiluted solution (as measured from the 15 mL centrifuge cone samples above) was used to calculate a volumetric dilution factor. The analytical data reported in Section 3 have been adjusted to account for this dilution, where appropriate.

The liquid samples held in the 15 mL cones at 45 °C for long-term observation did not, for the most part, form solids. The cones were observed after 19 days in the 45 °C heater block, just after the heater block failed and the samples began to cool. By the time the samples were examined for the presence of solids, the temperature had dropped to approximately 36 °C. At that point, cones A and B contained approximately 0.4 mL of light (off-white) solids, cones C-F contained a trace of off-white solids, and cones G and H were clear. The solids that were present were believed to have precipitated because of the cooling. There was no evidence of the formation of $Al(OH)_3$ precipitation caused by dilution.

2.3.1 Dilutions of Supernatant Liquid

Aliquots of WTC sample from mixed composite jar T3 were transferred to four 50 mL centrifuge cones labeled V1-1, V1-2, V3-1, and V3-2. The samples were allowed to settle at 45 °C for 2 weeks. The supernatant liquid fractions were then decanted from all four cones into a 125 mL jar labeled 3AN-V1. From there, the liquid was re-divided into six smaller (15 mL) centrifuge cones labeled 3AN-AA, -BB, -DD, -EE, -GG, and -HH. (The settled solids became viscosity samples V2 and V3 – see section 2.6.) Two of the supernatant liquid samples (–AA and –BB) were left undiluted. The samples in cones

–DD and –EE were diluted 10% by volume by adding 0.9 mL H_2O to each cone. Similarly, cones –GG and –HH were diluted 20% by volume with water.

Volumes and densities of samples in all six cones were recorded. Cones –AA, –DD, and –GG (0%, 10%, 20% dilution, respectively) were placed in a rack at ambient temperature. Cones –BB, –EE, and –HH (0%, 10%, 20% dilution) were placed in a heater block at 45 °C. (The analogous test planned for 65 °C was not completed due to limitations in the amount of sample available.) All of the cones were monitored for 10 days to watch for the formation of solids. Cones –AA, –BB, –DD, and –GG all formed significant amounts of solids, which were subsequently analyzed by PLM.

2.4 DILUTION TESTING, SETTLED SOLIDS SAMPLES, 25 °C AND 65 °C

The procedure for the dilution testing of the settled solids samples at 25 °C and 65 °C was the same as that described for the testing at 45 °C, except for the number of samples. Two (duplicate) samples –K and –L were tested at 65 °C, 80% dilution, and two (duplicate) samples –M and –N were tested at 25 °C, 80% dilution. (Actual dilution levels achieved were 66%, 77%, 91%, and 77% for cones K, L, M, and N, respectively.) The supernatant liquid analytical samples at 65 °C were diluted to keep solids from precipitating on cooling, as described in Section 2.3.

After 26 days, none of the liquid samples held for long term observation had formed significant solids. Samples –K and –L each contained approximately 2% by volume settled solids. Samples –M and –N each contained a barely discernable trace of solids.

2.5 DILUTION TESTING, WHOLE-TANK-COMPOSITE SAMPLES, 45 °C

WTC Jar T2 was stirred with a magnetic stirrer to homogenize the sample. While the waste was stirring, 30 mL aliquots were transferred by the syringe method into tared 50 mL plastic centrifuge cones labeled 3AN-0 and 3AN-50. Both cones were placed in a heater block at 45 °C (±2 °C).

After the cones had been in the heater block for 4 days, the total sample volumes, settled solids volumes, and floating crust volumes were recorded. The sample in cone 3AN-50 was then diluted with 15 mL warm water (45 °C), representing a dilution of 50% by volume. Both cones were mixed five times at one-hour intervals, then left to settle overnight. Then the cones were mixed again three times at one hour intervals. For the next 6 days, the samples were allowed to settle undisturbed while the volume of settled solids was monitored and recorded.

After the settling period, the samples were centrifuged at 45 °C. The total sample volume and weight were determined for each cone. The supernatant liquid from each cone was divided among three sub-samples, as described for the settled solids dilution

samples. The two liquid samples for chemical analysis were diluted with water to prevent precipitation of solids on cooling. The cones were re-weighed to determine the weight of centrifuged solids remaining. The solids were also sampled as described earlier.

2.6 RHEOLOGY TESTING

The following samples were prepared for viscosity measurements:

V1 – undiluted supernatant liquid at 45 °C from cones V1-1, V1-2, V3-1, V3-3 (see Section 2.3.1)
V2 – undiluted settled solids at 45 °C from cones V1-1 and V1-2
V3 – 80% dilution by volume of settled solids from cones V3-1 and V3-2
V4 – supernatant liquid fraction from sample V3
V5 – undiluted WTC sample from WTC Jar T3
V6 – 50% dilution by volume of WTC sample V5
V7 – supernatant liquid fraction of sample V6
V8 – 20% dilution by volume of sample V7

Viscosity measurements were made with a Haake Rotovisco® RV20 viscometer with a CV20 sensor system, as described in the Test Plan (Jewett 1999). Measurements were made at 25, 45, and 65 °C. Results were described in an internal memo, which is included here as Appendix A. Table 3-8 shows a summary of the results.

3.0 RESULTS – RAW DATA

"Raw data" are values actually recorded for weight and volume measurements and physical/chemical analyses. They are recorded here for documentation purposes. Sample-to-sample comparisons should not be made on raw data measurements because of differences in initial sample weights and volumes. Comparisons must be based on normalized data, accounting for initial volume and weight differences. The normalized data are presented in Section 4.

3.1 VOLUME AND WEIGHT MEASUREMENTS

Physical data measurements for WTC sample dilutions at 0% and 50% dilution are shown in Tables 3-1 and 3-2. Measurements for settled solids dilutions at 0% to 125% dilution, 45 °C, are shown in Tables 3-3 and 3-4. Corresponding data for the settled solids samples at 80% dilution, 25 °C and 65 °C, are shown in Tables 3-5 and 3-6. Dilution data for the supernatant liquid samples are shown in Table 3-7.

Table 3-1. Volume and Weight Measurements for WTC Sample Dilution Tests
(volumes in mL; weights in grams)
H_2O Diluent, 45 °C

Dilution (Volume percent) →	0%	50%
Initial sample weight	48.042	48.195
Initial sample volume	30.0	30.5
Wt (approx Vol) of water added	0	15.835
Actual Vol% Dilution	0	52
Diluted sample weight	48.042	64.030
Diluted sample volume	29.5	45.0
SSol[a] volume at 24 hours	17.5	9.5
CSol volume (approximate)	10.0	3.5
CLiq density (g/mL)	1.580	1.443
CSol weight	19.934	5.639

[a] SSol = settled solids; CSol = centrifuged solids; CLiq = centrifuged supernatant liquid

Table 3-2. Settled Solids Volumes (mL) After Dilution
WTC Samples, H_2O Diluent, 45 °C

Time, hr[a]	0% Dilution	50% Dilution
0 (total volume)	29.5	45.0
0.5	27.5	cloudy
1.0	27.5	cloudy
1.5	27.0	cloudy
2.0	26.0	cloudy
3.5	23.0	15.0
5	22.0	14.0
7	20.0	12.5
24	17.5	9.5
54	17.0	8.5
78	16.5	8.5
145	15.5	8.5

[a] time in hours after final mixing

Table 3-3. Volume and Weight Measurements for Settled Solids Dilution Tests
(volumes in mL; weights in grams)
H_2O diluent, 45 °C

Intended dilution (vol%) →	0%	40%	80%	120%
Cone label →	3AN-A 3AN-B	3AN-C 3AN-D	3AN-E 3AN-F	3AN-G 3AN-H
Initial weight of WTC sample	81.661 73.474	75.695 76.237	76.394 76.409	59.901 54.190
Initial volume of WTC sample	50.0 46.5	47.5 47.0	47.0 47.5	38.0 34.0
WTC density (g/mL)	1.63 1.57	1.59 1.62	1.63 1.61	1.58 1.59
Volume SSol+crust after 6 days (before decanting)	29.0 27.5	27.5 26.0	28.5 30.5	25.5 23.7
Volume SSol after decanting	28.5 27.0	27.5 27.0	28.5 29.5	24.0 23.0
Weight SSol after decanting	49.933 44.837	46.045 45.007	47.436 47.800	38.451 36.552
SSol density (g/mL)	1.75 1.66	1.67 1.67	1.66 1.62	1.60 1.59
Weight water added	0.000 0.000	10.655 10.782	20.161 22.448	28.428 28.717
Total diluted sample weight	49.933 44.837	56.700 55.789	67.597 70.248	66.879 65.269
Vol% dilution	0 0	39 40	71 76	118 125
Diluted sample volume	28.5 27.0	37.5 37.0	47.5 49.0	50.0 48.0
SSol volume at 97 hours	23.5 22.0	20.0 19.5	14.0 12.5	6.0 6.5
CSol volume	16.5 15.0	7.0 6.5	3.5 *	1.5 1.5
CLiq density (g/mL)	1.54 1.56	1.52 1.52	1.43 1.41	1.35 1.34
CSol weight	30.462 27.078	11.176 11.752	7.569 *	2.895 3.134

* Portion of Sample F lost due to spill before final volumes were recorded.

Table 3-4. Settled Solids Volumes (mL) After Dilution
H_2O Diluent, 45 °C

Dilution →	0%	0%	39%	40%
Time, hr[1]	3AN-A	3AN-B	3AN-C	3AN-D
0 (total volume)	28.5	27.0	37.5	37.0
1	28.0	26.5	35.0	34.5
2	28.0	26.0	33.0	32.5
3	27.5	25.5	32.0	30.0
5	27.0	25.0	27.0	26.0
7	26.5	24.5	25.0	23.5
97	23.5	22.0	20.0	19.5
145	22.5	21.0	18.5	18.0
Dilution →	71%	76%	118%	125%
Time, hr[1]	3AN-E	3AN-F	3AN-G	3AN-H
0 (total volume)	47.5	49.0	50.0	48.0
1	cloudy	cloudy	15.0	11.0
2	cloudy	cloudy	14.0	9.0
3	25.0	cloudy	12.5	8.0
5	22.5	23.5	10.0	7.0
7	20.5	23.0	9.0	7.0
97	14.0	12.5	6.0	6.5
145	12.5	11.5	5.0	5.5

[1] time in hours after final mixing

Table 3-5. Volume and Weight Measurements for Settled Solids Dilution Tests
(volumes in mL; weights in grams)
H_2O diluent, 65°C and 25 °C

Intended dilution (vol%) →	80%	80%	80%	80%
Temperature →	65 °C	65 °C	25 °C	25 °C
Cone label →	3AN-K	3AN-L	3AN-M	3AN-N
Initial weight of WTC sample	73.341	72.098	70.622	69.704
Initial volume of WTC sample	46.0	46.0	45.0	45.5
WTC density (g/mL)	1.59	1.57	1.57	1.53
Volume SSol+crust after 6 days (before decanting)	34.0	31.5	35.5	36.0
Volume SSol after decanting	27.5	20.5	25.0	26.5
Weight SSol after decanting	46.412	33.524	44.159	45.898
SSol density (g/mL)	1.69	1.64	1.77	1.73
Weight water added	19.233	17.531	22.762	20.391
Total diluted sample weight	65.645	51.055	66.921	66.289
Diluted sample wt after equil[1]	64.614	49.355	66.900	66.291
Vol% dilution before equil	70	86	91	77
Vol% dilution after equil	66	77	91	77
Diluted sample vol after equil	44.0	34.0	46.5	46.5
SSol volume at 24 hours	10.0	6.0	10.5	14.0
CSol volume (approximate)	2.5	1.5	3.0	3.0
CLiq density (g/mL)	1.446	1.425	1.423	1.426
CSol weight	4.936	2.039	4.226	4.753

[1] Samples at 65 °C lost a small amount of water due to evaporation during the equilibration period.

Table 3-6. Settled Solids Volumes (mL) After Dilution
H_2O Diluent, 65 °C and 25 °C

Time, hr[1]	66%	77%	91%	77%
	65 °C	65 °C	25 °C	25 °C
	3AN-K	3AN-L	3AN-M	3AN-N
0 (total volume)	46.0	37.0	47.0	46.5
1	cloudy	cloudy	cloudy	cloudy
2	cloudy	11.5	cloudy	cloudy
3.5	10.5	9.5	19.5	22.5
5	13.5	7.5	16.5	21.0
7	13.5	6.5	15.0	19.5
24	10.0	6.0	10.5	14.0
57	9.0	5.0	9.0	12.0
75	8.0	4.5	8.0	10.0
145	7.5	4.0	7.5	9.5

[1] time in hours after final mixing

Table 3-7. Dilution Volumes (mL) for Supernatant Liquid Samples

Temp		3AN-AA	3AN-DD	3AN-GG
25 °C	Vol Supernate	8.1	8.0	8.0
	Vol Water Added	0.0	0.79	2.08
	Vol% Dilution	0	10	26
		3AN-BB	3AN-EE	3AN-HH
45 °C	Vol Supernate	9.0	8.5	8.0
	Vol Water Added	0.0	1.19	2.08
	Vol% Dilution	0	14	26
		3AN-CC	3AN-FF	3AN-II
65 °C	Vol Supernate	insufficient sample		
	Vol Water Added			
	Vol% Dilution			

3.2 RHEOLOGY AND PARTICLE SIZE DISTRIBUTION

An internal memo was issued earlier this year with the results of the rheology measurements. The report is attached here as Appendix A. Results are summarized below. Particle size distribution measurements were not completed due to unresolved issues that developed with the procedure and equipment used for the analysis.

3.2.1 Rheology Results

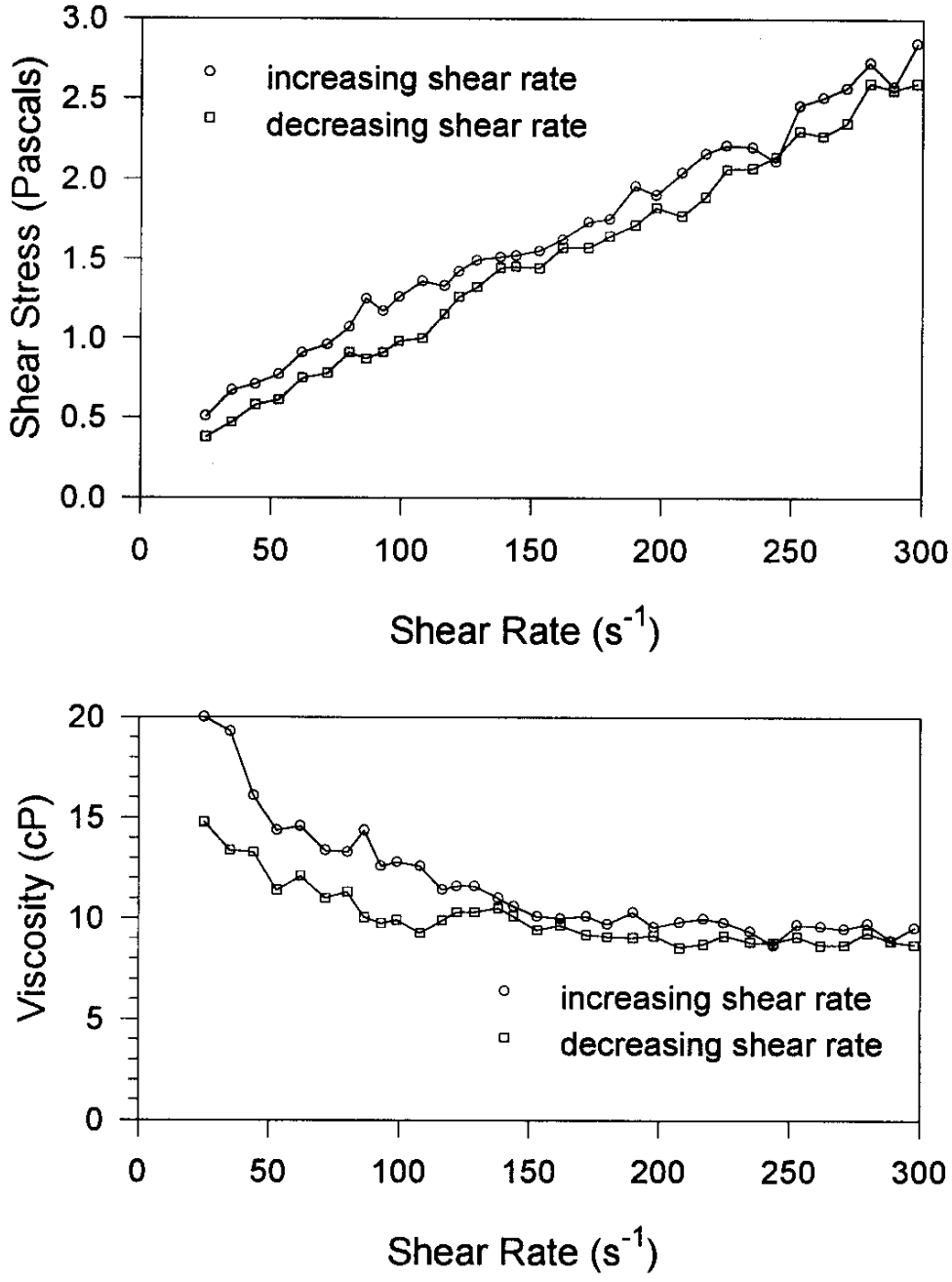
Preparation of the eight rheology samples was described in Section 2.6. All of the samples (with the possible exception of sample V2) showed essentially Newtonian behavior above shear rates of 100 s^{-1}, i.e., shear stress increased linearly with increasing shear rate, so the viscosity did not vary with shear rate. The instrument failed to measure the viscosity of sample V2.

Figure 3-1 shows graphs of shear stress vs. shear rate (top) and viscosity vs. shear rate (bottom) at 25 °C for the WTC sample diluted 50% by volume with water. Shear stress and viscosity graphs for the other samples are very similar in shape to the one shown here. Table 3-8 shows the viscosity measurement results for all samples.

Table 3-8. Viscosity Results for Rheology Samples.

Sample	Temperature (°C)	Mean Viscosity (cP)
V1 Undiluted Supernatant Liquid (separated at 45 °C)	ambient	27.4
	45	13.0
	65	7.6
V2 – Undiluted Settled Solids	ambient	failed
V3 Diluted Settled Solids (80% dilution by volume)	ambient	19.6
	45	10.8
	65	6.0
V4 Diluted Supernatant Liquid (from sample V3)	ambient	11.6
	45	6.7
	65	4.6
V5 Undiluted WTC	ambient	35.3
	45	20.3
	65	11.9
V6 Diluted WTC (50% dilution by volume)	ambient	9.4
	45	5.8
	65	4.0
V7 Diluted WTC Supernatant Liquid (liquid from sample V6)	ambient	8.8
	45	5.9
	65	4.0
V8 Diluted Supernatant Liquid (20% dilution of sample V6)	ambient	7.8
	45	5.4
	65	3.7

Figure 3-1. Shear Stress (top) and Viscosity (bottom) vs. Shear Rate
WTC Sample diluted 50% with water, 25 °C



3.3 CHEMICAL ANALYSES

Chemical analysis results are shown in Tables 3-9 through 3-13. Some of the analytical values that were reported were unrealistic, i.e., they were not consistent with the clear and expected trends established by the preponderance of the data. Those values are included in the tables, but are designated by placing the values inside parentheses ( ).

Mass balance and charge balance calculations can be done on the supernatant liquid fractions, because all of the known components of the liquid were analyzed. The formulas used for these calculations are:

$$\text{Mass Balance} = \%H_2O + (\Sigma_i C_i + 3C_{TOC} + 5C_{TIC} + 2.2C_{Al})/(10{,}000 \times \text{Density})$$

where the C_i values are concentrations expressed in μg/mL as shown in Tables 3-9 through 3-13; Density is in g/mL; and i = OH^-, Cr, K, Na, F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}. The TOC concentration is multiplied by 3 to account for the mass of oxygen, nitrogen, and hydrogen associated with the carbon in typical organic complexants. This is an approximate factor. For the centrifuged solids samples in which virtually all of the TOC comes from oxalate, the oxalate concentration is used instead of the TOC in the mass balance calculation. The TIC concentration is multiplied by 5 and the Al concentration is multiplied by 2.2 to account for the mass of oxygen in carbonate and aluminate (AlO_2^-), respectively. These are exact factors. The aluminate is used as the anhydrous AlO_2^- rather than the hydrated $Al(OH)_4^-$ because the hydration water is included in the $\%H_2O$ factor.

$$\text{Charge Balance (cation/anion)} = \Sigma_+(C_+/W_+)/\Sigma_-(C_-Z_-/W_-)$$

where the C_+ values are the concentrations of Na and K in μg/mL (Tables 3-9 through 3-13); W_+ are the respective atomic weights; C_- are the concentrations of anionic species (OH^-, TOC, TIC, Al, F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}); Z_- are the charges on the respective anions; and W_- are the formula weights of the anions. The Z_- for TOC is taken to be 0.5, assuming a typical mixture of organic compounds in solution that have an average of two carbon atoms per negative charge (e.g., acetate). The Z_- for TIC is 2. Aluminum is assumed to be present as aluminate ion, $Al(OH)_4^-$, but 27 is used as the formula weight because the concentration is expressed in the tables as Al, not $Al(OH)_4^-$.

Mass balance values should be (and generally are, where the data are reliable) near 100%. Charge balance values should be near 1.00, but are typically lower than that (averaging approximately 0.95) for reasons that the author does not yet understand. The same trend was observed for the 105-AN, 104-AN, and 101-AW samples in previous tests (Herting 1997, 1998, and 1999).

Table 3-9. Chemical Analysis Results, WTC Samples, 45 °C
(page 1 of 2)

	Supernatant Liquid			Centrifuged Solids		
Dil'n, Vol%:	0	50		0	50	
Sample ID:	3AN-0	3AN-50	units	3AN-0	3AN-50	units
Density	1.580	1.443	g/mL			g/mL
%H_2O	(47.1)	52.1	wt%	26.8	44.0	wt%
OH^-	92,400	49,100	µg/mL	32,000	31,700	µg/g
TOC	2,610	1,570	µg/mL	2,990	7,120	µg/g
TIC	924	3,700	µg/mL	8,830	10,700	µg/g
Ag	22	13	µg/mL	13	14	µg/g
Al	43,900	45,200	µg/mL	70,900	35,200	µg/g
As	< 110	< 80	µg/mL	< 100	< 50	µg/g
B	59	< 40	µg/mL	< 50	54	µg/g
Ba	< 55	< 40	µg/mL	< 50	< 25	µg/g
Be	< 6	< 4	µg/mL	< 5	< 3	µg/g
Bi	< 110	< 80	µg/mL	< 100	< 50	µg/g
Ca	< 110	< 80	µg/mL	280	1,020	µg/g
Cd	< 6	< 4	µg/mL	< 50	40	µg/g
Ce	< 110	< 80	µg/mL	< 100	< 50	µg/g
Co	< 22	< 16	µg/mL	< 20	< 10	µg/g
Cr	338	153	µg/mL	844	3,240	µg/g
Cu	< 11	< 8	µg/mL	< 10	< 5	µg/g
Fe	< 55	< 40	µg/mL	180	751	µg/g
K	17,100	9,020	µg/mL	6,130	5,580	µg/g
La	< 55	< 40	µg/mL	< 50	< 25	µg/g
Li	44	< 8	µg/mL	27	124	µg/g
Mg	< 110	< 80	µg/mL	< 100	< 50	µg/g
Mn	< 11	< 8	µg/mL	< 10	39	µg/g
Mo	118	61	µg/mL	< 50	40	µg/g
Na	318,000	209,000	µg/mL	228,000	186,000	µg/g
Nd	< 110	< 80	µg/mL	< 100	< 50	µg/g
Ni	< 22	< 16	µg/mL	24	109	µg/g
P	783	452	µg/mL	413	425	µg/g
Pb	114	< 80	µg/mL	< 100	71	µg/g
S	452	570	µg/mL	1,420	2,290	µg/g
Sb	< 66	< 48	µg/mL	< 60	< 30	µg/g
Se	< 110	< 80	µg/mL	< 100	< 50	µg/g
Si	505	336	µg/mL	872	537	µg/g

(continued on next page)

Table 3-9, continued
(page 2 of 2)

	Supernatant Liquid			Centrifuged Solids		
Dil'n, Vol%:	0	50		0	50	
Sample ID:	3AN-0	3AN-50	units	3AN-0	3AN-50	units
Sm	< 110	< 80	µg/mL	< 100	< 50	µg/g
Sr	< 11	< 8	µg/mL	< 10	< 5	µg/g
Ti	< 11	< 8	µg/mL	< 10	< 5	µg/g
Tl	< 220	< 160	µg/mL	< 200	< 100	µg/g
U	< 550	< 400	µg/mL	< 500	293	µg/g
V	< 55	< 40	µg/mL	< 50	< 25	µg/g
Zn	17	9	µg/mL	20	34	µg/g
Zr	< 11	< 8	µg/mL	< 10	16	µg/g
F^-	781	528	µg/mL	810	1,230	µg/g
Cl^-	10,500	6,040	µg/mL	3,490	3,110	µg/g
NO_2^-	174,000	98,100	µg/mL	58,600	52,700	µg/g
NO_3^-	213,000	165,000	µg/mL	169,000	83,900	µg/g
PO_4^{3-}	2,390	1,360	µg/mL	1,310	< 900	µg/g
SO_4^{2-}	< 1,050	1,070	µg/mL	3,470	5,830	µg/g
Oxalate	< 800	< 580	µCi/mL	6,170	22,300	µg/g
AT	< 0.009	< 0.007	µCi/mL	< 0.009	< 0.033	µCi/g
$^{89/90}Sr$	0.007	0.011	µCi/mL	4.77	16.6	µCi/g
^{99}Tc	0.18	0.077	µCi/mL	0.26	0.90	µCi/g
^{137}Cs	676	397	µCi/mL	250	290	µCi/g
^{60}Co	< 0.016	< 0.012	µCi/mL	< 0.132	< 0.120	µCi/g
^{154}Eu	< 0.055	< 0.040	µCi/mL	< 0.395	< 0.424	µCi/g
^{155}Eu	< 0.206	< 0.134	µCi/mL	< 0.354	< 0.384	µCi/g
^{241}Am by GEA	< 0.175	< 0.115	µCi/mL	< 0.326	< 0.342	µCi/g
Mass Bal	106.5	98.0	wt%	98.2	97.6	wt%
Charge Bal	0.95	0.90	--	0.98	0.99	--

(end of Table 3-9)

Table 3-10. Chemical Analysis Results, Supernatant Liquid Samples, Settled Solids Sample Dilutions, 45 °C. (page 1 of 2)
results adjusted for dilution required to prevent precipitation of solids on cooling
(units in µg/mL except as noted)

Sample >	3AN-A	3AN-B	3AN-C	3AN-D	3AN-E	3AN-F	3AN-G	3AN-H
Vol% >	0	0	39	40	71	76	118	125
density[a]	1.54	1.56	1.52	1.52	1.43	1.41	1.35	1.34
%H_2O[b]	40.2	40.7	44.7	45.3	52.7	53.1	61.4	62.2
OH^-	97700	105000	53700	54400	44200	39800	33100	33400
TOC	2650	2660	1560	1540	1320	1320	1120	1150
TIC	932	989	1780	1900	5160	6220	4770	4540
Ag	28	34	21	25	18	17	16	14
Al	38200	38000	75600	77900	49600	49100	37700	39200
As	< 112	< 124	< 92	< 90	< 71	< 57	< 64	< 64
B	67	62	< 46	< 45	< 36	< 29	< 32	< 32
Ba	< 56	< 62	< 46	< 45	< 36	< 29	< 32	< 32
Be	< 6	< 6	< 5	< 4	< 4	< 3	< 3	< 3
Bi	< 112	< 124	< 92	< 90	< 71	< 57	< 64	< 64
Ca	< 112	< 124	< 92	< 90	< 71	< 57	< 64	< 64
Cd	< 6	< 6	< 5	< 4	< 4	< 3	< 3	< 3
Ce	< 112	< 124	< 92	< 90	< 71	< 57	< 64	< 64
Co	< 22	< 25	< 18	< 18	< 14	< 11	< 13	< 13
Cr	359	370	189	186	127	122	95	103
Cu	< 11	< 12	< 9	< 9	< 7	< 6	< 6	< 6
Fe	< 56	< 62	< 46	< 45	< 36	< 29	< 32	< 32
K	19000	18000	9780	9830	7920	7610	5890	6330
La	< 56	< 62	< 46	< 45	< 36	< 29	< 32	< 32
Li	73	75	< 9	< 9	< 7	< 6	< 6	< 6
Mg	< 112	< 124	< 92	< 90	< 71	< 57	< 64	< 64
Mn	< 11	< 12	< 9	< 9	< 7	< 6	< 6	< 6
Mo	115	118	65	63	50	50	40	42
Na	328000	320000	261000	262000	209000	210000	162000	170000
Nd	< 112	< 124	< 92	< 90	< 71	< 57	< 64	< 64
Ni	< 22	< 25	< 18	< 18	< 14	< 11	< 13	< 13
P	943	930	514	513	453	459	364	390
Pb	154	190	101	96	82	72	69	< 64
S	483	498	459	477	753	841	741	750
Sb	< 67	< 75	< 55	< 54	< 43	< 34	< 39	< 39
Se	< 112	< 124	< 92	< 90	< 71	< 57	< 64	< 64
Si	500	563	457	457	326	316	270	268
Sm	< 112	< 124	< 92	< 90	< 71	< 57	< 64	< 64
Sr	< 11	< 12	< 9	< 9	< 7	< 6	< 6	< 6

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Table 3-10, continued
(page 2 of 2)

Sample >	3AN-A	3AN-B	3AN-C	3AN-D	3AN-E	3AN-F	3AN-G	3AN-H
Vol% >	0	0	39	40	71	76	118	125
Ti	< 11	< 12	< 9	< 9	< 7	< 6	< 6	< 6
Tl	< 225	< 250	< 180	< 180	< 140	< 110	< 130	< 130
U	< 560	< 620	< 460	< 450	< 360	< 290	< 320	< 320
V	< 56	< 62	< 46	< 45	< 36	< 29	< 32	< 32
Zn	31	44	16	13	11	9	8	8
Zr	< 11	< 12	< 9	< 9	< 7	< 6	< 6	< 6
F^-	733	650	231	410	211	552	500	493
Cl^-	10800	10600	5540	5780	4620	4230	3500	3400
NO_2^-	173000	173000	89200	93400	74700	69900	57100	56400
NO_3^-	216000	214000	209000	221000	173000	156000	127000	122000
PO_4^{3-}	2330	2050	1210	1680	(< 453)	1050	807	729
SO_4^{2-}	< 820	< 910	< 680	732	1870	1970	1960	1800
Oxalate	< 630	< 690	< 510	< 500	< 400	< 320	542	610
AT[c]	< 0.008	(0.011)	< 0.005	< 0.009	< 0.006	< 0.005	< 0.004	< 0.007
$^{89/90}Sr$[c]	0.009	(0.021)	0.007	0.007	0.018	0.019	0.014	0.014
^{99}Tc[c]	0.17	0.19	0.09	0.09	0.06	0.06	0.05	0.05
^{137}Cs[c]	705	697	392	392	312	303	242	239
^{60}Co[c]	< 0.017	< 0.020	< 0.005	< 0.005	< 0.003	< 0.003	< 0.003	< 0.003
^{154}Eu[c]	< 0.058	< 0.064	< 0.016	< 0.014	< 0.011	< 0.010	< 0.011	< 0.011
^{155}Eu[c]	< 0.67	< 0.70	< 0.19	< 0.19	< 0.15	< 0.13	< 0.13	< 0.12
^{241}Am[c]	< 1.6	< 1.7	< 0.45	< 0.44	< 0.35	< 0.31	< 0.30	< 0.29
MassBal[d]	101.6	101.1	98.2	100.4	98.4	98.0	98.5	100.1
ChgBal[e]	0.98	0.93	0.97	0.94	0.93	0.98	0.94	1.00

[a] density in g/mL
[b] $\%H_2O$ in weight percent
[c] radionuclides in μCi/mL
[d] mass balance in weight percent
[e] charge balance in cation/anion equivalent ratio (unitless)

Table 3-11. Chemical Analysis Results, Centrifuged Solids Samples, Settled Solids Sample Dilutions, 45 °C. (page 1 of 2)
(units in μg/g except as noted)

Sample >	3AN-A	3AN-B	3AN-C	3AN-D	3AN-E	3AN-F	3AN-G/H[a]
Vol% >	0	0	39	40	71	76	~ 120
%H_2O[b]	31.9	29.6	42.4	37.7	49.1	47.2	56.6
OH^-	33300	28500	23100	24900	24600	25800	23600
TOC	4790	4180	6970	7060	8930	12800	12000
TIC	13300	12800	24900	24300	13600	5990	3580
Ag	14	15	16	16	14	15	14
Al	72600	83400	36400	380000	33000	37100	37400
As	< 60	< 60	< 60	< 60	< 60	< 60	< 60
B	< 280	75	104	86	89	92	100
Ba	< 30	< 30	< 30	< 30	< 30	< 30	38
Be	< 3	< 3	< 3	< 3	< 3	< 3	< 3
Bi	< 60	< 60	< 60	< 60	< 60	< 60	< 60
Ca	300	305	693	622	1050	1570	2100
Cd	9	10	23	22	38	61	84
Ce	< 60	< 60	< 60	< 60	< 60	< 60	< 60
Co	< 12	< 12	< 12	< 12	< 12	< 12	14
Cr	1000	1060	2020	1870	3220	5230	6990
Cu	< 6	< 6	< 6	< 6	< 6	6	11
Fe	143	162	362	350	586	926	1200
K	5160	5490	3970	4240	4020	4140	3870
La	< 30	< 30	< 30	< 30	< 30	< 30	< 30
Li	26	28	66	78	149	275	380
Mg	< 60	< 60	< 60	< 60	62	100	148
Mn	12	12	25	23	39	63	84
Mo	36	40	31	29	31	31	< 30
Na	195000	214000	205000	198000	170000	154000	138000
Nd	< 60	< 60	< 60	< 60	< 60	< 60	< 60
Ni	39	37	75	70	116	188	249
P	379	391	317	304	325	414	265
Pb	< 60	65	< 60	< 55	81	99	171
S	1510	1700	2930	2650	2000	1730	480
Sb	< 34	< 36	< 36	< 36	< 36	< 36	39
Se	< 56	< 60	< 60	< 60	< 60	< 60	< 60
Si	1040	1190	2040	1970	2790	3730	4210
Sm	< 56	< 60	< 60	< 60	< 60	< 60	< 60
Sr	< 6	< 6	< 6	< 6	< 6	7	10

(continued on next page)

Table 3-11, continued
(page 2 of 2)

Sample >	3AN-B	3AN-A	3AN-C	3AN-D	3AN-E	3AN-F	3AN-G/H
Vol% >	0	0	39	40	71	76	~ 120
Ti	< 6	< 6	< 6	< 6	< 6	8	9
Tl	< 120	< 120	< 120	< 120	< 120	< 120	< 120
U	< 300	< 300	< 300	< 300	< 300	443	565
V	< 30	< 30	< 30	< 30	< 30	< 30	< 30
Zn	< 56	< 6	15	14	33	58	108
Zr	6	< 6	9	9	15	25	34
F^-	721	640	2460	2340	1110	990	263
Cl^-	3780	3110	2600	2740	2640	2490	2370
NO_2^-	62200	50600	42900	44700	44100	40900	39200
NO_3^-	(76300)	147000	106000	108000	101000	97900	88300
PO_4^{3-}	< 500	< 500	< 500	< 500	< 500	< 500	< 500
SO_4^{2-}	4940	4140	8660	8640	6190	4980	1360
Oxalate	10100	7740	19500	18600	29300	45200	55800
AT[c]	< 0.014	< 0.015	< 0.017	< 0.018	< 0.026	0.021	0.035
$^{89/90}Sr$[c]	5.4	5.8	12.5	11.4	19.1	29.8	40.2
^{99}Tc[c]	0.31	0.32	0.56	0.52	0.92	1.46	1.74
^{137}Cs[c]	244	256	226	224	248	305	319
^{60}Co[c]	< 0.011	< 0.012	< 0.013	< 0.012	< 0.018	< 0.027	< 0.055
^{154}Eu[c]	< 0.034	< 0.036	< 0.035	< 0.033	< 0.034	< 0.071	< 0.068
^{155}Eu[c]	< 0.083	< 0.086	< 0.081	< 0.078	< 0.085	< 0.136	< 0.140
^{241}Am[c]	< 0.076	< 0.080	< 0.075	< 0.073	< 0.078	< 0.125	< 0.130
MassBal[d]	94.0	100.9	105.2	100.3	103.0	98.3	104.8
ChgBal[e]	0.87	0.88	0.87	0.84	0.89	0.90	0.87

[a] solids from samples G and H combined.
[b] $\%H_2O$ in weight percent
[c] radionuclides in μCi/g
[d] mass balance in weight percent
[e] charge balance in cation/anion equivalent ratio (unitless)

Table 3-12. Chemical Analysis Results, Supernatant Liquid Samples, Settled Solids Sample Dilutions, 25 and 65 °C. (page 1 of 2)
(units in µg/mL except as noted)

	SSol Dilution at 65 °C		SSol Dilution at 25 °C	
	3AN-K	3AN-L	3AN-M	3AN-N
	66%	77%	91%	77%
density[a]	1.446	1.425	1.472	1.514
$\%H_2O$[b]	52.3	54.3	54.8	53.9
OH^-	42400	40600	37500	38400
TOC	1420	1370	1270	1290
TIC	4600	5690	5020	5080
Ag	17	18	15	16
Al	55400	50800	49300	48200
As	< 72	< 97	< 60	< 60
B	< 36	< 49	< 30	< 30
Ba	< 36	< 49	< 30	< 30
Be	< 4	< 5	< 3	< 3
Bi	< 72	< 97	< 60	< 60
Ca	< 72	< 97	< 60	< 60
Cd	< 4	< 5	< 3	< 3
Ce	< 72	< 97	< 60	< 60
Co	< 14	< 19	< 12	< 12
Cr	226	197	72	76
Cu	< 7	< 10	< 6	< 6
Fe	< 36	< 49	< 30	< 30
K	9380	7840	7930	7990
La	< 36	< 49	< 30	< 30
Li	< 7	< 10	< 6	< 6
Mg	< 72	< 97	< 60	< 60
Mn	< 7	< 10	< 6	< 6
Mo	57	49	49	51
Na	246000	212000	229000	217000
Nd	< 72	< 97	< 60	< 60
Ni	< 14	< 19	< 12	< 12
P	373	430	255	201
Pb	< 72	< 97	< 60	< 60
S	803	814	807	719
Sb	< 43	< 58	< 36	< 36
Se	< 72	< 97	< 60	< 60
Si	278	252	334	346
Sm	< 72	< 97	< 60	< 60
Sr	< 7	< 10	< 6	< 6

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Table 3-12, continued
(page 2 of 2)

	SSol Dilution at 65 °C		SSol Dilution at 25 °C	
	3AN-K	3AN-L	3AN-M	3AN-N
	66%	77%	91%	77%
Ti	< 7	< 10	< 6	< 6
Tl	< 140	< 190	< 120	< 120
U	< 360	< 480	< 300	< 300
V	< 36	< 49	< 30	< 30
Zn	10	13	8	6
Zr	< 7	< 10	< 6	< 6
F^-	587	675	459	512
Cl^-	4840	4580	4070	4840
NO_2^-	79800	74100	76100	93300
NO_3^-	187000	162000	176000	181000
PO_4^{3-}	1700	1430	< 500	< 500
SO_4^{2-}	1640	1680	1470	1520
Oxalate	< 500	< 700	< 400	< 400
AT[c]	< 0.006	< 0.003	< 0.005	< 0.005
$^{89/90}Sr$[c]	0.034	0.042	0.012	0.013
^{99}Tc[c]	0.102	0.099	0.058	0.059
^{137}Cs[c]	339	302	289	310
^{60}Co[c]	< 0.011	< 0.015	< 0.009	< 0.008
^{154}Eu[c]	< 0.032	< 0.047	< 0.028	< 0.029
^{155}Eu[c]	< 0.119	< 0.131	< 0.100	< 0.100
^{241}Am[c]	< 0.100	< 0.111	< 0.085	< 0.087
MassBal[d]	102.2	99.9	100.4	98.9
ChgBal[e]	1.05	0.97	1.05	0.95

[a] density in g/mL
[b] $\%H_2O$ in weight percent
[c] radionuclides in μCi/mL
[d] mass balance in weight percent
[e] charge balance in cation/anion equivalent ratio (unitless)

Table 3-13. Chemical Analysis Results, Centrifuged Solids Samples, Settled Solids Sample Dilutions, 25 and 65 °C. (page 1 of 2)
(units in µg/g except as noted)

	SSol Dilution at 65 °C	SSol Dilution at 25 °C
	3AN-K/L[a]	3AN-M/N[a]
	~ 70%	~80%
$\%H_2O$[b]	36.8	45.1
OH^-	25000	25700
TOC	9450	6890
TIC	11800	3470
Ag	17	13
Al	40700	38600
As	< 50	< 50
B	63	58
Ba	< 25	< 25
Be	< 3	< 3
Bi	< 50	< 50
Ca	1470	1380
Cd	55	54
Ce	< 50	< 50
Co	< 10	< 10
Cr	4200	4830
Cu	6	8
Fe	969	1070
K	4940	4750
La	< 25	< 25
Li	79	243
Mg	66	71
Mn	60	54
Mo	34	34
Na	214000	166000
Nd	< 50	< 50
Ni	176	151
P	351	3340
Pb	79	105
S	1700	968
Sb	< 30	34
Se	< 50	< 50
Si	611	536
Sm	< 50	< 50
Sr	6	6

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Table 3-13, continued
(page 2 of 2)

	SSol Dilution at 65 °C	SSol Dilution at 25 °C
	3AN-K/L[a]	3AN-M/N[a]
	~ 70%	~80%
Ti	6	5
Tl	< 100	< 100
U	444	417
V	< 25	< 25
Zn	45	62
Zr	24	22
F^-	948	1910
Cl^-	2660	2500
NO_2^-	45700	47700
NO_3^-	102000	103000
PO_4^{3-}	< 912	9980
SO_4^{2-}	4570	2630
Oxalate	35000	34400
AT[c]	< 0.003	0.018
$^{89/90}Sr$[c]	25.7	21.9
^{99}Tc[c]	1.05	1.15
^{137}Cs[c]	304	260
^{60}Co[c]	< 0.13	< 0.14
^{154}Eu[c]	< 0.43	< 0.46
^{155}Eu[c]	< 0.40	< 0.38
^{241}Am[c]	< 0.36	< 0.34
MassBal[d]	96.8	96.8
ChgBal[e]	1.09	0.97

[a] solids from samples 3AN-K and 3AN-L combined.
[b] $\%H_2O$ in weight percent
[c] radionuclides in μCi/g
[d] mass balance in weight percent
[e] charge balance in cation/anion equivalent ratio (unitless)

4.0 DILUTION RESULTS, VOLUME AND WEIGHT MEASUREMENTS

All results quoted in this section have been "normalized" to a common basis for comparison. The common basis is defined in each sub-section as appropriate.

4.1 WHOLE-TANK-COMPOSITE SAMPLE DILUTIONS

Two dilution tests (0% and 50% dilution, 45 °C) were done with WTC samples to represent the dilution scenario in which mixer pumps are used to homogenize the tank waste before any diluent is added. These two tests duplicate tests done earlier on samples from tanks 241-AN-104 (Herting 1998), 241-AN-105 (Herting 1997), and 241-AW-101 (Herting 1999).

Measurements of the volume of settled solids as a function of time were made on both samples (see section 3.1). The raw data can be normalized by using the diluted sample volume (settled solids plus supernatant liquid) as a common basis, i.e., each raw data value is divided by the diluted sample volume. The result is expressed as a volume percent settled solids.

Table 4-1 shows the volume percent settled solids measurements at 24 hours after mixing for the two WTC samples. The table also shows all of the other volume/weight measurements for the two tests. The "True Wt% Solids" data indicate that roughly 90% of solids present at 0% dilution are dissolved at 50% dilution, though the solids at 50% dilution retain much more interstitial liquid than the solids at 0% dilution (based on the "Wt% CSol" data).

Table 4-1. WTC Solids Volume and Weight Measurements[1] at 45 °C

Dilution, Vol% →	0%	50%
Vol% Settled Solids at 24 hr	59	21
Vol% CSol	34	8
Wt% CSol	41.5	8.8
Wt% CSol relative to undiluted sample	41.5	11.7
True Wt% Solids	25	1.8
True Wt% Solids relative to undiluted sample	25	2.4

[1] relative to diluted sample weight or volume, except as noted

4.1.1 True Weight Percent Solids

True weight percent solids is defined as 100 times the weight of actual solid phase material present in the sample divided by the total sample weight. It is not possible to measure the true weight percent solids directly, because perfect solid/liquid separations are not possible by any laboratory technique. Some liquid inevitably adheres to the solid particles or is held by capillary forces between the particles. Measurement of percent moisture does not give true solids directly by difference, because the water responsible for the weight loss contains dissolved salts which precipitate as the sample is dried.

There are two ways to determine the true weight percent solids. Both are indirect methods. One method is to measure the moisture content of both the centrifuged solids and the centrifuged liquid. Then, if the assumption is made that the true solids do not contain hydrated crystals that lose water at the drying temperature, it is possible to calculate the weight percent true solids by the following formula, where wt = weight in grams, cs = centrifuged solid, and liq = liquid:

$$\text{wt\% true solid} = 100\times[(\text{wt cs}) - (\text{wt cs})\times(\%H_2O_{cs}/\%H_2O_{liq})]/\text{total sample wt}$$

For the three tank wastes tested previously (104-AN, 105-AN, and 101-AW), this assumption was close to being true. In the current study, however, the data clearly show that the assumption is not valid, as a large fraction of the solids are hydrated crystals, mainly sodium aluminate, $NaAl(OH)_4$ or $NaAlO_2 \cdot 2H_2O$.

The second method for measuring the true weight percent solids, which is based on chemical analyses, is described in the Solid Phase Analysis Section 6. Results are shown in Tables 6-1 through 6-3, as well as in Table 4-1.

4.2 SETTLED SOLIDS SAMPLE DILUTIONS

The settled solids sample dilution tests were designed to model the dilution behavior of the tank waste if the supernatant liquid is removed from the tank before diluent is added. Dilutions (0% to 125% by volume) in these tests refer to the volume of diluent added relative to the volume of settled solids remaining after decanting the supernatant liquid from the settled WTC samples.

Measurements of settled solids volumes following dilution were made after 97 hours of settling for all samples. The raw data can be normalized by using total sample volume (settled solids plus diluent) as a common basis, i.e., each "raw data" settled solids volume is divided by the total sample volume. The result is expressed as a volume percent settled solids.

Table 4-2 shows a listing of all of the volume percent settled solids measurements at 97 hours after mixing. The table also shows other volume/weight measurements for the Settled Solids sample tests. Some of these data are plotted in Figure 4-1.

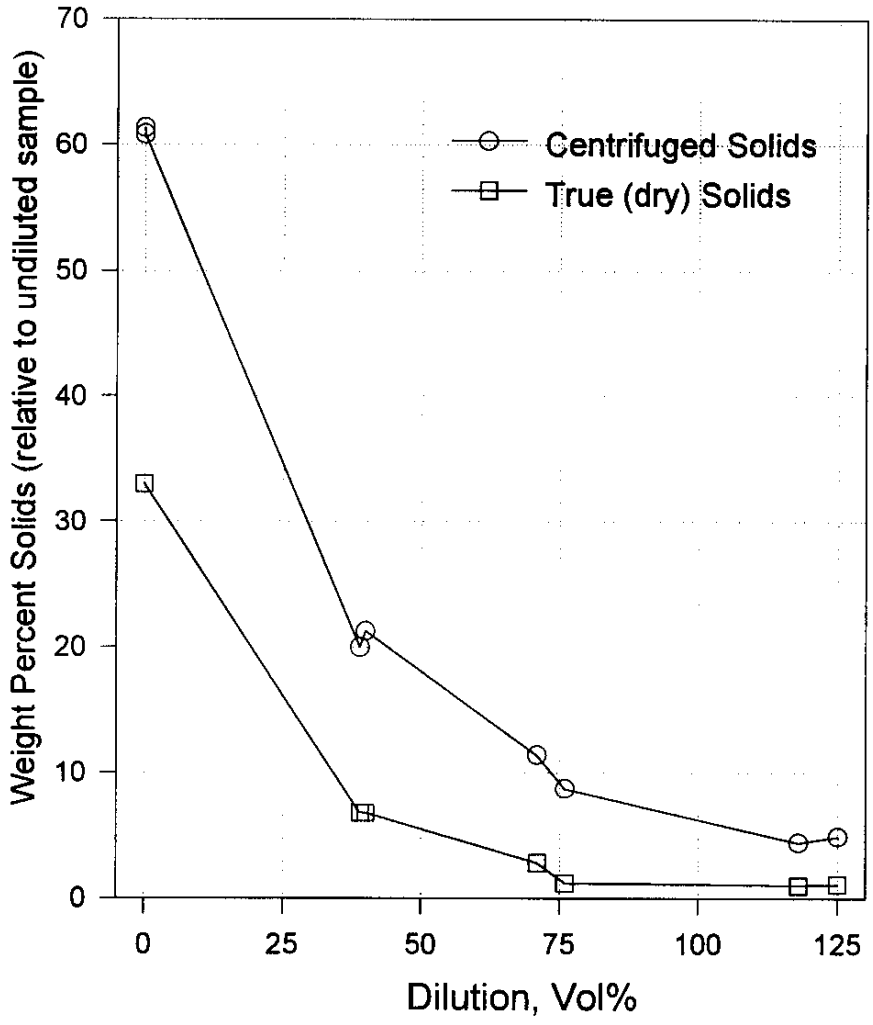
Temperature appears to have a predictable effect on the weight of centrifuged solids (see Table 4-2), though the effect is very small compared to the effect of dilution.

Table 4-2. Settled Solids Samples Volume and Weight Measurements[a] (at 45 °C except as noted)

Dilution, Vol% →	0%	0%	39%	40%	71%	76%
Vol% SSol at 97 hr	82	81	53	53	29	26
Vol% Csol	57	56	19	18	8	6
Wt% Csol	61.3	60.8	20.0	21.3	11.4	8.7
Wt% Csol relative to undiluted sample	61.3	60.8	24.3	26.1	16.0	*
True Wt% Solids	(25)	33	5.6	5.6	2.0	0.9
True Wt% Solids relative to undiluted sample	(25)	33	6.8	6.8	2.8	1.2
Dilution, Vol% →	66% 65 °C	77% 65 °C	77% 25 °C	91% 25 °C	118%	125%
Vol% SSol at 97 hr	17	12	22	17	12	14
Vol% Csol	6	4	6	6	3	3
Wt% Csol	7.7	4.1	7.2	6.3	4.4	4.9
Wt% Csol relative to undiluted sample	10.7	6.1	10.4	9.6	7.5	8.6
True Wt% Solids	1.6	0.9	1.0	0.6	0.6	0.6
True Wt% Solids relative to undiluted sample	2.3	1.3	1.5	1.0	1.0	1.1

[a] relative to diluted sample weight or volume, except as noted

Figure 4-1. Wt% Solids, Settled Solids Sample Dilutions at 45 °C



5.0 CHEMICAL COMPOSITION TRENDS

Gross sample behavior with dilution (i.e., volume of solids, viscosity) can be understood in terms of what happens to individual sample components. Most of the trends described in the following sections can be observed in Tables 3-9 through 3-13.

The behaviors of individual components can be grouped into four categories here for the purposes of discussions. The four categories can be defined as:

Category I: components that are present in the liquid phase below their saturation limits at zero dilution.

Category II: components that are virtually insoluble in the supernatant liquid at all dilution levels.

Category III: components that are relatively soluble, but have excess undissolved material in the solid phase at zero dilution.

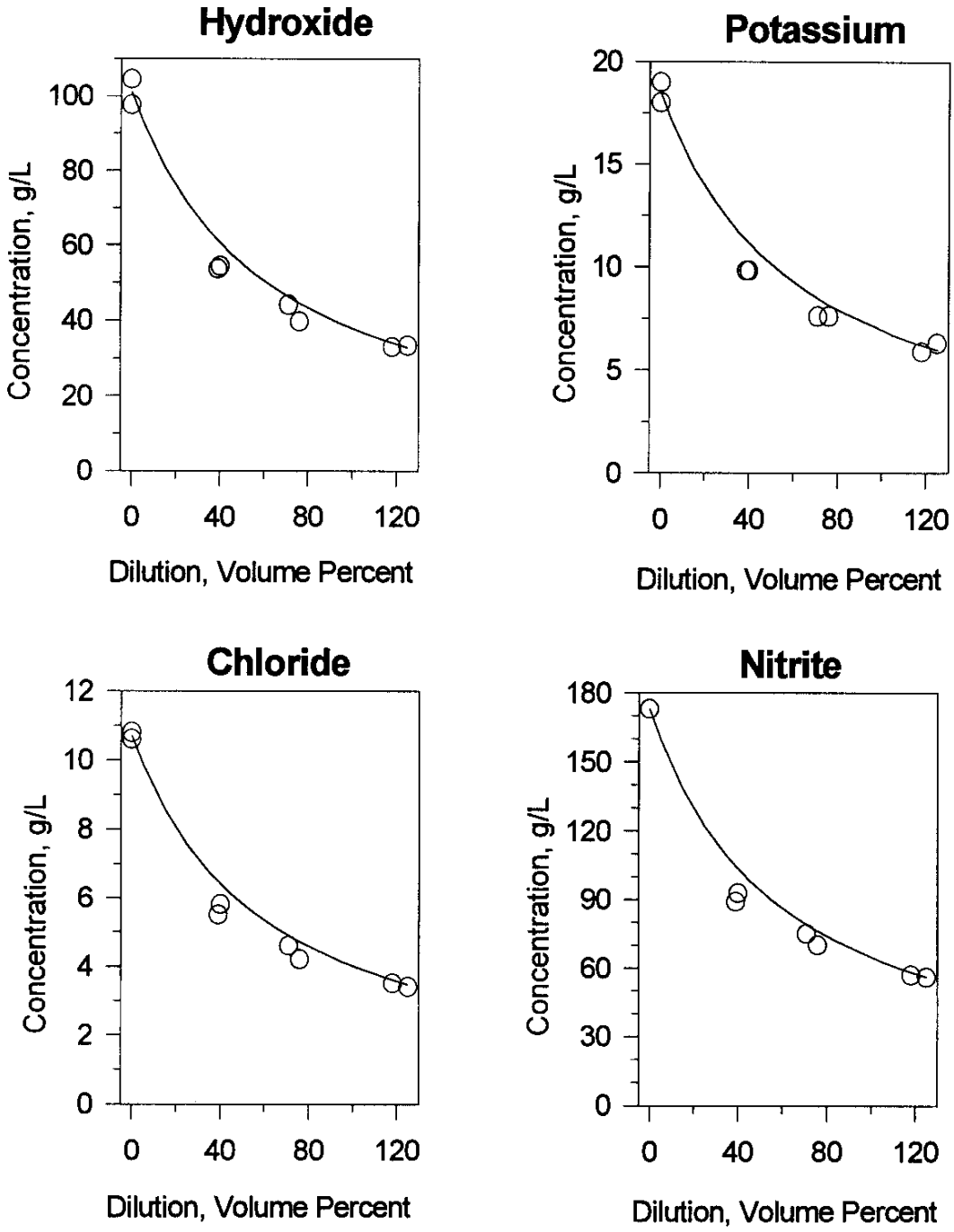
Category IV: components that have both soluble compounds and insoluble compounds present in the sample.

5.1 UNSATURATED CHEMICAL COMPONENTS, CATEGORY I

Category I components are present in the liquid phase but not the true solid phase. Their liquid phase concentrations decrease in direct proportion to the amount of diluent added. The prime examples for most tank waste samples are **potassium** and **chloride**. Other components that fall into category I for this particular tank waste include **hydroxide** and **nitrite**. Concentrations of all these components decrease smoothly as a function of dilution in both the supernatant liquids (Table 3-10, Figure 5-1) and centrifuged solids (Table 3-11).

The liquid phase data from the Settled Solids sample dilutions (Table 3-10) are shown in Figure 5-1 for several of the Category I components. The lines in Figure 5-1 represent the expected concentrations based on dilution effects alone, using the average measured value at 0% dilution as the point from which other dilutions are calculated. All of the data for the Category I components follow these lines fairly well, within the expected ±10% accuracy of the analytical data. The deviations from the smooth curves are likely due to the effect of the changes in solution volume as large amounts of salt dissolve. That is, the partial molar volumes of the dissolving salts are not taken into account in the simple dilution calculations.

Figure 5-1. Supernatant Liquid Concentrations, Category I Components



Centrifuged solids concentrations (Table 3-11) also tend to decrease with increasing dilution. These components are present in the centrifuged solids only as interstitial liquid. The numerical values of the concentrations in the centrifuged solids are lower than the corresponding supernatant liquid samples because (a) the units are different (μg/mL vs. μg/g), and (b) one gram of centrifuged solids contains less than one gram of interstitial liquid.

A good indicator for the presence or absence of a component in the solid phase is the arithmetic ratio of the supernatant liquid concentration to the centrifuged solids concentration, as shown in Table 5-1 for the major components. The ratio for Category I components is consistent within a given sample, but changes from sample to sample. For sample 3AN-A, the ratio is 2.9 ±0.1 (though K is anomalous). For less soluble components that are present more in the solid phase than the liquid phase, the ratio is much lower.

Table 5-1. Arithmetic Ratio of Supernatant Liquid Concentration to Centrifuged Solids Concentration (Table 10 value divided by Table 11 value)
(the lower the value, the higher the percentage in the solid phase)

Vol% Dilution →	0% 3AN-A	0% 3AN-B	39% 3AN-C	40% 3AN-D	71% 3AN-E	118% 3AN-G
OH^-	2.9	3.7	2.3	2.2	1.8	1.4
K	3.7	3.3	2.5	2.3	1.9	1.5
Cl^-	2.8	3.4	2.1	2.1	1.8	1.5
NO_2^-	2.9	3.4	2.1	2.1	1.7	1.5
NO_3^-	2.8	1.5	2.0	2.0	1.7	1.4
TIC	0.1	0.1	0.1	0.1	0.4	1.3
P	2.5	2.4	1.6	1.7	1.4	1.4
S	0.3	0.3	0.2	0.2	0.4	1.5
F^-	1.1	1.0	0.1	0.2	0.2	1.9
Al	0.5	0.5	2.1	2.1	1.5	1.0
Cr	0.4	0.3	0.1	0.1	0.04	0.01
Na	1.7	1.5	1.3	1.3	1.2	1.2
Oxalate	--	--	--	--	--	0.01
^{99}Tc	0.55	0.59	0.16	0.18	0.06	0.03
^{137}Cs	2.9	2.7	1.7	1.7	1.3	0.8

5.2 INSOLUBLE CHEMICAL COMPONENTS, CATEGORY II

Liquid phase concentrations of Category II components are at or below detection limits, but they are present in the solid phase. Their concentrations in the centrifuged solids (Table 3-11) increase as a function of dilution because of the dissolution of the Category III components from the solids. Examples from this study include **calcium, iron, nickel, uranium, and ^{90}Sr**. (Elements present in the centrifuged solids at concentrations less than 0.1% by weight are not included in this list, except for the radionuclides.)

5.3 SATURATED SOLUBLE CHEMICAL COMPONENTS, CATEGORY III

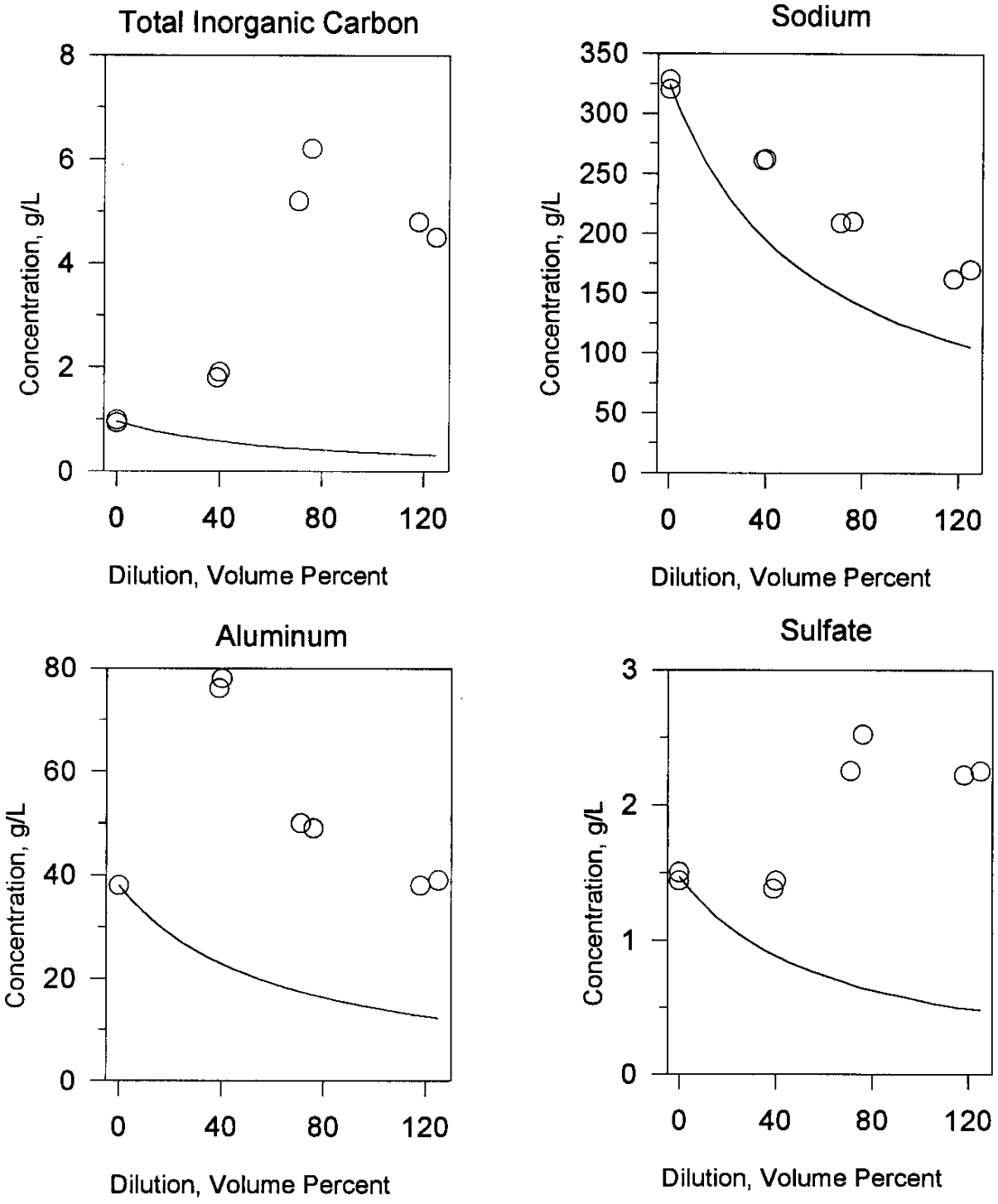
Solubility limits of Category III components change with dilution due to ionic strength and common ion effects, so concentrations in solution (Table 3-10) vary with dilution, but not in direct proportion to the amount of diluent added. These components include **TIC (carbonate), aluminum (aluminate), sodium, fluoride, nitrate, sulfate, and organic carbon (oxalate)**. Some examples are shown in Figure 5-2.

The trend for aluminum is classic. The solubility (liquid phase concentration) of the sodium aluminate doubles from 0% to 40% dilution, due to the decrease in ionic strength and sodium ion concentration. At higher dilution levels, there is no more sodium aluminate solid to dissolve, so the concentration in the liquid phase begins to decrease, following the same dilution pattern as for a Category I component. There also appear to be some insoluble aluminum compounds present, based on the low liquid:solid ratio at 118% dilution (Table 5-1), but these are minor compared to the amount of soluble aluminate present.

The sodium graph in Figure 5-2 looks very much like a Category I component graph, but the sodium concentration at high dilution is consistently above the predicted dilution-only curve. That is due to the dissolution of sodium salts (primarily aluminate, nitrate, and carbonate). There are also some insoluble sodium compounds, as shown by the Table 5-1 data, but again they are minor compared to the soluble sodium.

Sulfate and TIC (carbonate) follow a pattern similar to aluminate, but they are not dissolved until dilutions of about 80% or more. At 71% dilution, the sulfate and TIC concentration ratios in Table 5-1 are still much lower than the fully-soluble components (0.4 for sulfate and TIC vs. 1.7-1.8 for Category I components). At 118% dilution, the ratios for sulfate and TIC are about the same as the Category I components, indicating complete or nearly complete dissolution of sulfate and carbonate.

Figure 5-2. Supernatant Liquid Concentrations, Category III Components



The nitrate data are inconclusive, due to the large discrepancy (factor-of-two) between the analytical results for the centrifuged solids from the two duplicate samples at 0% dilution (see 3AN-A and -B in Table 3-11). The samples were re-run, but had the same results a second time. The supernatant liquid data strongly support the results for sample 3AN-B, in which a large amount of nitrate is present in the solid phase. (In sample 3AN-A, phase distribution calculations indicate no nitrate in the solids – see Appendix B.) The supernatant liquid samples have about the same nitrate concentration at 40% dilution as at 0% dilution (samples 3AN-A through -D, Table 3-10), implying that solids must be dissolving.

The fluoride data (not plotted) from Tables 3-10 and 3-11 are rather scattered, and near detection limits.

Total organic carbon (TOC) is a mixture of oxalate and other organic compounds. The liquid phase contains mainly the soluble organic compounds, and oxalate dominates the solids. The oxalate does not dissolve appreciably at any of the dilution levels tested, though its liquid phase concentration is above the detection limit at 118-125% dilution. At those dilutions, 85% of the oxalate is still in the solid phase, where sodium oxalate represents over half of the total undissolved solids.

5.4 CATEGORY IV

Category IV components are **chromium, silicon, ^{99}Tc, and ^{137}Cs**. Each of these elements appears to be represented by two species, one following Category I behavior and the other following Category II behavior. Thus, supernatant liquid concentrations (Table 3-10) for each of these components decreases smoothly with increasing dilution like Category I components, but the centrifuged solids concentrations (Table 3-11) increase with dilution like Category II components. In Table 5-1, the concentration ratios decrease steadily with increasing dilution. Possible identities of the soluble and insoluble species have been discussed previously (Herting 1998), where similar patterns were observed in the tank 104-AN studies.