1246844
[0067762H]

RHO-RE-SR-83-26
Book B

Process Aids

A Compilation of Technical Letters
Evaporator and Tank Farm Processes,
Advanced Waste Planning

Volume 15

Approved for Public Release;
Further Dissemination Unlimited
9/15/04

1983

Compiled by
P. J. Mulvey
Process Development Group

Prepared for the U.S. Department of Energy
under Contract DE-AC06-77RL01030

Rockwell International
Rockwell Hanford Operations
Energy Systems Group

RECEIVED
NOV 13 2017
EDMC

Book B

Title	Author	Date	Page
Evaporator Process			
Evaporator/Crystallizer Processing of Future Wastes	B. D. Bullough	01/03/83	453-454
242A Ion Exchange Resin	M. T. Jansky	08/18/83	455
Clarification of 242A Ion Exchange	M. T. Jansky	08/26/83	456
Resin Sample from 242A Evaporator	M. T. Jansky	09/19/83	457-458
Re-Evaluation of 242A Resin	M. T. Jansky	10/11/83	459-461
Capacity of 242A Ion Exchange Resin	M. T. Jansky	11/28/83	462-464
102AW Feed for Run #83-3	M. T. Jansky	01/24/83	465-469
Run 83-4 Boildown Product	M. T. Jansky	02/09/83	470
Additional Boildown Data for Evaporator Run 83-4	M. T. Jansky	04/01/83	471-474
Tank 102AW Samples: R5001 and R5002	M. T. Jansky	04/07/83	475-483
Customer Waste Sample from Tank 102AW (Sample #R6875)	M. T. Jansky	08/18/83	484
Composition of 102AW - Customer Waste	M. T. Jansky	09/22/83	485-486
Laboratory Results on Customer Waste 242A Evaporator Feed Samples, Run 83-6	M. T. Jansky	09/22/83	487-492
Chemical Composition of Tank 106AN Waste (Run 84-1)	M. T. Jansky	11/28/83	493-495
Laboratory Data for Evaporator Run 84-2	M. T. Jansky	11/28/83	496-500
Flash Point of Turco Oil	D. L. Herting	04/26/83	501
Separable Oil from TURCO Inhibited Phosphoric Acid	J. R. Jewett	04/26/83	502-504
Laboratory Support for Customer Waste Waste Volume Reduction	M. T. Jansky	05/05/83	505-524
Thermal Analysis of Synthetic Customer Waste	M. T. Jansky	05/13/83	525-526
Laboratory-Scale Boildown of Actual Customer Waste	M. T. Jansky	08/23/83	527

Title	Author	Date	Page
Boildown of Synthetic Current Acid Waste (CAW)	M. T. Jansky	04/04/83	528-532
Ammonia Content in Decladding Waste Supernatant	M. T. Jansky	04/08/83	533-535
Laboratory Boildowns of Synthetic Decladding Waste Supernatant Liquor	M. T. Jansky	03/23/83	536-540
Solubility Phase Diagram - Interim Report	D. L. Herting	03/08/83	541-546
Phase Diagram for the WB Program	R. A. Zinsli	07/15/83	547-562
SD-WM-TI-078, Solubility Phase Diagram - Final Report	D. L. Herting/ R. M. Cleavenger	05/20/83	563-564
Laboratory Results from Slurry Pumpability Tests	M. T. Jansky/ H. R. Risenmay	11/11/83	565-574
September 1983 Pilot Plant Double-Shell Slurry Evaporator-Crystallizer Run - Data and Results	M. J. Schliebe/ M. T. Jansky	11/30/83	575-597
Composition of Scaling Material from Reboiler after Engineering Laboratory Double-Shell Slurry Run	M. T. Jansky	12/21/83	598-600
Evaluation of the Pilot Scale Double-Shell Slurry Pumping Test	D. M. Tulberg	12/30/83	601-615
Salt Well Liquor/Double-Shell Slurry Study, Phase I	M. T. Jansky	03/17/83	616-625
Composition Ranges of Waste Feeds to Transportable Grout Facility	M. J. Kupfer	05/25/83	626-630
Tank Farm Process			
Content of 244BX and 244 U	M. T. Jansky	03/23/83	631-632
Non-Routine Pu and ^{241}Am Determination in Tank 244 BX Samples	S. G. Metcalf	07/07/83	633-634
244-BX Jet Pump Liquors	M. T. Jansky	07/08/83	635-637
WR Vault Samples	M. T. Jansky	05/09/83	638-639
Additional Data for Solids in Tank 203B	M. T. Jansky	01/07/83	640-642
Samples from Tank 103AW	M. T. Jansky	03/31/83	643-646
Solids in Tank 103AW	M. T. Jansky	05/24/83	647-648

Title	Author	Date	Page
Waste Surface Level Changes in TK-101-SY	L. M. Sasaki	08/04/83	649-652
Tank 101AZ Sludge	M. T. Jansky	12/28/83	653-655
Characterization of 102AZ Waste Tank	J. S. Buckingham	07/28/83	656-658
Analysis of TK 102AZ Supernatant Liquid	J. S. Buckingham	08/19/83	659-660
102AZ Sludge Sample	M. T. Jansky	08/26/83	661-665
Corrected Radionuclide Content of TK 102AZ Sludge	M. T. Jansky	09/01/83	666-667
Corrosion of Tank H-101	J. R. Jewett	09/08/83	668-669
Source of NO_x Fumes in 241-A-702 Ventilation System, Final Report	R. B. Bendixsen	12/12/83	670-671
Laboratory Procedure for Determining Settling Rates of Neutralized Current Acid Waste (CAW/ZAW)	M. T. Jansky	02/18/83	672
Laboratory Support for Aging Waste Characterization	M. T. Jansky	03/21/83	673
Identification of Chemical and Physical Analyses in Support of Waste Tank Characterization	D. R. Bratzel	11/11/83	674-681
Summary of Laboratory Data for the Ninety-Day Rule Experiment	M. T. Jansky	01/20/83	682-704
Decladding Waste Addition/Dilution	B. D. Bullough/ C. R. Reichmuth	02/07/83	705-713
Mixing of Wastes: 103AW and Synthetic Decladding Waste	M. T. Jansky	04/11/83	714-717
"Scheduling" of the Mixing Study	M. T. Jansky/ H. R. Risenmay	05/12/83	718-719
Laboratory Results from the Waste Mixing Study	M. T. Jansky/ H. R. Risenmay	06/24/83	720-727
Supplemental Mixing Study Data	M. T. Jansky/ H. R. Risenmay	09/07/83	728-738
Laboratory Support for Decladding Supernatant/Salt Well Liquor Mixing	M. T. Jansky/ H. R. Risenmay	10/21/83	739-743
Laboratory Results from Neutralized Zirflex Acid Waste (NZAW) Study	M. T. Jansky/ H. R. Risenmay	09/09/83	744-757

Title	Author	Date	Page
Boiling Point of Neutralized Decladding Sludge	B. D. Bullough	02/22/83	758
Analysis of "Iron Oxide" Sludge	M. T. Jansky	08/12/83	759-760
Irradiation of Synthetic Iron Hydroxide Sludge	M. T. Jansky	08/15/83	761
Irradiation of Iron Hydroxide Sludge	M. T. Jansky	08/23/83	762
Irradiation of Synthetic Iron and Chrome Hydroxide Sludge	M. T. Jansky	11/09/83	763-764
Sulfate Solubility in Aging Waste	M. T. Jansky	11/21/83	765-766
Feed Make-Up for Sulfate Solubility Study	M. T. Jansky	11/23/83	767-770
Sulfate Precipitation in Aging Waste	M. T. Jansky/ H. R. Risenmay	12/14/83	771-772
Ever-Tite R Quick-Connect Fittings for Jet Pump Use	B. D. Bullough	02/22/83	772
Magnesium Hydroxide Neutralization Scouting Study	D. L. Herting/ K. J. Patterson	06/15/83	774-779
Stability of Decladding Waste Solids in Excess Caustic	D. L. Herting/ K. J. Patterson	08/09/83	780-783
Thermal Stability of $NaNO_3$ and $NaNO_2$	D. L. Herting	09/12/83	784-786
Return of the Missing Hydroxide	D. L. Herting	03/01/83	787-793
Hydroxide Concentration Analysis	B. D. Bullough	03/02/83	794
Composition of Gases Generated During Slurry Growth	M. T. Jansky/ B. A. Meissner	11/23/83	795-807
Laboratory Study for Evaluating Water Soluble Oil Use	M. T. Jansky	11/07/83	808-809
Laboratory Testing of Water Soluble Oil	M. T. Jansky/ H. R. Risenmay	11/30/83	810-815
Employee Suggestion 96215 - Water Soluble Oil	R. B. Bendixsen	11/29/83	816
<u>Advanced Waste Planning</u>			
WG Monthly Report, May 1983	D. R. Bratzel	05/31/83	817-819
WG Monthly Report, June 1983	D. R. Bratzel	06/27/83	820-825

Title	Author	Date	Page
WG Monthly Report, July 1983	D. R. Bratzel	08/01/83	826-834
WG Monthly Report, August 1983	D. R. Bratzel	08/31/83	835-840
Proposed FY-84 Laboratory Studies for BIPP Feed Preparation	D. R. Bratzel	11/01/83	841-844

SUBJECT INDEX

	Page
ACID WASTE	259
ACRYLIC FIBERS	413
AGING WASTE	673,765,771
AIR LINE	296
A.L. WASTE	449
ANALYSIS	156
AMERICIUM	633
PLUTONIUM	240
PUREX READINESS TESTS	193,195
ANION EXCHANGE	441
A-702	670
BCP CRIB	301
BIPP FEED	817,820,826,835,841
BLENDER	57
BORON CARBIDE	57
CALCINER	54,60,62,64
CALCIUM CARBONATE	62,64
CALCIUM NITRATE	44
CALCIUM OXALATE	18,30
CALIBRATION	80.82,85,98,106,111
CARBON TETRACHLORIDE	438
CAUSTIC STRIKE	307,309,327
CELL 18	326
CERIUM COVERGLASS	428,432
CESIUM	343,346
CESIUM CHLORIDE	420

CHROMIUM HYDROXIDE	763
CHROMIUM POWDER	13-17
COLE SOL 1113	163
CORROSION	225,237,668
CURIE	419
CURRENT ACID WASTE	528,672
CUSTOMER WASTE	484,485,505,525,527
DECAPPER	205
DECLADDING WASTE	11,278,533,536,705,714,739,758, 780
DILUENT	156,158,165,173,178,180,182, 183,190
DISSOLUTION	221
DISSOLVER	9
DOUBLE SHELL SLURRY	575,598,601,616
DUOLITE ARC-359	331
E CELL	428,532
ENHANCED READINESS TEST	193,195,230
ESSENTIAL MATERIAL	156
EVAPORATOR/CRYSTALLIZER	453,575,598
BOILDOWN DATA	471,496,505,527,528,536,575
FEED	465,487
PRODUCT	470
FEED	326
EVAPORATOR	465,487
GROUT	626
FLASHPOINT	180,501
FLUORIDE ION	278
GASKET MATERIAL	228

HEAD END	195
HEAT	419
HYDROXIDE	794
ION EXCHANGE RESIN	455,457,459,462
IRA-930 RESIN	443
IRON OXIDE/HYDROXIDE	759,761,762,763
IRRADIATION	761,762,763
JET PUMP	773
JET SAMPLER	10
LAUNDRY CRIB	415,418
LIGHT WATER	349
MAGNESIUM HYDROXIDE	276,774
MAGNESIUM OXIDE COATED ACRYLIC FIBERS	413
MATERIAL	219
M CELI	106
MISSING HYDROXIDE	787
MIXING WASTE	714,718,720,728,739
NEUTRALIZATION	217,259,276,372,759,774
NEUTRALIZED ZAW	744
NEW CONCEPTS	375,413
NINETY-DAY RULE	602
NORMAL PARAFFIN HYDROCARBON	156,158,162,163,165,173,178, 180,182,183,190
NO_2/NO_x	217,670
OIL	306
OIL, SOLUBLE	808,810,816
PFMP	1,9,12
PHASE DIAGRAM	541,547,563

PLUTONIUM	240,441,451
PLUTONIUM ANALYSIS	633
PLUTONIUM CALCINER	54,60
PLUTONIUM OXALATE	30,57,66,75
PRF WASTE	447
PROCEDURE	672
PRODUCT, EVAPORATOR	470
PUMPABILITY	565,601
QUICK-CONNECT FITTING	773
RARE EARTH STRIKE	312,314,316,318,320,322,324
RECIPE, SOLIDS	9
SALT WELL LIQUOR	616,739
SAMPLER	1,9,10
SEM	13
SETTLING RATE	672
SILICA GEL	178
SLUDGE	653,661,758,759,761,762,763,780
SLURRY	565,601
SLURRY GROWTH	649,795
SODIUM HYDROGEN SULFATE	283
SOL-GEL	351
SOLIDS	9,220,285
SOLUBILITIES	
PLUTONIUM OXALATE	46
SULFATE	765,767,771
WASTE	541,563
SOLVENT	162,163,165,170,171,172,173, 178,180

SPECIFIC GRAVITY	283
STICKY STUFF	425
STRONTIUM	301
SUGAR DENITRATION	241,257,259
SULFATE	765,767,771
SUPERNATANT LIQUID	659
TANK CALIBRATION	80.82,85,98,106,111
TANK E5	220
TANK F8	226
TANK H-101	225,668
TANK J1-300B	237
THERMAL ANALYSIS	525
THERMAL STABILITY	784
TK-E3	240
TK MNB-178	286
TK 101AZ	653
TK 101SY	659
TK 102AZ	656,659,661,666
TK 102AW	462,475,484,485
TK 103AW	643,647,714
TK 106AN	493
TK 203B	640
TK 244BX	631,633,635
TK 244U	631
TK 23-3	331
TK 25-1	285
TK 37-1	333
T-38-5	335

TMI	435
TRANSPORTABLE GROUT FACILITY	626
TURCO	501,502
UNH	222
VALVE	219
VAPOR PRESSURE	222
VENTILATION SYSTEM	670
WASTE DECLADDING	11
WASTE TANK CHARACTERIZATION	674
WR VAULT	638
ZAW	672,744
ZEOLON	328,332,337
ZIRCONIUM	221

Internal Letter

Rockwell International

Date January 3, 1983

No. 65453-83-001

TO (Name, Organization, Internal Address)
C. W. Manry/G. A. Beitel
Program Engineering
2750E/200 East

FROM (Name, Organization, Internal Address, Phone)
B. D. Bullough
Separations Process Development Unit
202-S/200 West
3-2967

Subject: Evaporator/Crystallizer Processing of Future Wastes

If any significant changes are made to the PUREX process, affecting the waste streams, existing data and experience on evaporator/crystallizer processing may be invalid. An increase of 5% in actual solids waste volume over or under predicted volume may be of significant consequence.* There could also be some unexpected changes related to crystal size, distribution, type, etc., or sludge volumes.

In response to possible questions related to these changes, batch boildowns of actual or simulated wastes will be of considerable aid. However, several runs on a larger scale evaporator with simulated waste will more effectively demonstrate evaporator/crystallizer operation, as well as waste volume reduction differences (a few selected wastes, under a number of parameters). The Separations Process Development Unit (SPDU) has the personnel and equipment to perform all of these experiments.

Process changes that may affect waste volume reduction, or possibly other factors, include the ammonia off-gas scrubber (installed after PUREX shut down, therefore solids and other wastes introduced via this facility haven't been dealt with, in practice), and neutralization changes (to direct or co-strike), enhanced sugar denitration, and alternate head-end facilities. From this list, it is evident that some deviations in speculated VWR might well occur in excess of 5%.

Small pilot scale evaporator runs of three to five days duration will most probably provide substantial data and can be performed without excessive problems. The existing equipment would require some upgrading, and some support would be required in developing "recipes" for waste types. Approximately 6 man months per waste type would be required (possibly less without equipment modifications).

If any questions arise, or the potential problems outlined in this letter are deemed worth investigation, please contact chemical engineering laboratory personnel in 202-S.

Bruce D. Bullough

B. D. Bullough
Engineer

BDB/naj

*A five percent change in predicted WVR of CAW supernate will be ≈100,000 gal, but a 5% change in predicted sludge (primarily decladding waste) volumes is ≈800,000 gal, based on reverse strike neutralization. [Calculations by L. D. Vanselow]

Rockwell International

cc:

J. F. Albaugh, B. N. Anderson, J. S. Buckingham, K. G. Carothers, K. A. Gasper, M. T. Jansky, L. Jensen, M. J. Kupfer, G. W. Reddick, Jr., D. A. Reynolds, L. H. Rodgers, M. J. Schliebe, R. A. Van Meter, D. G. Wilkins, R. D. Wojtasek, G. D. Wright, Process Aids, Letterbook

Internal Letter

Rockwell International

455

Date. August 18, 1983

No. 65453-83-206

TO: (Name, Organization, Internal Address)
. P. J. Certa
. Process Engineering
. 2750E/A105/200 E

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Chemical Laboratory Unit
. MO-037/200 W
. 3-1571

Subject: . 242A Ion Exchange Resin

The Chemical Laboratory Unit (CLU) received a sample of 242A evaporator ion exchange resin. A sieve test indicated that eight percent of the resin, by volume, went through a fifty-mesh seive, with the remaining 92% retained.

An aliquot of the resin was tested for efficiency, with a K_d of 1.41. A second aliquot was regenerated with 7 M sodium nitrate solution, with the regenerated resin having a K_d of 74. A sample of new resin that CLU had was also tested, having a K_d of 41.

These data may be compared to a resin sample taken from 242A on July 15, 1982. The as-received sample had a K_d of 2.17, whereas a new sample was reported to have a K_d of 4.81. (The low K_d of the new material indicates that the resin was probably not in the sodium form.) The sieve test for the 1982 sample gave 98 volume percent retained on a fifty-mesh sieve.

The data indicate that the existing resin has a significant quantity of fines, and needs either replacement or, at the very least, regeneration.

Please call if there are any questions regarding this work.

M. T. Jansky
Senior Chemist

MTJ:gij

cc: J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham JSB
D. L. Herting
R. D. Wojtasek
Process Aids
File: WB621

456

Internal Letter

Rockwell International

Date August 26, 1983

No. 65453-83-220

TO: (Name, Organization, Internal Address)
- P. J. Certa
- Process Engineering
- 2750E/A105/200 E

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Chemical Laboratory Unit
- MO-037/200 W
- 3-1571

Subject: Clarification of 242A Ion Exchange

Reference: Letter, 65453-83-206, M.T. Jansky to P.J. Certa, "242A Ion Exchange Resin", August 18, 1983

The referenced letter contains data pertaining to a sample of 242A ion exchange resin. Values were given for resin efficiency, which were reported as K_ds. The units for the K_d values are milliliters of feed per gram of resin.

Also, K_ds reported for a July 15, 1982, sample were reported as 2.17 (as received sample) and 4.81 (new sample) mL/g. A calculation error was made, and correct values should be 3.17 and 9.31 mL/g, respectively.

I hope this clarifies the referenced letter. In the future, I plan on "standardizing" the procedure to determine K_d, which should provide you with more relevent data. Please call if you have further questions or comments.

M. T. Jansky
Senior Chemist

MTJ:gij

cc: J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham JSB
D. L. Herting
R. D. Wojtasek
[redacted]
File: WB621

Internal Letter

Rockwell International

Date. September 19, 1983

No. 65453-83-235

TO: (Name, Organization, Internal Address)
. P. J. Certa
. Process Engineering
. 2750E/A105/200E

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Chemical Laboratory Unit
. MO-037/200W
. 3-1571

Subject: . Resin Sample From 242A Evaporator

A resin sample, labled "Fresh Resin" was received by the Chemical Laboratory Unit (CLU). The sample was dated August 30, 1983. The sample was subjected to a sieve test, with the results shown in Table I. The bulk density of the resin was found to be 0.811 (grams per cubic centimeter).

The resin was also examined for efficiency by contacting it with a slightly contaminated Cs^{137} solution. The efficiency (K_d), in milliliters of contact solution per gram of resin, was determined to be 145 mL/g. The K_d value was based on a feed stock Cs^{137} concentration of 1.70×10^{-4} microcuries per liter ($C_o = 1.70 \times 10^{-4}$ µCi/L).

The CLU is going to "standardize" the K_d measurements by modifying the cesium adsorption procedure from LE-215-102, Essential Materials Manual. The C_o value will be set at 5×10^{-1} µCi/L. This C_o value is necessary to provide accurate analyses using the small quantities of resin and contact solution, 0.5 grams and 5 milliliters, respectively. The calculation of K_d will remain the same:

$$K_d = \frac{(C_o - C)V}{g \cdot C}$$

C_o = initial concentration of feed solution, µCi/L

C = concentration of solution after contact, µCi/L

V = volume of contact solution, mL

g = grams of resin used, g

The units of this determination are milliliters of contact solution per gram of resin.

The "Fresh Resin" K_d will be re-evaluated when CLU receives a standardized feed solution, with C_o of 5×10^{-1} µCi/L. Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ/rr

cc: J. F. Albaugh
J. S. Buckingham JSB
K. G. Carothers
G. A. Gratney
D. L. Herting
K. J. Patterson
L. H. Rodgers
R. D. Wojtasek
[redacted]
File: WB621

Attachment

Table I

Sieve Test Results for "Fresh Resin"

Dated August 30, 1983

	Weight %	Volume %
Retained on 20 mesh	0.11	0.26
Retained on 50 mesh	99.02	98.19
Passed through 50 mesh	0.87	0.12

Internal Letter

Rockwell International

459

Date: October 11, 1983

No. 65453-83-260

TO: (Name, Organization, Internal Address)
P. J. Certa
Process Engineering
2750E/A105/200E

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Chemical Laboratory Unit
222S/MO-037/200W
3-1571

Subject: Re-evaluation of 242A Resin

Ref: Letter, 65453-83-235, M. T. Jansky to P. J. Certa, "Resin Sample from 242A Evaporator", September 19, 1983

As stated in the referenced letter, the Chemical Laboratory Unit (CLU) had received a resin sample from the 242A evaporator. The sample, dated August 30, 1983, was labled "Fresh Resin". The resin was tested for efficiency by contacting it with a slightly contaminated Cs^{137} solution. The K_d was determined to be 145 mL/g (see reference for explanation of K_d).

The low concentration of Cs^{137} made the data somewhat questionable because of the detection limits of the analytical method. Therefore, as stated in the reference, a standardized feed solution with $C_o = 5.64 \times 10^{-1}$ µCi/L was prepared and used for the contact. The K_d was re-evaluated, and is shown in Table I.

A second sample of resin, dated 9/03/83, was also received by the CLU. This sample was damp, indicating either regeneration or actual use. The sample was tested for efficiency, with the K_d shown in Table I. Table II contains results from a sieve test. The bulk density of the "wet" resin was determined to be 0.808 grams per cubic centimeter.

The data shows that the resins are comparable to one another in terms of efficiency. However, the "wet" resin has more fines in it, which may cause some transfer problems in the future. The cohesiveness of the resin should probably be monitored somewhat closely.

Please call if there are any questions or comments regarding this work.

M. T. Jansky
Chemist, Senior

MTJ/rr

cc: J. F. Albaugh
J. S. Buckingham JSB
K. G. Carothers
G. A. Gratney
D. L. Herting
K. J. Patterson
L. H. Rodgers
R. D. Wojtasek
[redacted]
File: WB53G

TABLE I

RE-EVALUATION OF K_d'S USING $C_o = 5.64 \times 10^{-1}$ µCi/L

Resin	C/C_o	K_d
Fresh (8/30/83)	0.324	19.58
Wet (9/03/83)	0.268	17.67

TABLE II

SIEVE TEST RESULTS FOR "WET RESIN"
Dated September 3, 1983

	Volume %
Retained on 20 mesh	1.09
Retained on 50 mesh	93.99
Passed through 50 mesh	4.92

462

Internal Letter

Rockwell International

Date November 28, 1983

No. 65453-83-298

TO: (Name, Organization, Internal Address)
. P. J. Certa
. Process Engineering
. 2750E/A105/200E

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Chemical Laboratory Unit
. 222S/MO-037/200W
. 3-1571

Subject . Capacity of 242A Ion Exchange Resin

The Chemical Laboratory Unit (CLU) recently received a sample of ion exchange resin from the 242A evaporator. The sample was dated 11/11/83 and labeled: 242A-IX Resin, R. Smith, R. Thompson. The resin was moist when received. The sample was subjected to a sieve test, with the results shown in Table I. The sieve data indicate that the resin has not broken down.

The sample was also subjected to efficiency testing, as measured by Cs^{137} exchange capacity. The data show that the resin must have been loaded with Cs^{137}, as after contact, more Cs was present than in the original feed solution. Contact with an earlier sample was conducted for comparison. The K_d data are shown in Table II. These data show that while the contact solution was 5.33×10^{-4} μCi/mL in Cs^{137}, after contact the same solution was almost 100 times as concentrated.

The data show that while the resin has not physically degraded, a large amount of cesium is loaded onto the resin. More of the resin is available for testing, having been archived by CLU.

Please call if you have questions, comments, or need additional information.

M. T. Jansky
Senior Chemist

MTJ/rr

Attachments

cc: J. F. Albaugh
J. S. Buckingham JSB
E. G. Gratny
D. L. Herting
D. W. Lindsey
L. H. Rodgers
R. A. VaMeter
R. D. Wojtasek
[redacted]
File Code WB53G

TABLE I

SIEVE TEST RESULTS FOR 242A IX RESIN
(11/11/83)

	Weight %	Volume %	Bulk Density
Retained on 20 - mesh	0.20	0.49	0.569
Retained on 50 - mesh	99.30	98.54	1.404
Pass Through 50 - mesh	0.50	0.97	0.72

TABLE II

K_d FOR 242A IX RESIN
(11/11/83)

Resin	Weight (g)	Cs^{137} (μCi/mL)	K_d
8/30/83	0.58898	1.70×10^{-4}	18.13
8/30/83*	0.53170	1.83×10^{-4}	19.58
11/11/83	0.58415	3.14×10^{-2}	-
11/11/83	0.45340	2.86×10^{-2}	-
11/11/83	0.50242	2.89×10^{-2}	-
Feed		5.33×10^{-4}	-

*Test results from earlier run on same 8/30 sample.

Internal Letter

Rockwell International

Date. January 24, 1983

No. 65453-83-024

TO: (Name, Organization, Internal Address)
P. J. Certa
Process Engineering
2750E/A105/200 East

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Separations Process Development Unit
222-S/MO-037/200 West
3-1571

Subject: 102AW Feed for Run #83-3

Two samples from Tank 102AW (Run #83-3) were received by the Separations Process Development Unit (SPDU) on December 20, 1982. The samples were to be used for chemical analyses and batch boildowns.

Both samples were clear, yellow liquids with only a trace of solids. An aliquot of the first sample was prepared for analyses and submitted to Analytical Laboratories. The results of the analyses are shown in Table I. The remainder of the sample was used for a batch boildown. Pressure verus temperature data are shown in Table II. Nucleation occurred at 49 percent waste volume reduction (WVR). The nucleated product's viscosity was approximately 300 centipoise at 51°C.

The second sample was also used for a batch boildown, but only reduced to a 40 percent WVR. Pressure versus temperature data for the second sample are provided in Table III. Additionally, viscosity versus temperature data for the 40 percent WVR product were gathered, and are shown in Table IV.

Please call if you have any questions or comments regarding this work.

M. T. Jansky
Senior Chemist

MTJ/naj

cc: (W/Attachments)

J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
K. G. Carothers
M. I. Fineman
D. L. Herting
D. A. Reynolds
L. H. Rodgers
R. A. VanMeter
R. D. Wojtasek
[redacted]
File Code: WB621
Letterbook

Table I

Composition of 102AW Feed

Run 83-3

Component	Concentration	
	Molarity	Wt. %
$NaAlO_2$	0.36	2.36
$NaOH^*$	0.633	2.02
$NaNO_2$	0.76	4.20
$NaNO_3$	1.91	12.97
Na_2CO_3	0.74	6.25
TOC(g/L)	10.43	2.48
Na_2SO_4	0.053	0.61
Na_3PO_4	0.045	0.59
Cs^{137} (μCi/L)	4.35×10^5	**
Sr^{90} (μCi/L)	4.88×10^4	**
Pu(g/L)	2.04×10^{-4}	**
Cs^{134} (μCi/L)	410	**
Co^{60} (μCi/L)	263	**
Ra^{226} (μCi/L)	6.0×10^3	**
Eu^{155} (μCi/L)	973	**
$\%H_2O$		68.8
SpG	1.25	

*Values corrected by factor of ten from referenced letter #65453-83-024

**Not included in weight percent calculations

Table II

Pressure versus Temperature Data

102AW Feed, 83-3

%WVR	Temperature(°C/°F)	Pressure(torr)
0	38.2/100.6	40
	45.4/113.6	60
	51.0/124.2	80
10	38.8/101.6	40
	46.0/115.0	60
	52.2/125.8	80
20	39.2/102.6	40
	47.0/116.6	60
	53.0/127.4	80
30	40.6/105.0	40
	48.4/119.2	60
	54.4/130.2	80
35	Seems to be getting thicker	
40	42.6/108.6	40
	50.2/122.4	60
	56.6/133.8	80
49*	44.2/111.6	40
	52.2/126.2	60
	60.6/141.0	80**

*Nucleation

**The waste "blurped" at 80 torr. When the sample was exposed to atmospheric pressure, a very thin layer (<2 volume %) of supernatant liquor was observed over the solids. The viscosity of the concentrated product (49% WVR) was ≈300 centipoise at 51°C.

Table III

Pressure versus Temperature Data

102AW Feed

83-3

% WVR	Temperature (°C/°F)	Pressure (torr)
0	38.2/100.6	40
10	38.8/101.6	40
20	39.4/102.8	40
30	40.6/105.0	40
35	41.4/106.6	40
40	42.6/108.6	40

Table IV

Viscosity versus Temperature Data
For 40% WVR Product
Run 83-3

Temperature (°C/°F)	Viscosity (centipoise)
51/123.8	9
41/105.8	11
30/86.0	13
25/77	15
21/69.8	17
15/59	21
10/50	25

470

Internal Letter

Rockwell International

Date February 9, 1983

No. 65453-83-040

TO: (Name, Organization, Internal Address)
M. I. Fineman
Process Design
2750E/A219/200 East

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Separations Process Development Unit
222-S/MO-037/200 West
3-1571

Subject: Run 83-4 Boildown Product

As per your verbal request, the Separations Process Development Unit (SPDU) examined the physical nature of the product slurry from a batch boildown of evaporator feed, Run #83-4.

The product slurry was prepared by reducing the feed (sample #4289) 67 volume percent. The product slurry specific gravity was 1.494 at 51°C. An aliquot was poured into a tared vial and stored overnight at ambient temperature. The slurry seemed to be slightly thicker when examined the following day, as expected (due to the lower temperature). The slurry was then warmed to 35°C (=95°F, tank temperature), and allowed to equilibrate for 24 hours. Although the slurry seemed slightly less viscous, no major changes were observed.

All data pertaining to the laboratory boildowns for Run 83-4 will be presented in a separate letter when analytical data are available.

Please call me if you have any further questions.

M. T. Jansky
Senior Chemist

MTJ/naj

cc:

J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
K. G. Carothers
P. J. Certa
D. L. Herting
D. A. Reynolds
L. H. Rodgers
R. A. VanMeter
R. D. Wojtasek
[redacted]

File Code: WB621
Letterbook

Internal Letter

Rockwell International

Date April 1, 1983

No. 65453-83-096

TO: (Name, Organization, Internal Address)
. M. I. Fineman
. Process Design
. 2750E/A219/200 East

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Separations Process Development Unit
. 222-S/MO-037/200 West
. 3-1571

Subject: . Additional Boildown Data for Evaporator Run 83-4

Ref: Letter, #65453-83-040, dated February 9, 1983, M. T. Jansky to M. I. Fineman, "Run 83-4 Boildown Product"

As per your verbal request, another boildown was conducted on a sample of 102AW feed, evaporator run #83-4. The referenced letter discussed the physical nature of the boildown product. The purpose of this letter is to present the analytical data from the boildown product.

The waste sample (102AW, #2, sample #4289) was a clear solution, with only a trace of light-colored solids present. An aliquot of the feed was submitted to Analytical Laboratories (AL) for analyses, and the analytical data are shown in Table I.

A 100 mL aliquot of the waste was vacuum reduced at 40 torr to a 67 percent waste volume reduction (WVR). The product was filtered, with total slurry, filtrate, and dissolved solids submitted to AL for analyses. The analytical data for the product are shown in Tables II and III.

Please call if you have questions or comments regarding these data.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachments

cc:

J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
K. G. Carothers
P. J. Certa
D. L. Herting
L. H. Rodgers
R. A. Van Meter
R. D. Wojtasek
[redacted]

File Code: WB621
Letterbook

Table I

Composition of 102AW Feed, #2

Component	Concentration (moles/Liter)
$NaAlO_2$	0.375
NaOH	1.19
$NaNO_2$	0.38
$NaNO_3$	1.26
Na_2CO_3	0.13
TOC (g/L)	1.36
Na_2SO_4	*
Na_3PO_4	0.03
Cs^{137} (μCi/L)	1.48×10^5
Sr^{90} (μCi/L)	7.18×10^2
SpG	1.18

*Too low to determine

Table II

Composition of 102AW Concentrated Product Slurry

(67% WVR)

Component	Concentration	
	Molarity	Weight %
$NaAlO_2$	1.40	7.68
NaOH	3.34	8.94
$NaNO_2$	1.17	5.41
$NaNO_3$	4.12	23.44
Na_2CO_3	0.412	2.92
TOC	4.36	0.87
Na_2SO_4	*	*
Na_3PO_4	0.04	0.44
SpG	1.494	
% H_2O		44.17

*Too low to determine

Table III

Composition of 102AW Concentrated Product Phases

Component	Concentration		
	Filtrate		Solids
	Molarity	Wt.%	Wt.%
$NaAlO_2$	1.36	7.80	
NaOH	3.32	9.29	
$NaNO_2$	0.58	2.78	57
$NaNO_3$	4.18	24.84	17
Na_2CO_3	0.25	1.88	26
TOC	4.40	0.91	
Na_2SO_4	*	*	
Na_3PO_4	0.02	0.23	
SpG	1.43		
% H_2O		45.5	

*Too low to determine

Internal Letter

Rockwell International

475

Date. April 7, 1983

No: . 65453-83-102

TO: (Name, Organization, Internal Address)
P. J. Certa
Process Engineering
2750E/A100/200 East

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Separations Process Development Unit
222-S/MO-037/200 West
3-1571

Subject: Tank 102AW Samples: R5001 and R5002

Two samples from Tank 102AW were received by the Separations Process Development Unit (SPDU). The samples, numbered R5001 and R5002, were dated January 28, 1983. Both samples contained a trace of settled, dark brown solids, approximately 2-5 volume percent. The detailed laboratory handling of the samples is discussed below.

An aliquot of R5001 was submitted to Analytical Laboratories (AL) for analysis. The analytical data are shown in Table I. The remainder of the sample was used for a batch boildown, generating pressure versus temperature (P/T) data. Nucleation may have occurred at 23 percent waste volume reduction (WVR), but was definitely observed at 25 percent WVR. The P/T data are shown in Table II.

An aliquot of the product was placed into a 50°C viscosity cup. Viscosity versus temperature data was recorded and is shown in Table III. A second aliquot was submitted to AL for analyses. The remainder of the product was filtered, the phases were prepared for analyses, and also submitted to AL. The analytical data for the product are shown in Tables IV and V.

A second boildown was requested in which the WVR be only 15 percent. Sample R5002 was used. The P/T data are shown in Table VI. The product (15% WVR) was subjected to a viscosity versus temperature determination, with the data shown in Table VII. The product was allowed to stand at 20°C overnight.

The next morning, the product was transferred to the boildown pot, as it was requested that the product be concentrated an additional 5 volume percent. At 40 torr, the material boiled at 44.0°C. When the total concentration was 18 percent (versus the 15 percent initially), the material immediately precipitated and turned into "green goo" (the temperature climbed to 51°C, still at 40 torr). When the pressure was increased to atmospheric and the heat was removed, immediately the product was some 80 volume percent settled solids.

The data presented in this letter were being relayed constantly, via telephone, to engineering personnel. No further data or work was requested on these 102AW samples.

Please call if you have questions or comments regarding this work.

M. T. Jansky
Senior Chemist

MTJ/naj

Rockwell International

P. J. Certa
Page 2
April 7, 1983

Attachments

cc:

J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
M. I. Fineman
R. E. Haaland
D. L. Herting
L. H. Rodgers
R. D. Van Meter
R. D. Wojtasek
File Code: WB621
[redacted]
Letterbook

Table I

Chemical Composition of 102AW Sample, #R5001

Component	Concentration (moles/Liter)
Al	0.87
OH	1.25
NO_2	1.46
NO_3	2.85
CO_3	0.64
TOC (g/L)	6.60
PO_4	0.047
SO_4	0.24
Cs^{137} (μCi/L)	5.85×10^{5}
Sr^{90} (μCi/L)	9.96×10^{3}
Pu (g/L)	4.11×10^{-5}
K	0.063
Cr	0.029
Ni	0.001
Zn	*
B	0.003
Si	0.002
Ca	0.002
SpG	1.36

* Below detection limits

Table II

Pressure *versus* Temperature of TK 102AW, R5001

%WVR	Temperature (°C/°F)	Pressure (torr)
0	41.6/106.8	40
	49.8/121.6	60
	55.4/131.6	80
10	43.0/109.4	40
	51.0/123.8	60
	57.4/135.2	80
20[a]	45.2/113.4	40
	53.6/128.4	60
	59.4/130.8	80
23	? Nucleation ?	
25[b]	45.4/114.0	40
	53.8/128.8	60
	60.0/140.0	80

(a) Material "clinging" to vessel

(b) Definite nucleation, waste yellowed

Table III

Viscosity *versus* Temperature of TK 102AW, R5001

25% WVR

T (°C)	RPM	Viscosity (cps)*
50	60	58
	30	75
40	60	70
	30	80
15	60	95
	30	100

*Brookfield LVT spindle viscometer, #2 spindle

Table IV

Chemical Composition of 102AW, R5001 Boildown Product

25%WVR, Slurry

Component	Concentration (moles/Liter)
Al	1.23
OH	2.10
NO_2	2.16
NO_3	4.32
CO_3	0.90
TOC (g/L)	9.35
PO_4	0.086
SO_4	0.10
Cs^{137} (μCi/L)	8.53×10^5
Sr^{90} (μCi/L)	1.39×10^4
Pu (g/L)	8.93×10^{-6}
K	0.11
Cr	0.04
SpG	1.52

Table V

Chemical Composition of 102AW, R5001 Boildown Product

25% WVR, Phases

Component	Concentration	
	Filtrate (moles/Liter)	Solids (weight%)
Al	1.11	70
OH	1.79	
NO_2	2.21	
NO_3	2.36	23
CO_3	0.41	7
TOC (g/L)	8.01	
PO_4	0.06	
SO_4	0.09	
Cs^{137} (μCi/L)	7.46×10^5	
Sr^{90} (μCi/L)	9.84×10^3	
Pu (g/L)	1.03×10^{-5}	
K	0.11	
Cr	*	
SpG	1.41	

*Below detection limits

Table VI

Pressure *versus* Temperature for Tk 102AW, R5002

% WVR	Temperature (°C/°F)	Pressure (torr)
0	41.6/106.6	40
10	43.0/109.2	40
	50.6/123.4	60
	56.8/134.4	80
15	43.8/110.8	40
	51.4/124.6	60
	57.6/135.8	80

TABLE VII

Viscosity *versus* Temperature of TK 102AW, R5002

15% WVR

Temperature (°C)	RPM	Viscosity (cps)*
51	60	9
41	60	11
20	60	23

484

Internal Letter

Rockwell International

Date August 18, 1983

No. 65453-83-207

TO: (Name, Organization, Internal Address)
. P. J. Certa
. Process Engineering
. 2750E/A105/200 E

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Chemical Laboratory Unit
. MO-037/200 W
. 3-1571

Subject. . Customer Waste Sample from Tank 102AW (Sample #R6875)

A sample of customer waste from Tank 102AW was received by the Chemical Laboratory Unit (CLU). The waste was a clear yellow solution containing no solids. There was no visible organic layer associated with the sample. The pH of the sample, as received, was 13.5. The waste was subjected to a batch boildown. At 40 torr, the solution boiled at 34.4°C/94.2°F. Nucleation occurred at 24 percent waste volume reduction (WVR), which was indicated by the solution turning cloudy. The sample was further concentrated to a total of 40 percent WVR, and allowed to stand, at room temperature for two days. The condensate was tested for organic carbon, with analytical results showing that organics were below detection limits. No organics were visibly observed in the condensate.

After two days, a trace of solids was visible in the original boildown product. No organic layer was observed. The waste was concentrated an additional 20 percent (a total of 60 percent WVR) when an organic appeared. Brown droplets floated on the surface of the waste. The droplets are believed to be a result of the Turco in the customer waste. The condensate of the continued boildown again contained no organics.

The Waste Management Process Technology Unit (WMPTU) has requested further testing of this waste. With the remainder of the sample, CLPDU will attempt to gather as much information as possible. You will be contacted when the results of the additional testing are available.

Please call if there are any questions or comments regarding this work.

M. T. Jansky
Senior Chemist

MTJ:gij

cc: J. F. Albaugh
R. B. Bendixsen
K. G. Carothers
E. G. Gratney
D. L. Herting
R. E. Haaland
D. G. Wilkins
R. D. Wojtasek
File: WB621
Process Aids
Letterbook
J. S. Buckingham JB

Internal Letter

Rockwell International

Date September 22, 1983

No 65453-83-244

TO: (Name Organization, Internal Address)
R. E. Haaland
Process Design
2750E/A227/200E

FROM: (Name Organization Internal Address, Phone)
M. T. Jansky
Chemical Laboratory Unit
MO-037/200W
3-1571

Subject: Composition of 102AW - Customer Waste

Reference: Letter, 65453-83-207, M. T. Jansky to P. J. Certa, "Customer Waste Sample from Tank 102AW (Sample # R6875)", August 18, 1983

The referenced letter describes some physical characteristics of a waste sample, customer waste, from Tank 102AW. Recently, as verbally requested by the Waste Management Process Technology Unit (WMPTU), the chemical analysis of the waste was completed. The data are provided in the attached table.

There was insufficient sample for any other determinations utilizing sample # R6875. Therefore, no further testing will be done. Please call if you have any questions regarding this sample.

M. T. Jansky
Senior Chemist

MTJ/rr

cc: J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
K. G. Carothers
P. G. Certa
E. G. Gratny
D. L. Herting
M. C. Teats
R. A. VanMeter
D. G. Wilkins
R. D. Wojtasek
[redacted]
File:WB621

COMPOSITION OF 102AW WASTE

(# R6875)

Component	Concentration (moles/Liter)
Al^{+3}	0.0067
OH^-	0.106
NO_2^-	0.019
NO_3^-	0.025
TOC (g/L)	*
CO_3^{-2}	0.0090
SO_4^{-2}	0.002
PO_4^{-3}	0.078
Na^+	0.30
Pu (g/L)	**
Sr^{90}(μCi/L)	*
GEA (μCi/L)	4.92×10^3
SpG	1.030
% H_2O	96.4

*Not Available
**Below Detection Limits

Internal Letter

Rockwell International

Date September 22, 1983

No. 65453-83-242

TO: (Name, Organization, Internal Address)
- E. G. Gratny
- Process Engineering
- 2750E/A100/200E

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Chemical Laboratory
- 222S/MO-037/200W
- 3-1571

Subject: Laboratory Results on Customer Waste 242A Evaporator Feed Samples, Run 83-6

The Chemical Laboratory Unit (CLU) received two samples from Tank 102AW. The samples, customer waste to be used as feed for the upcoming 242A evaporator campaign, were delivered at approximately 2:00 p.m. on Friday, September 9. On graveyard, September 12, the CLU began working with the samples. The laboratory results are discussed below.

Two Tank 102AW samples were received by the CLU. One sample, R7811, was taken 4 feet below the surface of the waste. Approximately 79 milliliters of sample were available to work with. The sample was a pale yellow clear liquid, with a trace of dark solids on the bottom. An aliquot was removed for chemical analyses and submitted to Analytical Laboratories (AL). The remainder of the sample was used for a batch boildown. The waste was concentrated to a waste volume reduction (WVR) of 50 percent. Pressure versus temperature data are shown in Table I.

The 50 percent WVR product was placed into a thermally controlled bath and cooled to room temperature without agitation. After equilibration for approximately 30 minutes at 25°C, no major changes in the product were observed. The upper 5 volume percent of the product was perhaps slightly clearer, but the waste mixture was generally cloudy. Viscosity versus temperature data were gathered, and are shown in Table II. The rotation of the spindle on the viscometer provided the only agitation. After taking the viscosity reading at 47°C, the mixture was cooled to 20°C without agitation. As before, no changes in the waste were observed. The sample was then heated to 47°C while stirring, and equilibrated at 47°C for approximately 30 minutes. The sample was then concentrated an additional 10 volume percent (a total of 60 percent WVR). The P/T data at 60 percent WVR are also shown in Table I.

An aliquot of the 60% product was layered on top of an archived 106AN sample (R5553, 8' below). The ratio of 102AW:106AN was 1:2. Immediately, white crystalline needles formed at the interface of the mixture. After approximately 2 hours, there were approximately 50 volume percent bulk solids, i.e. phosphate needles, in the upper layer (102AW).

Rockwell International

The remainder of the 60 percent product was cooled to 25°C without stirring. When the spindle was placed into the mixture for viscosity determinations, and rotated, the mixture immediately solidified, with phosphate-like crystals forming. The mixture was stirred, and became increasingly "looser" as the material was stirred. Solids began to settle out, with the following volume percent of settled solids recorded at respective temperatures: 90%/30°C, 60%/40°C, 20%/50°C, ~10% after 10 minutes at 50°C.

The second 102AW sample, taken two feet from the bottom of the tank (R7812), was similar visually to the earlier sample. As before, a trace of solids was observed. An aliquot was removed and submitted to AL for analyses. The remainder was reduced in volume to a 50 percent WVR. The sample had a boiling temperature of 33.8°C at 40 torr during reduction. The sample became cloudy at ~30 percent WVR, with nucleation occurring at ~41 percent WVR.

A portion of the 50 percent WVR product was removed. Half was cooled to room temperature and added to the archive sample of 106AN in a 1:2 102AW:106AN ratio. The other half was added, in the same ratio, to another portion of 106AN, but while the 102AW was at temperature (33.8°C). Both "mixtures" had two layers; the 102AW sample on top. The cooler sample formed phosphate needles at the interface. The warm sample had no precipitation, and eventually appeared to diffuse into a single phase.

The remainder of the sample was concentrated further to a total of 55 percent WVR. The viscosity of the 55 percent product was 2 cps at 50°C, and 3 cps at 20°C. The material was then further reduced to a total WVR of 65 percent. The material, at that point, immediately "burped", turning into "green goo".

The analytical data pertaining to the composition of the 102AW feeds are shown in Table III. The waste appears to be a dilute customer waste. Analyses are generally consistent, indicating that the samples are, relatively, the same. At no time were organics visible, even after a volume reduction of 67 percent, or mixing with the 106AN samples.

The "mixtures" (102AW and 106AN mixtures) were shaken after approximately one week. The solids at the interface were a hard, crystalline layer. The solids were broken up and settled to the bottom, with no apparent increase in bulk volume.

Rockwell International

E. G. Gratny
Page 3
September 22, 1983

The entire volumes of samples were utilized to gather the data presented in this letter. Therefore no further work is planned. Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ/pjm

cc: J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham JSB
K. G. Carothers
P. J. Certa
R. E. Haaland
D. L. Herting
K. P. Nelson
M. C. Teats
R. D. Van Meter
D. G. Wilkins
R. D. Wojtasek
File Code WB621
[redacted]

TABLE I

PRESSURE VS. TEMPERATURE OF TANK 102AW WASTE

CUSTOMER WASTE, R7811, 4' BELOW SURFACE

% WVR	PRESSURE (torr)	Temperature °C/°F
0	40	33.8/92.8
	60	41.0/105.8
	80	46.6/115.8
10	40	34.0/93.4
	60	41.0/105.8
	80	46.8/116.2
20	40	34.0/93.6
	60	41.0/105.8
	80	46.8/116.2
20	40	34.0/93.6
	60	41.0/105.8
	80	46.8/116.0
30	40	34.0/93.6
	60	41.0/105.8
	80	46.8/116.4
38.5	40	Nucleation
40	40	34.4/94.0
	60	41.2/105.6
	80	47.0/116.8
50	40	34.4/94.0
	60	41.6/107.0
	80	47.0/116.8
60	40	35.6/95.2
	60	42.6/108.6
	80	48.2/118.6

TABLE II

VISCOSITY VS. TEMPERATURE, R7811

50% WVR PRODUCT

Temperature (°C)	Viscosity (cps)
26	5
35	3
47	2

TABLE III

CHEMICAL COMPOSITION OF TANK 102AW FEEDS

CUSTOMER WASTE, RUN 83-6

Component	Concentration (Moles/Liter) 4' Below	2' Above
Al^{+3}	0.0121	0.0119
OH^-	0.045	0.0293
NO_2^-	0.036	0.046
NO_3^-	0.0827	0.0818
PO_4^{-3}	0.231	0.279
SO_4^{-2}	0.0169	0.0014
CO_3^{-2}	NA*	NA
TOC (g/L)	0.69	0.74
Cs^{137} (μCi/L)	8.89×10^3	9.02×10^3
Sr^{90} (μCi/L)	2.14×10^{-2}	2.39×10^{-2}
Pu (g/L)	**	**
SpG	1.015^4	1.021^2
$\%H_2O$	96.0	95.6

*Not available.
**Below detection limit.

Internal Letter

Rockwell International

Date. November 28, 1983

No. 65453-83-297

TO: (Name, Organization, Internal Address)
. E. G. Gratny
. Process Engineering
. 2750E/A100/200E

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Chemical Laboratory Unit
. 222S/MO-037/200W
. 3-1571

Subject. . Chemical Composition of Tank 106AN Waste (Run 84-1)

Two waste samples from Tank 106AN were received by the Chemical Laboratory Unit (CLU). The waste was to be used in evaporator run 84-1. Tank Farm and Evaporator Process Control (TFEPC) personnel initially requested viscosity data, chemical data, and boildown data. The boildown data request was subsequently cancelled.

Both samples, 8501 (surface) and 8500 (six foot), were at 50°C when received by CLU. They were amber in color, with no visible solids. Aliquots of each were subjected to viscosity versus temperature determinations, with the data shown in Table I. After completion of viscosity determinations, aliquots were taken and prepared for chemical analyses. The analytical data are shown in Table II.

The remainder of each of the samples was returned to the 50°C water bath. With the sample bottles capped, each sample was allowed to cool to room temperature (24°C). Solids did not precipitate. Each sample bottle was opened to the air. No change was observed in the deeper sample, but solids immediately formed in the surface sample. Approximately 25 volume percent solids were observed. However, after two days, the solids were no longer present. Since the solids appeared to be sodium phosphate (long needles), they either melted or redissolved into the solution.

Both samples are in our archive. Please contact me if you have further need for the samples (further work) or if you have any questions or comments regarding these data.

M. T. Jansky
Senior Chemist

MTJ/rr

cc: J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham JSB
K. G. Carothers
P. J. Certa
R. A. Haaland
D. L. Herting
L. H. Rodgers
M. C. Teats
R. A. VanMeter
R. D. Wojtasek
[redacted]
File Code WB53G

TABLE I

TEMPERATURE VERSUS VISCOSITY OF TANK 106AN WASTES
(Run 84-1)

Temperature (°C)	RPM	Viscosity (Cps)* 8501/Surface	8500/6 foot
5	60	8	-
	30	5	
10	60	5	-
	30	**	
20	60	2	4
30	60	**	2

*Brookfield LVT spindle viscometer, #2 spindle.

**Too low to determine.

TABLE II

CHEMICAL COMPOSITION OF TANK 106AN WASTE
(Run 84-1)

Component	Concentration 8501/Surface	8500/6 foot
Al^{+3} (M)	0.027	0.0355
OH^- (M)	0.097	0.102
NO_2^- (M)	0.082	0.100
NO_3^- (M)	0.146	0.197
CO_3^{-2} (M)	0.0398	0.0492
TOC (g/L)	1.45	1.61
PO_4^{-3} (M)	0.370	0.388
SO_4^{-2} (M)	0.0031	0.0034
Cs^{137} (μCi/L)	1.013×10^3	1.34×10^3
Sr^{90} (μCi/L)	28.71	6.56
Pu (g/L)	2.32×10^{-7}	1.87×10^{-7}
Co^{60} (μCi/L)	-	8.02

496

Internal Letter

Rockwell International

Date November 28, 1983

No. 65453-83-299

TO: (Name, Organization, Internal Address)
- E. G. Gratny
- Process Engineering
- 2750E/A100/200 E

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Chemical Laboratory Unit
- MO-037/200 W
- 3-1571

Subject: Laboratory Data for Evaporator Run 84-2

Two samples from Tank 102AW were recently sent to the Chemical Laboratory Unit (CLU). The samples, numbers R8555 and R8556, were taken from the surface of the waste and from six feet below the surface, respectively. The surface sample was an amber liquid with a trace of gray solids on the bottom of the sample bottle. The deeper sample was also an amber liquid, but contained approximatley 25 volume percent settled, dark fluffy solids. The solids visually looked like iron hydroxide.

Aliquots of each slurry were taken, and specific gravities of the various components measured. The specific gravity data are shown in Table I. Aliquots of the supernatants were analyzed, with the analytical data presented in Table II.

A batch boildown was conducted on the surface sample. Pressure versus temperature data are shown in Table III. The material would foam when subjected to reduced pressure. However, once reduced from atmospheric, the foaming dissipated. The sample was intermittently cooled to room temperature (while stirring) to observe viscosity increase or nucleation. None was observed up to 60 percent waste volume reduction (WVR). The sample instantaneously nucleated at 75 percent WVR.

A second boildown was conducted on the deep sample. The temperature, during the boildown, was fluctuating quite a bit. Any changes in pressure caused the material to "foam"in the vessel, probably due to surface tension properties of the mixture because of the solids. The pressure/temperature data are shown in Table IV. Although the deep sample was completely opaque due to the suspended solids, nucleation was observed at 75 percent WVR.

Both samples nucleated at 75 percent WVR. Homogenizing the tank contents, by efficient mixing, should reduce any "foaming" that may be encountered when processing the waste.

Please call if you have any questions or comments regarding this work.

M. T. Jansky
Senior Chemist

MTJ:gij

Attachments

cc: J.F. Albaugh
R.B. Bendixsen
J.S. Buckingham JSB
K.G. Carothers
P.J. Certa
M.I. Fineman
R.A. Haaland
D.L. Herting
H.R. Risenmay
L.H. Rodgers
M.C. Teats
R.A. Van Meter
R.D. Wojtasek
[redacted]
File: WB

Table I

SPECIFIC GRAVITIES OF TANK 102AW WASTES

(Run 84-2)

	#8555 (Surface)	#8556 (6 Feet)		
	"slurry"	slurry	supernatant	solids*
sp.6.	1.0219	1.0315	1.0283	1.124

*Bulk density of centrifuged solids, includes interstitial liquor.

Table II

COMPOSITION OF TANK 102AW WASTE

(Run 84-2)

Component	Concentration	
	8555 (Surface)	8556 (6 Feet)
Al^{+3} (M)	0.0021	0.0055
OH^- (M)	0.034	0.041
NO_2^- (M)	0.016	0.032
NO_3^- (M)	0.013	0.043
CO_3^{-2} (M)	0.011	0.0213
TOC (g/L)	0.79	0.98
PO_4^{-3} (M)	0.191	0.189
SO_4^{-2} (M)	*	*
Cs^{137} (μCi/L)	2.82×10^3	8.80×10^4
Sr^{90} (μCi/L)	0.823	7.65
Pu (g/L)	3.05×10^{-6}	2.66×10^{-7}

*Below detection limits.

Table III

PRESSURE VERSUS TEMPERATURE DATA FOR 102AW FEED

RUN 84-1/R8555/SURFACE

% WVR	Temperature (°C/°F)	Pressure (torr)
0	33.4/92.4	40
	41.4/106.6	60
	47.0/116.8	80
10	33.6/92.4	40
	41.4/106.6	60
	46.8/116.2	80
20	33.6/92.4	40
30*	33.8/93.0	40
	41.4/106.6	60
	46.8/116.2	80
40	33.6/92.6	40
50*	34.2/93.6	40
	41.2/106.2	60
	64.8/116.8	80
60*	34.2/93.8	40
	41.2/106.2	60
	47.0/116.8	80
70	34.2/93.8	40
	Material getting thicker Brown, insoluble globs (organic) showing up	
75	∿35.6	40
	Instantaneous Nucleation	

*After P/T data, sample cooled to room temperature (25°C) with stirring. No apparent nucleation or significant increase in viscosity observed.

Table IV

PRESSURE VERSUS TEMPERATURE DATA FOR 102AW FEED

RUN 84-1/R8556/DEEP

% WVR	Temperature (°C/°F)	P (torr)
0*	36.0/97.0	40
	42.2/108.0	60
	47.4/117.8	80
10	36.0/97.0	40
20	36.0/96.8	40
30	36.0/97.0	40
40**	35.0/95.6	40
	42.2/108.0	60
	48.0/118.0	80
50***	35.0/95.6	40
	42.6/108.4	60
	48.0/118.6	80
55	35.0/Thicker???	40
60***	35.2/96.0	40
	42.4/108.0	60
	48.0/118.6	80
70	Thicker	40
75	Nucleation	

*Temperature fluctuating.
**Temperature seems to have stabilized.
***After P/T data, sample cooled to room temperature (25°C) with stirring. No apparent nucleation or significant increase in viscosity observed.

Internal Letter

Rockwell International

Date: April 26, 1983

No. 65453-83-126

TO: (Name, Organization, Internal Address)
.K. G. Carothers
.Waste Management Process Technology Ut
.2750E/A204/200 East

FROM: (Name, Organization, Internal Address, Phone)
. D. L. Herting
. Separations Process Development Unit
. 222-S/MO-037/200 West
. 3-2532

Subject: .Flash Point of Turco Oil

The following information appeared in the Weekly Report for the period ending June 10, 1981, J. S. Buckingham to L. C. Brown. The work was performed by myself and K. J. Patterson.

Neutralization to pH 10 of 150g of Turco 4512-14A at 70°C gave 4.8 g of an immiscible dark oil phase. Therefore, the Turco is at least 3.2% by weight insoluble oil. The oil density was about 1.0 g/mL. An annual shipment of 500,000 gallons of customer waste (6% by weight Na_2HPO_4) would include at least 1100 gallons of oil.

Flash point determinations were made on light and dark samples of Turco oil. (The light sample was obtained from low temperature Turco neutralization, the dark sample from high temperature neutralization. Neither sample could be ignited with a propane flame up to 200°C. Differential thermal analysis (DTA) spectra of the two samples showed no exotherms in the range of 22° to 500°C.)

D. L. Herting
Chemist

DLH/naj

cc:

J. S. Buckingham
R. E. Haaland
M. T. Jansky
[redacted]
File Code: WB
Letterbook

502

Internal Letter

Rockwell International

Date: April 26, 1983

No. 65453-83-127

TO: (Name, Organization, Internal Address)
K. G. Carothers
Waste Management Process Technology Ut
2750E/A204/200 East

FROM: (Name, Organization, Internal Address, Phone)
J. R. Jewett
Separations Process Development Unit
222-S/MO-037/200 West
3-1972

Subject: Separable Oil from TURCO Inhibited Phosphoric Acid

In the maintenance of N-reactor, UNC uses large amounts of inhibited phosphoric acid purchased from TURCO Products, Carson, CA. During use, this material becomes contaminated, and has normally been disposed to underground storage (UGS) by Rockwell.

The pH specification for UGS has recently been raised. When caustic is added to the inhibited phosphoric acid to reach the new specification, a separate oil layer is formed. This layer did not form under the old specification.

Thermogravimetric analyses were performed on a sample of the oily layer. In one run (Figure 1) the temperature was increased at 2°C/min; in the other, (Figure 2) by 10°C/min. These show that 65% to 70% of the layer is quite volatile. The initial slope indicates that the evaporation rate is about 5g/da per square foot of surface, even at 30°C. A boiling point for the component cannot be established from this data, but it is $\geq$ 143°C.

Most of the remaining material volatilizes at temperatures >200°C, but ≈4% remained, even at 800°C. The oil sample provided was not well separated from the aqueous material. Some flocculent solid material was also present. The different proportions of the components determined in the two samples are probably due to sample inhomogeneity.

This analysis is all that was requested for this material. If you need further work, let me know.

J. R. Jewett
Chemist

JRJ/naj

Attachments

cc:

J. S. Buckingham
D. A. Reynolds
L. H. Rodgers
R. E. Haaland
File: WB621
[redacted]
Letterbook

Figure 1

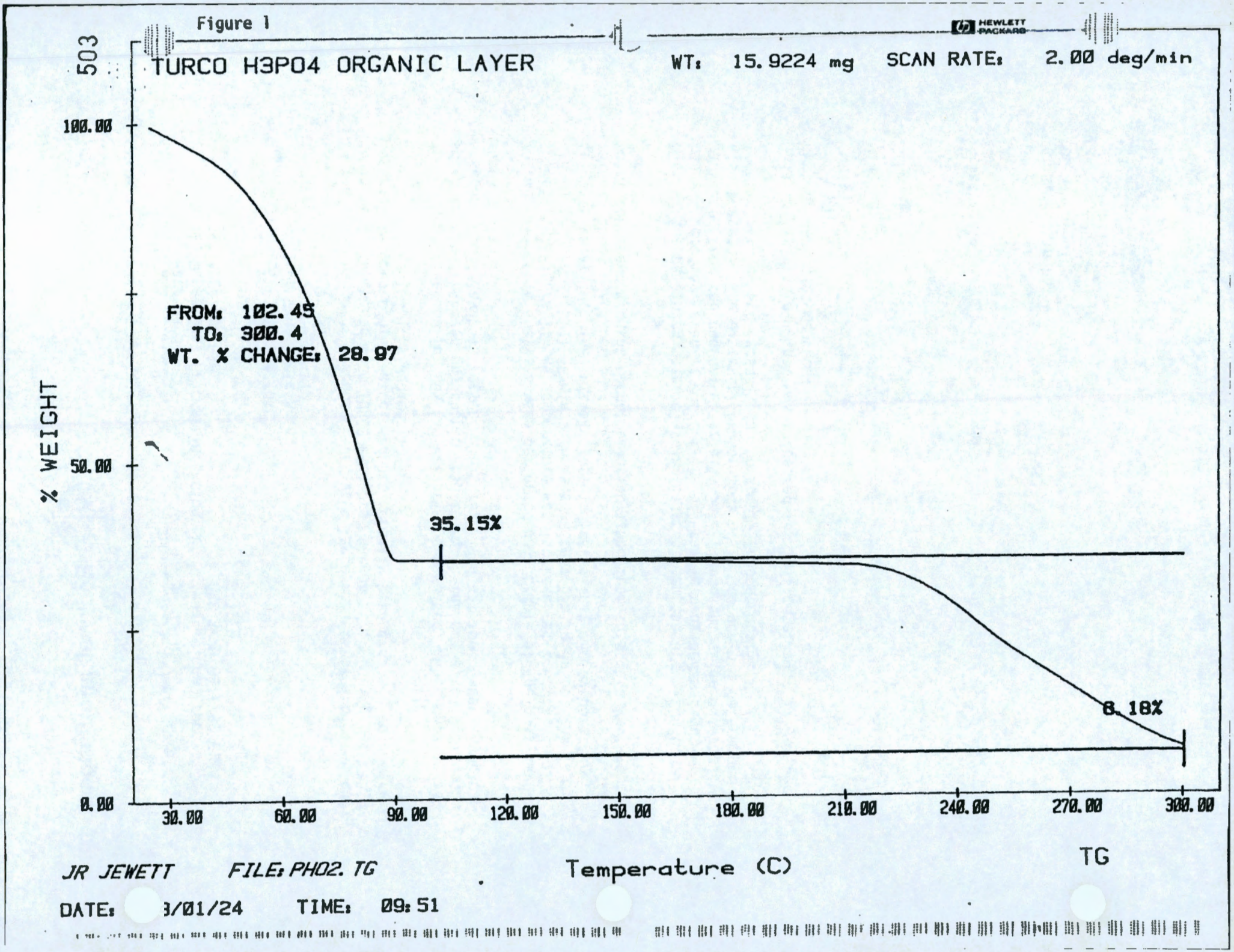
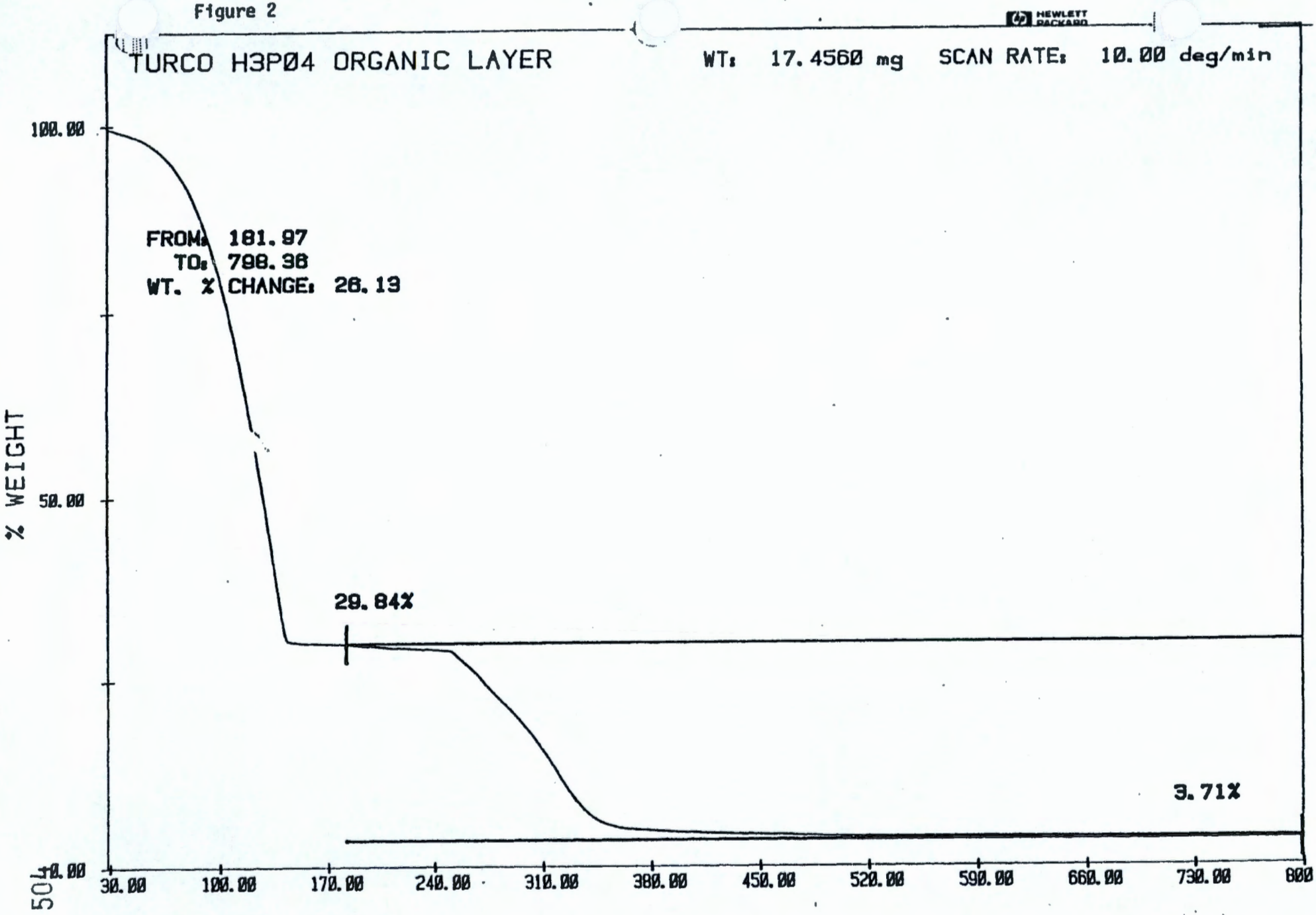

503
TURCO H3PO4 ORGANIC LAYER
WT: 15.9224 mg
SCAN RATE: 2.00 deg/min
100.00
50.00
0.00
% WEIGHT
FROM: 102.45
TO: 300.4
WT. % CHANGE: 28.97
35.15%
8.18%
30.00
60.00
90.00
120.00
150.00
180.00
210.00
240.00
270.00
300.00
Temperature (C)
TG
JR JEWETT
FILE: PH02.TG
DATE: 3/01/24
TIME: 09:51

Figure 2



JR JEWETT FILE: PHO10. TG

DATE: 83/01/25 TIME: 07:58

Internal Letter

Rockwell International

Date: May 5, 1983

No. 65453-83-135

TO: (Name, Organization, Internal Address)
R. E. Haaland
Process Design
2750E/A227/200 East

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Separations Process Development Unit
222-S/MO-037/200 West
3-1571

Subject: Laboratory Support for Customer Waste
Waste Volume Reduction

Refs: (1) Letter, #65411-83-088, dated April 18, 1983, R. E. Haaland to M. T. Jansky, "Synthetic Waste Volume Reduction Study for N Reactor Decontamination Waste"

(2) Letter, #65453-83-102, dated April 7, 1983, M. T. Jansky to P. J. Certa, "Tank 102AW Samples: R5001 and R5002"

As per your request in Reference 1, the Separations Process Development Unit (SPDU) performed several laboratory-scale batch boildowns using synthetic customer waste and synthetic tank farm waste. The synthetic customer waste was prepared using TURCO, received from United Nuclear Industries (UNC), with the preparation shown in Table I. The synthetic tank farm waste was prepared based on analytical data for Tank 102AW (Reference 2). The composition of the synthetic waste is shown in Table II.

Originally, three boildowns were requested. The boildowns were to be conducted on solutions using the following UNC:102AW volume ratios: 7.5:1, 1:0, and 7.5:0.8:0.2 (UNC:102AW:water). The requested data are shown in Tables III-V.

At this point, a "new" recipe for customer waste was provided. The "new" recipe is shown in Table VI. The new UNC was used for a boildown, with the data shown in Table VII. A 22:1 UNC:102AW mixture was requested; however, a 9:1 ratio was used instead. Those data are shown in Table VIII.

Yet another boildown was requested, this time using a diluted 102AW synthetic (1:10 102AW:H_2O). The requested ratio of UNC to diluted 102AW was 22:1. Those data are shown in Table IX. Table X contains data (requested for "confirmatory purposes") pertaining to a 7.5:1 UNC:undiluted synthetic 102AW.

A boildown on a 22:0.5:0.5 mixture of UNC:Actual 102AW waste:water was requested, with the data shown in Table XI. The data are very similar to studies using the synthetic. Also, Table XII contains data from a UNC:synthetic 102AW ratio of 22:1.

In all cases, the final boildown product was a light-colored, creamy material which solidified when cooled even a few degrees. The cooled product definitely was a crystalline mass, with long, needle-like crystals; sodium phosphate crystals. The creamy material was not visually crystalline. After allowing the boildown products to sit at room temperature for several days, only minute traces of organic oil were seen in some products; none was seen in most of the final products.

Rockwell International

No additional data were requested. If further work is needed, please call.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachments

cc:

J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
K. G. Carothers
P. J. Certa
D. L. Herting
L. H. Rodgers
R. D. Wojtasek
[redacted]
File Code: WB621
Letterbook

Table 1

Preparation of Synthetic UNC Waste

1. 30 ml of Turco 4512-A solution is mixed with 330 ml of water.
2. Product of Step 1 is mixed with 425 ml of water.
3. Using a 19M aqueous solution of NaOH, the product of Step 2 is neutralized to a pH of 12 at 20 - 25°C.
4. 0.75g $NaNO_2$ is dissolved into the neutralized solution.
5. Product of Step 4 is mixed with 167 ml of water.

Table II

Composition of Synthetic 102AW Waste

Component	Concentration (moles/Liter)
$NaAlO_2$	0.45
NaOH	0.66
$NaNO_2$	0.70
$NaNO_3$	1.38
Na_2CO_3	0.3
Na_2SO_4	0.028
Na_3PO_4	0.022
TOC* (g/L)	3

*TOC is Total Organic Carbon

Table III

UNC: 102AW = 7.5:1

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
0	40	36.6	
	50	39.6	
	80	48.2	
5	40	35.8	
	50	39.6	5
	80	48.2	
10	40	36.4	
	50	40.6	13
	80	48.2	
15	40	36.8	
	50	39.8	27
	80	48.0	
20	40	36.0	
	50	40.2	40
	80	48.2	
25	40	36.4	
	50	39.8	50
	80	48.2	
30	40	36.2	
	50	40.2	59
	80	48.2	
35	40	35.6	
	50	39.6	54
	80	48.2	
40	40	35.8	
	50	40.2	75
	80	48.4	
45	40	35.6	
	50	40.2	86
	80	48.8	
50	40	36.0	
	50	39.6	94
	80	48.8	

Table III (continued)

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
55	40	36.0	
	50	39.6	103
	80	48.8	
60	40	37.0	
	50	40.2	114
	80	49.0	
65*	40		
	50	39.2	127
	80		

Product Data

Slurry Viscosity (cps)	Solids settled too rapidly.		
Slurry SpG (40°C)	=	1.198	
Volume % Settled Solids	.40°C	=	33
	.Room Temperature	=	74

*Nucleation

Table III - (Continued)

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
60	40	35.6	
	50	39.2	115
	80	47.8	
65	40	35.8	
	50	39.6	123
	80	48.6	
70*	40	35.8	
	50	40.2	133
	80	48.4	
75	50	39.2	143

Product Data

Slurry Viscosity (cps) (40°C) = 9

Slurry SpG (40°C) = 1.256

*Nucleation occurred at 68.5% WVR

Table IV

UNC: 102AW = 1:0

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
0	40	35.6	
	50	39.4	
	80	47.8	
5	40	36.2	
	50	39.6	3
	80	48.2	
10	40	35.6	
	50	40.2	14
	80	48.4	
15	40	36.6	
	50	39.4	24
	80	48.2	
20	40	36.2	
	50	39.8	34
	80	48.2	
25	40	36.0	
	50	39.6	43
	80	48.2	
30	40	36.0	
	50	39.2	53
	80	47.8	
35	40	35.2	
	50	39.6	64
	80	48.0	
40	40	35.8	
	50	39.8	73
	80	48.0	
45	40	35.6	
	50	39.2	82
	80	47.8	
50	40	35.4	
	50	39.2	94
	80	48.0	

Table V

UNC: 102AW: H_2O = 7.5: 0.8:0.2

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
0	40	36.4	
	50	40.4	
	80	48.6	
5	40	36.2	
	50	40.8	7
	80	48.4	
10	40	36.6	
	50	40.4	18
	80	48.4	
15	40	36.4	
	50	39.6	31
	80	48.4	
20	40	36.4	
	50	39.8	41
	80	48.4	
25	40	36.4	
	50	40.6	51
	80	48.4	
30	40	36.6	
	50	40.0	63
	80	48.0	
35	40	36.4	
	50	40.0	74
	80	48.2	
40	40	36.4	
	50	40.2	83
	80	48.4	
45	40	36.8	
	50	40.6	95
	80	48.6	
50	40	36.2	
	50	39.6	117
	80	48.8	

Table V - (Continued)

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
55	40	36.6	
	50	40.0	128
	80	48.6	
60	40	36.8	
	50	40.8	138
	80	48.6	
65	40	36.8	
	50	40.2	149
	80	49.2	
70	40	36.8	
	50	41.4	159
	80	49.2	
78.4*	50	43.8	167

Product Data

Slurry Viscosity (cps)** Solids Settled Rapidly

Slurry SpG (40°C) 1.312

* Nucleation

**Product became very thick; however, with stirring it became pourable.

Table VI

"New" Recipe for Synthetic UNC Waste

1. Mix together: 30 mL Turco
   330 mL H_2O
   425 mL H_2O

2. Neutralize (1) with 46 mL 19M NaOH.

3. Add 0.75 g $NaNO_2$ to (2).

4. Add 167 mL H_2O to (3).

5. *Decant organic layer.

*Note that no organic layer was observed.

Table VII

"New" UNC: 102AW = 10

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
0	40	36.4	
	50	40.2	
	80	48.2	
10	40	35.2	
	50	40.0	10
	80	48.2	
20	40	36.4	
	50	40.2	
	80	48.0	
30	40	35.2	
	50	39.8	
	80	48.0	
40	40	35.6	
	50	39.8	≈35
	80	47.8	
50	40	36.6	
	50	39.6	43
	80	47.4	
60	40	35.6	
	50	40.6	55
	80	48.2	
70	40	35.2	
	50	39.4	66
	80	47.8	
76*	50	40.6	72
82	50	41.0	

Product Data

Slurry Viscosity (cps) (40°C) = 10

Slurry SpG (40°C) = 1.217

*Nucleation

Table VIII

UNC: 102AW = 9:1

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
0	40	36.6	
	50	40.0	
	80	48.0	
5	40	36.0	
	50	40.0	3
	80	48.2	
10	40	35.8	
	50	40.6	10
	80	48.2	
15	40	36.2	
	50	40.2	15
	80	47.8	
20	40	35.6	
	50	40.0	20
	80	47.8	
25	40	35.6	
	50	39.6	26
	80	47.8	
30	40	35.8	
	50	39.8	32
	80	47.4	
35	40	36.2	
	50	39.6	38
	80	47.8	
40	40	36.2	
	50	40.2	43
	80	48.0	
45	40	36.8	
	50	39.8	49
	80	48.0	
50	40	36.6	
	50	39.2	60
	80	47.6	

Table VIII - (Continued)

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
55	40	35.0	
	50	39.4	66
	80	48.2	
60	40	37.6	
	50	40.0	71
	80	47.8	
65	40	36.6	
	50	39.6	77
	80	48.4	
70*	40	37.0	
	50	40.6	81
	80	48.8	
75	40	36.8	
	50	41.2	90
	80	48.4	
77.3	50	41.2	96

Product Data

Slurry Viscosity (cps)**(40°C)	16
Slurry SpG (40°C)	1.269

*Nucleation

**Product had "heavy" solids that dropped rapidly.

Table IX

UNC: Diluted 102AW = 22:1

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
0	40	36.4	
	50	40.6	
	80	48.4	
5	40	36.8	
	50	40.6	5
	80	48.6	
10	40	37.2	
	50	40.6	17
	80	48.2	
15	40	35.2	
	50	40.2	28
	80	47.8	
20	40	36.6	
	50	40.4	37
	80	48.0	
25	40	36.6	
	50	40.0	46
	80	48.0	
30	40	35.8	
	50	40.2	57
	80	47.6	
35	40	37.0	
	50	40.4	67
	80	47.4	
40	40	35.0	
	50	39.2	71
	80	48.2	
45	40	36.8	
	50	39.8	79
	80	47.8	
50	40	35.6	
	50	39.4	87
	80	48.2	

Table IX - (Continued)

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
55	40	36.4	
	50	40.2	93
	80	47.8	
60	40	36.4	
	50	39.2	99
	80	47.2	
65	40	36.2	
	50	39.6	105
	80	48.2	
70	40	35.6	
	50	39.0	114
	80	48.2	
72*	50	39.4	119
75	40	36.6	
	50	39.2	121
	80	48.0	
80	50	39.6	127

Product Data

Slurry Viscosity (cps) (40°C)	12
Slurry SpG (40°C)	1.212

*Nucleation

Table X

UNC: 102AW = 7.5:1

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
0	40	35.6	
	50	40.0	
	80	48.0	
5	40	36.6	
	50	40.2	5
	80	48.0	
10	40	36.2	
	50	40.6	8
	80	48.0	
15	40	36.6	
	50	40.0	12
	80	48.0	
20	40	36.6	
	50	40.0	15
	80	--	
62*	40	36.6	
	50	40.6	43
	80	48.8	
70	40	37.4	
	50	40.0	
	80	48.8	
75	50	41.2	68

Product Data

Slurry Viscosity (cps)	Solids dropped too rapidly
Slurry SpG (40°C)	1.737

*Nucleation

Table XI
Hot Boildown
UNC: Actual 102AW:H_2O = 22:0.5:0.5

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
0	40	34.2	
	50	37.4	
	80	46.6	
10	40	34.6	
	50	38.2	5
	80	47.2	
20	40	34.2	
	50	37.8	17
	80	47.0	
30	40	34.8	
	50	38.6	27
	80	47.2	
40	40	34.8	
	50	38.4	38
	80	47.6	
50	40	35.2	
	50	39.0	49
	80	46.6	
60	40	35.2	
	50	38.2	58
	80	48.4	
64*	50	38.8	73
86	50	39.8	81

Product Data

Slurry Viscosity (cps)	Solids dropped too rapidly
Slurry SpG (40°C)	1.249

*Nucleation

Table XII

UNC: 102AW = 22:1

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
0	40	36.4	
	50	40.2	
	80	47.8	
5	40	36.8	
	50	40.2	4
	80	48.2	
10	40	--	
	50	39.6	12
	80	48.0	
15	40	36.6	
	50	39.2	18
	80	48.2	
20	40	35.2	
	50	39.4	27
	80	48.0	
25	40	36.8	
	50	39.2	33
	80	48.2	
30	40	36.6	
	50	39.8	40
	80	48.0	
35	40	35.6	
	50	39.2	48
	80	48.0	
40	40	36.4	
	50	39.6	53
	80	48.0	
45	40	35.8	
	50	39.2	59
	80	48.0	
50	40	35.8	
	50	39.6	68
	80	47.8	

Table XII - (Continued)

% WVR	Pressure (torr)	Temperature(°C)	Elapsed Time (minutes)
55	40	36.4	
	50	39.2	72
	80	48.2	
60	40	--	
	50	39.8	79
	80	--	
65	50	39.8	83
70	50	39.8	88
72*	50	40.0	89
75	50	40.2	92
79	50	40.8	98

Product Data

Slurry Viscosity (cps) (40°C)	23
Slurry SpG (40°C)	1.24

*Nucleation

Internal Letter

Rockwell International

Date: May 13, 1983

No. 65453-83-143

TO: (Name, Organization, Internal Address)
. P. J. Certa
. Process Engineering
. 2750E/A106/200 East

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Separations Process Development Unit
. 222-S/MO-037/200 West
. 3-1571

Subject: . Thermal Analysis of Synthetic Customer Waste

As per a verbal request, the Separations Process Development Unit (SPDU) examined the "aqueous phase" of neutralized TURCO using thermal analysis. The temperature range from ambient to 500°C did not display an exotherm, using differential thermal analysis (DTA, see attachment).

We hope to utilize actual customer waste to verify these results. Please let me know when a sample is available.

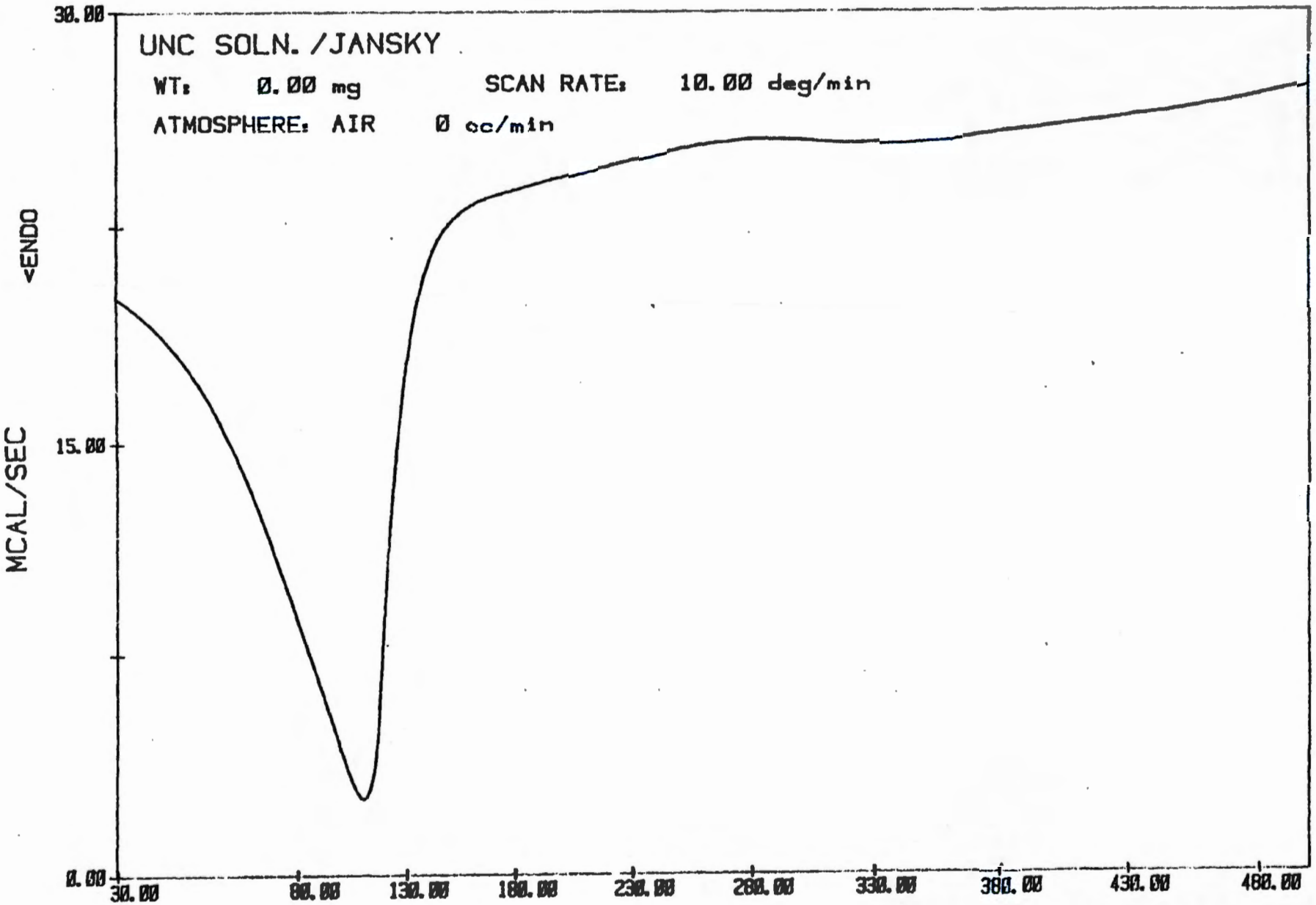
M. T. Jansky
Senior Chemist

MTJ/naj

Attachment

cc:

J. S. Buckingham
K. G. Carothers
R. E. Haaland
D. L. Herting
L. H. Rodgers
R. D. Wojtasek
File Code: WB621
[redacted]
Letterbook



RC FILE: QSAVE.DT

DATE: 93/05/03 TIME: 14:09

Internal Letter

Rockwell International

Date August 23, 1983

No. 65453-83-216

TO: (Name, Organization, Internal Address)
R. E. Haaland
Process Design
2750E/A227/200 East

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Chemical Laboratory
222-S/MO-037/200 West
3-1571

Subject: Laboratory-Scale Boildown of Actual Customer Waste

You have recently requested, verbally, that the Chemical Laboratory Unit (CLU) perform a batch boildown on actual customer waste from UNC. The purpose of this letter is to outline CLU's understanding of your verbal request to insure that the proper data are obtained. The procedure is described below:

1. In the following ratios: to 785 mL of TURCO (from UNC and AL) add 54 mL of 19M NaOH. Allow the mixture to equilibrate at 32°C, also allowing solids to settle.

2. Decant the supernatant, let cool to room temperature, add 0.75 grams $NaNO_2$, mix with 167 and H_2O. This provides approximately one liter of feed.

3. Add the UNC customer waste solution (from part #2) to actual 102AW heel (which CLU has archived). The volume ratio of UNC:102AW should be 22:1.

4. Perform a batch boildown, at 50 torr, to a waste volume reduction (WVR) of 40 percent. Observe temperature versus time versus WVR, nucleation point, viscosity versus temperature of product, volume percent solids, and other physical observations. Save product for potential future use.

Please indicate your concurrence of this work by initialing a copy of the letter and returning it to me. Work will commence upon receipt of the initialed letter.

M. T. Jansky
Senior Chemist

MTJ/naj

cc:

R. B. Bendixsen
J. S. Buckingham JSB
K. G. Carothers
P. J. Certa
D. L. Herting
M. J. Kupfer
H. R. Risenmay
L. H. Rodgers
D. G. Wilkins
File Code: WB621
[redacted]
Letterbook

528

Internal Letter

Rockwell International

Date. April 4, 1983

No: . 65453-83-099

TO: (Name, Organization, Internal Address)
.K. M. Hodgson
.Process Design
.2704E/16/200 East

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Separations Process Development Unit
. 222-S/MO-037/200 West
. 3-1571

Subject: .Boildown of Synthetic Current Acid Waste (CAW)

As per your verbal request, the Separations Process Development Unit (SPDU) performed a laboratory-scale, batch boildown on synthetic current acid waste (CAW). The material was supplied by M. J. Kupfer of SPDU. The boildown was conducted at atmospheric pressure, to a waste volume reduction (WVR) of 75 percent. Requested data are shown in Tables I and II.

A second boildown was conducted for comparison and verification of data. The data from the second boildown are shown in Tables III and IV.

Both boildown products were black in color, and extremely viscous at room temperature. The exact chemical composition of the solids was not determined.

Please call if you have any questions or comments regarding this work, of if SPDU may be of additional assistance.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachments

cc:

J. S. Buckingham
D. L. Herting
J. O. Honeyman
M. J. Kupfer
R. J. Thompson
[redacted]
Letterbook

Table I

Boildown of Synthetic CAW

% WVR	Temperature (°C)	Elapsed Time (minutes)
0	Ambient	0
0	103.8[a]	0
5	103.8	8
10	104.2	15
15	104.4	22
20	104.8	29
25	105.4	36
30	105.8	42
35	106.6	49
40	107.4	56
45	108.6	63
50	110.0	69
55	111.8	77
60	114.2	84
63[b]	116.0	88
65	116.8	95
70	120.2	103
75[c]	123.6	112

(a) Atmospheric boiling point

(b) End of shift, started again the next morning

(c) Nucleation. Product started frothing

Table II

Physical and Chemical Properties of Synthetic CAW

	Starting Material*	75% WVR Product	
		50°C	Room Temperature
SpG	1.163	1.593	--
Viscosity (cps)	6	26	165
Al (M)	0.88	**	
NO_3 (M)	4.06	**	

*SpG and viscosity measured at room temperature

**Unavailable

Table III

Synthetic Boildown of Synthetic CAW

% WVR	Temperature (°C)	Elapsed Time (min)
0	Ambient	0
0	103.0*	0
10	103.8	16
20	104.8	28
30	105.6	40
40	107.2	53
50	109.8	68
60	113.6	82
70	119.6	98
74**	122.6	105
76	123.8	108
77.5	--	--

*Atmospheric boiling point

**Froth, black solids

Table IV

Physical and Chemical Properties of Second Boildown Product

	77.5% WVR Product
SpG	1.590 (at ≈60°C)
Viscosity (cps)	40 (at 80°C), ≈320 (at R.T.)
Al (M)	3.83
NO_3 (M)	*

*Unavailable

Internal Letter **Rockwell International** 533

Date. April 8, 1983 No: . 65453-83-105

TO: (Name, Organization, Internal Address)
- M. I. Fineman
- Process Design
- 2750E/A219/200 East

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Separations Process Development Unit
- 222-S/MO-037/200 West
- 3-1571

Subject: . Ammonia Content in Decladding Waste Supernatant

Ref: Letter, February 17, 1983, M. I. Fineman to M. T. Jansky

As you requested in your referenced letter, the Separations Process Development Unit (SPDU) investigated the potential for gaseous ammonia to "flash" during a boildown of synthetic decladding supernatant liquor. We found no reason to believe an explosive mixture formed in the vapor phase above the liquor. Laboratory details are discussed below.

A solution was prepared which was 1.24 moles per Liter (M) ammonium chloride and pH 12. The solution was taken to 40 torr pressure, and then heated to boiling. The solution was concentrated in 5 volume percent increments to a waste volume reduction (WVR) of 50 percent. Each 5 percent increment of condensate was analyzed for ammonia. The final product was analyzed for ammonia as well. Relevant requested data are shown in Tables I and II.

No evidence of an explosive mixture was observed during the experiment, i.e., flashing, bumping, violent eruptions of the liquor. The potential for an explosion is most likely virtually eliminated by (a) the great amount of water vapor above the mixture, and (b) the action of the vacuum rapidly removing gaseous ammonia.

I hope this information will prove useful. Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachments

cc:

J. S. Buckingham
K. G. Carothers
D. L. Herting
D. M. Tulberg
File Code: WB621
[redacted]
Letterbook

Table I

Reduction of NH_3 Concentration in Synthetic Wastes

% WVR	Pressure (torr)	Temperature (°C)	Total Time Elapsed (min)	NH_3 (M)
0	Atmospheric	Ambient	0	1.24
0	40	Ambient	5	1.13
0	40	36.2	10	0.24
50	40	36.0	118	*

*Below detection limits

Table II

Concentration of Ammonia in Condensate

% WVR	NH_3 (M)*	Total time of Boiling (min)
5	0.77	10
10	0.29	18
15	0.28	23
20	0.11	33
25	0.037	39
30	0.008	55
35	0.003	73
40	0.001	89
45	0.001	105
50	0.001	113

*Concentration determined for individual 5 mL aliquots

Internal Letter

Rockwell International

Date. March 23, 1983

No. 65453-83-083

TO: (Name, Organization, Internal Address)
. D. M. Tulberg
. Process Design
. 2750E/A227/200 East

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Separations Process Development Unit
. 222-S/MO-037/200 West
. 3-1571

Subject: . Laboratory Boildowns of Synthetic Decladding Waste Supernatant Liquor

Ref: DSI, dated January 11, 1983, D. M. Tulberg to M. T. Jansky

The referenced DSI was a request for laboratory boildowns on synthetic decladding waste supernatant liquor. The emphasis on the work developed into determining the waste volume reduction (WVR) required to produce (a) 8 M hydroxide in the supernatant and/or (b) 30 volume percent settled solids. The Separations Process Development Unit (SPDU) determined that an 89 percent WVR produced a supernatant liquor which was 7.86 M hydroxide, with the total slurry containing 26 volume percent settled solids. Specific laboratory details are discussed below.

Pilot plant decladding supernatant liquor was supplied by SPDU's Engineering Laboratory. The supernatant had been analyzed by Analytical Laboratories, with the results shown in Table I. Aliquots of the supernatant were concentrated at 60 torr to various WVRs attempting to reach 8 M hydroxide and/or 30 volume percent settled solids. The data are shown in Table II.

The hydroxide data shown in Tables I and II are biased somewhat due to the presence of ammonia in the solution. The exact extent of the bias is not quantified at this time because the specific chemistry is not defined. However, Table III reflects reasonable estimates of "free" hydroxide in the boildown product supernatants. The assumptions made to determine the hydroxide concentrations are as follows:

(1) The initial concentration of hydroxide was 0.64 M (0.90 M reported less 0.26 M NH_3).

(2) The volume percent solids reduces the amount of supernatant accordingly.

The bulk of the ammonia was probably driven off by elevated temperature/reduced pressure by 88% WVR. At 92% WVR, however, hydroxide solids are precipitating and/or the void volume in the settled solids is playing a role in actual volume of liquor.

The particle size distribution of the precipitated solids (88% WVR) was measured, with the average weight percent diameter 10.4 micrometers. Settling rate data were not available due to the extremely rapid settling or the formation of multiple phases (heavy solids that immediately settled, suspended particles, clear supernatant). The small product volumes available were not sufficient to utilize for viscosity determinations.

Rockwell International

D. M. Tulberg
Page 2
March 23, 1983

Another interesting phenomenon was discovered when the various concentrated products were examined using the microscope. Up until 90 percent WVR, the crystal structures were consistent with those of NaF or KF (both cubic, non-distinguishable under the microscope). However, the 92 percent WVR product contained an additional phase. The composition of the additional phase was not determined.

I hope the information will prove useful. Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachments

cc:

R. B. Bendixsen
J. S. Buckingham
K. G. Carothers
R. D. Claghorn
M. I. Fineman
D. L. Herting
R. D. Wojtasek
File Code: WX63G
[redacted]
Letterbook

Table I

Composition of Decladding Supernatant Liquor

Component	Concentration (moles/Liter)
OH^-	0.969
NH_3	0.257

Table II

Waste Volume Reductions of Decladding Supernatant

% WVR	OH^- (M)	% Settled Solids
0	0.90	0
85	5.34	15
88	6.48	18
89	7.86	26
90	9.98	30
92	14	60

Table III

Adjusted WVR/[OH^-] Data

% WVR	Adjusted OH^- (M)
0	0.64
85	5.02
88	6.50
89	7.99
90	9.29
92	20.3

Internal Letter

Rockwell International

Date. March 8, 1983

No. 65453-83-059

TO: (Name, Organization, Internal Address)
. D. A. Reynolds
. Waste Management Process Technology
. 2750E/A110/200E

FROM: (Name, Organization, Internal Address, Phone)
. D. L. Herting
. Separations Process Development
. 222S/MO-037/200W
. 3-2532

Subject: . Solubility Phase Diagram - Interim Report

Reference: SD-WM-DTP-004 (Supporting Document), "Laboratory Test Plan for Hanford Waste Solubility Phase Diagram Study," D. L. Herting, September 17, 1982

This is the first interim report on the laboratory data from the solubility phase diagram study. The report covers solubility of sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$) at three levels of sodium hydroxide (NaOH), two levels of sodium aluminate ($NaAlO_2 \cdot 2H_2O$), and two temperatures (60° and 80°C). Please refer to the laboratory test plan for experimental details (reference). Some minor deviations from the test plan have been necessary; they will be described fully in the final report.

The results to date have been very reproducible, internally consistent, and readily interpretable. Briefly, the major conclusions are:

1) Temperature is the major factor influencing the solubility of $NaNO_3$. Increasing the temperature from 60° to 80°C causes the $NaNO_3$ solubility to increase by 40-50%.

2) Hydroxide concentration has the second-largest effect on $NaNO_3$ solubility. Decreasing the NaOH concentration from 11.3 molal (m) to 8.9 m causes an increase in $NaNO_3$ solubility of roughly 15%. Decreasing NaOH from 8.9 m to 5.3 m has the same effect.

3) Aluminate has a small but detectable effect. Raising the aluminate concentration from 1.2 m to 2.0 m causes a slight decrease in $NaNO_3$ solubility.

4) A large increase in $NaNO_2$ concentration (from about half-saturated to near-saturated) causes a slight <u>increase</u> in $NaNO_3$ solubility. This may be the most surprising result to date.

5) In conclusions 1-4, $NaNO_3$ can be replaced by $NaNO_2$ (and vice-versa) without changing the veracity of any statement.

The data that support these conclusions are shown in Figures 1-4. Each point on the graphs represents one solubility determination; $NaNO_3$

Rockwell International

solubility values are plotted with the symbol "+", and $NaNO_2$ values are plotted with the symbol "O". All of the points on any particular graph were measured at a single temperature and aluminate concentration. The three sets of intersecting lines on each graph represent the three hydroxide concentrations - 11.3 m, 8.9 m, and 5.3 m.

Conclusion 1 is best observed by overlaying Figures 1 and 3, and/or 2 and 4. (Take careful note, when overlaying the figures for comparison, that values of x and y at the origin are not always the same. The scale, however, is constant for all four figures.) With the axes properly aligned, all of the 60° data fall completely under the 80° data. Conclusion 3 is best observed by overlaying Figures 1 and 2, and/or 3 and 4. The aluminate effect appears to be just larger than the scatter in the data. A statistical analysis will be needed to verify the visual conclusion. Conclusions 2 and 4 can be observed directly from the graphs.

The remainder of the phase diagram work is progressing pretty much according to schedule. The problems associated with $NaNO_3/NaNO_2$ solubility measurements at 100°C have been overcome, so a smooth conclusion to that part of the study is expected. The 80°C portion of the aluminate solubility study is nearly complete. The data are not as precise as for the nitrate/nitrite measurements, but are still quite interpretable. In some of the 60° and 100° aluminate studies, the sodium aluminate has been very reluctant to relieve the supersaturation and precipitate. Although we are slightly behind schedule in this area, we are confident that we will catch up before the final laboratory milestone date of May 23.

Please call if you have any questions or comments.

D. L. Herting
Chemist

DLH/pjm

cc: R. B. Bendixsen
J. S. Buckingham
K. G. Carothers
P. J. Certa
M. T. Jansky
L. Jensen
A. M. Liebetrau
L. H. Rodgers
D. G. Wilkins
File: WB
[redacted]
Letterbook

Figure 1

HYDROXIDE EFFECT, 60 C, 1.2 m ALO2

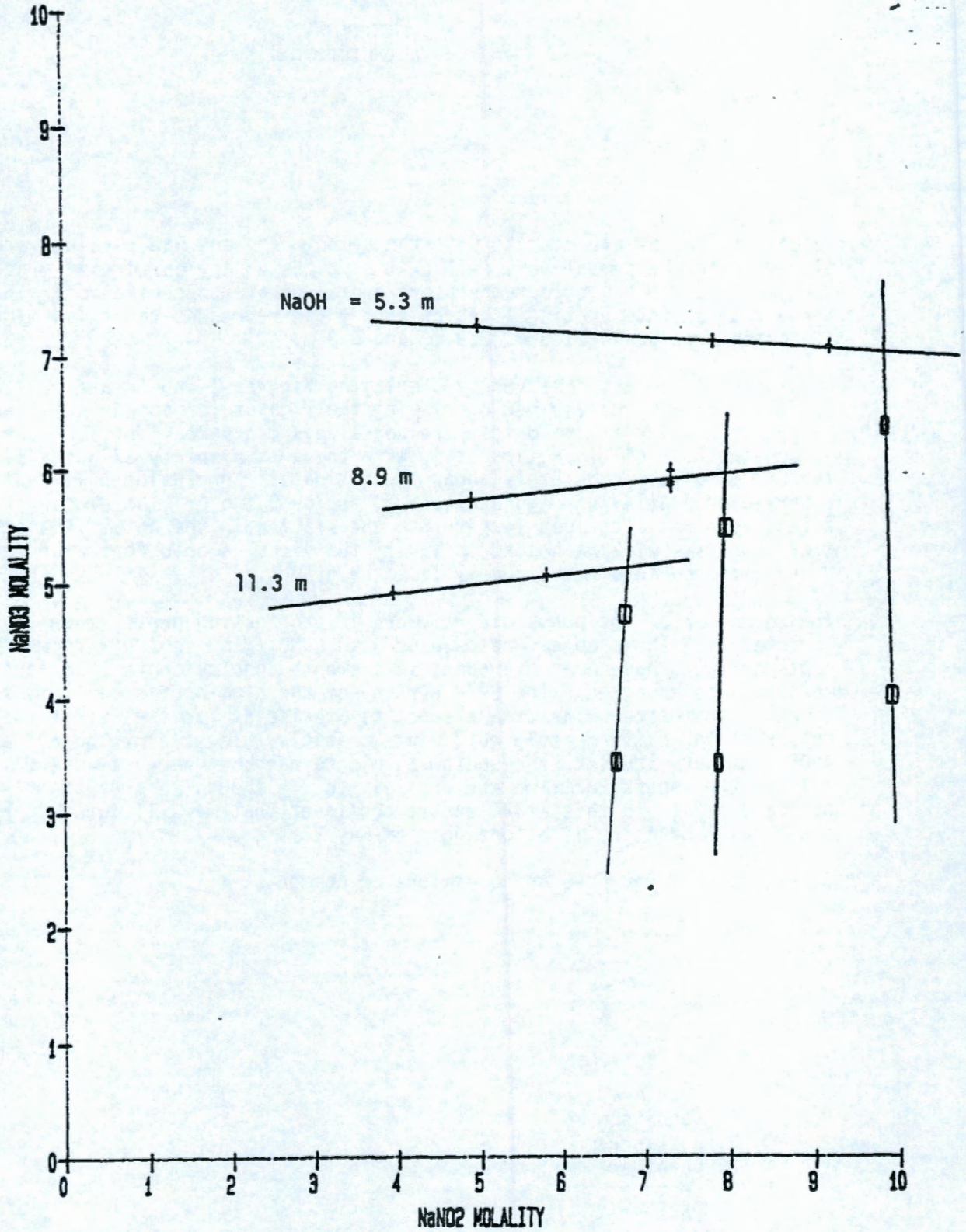


Figure 2

HYDROXIDE EFFECT, 60 C, 2 m AlO2

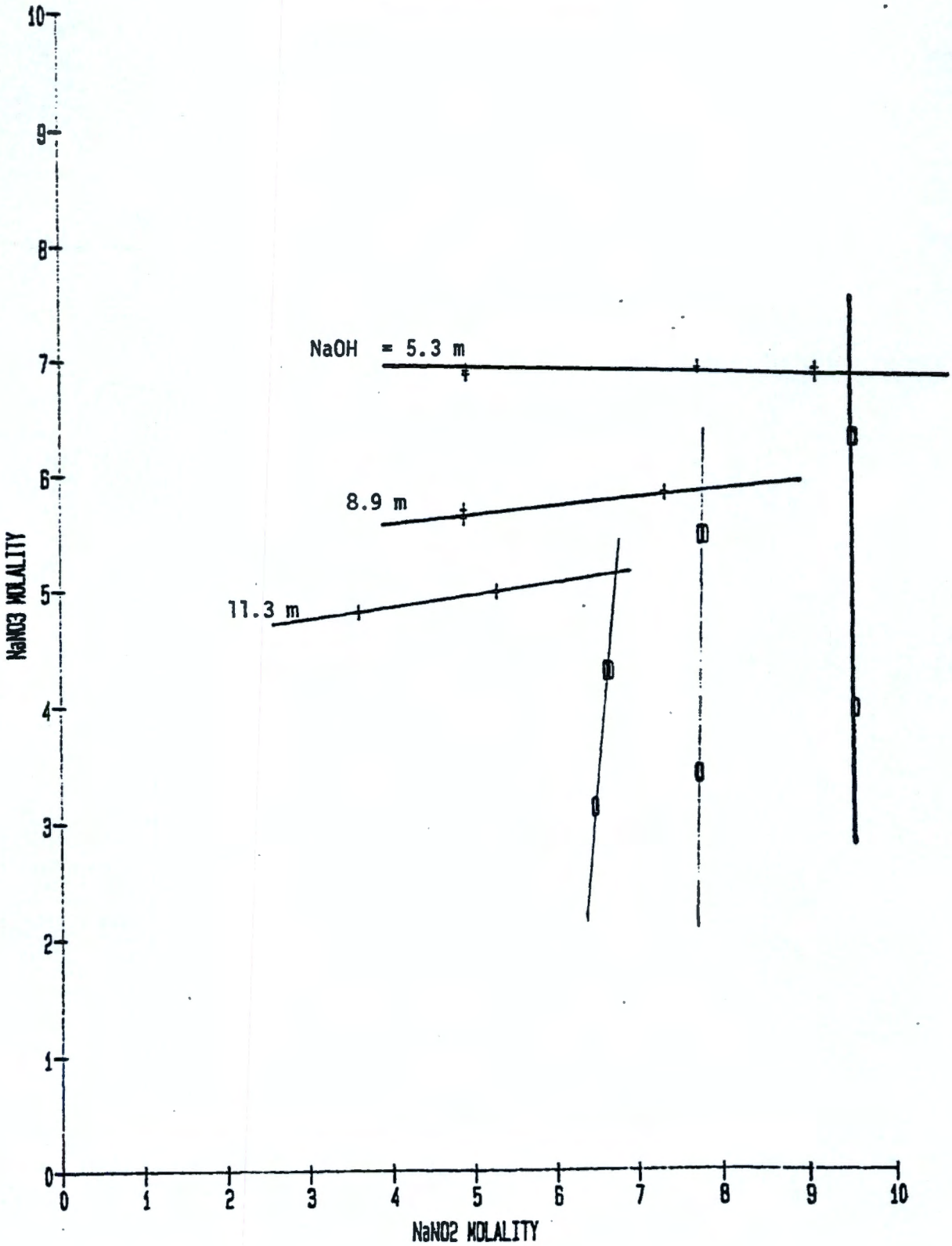


Figure 3

HYDROXIDE EFFECT, 80 C, 1.2 m ALO2

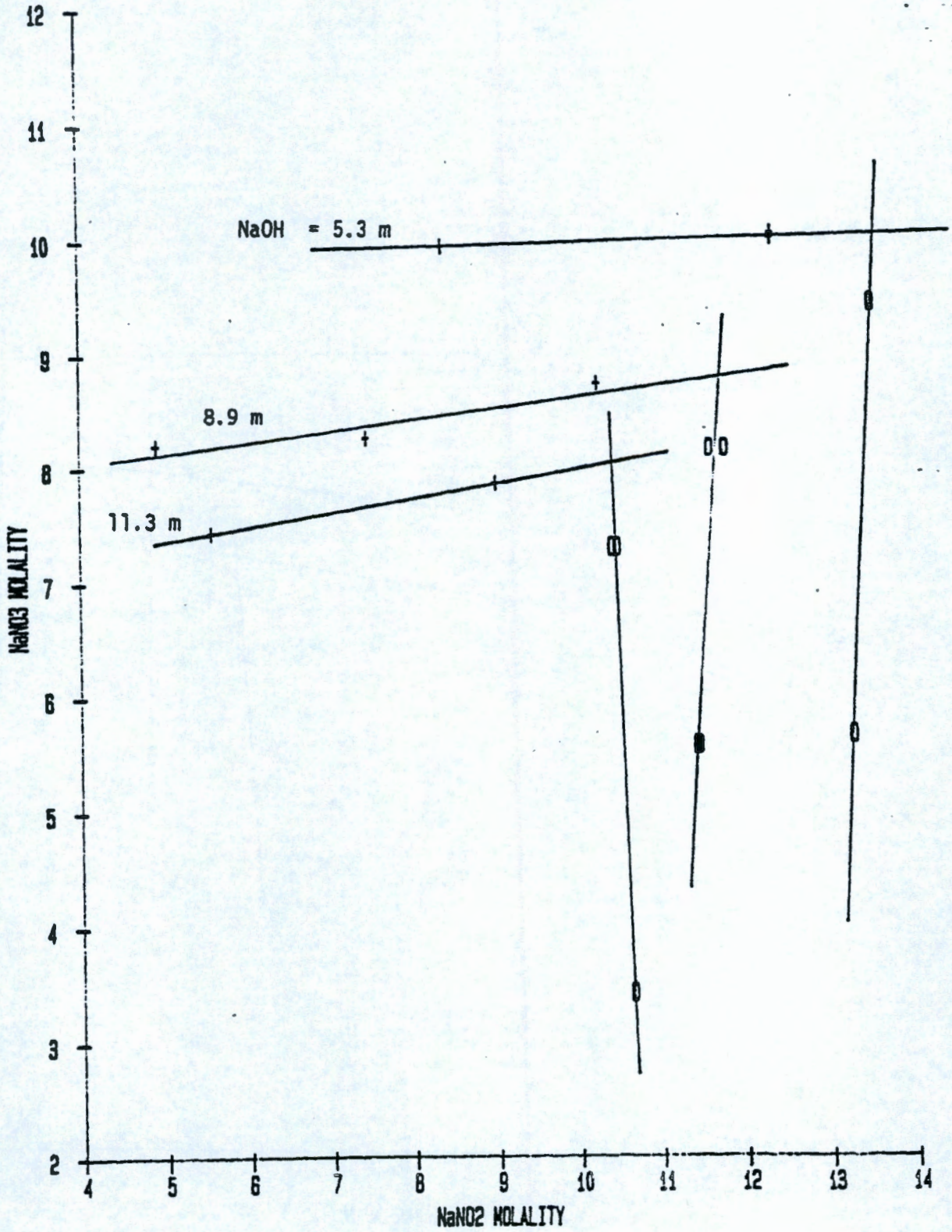
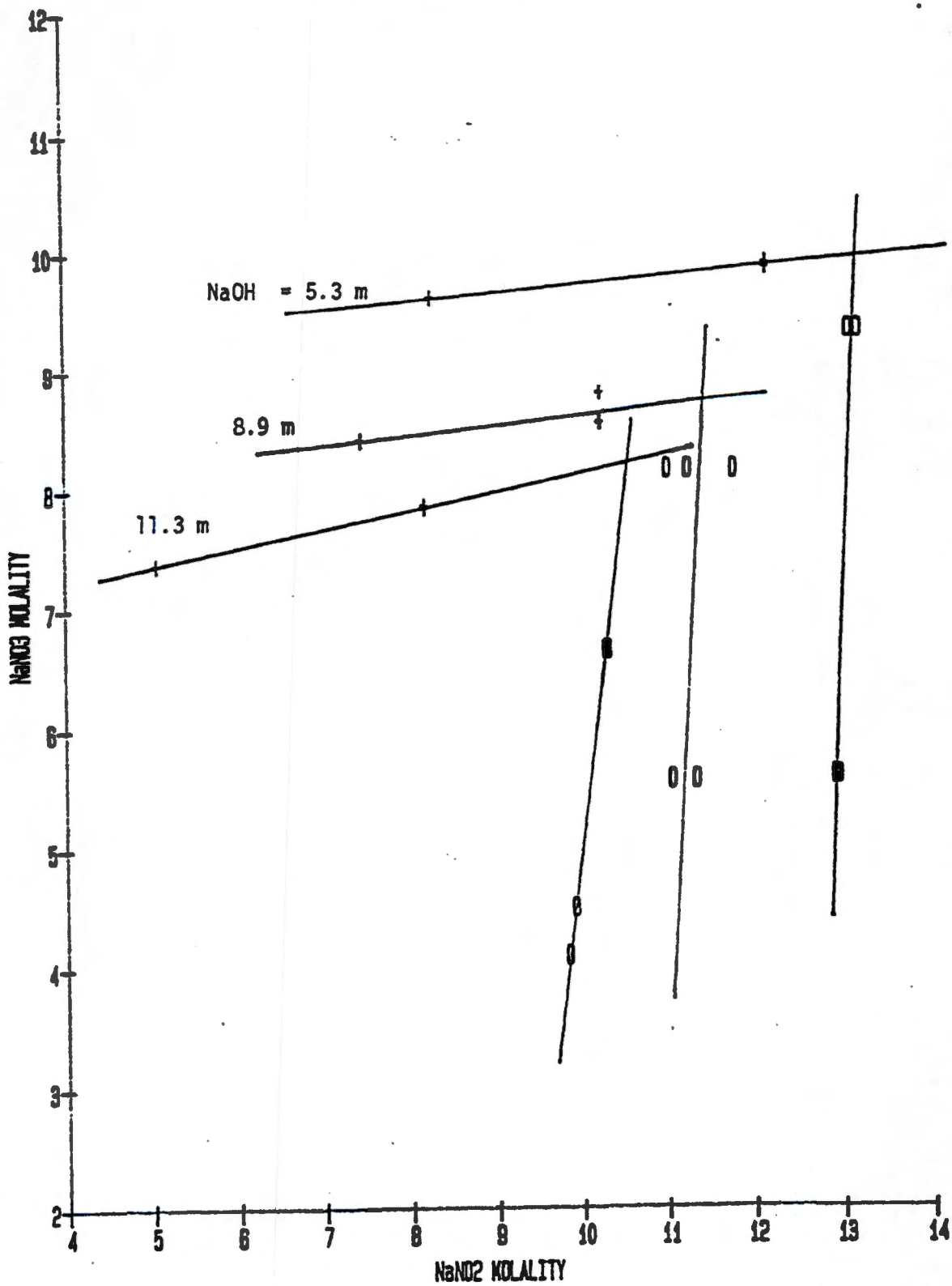


Figure 4

HYDROXIDE EFFECT, 80 C, 2 m ALO2



547

OUTGOING LTR. NO.
R83-2627

INCOMING LTR. NO.

ACTION
ZINSLI

REPLY DUE
—

DIST:	LTR.	ENCL.	APPR.
Bartholomew, D.C.			
Bellofatto, M.			
Carey, J.M.			
Cosheron, G.J.	X		
Crawford, A.C.			
Goss, R.A.			
Goodman, J.L.			
Gunchus, J.W.			
Gunsorn, R.J.			
Grubb, R.E.			
Hammond, R.D.			
Hanneman, R.E.			
Kinzor, J.E.			
Knight, S.E.			
Larson, M.P.			
Iossoni, P.E.	X	X	
Gerwood, R.J.			
Ogborne, L.R.			
Pasco, K.J.			
Patterson, J.W.	X	X	
Parham, J.D.			
Rossbar, J.H.	X	X	
Salmo, C.M.			
Shaw, H.P.			
Weil, V.R.			
Zahn, L.L.			
Contract Administrator	X	X	
Central Files	X	X	
REYNOLDS			
WILKINS	X	X	X
RODGERS	X	X	X
ALBAUGH	X	X	
ZINSLI	X	X	X
CARTHERS	X	X	X
UHL, D.L.	X	X	
GASPER	X	X	

DATE JUL 15 1983

I + cc's

Rockwell Hanford Operations
Energy Systems Group
P.O. Box 800
Richland, WA 99352

Rockwell International

In reply, refer to letter R83-2627

JUL 15 1983

Mr. J. J. Schreiber, Director
Waste Management Division
Department of Energy
Richland Operations Office
Richland, Washington 99352

Dear Mr. Schreiber:

PHASE DIAGRAM FOR THE WB PROGRAM
(Contract DE-AC06-77RL01030)

An extensive laboratory study has been completed to add to our knowledge of double-shell slurry and enhance our ability to conserve tank storage space. The data generated have been used to clarify the solubility (phase boundary) of the major components in the waste.

This letter represents the data both in diagrammatic forms and predictive equations. A letter with attached diagrams will meet the July 15, 1983 Phase Diagram milestone for the WB program. A document will be written to give greater details on experimental results and interpretations.

This study evaluated the solubility of three major components in the Hanford waste -- sodium nitrate, sodium nitrite, and sodium aluminate. These compounds were studied under three temperatures and three sodium hydroxide concentrations. The solubility of the compound of interest was measured as the other two compounds varied at two levels at each temperature-hydroxide combination. Therefore, each of the compounds had four factors influencing solubility.

The experiments were performed using molality (moles of salt/1000 g water) as the basic unit of concentration. At the end of each experiment, density measurements were made which allows conversion between molality and molarity.

In all cases, the temperature and hydroxide concentrations had the most powerful effect on the equilibrium concentration. Figures 1 to 3 represent a three-dimensional surface of the compounds as a function of temperature and hydroxide. These diagrams illustrate how the temperature and hydroxide interact.

Rockwell International

Figures 4, 5 and 6 show the solubilities of the three chemical species on the molality scale. In Figure 4, the area below a given temperature curve represents an unsaturated solution. There will be no solid phase present. As more sodium nitrate is added, or water removed, the concentration increases until the curve is reached. The curve is the equilibrium line at which a solid sodium nitrate is in equilibrium with a saturated solution of the composition given by the curve. The area above the curve represents a supersaturated solution or a mixture of solid and saturated solution. The curves indicate the way the equilibrium varies with hydroxide and temperature.

Figures 7, 8 and 9 are similar curves on the molarity scale. The solid lines are very concentrated solutions with all compounds at/or near saturation. The dotted lines represent less concentrated solutions. The solution is not saturated in other compounds. The figures for sodium nitrate and sodium nitrite show the strong dependency on temperature, hydroxide concentration and other compounds. Aluminate requires some explanation. Figure 9 shows that the aluminate solubility seems to have an inverse solubility with temperature. The solubility of aluminate apparently decreases as the temperature increases. The solid lines once again are highly concentrated solutions. Apparently, aluminate is very dependent on the total salt concentration. At the high temperatures, the concentration of the other salts is much greater. The added solubility of the other salts suppresses the solubility of aluminate. The dotted lines are lower concentrations and aluminate shows a "normal" solubility. Aluminate solubility increases with increasing temperature. The other ions do not suppress the aluminate solubility as they are relatively weak.

The figures are helpful in visualizing the solubility of each species. However, only three dimensions can be given on a plot (salt, hydroxide and temperature). All of the salts showed variation with more than two variables. Therefore, the equations in Tables 1, 2, and 3 should be used for predictive work. Most of the equations have linear effects, squared effects for temperature and hydroxide that indicate curvature, and some interactions. Generally two equations are given for each specie. The more complicated equation has all terms included that were statistically significant. As some of these equations are very long, an abbreviated version is given. It is expected that the long equation will be useful on computer applications while the short equation will be useful on hand calculators. It should be pointed out that the equations are strictly valid only for the ranges of variables listed. Extrapolation beyond the ranges should be done with caution.

Rockwell International

The enhanced predictive capabilities that this study provides will allow for better evaporator operation. It is expected that evaporator campaigns will be planned better and the operation of the evaporator will be closer to the expected products. This should improve our ability to concentrate the waste to lower overall volume with fewer areas of uncertainty.

If you have any questions concerning the application of these equations, please contact me or D. A. Reynolds at 373-3119.

Very truly yours,

R. A. Zinsli

R. A. Zinsli, Program Manager
Radioactive Waste Operations

RAZ:DAR:wrj

Att.

cc: P. E. Rasmussen - DOE-RL

Table 1
SODIUM NITRITE

MOLALITY UNITS

$[NaNO_2]$ = 14.3211
-.103584(TEMP)
-.931492[OH]
-.267858[NO3]
-.513876[ALO2]
+.00174871(TEMP)2
+.0216164[OH]2
+.00320869(TEMP)[NO3]
+.00567246(TEMP)[ALO2]
+.0140477[OH][NO3]

MULT. R =.99945
R SQUARED =.9989
STD. ERROR =.1307

[NaNO2] = 7.3146
-.48852[OH]
+.001329[NO3](TEMP)
+.0012349(TEMP)2

MULT. R =.9982
R SQUARED =.9964
STD. ERROR =.228

Ranges
TEMP from 60 C to 100 C
OH from 5 m to 11.5 m
NO3 from 3 m to 12 m
ALO2 from 1 m to 3 m

Molarity Units

[NaNO2] = 7.5494
-.49507[OH]
-.336315[NO3]
-.641674[ALO2]
+.000424249(TEMP)2

MULT.R =.9954
R SQUARED =.9908
STD.ERROR =.1334

RANGES
TEMP from 60 C to 100 C
OH from 2 M to 7.5 M
NO3 from 2 M to 5.5 M
ALO2 from .5 M to 1.6 M

Table 2

Sodium Nitrate Solubility

Molality Units

```
[NaNO3] = 9.19205
          -.0457708(TEMP)
          -.648307[OH]
          -.204878[NO2]                MULT. R =.99955
          -.487277[ALO2]               R SQUARED =.9991
          +.00124039(TEMP)2            STD. ERROR =.0908
          +.0214090[OH]2
          -.00229276(TEMP)[OH]
          +.0017593(TEMP)[NO2]
          +.00579748(TEMP)[ALO2]
          +.0175072[OH][NO2]

[NaNO3] = 4.9399
          -.33255[OH]                  MULT. R =.9983
          +.00091845(TEMP)[NO2]        R SQUARED =.9965
          +.00094992(TEMP)2            STD.ERROR =.1711
```

Ranges

TEMP from 60 C to 100 C
OH from 5 m to 11.5 m
NO2 from 3.5 m to 14.5 m
ALO2 from 1 m to 3 m

Molarity Units

```
[NaNO3] = 5.53679
          +.0223925(TEMP)
          -.627270[OH]
          -.269967[NO2]            MULT. R =.9980
          -.754656[ALO2]           R SQUARED = .9960
          +.00020753(TEMP)2        STD. ERROR =.06966
          +.0159733[OH]2
          +.0146144[OH][NO2]
          +.0584659[OH][ALO2]

[NaNO3] = 5.55204
          -.20457[NO2]             MULT. R =.9974
          -.49885[ALO2]            R SQUARED =.9949
          -.36200[OH]              STD. ERROR =.0767
          +.00034707(TEMP)2
```

Ranges

TEMP from 60 C to 100 C
OH from 2 M to 7.5 M
NO2 from 2 M to 7 M
ALO2 from .5 M to 1.7 M

TABLE 3

SODIUM ALUMINATE SOLUBILITY

Molality Units

```
[NaALO2] =9.35888
          -.0898752(TEMP)
          -.567107[OH]                MULT. R =.9710
          +.000628658(TEMP)2          R SQUARED =.9429
          +.0030425(TEMP)[OH]         STD. ERROR =.2202
          -.00534453[NO2][NO3]

[NaALO2] =6.47113
          -.67085[OH]                 MULT. R =.9441
          -.00598[NO2][NO3]           R SQUARED =.8914
          +.0042449(TEMP)[OH]         STD. ERROR =.3074
```

Ranges

TEMP from 60 C to 100 C
OH from 5 m to 11.5 m
NO2 from 3.7 m to 14.5 m
NO3 from 3 m to 12 m

Molarity Units

```
[NaALO2] =5.30412
          -.0550088(TEMP)
          -.502164[OH]                MULT. R =.9235
          +.000413064(TEMP)2          R SQUARED =.8529
          +.00282364(TEMP)[OH]        STD. ERROR = .1472
          -.00189116(TEMP)[NO3]
          -.00149886(TEMP)[NO2]

[NaALO2] = 2.38608
          -.04828[NO2][NO3]           MULT. R =.8664
          -.03783[OH]2                R SQUARED =.7507
          +.000069508(TEMP)2          STD.ERROR =.2031
```

Ranges

TEMP from 60 C to 100 C
OH from 2 M to 6.5 M
NO2 from 2 M to 6.2 M
NO3 from 1.7 M to 5 M

FIGURE 1

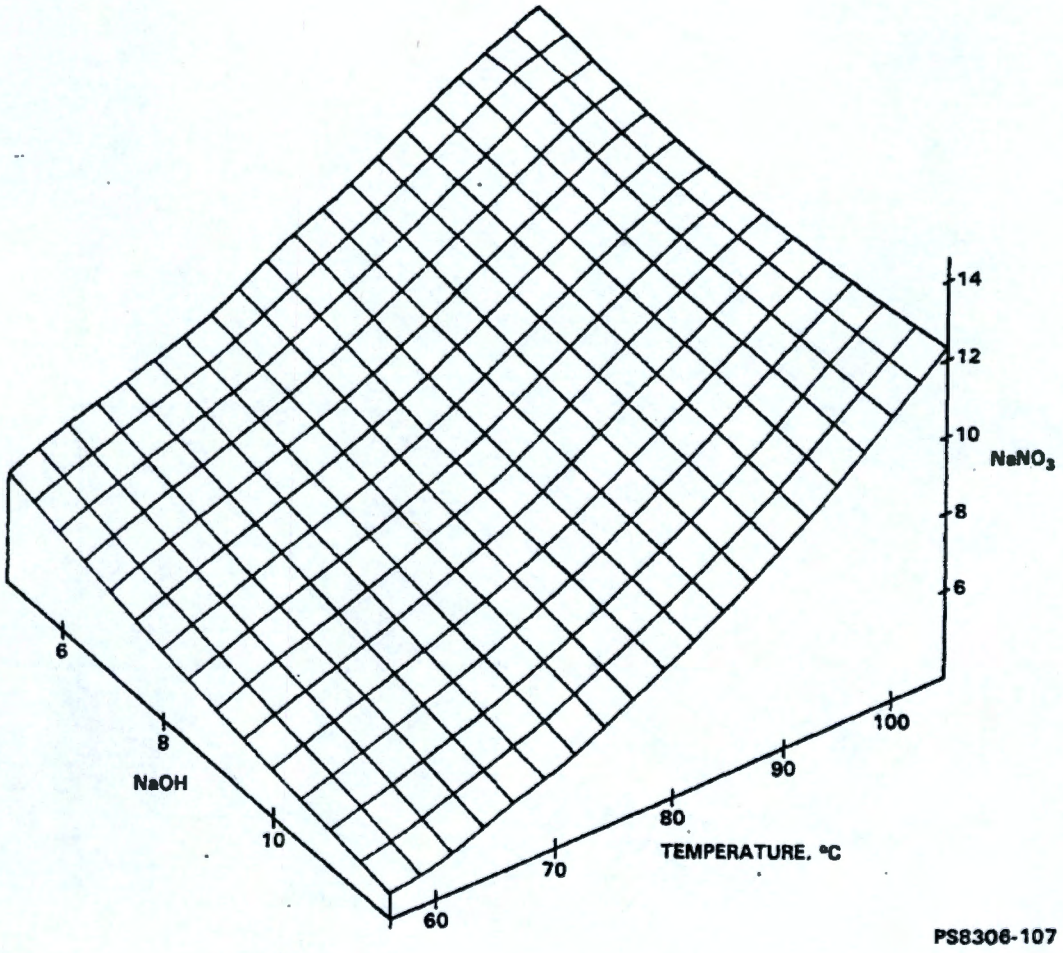

14
12
10
NaNO3
8
6
6
8
NaOH
10
100
90
80
TEMPERATURE, °C
70
60
PS8306-107

FIGURE 2

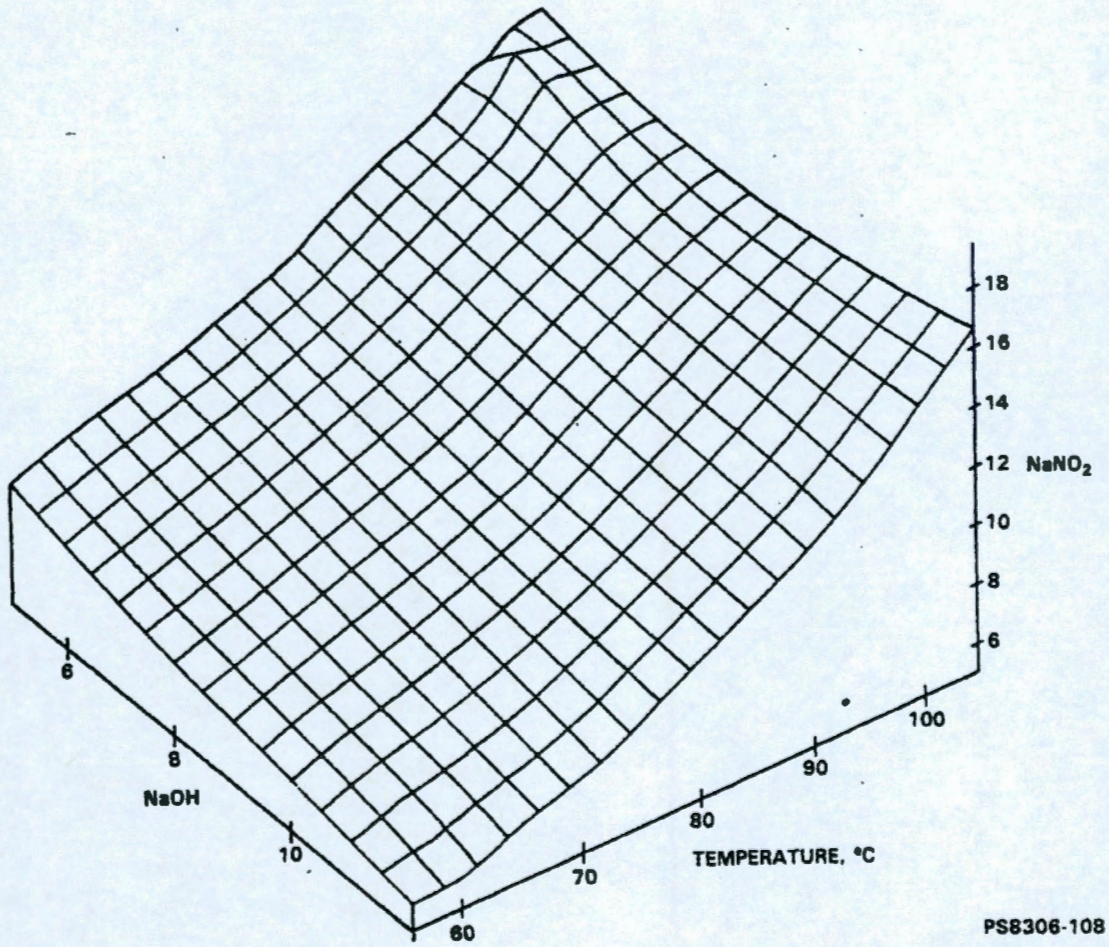

18
16
14
12 $NaNO_2$
10
8
6
6
8
NaOH
10
60
70
80
90
100
TEMPERATURE, °C
PS8306-108

FIGURE 3

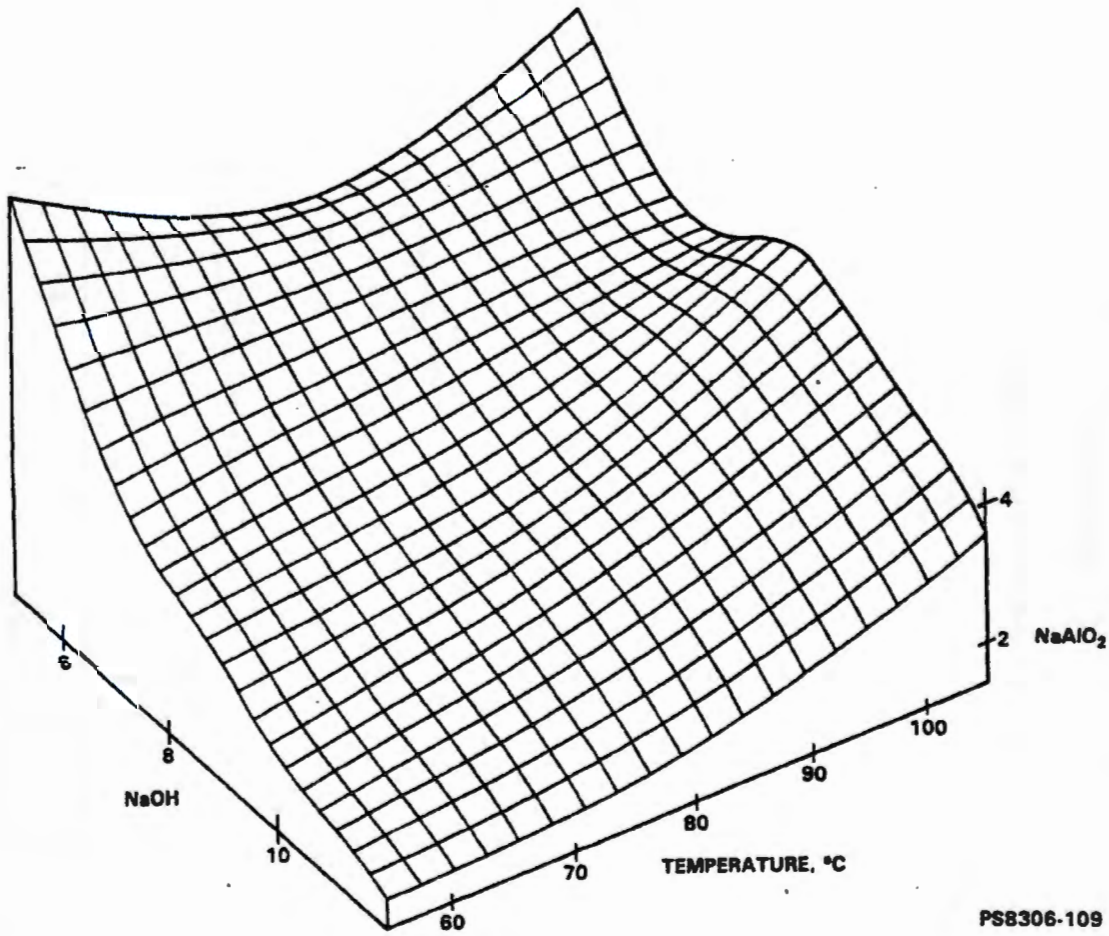


FIGURE 4

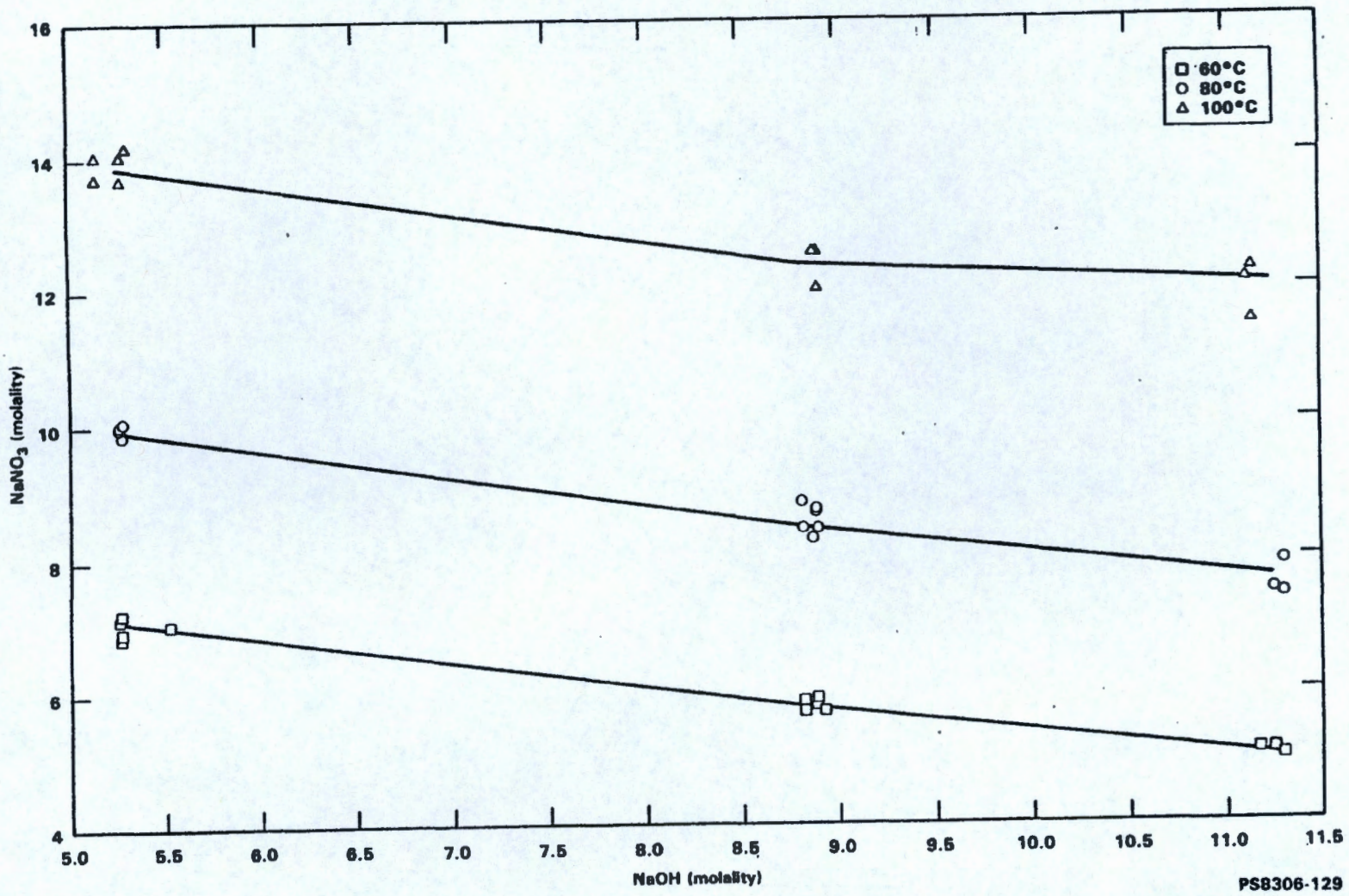
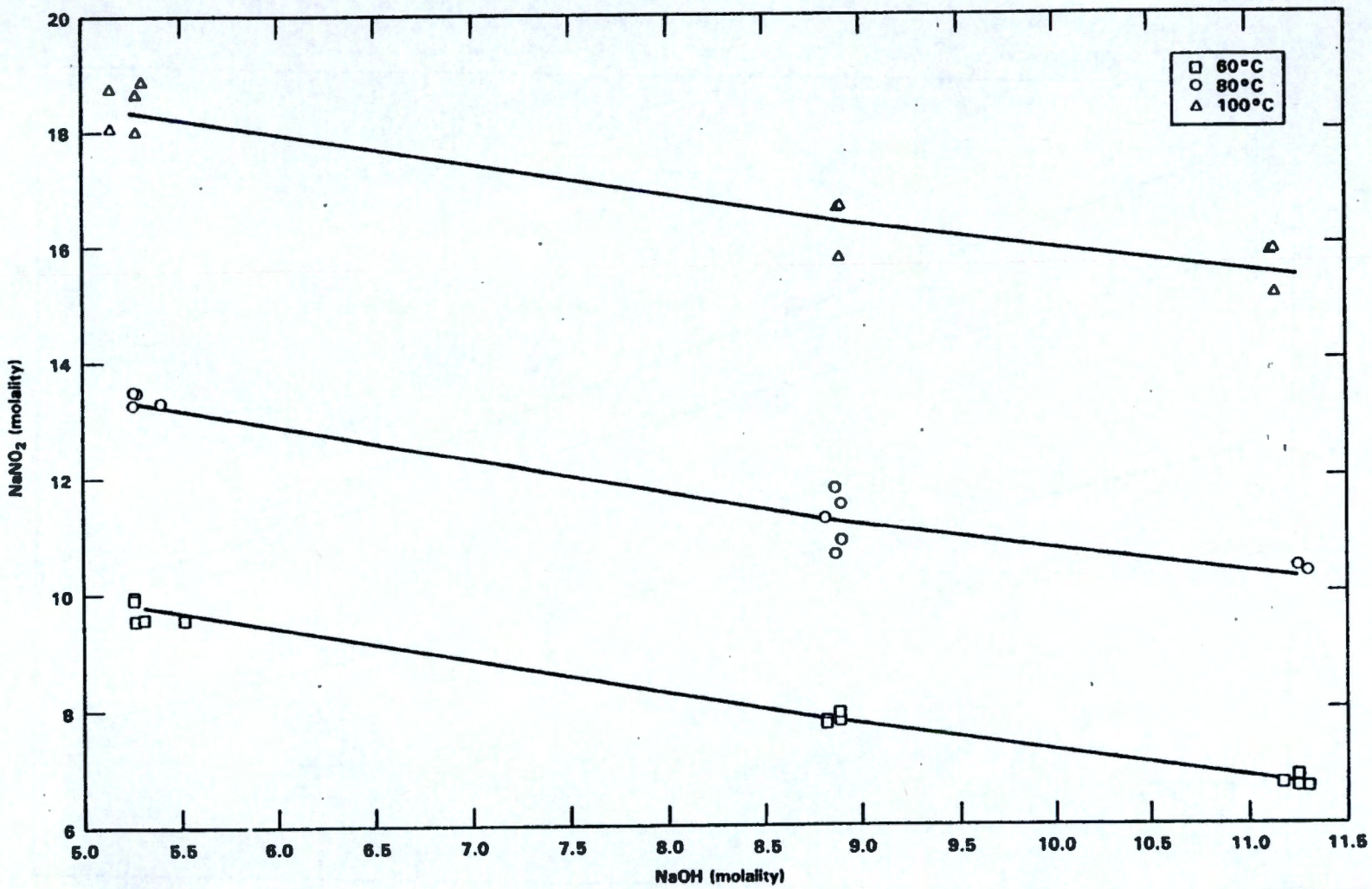
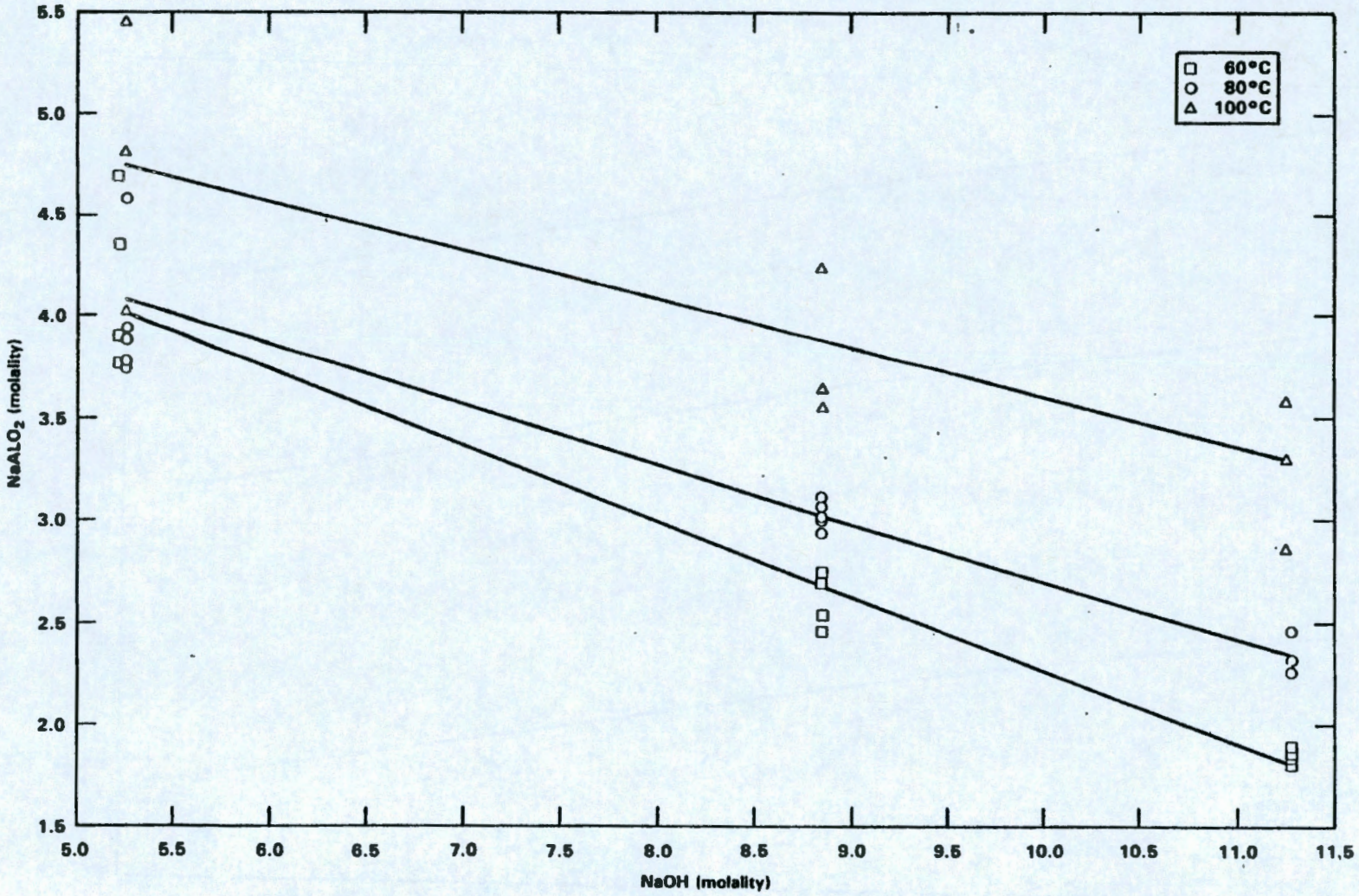

60°C
80°C
100°C
16
14
12
10
8
6
4
$NaNO_3$ (molality)
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
NaOH (molality)
PS8306-129

FIGURE 5



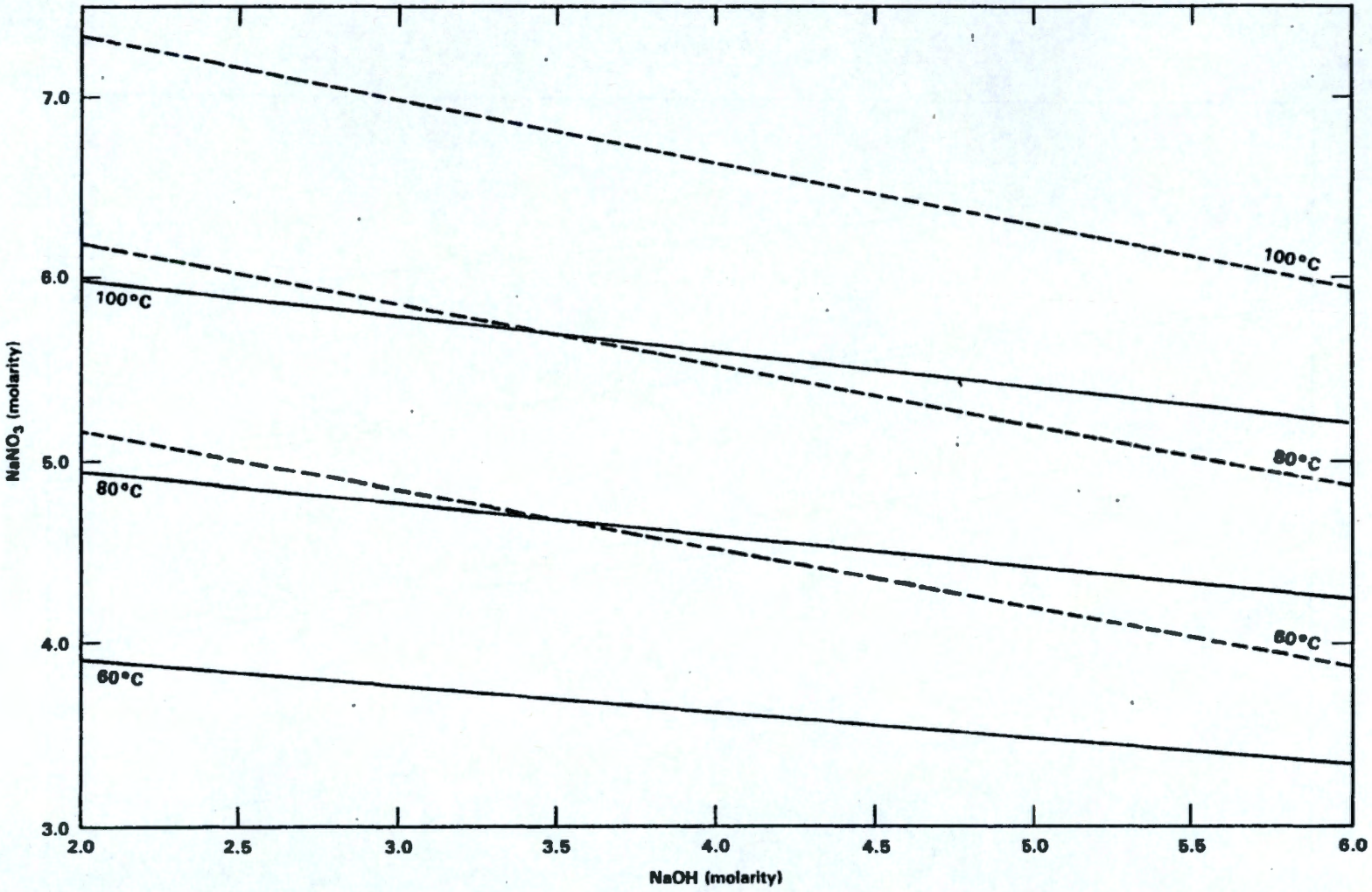
PS8306-130

FIGURE 6



PS8306-131

FIGURE 7



PS8306-132

FIGURE 8

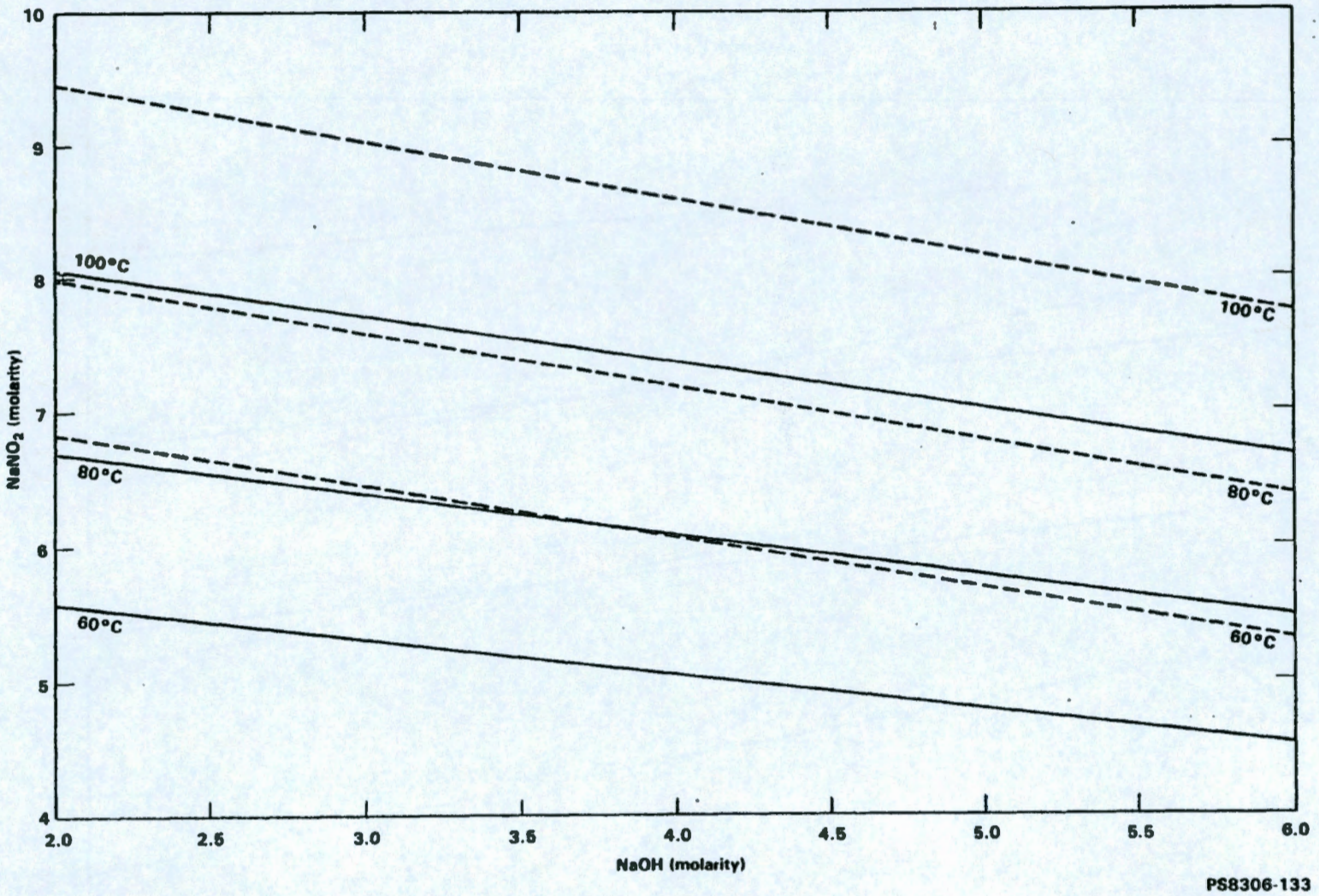
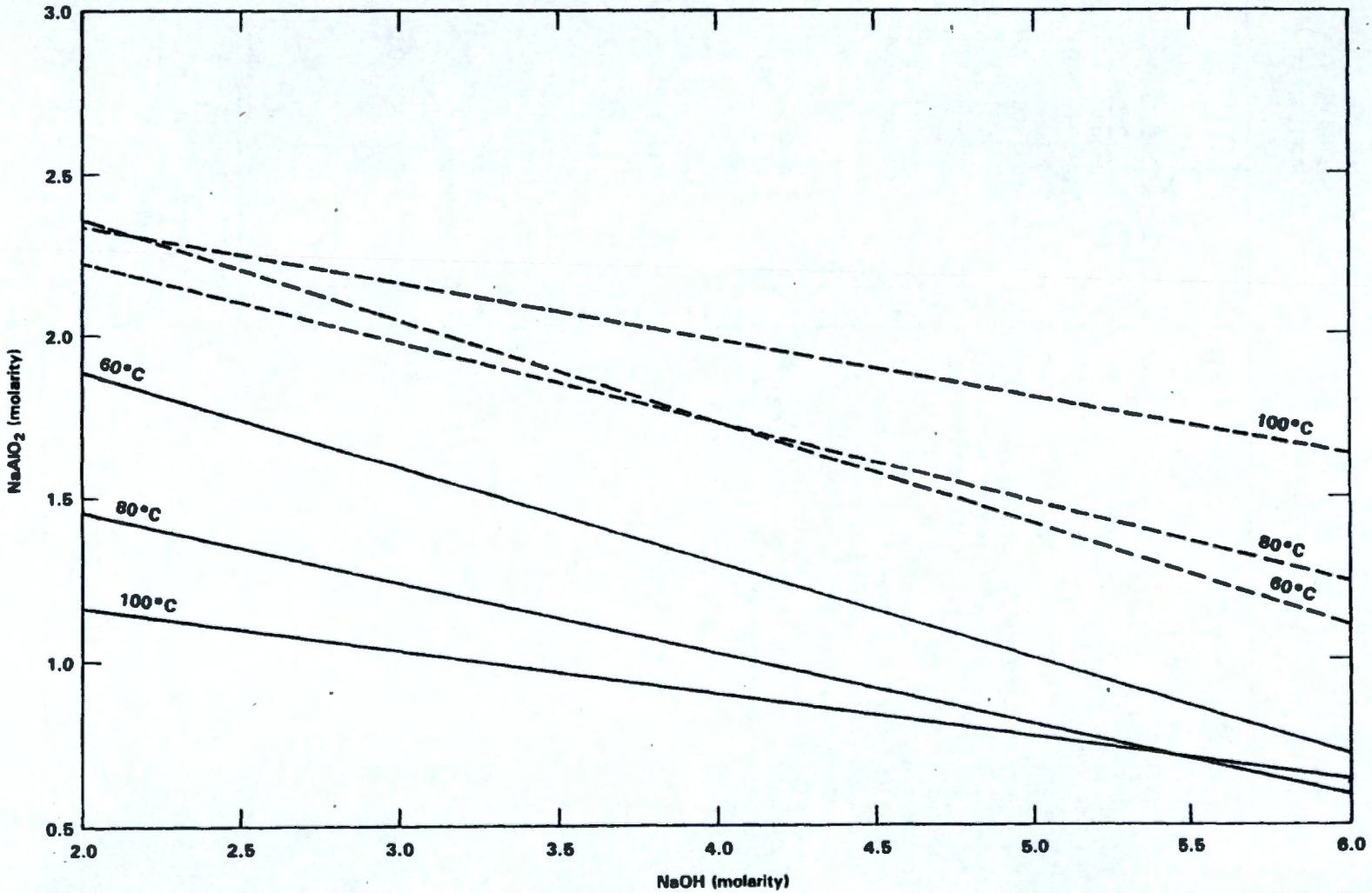

10
9
8
7
6
5
4
$NaNO_2$ (molarity)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
NaOH (molarity)
100°C
80°C
60°C
100°C
80°C
60°C
PS8306-133

FIGURE 9



PS8306-134

Rockwell Hanford Operations

SUPPORTING DOCUMENT	Number	Rev. Ltr./ Chg. No.	Page 1 of Total Pages
PROGRAM: Waste Concentration (WB)	SD-WM-TI-078	00	47

Document Title:

Solubility Phase Diagram - Final Report

Baseline Document ☐ Yes ☒ No

WBS No. or Work Package No. WB625

Key Words:
Phase Diagram, Double Shell Slurry, Sodium Aluminate, Sodium Nitrate, Sodium Nitrite, Solubility

Prepared by (Name and Dept. No.)
D. L. Herting/R. M. Cleavenger
65450

Date 5-20-83

See reverse side for additional approvals

THIS DOCUMENT IS FOR USE IN PERFORMANCE OF WORK UNDER CONTRACTS WITH THE U.S. DEPARTMENT OF ENERGY BY PERSONS OR FOR PURPOSES WITHIN THE SCOPE OF THESE CONTRACTS. DISSEMINATION OF ITS CONTENTS FOR ANY OTHER USE OR PURPOSE IS EXPRESSLY FORBIDDEN.

Abstract

Solubilities were determined for sodium nitrate, sodium nitrite, and sodium aluminate in synthetic waste liquor. Solubilities were determined as a function of temperature and solution composition (concentrations of sodium hydroxide, nitrate, nitrite, and aluminate). Temperature had the largest effect on solubilities of sodium nitrate and nitrite, and a somewhat smaller effect on sodium aluminate solubility. Hydroxide had a large effect on the solubilities of all three salts. Other solution components had minor effects.

*	Distribution Name	Mail Address
*	J. O. Albaugh	2750E/A107/200E
*	G. S. Barney	MO-037/2101M/200W & E
*	D. J. Bates	2704-S/200W
*	R. B. Bendixsen	2750E/A110/200E
*	J. S. Buckingham	222-S/MO-037/200W
*	G. B. Burch	222-S, 200W
*	K. G. Carothers	2750E/A204/200E
*	R. M. Cleavenger	202-S/200W
*	C. H. Delegard	234-5/200W
*	D. L. Herting (3)	222-S/MO-037/200W
*	J. O. Honeyman	2704E/14/200E
*	M. T. Jansky	222-S/MO-037/200W
*	L. Jensen	2704-S/200W
*	J. H. Lawler	2750E/D228/200E
*	A. M. Liebetrau	2704-S/200W
*	L. H. Rodgers	2750E/A222/200E
*	L. M. Sasaki	2750E/200E
*	W. W. Schulz	2750E/A210/200E
*	M. C. Teats	2750E/A100/200E
*	D. L. Uhl	2704-S/200W
*	D. G. Wilkins	2750E/A207/200E
*	G. D. Wright	MO-405/141A/200E
*	R. A. Zinsli	2750E/A139/200E
**	File: WB	
**	Process Aids	
**	Letterbook	
**	Send to 222-S/MO-037/200W C/O Nancy Jones	

(Continued on reverse side)

*COMPLETE DOCUMENT
(No asterisk, title page/summary of revision page only)

Release Stamp

Prepared By: _____

Used By: _____

1

564

Rockwell Hanford Operations

Page	Number	SUPPORTING DOCUMENT
2	SD-WM-TI-078	

Approvals

- ☐ _____ Program Office
- ☐ _____ Research and Engineering
- ☐ _____ Plant Operations
- ☐ _____ Health, Safety and Environment
- ☐ _____ Quality Assurance
- ☐ _____ Training
- ☐ _____ End Function
- ☐ _____ End Function
- ☐ _____
- ☐ _____
- ☐ _____
- ☐ _____
- ☒ B Buckingham — Approval Authority J. S. Buckingham

* Distribution	Name	Mail Address

A-6400-073R (2-83)

Internal Letter

Rockwell International

Date: November 11, 1983

No 65453-83-288

TO: (Name, Organization, Internal Address)
D. M. Tulberg
Process Design
2750E/A227/200E

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky/H. R. Risenmay
Chemical Laboratory Unit
222S/MO-037/200W
3-1571/3-3612

Subject: Laboratory Results from Slurry Pumpability Tests

As per your verbal request, the Chemical Laboratory Process Development Unit (CLPDU) performed viscosity determinations on several synthetic double shell slurry (DSS) products. The purpose of the experiment was two-fold. Primarily, viscosity data were to be gathered to assess slurry pumpability. However, of equal interest was to compare viscosity measurements utilizing two instruments: the Haake absolute viscometer and the Brookfield LVT relative viscometer. The data indicate that DSS is a Newtonian mixture; i.e. viscosity is independent of shear rate. The data also shows that the two instruments provide significantly different viscosity determinations when solids are present. The difference is most likely due to sample containment geometry. Specific laboratory details are discussed below.

Viscosity versus temperature data were gathered on Engineering laboratory DSS feeds. The data were taken using both the Haake absolute viscometer and the Brookfield LVT spindle viscometer (#2 spindle, relative measurements). The data are shown in Table I.

Batch boildowns were conducted on the DSS feed to 41 percent waste volume reduction (WVR) and 44 percent WVR. Temperature versus WVR data (at 60 torr) were gathered and are presented in Table II. Each product was subjected to viscosity versus temperature determinations, with those data shown in Tables III and IV. It should be pointed out here that the viscosity data from the Haake are reported as the shear rate was increased. When the rate was subsequently decreased and readings taken, the readings were consistently $\leq$ 5 percent of the initial readings. The repeat of viscosity versus increasing shear rate was consistent with the initial readings. (See Table V for increase versus decrease).

The 44 percent WVR DSS product was also reheated, with viscosity versus temperature measurements taken. The heating data are shown in Table VI.

As further comparison, synthetic DSS produced from the Engineering laboratory was tested for viscosity versus temperature. The DSS was a product taken approximately three-fourths of the way through the Engineering laboratory run. The fresh product was tested immediately for viscosity versus temperature using the Brookfield. Subsequently, after storage for approximately 2 months, the DSS was used for this comparison. The relevant data are shown in Table VII. Additionally, data are presented in Table VIII pertaining to the viscosity of the 41 percent, WVR DSS product supernatants.

Rockwell International

The absolute viscosity data indicate that DSS is approximately Newtonian. A Newtonian material is one which has a constant viscosity independent of shear rate. The trend in the data is a constant viscosity, ± 5 percent, for DSS slurry. The "relative" data are not similar to the absolute, a phenomenon that may be attributed primarily to sample containment geometry. The Haake does not allow excessive settling of solids, whereas crystalline build-up on the spindle causes increased viscosity readings.

Similar statements may be made for both the feed and the supernatant. At lower temperatures, precipitation may be occurring. Temperature and shear rate may effect crystallization, and subsequently viscosity determinations.

Please call if you have questions or comments regarding this work.

M. T. Jansky, Senior Chemist

H. R. Risenmay, Chemist

MTJ/HRR/rr

Attachments

cc: J. S. Buckingham JSB
K. G. Carothers
D. L. Herting
J. H. Lawler
L. H. Rodgers
Process Aids
File Code

TABLE I

VISCOSITY VERSUS TEMPERATURE FOR FEED

	Haake			Brookfield*	
Temperature (°C)	Shear Rate (Sec^{-1})	Stress (Pa)	Viscosity (Cps)	RPM	Viscosity (Cps)
70	346.2	3.52	10.16	60	9
	692.5	5.28	7.62		
	1385	9.97	6.55		
60	346.2	2.67	7.70	60	10
	692.5	5.86	8.47		
	1385	11.19	8.09		
	2770	21.85	7.90		
50	346.2	4.26	12.33	60	11
	692.5	8.53	12.33		
	1385	15.99	11.55		
	2770	28.78	10.40		
40	346.2	5.86	16.95	60	12
	692.5	11.19	16.18		
	1385	21.32	15.41		
	2770	43.17	15.60		
30	346.2	9.06	26.19	60	18
	692.5	17.06	24.65		
	1385	32.51	23.49		
	2770	69.29	25.04		

*#2 spindle

TABLE II

TEMPERATURE VERSUS WVR DATA FOR
PILOT PLANT FEED BATCH BOILDOWNS

(.60 Torr Constant Pressure)

Temperature (°C)	% WVR 41	% WVR 44
0	55.0	54.6
5	55.4	55.6
10	56.4	57.0
15	58.6	58.2
20	59.8 (60.8)*	60.0
25	62.4	61.8
30	64.8	64.4
35	66.8	67.2
40	-	70.6**
41	70.2	-
44	-	73.8

*Allowed to reflux overnight, temperature increase the next morning.

**Nucleation occurred at approximately 37% WVR, 69°C.

TABLE III

VISCOSITY VERSUS TEMPERATURE OF DSS PRODUCT, 41% WVR

	Haake			Brookfield*	
Temperature (°C)	Shear Rate (Sec^{-1})	Stress (Pa)	Viscosity (Cps)	RPM	Viscosity (Cps)
70	346.2	8.53	24.66	60	29
	692.5	16.88	24.39		
	1385	32.16	23.23		
	2770	67.87	24.52		
60	346.2	15.28	44.17	60	42
	692.5	28.60	41.33		
	1385	54.76	39.54		
	2770	111.93	40.44		
50	346.2	26.30	76.00	60	90
	692.5	52.06	75.23		
	1385	103.93	75.10		
	2770	202.54	73.18		
40	346.2	53.3	154.06	60	183
	692.5	102.87	148.67		
	1385	200.41	144.82		
	2770	379.50	137.12		
30	346.2	106.60	308.13	60	457
	692.5	212.13	306.58		
	1385	415.21	300.04		
20	346.2	252.64	730.26	12	1325
	692.5	495.16	715.62		

*#2 Spindle

TABLE IV

VISCOSITY VERSUS TEMPERATURE OF DSS PRODUCT, 44% WVR

	Haake			Brookfield*	
Temperature (°C)	Shear Rate (Sec^{-1})	Stress (Pa)	Viscosity (Cps)	RPM	Viscosity (Cps)
70	346.2	13.14	38.00	60	38
	692.5	24.70	35.69		
	1385	46.72	33.77		
	2770	111.93	40.44		
60	346.2	23.81	68.81	60	96
	692.5	45.48	65.73		
	1385	88.12	63.68		
	2770	165.23	59.70		
50	346.2	44.24	127.87	60	216
	692.5	88.12	127.36		
	1385	170.91	123.51		
	2770	321.93	116.32		
40	346.2	90.08	260.37	30	641
	692.5	176.96	255.74		
	1385	334.19	241.49		
30	173.12	90.08	520.73	12	1663
	346.2	180.15	520.73		
	692.5	349.12	504.55		

*#2 Spindle

TABLE V

VISCOSITY DETERMINATIONS FROM INCREASING VERSUS DECREASING SHEAR, 44% WVR

Temperature (°C)	Shear Rate (sec^{-1})	Viscosity (Cps) Increasing Shear	Viscosity (Cps) Decreasing Shear*
60	346.2	68.81	65.73
	692.5	65.73	63.94
	1385	63.68	63.04
	2770	59.70	
50	346.2	127.87	124.79
	692.5	127.36	121.45
	1385	123.51	120.17
	2770	116.32	
40	346.2	260.37	240.34
	692.5	255.74	233.40
	1385	241.49	231.09

*After increasing shear rate, the rate was decreased the same intervals.

TABLE VI

VISCOSITY VERSUS TEMPERATURE OF DSS PRODUCT, 44% WVR, HEATING

Temperature (°C)	Haake Shear Rate (Sec^{-1})	Haake Stress (Pa)	Haake Viscosity (Cps)	Brookfield* RPM	Brookfield* Viscosity (Cps)
40	346.2	79.95	231.09	30	416
	692.5	155.64	224.93		
	1385	304.88	220.31		
	2770	548.99**	198.36		
50	346.2	41.93	121.20	60	179
	692.5	81.37	117.60		
	1385	158.83	114.78		
	2770	298.48	107.84		
60	346.2	25.59	73.96	60	82
	692.5	49.03	70.87		
	1385	94.88	68.56		
	2770	245.18	88.59		
70	346.2	15.99	46.22	60	49
	692.5	31.09	44.93		
	1385	60.59	43.78		
	2770	159.90	57.78		

*#2 Spindle
**At high end of scale, questionable reading.

TABLE VII

VISCOSITY VERSUS TEMPERATURE OF DSS PRODUCT, FROM ENGINEERING LABORATORY

	Haake			Brookfield*			
Temperature (°C)	Shear Rate (Sec^{-1})	Stress (Pa)	Viscosity (Cps)	RPM	Current Viscosity	RPM	Initial Viscosity
70	346.2	27.36	79.09	60	294	60	72
	692.5	41.58	60.09	30	434		
	1385	70.18	50.71	12	695		
	2770	154.04	55.66				
60	346.2	34.64	100.14	60	>500	60	280
	692.5	60.77	87.81	30	714	30	380
	1385	112.82	81.52	12	1246		
	2770	209.47	75.68				
50	346.2	76.16	194.12	60	>500	60	>500
	692.5	121.17	175.12	30	821	30	820
	1385	220.66	159.45	12	1123	12	990
	2770	366.70	132.49				
40	346.2	144.27	417.00	60	>500		
	692.5	238.25	344.23	30	>1000		
	1385	385.36	278.47	12	1670		
30	346.2	222.79	643.98	60	>500		
	692.5	376.30	543.84	30	>1000		
				12	>2500		
				6	3992		

*# 2 Spindle

TABLE VIII

VISCOSITY VERSUS TEMPERATURE OF DSS PRODUCT SUPERNATANT, 41% WVR

	Haake			Brookfield*	
Temperature (°C)	Shear Rate (Sec^{-1})	Stress (Pa)	Viscosity (Cps)	RPM	Viscosity (Cps)
80	86.56	1.24	14.4	12	20
	173.12	2.66	15.4	30	18
	346.24	5.69	16.4	60	22
	692.48	11.37	16.4		
	1385	21.50	15.5		
	2770	42.64	15.4		
70	86.56	1.78	20.5	12	23
	173.12	4.09	23.6	30	25
	346.24	8.71	25.2	60	28
	692.48	15.99	23.1		
	1385	30.56	22.1		
	2770	60.23	21.8		
60	86.56	4.44	51.4	12	45
	173.12	8.35	48.3	30	43
	346.24	15.63	45.2	60	48
	692.48	28.96	41.9		
	1385	55.08	39.8		
	2770	136.80	49.4		
50	86.56	8.88	102.7	12	90
	173.12	15.81	91.4	30	107
	346.24	28.43	82.2	60	97
	692.48	53.83	77.8		
	1385	102.69	74.2		
	2770	197.74	71.4		

*#2 Spindle

Internal Letter

Rockwell International

Date. November 30, 1983

No. 65455-83-073

TO: (Name, Organization, Internal Address)
- M. G. Kelly
- Waste Management Process Design
- 2750E/A219/200E

FROM: (Name, Organization, Internal Address, Phone)
- M. J. Schliebe/M. T. Jansky
- Process Development
- MO-922/200E, MO-037/200W
- 3-3513, 3-1571

Subject: September 1983 Pilot Plant Double-Shell Slurry Evaporator-Crystallizer Run - Data and Results

Attached is a report summarizing the September, 1983 pilot evaporator-crystallizer run. During the 30 hour run, ∿2400 gallons of dilute, synthetic feed were processed, producing ∿1200 gallons of double-shell slurry (DSS). The DSS is to be used in future (FY-84) test efforts.

M. J. Schliebe
Engineer

M. T. Jansky
Scientist

MJS/pjm

cc: J. S. Buckingham
K. G. Carothers
W. R. Dworzak WRD
T. A. Lane
R. B. Bendixson
M. I. Fineman
L. M. Saski
D. M. Tulberg

- PILOT SCALE EVAPORATOR-CRYSTALLIZER RUN -

September 14-15, 1983

1.0 INTRODUCTION

In May of 1983, a proposal was submitted to Program Engineering outlining pilot plant work involving the recovery of double-shell-slurry (DSS) from a waste tank (reference 1). In order to satisfy the objectives of this proposal, synthetic DSS was needed. A pilot evaporator-crystallizer (EC) run plan was prepared (reference 2) and distributed for comment. The feed composition suggested, listed in reference 2, was negotiated with the Waste Management Process Technology Unit, the final target feed composition is shown in Table 0. In addition, the target waste volume reduction (WVR) for the run was increased so that a more representative product would be produced (reference 3). The run took place on 9/14-9/15, 1983. This report summarizes the pilot plant run performed to make DSS for WG FY84 program needs.

2.0 SUMMARY

The run lasted ~30 hours. Approximately 2400 gallons of feed were processed to produce ~1200 gallons of DSS product. The nominal steady state EC operating temperature and pressure were 165-170 degrees F and 60 torr. The average feed and condensate rates were 1.20 and 0.55 gpm respectively. The objective of this run was to produce DSS for FY84 testing needs. In addition, process and laboratory data were requested as described in reference 4. Process data and laboratory data were obtained and are presented in this report. Slurry growth experiments were also requested (reference 5); this experiment is on-going and data are not reported at this time. Slurry transfer pressure drop data were recorded during the transfer of DSS to storage tanks; this information is documented in reference 6.

In general, the run went smoothly. No DSS transfer lines were plugged. The dip tubes in the evaporator, used to monitor the slurry specific gravity and liquid level in the evaporator, did plug periodically. Steam purging was successfully used to unplug the dip tubes.

Two previously untested process instruments were used during this run, an online viscometer and densometer. The viscometer, a Nametre (trade name) , has a vibrating sphere senor tip which is immersed in the process fluid. The power required to maintain a constant amplitude-oscillation is measured. This signal is proportional to the viscosity of the fluid. The features of this method are a) viscosity measurements can be made online and b) viscosity measurements are made at the same shear rate. The densometer, an Automation Products, Inc Dynatrol model (trade

name) has a vibrating U tube. The solution to be measured flows through the U tube and dampens the vibration of the tube. The dampened oscillation is proportional to the fluid density. Both instruments appeared to work satisfactorily, but plugged within ~9 hours of operation.

3.0 TEST RESULTS

Although the primary objective of this pilot plant run was to produce DSS, the run provided an opportunity to gain additional data relevant to processing actual DSS feeds. For this reason, process and laboratory data were obtained. The following test results are divided into two parts: process data and results and laboratory data and results.

3.1 Process Data & Results

The pilot plant EC run began at ~9:20 a.m. on 9/14/33 and lasted for ~ 30 hours. The recirculation rate in the EC was maintained at ~150 gpm. The average feed and condensate rate were 1.20 and 0.55 gpm respectively. (Approximately 540 gallons of feed were saved for future use.) Online viscosity and density measurements were obtained for ~9 hours, after which, the product lines to and from the instruments plugged. The operating pressure of the EC was 60 torr.

The process was operated continuously for 30 hours with no major problem or process upsets. During initial concentration of the dilute feed (~4 hours), no slurry was removed form the system. After initial concentration (to the approximate target WVR) slurry was removed semi-continuously in nominal 30-40 gallon increments.

Process "strip chart" data are not presented in this report, but will be maintained on file through FY84. Copies are available on request (contact M. J. Schliebe).

Slurry samples were collected periodically during the run. These samples were collected form the discharge side of the slurry recirculation pump. A Bristol Isolok (trade name) sampler was used to obtain samples. The company claims isokinetic sampling is acheived using their equipment. The analysis of the samples are included in the Laboratory Data & Results section of this report.

Condensate samples were taken during the latter half of the run. The conductivity of the samples was ~80-100 micromhos. These data were taken using a portable conductivity instrument maintained in the CELPDU. (The instrument had been calibrated with standard solutions).

Slurry was transfered from the EC to an intermediate slurry

receiver tank, (~60 gallons) and then transfered to a final storage tank or barrel. After each slurry transfer, the lines and intermediate slurry receiver tank were flushed with water, preventing potential line plugage.

Approximately 720 gallons of DSS were transfered to an insulated storage tank equiped with a temperature controlled steam jacket. This material will be maintained at ~175 degrees F until testing is completed. An additional 375 gallons of DSS were transfered to 55 gallon drums and stored (unheated) for future use. (The first ~30 gallons and last ~30 gallons of DSS were sewered due to lack of storage drums.)

Tables 1-3 summarize the process data collected during the run. Questions concerning these data should be directed to M. J. Schliebe (3-3513).

3.2 Laboratory Data & Results

Feed solution was received by the Chemical Laboratory Unit (CLU) from the pilot plant . Viscosity *versus* temperature data were taken, and are shown in Table 4. The specific gravity of the feed, at 40 degrees C, was 1.4456. Interest was expressed in the properties of the feed during concentration. To that end, a batch boildown was conducted on the feed, Initially, a 40 percent waste volume reduction was requested. The boildown data, at a constant pressure of 60 torr, are shown in Table 5. The specific gravity of the 40 percent WVR product was 1.6515, at 71.6 degrees C. The sample was further reduced to a total of 50 percent WVR. The 50 percent product's viscosity was 151 centipoise (60 RPM) at 30 degrees C, and 3500 centipoise (6 RPM) at 70 degrees C.

A second boildown was conducted on the feed to a 40 percent WVR. Temperature *versus* WVR data are shown in Table 6, with viscosity *versus* temperature data (40 percent WVR) shown in Table 7.

Two more samples of feed were received from the pilot plant by CLU. The samples were taken from the two feed tanks, TK505 and TK509. The samples were analysed by Analytical Laboratories (AL). The analytical results are shown in Table 8. Aliquots of each sample were blended such that a 50:50 mixture was obtained. The mixture was subjected to a batch boildown at 60 torr, concentrating to a 45 percent WVR. Temperature *versus* WVR data are shown in Table 9. Nucleation occurred at 30 percent WVR, the material was reduced to a total of 45 percent WVR. The specific gravity of the product was 1.7014 at 74.2 degrees C. The product was then transferred to a jacketed vessel for viscosity *versus* temperature determinations. Those data are shown in Table 10.

Four samples were taken during the actual run for handling by CLU. Each sample was handled in a similar fashion. The sample

was taken, and immediately transfered to a 70 degrees C oven. An aliquot of the product was dissolved and submitted to AL for chemical analysis. A second aliquot was filtered, with the filtrate and dissolved solids also analyzed by AL. A third aliquot was utilized for viscosity determinations using the Brookfield LVT, spindle viscometer (# 2 spindle). Analytical data ate shown in Tables 11-14. Viscosity versus temperature data are shown in Tables 15-18.

The data presented here are gathered during the run. Questions should be directed to Mike Jansky (3-1571). Since completion of the run, archieved samples have been tested for changes in viscosity, concentration, and other parameters. The post-run data will be presented in a separate letter.

4.0 REFERENCES

1] Internal Letter # 65454-83-156, May 31, 1983, J. S. Buckingham to J. J. Goldin, "Pilot Plant Work for Recovering Double Shell Slurry for a Waste Tank"

2] Internal Letter # 65455-83-009, July 13, 1983, M. J. Schliebe to J. J. Goldin, "Double-Shell Slurry Production Using the 202S Pilot Scale Evaporator-Crystallizer"

3] DSI #65450-83-075, July 21, 1983, M. J. Kupfer to J. J. Goldin, "Double-Shell Slurry Production"

4] Internal Letter # 65411-83-161, August 10, 1983, M. G. Kelly to M. J. Schliebe, "Double-Shell Slurry Production Using the 202S Pilot Scale Evaporator-Crystallizer"

5] Internal Letter # 65411-83-160, August 15, 1983, L. M. Sasaki to M. J. Schliebe, "Slurry Growth Experiments with DSS from the 202S Pilot Scale Evaporator-Crystallizer"

6] Internal Letter 3 65455-83-070, November 18, 1983, K. H. Lee to D. M. Tulberg, "Pilot Scale Evaporator"

TABLE 1

PROCESS DATA

Feed, Condensate, and Product Volumes

Date	Time	Feed Rate (GPM)	Cumulative Feed (gal)	Condensate Rate (GPM)	Cumulative Condensate (gal)	Cumulative Product (~gal)
9/14/83	9:20	0	240	0	0	0
	11:00	0.720	312	0.740	74	
	12:00	1.500	402	0.533	106	
	13:00	1.550	495	0.567	140	
	14:00	0.950	552	0.500	170	31 gal sewered
	15:00	1.750	657	0.500	200	
	16:00	1.050	720	0.483	229	
	17:00	1.217	793	0.500	259	
	18:00	1.283	870	0.508	289.5	
	19:00	1.167	940	0.575	324	
	20:00	1.125	1007	0.650	363	
	21:00	1.300	1085	0.483	392	
	22:00	1.500	1175	0.517	423	720 gallons total
	23:00	1.667	1275	9.650	462	in TK408
	24:00	1.417	1360	0.600	498	~30 gal. increments
9/15/83	1:00	1.333	1440	0.567	532	
	2:00	1.217	1513	0.583	567	
	3:00	1.333	1593	0.583	602	
	4:00	1.367	1675	0.583	637	
	5:00	1.233	1749	0.567	671	
	6:00	1.167	1819	0.600	707	
	7:00	1.000	1879	[1]0.500	737	
	8:00	0.917	1934	0.450	764	
	9:00	0.967	1992	0.467	792	
	10:00	1.000	2052	0.467	820	375 gallons in
	11:00	1.133	2120	0.483	849	55 gal. drums
	12:00	1.000	2180	0.538	881	
	13:00	1.033	2242	0.442	907.5	
	14:20	1.113	2331	0.500	947.5	
	15:00	1.125	2376	0.550	969.5	
	15:40	0.625	2401	0.425	986.5	
						80 gal. sewered

[1]Estimated rate

TABLE 2

PROCESS DATA

SpG, Viscosity, WVR

Date	Time	[1]Specific Gravity (g/cc)	[2]Viscosity (Centipoise)	[3]Incremental WVR (%)	[3]Cumulative WVR (%)
9/14/83	9:20	1.4456	11.5		0
	11:00	1.577	22.5		23.7
	12:00	1.608	41	35.5	26.4
	13:00	1.616	36	36.6	28.3
	14:00	1.670	40	52.6	30.8
	15:00	1.685	38	28.6	30.4
	16:00	1.685	42	46.0	31.8
	17:00	1.682	43	41.1	32.7
	18:00	1.686	43	39.6	33.3
	19:00	1.693/1.696*	45	49.3	34.5
	20:00	1.708	Instrument	57.8	36.0
	21:00	1.718	Plugged	37.2	36.1
	22:00	1.72	"	34.5	36.0
	23:00	1.667*	"	39.0	36.2
	24:00	--	"	42.3	36.6
9/15/83	1:00	1.676*	"	42.5	36.9
	2:00	1.691*	"	47.9	37.5
	3:00	1.696*	"	43.8	37.8
	4:00	--	"	42.6	38.0
	5:00	--	"	46.0	38.4
	6:00	1.72*	"	51.4	38.9
	7:00	1.72*	"	50.0	39.2
	8:00	--	"	49.1	39.5
	9:00	--	"	48.3	39.8
	10:00	--	"	46.7	40.0
	11:00	1.727*	"	48.3	40.0
	12:00	1.725*	"	53.8	40.4
	13:00	1.722*	"	42.8	40.5
	14:20	1.710*	"	44.9	40.6
	15:00	1.705*	"	48.9	40.8
	15:40	1.705*	"	68.0	41.1

[1]Dynatrol reading unless flagged with "*".
[2]Nametre online viscometer

[3]Based on condensate, i.e., $WVR = \frac{\text{unit volume condensate}}{\text{unit volume feed}}$

TABLE 3

RUN SUMMARY

Processing Data

Feed processed:	2,400 gal
Volume DSS produced:	1,206 gal
Volume of condensate produced:	986 gal
Feed composition:	See Table 8
Average feed rate:	1.20
Processing time:	30.33/hr.
Control pressure:	60 torr
Control temperature:	165-170°F
Feed temperature:	~100°F
WVR:	40.1% (based on condensate) 50% (based on product)

TABLE 4

VISCOSITY VERSUS TEMPERATURE OF PILOT PLANT FEED

Temperature (°C)	Viscosity (cps)*
20	29
30	20
40	15
50	13
60	11
70	9

*Brookfield LVT Spindle Viscometer, #2 spindle, 60 RPM.

TABLE 5

WVR VERSUS TEMPERATURE OF PILOT PLANT FEED

(60 torr pressure)

% WVR	Temperature (°C)
0	55.8
5	57.2
10	58.6
15	59.8
20	61.8
25	63.6
30*	65.8
35	68.4
40	71.6

Specific Gravity Data Obtained
Continued WVR

40	71.6
45	75.6
50	80.0

*Nucleation at 31% WVR, 66.2°C

TABLE 6

WVR VERSUS TEMPERATURE DATA OF PILOT PLANT FEED

(60 torr pressure)

% WVR	Temperature (°C)
0	55.8
5	56.8
10	58.2
15	59.4
20	61.0
25	63.2
30	65.2
35*	68.2
40	71.4

*Nucleation occurred at 34% WVR, 67.2°C.

TABLE 7

VISCOSITY VERSUS TEMPERATURE OF PILOT PLANT DSS PRODUCT

(40% WVR)

Temperature (°C)	RPM	Viscosity (cps)
80	60	24
70	60	34
60	60	54
50	60	131
40	60	305
30	30	880
20	6	2500
	Reheated	
80	60	26

TABLE 8

COMPOSITION OF PILOT PLANT FEED

Component	Concentration (M) TK-505	TK-509
Al	1.225	1.235
OH	3.40	3.42
NO_2	2.18	2.115
NO_3	2.54	2.50
CO_3	0.159	0.157
PO_4	0.041	0.027
SO_4	<0.052	<0.052
F	0.062	0.05
Cl	0.115	0.103
HEDTA	*	*
EDTA	*	*
$Cr_2O_7^=$	0.106	0.0983

*Unavailable.

TABLE 9

WVR VERSUS TEMPERATURE OF PILOT PLANT FEED

(60 torr pressure)

WVR (%)	Temperature (°C)
0	55.2
5	56.2
10	57.6
15	59.0
20	60.6
25	62.4
30*	65.0
35	67.4
40	70.2
45	74.2

*Nucleation.

TABLE 10

VISCOSITY VERSUS TEMPERATURE OF DSS PRODUCT

(45% WVR)

Temperature (°C)	RPM	Viscosity (cps)*
80	60	32
70	60	49
60	60	100
55	60	226
50	60	413
45	30	655
40	12	1200
35	12	1865
30	6	3400
25	3	6100
	Reheat	
75	60	49
80	60	41

*Brookfield LVT spindle viscometer, #2 spindle.

TABLE 11

COMPOSITION OF PILOT PLANT SAMPLE #1
(Sample taken at 3:10pm, 9/14)

Component	Slurry (M)	Filtrate (M)	Solids (Wt %)
Al	2.11	2.26	
OH	5.28	5.4	
NO_2	3.70	3.88	
NO_3	3.90	2.93	96
EDTA	*	*	
HEDTA	*	*	
SpG**	1.674	1.612	

*Not analyzed.
**At 70°C.

TABLE 12

COMPOSITION OF PILOT PLANT SAMPLE #2
(Sample taken at 9:15, 9/15)

Component	Slurry (M)	Filtrate (M)	Solids (Wt %)
Al	2.28	2.32	11
OH	5.48	5.75	6
NO_2	3.83	4.05	8
NO_3	3.15	1.28	73
EDTA	0.078	0.033	
HEDTA	0.138	0.125	
SpG*	1.664	1.637	

*At 70°C.

TABLE 13

COMPOSITION OF PILOT PLANT SAMPLE #3
(Sample taken at 1:30pm, 9/15)

Component	Slurry (M)	Filtrate (M)	Solids (Wt %)
Al	2.25	1.78	30
OH	5.5	5.98	7
NO_2	3.95	4.40	
NO_3	3.43	3.33	40
EDTA	*	*	
HEDTA	*	*	
TOC (g/L)	0.34	0.31	21
SpG**	1.665	1.623	

*Not analyzed.
**At 70°C.

TABLE 14

COMPOSITION OF PILOT PLANT SAMPLE #4
(sample taken at 3:20pm, 9/15)

Component	Slurry (M)	Filtrate (M)	Solids (Wt %)
Al	2.23	1.63	46
OH	5.5	5.78	
NO_2	2.95	4.23	
NO_3	4.68	3.18	21
EDTA	*	*	
HEDTA	*	*	
TOC	0.325	0.313	25
SpG**	1.662	1.619	

*Not analyzed.
**At 70°C.

TABLE 15

VISCOSITY VERSUS TEMPERATURE DATA FOR PILOT PLANT DSS PRODUCT

Sample 1

Temperature (°C)	RPM	Viscosity (cps)
76	60	34
	30	28
71	60	40
	30	40
64.5	60	53
	30	54
60	60	82
	30	84
55	60	110
	30	122
50	60	196
	30	216
45	60	320
	30	310
40	60	>500
	30	644
	12	650
35	60	>500
	30	900
	12	945
30	60	>500
	30	>1000
	12	1600
75*	60	49
	30	57

*Left sample stirring overnight at 30°C, heated to 75°C, and determined viscosity.

TABLE 16

VISCOSITY VERSUS TEMPERATURE DATA FOR PILOT PLANT DSS PRODUCT

Sample 2

Temperature (°C)	RPM	Viscosity (cps)
80	60	37
75	60	52
69.5	60	76
65	60	147
	30	166
59.5	60	375
	30	320
54.5	60	>500
	30	670
	12	708
50	60	>500
	30	>1000
	12	1300
	(stir & remeasure)	
	60	>500
	30	700
	12	925
45	60	>500
	30	>1000
	12	1875
	Heat	
72	60	275
	30	295
80	60	126
	Stir	
	60	82

TABLE 17

VISCOSITY VERSUS TEMPERATURE DATA FOR PILOT PLANT DSS PRODUCT

Sample 3

Temperature (°C)	RPM	Viscosity (cps)
80	60	47
75	60	50
70	60	72
65	60	125
60	60	280
	30	380
	stir	
	60	315
	30	322
55	60	430
	30	500
	stir	
	60	475
	30	500
50	60	>500
	30	820
	12	990
45	60	>500
	30	>1000
	12	1500
	heat	
80		51

TABLE 18

VISCOSITY VERSUS TEMPERATURE FOR PILOT PLANT DSS PRODUCT

Sample 4

Temperature (°C)	RPM	Viscosity (cps)
80	60	43
75	60	71
70	60	66
65	60	98
	30	105
60	60	173
	30	210
55	60	270
	30	310
50	60	478
	30	490
	60	460
45	60	>500
	30	>1000
	12	1300
	stir	
	30	>1000
	12	1500

598

Internal Letter

Rockwell International

Date. December 21, 1983

No. 65453-83-308

TO: (Name, Organization, Internal Address)
- M. I. Fineman
- Waste Management Process Technology
- 2750E/A219/200E

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Chemical Laboratory
- 222S/MO-037/200W
- 3-1571

Subject: Composition of Scaling Material from Reboiler After Engineering Laboratory Double Shell Slurry Run

The Engineering Laboratory (EL) conducted a pilot plant double shell slurry (DSS) run in September, 1983. Physical and chemical data were gathered both during and after the run. Additionally, after the run, the reboiler was dismantled, and several samples of "scale" and "plug" material were taken. The samples were given to the Chemical Laboratory Unit (CLU) for submission for X-ray analysis. The results of the analyses are shown in Table I. The data show that sodium nitrate ($NaNO_3$) is the major component formed in the reboiler.

As a supplemental test, the Waste Management Process Development Unit (WMPTU) requested that a sample of reboiler scale be subjected to boiling water to determine if the scale would dissolve in water. The sample was allowed to reflux at atmospheric pressure overnight, with minimal dissolution. After 5 days at boiling, approximately 70 percent of the sample appeared to dissolve. The insoluble fraction was then dissolved in hot, dilute nitric acid.

The acid soluble fraction was analyzed for metal ions. Table II shows the ions detected, and are reported in an ion to aluminum ion ratio (i.e. there were 1.23 times as many sodium ions in solution as there were aluminum ions). The water soluble fraction was not analyzed. These data show that sodium is the most prevalent cation, which is not surprising when the X-ray data are considered.

The data indicate that $NaNO_3$ is probably the scale material that forms during evaporator operation. Apparently steam would not be a rapid means to remove reboiler scale. A flush with some material, not detrimental to evaporator operations, might provide adequate cleansing of the scale. Should you require a determination of such a "cleansing" agent, or have questions regarding this work, please call me on 3-1571.

M. T. Jansky
Chemist

MTJ/pjm

cc: J. S. Buckingham JSB
K. G. Carothers
P. J. Certa
D. L. Herting
M. G. Kelly
H. R. Risenmay
M. J. Schliebe
File Code WB
Process Aids

TABLE I

X-RAY ANALYSES OF PILOT PLANT SOLIDS

Sample Description	Major Component	Minor Component	Trace
Reboiler tube plug*	$NaNO_3$	$Na\text{-}Al\text{-}Si\text{-}O \cdot H_2O$	?
Plug	$NaNO_3$		?
Reboiler tube sheet scale	$NaNO_3$ $(NH_4)_2Al_6O_9(SO_4)_4 \cdot H_2O$	$Na\text{-}Al\text{-}Si\text{-}O \cdot H_2O$	$AlSO_4OH \cdot 5H_2O$
Reboiler tube sheet top surface scale	Same as reboiler tube sheet scale		
Reboiler scale after flushing	$NaNO_3$ $Ca_5F(PO_4)_3$		

*Three samples submitted.

TABLE II

IONS IN ACID SOLUBLE FRACTION OF PILOT PLANT SCALE

Ion	Ion/Al Ion Ratio
Na^{+}	1.23
Al^{+3}	1.00
Si^{+4}	0.69
Ca^{+2}	0.26
Mg^{+2}	0.15
Fe^{+3}	0.01
Ba^{+2}	<0.01
Sr^{+2}	<0.01

Internal Letter

Rockwell International

Date December 30, 1983

No. 65611-83-236

TO Name, Organization, Internal Address:
K. G. Carothers

FROM Name, Organization, Internal Address, Phone
D. M. Tulberg
Waste Management Process
Technology Unit
2750-E/A-227/3-3429

Subject: Evaluation of the Pilot Scale Double-Shell Slurry Pumping Test

References:

(a) Letter, 65455-83-073, November 30, 1983, M. J. Schliebe/ M. T. Jansky to M. G. Kelly, "September 1983 Pilot Plant Double-Shell Slurry Evaporator-Crystallizer Run-Data and Results"

(b) Letter, 65453-83-288, November 11, 1983, M. T. Jansky/ H. R. Risenmay to D. M. Tulberg, "Laboratory Results from Slurry Pumpability Tests"

(c) Letter 65455-83-070, November 18, 1983, K. H. Lee to D. M. Tulberg, "Pilot Scale Evaporator"

(d) William B. Hooper, "The Two-K Method Predicts Head Losses in Pipe Fittings," Chemical Engineering (August 24,1981)

(e) J. A. Robertson and Clayton T. Crowe, Engineering Fluid Mechanics, 2nd edition, p 373, Houghton Mifflin Company, Boston (1980)

(f) Letter, 65611-83-233, December 16, 1983, R. E. Haaland to K. G. Carothers, "The Potential for Line Plugging During Transport of Double-Shell Slurry Evaporator Products"

(g) ARH-F-101, August 1976, W. E. Ogren and R. E. Van der Cook, "Vacuum Evaporator-Crystallizer Flowsheet for Waste Liquors"

(h) G. A. Hughmark, "Aqueous Transport of Settling Slurries and Engineering Chemistry (May 1961)

(i) A. R. Oroskar and R. M. Turian, "The Critical Velocity in Pipeline Flow of Slurries," AIChE Journal (July 1980)

(j) L. A. DeFrate, A. W. Etchells and B. J. Tilley, Chemical Engineering Applications of Modern Fluid Dynamics," AIChE Today Series (1981)

(k) A. Einstein, Ann. Physik 19, p. 289 (1906)

(l) V. V. Jinescu, "The Rheology of Suspensions," International Chemical Engineering (July 1974)

Rockwell International

SUMMARY

In an effort to further understand the rhelological properties of double-shell slurry(DSS), the product from the pilot scale evaporator-crystallizer run was evaluated. The effective pipeline viscosity calculated for the most concentrated product ranged between 52 to 56 cp (Table 1). This viscosity is in close agreement with the viscosities taken on samples (Ref. a) from the pilot run. The viscosity of the samples did not agree well with the viscosity of a laboratory boildown product (Ref. b).

The laboratory product had about one half the viscosity but was believed to be concentrated further then the pilot scale samples. Additional study is required to determine if laboratory studies will be useful in determining DSS viscosities of the evaporator.

Figure 1 shows the operating region that is required to process DSS within the bounds of the pump casing pressure limits (270 psi) and a minimum Reynolds number (Re) of 2400 at the conditions shown on the figure. A viscosity of 56 cp could be processed if the slurry flowrate is maintained between 52 and 67 gpm. It is advisable to operate at 67 gpm to give the flow the highest possible turbulence (Re=3100). At 3100 Re some laminar characteristics still exist therefore there is a risk of solids settling.

To increase the turbulence of the DSS products when transferred, the viscosity of the suspension must be modified. In the discussion of pumpability, several parameters that contribute to viscosity are discussed. Insufficient data exists on the physical characteristics of DSS solids to evaluate their effect. Control of slurry temperature to its maximum achievable limit is one of the major methods presently available for viscosity control. It must be noted however that if increased temperature caused more aluminum precipitation, viscosity could increase. Another parameter influencing viscosity that may be controlled is the volume percent solids. Precipitating and settling solids during intermediate stages of concentration (before production of DSS) may be achieved by controlling the operating temperature to maximize solids produced during these stages.

Recommendations

- It is desirable to transfer slurry at a flow rate that produces at least a Re of 4,000. Since WVR may be restricted by this high flow rate, a minimum Re of 2500 should be set.

- Since a risk of plugging is present, especially when operating below a 4,000 Re, control methods for determining if solids settling is occuring should be developed as a means for identifying the onset of line plugging. A recourse should be developed too.

Rockwell International

- The 270 psi operating specification will be the limit on the maximum achievable Re at a given viscosity. This specification should be investigated to determine if it can be raised.

- Additional study is required to determine if laboratory boil-downs of evaporator feed samples can be used to evaluate double-shell slurry viscosities. Included in this is an evaluation of particle size and distribution difference between laboratory scale and full scale evaporator operations.

- Additional study is required to evaluate the effects of aluminum precipitation on slurry viscosities.

- Evaporator operating schemes should be developed that would minimize the solids concentration in DSS. Possible methods are to run the evaporator process at elevated temperatures and to precipitate solids before the DSS process step.

- Haake absolute viscosities should be used when evaluating DSS viscosities.

- The best methods for determining critical velocities is by pilot scale experimentation. An evaluation of the feasibility of pilot scale study should be done. If the study is feasable and it is determined that the evaporator must operate at low flows to achieve a maximum WVR, a pilot scale test should be performed.

DISCUSSION OF EXPERIMENTAL RESULTS

During the September 1983 pilot evaporator DSS run, three slurry transfers to TK-48 were monitored. The data taken during these transfers are summarized in Table 2. Additionally, three water runs through the same transfer route were taken just prior to the pilot evaporator run. These data are also listed in Table 2. After initial analysis of these data, it was determined that additional knowledge of the pipelines roughness was required because of its large sensitivity in the calculations. Reference c lists the data taken to determine the roughness factor and the conditions of which the results were measured. Table 3 presents the results of the roughness calculations. It must be noted that two 45 bends were in the 15.25 ft length of line over which the pressure difference was measured. The two K method for head loss determination (Ref. d) was used to adjust the pressure drop to a straight length of pipe.

The roughness factors ranged from .000013 to .00021 ft. The largest roughness factor produced results not physically possible and therefore was not carried through in subsequent calculations.

Rockwell International

Roughness factors of .00005 ft. for stainless steel (Ref. d) and 0 for smooth pipe were carried through in further calculations for comparison purposes.

The next step in the calculations was the determination of an overall system head loss due to bends. Using the water tests that were made prior to th slurry transfers, head loss coefficients were calculated for each roughness factor and are listed in Table 1.

Effective pipeline viscosities were then calculated based on the range of roughness factors and head loss coefficients determined for water. A computer algorithm, which uses the Darcy equation, was used to determine friction factors. Laminar and turbulent viscosities were calculated based on the friction factors. Using the friction factor chart presented in reference e., it was determined that the flow for the slurry transfers must be in the laminar region. The slurry viscosity (Table 1), therefore, may be as high as 56 cp.

Comparison viscosities were taken during the pilot evaporator campaign using the Brookfield viscometer. A summary of the data in reference a is presented in Table 4. Additional viscosity information (Ref. b) from laboratory boildowns on the pilot feed is presented in Table 4. Viscosities from the Haake absolute viscometer were also taken in the laboratory study to make a comparison between absolute viscosities and the apparent viscosities given by the Brookfield. Figure 3 shows Brookfield viscosities versus Haake viscosities.

One of the major implications of the data in figure 3 is that Brookfield viscosities for different solutions cannot be correlated to give an absolute viscosities. Each solution measured had a different relationship between apparent and absolute viscosity. Another finding is that the Brookfield apparent viscosities tend to be higher than the absolute viscosities. As the absolute viscosity increases the differences between the viscosities tend to increase. Conversly, except for one solution that contained aluminate solids and slurry growth gases, the viscosities tend to converge near 50 cp.

The pilot scale evaporator was operated between 74° and 77° C (Ref a). At this slurry temperature, the Brookfield viscosities taken during the run are in good agreement with calculated effective pipeline viscosities. The good agreement may be due to two factors. First, the Brookfield viscosities are nearly the same as absolute viscosities at this point. Secondly, at this consistency, the slurry tends to behave as a Newtonian fluid (Ref. b).

One observation that is not explained is the difference between the laboratory boildown product viscosities and the pilot evaporator product viscosities. The 44% WVR boildown that was made on the same feed as processed through the pilot evaporator had a higher endpoint hydroxide and aluminum concentration than the pilot samples. The apparent viscosity of this boildown was only one half that of the pilot plant viscosities from samples 2, 3 and 4 but was similar that of sample 1. The major difference between sample 1 and the others, besides being somewhat less concentrated, was that aluminum precipitated from the latter three. If in fact aluminum is the cause for the observed differences and didn't precipitate from the laboratory boildown, it would indicate that these boildowns could not be confidently used to predict evaporator viscosities using the present laboratory technique. Further work is required in this area to conclusively determine how laboratory boildown viscosities relate to the evaporator product viscosities, particulary with regard to aluminum precipitation and the time frames required to produce a measurable affect.

DISCUSSION OF SLURRY PUMPABILITY

Slurries that are fast settling must be pumped in turbulent flow to maintain suspended solids in solution. A qualitative way of determining if a slurry is fast settling is to examine a slurry sample for a rapid solids bed accumulation in the sample container. Examination of slurries generated in the laboratory indicate that a percentage of the solids do settle rapidly, therefore the slurry must be treated as fast settling and turbulent flow is required during transfers.

The transition between turbulent and laminar flow is dependent on the individual slurries. Reference f indicates that this transition point could be as high as Re of 2400. At the transition point the flow is largely laminar with some turbulent characteristics. The fluid takes on more turbulent behavior until it reaches a Re of 4000 at which point the laminar characteristics are generally negligable. Ideally, to assure no settling, solutions should be pumped at a Re greater than 4,000. From a practical standpoint a Re this large would probably limit WVR because of the 270 psi pump casing pressure limits. It is possible that past DSS campaigns may have pumped slurries at a Re less than 4,000. Therefore, to give a maximum WVR, pumping DSS down to the 2400 Re level may be desirable.

It must be noted that approaching the laminar flow boundary introduces risk into the transfer process. Since past DSS runs may have transferred in or near the laminar flow regions, it is assumed that the risks are less than the gains in increased WVR. To insure that the risk of plugging remains small, additional study should be done to evaluate ways of detecting if solids are settling in the line. One method would be to monitor PB-2 pressure for increases. (Ref. g) Pressure sensitivity to flow changes must be evaluated to utilize this method in a process control scheme.

Rockwell International

The point at which solids settle is called the critical velocity Reference h is the correlation that was used in the past for determining critical velocities. Reference i developes a new correlation that is expected to yield better results (Ref j). Both correlations yield nearly the same critical velocity, but these results yield laminar flow. Since the correlations were developed for turbulent flow, the results are invalid. The best method for determining critical velocities is by pilot scale experimentation (Ref. j). As indicated earlier, it may not be possible to simulate evaporator condition in smaller operations. Therefore, the feasibility and usefulness of doing pilot scale work should be evaluated before proceeding to pilot tests.

Without equipment or specification modifications, the two controlling factors that will define DSS pumpability are the turbulent flow requirment and the 270 psi operating specification on PB-2 casing pressure. Figure 1 graphically presents the boundaries defined by these control limits. Additional boundaries are plotted on Figure 2 to show the affects of raising the Re requirement and making the casing pressure specification less restrictive. It should be noted that the pressure limit boundaries are for the conditions that are listed on the figures. The maximum viscosity that can be The maximum viscosity that can be pumped at the conditions presented is 70 cp. If higher turbulence (Re=4000) is requird the maximum viscosity is limited to 45 cp. Raising the pressure limit to 350 psi would raise the maximum viscosity limits to 80 and 51 cp for Re's of 2500 and 4000, respectively, lessening the length of pipe of the transfer route will have similar affects.

Control of DSS product viscosity will be a primary method of achieving pumpability. There are several parameters that affect the rheology of suspensions. Among these are solids concentration, particle dimension, particle shape, particle size distribution, particle surface nature, dispersion medium effects, electostatic effects and temperature. Solids concentration is one of the primary factors that determines viscosity. Einstein derived the following equation that gives the contribution of solids to viscosity (Ref k).

$$\mu_r = \frac{\mu_s}{\mu} = 1 + 2.5$$

μ_r = relative viscosity

μ_s = suspension viscosity

μ = dispersion medium viscosity

Φ = volume fraction of solids

For solutions that have a high concentration of solids, the coefficient for volume fraction of solids increases to as high as 5.5 (Ref 1).

Rockwell International

Solids concentration can be controlled by changes in temperature, chemical composition and volume reduction. Component solubilities are very temperature sensitive, therefore evaporator pot temperature can be used to keep the solids dissolved. Chemical composition can be controlled by precipitating solids prior to making DSS. As a last resort, a reduction in WVR will decrease the solids concentration.

Physical characteristics of the particles can also have a large affect on viscosity. Needle-like crystals from phosphates have been a common viscosity problem in the past. The plate crystals of aluminate are also believed to increase slurry viscosities. Particle size also can change viscosity. Particles of 10μ size have the least affect on viscosity. For larger than 10μ particles, the viscosity increases lineraly with particle size. Particles with less than 10μ size increase the viscosity rapidly as size decreases (Ref 1). Slurries with large crystal size distributions also have a lower viscosity than a slurry with a narrow particle size range.

Control over the physical characteristics is limited because most are a function of the evaporator properties. Inhibiting the precipitation of solids of harmful shape or size is the only control method. Additional study of aluminum precipitate would be required to take advantage of this method.

Among the remaining factors that contribute to viscosity, little is known about the contribution of particle surface nature and electrostatic effects. The dispersion medium for DSS has a viscosity of about 20 cp at 70°C. The high medium viscosity is a major contributor to the overall suspension viscosity. Since chemical composition controls the medium viscosity there is generally little control over this factor. The last parameter that affects visocisty is temperature. In addition to controlling the percent solids, temperature can also be used to control the dispersion medium viscosity. Operating at the maximum achievable temperature is therefore required if the viscosity is to be minimized.

Rockwell International

Any questions or comments regarding further work, please contact D. M. Tulberg on 373-3429.

KG Carothers for
D. M. Tulberg, Engineer
Waste Management Process Technology Unit

DMT:wrj

Att.

Distibution

R. B. Bendixsen
J. S. Buckingham ✓
P. J. Certa
R. D. Claghorn
G. T. Dukelow
M. I. Fineman
E. G. Gratney
R. E. Haaland
M. T. Jansky
M. G. Kelly
D. W. Lindsey
D. A. Reynolds
L. H. Rodgers
M. C. Teats
D. G. Wilkins
R. A. Zinsli
File/LB

TABLE 1 DOUBLE-SHELL SLURRY VISCOSITY RESULTS

Slurry run	Roughness factor $x10^5$ (ft)	Overall Head Loss Co-efficient	Total Bend Head Loss (PSI)	Straight Line Head Loss (PSI)	Friction factor	Effective Viscosity-Laminar (CP)	Effective Viscosity-turbulent (CP)
1	0	11.54	9.5	81.5	.04535	48.3	24.9
	1.3	9.91	8.1	82.9	.04645	50.0	26.5
	2.5	8.56	7.0	84.0	.04731	50.9	27.7
	3.3	7.72	6.3	84.7	.04785	51.5	28.5
	5	6.06	5.0	86	.04887	52.7	30.0
2	0	11.54	10.1	85.9	.04548	50.9	26.07
	1.3	9.91	8.7	87.3	.0465	52.0	27.6
	2.5	8.56	7.5	88.5	.04738	53.0	28.9
	3.3	7.72	6.8	89.2	.04789	53.5	29.6
	5.0	6.06	5.3	90.7	.04898	54.7	31.3
3	0	11.54	10.5	88.1	.04553	52.0	26.7
	1.3	9.91	9.0	89.6	.04659	53.1	28.3
	2.5	8.56	7.8	90.8	.0474	54.1	29.6
	3.3	7.72	7.0	91.6	.04801	54.8	30.8
	5.0	6.06	5.5	93.1	.04907	56.1	32.21

* Flow was determined to be laminar.Turbulent viscosities are only for comparison.

TABLE 2 PILOT EVAPORATOR TRANSFER DATA

	SP.GR	ΔP (PSI)	Corrected ΔP	Slurry level	Calculated Flow Rate (GPM)
Run 1 Slurry	1.691	90	91	45 to 20	8.03
Run 2 Slurry	1.696	95	96	45 to 20	8.30
Run 3 Slurry	1.72	100→95	98.6	40 to 15	8.36
Run 1 water	.997	61→60.2	61.4	40 to 20	12.19
Run 2 water	.997	61→60	61.4	40 to 20	12.19
Run 3 water	.997	61→60	61.4	40 to 20	12.19

*Calculated from gauge calibration curve

TABLE 3 CALCULATED PIPELINE ROUGHNESS FACTORS

Flow Rate (GPM)	Measured ΔP (PSI)	Adjusted* ΔP (PSI)	Roughness factor (ft)
6.36	3.20	2.87	.00021
8.07	3.88	3.35	.000019
9.44	5.21	4.49	.000022
10.51	6.20	5.31	.000013
8.72	4.61	3.99	.000033
9.29	5.18	4.48	.000033

*Pressure drop was corrected by subtracting the headloss due to 2-45° exbows

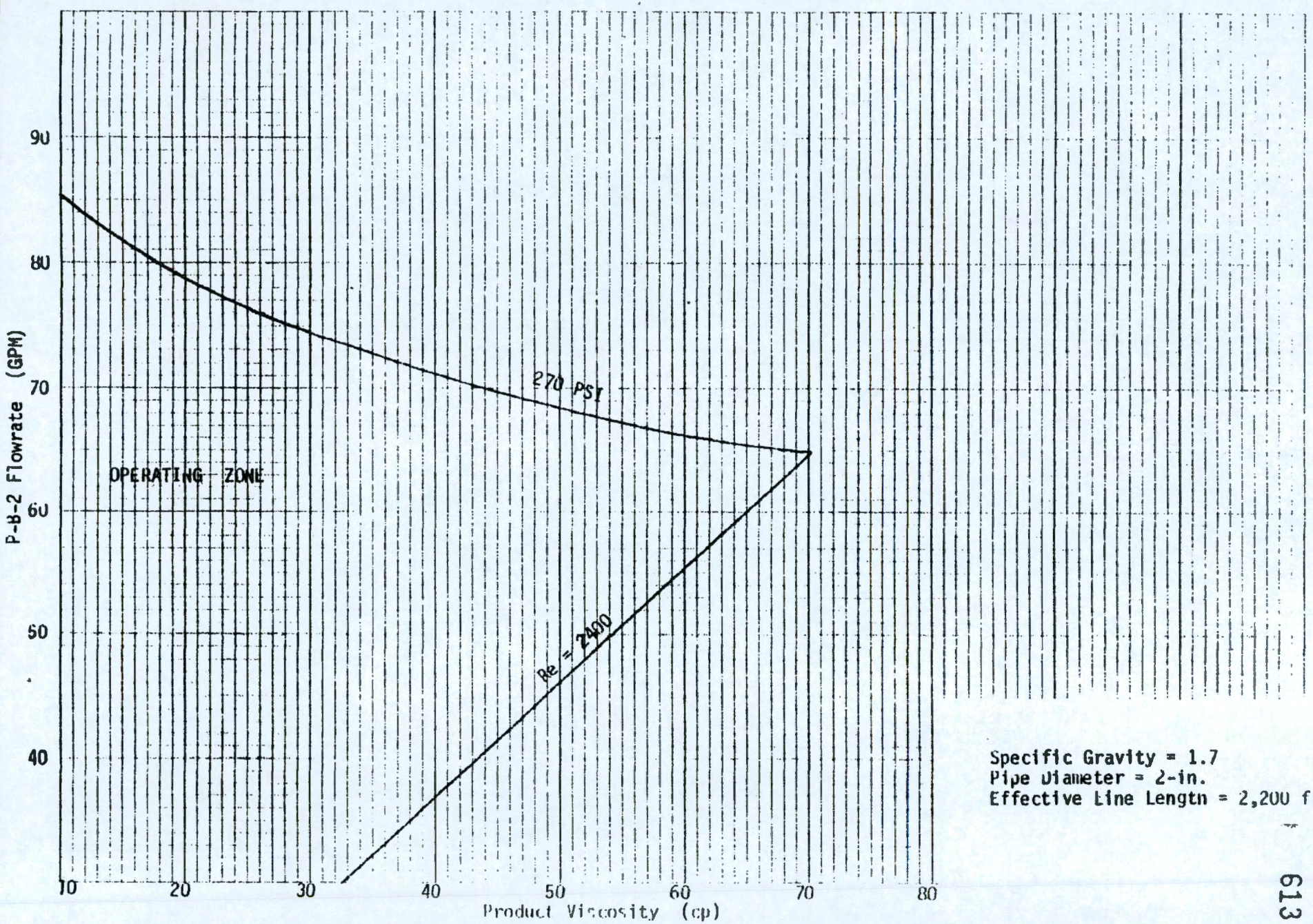
TABLE 4 SLURRY SAMPLE VISCOSITIES

	Method*	Viscosity 75°C** (CP)	Viscosity 70°C (CP)	SP.GR
P.P. Sample 1	Brookfield	35	44	1.685
P.P. Sample 2	Brookfield	52	74	---
P.P. Sample 3	Brookfield	50	72	1.722
P.P. Sample 4	Brookfield	51	66	1.71
Lab 41% WVR	Brookfield	---	29	---
Lab 41% WVR	Haake	---	24	---
Lab 44% WVR	Brookfield	---	38	---
Lab 44% WVR	Haake	---	36	---

*Brookfield viscosities are taken with a #2 spindle at 60 rpm.
Haake viscosities are at a shear rate of 692.5 sec -1

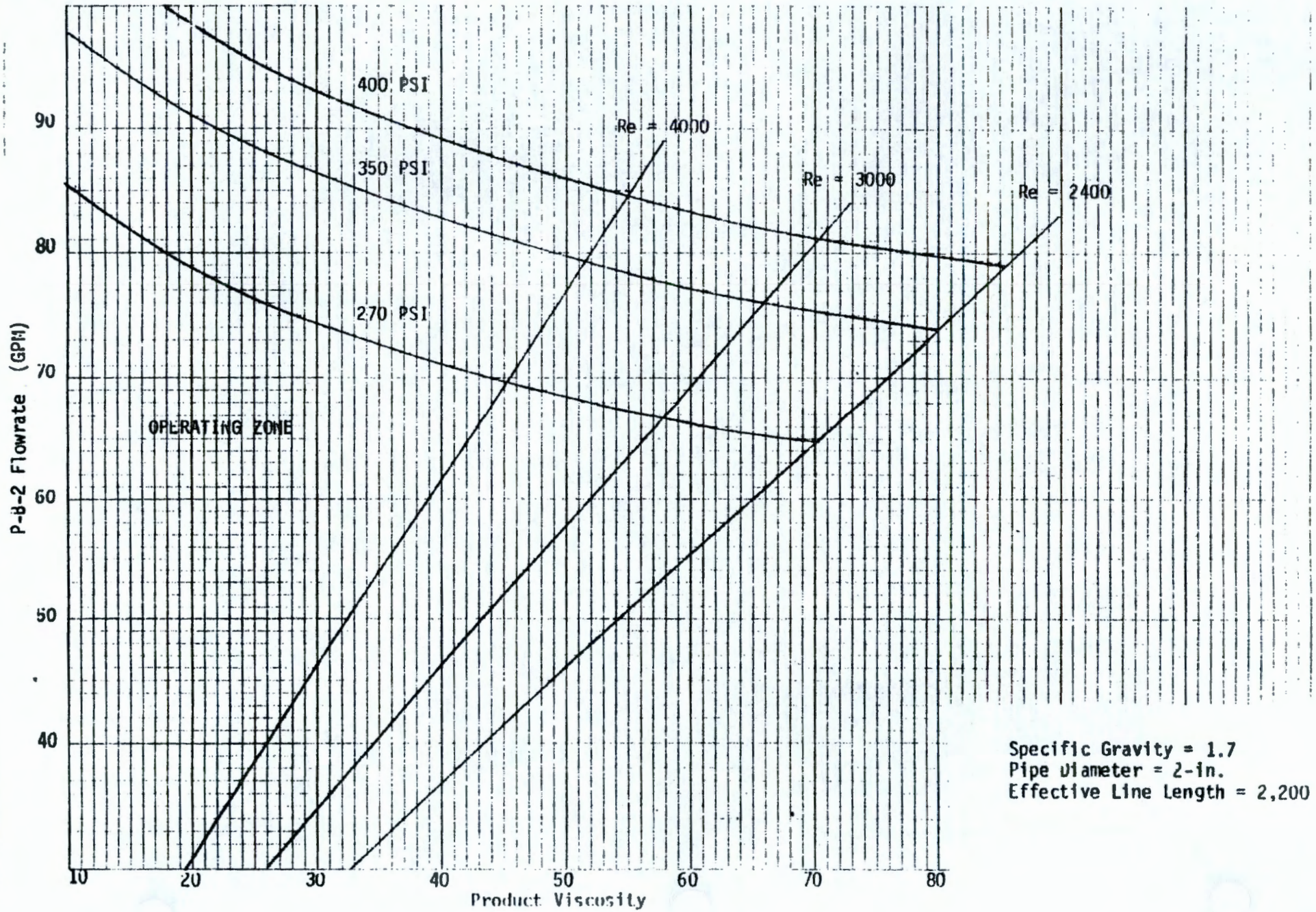
**The pilot evaporator operated between 74 and 77°C.

FIGURE 1. Double-Shell Slurry Operating Boundaries



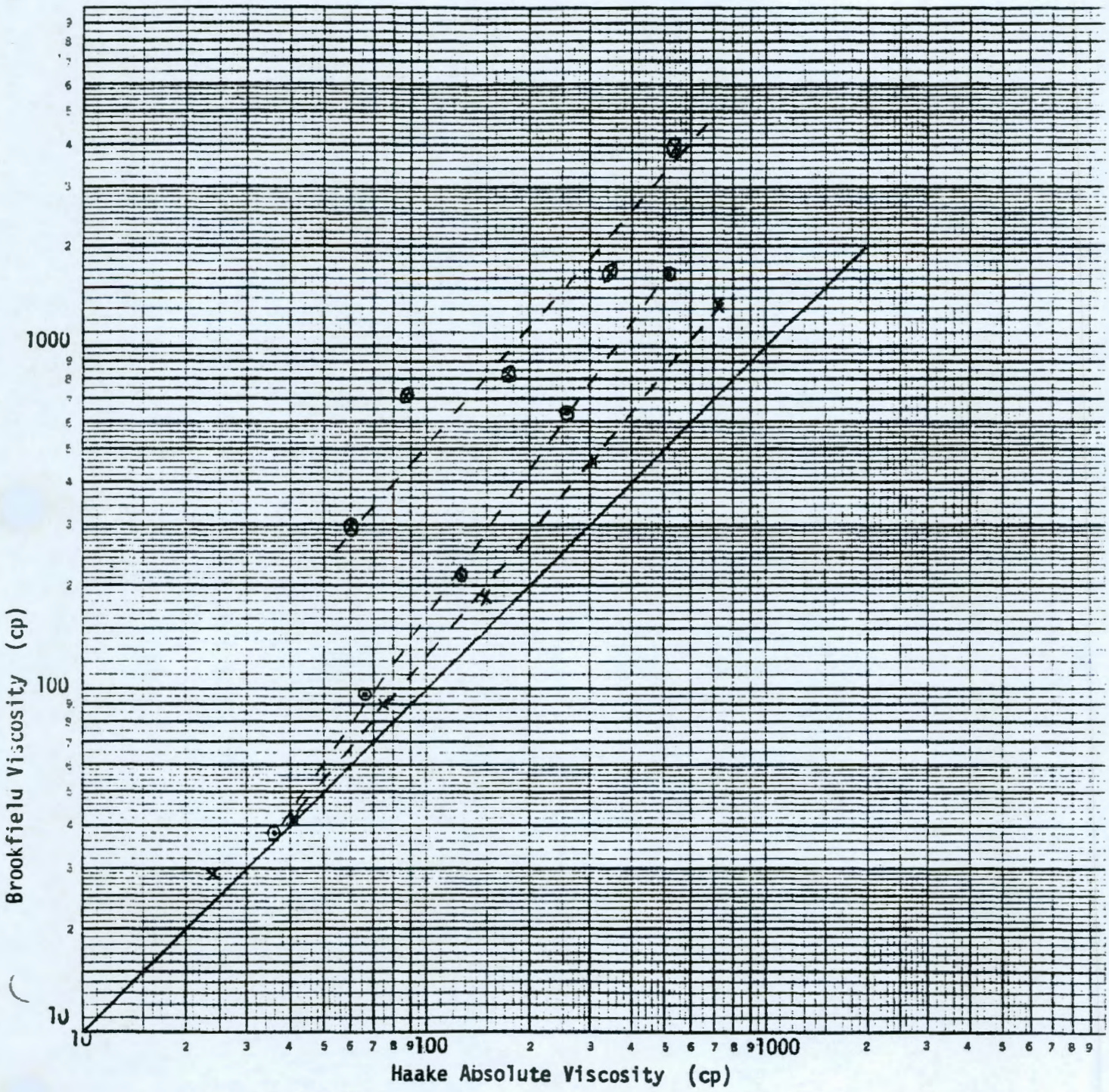
Specific Gravity = 1.7
Pipe Diameter = 2-in.
Effective Line Length = 2,200 ft.

FIGURE 2. Alternate Double-Shell Slurry Operating Boundaries



Specific Gravity = 1.7
Pipe Diameter = 2-in.
Effective Line Length = 2,200 ft.

FIGURE 3. Haake Viscosity vs Brookfield Viscosity



× 41% WVR
⊙ 44% WVR
⊗ Aged P.P. Sample 3

616

Internal Letter

Rockwell International

Date. March 17, 1983

No. 65453-83-070

TO: (Name, Organization, Internal Address)
. R. E. Haaland
. Process Design
. 2750E/A227/200 E

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Separations Process Development Unit
. MO-037/200 W
. 3-1571

Subject: . Salt Well Liquor/Double-Shell Slurry Study, Phase I

Reference: Letter, #65411-83-015, dated January 20, 1983, R.E. Haaland to M.T. Jansky, "Request for Synthetic Boildown Study with TX Salt Well Liquor"

As per your request in the reference letter, the Separations Process Development Unit (SPDU) investigated the chemical and physical properties of synthetic TX salt well liquor (SWL). This letter summarizes the initial data obtained from the investigations. The experimental details are discussed below.

Synthetic TX SWL was prepared. The chemical composition is shown in Table I. The material was concentrated at 60 torr to a 25% waste volume reduction (WVR). Relevant requested data for the boildown are shown in Tables II and III.

The product slurry was equilibrated at 38°C for 24 hours. The sample volume decreased 1.2%. There were 17 volume percent settled solids, and the equilibrated slurry density was 1.498. The slurry was separated into liquid/solid fractions, and each phase analyzed. Relevant requested data for each phase are shown in Table IV.

At this point, the concentrated TX SWL product supernatant was used for further study. The supernatant was to be used to prepare double-shell slurry (DSS); therefore, it is called DSS Feed (DSSF). Synthetic DSSF was prepared based on the chemical analyses shown in Table IV. The DSSF theoretical composition is shown in Table V.

The DSSF was subjected to a boildown at 40 torr to 35 percent WVR. The concentrated DSSF was held at the boiling temperature for 20 minutes to allow equilibration. The relevant requested boildown data are shown in Tables VI and VII.

Rockwell International

The DSSF boildown product was separated into three separate aliquots. One aliquot was filtered at 70°C and each phase analyzed. The relevant data are shown in Table VIII.

The remaining two aliquots were placed into a 38°C oven for observation. The requested data from those two aliquots will be reported in a separate letter.

Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ:giw

cc: J. S. Buckingham
K. G. Carothers
D. L. Herting
M. J. Kupfer
D. A. Reynolds
D. G. Wilkins
File Code: WB621
[redacted]

Attachments

TABLE I

SYNTHETIC TX SALT WELL LIQUOR COMPOSITION

Component	Theoretical	Experimental
Al	1.36	1.33
OH	2.99	3.59
NO_3	3.03	3.35
NO_2	1.89	1.82
CO_3	0.164	0.194
PO_4	0.047	0.0400
SO_4	0.026	0.042
Na	9.58	9.88
Viscosity (cps)*		12 (60 RPM), 8 (30 RPM)
Density*		1.385

*Measured at 38°C

TABLE II

WVR VS. TEMPERATURE DATA

(60 torr, Synthetic TX SWL)

% WVR	Temperature	Time Elapsed (minutes)
0	26.6	0
0	54.0	0
5	55.6	6
10	56.8	10
15	58.2	14
20	59.8	18
25*	61.8	23

*Nucleation occured at 25% WVR.

TABLE III

COMPOSITION OF TX SWL BOILDOWN PRODUCT

Component	Concentration (moles/liter)
Al	1.77
OH	4.00
NO_3	4.38
NO_2	2.32
CO_3	0.27
PO_4	0.070
SO_4	0.060
Na	12.5
Viscosity (cps)*	14 (60 RPM); 10 (30 RPM)
Density*	1.490

*Measured at 61.8°C

TABLE IV

COMPOSITION OF EQUILIBRATED, CONCENTRATED SYNTHETIC TX SWL

Component	Concentration	
	Supernatant (moles/liter)	Solids (weight %)[a]
Al	1.90	--
OH	5.40	--
NO_3	2.64	85
NO_2	2.38	--
CO_3	0.002	10
PO_4	0.062	2
SO_4	0.04	3
Na	11.64	--
Viscosity (cps)[b]	27 (60 RPM); 25 (30 RPM)	
Density[b]	1.459	

Centrifuged volume % solids = 23

"True" volume % solids = 6

Weight percent solids = 9

[a]Weight percent calculated as sodium salts

[b]Measured at 38°C

TABLE V

COMPOSITION OF SYNTHETIC DSSF

Component	Concentration (moles/liter) theoretical
Al	1.90
OH	4.10
NO_3	2.64
NO_2	2.38
CO_3	0.15
PO_4	0.06
SO_4	0.04
Na	11.2
Density*	1.447
Viscosity (cps)*	24 (60 RPM), 16 (30 RPM)

*Measured at 38°C

TABLE VI

WVR VS. TEMPERATURE DATA

40 torr, Synthetic DSSF

% WVR	Temperature (°C)	Time Elapsed (minutes)
0	29.0	0
0	53.2	0
5	54.8	5
10	56.4	6
15	59.0	35
21	61.8	46
25	64.6	52
30*	66.8	65
35	70.4	82

Product Density** 1.695

Product Viscosity (cps)** 34 (60 RPM)
33 (30 RPM)
60 (12 RPM)

*Nucleation, granules adhering to vessel.
**Measured at 70°C.

TABLE VII

COMPOSITION OF DSSF BOILDOWN PRODUCT

Component	Concentration (moles/liter)
Al	2.38
OH	6.5
NO_3	8.9
NO_2	1.7
CO_3	0.04
PO_4	*
SO_4	*
Na	17.3
SpG	1.695

*Unavailable

TABLE VIII

COMPOSITION OF CONCENTRATED DSSF

Component	Concentration: Supernatant (moles/liter)	Concentration: Solids (weight %)[a]
Al	2.47	34
OH	6.9	
NO_3	4.0	66
NO_2	3.6	
CO_3	0.08	
PO_4	Unavailable	
SO_4	Unavailable	
Na	17.04	

Viscosity (cps)[b] 27 (60 RPM), 21 (30 RPM), 17 (12 RPM)

Density[b] 1.652

Centrifuged volume % solids = c
"True" volume % solids = 2.75
Weight percent solids = 1.74

[a]Weight percent calculated as sodium salts
[b]Measured at 70°C
[c]Completely solidifies when cooled even a few degrees.

626

Internal Letter

Rockwell International

Date. May 25, 1983

No. 65450-83-130

TO: (Name, Organization, Internal Address)
. J. J. Goldin
. Program Engineering
. 2750E/200E

FROM: (Name, Organization, Internal Address, Phone)
. M. J. Kupfer
. Process Development
. 222S/MO-037/200W
. 3-2162

Subject: . Composition Ranges of Waste Feeds to Transportable Grout Facility

Refs:
1) Letter, #65410-83-052, D. G. Wilkins to R. E. Smith, "Composition of Waste Feeds to Transportable Grout Facility".
2) Eding, J. H., "Waste Volume Reduction Factors", RHO-CD-81-1164, October, 1981.
3) Letter, #65453-83-070, March 17, 1983, M. T. Jansky to R. E. Haaland, "Salt Well Liquor/Double Shell Slurry Study, Phase I".
4) Letter, #65453-80-348, November 20, 1980, M. T. Jansky to D. E. Bowers, "Second Double-Shell Slurry Campaign Products".
5) Letter, #65453-82-088, March 15, 1982, M. T. Jansky to M. R. Fox, "Updated Analyses of 244-TX Samples".
6) Allen, G. K., Jacobs, L. L., Reberger, D. W., "PUREX Flowsheet - Processing N Reactor Fuels", PFD-P-020-0001, September, 1982.
7) Claghorn, R. D., Telephone Communication with M. J. Kupfer, May 19, 1983.

Typical compositions of double-shell slurry (DSS), zirflex decladding waste, and customer waste feeds to the Transportable Grout Facility (TGF) were given in reference 1. To facilitate evaluation of the effects of waste components on grout properties, the expected concentration ranges of the components in the wastes were defined. Composition ranges for DSS are shown in Table 1. Composition ranges were based on information from references 2-5.

The concentration ranges of components in zirflex decladding waste should vary no more than ±20 percent of the flowsheet values shown in Table 2. The composition is based on data from reference 6. It should be noted that addition of sufficient $Ca(NO_3)_2$ or $Mg(NO_3)_2$ to precipitate the fluoride in this waste would likely be required prior to incorporation of the waste in grout. Free fluoride in the waste would prevent the grout from setting-up properly. Calcium or magnesium waste components are not shown in the table.

Rockwell International

The composition ranges expected for phosphate customer waste are shown in Table 3. A reference composition for sulfate customer waste is no longer needed since recent information indicates that it is unlikely that this waste would constitute feed to the TGF. Sulfate customer waste will probably be mixed with other dilute, non-complexed wastes, which would be converted to DSS (ref. 7).

Future waste management plans include possible mixing of wastes, or containment of more than one type of waste in double-shell tanks. It is thus quite likely that grout matrix development tests must encompass various mixtures of the waste streams shown in Tables 1-3. Possible mix combinations will be defined at a later date.

If you have any questions or require more information on the waste compositions, feel free to call me.

M. J. Kupfer
Staff Chemist

MJK/pjm

cc: J. S. Buckingham
D. L. Uhl
L. D. Vanselow
D. G. Wilkins
Process Aids

TABLE 1

Ranges in Concentration of Double-Shell Slurry Waste Components

Component	Concentration Range (molarity)
$NaAlO_2$	2.4 - 3.4
NaOH	3.6 - 6.5
$NaNO_3$	5.0 - 5.7
$NaNO_2$	4.0 - 5.4
Na_2SO_4	0.05 - 0.30
Na_3PO_4	0.05 - 0.50
Na_2CO_3	0.05 - 0.30
Na_2CrO_4	0.00 - 0.50
NaCl	0.10 - 0.40
NaF	0.00 - 0.20
TOC*	5 g/L - 20 g/L

*12.0 g/L total organic carbon (TOC) is equivalent to any one of the following: 0.10 M HEDTA, 0.10 M EDTA, 0.1667 M sodium citrate, 0.5 M sodium acetate, or 0.5 M sodium oxalate. It is assumed that 30% of the organic carbon contribution is from HEDTA, 10% from EDTA, 40% from sodium citrate, 10% from sodium acetate, and 10% from sodium oxalate. Following are gram amounts to be dissolved in one liter to give a TOC concentration of 12.0 g/L:

Component	g/L
HEDTA (N-hydroxyethylethylenediaminetriacetic acid, trisodium salt (MW-344.2)	10.33
EDTA (ethylenediaminetetracetic acid, tetra-sodium salt dihydrate (MW-416.2)	4.16
sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) - MW = 294.10	19.61
sodium acetate ($NaC_2H_3O_2$) - MW = 82.03	4.10
sodium oxalate ($Na_2C_2O_4$) - MW = 134.0	6.70

TABLE 2

Zirflex Decladding Waste

	Molarity*	
	Sludge + Supernatant	Supernatant
$ZrO_2 \cdot XH_2O$	0.18	--
OH^-	0.73	0.81
F^-	1.39	0.60
NO_3^-	0.024	0.027
Na^+	1.66	0.90
K^+	0.47	0.52
NH_3/NH_4^+	0.52	0.40

*Maximum ranges of molarity are ±20% of values shown.

TABLE 3

Composition of Phosphate Customer Waste

Component	Concentration Range (Molarity)
Na_2HPO_4	0.20 - 0.50
Na_3PO_4	0.007 - 0.018
NaOH	0.008 - 0.012
$NaNO_2$	0.011 - 0.028

Internal Letter

Rockwell International

631

Date. March 24, 1983

No. 65453-83-082

TO: (Name, Organization, Internal Address)
. J. G. Riddelle
. Process Engineering
. 2750E/A103/200 East

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Separations Process Development Unit
. 222-S/MO-037/200 West
. 3-1571

Subject: . Content of 244BX and 244U

Two samples were received by the Separations Process Development Unit (SPDU). One, from 244BX, was dated March 8, 1980. The second sample, from 244U, was dated March 2, 1983. Neither sample contained solids. As per your verbal request, the samples were analyzed for pH, hydroxide, nitrite, total alpha, and total beta. Additional analyses were available, and are included with requested data in the attached table.

Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachment

cc:

J. F. Albaugh
J. S. Buckingham
D. E. Cline
D. L. Herting
S. J. Joncus
R. A. Van Meter
R. D. Wojtasek
File Code: WB621
[redacted]
Letterbook

TABLE

Composition of 244BX and 244U

Component	Composition	
	244BX	244U
pH	11.75	12.28
OH^- (M)	9.42×10^{-3}	2.44×10^{-2}
NO_2^- (M)	3.56×10^{-2}	$<4.8 \times 10^{-5}$
Total Alpha (μCi/L)	$<2.42 \times 10^{-3}$	$<3.88 \times 10^{-3}$
Total Beta (μCi/L)	0.102	0.934
NO_3^- (M)	7.25×10^{-4}	7×10^{-3}
PO_4^{-3} (M)	--	6.53×10^{-3}

Internal Letter

Rockwell International

633

Date July 7, 1983

No. 65452-83-070

TO: (Name, Organization, Internal Address)
M. T. Jansky
Chemical Lab. Proc. Development Unit
MO-037/200 W

FROM: (Name, Organization, Internal Address, Phone)
S. G. Metcalf
Anaytical Process Development Unit
MO-037/200 W
3-1213

Subject: Non-Routine Pu and ^{241}Am Determination in Tank 244 BX Samples

Reference: "Determination of Plutonium and Americium in Hanford Defense Waste", SD-RE-LB-002, S.G. Metcalf, September 1982

Non-routine Pu and ^{241}Am analyses were performed on four samples of waste from Tank 244BX. The results, corrected for spike recovery, are given in the table.

The samples were analyzed by the method described in the reference. Each sample was analyzed in duplicate, spiked with appropriate activities of Pu and ^{241}Am and reanalyzed in duplicate. The average spike recovery for Pu and ^{241}Am were 97.6% and 91.1%, with relative standard deviation of 4.6% and 2.4%, respectively.

Analytical Laboratories is preparing to provide routine Pu and ^{241}Am determinations. Until that time, please contact me for additional non-routine support you might require.

D A Dodd

for S. G. Metcalf
Staff Chemist

SGM:gij

cc: S. A. Catlow
D. A. Dodd
J. S. Buckingham
C. H. Hunter
W. H. Sant
D. L. Uhl

Table 1

ANALYTICAL RESULTS FOR TANK 244BX

Sample Number	Pu, μCi/mL	^{241}Am, μCi/mL
K205	3.41×10^{-2}	$<5.1 \times 10^{-3}$
K206	1.61×10^{-2}	$<4.1 \times 10^{-3}$
K212	4.59×10^{-2}	$<6.0 \times 10^{-3}$
K224	3.05×10^{-2}	$<5.7 \times 10^{-3}$

Internal Letter

Rockwell International

Date: July 8, 1983

No. 65453-83-180

TO: (Name, Organization, Internal Address)
. J. G. Riddelle
. Process Engineering
. 2750E/A119/200 East

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Chemical Laboratory
. 222-S/MO-037/200 West
. 3-1571

Subject: . 244-BX Jet Pump Liquors

Several 244-BX samples have been received by the Chemical Laboratories Process Development Unit (CLPDU). The samples originated from the BY tank farm during jet pump operations. The Tank Farm and Evaporator Process Control Group (TFEPC) requested that CLPDU provide viscosity versus temperature data and plutonium and americium-241 analyses. This letter provides the requested data.

Three samples from 244-BX have been examined by CLPDU. The samples were dated May 26, June 5, and June 12. The sample dated May 26 contained a trace of solids when received; therefore analyses were conducted on both the supernatant and slurry (mixture of solids and supernatant). The other two samples contained no visible solids. Viscosity versus temperature data are shown in Table I. Table II contains the plutonium and americium-241 data.

It should be pointed out that the data in Table II indicate Pu concentrations higher in the supernatant than in the slurry. The difference is real, but the reverse of what one might expect. No explanation for this phenomenon is available at this time.

Additional samples have been received by CLPDU and are being processed. As data become available, they will be transmitted to you. Also, future samples will be treated in the same fashion.

Please call if you have any questions or comments regarding this work.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachments

cc:

J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
K. G. Carothers
P. J. Certa
D. L. Herting
D. M. Tulberg
R. A. Van Meter
[redacted]
File Code: WB621
Letterbook

Table I

Viscosity Verus Temperature Data From
244-BX Samples

	Viscosity (cps)*		
Temperature(°C)	5/26**	6/5	6/12
50	17	11	11
40	10	15	13
30	12	20	19
20	16	27	25
10	22	46	42
5	27	61	59

*Brookfield LVT spindle viscometer, #2 spindle

**Mixture; solids included

Table II

244-BX Pu/Am Samples

Sample Date	Pu (μCi/mL)	^{241}Am (μCi/mL)
5/26 (Supernatant)	3.41×10^{-2}	$<5.1 \times 10^{-3}$
5/26 (Slurry)	1.61×10^{-2}	$<4.1 \times 10^{-3}$
6/5	4.59×10^{-2}	$<6.0 \times 10^{-3}$
6/12	3.05×10^{-2}	$<5.7 \times 10^{-3}$

638

Internal Letter

Rockwell International

Date: May 9, 1983

No. 65453-83-137

TO: (Name, Organization, Internal Address)
J. G. Riddelle
Process Engineering
2750E/A119/200 East

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Separations Process Development Unit
222-S/MO-037/200 West
3-1571

Subject: WR Vault Samples

Two samples from the WR vault were received by the Separations Process Development Unit (SPDU) at the end of February, 1983. The samples were labeled 001-WR-Sump and 002-WR-Vault. Both samples had a thin layer of "gray fluff" on the bottom of the sample bottle, as well as some sand. The "gray fluff" was easily suspended when the sample was agitated. As per your request, the samples were analyzed for various components. The analytical results are shown in the attached table.

Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachment

cc:

J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
D. L. Herting
S. J. Joncus
R. D. Wojtasek
File Code: WB621
[redacted]

Content of WR Vault Samples

Component	Concentration	
	001-WR-Sump	002-WR-Vault
Total Beta (μCi/L)	612	77.6
Total Alpha (μCi/L)	2.09×10^{-2}	$<3.26 \times 10^{-3}$
Cs^{137} (μCi/L)	1.50	5.27
Sr^{90} (μCi/L)	187	57.3
Pu (g/L)	1.18×10^{-6}	7.22×10^{-7}
U (g/L)	2.66×10^{-4}	3.14×10^{-3}
Th (g/L)	$<2.7 \times 10^{-4}$	$<2.7 \times 10^{-4}$
NO_2 (molar)	0.0198	8.96×10^{-5}
NO_3 (molar)	0.286	0.114
pH	7.73	8.75
SpG	0.991	0.983

640

Internal Letter

Rockwell International

Date January 7, 1983

No. 65453-83-010

TO: Name, Organization, Internal Address,
D. E. Bowers
Process Engineering
2750E/A100/200 East

FROM: Name, Organization, Internal Address, Phone
M. T. Jansky
Separations Process Development Unit
222-S/MO-037/200 West
3-1571

Subject: Additional Data for Solids in Tank 203B

Ref: Letter, #65453-82-452, dated December 30, 1982, M. T. Jansky to D. E. Bowers, "Solids in Tank 203B"

Solids present in Tank 203B were previously isolated and characterized by the Separations Process Development Unit (SPDU). The referenced letter discussed the analytical results. A few corrections and additions to Table I of the referenced letter need to be made. Therefore, a new Table I is enclosed herein, which should replace the Table in the original letter.

Table I (this letter) includes solubility data that have been corrected for a dilution factor. Table II reports specific radioisotope content per gram of centrifuged solids (water-soluble or acid-soluble). Additionally, the latest results on the washed solids show that the water-insoluble solids are high in siliceous material. The exact quantitative and qualitative values are not available, however.

No further work is planned for this sample. I understand that an attempt to obtain a sludge sample is presently underway. Please call when the sample is ready, or if there are any questions regarding the completed work.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachments

cc:

J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
J. L. Deichman
K. A. Gasper
W. F. Heine
E. J. Kosiancic
W. L. Louk
W. H. Sant
C. P. Sutter
R. A. VanMeter
R. D. Wojtasek
File Code: WB621
[redacted]
Letterbook

TABLE I

Composition of Solids in Tank 203B
(as weight percent of centrifuged solids)

Component	Water-Soluble*	Acid-Soluble*
Ba	0.02	2.90
Fe	0.43	3.68
Mn	0.06	1.03
Hg	1.37	1.38
Al	0.19	3.29
Cr	0.10	0.27
Ni	**	0.03
Zn	4.7×10^{-3}	0.03
Na	8.8	17.55
Ca	0.12	5.80
K	2.80	1.32
Pb	**	0.13
Zr	**	0.06
Cd	**	**
La	0.05	1.16
Sn	**	**
P	0.33	0.70
Bi	0.20	3.10
Mg	0.05	3.91
Sr (total)	0.01	0.09
Sr^{90}	7.56×10^{-6}	**
Cs^{137}	3.1×10^{-8}	**
U	0.01	0.03
NO_2	0.42	0.25
NO_3	14.60	--
Pu	1.17×10^{-4}	**

*60-75 weight percent of solids is water

**Below detection limits

TABLE II

Radioisotope Content of Solids in Tank 203B
(per gram of centrifuged solids)

Isotope	Water-Soluble Solids	Acid-Soluble Solids
Sr^{90}	10.74 μCi	2.38 μCi
Cs^{137}	0.03 μCi	*
U	7.29×10^{-5} g	2.87×10^{-4} g
$Pu^{239/240}$	1.17×10^{-6} g	*

*Not detected

Internal Letter

Rockwell International

643

Date March 31, 1983

No. 65453-83-094

TO: (Name, Organization, Internal Address)
- M. C. Teats
- Process Engineering
- 2750E/A100/200 East

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Separations Process Development Unit
- 222-S/MO-037/200 West
- 3-1571

Subject: Samples from Tank 103AW

Two samples of waste from Tank 103AW were received by the Separations Process Development Unit (SPDU). One sample was taken two feet below the surface, and the other was taken from the bottom of the waste (both dated March 20, 1983). Neither sample had an abundance of solids, with the bottom sample containing less than one volume percent (virtually none in the 2-foot sample). As per your verbal request, the samples were prepared for analyses and submitted to Analytical Laboratories. The analytical data, and viscosity data, are shown in the attached tables.

There are several issues to point out concerning the analytical data for the 103AW bottom sample. Table II shows extremely low aluminum and nitrite concentrations. Apparently, some interferences were created by the "trace" of solids or the matrix used to dissolve the solids. The filtrate data in Table III is very similar to the data shown in Table I. Therefore, Al^{+3} and NO_2^- data in Table II are definitely suspect.

Also, the solids analyses indicate that the solids are 54 weight percent sodium aluminate, with the remainder of the solids organic material. Although a similar phenomenon has occurred in a previous sample, no explanation was (or is) available. It is interesting that although approximately half of the mass of solids are attributed to organic carbon, no HEDTA or EDTA were observed.

Finally, data is as yet unavailable on metallic ion content (inductively coupled plasma [ICP] analyses). The data will be transmitted to you when they become available.

Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ/naj

cc: (W/Attachments)

J. F. Albaugh, R. B. Bendixsen, J. S. Buckingham, K. G. Carothers, D. R. Groth, D. L. Herting, L. H. Rodgers, D. M. Tulberg, R. D. Wojtasek, [redacted]
File Code: WB621, Letterbook

TABLE I

Tank 103AW, 2-foot sample

3/20/83

Component	Concentration (moles/Liter)
Al	0.69
OH	1.25
NO_2	1.42
NO_3	2.61
CO_3	0.109
TOC (g/L)	3.78
HEDTA/EDTA	*
PO_4	0.039
SO_4	*
F	0.136
Cs^{137} (μCi/L)	8.60×10^4
Sr^{90} (μCi/L)	2.57×10^2
SpG	1.265
Viscosity (cps)	5

*Below Detection Limits

TABLE II

Tank 103AW, Bottom Sample, "Slurry"

3/20/83

Component	Concentration (moles/Liter)
Al	0.16
OH	1.03
NO_2	0.031
NO_3	3.36
CO_3	0.1
TOC (g/L)	4.58
HEDTA/EDTA	*
PO_4	*
SO_4	*
F	0.15
Cs^{137} (μCi/L)	2.28×10^5
Sr^{90} (μCi/L)	78.7
SpG	1.271
Viscosity (cps)	6

*Below Detection Limits

Table III

Tank 103AW, Bottom Sample, "Phases"

3/20/83

Component	Concentration	
	Filtrate (moles/L)	Solids (weight %)
Al	0.69	54
OH	1.31	
NO_2	1.08	
NO_3	2.90	
CO_3	0.11	
TOC (g/L)	3.68	46
HEDTA/EDTA	*	
PO_4	0.04	
SO_4	*	
F	0.15	
Cs^{137} (μCi/L)	2.17×10^5	
Sr^{90} (μCi/L)	2.51×10^2	
SpG	1.281	
Viscosity	6	

*Below Detection Limits

Internal Letter

Rockwell International

647

Date: May 24, 1983

No. 65453-83-149

TO: (Name, Organization, Internal Address)
- D. M. Tulberg
- Process Design
- 2750E/A227/200 East

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Separations Process Development Unit
- 222-S/MO-037/200 West
- 3-1571

Subject: Solids in Tank 103AW

Ref: Letter, #65453-83-094, dated March 31, 1981, M. T. Jansky to M. C. Teats, "Samples from Tank 103AW"

A sample from Tank 103AW was received by the Separations Process Development Unit (SPDU). The sample was found to be a dark green mixture, with virtually 100 percent suspended solids. A slight trace of supernatant liquor was observed over the solids. An aliquot was centrifuged to separate phases, with the supernatant and dissolved solids submitted to Analytical Laboratories for analyses. The analytical results are shown in the attached table.

The analytical data are in good agreement with earlier data (Reference) regarding the composition of the solids. As before, the two components comprising the solids were aluminum and total organic carbon. The earlier work did not have a large quantity of solids to work with, which may account for the differences in weight percent of the components (Al/TOC was 45/55 in this sample compared to 55/45 in the earlier work).

We will examine our sample archive to see if any 103AW sample remains. If so, as per your verbal request, the solids will be analyzed for determination of the organic compounds present. All information will be reported to you as it becomes available.

Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ/naj

cc: (W/Attachment)

J. S. Buckingham
K. G. Carothers
P. J. Certa
D. L. Herting
M. C. Teats
R. D. Wojtasek
File Code: WB621
[redacted]
Letterbook

648

Tank 103AW, Bottoms
R5467 - 4/12/83

Component	Concentration	
	Supernatant (Molarity)	Solids (Wt.%)
Al	1.43	45
OH	2.64	
NO_2	2.25	
NO_3	3.27	
CO_3	0.15	
TOC (g/L)	7.71	55
PO_4	*	
SO_4	*	
Cs^{137} (μCi/L)	4.96×10^5	
Sr^{90} (μCi/L)	Unavailable	
SpG	1.42	

*Below Detection Limits

Internal Letter **Rockwell International**

J.S. BUCKN... 10 1984 RECEIVED

Date August 4, 1983 65411-83-157

TO: (Name, Organization, Internal Address)
C. M. Walker
Tank Farm and Evaporator
Process Control
2750-E/A-108/200E

FROM: (Name, Organization, Internal Address, Phone)
L. M. Sasaki
Waste Management Process
Technology Unit
2750-E/A-227/3-3429

Subject: Waste Surface Level Changes in TK-101-SY

References: (a) Letter 65950-83-1286, July 21, 1983, C. M. Walker to W. F. Heine, "Waste Surface Level Changes in Tank 101-SY"

(b) Document, "Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101", RHO-LD-124, C. H. Delegard, December 1980

(c) Letter 60120-79-012, January 24, 1979, T. A. Lane to K. G. Carothers, "Synthetic Double Shell Slurry Gas Identification"

(d) Document, "Laboratory Plan to Study Gas Generation During Slurry Growth," SD-RE-DTP-007, M. T. Jansky, May 1983

This letter presents some of the engineering analysis done subsequent to the July 4, 1983 release of gases from the slurry into the vapor space of Tank 101-SY and addresses recommendations made in your letter on the subject (a).

Laboratory experiments with simulated double-shell slurry have shown that both HEDTA and glycolic acid react to form gases which become entrapped in the slurry, causing slurry growth. Gas composition analyses show varying results; H_2 concentrations, for example, have been reported to be as low as 4.8% or as high as 34% (b, c).

The amount of gas released during the pressurization of the tank is estimated to be between 2000 and 6000 moles. The actual value is probably closer to the 2000 mole figure considering the rapid rise and fall of the vapor space pressure. Calculations show that the H_2 concentration in the tank may have been as high as 1.65% after the release of the gases; this is near the specification limit of 2% (one half the lower flammability limit of H_2 in air) (see attachment for calculations). Knowledge of the ventilation rates in the tank would allow a more precise estimate of the amount of gas released. Gas generation experiments (d) will provide more information on the composition of the generated gases.

In general, Waste Management Process Technology Unit (WMPTU) agrees with all your recommended actions except the changing of the gas generation study (Item 4 in reference (a)); below are several comments and suggestions.

Rockwell International

1. Analysis of slurry samples from Tank 101-SY in July 1980 showed stratification of wastes, but the uniform temperature profiles obtained after the second double-shell slurry (DSS) campaign in November 1980 indicate that the layers may have mixed. Slurry samples from several levels should be analyzed to determine if layering of wastes exists. Sampling can be done in conjunction with, or perhaps in lieu of, lancing the tank waste. Gas sampling equipment should be in place and ready for use in the event that pressurization (a gas release) occurs at the time of lancing.

2. The planned gas generation experiments (d) are part of the on-going slurry growth studies and should not be changed. These experiments will provide information on gas generation and slurry growth rates as well as gas compositions. If slurry sampling shows the existence of "duplex waste" a separate set of experiments can be conducted to study the behavior of such waste.

3. If gas sampling at the time of the next gas release is feasible, samples should be taken at different times and at different heights above the liquid level. The first samples should be taken as soon as possible after the gas release. Perhaps the equipment can be set up such that a sudden increase in tank vapor space pressure triggers gas sampling. Since the duration of a pressure spike is relatively short, waiting for an operator, radiation monitor and engineer to get prepared and out in the tank farm to do the sampling after a gas release has occurred will not be practical. Also, since the tank could become pressurized, the current procedure of dropping flexible tubing through an open riser to sample the vapor space should not be followed.

L. M. Sasaki

L. M. Sasaki, Engineer
Waste Management Process Technology Unit

LMS:wrj

cc: J. F. Albaugh
[redacted]
K. G. Carothers
D. A. Reynolds
T. S. Vail
R. A. Van Meter
D. G. Wilkins
File/LB

L.M. Sasak,
T 12 July 1983

Calculations

Tank 101-SY vapor space pressurization/gas release 4 July 1983

Data initial pressure, $P_i = -0.8$ "wg $= 406.0$ "w 1 gal = 0.1337 ft³

final pressure, $P_f = +1.0$ "wg $= 407.8$ "w

($P_{atm} = 406.8$ "w)

gas constant $R = 1.18$ ft³ "w/gmol °K

initial liquid level, $h_i = 410.75$"

final liquid level, $h_f = 406.1$"

Assumptions: temperature $T = 140°F = 333°K$

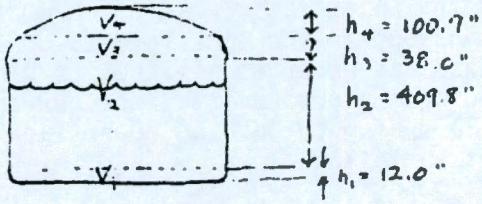
instantaneous release of gas

ideal gas law applicable $PV = nRT$

specific gravity of slurry = 1.7

Vapor Space Calculation:

reference: Letter, J.A. Reid to D.R. Ellingson, "Boiling Waste Tank Volume Calculations AZ Farm", 6 December 1982.



$V_4 = 143{,}555.9$ gal $= 19{,}191.5$ ft³

$V_3 = 102{,}155.6$ gal $= 13{,}656.8$ ft³

$V_2 = 1{,}128{,}538.4$ gal $= 150{,}870.1$ ft³

V_2 is a right cylinder

$V_1 = 32{,}670.53$ gal $= 4{,}367.60$ ft³

$V_{TOTAL} = 1{,}406{,}921$ gal $= 188{,}086$ ft³

vapor space volume, $V = V_4 + V_3 + (V_2 \times$ fraction of V_2 occupied by vapor)

$$\boxed{V = V_4 + V_3 + V_2\left(1 - \frac{h-12}{409.8}\right)}$$

h = liquid level in inches

Before Gas Release:

$$V_i = 19{,}191.5 + 13{,}656.8 + 150{,}870.1\left(1 - \frac{410.75-12}{409.8}\right) \text{ ft}^3$$

$$V_i = 36{,}916.4 \text{ ft}^3$$

using ideal gas law

$$n_i = P_i V_i / RT$$

$$= (406.0)(36{,}916.4)/(1.18)(333)$$

$$n_i = 38{,}143.4 \text{ gmol air in Tank originally}$$

After gas Release:

$$V_f = 19{,}191.5 + 13{,}656.8 + 150{,}870.1\left(1 - \frac{406.1-12}{409.8}\right) \text{ ft}^3$$

$$V_f = 33{,}628.3 \text{ ft}^3$$

652

$n_f = PV/RT$

$= (407.8)(38,628.3)/(1.18)(333)$

$n_f = 40,089.0$ gmoles (air+gas) in tank after release

$\Delta n = 40,089.0 - 38,143.4$ gmole

$\boxed{\Delta n = 1945.6 \text{ gmole gas released}}$

(1,379 ft^3 at NTP)

This is a conservative estimate of the # of moles of gas released

Hydrogen Concentration in the Vapor Space:

assumptions: complete mixing of gas and air

released gases contain 34% H_2 (max. amount found in expts)

$$\frac{(1945.6 \text{ moles gas released})(0.34 \text{ mole } H_2/\text{mole gas})}{(40,089 \text{ moles gas+air})} \times 100\% = \boxed{1.65\% \ H_2 \text{ in vapor space}}$$

Alternate calculation for gas released.

the pressure was essentially back to its original level 20 minutes after the gas release began.

assumption: ~~apt~~ exhauster operated at a constant 180 ft^3/min for the 20 minutes (NTP assumed)

moles of gas released = moles of gas exhausted + moles of additional vapor space due to liquid level decrease

volume of gas exhausted = (180 ft^3/min)(20 min)

= 3600 ft^3

→ 4163 gmole gas removed @ NTP

increase in vapor space volume = (368.2 ft^3/in tank space)(4½" l.l. drop)

= 1657 ft^3

→ 1712 gmoles @ −0.8" wg, 333K

moles of gas released = 4163 + 1712

= $\boxed{5875 \text{ moles gas released}}$

Internal Letter

Rockwell International

Date: December 28, 1983

No. 65453-83-311

TO: (Name, Organization, Internal Address)
- T. M. Kady
- Process Engineering
- 2750E/A118/200 E

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Chemical Laboratory Unit
- MO-037/200 W
- 3-1571

Subject: Tank 101AZ Sludge

A sludge sample from Tank 101AZ was received by the Chemical Laboratory Unit (CLU) on August 29, 1983. The sample, #R7788, came in a split-tube sampler. There was approximately two inches of sludge and 50 milliliters of liquor. The liquor was not retrieved when the sampler was opened.

An aliquot of the sludge was centrifuged. The sludge was 78.3 volume percent, and 68.96 weight percent, solids. The solids had a bulk density of 1.51 grams/mL. The supernatant had a density of approximately 1 g/mL. The supernatant was analyzed, with the analytical data shown in Table I.

The centrifuged sludge was contacted with 2x volumes of water to determine solubility. Approximately 6 volume percent of the solids dissolved at 23°C, 15 percent dissolved at 50°C, and 23 percent at 70°C. The aqueous phase was analyzed, also those analytical data are also shown in Table I. The water-insoluble fraction was dissolved in acid, with the data presented in Table II.

The data show that the 101AZ solids are high in nitrate and aluminum. The water-soluble fraction, not surprisingly, consists primarily of nitrate and nitrite. The high caustic value may be attributable to aluminum hydroxide (gibbsite) which is slightly soluble. Gibbsite was found to be the most prevalent material present in the dried sludge, as determined by x-ray diffraction. The gibbsite would naturally be soluble in acid, which accounts for the high aluminum content in the acid-soluble fraction.

Archived samples of the 101AZ are available should further work be requested. Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ:gij

cc: R. B. Bendixsen
J. S. Buckingham JSB
M. I. Fineman
D. L. Herting
D. W. Lindsey
D. J. Swanberg
File: WB
[redacted]

Attachments

TABLE I

COMPOSITION OF TANK 101AZ SLUDGE

Component	Concentration: Interstitial Liquor (M)	Concentration: H_2O Soluble Solids (wt%)
Al	0.077	
OH	0.19	13**
NO_2	0.27	18
NO_3	0.77	35
CO_3		
TOC	0.731	30
PO_4	0.077	
SO_4	0.01	
Fe	0.002	
Cr	0.006	
Pu (g/L)	3.55×10^{-3}	
Am (μCi/L)	*	
Cs^{137} (μCi/L)	2.34×10^{5}	
Sr^{90} (μCi/L)	1.11	
HEDTA	*	*
EDTA	*	*

*Below detection limits.
**See text.

TABLE II

COMPOSITION OF ACID-SOLUBLE (WATER-INSOLUBLE) 101-AZ SLUDGE

Component	Weight %
Na	13
Al	27
Fe	4
Cr	1
C	8

656

Internal Letter

Rockwell International

Date July 28, 1983

No. 65453-83-191

TO: (Name, Organization, Internal Address)
T. M. Kady
Tank Farm and Evaporator Process Control
2750E/A118/200 East

FROM: (Name, Organization, Internal Address, Phone)
J. S. Buckingham
Chemical Laboratory Process
222-S/MO-037/200 West
3-2487

Subject: Characterization of 102AZ Waste Tank

Tank 102AZ has been designated as the receiver tank for neutralized PUREX waste when PUREX begins operations. Before new waste can be added to the tank the contents of the tank must be transferred to another tank. Prior to the transfer supernatant liquid and sludge samples were taken for characterization. As I understand the samples were taken using the "bottle on a string" technique.

Examination of the two samples indicated they both were slurry samples of the light flocculant slurry in the tank rather than a sample of the supernatant liquid and the sludge. Because the two samples appeared to be the same a complete analysis was not performed on the sludge sample sent to the Chemical Laboratory Process Development Unit (CLPDU). The results from the supernatant liquid sample sent to the 222-S Analytical Laboratory combined with the limited results from CLPDU are shown in Table 1. The viscosity of the slurry as a function of temperature is shown in Table 2. It was found that 60 percent of the solid centrifuged from the slurry was soluble in water at a ratio of two volumes of water to one volume of sludge.

Please call me if you have any questions regarding this work.

JS Buckingham

J. S. Buckingham, Acting Manager
Chemical Laboratory Process Development Unit

JSB/naj

cc:

G. Burch
M. T. Jansky
L. H. Rodgers
T. S. Vail
S. Yoo
R. D. Woitasek
[redacted]
Letterbook
K. G. Carothers

Attachments

Table 1

102AZ Supernatant Liquid

	AL	CLPDU	WT.%
Vol. Solids in Slurry	10%	6.76%	
SpGr	1.410 g/ml		
H_2O	52.0%		52.0
pH		10.8	
NaOH	0.82M		7.3
$NaAlO_2$	0.135M		0.8
$NaNO_2$	0.536M	0.53M	2.6
$NaNO_3$		3.72M	22.4
Na_2CO_3	0.832M		6.3
Na_3PO_4	0.01M		0.1
TOC	70 g/L		9.6*
Na	8.51M		
^{137}Cs	3.14×10^5 µCi/L		
^{90}Sr	2.65×10^5 µCi/L		
Total			96.1

*Assumes all TOC is mixture of HEDTA and EDTA

Table 2

Viscosity of 102AZ Slurry

Temperature	Viscosity, centipoise*
5	27
10	19.8
20	15.5
30	12.9
40	10.0
50	5

*Brookfield Rotoviscometer, No. 2 spindle, 60 RPM

Internal Letter

Rockwell International

Date August 19, 1983

No. 65453-83-[redacted]

TO: (Name, Organization, Internal Address)
. Distribution
.
.

FROM: (Name, Organization, Internal Address, Phone)
. J. S. Buckingham
. Chemical Laboratory Unit
. MO-037/200 W
. 3-2487

Subject: . Analysis of TK 102AZ Supernatant Liquid

The waste currently in the 102AZ tank is classified as complexant waste concentrate. That is the waste has been through B-Plant for the removal of ^{90}Sr and ^{137}Cs. Since 1979, the supernatant liquid waste in 102AZ has been sampled four times for various tasks. Different organizations were interested in the data for different reasons; therefore, not all analyses were performed each time. I thought it might be helpful and interesting to record all of the analyses in one letter so those interested can compare results obtained over a period of time. It is interesting to note the consistency of the SpGr, H_2O, OH^-, NO_3^-, and ^{137}Cs analyses. With an exception, the ^{90}Sr analysis is fairly consistant.

At the present time, a sample of sludge from TK 102AZ is being analyzed by the Process Development Group. The results of that analysis will be reported later. Please call me if you have any questions regarding the data presented here.

JS Buckingham

J. S. Buckingham
Acting Manager
Chemical Laboratory Unit

JSB:gij

Distribution: R. B. Bendixson
D. A. Dodd
M. T. Jansky
F. M. Jungfleisch
M. J. Kupfer
T. M. Kady

CORRECTED ATTACHMENT FOR LETTER #65453-83-213

660

TK 102AZ ANALYSES

Analyte	(1) 6/26/79	(2) 8/27/81	(3) 9/20/82	(4) 7/28/83
SpGr, g/mL	1.392	1.391	1.390	1.410
H_2O, %	48.5	51.0		52.0
OH^-, M	1.03	1.10	0.998	0.82
No_2^-, M	0.20	0.057		0.53
No_3^-, M	4.26	4.08		3.72
Co_3^{-2}, M	0.81	1.25		0.832
PO_4^{-3}, M	0.011	0.006		0.01
SO_4^{-2}, M	0.904			
F^-, M	0.009		0.0165	
Cl^-, M	0.005			
Al, M	0.18	0.031	0.024	0.135
Na^+, M	3.0		8.14	8.51
TOC, g/L	121.8		76	70
HEDTA, M			0.2062	
EDTA, M			0.0585	
^{137}Cs, Ci/L	0.331	0.375	0.220	0.314
^{155}Eu, μCi/L	2.11×10^4	5.85×10^3		
^{90}Sr, Ci/L	0.244	0.292	0.072	0.265
^{99}Tc, μCi/L			100.	
$^{239/240}Pu$, g/L	0.0024	0.00106	0.0036	

(1) Routine sample analyzed by 222S Analytical Laboratories (AL).
(2) Special sample analyzed by M. T. Jansky.
(3) Special sample analyzed by M. T. Jansky, primarily for complexants, Tc, and actinides.
(4) Special sample analyzed by J. S. Buckingham and AL for pumping assesment.

Internal Letter

Rockwell International

Date August 26, 1983

No. 65453-83-221

TO: Name Organization, Internal Address,
- T. M. Kady
- Process Engineering
- 2750E/A118/200 E

FROM: Name Organization Internal Address Phone.
- M. T. Jansky
- Chemical Laboratory Unit
- MO-037/200 W
- 3-1571

Subject: 102AZ Sludge Sample

References: 1) Letter, 65950-83-1304, T.M. Kady to J.S. Buckingham, "102-AZ Sludge Sample Analysis" July 29, 1983

2) Letter, 65453-83-191, J.S. Buckingham to T.M. Kady, "Characterization of 102AZ Waste Tank" July 28, 1983

Tank 102AZ may be used as the receiver tank for neutralized PUREX waste after PUREX Startup. The waste presently in the tank needs to be characterized prior to adding the PUREX waste. Samples from Tank 102AZ have been taken for that purpose. Reference 1 discusses desired information regarding existing waste in Tank 102AZ. The purpose of this letter is to document the requested data.

As it turns out, four samples were taken from Tank 102AZ. The first "sludge" sample was insufficient for analyses. The next two were not sludge samples, but light flocculant slurry samples. They were analyzed and the results reported in Reference 2. The fourth sample, taken utilizing a "bottle on a string" technique, was indeed a sludge sample. Relevant data are discussed below.

The sludge sample contained approximately 90-95 volume percent settled solids, with a small layer of very dark supernatant. The sludge sample was transferred to a jacketed vessel for mixing and viscosity determinations. It was noted that the material was rather viscous, having to be scoped out of the sample bottle. The sludge was well stirred, and an aliquot was taken for solubility measurements and analyses. The remainder of the sample was used to determine viscosity versus temperature (those data are shown in Table I).

The aliquot taken for solubility determinations was centrifuged (50 volume percent centrifuged solids). The slurry specific gravity was found to be 1.421. The supernatant was decanted, and the bulk density of the centrifuged solids was determined to be 1.50. The centrifuged solids were contacted with twice the volume of water (2:1, H_2O:solids). At 26°C, 18 volume percent of the solids dissolved, 23 percent dissolved at 50°C, and 30 percent dissolved at 70°C. The aqueous phase was decanted and analyzed for chemical content. The remainder of the solids were dissolved in dilute hydrochloric acid and also analyzed. The interstitial liquor was "backed out" of the solids analyses, (using supernatant analyses from Reference 2), and the weight percent of remaining compounds calculated (assuming sodium salts of aluminum, nitrite, nitrate, and phosphate). The composition of the solids is shown in Table II.

Rockwell International

Table III contains data for radionuclide content of the sludge. The data presented here are centrifuged solids containing interstitial liquor. The data are presented this way because supernatant liquor analyses are not available, i.e., the interstitial liquor was not "backed out". Please note that if a representative aliquot of the as-received sludge was analyzed, the radionuclide content would be considerably higher because the supernatant liquor would necessarily be included.

It was requested, after several days, that the Chemical Laboratory Unit (CLU) warm the sample further, past 70°C. Tank farms had experienced NO_x generation, noting the heating of 102AZ as a possible cause. The sludge sample was warmed to 100°C, with no evidence of NO_x generation. The vapor space above the heated sludge was tested for NO_x using Draher tubes capable of detecting less than 0.5 parts per million (ppm) NO_x. The sludge then had air bubbled through it, with subsequent testing for NO_x. As before, no evidence of NO_x generation was observed. The CLU concluded that Tank 102AZ was not the source of NO_x generation in the tank farms.

The data clearly indicate that the sludge contains a large quantity of precipitated organic compounds. Specific complexant analyses showed that HEDTA and EDTA are not present in the sludge. The conclusion is that the organic is some degradation product from complexant destruction. The specific nature of the organic might be oxalate or acetate, both of which are notoriously soluble in water. However, other possibilities do exist, but the capability of determining the nature of the organic material is not presently available in Rockwell.

Please call if you have any questions or comments regarding this or future work with Tank 102AZ sludge.

M. T. Jansky
Senior Chemist

MTJ:gij

attachment

cc: J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham JSB
K. G. Carothers
P. J. Certa
D. L. Herting
M. J. Kupfer
R. S. McBeath
L. H. Rodgers
L. M. Sasaki
T. S. Vail
R. E. Van Meter
D. G. Wilkins
R. D. Wojtasek
File: WX63G
[redacted]

TABLE I

VISCOSITY VERSUS TEMPERATURE OF 102AZ SLUDGE

Temperature (°C)	RPM	Viscosity* (Centipoise)
20	30	937
30	30	820
	12	1025
40	30	630
	12	800
50	60	400
	30	480
60	60	300
	30	380
70	60	239
	30	300

*Used Brookfield spindle viscometer, #2 spindle

TABLE II

COMPOSITION OF 102AZ SLUDGE
(Centrifuged Solids)

Component	Weight %	
	Water Soluble	Acid Soluble
$NaAlO_2$		38
$NaNO_2$	6	
$NaNO_3$	50	
Na_3PO_4		61
TOC*	43	

*Total Organic Carbon

RADIONUCLIDE CONTENT OF TANK 102AZ SLUDGE
(Per Liter of Centrifuged Solids)

Component	Content		
	Water Soluble	Acid Soluble	Total
Cs^{137} (μCi)	1.25×10^{5}	1.29×10^{5}	2.54×10^{5}
Sr^{90} (μCi)	8.34×10^{4}	1.35×10^{5}	2.19×10^{5}
Pu (g)	3.72×10^{-2}	4.75×10^{-1}	0.512
Am (g)	1.42×10^{-2}	1.47×10^{-4}	2.05×10^{-4}
Tc^{99} (μCi)	22.62	20.08	42.70
Pm (μCi)	1.30×10^{5}	1.32×10^{5}	2.62×10^{5}

*As received sludge sample may contain more of these radionuclides. As noted in the text, the data presented here are based on centrifuged sludge solids, containing an unknown amount of interstitial liquor; however, supernatant liquid has been removed.

666

Internal Letter

Rockwell International

Date September 1, 1983

No. 65453-83-228

TO: (Name, Organization, Internal Address)
· Those Listed

FROM: (Name, Organization, Internal Address, Phone)
· M. T. Jansky
· Chemical Laboratory Unit
· MO-037/200 W
· 3-1571

Subject · Corrected Radionuclide Content of Tank 102AZ Sludge

Reference: Letter, #65453-83-221, M.T. Jansky to T.M. Kady, "102AZ Sludge Sample" August 26, 1983

The referenced letter contained information regarding chemical and physical characteristics of Tank 102AZ. The data for the radionuclide content of Tank 102AZ sludge needs to be corrected, specifically for plutonium and americium. The data in the reference letter were based on Analytical Laboratories data, which were incorrectly reported to the Chemical Laboratory Unit. Correct data have been supplied, with corresponding corrections shown in the attached table.

Please discard the radionuclide data in the referenced letter and include the attached Table III. Please call if you have any questions regarding 102AZ.

M. T. Jansky
Senior Chemist

MTJ:gij

cc: J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham JSB
K. G. Carothers
P. J. Certa
D. L. Herting
T. M. Kady
M. J. Kupfer
W. L. Louk
R. S. McBeath
L. H. Rodgers
L. M. Sasaki
C. P. Sutter
T. S. Vail
R. E. Van Meter
D. G. Wilkins
R. D. Wojtasek
File: WX63G
[redacted]

Attachment

TABLE III

RADIONUCLIDE CONTENT OF TANK 102AZ SLUDGE, CORRECTED

(Per Liter of Centrifuged Solids)

Component	Content		
	Water Soluble	Acid Soluble	Total
Cs^{137} (μCi)	1.25×10^{5}	1.29×10^{5}	2.54×10^{5}
Sr^{90} (μCi)	8.34×10^{4}	1.35×10^{5}	2.19×10^{5}
Pu (g)**	3.72×10^{-2}	2.98×10^{-2}	0.0671
Am (g)**	1.42×10^{-4}	1.47×10^{-4}	2.90×10^{-4}
Tc^{99} (μCi)	22.62	20.08	42.70
Pm (μCi)	1.30×10^{5}	1.32×10^{5}	2.62×10^{5}

*As received sludge sample may contain more of these radionuclides. As noted in the text, the data presented here are based on centrifuged sludge solids, containing an unknown amount of interstitial liquor; however, supernatant liquid has been removed.

**Note corrected values.

668

Internal Letter

Rockwell International

Date September 8, 1983

No. 65452-83-232

TO: (Name, Organization, Internal Address)
. G. J. Carter
. B-Plant Process Control
. 271-B/Trl./200 East

FROM: (Name, Organization, Internal Address, Phone)
. J. R. Jewett
. Chemical Lab. Unit
. MO-037/200 W
. 3-1972

Subject: . Corrosion of Tank H-101

Reference: Metals Handbook, 8th ed., Taylor Lyman, ed., (American Society for Metals, 1961), Vol. 1, pp. 570-3.

Introduction and Summary

Solutions of hydrogen sulfate ($NaHSO_4$) are prepared in the H-101 tank for the Rare Earth Strike recovery of strontium from Sulfate Strike waste. Recently, a good deal of corrosion has occurred in the piping associated with this tank. Analyses of the $NaHSO_4$ crystals and of the 4.5 M $NaHSO_4$ solution from the H-101 tank show large amounts of chloride present. The combination of chloride, sulfate, and acid is highly corrosive toward stainless steels.

Experimental Results

Crystals of $NaHSO_4$ obtained directly from the vendor's drum were mixed with laboratory distilled water to a concentration of 4.5 M. This solution, along with the 4.5 M $NaHSO_4$ solution taken from TK H-101, was analyzed by Analytical Laboratories using ion chromatography. Chromatographic peaks corresponding to chloride were somewhat overlapped with peaks of unknown identity. Re-analysis of the samples, after precipitating the chloride with silver, confirmed the identification of the chloride peaks. The chloride concentrations found were 0.0065 M in the solution prepared with laboratory water and 0.030 M in the TK H-101 solution.

Discussion

If these measurements are truly representative of the chloride concentration in this tank, it is not surprising that corrosion has occurred. $NaHSO_4$ solution is quite acidic; the dissociation of 4.5 M hydrogen sulfate ion (HSO_4) yields on the order of 0.6 M free acid. The concentrations of chloride found in this acid solution are well within the range known to be incompatible with stainless steels.

The corrosion problem is exacerbated by the additional presence of sulfate. According to Reference 1:

Rockwell International

G. J. Carter
Page 2
September 8, 1983

"one to 5% [0.1 - 0.5 M] sulfuric acid at ambient temperature should not be stored in vessels of molybdenum-free stainless steels. Type 316 may be used for this purpose; 317, with a higher molybdenum content, may be used safely in this range of acid concentration at temperatures as high as 150 F."

TK H-101 and the associated piping are made of Type 304, a molybdenum-free stainless steel. The use of 316 (2%-3% Mo) would presumably reduce attack by sulfate; however, the chloride problem would remain.

J. R. Jewett
Chemist

JRJ:gij

cc: J.S. Buckingham JSB
J.O. Honeyman
I.E. Reep
W.R. Dworzak
File:WD631
[redacted]

670

Internal Letter

Rockwell International

Date: December 12, 1983

No. 65950-83-1696

TO: (Name, Organization, Internal Address)
J. F. Albaugh, Manager
Process Engineering Department
2750-E A-107 200-E

FROM: (Name, Organization, Internal Address, Phone)
R. B. Bendixsen
Tank Farm & Evaporator
Process Control Group
3-1018

Subject: SOURCE OF NO_X FUMES IN 241-A-702 VENTILATION SYSTEM, FINAL REPORT

Reference: Letter, September 29, 1983, R. B. Bendixsen to R. D. Wojtasek, "Source of NO_X Fumes in 241-A-702 Ventilation System"

The source of NO_X emissions, visually observed in the 241-A-702 exhaust stack (296-A-17) during September and October, is degradation of complexant waste in Tank 102-AZ. Several NO_X and NH_3 concentration measurements using Draeger tubes (Table 1) support the conclusion of the reference letter that the hot liquid in 102-AZ causes NO_X emissions. Inspection of the data in Table 1 shows a general correlation of higher liquid temperature in 102-AZ producing higher NO_X concentrations in the A-702 exhaust stack. In addition, the before and after measurements of NO_X concentrations in the AN Tank Farm ventilation system indicate that the 200 inches of hot AZ-102 liquid transferred into 107-AN also caused NO_X emissions from the AN Farm ventilation system of 1 ppm (part per million).

The concentrated complexant in 102-AZ had a September 1983 analysis measuring .21 and .06 moles/liter of, respectively, HEDTA and EDTA (sodium salts of N- (2-hydroxyethyl) ethylene- and ethylene- diaminetriacetic acid). Calculations indicate that about 4% of the HEDTA and EDTA have degraded in the 102-AZ solution due to NO_X emission. It is not known how much of the NO_X was absorbed by reaction with caustic in the solution to form nitrate/nitrite salts. Therefore, analysis of samples of 102-AZ solution (contained in 107-AN) are recommended to check for organic degradation and to determine if the solution is complexed or can be processed as noncomplexed waste. This suggestion would require a hot boildown experiment by the Process Design Group. A significant cost saving in double shell tank space will result if the 102-AZ waste has been degraded enough to be reclassified as noncomplexed waste.

R. B. Bendixsen, Staff Engineer
Tank Farm & Evaporator Process Control

RBB:ra

cc: J. S. Buckingham
K. G. Carothers
G. T. Dukelow
R. B. Gelman
D. W. Lindsey
M. T. Jansky
M. C. Teats
D. G. Wilkins
File
R. A. Van Meter

Table 1

Tank Farm NO_x Emissions

	241-A-702		AW Farm		AN Farm		AZ-102	
Date	NO_x[1]	NO_3[2]	NO_x	NH_3	NO_x	NH_3	Temp. °F	Comments
09/02/83	300-400	-[3]	-	-	-	-	195	Light yellow plume, A-702
09/09/83	90-200	.04	-	-	-	-	193	Light yellow plume, A-702
09/13/83	100	-	-	-	-	-	179	Plume not visible
09/21/83	3	0	0	.03-.04	0	0	179	Base line of AW and AN Farms
10/03/83	30	.01-.02	-	-	-	-	180	102-AZ agitator pump is on
10/10/83	300	.05	-	-	-	-	203	102-AZ agitator pump is on
10/12/83	200	.03	-	-	-	-	205	102-AZ agitator pump is on
10/28/83	90	.02	0	.03	1	0	180	Transferring 102-AZ to 107-AN

1. Units are volume fraction, parts per million in the air flow.
2. Units are volume percent.
3. Data not taken.

672

Internal Letter

Rockwell International

Date February 18, 1983

No. 65453-83-046

TO: (Name, Organization, Internal Address)
- J. A. Reid
- Process Engineering
- 2750E/A116/200 East

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Separations Process Development Unit
- 222-S/MO-037/200 West
- 3-1571

Subject: Laboratory Procedure for Determining Settling Rates of Neutralized Current Acid Waste (CAW/ZAW)

The general laboratory technique for determining "settling rates" for neutralized PUREX current acid waste (CAW/ZAW) is discussed below.

Fifty mL of waste slurry is placed into a 50 mL graduated cylinder (2 cm. I.D., 15.2 cm. long). The slurry consists of interstitial liquor and suspended solids. The volume of "settled solids" versus time is monitored; i.e., the solids/supernatant interface is recorded as a function of time. The data are generally reported in graph form as volume percent settled solids versus time.

Please call if you need additional information.

M. T. Jansky
Senior Chemist

MTJ/naj

cc:

J. F. Albaugh
[redacted]
D. L. Herting
N. W. Kirch
R. D. Wojtasek
Letterbook

Internal Letter Rockwell International 673

Date. March 21, 1983 No. 65453-83-077

TO: (Name, Organization, Internal Address)
- D. W. Lindsey
- Process Engineering
- 2750E/A116/200 East

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky
- Separations Process Development Unit
- 222-S/MO-037/200 West
- 3-1571

Subject: Laboratory Support for Aging Waste Characterization

PUREX is scheduled to start processing nuclear fuels in 1984. The waste from the processes will either be put directly into tanks to age for 5-7 years, or processed through B-Plant and then put into tanks. Regardless, the waste will need to be intermittantly sampled to provide information pertaining to waste composition, stability, and behavior. Since the waste samples will contain solids, and also since the samples will be taken on a non-routine, as-needed basis, they should be sent to me or Separations Process Development Unit (SPDU) personnel.

In the past, it has been SPDU's responsibility to handle tank farm and evaporator samples that contain solids. Typically, we provide data regarding viscosity, weight and volume percents of each phase, particle size dimensions, temperature-dependent parameters, as well as other physical measurements. We also separate the phases and have them analyzed by Analytical Laboratories (AL) to determine chemical compositions. Being as the samples we receive are "non-routine", SPDU is somewhat more flexible than AL in procedures. Also, again because of our flexibility, we can adapt and modify our capabilities to meet your specific needs. The SPDU reviews and interprets the data to insure they make sense and then reports the data (generally in internal letterform) to the customer.

The Process Engineering Department should provide SPDU with a complete list of specific needs, i.e., data, that they desire, as well as a sample schedule. Proper planning will insure accurate results and timely turnaround.

Please call if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ/naj

cc:

J. F. Albaugh
J. S. Buckingham JSB
G. Burch
D. L. Herting
L. Jensen
W. L. Louk
L. H. Rodgers
D. Swanberg
R. D. Wojtasek
[redacted]
File Code: WB
Letterbook

674

Internal Letter

Rockwell International

Date November 11, 1983

No · 65453-83-289

TO: (Name Organization, Internal Address)

· C.J. Geier
· Waste Management Program Office
· 2750E/200 E

FROM: (Name, Organization, Internal Address, Phone)

· D.R. Bratzel
· Chemical Proc. Unit
· MO-037/200 W
· 3-1228

Subject: · Identification of Chemical and Physical Analyses in Support of Waste Tank Characterization

References:
1. Letter, #65462-83-063, F.M. Jungfleisch to J.S. Buckingham and D.A. Dodd, "Request for Review and Cost Estimation of the Proposed Analysis of Waste Core Samples", September 28, 1983.
2. Letter, #65452-83-144, D.A. Dodd to V.W. Hall, "Chemical and Physical Measurements for Waste Tank Characterization", November 8, 1983.

Reference 1 cites analytical method requirements, detection limits, and minimum measurement criteria for the characterization of waste tank core samples in support of the WG85 work package. Reference 2 identifies chemical and physical measurements defined in Reference 1 which require analytical development and documentation. Based on user organization meetings to clarify waste characterization requirements, the following letter documents a finalized list of waste characterization radionuclide analyses, chemical analyses, and physical measurements to fulfill a November 15 milestone.

Core Segment Breakdown

Typical full-depth cores recovered from underground waste storage tanks will consist of a series of core segments composed of solid waste phases and interstitial liquid. Once the core segment sampler is received in the laboratory, the waste sample will be extruded from the sampler in a laboratory hot cell, photographed for a permanent visual record, and visually examined to determine decision criteria regarding the laboratory characterization scheme. Visual examination includes general appearance, identification of continuous phase types, stratification, color, general morphology (crystalline or amorphous phases), and evaluation of preservation of core sampling integrity.

Rockwell International

Based upon visual identification of phase differentiation, decision criteria regarding the analysis of seperate phases is determined. Continuous phases which account for >20% of the total segment volume will be independantly characterized for radionuclide activity, chemical constituents, and physical measurements.

After visual examination of the core segment sample, drainable liquor will be collected, the volume recorded, and characterized for chemical and radionuclide composition. The mass and approximate volume of the solid phase will also be recorded. Continuous major phases will be blended, sampled, dissolved (10 grams of waste sample per liter of solution), and characterized.

Physical Analyses

Physical analyses will be performed on each core segment or principal waste phase in an attempt to quantify tank stratification. Routine physical analyses to be performed on the solid waste sample and drainable liquor are shown in Table 1. Requested analysis methods are discussed in Reference 1 and include drainable liquor volume, percent moisture, bulk density, particle density, particle size distribution, sample viscosity (rheology), supernatant viscosity, water solubility, and softening point. As discussed in Reference 2, method development is required for determination of softening point. All other analyses have been demonstrated on high-level waste samples.

Drainable liquor analyses determines the volume of liquid collected from the core sampler during sample breakdown in the hot cell.

Percent moisture analyses will be determined on both the solid waste and drainable liquor samples. After centrifugation of sludge samples to decant drainable liquor, percent moisture was previously determined by the weight loss after heating the sample for at least 8 hours at 110°C in a laboratory oven. Thermogravimetric analysis (TGA) has been suggested as a replacement method for determination of percent moisture as well as crystal lattice water and water of hydration.

Bulk density is determined on a centrifuged, solid waste sample by measuring the mass to volume ratio. Particle density is determined using the dried sample from the percent moisture analysis. Particle density is calculated by the addition of a specified volume of normal paraffin hydrocarbon (NPH) to the dried sample (to correct for void volume) and measuring the mass to volume ratio. The specific gravity (SpG) of the drainable liquor will also be determined.

Rockwell International

Particle size distribution will be conducted on the sludge sample for determination of the population distribution of particle size ranges.

Viscosity analyses will be performed on both the drainable liquor and phase sample as a function of temperature.

Water solubility analyses will quantitatively and qualitatively determine chemical and radionuclide constituents which are water soluble upon contacting a fraction of the sludge with deionized water. Reference 1 discusses the possibility of three successive water contacts with a known amount of sludge sample.

Softening point will be defined as the temperature at which a solid phase sample begins to "flow". As previously mentioned, this is the only physical measurement which requires method development.

Radionuclide Analyses

Radionuclide analyses which will be routinely performed on drainable liquor and dissolved solid phase samples are listed in Table 2. The basis for selecting these radionuclides is based upon regulatory guidelines and estimates of average radionuclide concentrations in the waste inventory as detailed in Reference 1. Radionuclide analyses which require analytical development are discussed in Reference 2 and include carbon-14, technitium-99, and plutonium-241. These radionuclides are determineed by solvent extraction or ion-exchange techniques to seperate the desired radionuclide(s) from the dissolved solid phase sample or drainable liquor. Radionuclide counting techniques include alpha energy analysis (AEA), beta counting, and gamma energy analysis (GEA). A total alpha analysis will be performed in addition to a total beta anlaysis to determine individual radionuclide contributions to the total activity, that off-standard conditions are identified, and independant methods are verified (Reference 1).

In addition, reference 1 discusses the need for special analyses (neptunium-237, uranium-236, uranium-233, and uranium-238) for waste associated with special fuel reprocessing.

Rockwell International

Chemical Analyses

Table 3 identifies non-radioactive chemical constituents and requested detection limits which will be determined in both dissolved solids and drainable liquor. Of the twenty-six constituents listed, seven methods are required. Chemical analyses which require analytical method development include selenium and free hydroxide (Reference 2). Free hydroxide (defined as the unbound hydroxide ion concentration of the drainable liquor) will only be performed on drainable liquor samples >pH 10.

The need for optimization of ion chromatography (Dionex) methods for determination of anions is also discussed in Reference 2. Previous waste characterization laboratory experience has shown dilution factors often decrease the anion concentration below effective detection limits.

Please call if there are any questions or comments.

D.R. Bratzel

D. R. Bratzel
Chemist

attachments

DRB:gij

cc: J.S. Buckingham JSB
F.M. Jungfleisch
T.A. Lane
R.S. McBeath
W.H. Sant
T.S. Vail
D.G. Wilkins
File: WG

Table 1

Physical Analyses

Sludge Phase	Drainable Liquor
Visual	Visual
Photograph	Volume
Volume	Specific Gravity
Mass	Percent Moisture
Bulk Density	Viscosity
Particle Density	
Thermogravimetric Analysis	
Percent Moisture	
Water of Hydration and Crystallization	
Particle Size Distribution	
Viscosity (Rheology)	
Softening Point	

Table 2

Radionuclide Analyses

Radionuclide	Detection Limit (Ci/L)*
Carbon-14**	$7x10^{-7}$
Strontium-90	$3x10^{-7}$
Technitium-99**	$2x10^{-5}$
Cesium-137	$2x10^{-6}$
Plutonium-239&240	$4x10^{-7}$
Plutonium-241**	$3x10^{-5}$
Americium-241	$4x10^{-8}$
Total Alpha	$4x10^{-8}$
Total Beta	$2x10^{-6}$
Gamma Energy Analysis	$2x10^{-6}$

*Assumes 10 grams of solid sample per liter of solution

**Requires method development (Reference 2)

Table 3

Chemical Analyses

Analyte	Required Detection Limit (g/L)	Method
Total Uranium	$1x10^{-1}$	Fluorimetry
Chloride	$1x10^{-2}$	Ion Chromatography
Fluoride	$1x10^{-1}$	Ion Chromatography
Nitrite	$1x10^{-1}$	Ion Chromatography
Sulfate	$1x10^{-1}$	Ion Chromatography
Aluminum	$1x10^{-1}$	ICP*
Silver	$5x10^{-5}$	ICP
Bismuth	$1x10^{-2}$	ICP
Cadmium	$5x10^{-5}$	ICP
Chromium	$5x10^{-5}$	ICP
Iron	$1x10^{-2}$	ICP
Manganese	$1x10^{-2}$	ICP
Sodium	$1x10^{-2}$	ICP
Nickel	$3x10^{-3}$	ICP
Phosphorous	$1x10^{-1}$	ICP
Lead	$5x10^{-5}$	ICP
Silicon	$1x10^{-2}$	ICP
Zirconium	$1x10^{-2}$	ICP
Mercury	$2x10^{-6}$	AA**
Selenium	$1x10^{-5}$	AA

*ICP - Inductively Coupled Plasma Spectrometry

**AA - Atomic Absorption Spectrometry

Table 3 (cont.)

Chemical Analyses

Analyte	Required Detection Limit (g/L)	Method
EDTA	$8x10^{-3}$	Liquid Chromatography
HEDTA	$4x10^{-2}$	Liquid Chromatography
Carbonate	$1x10^{-2}$	Infrared Absorption
Total Organic Carbon	$2x10^{-2}$	Infrared Absorption
Free Hydroxide	$1x10^{-4}$	(MD)

MD - Requires method development (Reference 2)

682

Internal Letter

Rockwell International

Date January 20, 1983

No. 65453-83-023

TO: (Name, Organization, Internal Address)
C. M. Kronvall
Process Design
2750E/A219/200 East

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Separations Process Development Unit
222-S/MO-037/200 West
3-1571

Subject: Summary of Laboratory Data for the Ninety-Day Rule Experiment

Refs: 1) Supporting Document #SD-RE-DTP-006, "Modified Laboratory Plan for the Ninety-Day Rule", M. T. Jansky, September 1, 1982

2) Letter, #65453-82-032, dated January 28, 1982, M. T. Jansky to C. M. Kronvall, "Direct Neutralization of PUREX Current Acid Waste (CAW/ZAW)"

3) Letter, #65453-81-386, dated December 28, 1981, M. T. Jansky to J. S. Linck, "Optimum Neutralization Parameters for PUREX Zirflex Acid Waste (ZAW)"

For the past three-plus months, the Separations Process Development Unit (SPDU) has been investigating the "ninety-day rule". The rule states that if a tank containing aging waste sits idle, without additions, for more than ninety days, no more waste may be added to that tank. The data presented in this letter indicate that there is no chemical basis for the "ninety-day rule". No chemical shifts were noted, and no major changes were observed in the boiling wastes over ninety-one days. Laboratory details are discussed below.

Experimental

The detailed experimental procedure may be found in Reference 1. Seven liters of synthetic 12 percent and 6 percent CAW/ZAW were prepared. The compositions are shown in Table I. Two 2.5L aliquots of each waste were taken. Each aliquot was placed into a stainless steel cooker and warmed to 70°C. Sodium hydroxide (concentrated, 19M) was added to each pot such that there was one mole excess free hydroxide per liter of synthetic CAW/ZAW (stoichiometric calculation, see initial studies, References 2 and 3). The 12 percent fuel required 0.685L of concentrated sodium hydroxide (NaOH). The 6 percent fuel required 0.865L of 19M NaOH. The mixtures were well-mixed and aliquots taken. The lids were put on the cookers and sealed using a silicon sealant. The final apparatus is shown in Figure 1.

The mixtures were heated to boiling at atmospheric pressure, and constantly air-sparged at approximately 0.007 CFH/gal. The mixtures were allowed to boil for ninety-one days (thirteen weeks). The liquid levels were checked daily to insure that water loss, through evaporation, did not exceed 300 milliliters in any twenty-four hour period. Distilled water was added as needed to maintain a constant liquid level. Samples of each mixture were taken prior to boiling, after three (3) weeks, after six (6) weeks, after nine (9) weeks, and after thirteen (13) weeks. Each aliquot was examined for various parameters. The parameters are discussed below.

Rockwell International

Chemical Shifts

No chemical shifts were observed in any sample over the time-span of the study. There were no consistent color changes, no "bumping", no vast change in physical appearances.

Two phenomena did occur, but are not defined as due to chemical shifts. In one instance, one of the 6 percent mixtures seemed to become slightly lighter in color at ca. 6 weeks of boiling, but the probable cause was insufficient mixing of the mixture prior to observation. No change was observed for the other 6 percent mixture or the two 12 percent mixtures.

Additionally, an "explosion" occurred in one 12 percent mixture (Sample A) after seven weeks. An ice plug was observed in the reflux condenser at that time. The explosion was most likely due to the pressurization of the vessel when the sparged air had no vent (the ice plug prevented air from venting through the reflux condenser). The experiment was continued using the three remaining vessels. No problems were encountered during the remainder of the experiment.

Physical Parameters

Various physical parameters were measured on each mixture's aliquot after sampling. The parameters included slurry viscosity, density measurements, and particle size distribution (HIAC particle counter). The data are shown in Tables II-V. Although there are slight variations in the data, no real changes occurred. The variations are attributed to the inherent inaccuracies of (1) maintaining a constant liquid level, (2) gathering a representative sample, and (3) consistent sample handling over a three-month period.

Chemical Analyses

Aliquots of each mixture were submitted to Analytical Laboratories (AL) for analyses after sampling. A portion of each aliquot was filtered, with filtrate and dissolved solids also submitted to AL for analyses. The results of all analyses are shown in the Appendix. The data show that no major changes in chemical composition occurred over the ninety-one day experimental period.

The overall results of the analytical data, although not in as narrow a range as one would like to have to draw exact conclusions, are good. The increase in carbonate levels are expected due to sparging the caustic mixtures. The relative ratios between iron and chromium present in the waste remain fairly constant. Analyses are especially sensitive to the inherent factors mentioned earlier, i.e., volume changes, representative sampling, and consistent handling of samples over time.

Rockwell International

Microscopic Analyses

The aliquots examined using microscopic techniques did not exhibit any particularly interesting characteristics. The samples looked like amorphous hydroxide "gels", apparently experiencing no changes throughout the course of the experiment.

Summary

The data (chemical analyses, observations, etc.) indicate that no chemical shift occurred, no "bumping" was observed, and no gross changes took place in the synthetic waste over the test period. Therefore, the conclusion that there is no chemical basis for the ninety-day rule is justified. An in-tank process test is recommended should waste additions be such that a violation of the "rule" would occur.

This letter completes the January internal milestone for SPDU concerning the ninety-day rule.

Please call me if you have questions or comments regarding this work.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachments

cc:

J. F. Albaugh, R. B. Bendixsen, J. S. Buckingham, B. D. Bullough, K. G. Carothers, J. F. Durnil, N. W. Kirch, J. H. Lawler, L. H. Rodgers, File Code: WX63G, [redacted], Letterbook

Table I

Compositions of 12% and 6% CAW/ZAW

Component	Concentration (Moles/Liter) 12%	6%
HF	0.15	0.21
H_2SO_4	0.20	0.08
HNO_3	0.40	0.94
$Cr(NO_3)_3 \cdot 9H_2O$	0.013	0.018
$Fe(NO_3)_3 \cdot 9H_2O$	0.12	0.09
$Al(NO_3)_3 \cdot 9H_2O$	0.72	0.99
$NaNO_3$	0.18	0.20

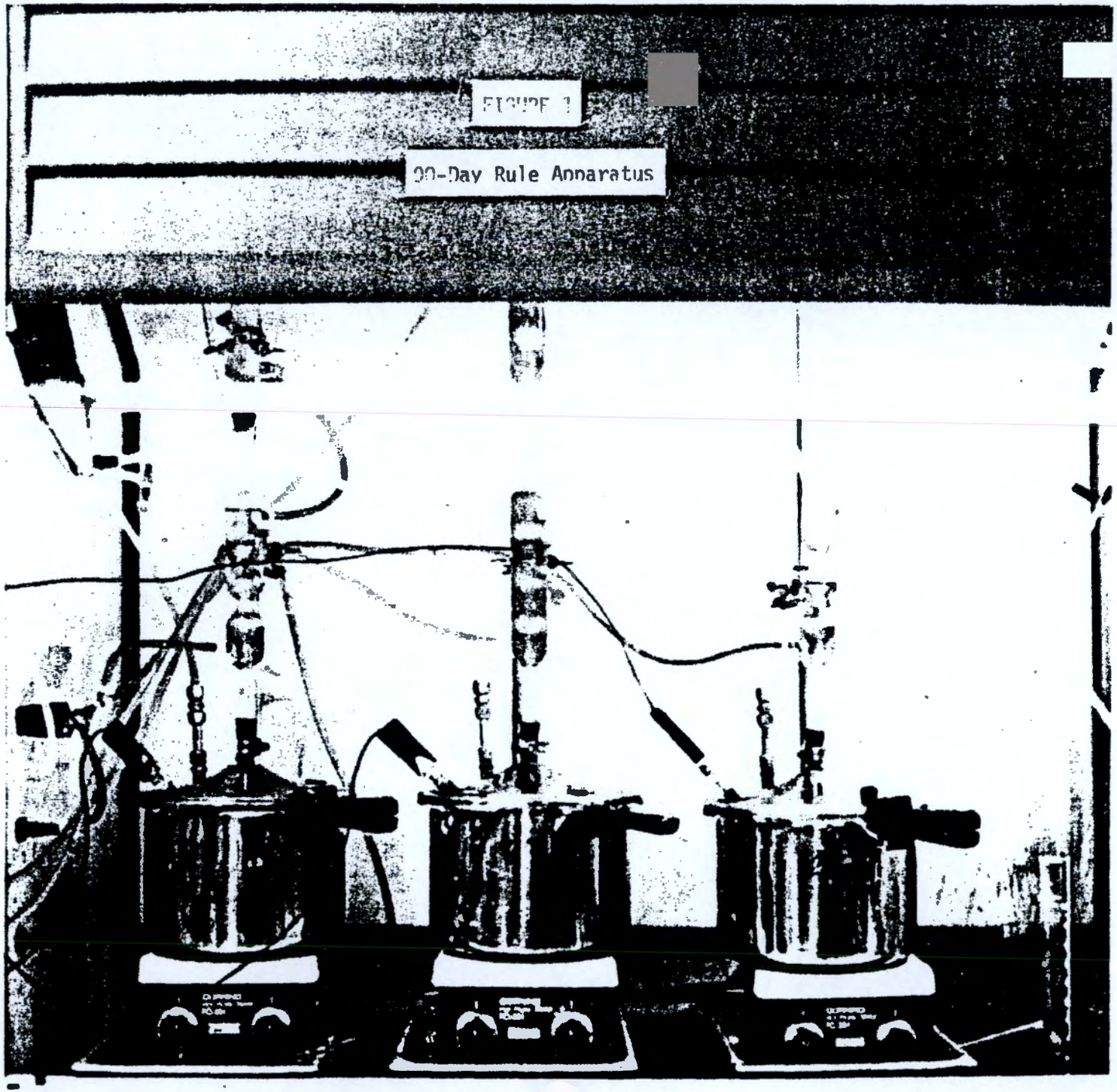


FIGURE 1

90-Day Rule Apparatus

Table ..

6% CAW/ZAW - Sample A

Parameter	Initial	3 weeks	6 weeks	9 weeks	91 days
o Slurry Viscosity(cps) at 50°C	10	8	9	9	8
o Specific Gravity					
o Slurry	1.21	1.32	1.26	1.27	1.23
o Supernatant	1.21	1.32	1.33	1.27	1.24
o Solids	1.24	1.34	1.25	1.31	1.16
o Solids					
o Volume % (centrifuged)	9	11	6	10	10
o Volume % (settled after one day)*	39	24	19	30	25
o Mean particle diameter (micrometers)	25	24	27	29	28

*Measured after 4 days for 3 weeks aliquot

Table III

6% CAW/ZAW - Sample B

Parameter	Initial	3 weeks	6 weeks	9 weeks	91 days
o Slurry Viscosity(cps) at 50°C	10	16	6	7	7
o Specific Gravity					
o Slurry	1.24	1.29	1.23	1.24	1.22
o Supernatant	1.24	1.44**	1.23	1.24	1.22
o Solids	1.26	1.25	1.28	1.29	1.21
o Solids					
o Volume % (centrifuged)	10	20	4	7	8
o Volume % (settled after one day)*	38	45	12	19	17
o Mean particle diameter (micrometers)	21	41	27	30	34

*Measured after 4 days for 3 weeks aliquots

**Suspect

Table IV

12% CAW/ZAW - Sample A

Parameter	Initial	3 weeks	6 weeks	9 weeks	91 days
o Slurry Viscosity(cps) at 50°C	10	12	7		
o Specific Gravity					
o Slurry	1.19	1.21	1.21		
o Supernatant	1.20	1.21	1.21		
o Solids	1.16	1.23	1.28		
				"Explosion"	
o Solids					
o Volume % (centrifuged)	9	7	5		
o Volume % (settled after one day)*	33	18	16		
o Mean particle diameter (micrometers)	29	25	27		

*Measured after 4 days for 3 weeks aliquot

Table V

12% CAW/ZAW - Sample B

Parameter	Initial	3 weeks	6 weeks	9 weeks	91 days
o Slurry Viscosity(cps) at 50°C	11	12	8	7	7
o Specific Gravity					
o Slurry	1.19	1.25	1.22	1.21	1.20
o Supernatant	1.19	1.25	1.22	1.21	1.20
o Solids	1.16	1.28	1.26	1.26	1.13
o Solids					
o Volume % (centrifuged)	8	7	6	6	7
o Volume % (settled after one day)*	37	23	26	23	25
o Mean particle diameter (micrometers)	24	24	26	29	23

*Measured after 4 days for 3 weeks aliquot

APPENDIX

CHEMICAL ANALYSES OF NINETY-DAY RULE SAMPLES

The following tables contain analytical data pertaining to the ninety-day rule experiment. A brief explanation of the tables follows.

Two types of waste were examined: 6% and 12% CAW/ZAW. Two aliquots of each were investigated; thus A and B samples.

The slurry is representative of an aliquot containing both interstitial liquor and precipitated solids. The symbol (<) indicates that the concentration of a component was below the detection limit of the analytical method. The symbol (*) indicates that analytical results were unavailable.

The filtrate is the interstitial liquor with solids removed. The explanation of symbols is the same as for the slurry.

The solids analyses are indicative of actual solids content. The values shown, as weight percent component per gram of dry solids, were obtained by (a) "backing out" any residual interstitial liquor present with the dissolved solids, and (b) subsequent normalization of the weights.

6% CAW/ZAW Slurry[a]

Sample A

Component	Theoretical	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	0.73	0.58	0.70	0.54	0.50	0.42
OH	0.74	0.45	0.87	*	0.77	0.59
CO_3	Ø	0.08	0.03	*	0.01	0.05
Cr^{+6}	Ø	<	<	<	<	<
Cr^{total}	0.013	0.01	0.01	0.008	0.011	0.007
F	0.16	0.25	0.14	0.05	0.08	0.04
Fe^{+2}	Ø	<	<	<	<	<
Fe^{total}	0.07	0.06	0.05	0.05	0.08	0.05
Na	5.04	4.90	2.94	4.75	4.75	4.09
NO_3	3.28	3.20	3.60	*	3.28	2.98
SO_4	0.013	0.03	0.06	0.04	*	0.08
SpG		1.21	1.32	1.26	1.27	1.23
Viscosity(cps)		10	8	9	9	8
% cent. solids		9	11	6	10	10

[a]Concentrations expressed in moles component per liter of solution

6% CAW/ZAW Filtrate[a]

Sample A

Component	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	0.621	0.73	0.49	0.54	0.41
OH	0.67	0.96	0.84	0.90	0.78
CO_3	0.01	0.01	0.01	0.01	0.02
Cr^{+6}	<	<	<	<	<
Cr^{total}	<	<	<	<	<
F	0.14	0.08	0.16	0.02	0.02
Fe^{+2}	<	<	<	<	<
Fe^{total}	<	<	<	<	<
Na	4.73	6.26[c]	4.20	4.96	4.36
NO_3	3.42	4.60	2.72	3.62	3.16
SO_4	0.08	0.04	0.07	0.05	0.05
SpG	1.24	1.32	1.25	1.27	1.24

[a]Concentrations expressed in moles component per liter of solution

[c]Suspect

6% CAW/ZAW Solids[b]

Sample A

Component	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	8	9	25	18	20
OH	--	--	--	--	--
CO_3	--	7	*	16	17
Cr^{+6}	--	--	--	--	--
Cr^{total}	11	9	12	6	6
F	--	--	--	--	--
Fe^{+2}	--				
Fe^{total}	81	73	63	47	53
Na	--	--	--	--	--
NO_3	--	--	--	--	--
SO_4	--	1	*	5	4

[b]Composition in normalized weight percent (See Appendix discussion)

6% CAW/ZAW Slurry[a]
Sample B

Component	Theoretical	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	0.73	0.57	0.50	0.42	0.50	0.34
OH	0.74	0.50	0.34	*	0.55	0.55
CO_3	Ø	0.08	0.05	*	0.13	0.09
Cr^{+6}	Ø	<	<	<	<	<
Cr^{total}	0.013	0.01	0.018	0.006	0.009	0.006
F	0.16	0.13	0.14	0.15	0.04	0.05
Fe^{+2}	Ø	<	<	<	<	<
Fe^{total}	0.07	0.08	0.09	0.04	0.05	0.04
Na	5.04	4.34	5.62	4.11	4.43	4.17
NO_3	3.28	3.17	4.28	*	2.98	2.85
SO_4	0.013	0.08	0.07	0.06	0.09	0.07
SpG		1.24	1.29	1.23	1.24	1.22
Viscosity		10	16	6	7	7
% cent. solids		10	20	4	7	8

[a]Concentrations expressed in moles component per liter of solution

6% CAW/ZAW Filtrate[a]

Sample B

Component	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	0.67	0.68	0.41	0.45	0.34
OH	0.66	0.78	0.80	0.81	0.72
CO_3	0.01	0.01	0.01	0.01	0.02
Cr^{+6}	<	<	<	<	<
Cr^{total}	<	<	<	<	<
F	0.14	0.13	0.05	0.02	0.03
Fe^{+2}	<	<	<	<	<
Fe^{total}	<	<	<	<	<
Na	4.94	4.84	4.64	4.48	4.12
NO_3	3.35	3.30	3.16	3.20	2.85
SO_4	0.10	0.07	0.08	0.05	0.04
SpG	1.24	1.25	1.23	1.24	1.22

[a]Concentrations expressed in moles component per liter of solution

6% CAW/ZAW Solids[b]

Sample B

Component	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	8	9	28	25	20
OH	--	--	--	--	--
CO_3	4	14	26	21	25
Cr^{+6}	--	--	--	--	--
Cr^{total}	10	5	8	6	5
F	--	--	1	--	--
Fe^{+2}	--	--	--	--	--
Fe^{total}	78	69	41	46	49
Na	--	--	--	--	--
NO_3	--	--	--	--	--
SO_4	--	1	*	3	--

[b]Composition in normalized weight percent (See Appendix discussion)

12% CAW/ZAW Slurry[a]

Sample A

Component	Theoretical	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	0.56	0.66	0.57	0.54		
OH	0.78	0.59	0.52	*		
CO_3	Ø	0.12	0.03	*		
Cr^{+6}	Ø	<	<	<		
Cr^{total}	0.01	0.01	0.01	0.009		
F	0.12	0.13	0.10	0.18		
Fe^{+2}	Ø	<	<	<		
Fe^{total}	0.09	0.09	0.09	0.07		
Na	4.22	4.60	4.71	4.10		
NO_3	2.45	2.99	2.67	*		
SO_4	0.16	0.21	0.15	0.14		
SpG		1.19	1.21	1.21		
Viscosity		10	12	7		
% cent. solids		9	7	5		

[a]Concentrations expressed in moles component per liter of solution

ICE PLUG

700

12% CAW/ZAW Filtrate[a]
Sample A

Component	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	0.45	0.47	0.52		
OH	0.70	0.71	0.76		
CO_3	0.01	0.01	0.01		
Cr^{+6}	<	<	<		
Cr^{total}	<	<	<		
F	0.11	0.10	0.13		
Fe^{+2}	<	<	<		
Fe^{total}	<	<	<		
Na	4.11	4.01	3.93		
NO_3	2.47	2.44	2.18		
SO_4	0.18	0.16	0.16		
SpG	1.20	1.21	1.21		

[a]Concentrations expressed in moles component per liter of solution

ICE PLUG

12% CAW/ZAW Solids[b]

Sample A

Component	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	--	--	--		
OH	--	--	--		
CO_3	--	7	20		
Cr^{+6}	--	--	--		
Cr^{total}	9	7	7		
F	--	--	--		
Fe^{+2}	--	--	--		
Fe^{total}	91	86	73		
Na	--	--	--		
NO_3	--	--	--		
SO_4	--	--	--		

[b]Composition in normalized weight percent (See Appendix discussion)

ICE PLUG

12% CAW/ZAW Slurry[a]

Sample B

Component	Theoretical	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	0.56	0.54	0.61	0.61	0.48	0.49
OH	0.78	0.41	0.77	*	0.55	0.49
CO_3	Ø	0.01	0.03	*	0.08	0.08
Cr^{+6}	Ø	<	<	<	<	<
Cr^{total}	0.01	0.01	0.01	0.01	0.009	0.008
F	0.12	0.13	0.10	0.32	0.01	0.01
Fe^{+2}	Ø	<	<	<	<	<
Fe^{total}	0.09	0.09	0.095	0.098	0.088	0.079
Na	4.22	3.86	5.57	4.19	3.94	3.85
NO_3	2.45	2.26	2.78	*	2.42	2.36
SO_4	0.16	0.17	0.16	0.05	0.16	0.17
SpG		1.19	1.25	1.22	1.21	1.20
Viscosity		11	12	8	7	7
% cent. solids		8	7	6	6	7

[a]Concentrations expressed in moles component per liter of solution

12% CAW/ZAW Filtrate[a]
Sample B

Component	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	0.52	0.58	0.56	0.55	0.51
OH	0.67	0.84	0.74	0.72	0.72
CO_3	0.01	0.01	0.01	0.01	0.01
Cr^{+6}	<	<	<	<	<
Cr^{total}	<	<	<	<	<
F	0.12	0.11	0.02	*	0.01
Fe^{+2}	<	<	<	<	<
Fe^{total}	<	<	<	<	<
Na	4.13	4.60	4.20	4.18	4.24
NO_3	2.52	2.91	2.48	2.56	2.66
SO_4	0.18	0.17	0.15	0.15	0.15
SpG	1.19	1.25	1.22	1.21	1.20

[a]Concentrations expressed in moles component per liter of solution

12% CAW/ZAW Solids[b]

Sample B

Component	Initial	3 weeks	6 weeks	9 weeks	91 days
Al	--	--	--	--	--
OH	--	--	--	--	--
CO_3	--	6	28	25	24
Cr^{+6}	--	--	--	--	--
Cr^{total}	9	7	7	6	6
F	--	--	--	--	--
Fe^{+2}	--	--	--	--	--
Fe^{total}	91	87	64	68	69
Na	--	--	--	--	--
NO_3	--	--	--	--	
SO_4	--	--	--	--	

[b]Composition in normalized weight percent (See Appendix discussion)

Internal Letter

Rockwell International

705

Date. February 7, 1983

No. 65453-83-036

TO: (Name, Organization, Internal Address)
. D. M. Tulberg
. Process Design
. 2750E/A227/200 East

FROM: (Name, Organization, Internal Address, Phone)
. B. D. Bullough/C. R. Reichmuth
. Separations Process Development Unit
. 202-S/200 West
. 3-2967

Subject: . Decladding Waste Addition/Dilution

Refs: 1) Letter, #65411-82-233, D. M. Tulberg to L. H. Rodgers, "Proposed Pilot Plant Study of PUREX Decladding Waste Characteristics at Settling Tank Concentrations"

2) SD-WM-DTP-001, "PUREX Decladding Waste Neutralization Pilot Plant Study", T. H. May, January 13, 1982

3) SD-RE-TPL-006, "PUREX Pilot Scale Decladding Waste Characteristics at Settling Tank Concentrations", C. R. Reichmuth, December 17, 1982

As requested in Reference 1, the Separations Process Development Unit (SPDU) engineering laboratory performed a simulation of the addition to underground storage tanks of PUREX decladding waste.

Two identical batches of Zircalloy were dissolved in AFAN solution to produce synthetic "waste"; each batch consisted of 2392 g of Zircalloy II in a solution of 1230 g of NH_4NO_3 and 6360 g of NH_4F in 7.7 gal of H_2O. The process used was that described in Reference 2. Neutralization and addition of the waste was performed in batches, following the procedure in Table 1 of the Test Plan (Reference 3). Following the prescribed method, neutralization was performed at 55-60 degrees C. Decladding waste solutions of ≈0.34 M and ≈0.15 M Zr, as well as a sodium nitrite solution and a spent metathesis solution, were added to the tank for simulation purposes.

The simulation vessel was a 12" diameter section of glass pipe, approximately six feet high. Prior to adding simulated waste, about one inch of synthetic interstitial liquor was added to the bottom of the tank; as waste was added, the temperature of the waste was maintained at ≈35 degrees C. The vessel was kept covered to prevent gross amounts of evaporation and ammonia loss.

Observations and Results

Physical observations and data that were requested include layering, settling times, types of solids, and pumpability of the precipitate and supernate. Boildown information was also requested, and will be addressed by M. T. Jansky in a separate letter. Laboratory analyses are ongoing, and data received to date will be presented here.

Layering of the waste was noticed very early. Details of the solids levels, and layering are presented in Table 1. Table 2 presents the data obtained on settling rates. In general, each layer corresponds to a waste addition

Rockwell International

"batch". Solids that were generated by waste neutralization and addition were of three types:

- o Heavy.....drop out immediately (<5 min.)
- o Intermediate.....drop out w/in 45 min.
- o Light.....drop out w/in ≈8 hr.

After waste additions were completed, the solids level was observed to determine a compaction rate. The rate was generally a smooth, exponential curve, with one exception. An unrelated test was being performed adjacent to this one; the other test required that a centrifuge be used, and the centrifuge began to vibrate violently. The vibrations apparently were sufficient to cause an estimated 5 to 7 days of settling overnight! When settling had, for all practical purposes, finished, the final height was where it was projected to be one week later.

Chemical analysis of the final supernate and solids were not complete at the time this letter was released. Results from Analytical Laboratories that were available are presented in Table 3. Two separate analyses were performed on the feed solution, and there is some discrepancy in the results. The first Zr analysis (of fresh solution) showed a 0.375 M solution, the second (of remaining solution after completion of tests) was 0.458 M. The latter result is much closer to previous numbers from similar solutions generated under the same conditions.

Observations in waste pumpability were initiated by examination of lowering a pancake through the supernate onto the sludge. The pancake consisted of 4 inch diameter 1/4 inch plate steel weighing 540 g. The pancake settled from the 39-1/2 L level to approximately a level of 22 L, through the settled solids. Allowing the solids to resettle, pumping of the supernate was achieved by removing supernate with a centrifugal pump removing 10 L/min through a .25" i.d. tube. At a distance of about 1/2" from the solid/liquid interface, solids were drawn upwards. Pumping of the slurry continued until the flow rate had stopped. The volume of solids remaining was approximately 23 L.

If more information is required, or additional testing is needed, please contact me.

Bruce D. Bullough
B. D. Bullough, Engineer

C. R. Reichmuth, Engineer

BDB:CRR:naj
Attachments

Rockwell International

D. M. Tulberg
Page 3
February 7, 1983

cc:

J. F. Albaugh
J. S. Buckingham
K. G. Carothers
M. T. Jansky
G. W. Reddick, Jr.
L. H. Rodgers
R. A. Van Meter
D. G. Wilkins
G. D. Wright
[redacted]
Letterbook

Table 1

Periodic Solids Level Measurements

Date	Addition cycles completed	Total volume (L)	Solids volume (L)	% solids
1-10-83 am*	2	12.33	5.5	44.6
1-10-83 pm	6	30L	--	--
1-11-83 am	6	29.75	14L	47.1
1-11-83 pm	12.8	68.67	--	--
1-12-83 am	12.8	68.5	34.67	50.6
1-12-83 pm	16	85.75	44	51.3
1-13-83 am	16	85.67	40.33	47.1
1-14-83 am**	18.8	100	44.5	44.5
1-14-83 pm	19	101	44.67	44.2
		Waste Additions Completed		
1-17		101	42.25	43.[illegible]
		1.42 L of Supernate samples taken on 1-17-83 and 1-18-83		
1-18		--	41.8	41.9
1-19		99.6	41.4	41.6
1-20		99.6	41.1	41.3
1-21		99.6	40.8	41.0
harp drop 1-24		99.6	40.2	40.4
1-25		99.6	39.7	39.9
1-26		99.6	39.5	39.7
1-27		99.6	39.4	39.6

"Pancake" sludge level detection was dropped--it settled at the 23L mark.

*Waste addition cycles were begun on 1-7-83. Two cycles were completed. Prior to waste addition, two liters of synthetic interstitial liquor were added.

**The final cycle of waste addition run 19 was added after allowing the supernate to clear. This was done to observe settling rates.

Table 2 - SETTLING RATES

Run #1 - Settling Data for Different Zr Soln's

Samples were agitated prior to taking readings.

Readings were taken simulataneously.

Time/Min.		Solids level/ml			
		.34 Zr	.15 Zr	.19 Zr	
15:06-1/10/83	0	830/830	750/750	1000/1000	
	2 Min.	820	745	980	
	4	815	744	950	
	6	810	740	900	
	8	805	735	860	
	10	803	728	840	
	12	800	720	825	
	14	798	715	810	
	16	795	705	800	
	18	790	700	792	
	20	790	695	785	
	22	785	690	780	
	24	780	683	773	
	26	780	677	769	
	28	775	670	764	
	30	775	665	760	
	35	770	650	750	
	40	755	638	742	
	45	750	627	738	
08:00-1/11/83		505/810	450/740	667/985	16 Hrs. 54 Min.
08:00-1/12/83		505	440	650	49 " 54 "
08:00-1/13/83		500	435	647	64 " 54 "
08:00-2/15/83		480/810	415/740	625/985	880 " 54 "

Table 2 (Continued)

Run #2 - Settling Data for Different ZR Sol's

Solids Level [ml]

	Min.	[0945] .34 Zr	[1015] .15 Zr	[1045] .19 Zr	
0945 - 1/13/83	0	795/795	725/725	1010/1010	Samples were preparec 1/2 hr. apart
	2	795	725	1005	
	4	795	725	998	
	6	792	724	988	37mm/100ml
	8	790	723	975	
	10	789	720	955	
	12	787	718	935	
	14	785	715	915	
	16	782	712	895	
	18	780	710	880	
	20	778/792	705/725	865/1005	
	22	775	700	855	
	24	771	697	845	
	26	769	695	839	
	28	765	693	830/1002	
	30	760	690	822	
	35	750	670	810	
	40	739/791	660	798	
	45	728/790	645	788	
	50	715	635	780	
	55	703	630	772	
	60	690	620	765	
	65	680	615		
	70	670	605		
	75	658	600		
	80	645	595		
	85	637	590		
	90	630	585		
	95	620			
	100	618			
	105	610			
	110	605			
	115	600			

Table 2 (Continued)

Run #2 - Settling Data for Different ZR Sol's

Solids Level [ml]

		[0945]	[1015]	[1045]	
	Min.	.34 Zr	.15 Zr	.19 Zr	
0945 - 1/13/83	120	595		720/1000	
	150		545/723		
	180	570		700	
	210		520		
	240	555		689	
	270		510/722		
	300	550		678	
	330		490		
	360	540		672	
	390		483		
	420	537		666	
	450		475		
	480	533		660	
	510		466		
	540	528		655	
	570		460		
	600	525			
1330 - 1/14/83	[1665]	510 [1635]	440 [1605]	640	
1500 - 1/18/83	[7515]	500/790	425/722	620/100	Note: 30 min betwe sample
0800 - 2/15/83	33 days	485/790	405/722	600/1000	

Table 2 (Continued)

Settling Rates in 1' Glass Column

Time Min	Trailing Edge Location (L)
3	92
9	94
12	87
15	85
*24	85
25	83
30	76
35	63
40	52
45	45

*Metathesis sol'n added after 20 min, mixing occurred after this point.

Table 3

Analytical Information

Feed Make-up:

	Batch 1	Batch 2
Zr	.375M, 0.458M	.395M
NH_3/NH_4^+	1.11M	1.29M
SpG	1.05	1.06
pH	6.02	7.0

NaOH for Neutralization: 19.95M

Neutralized Decladding Waste:

	Supernate	Precipitate
Na^+	1.08M	
K^+	0.374M	
F^-	0.840M	
OH^-	0.969M	
viscosity	1.87 cp	252 cp
Zr	$<1.1\times10^{-4}$M	
NH_3/NH_4^+	0.257M	
SpG	1.062	1.173
% H_2O	91.75	75.75
pH	13.3	12.8

714

Internal Letter

Rockwell International

Date. April 11, 1983

No: . 65453-83-106

TO: (Name, Organization, Internal Address)
.D. M. Tulberg
.Process Design
.2750E/A227/200 East

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Separations Process Development Unit
. 222-S/MO-037/200 West
. 3-1571

Subject: .Mixing of Wastes: 103AW and Synthetic Decladding Waste

As per your verbal request, the Separations Process Development Unit (SPDU) examined the effects of mixing actual tank waste with synthetic neutralized decladding waste. The volume percent settled solids and chemical analyses of phases were examined. Laboratory details are discussed below.

The first test utilized actual waste from Tank 103AW (3-20-83), and synthetic neutralized decladding waste. Twenty-five milliliters of TK-103AW waste (bottom sample) were placed into a 100 mL boildown pot. Synthetic neutralized decladding waste was added, dropwise. The decladding waste, provided by the Engineering Laboratory, was a total of 25 mL. The decladding waste was prepared such that there was 36.5 volume percent solids and 63.5 volume percent supernatant. No temperature change occurred when the two materials were mixed. The decladding waste remained suspended as a separate phase immediately after adding the entire 25 mL. After approximately 5 minutes, it appeared that there were three separate phases as the decladding waste began to "mix" with the 103AW material. The total mixture was allowed to stand (i.e., settle) overnight. After settling overnight, the resulting mixture was 24 volume percent while settled solids, with a clear, yellow supernatant. A portion of the supernatant was removed and submitted for analyses. The remainder of the supernatant was then removed to "isolate" the solids. An aliquot of the solids were washed with water, and a second aliquot was washed with a 0.1 M NaOH solution. The solids were dried overnight, and then submitted for X-ray analyses. The analytical data are shown in Table I.

For a separate test, 20 mL aliquots of TK-103AW waste were placed into 3 100 mL graduated cylinders. Synthetic neutralized decladding waste were added, dropwise, such that the ratio of 103AW: decladding was: 1:0.5, 1:2, and 1:4. To a fourth graduated cylinder, 50 mL of the decladding waste was added for a blank. The mixtures were allowed to settle overnight. The following morning, volume percent settled solids were recorded. The results are shown in Table II. Note that the solids settled smoothly into a flat layer in three of the five determinations. However, a "snowdrift" effect was observed in the 1:2 and 1:4 mixtures. No definite explanation for the differences can be made; possibly ammonia channeling out of the mixture or viscosity/specific gravity differences between the two materials.

Based on both the measured volumes of the solids, and on analytical data (x-ray), no change occurred in the solids. The x-ray analyses of the "washed" solids were virtually identical. The only crystalline material

Rockwell International

present was sodium fluoride, with an amorphous zirconium compound (hydrated zirconium oxide) also present. This was verified by an X-ray analysis of the decladding solids that had not been contacted with 103AW.

I understand that another sample of TK103AW will be taken in the future, in an attempt to get solids from the tank. Please call when the sample is ready and you have defined your requirements. Also, if you have any comments or questions regarding the data presented in this letter, please contact me.

M. T. Jansky
Senior Chemist

MTJ/naj

Attachments

cc:

J. F. Albaugh
R. B. Bendixsen
J. S. Buckingham
K. G. Carothers
P. J. Certa
D. L. Herting
M. C. Teats
R. A. Van Meter
R. D. Wojtasek
[redacted]
File Code: WB621
Letterbook

TABLE I

Composition of TK103AW/Synthetic Decladding Mixture

50:50 Mixture

Component	Supernatant (Moles/Liter)
Al	0.322
OH	1.06
NO_2	0.602
NO_3	1.39
TOC (g/L)	1.88
CO_3	0.0646
PO_4	**
SO_4	**
F	0.347
Cl	0.046
NH_3	0.0355
Cs^{137} (μCi/L)	1.13×10^5
Sr^{90} (μCi/L)	Unavailable
SpG	1.235

*Solids analyzed qualitatively by X-ray; see text

**Below detection limits

Table II

Volume Percent Settled Solids of TK103AW/Synthetic Decladding Mixture

103AW: Decladding Ratio	Volume % Settled Solids After Overnight Settling	
	Experimental	Theoretical*
0:1 (blank)	44	
1:1**	24	22
1:0.5	13	13
1:2	29	29
1:4	35	34

*Based on experimental value for blank

**The initial test did not use graduated cylinders; used ruler to measure retentive volumes

718

Internal Letter

Rockwell International

Date: May 12, 1983

No. 65453-83-142

TO: (Name, Organization, Internal Address)
D. M. Tulberg
Process Design
2750E/A227/200 East

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky/H. R. Risenmay
Separations Process Development Unit
222-S/MO-037/200 West
3-1571 - 3-1972

Subject: "Scheduling" of the Mixing Study

Ref: Letter, #65411-83-092, dated April 21, 1983, D. M. Tulberg to M. T. Jansky, "Decladding of Supernate-Salt Well Liquor Mixing Study"

The referenced letter requested work concerning the mixing of synthetic decladding supernatant liquor and synthetic salt well liquor. The Separations Process Development Unit (SPDU) will provide the requested data as per the attached "schedule".

To aid you in meeting your July 8 milestone SPDU will have all data available by June 17. An internal letter summarizing the data will be issued no later than June 22.

If there are any problems or questions concerning the timing of this work, please call.

M. T. Jansky
Senior Chemist

H. R. Risenmay
Chemist

MTJ/naj

cc: (W/Attachment)

J. S. Buckingham
K. G. Carothers
P. A. Certa
D. L. Herting
M. I. Fineman
L. H. Rodgers
R. D. Wojtasek
File Code: WB621
[redacted]
Letterbook

"SCHEDULE"

WEEK OF	WORK TO BE COMPLETED
May 9	o Define compositions o Prepare mixtures o Prepare apparatus
May 16	o P/T data on 50% WVR o SpG data on 50% WVR o Viscosity data on 50% WVR o Prepare solids and solutions for analyses
May 23	o May 16 data for DSS
May 30	o May 16 data for DSS
June 6	o Data for mixtures containing decladding sludge o Analyze analytical data
June 13	o "Fine-tuning" and "tweaking"
June 20	o Issue internal letter

720

Internal Letter

Rockwell International

Date June 24, 1983

No. 65453-83-175

TO: (Name, Organization, Internal Address)
D. M. Tulberg
Process Design
2750E/A227/200 East

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky/H. R. Risenmay
Chemical Laboratory
222-S/MO-037/200 West
3-1571

Subject: Laboratory Results from the Waste Mixing Study

Refs: (1) Letter, #65411-83-092, dated April 21, 1983, D. M. Tulberg to M. T. Jansky, "Decladding Supernate-Salt Well Liquor Mixing Study"

(2) Letter, #65453-83-142, dated May 12, 1983, M. T. Jansky/ H. R. Risenmay to D. M. Tulberg, "Scheduling of the Mixing Study"

(3) Letter, #65453-83-168, dated June 10, 1983, M. T. Jansky to D. M. Tulberg, "Chemical Analyses of Mixing Study Samples"

Future operating restrictions, specifically tank space availability, may require that decladding supernatant (DSP) and salt well liquor (SWL) be mixed together. The Waste Management Process Technology Unit (WMPTU) has requested physical and chemical data concerning various mixtures of DSP and SWL (Reference 1). The Chemical Laboratory Process Development (CLPD) has completed the data gathering (Reference 2). The purpose of this letter is to formally provide the data, included in the letter, to WMPTU.

Feeds Make-Up

Five different feeds were prepared. Each feed was made using synthetic TX salt well liquor (SWL). The composition of SWL is shown in Table I. Note that the operating processes will have the SWL diluted by a factor of 1.8.

The mixtures were prepared by mixing SWL with synthetic decladding supernatant (DSP). The DSP was provided by the Engineering Laboratory, and its composition is shown in Table II. The mixtures were prepared in the following SWL:DSP ratios--100:0, 85:15, 70:30, 55:45, 40:60. The feeds were analyzed, and the results are shown in Table III.

Waste Volume Reduction (WVR)

Each feed was subjected to batch boildowns, following the waste volume reduction (WVR) scheme shown in Figure 1. The general procedure is discussed below.

A feed was placed into a batch boildown vessel, and pressure/temperature (P/T) data were gathered. The feed was then reduced in volume, to the indicated point in Figure 1, at 60 torr, continually gathering temperature/WVR data. At the end point, P/T data were gathered. The product was split into separate aliquots and stored at various temperatures overnight for equilibration. After equilibration, each aliquot was examined for volume percent settled solids, and the phases separated and analyzed.

Rockwell International

A separate boildown was conducted to the endpoint, and the product stored at 35°C overnight. If solids were present, the supernatant was decanted and subsequently used as the feed for the next boildown. The various percent WVR's for the five feeds are shown in Table IV.

Physical and chemical data concerning the mixing study products are shown in the Appendices. Appendix I contains P/T data. The data contain some duplicate runs, which indicate that the thermocouple, tested initially, developed a bias during the first 50 percent WVR's. Therefore, the replicate data are probably more representative of actual P/T data.

Appendix II contains data pertaining to specific gravity, viscosity (centipoise) and percent solids: volume percent settled, dry weight, and dry volume percents. The "dry" values were obtained by using analytical results for percent waters and then "backing out" the supernatant.

Appendix III contains the analyses of the various supernatant liquors. Appendix IV shows the composition of the solids, as moles of component per gram of dry solid.

Appendix V contains data concerning physical measurements of mixtures containing solids that were subjected to a 50 percent WVR.

It should be pointed out that, as requested in the letter, volume balances were obtained for the condensate and the slurry product. As a general rule, the additive volumes of the two were off no more than ± 2 percent from the starting volumes.

Also, the calculations involving the "backing out" of supernatant liquor are highly dependent on percent water analyses. Several instances arose where water content of the solids was higher than that of the corresponding supernatant, or there was insufficient supernatant for analysis. These particular problems will be addressed in the SD document mentioned below.

Additional data that has been requested will be included in an SD document. The data consists of additional analyses (Reference 3), microscopic analyses, particle size distributions, and calculated values of solids compositions based on assumptions (e.g., insufficient supernatant volumes precluded some calculations). The document will also include a detailed discussion of the data and observations gathered during the experiment.

Please call if there are questions or comments regarding the data.

Rockwell International

D. M. Tulberg
Page 3
June 24, 1983

M. T. Jansky
Senior Chemist

MTJ for HRR
H. R. Risenmay
Chemist

MTJ:HRR:naj

cc: (W/Appendices)

P. G. Certa
R. E. Haaland
M. I. Fineman
D. A. Reynolds

cc: (W/O Appendices)

R. B. Bendixsen
J. S. Buckingham
G. Burch
K. G. Carothers
R. D. Claghorn
D. L. Herting
M. G. Kelly
M. J. Kupfer
J. H. H. Lawler
[redacted]
L. H. Rodgers
M. C. Teats
D. G. Wilkins
R. D. Wojtasek
File Code: WX63G
Process Aids
Letterbook

Table I

Composition of Synthetic SWL

Component	Concentration (Moles/Liter)		
	Desired		Found
	Undiluted	Diluted	
$NaAlO_2$	1.36	0.76	0.81
NaOH	2.99	1.66	1.70
$NaNO_2$	1.89	1.05	1.08
$NaNO_3$	3.03	1.68	1.57
Na_2CO_3	0.164	0.091	0.117
Na_3PO_4	0.047	0.026	0.0297
Na_2SO_4	0.026	0.014	0.0147
Na	9.79	5.44	5.73
SpG			1.266

Table II
Composition of Synthetic DSP

Component	Concentration (Moles/Liter)
Al^{+3}	--
OH^{-}	0.80
NO_2^{-}	0.0165
NO_3^{-}	0.0202
CO_3^{-2}	0.0154
PO_4^{-3}	*
SO_4^{-2}	0
Na^{+}	1.00
K^{+}	0.388
SpG	1.065

* Below Detection Limits

Table III

Compositions of Mixing Study Feeds

Component	Mixture Ratio (SWL:DSP), M				
	100:0	85:15	70:30	55:45	40:60
Al^{+3}	0.81	0.67	0.57	0.46	0.35
OH^-	1.70	1.55	1.16	1.24	1.10
NO_2^-	1.08	0.905	0.746	0.595	0.437
NO_3^-	1.57	1.39	1.28	1.01	0.769
CO_3^{-2}	0.117	0.102	0.0873	0.0708	0.0537
PO_4^{-3}	0.0297	0.0243	0.0240	0.0134	0.0037
SO_4^{-2}	0.0147	0.0137	0.0115	0.0087	0.0067
F^-	0.001	0.123	0.248	0.364	0.501
Na^+	5.73	4.81	3.82	3.35	2.66
K^+	--	0.0573	0.141	0.165	0.247
NH_3	0.0554	0.0184	0.0432	0.0626	0.0877
SpG*	1.266	1.237	1.208	1.178	1.147
$\%H_2O$	65.03	70.34	73.11	76.56	79.90

*Room Temperature

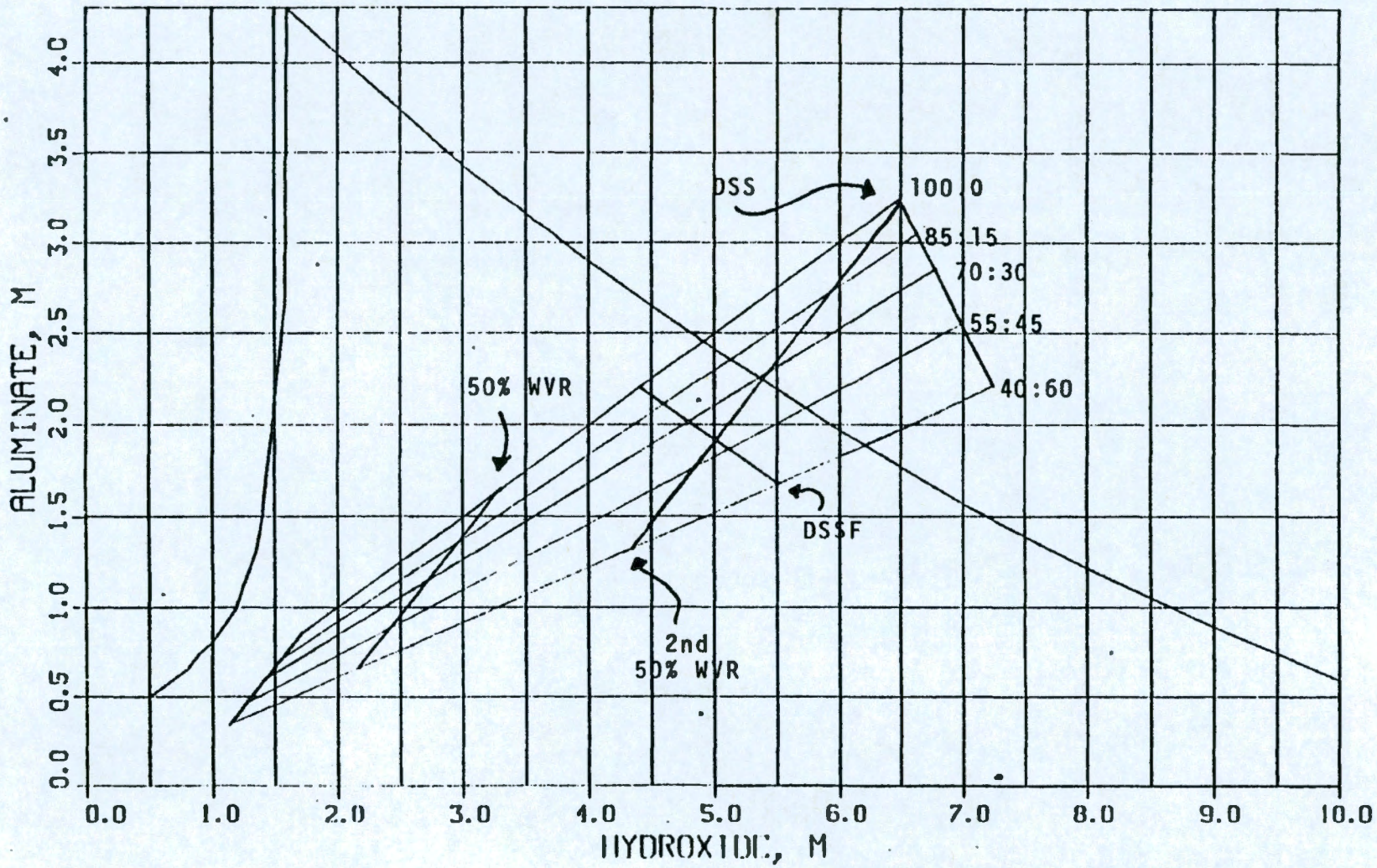
Table IV

WVR of Mixing Study Mixtures

Mixture (SWL:DSP)	% WVR 1st 50% Cut	2nd 50% Cut	DSSF	DSS
100:0	50	--	24	31
85:15	50	--	33	29
70:30	50	--	41	30
55:45	50	--	50	27
40:60	50	50	22	23

FIGURE 1

SWL:DSP Mixture Operating Lines



728

Internal Letter

Rockwell International

Date. September 7, 1983

No. 65453-83-234

TO: (Name, Organization, Internal Address)
- D. M. Tulberg
- Waste Management Process Technology
- 2750E/A227/200E

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky/H. R. Risenmay
- Chemical Laboratory Process
- 222S/MO-037/200W
- 3-1571/3-3612

Subject. Supplemental Mixing Study Data

Ref: 1) Letter, #65453-83-175, June 24, 1983, M. T. Jansky/H. R. Risenmay to D. M. Tulberg, "Laboratory Results from the Waste Mixing Study"

2) Letter, #65411-83-164, August 15, 1983, D. M. Tulberg to M. T. Jansky, "Supplemental DSP-SWL Mixing Study"

The storage of waste, after PUREX startup, will involve the mixing of decladding supernatant liquors with existing wastes. One scenario in particular is potentially mixing decladding supernatant liquor with salt well liquor and concentrating the mixture to double shell slurry (DSS). Reference 1 discussed laboratory data pertaining to the production of DSS from five different mixtures of decladding supernatant liquor and salt well liquor (SWL). Those data were used to develop various flowsheet parameters for evaporator operations. Additional data are needed to verify the developed parameters. The purpose of this letter is to provide those supplementary data, as requested in Reference 2. The laboratory details are discussed below.

Five waste mixtures were prepared, as requested in Reference 2. The requested concentrations are shown in Table I. The resulting mixtures contained visible solids. The mixtures were well-mixed, and representative aliquots taken and analyzed to confirm the make-up. The analyses, aluminum and hydroxide concentrations shown in Table II, indicated that the aluminum values are within analytical error of the desired concentrations, but the hydroxides were low. This phenomenon is attributed to the composition of sodium aluminate used in laboratory studies. It is a technical grade, listed as roughly 65 weight percent aluminate and 0-20 weight percent hydroxide. The low hydroxide values were corrected for by butting the mixtures up with solid sodium hydroxide. The accompanying increase in volume was minimal, therefore maintaining a constant aluminum concentration. The specific gravity of each feed was determined, and they are given in Table III.

Each waste mixture was subjected to a batch boildown, at a constant pressure of 60 torr. Temperature versus waste volume reduction (WVR) data were recorded. Nucleation points were also recorded, with the data shown in Table IV. Each product slurry was analyzed for aluminum and hydroxide concentration, as well as specific gravity (at product boildown temperature). The Al/OH and Sp.G. data are given in Table V. Aliquots of the products were also used for viscosity versus temperature determinations, the temperature varying from 75°C down to 25°C. Viscosity versus temperature data are presented in Table VI.

Rockwell International

Separate aliquots of each product were placed into 100 mL graduated cylinders and stored at 75°C. Trailing edge settling rates on these products are listed in Table VII. After approximately two days, each supernatant was analyzed for aluminum and hydroxide content. The results of the analyses are given in Table VIII. Then, the cylinders were allowed to equilibrate for two more days, but at 37°C. Aliquots of the supernatant were taken and analyzed. The 37°C data are shown in Table IX. As per the referenced letter, these samples will be stored for some two (2) months at 37°C, at which time the supernatants will again be analyzed for Al/OH.

The data allow several observations to be made. First, the assumption that WVR may be measured using condensate volumes holds up very well. Second, lower temperature equilibration of saturated sodium aluminate causes the formation of many solids (presumably precipitation of $NaAlO_2$ (s)). Also, complexants tend to cause changes in many of the physical and chemical characteristics of the wastes. Finally, the synthetic wastes, under the conditions discussed in this letter, tend to reach a supernatant hydroxide equilibrium approaching 8M. The final point is crucial when considering tank farm specifications.

No further work is planned at this time. Please call if you have any questions or comments regarding the data in this letter.

M. T. Jansky
Senior Chemist

H. R. Risenmay
Chemist

MTJ/HRR/pjm

cc: J. S. Buckingham JSB
K. G. Carothers
P. J. Certa
M. I. Fineman
D. L. Herting
M. J. Kupfer
J. H. Lawler
L. H. Rodgers
D. G. Wilkins
R. D. Wojtasek
File Code WX63G
[redacted]

TABLE I

Chemical Compositions of Supplemental Mixing Study Feeds
SWL:DSP Mixtures

	Concentration (moles/Liter)				
	100:0	85:15	70:30	55:44	40:60
Al	1.70	1.66	1.62	1.54	1.41
OH	3.48	3.63	3.86	4.20	4.62
NO_2	2.24	2.21	2.15	2.08	1.88
NO_3	3.63	3.56	3.50	3.45	3.17
F	--	0.07	0.065	0.06	0.05
PO_4	0.062	0.059	0.058	0.055	0.051
SO_4	0.015	0.015	0.015	0.015	0.015
CO_3	0.11	0.11	0.11	0.11	0.11
Complexants	--	0.034	--	0.032	--
K	--	0.136	0.394	0.563	1.08
Na	11.49	11.48	11.21	11.24	10.46

TABLE II

Supplemental Mixing Study Feed Make-Up Analyses*

	SWL:DSP Mixtures Concentration (moles/Liter)				
Component	100:0	85:15	70:30	55:45	40:60
Al	1.66	1.64	1.60	1.56	1.44
OH	3.30	3.42	3.70	4.08	4.55

* See text for discussion of low hydroxide values. Feeds butted up with solid NaOH to reach desired concentration of OH as listed in Table I.

TABLE III

Specific Gravity of Supplemental Mixing Study Feeds

SWL:DSP	Specific Gravity
100:0	1.49^{7}
85:15	1.50^{9}
70:30	1.50^{0}
55:45	1.50^{2}
40:60	1.48^{2}

TABLE IV

WVR *versus* Temperature of Supplemental Mixing Study Feeds

	Temperature (°C)				
% WVR	100:0	85:15	70:30	55:45[a]	40:60
0	58.6	58.8	58.8	58.4	59.0
5	60.0	60.2	60.0	59.6	60.4
10	61.4	61.6	61.8	61.6	62.0
15	63.2	63.2	63.2	63.6	64.0
16			64*	64*	64*
17	64*				
18		65.0*			
20	65.0	65.6	65.4	65.6	65.6
25	66.4	67.2	67.8	68.6	68.2
27.8					70.2**
30	69.2	69.8	70.6		
30.5				71.6**	
33			72.4**		
34.5		72.6**			
35.5	72.8**				

* Nucleation.

** Final desired WVR.

(a) Feed "foamed" throughout the run. Note that this material contained complexant.

TABLE V

Al/OH/SpG of Supplemental Mixing Study Products

Component	Ratio (SQL:DSP) 100:0	85:15	70:30	55:45	40:60
Al (moles/L)	2.60	2.47	2.60	2.23	1.98
OH (moles/L)	5.60	5.60	5.65	6.15	6.55
Sp.G.*	1.73^{6}	1.69^{9}	1.66^{2}	1.67^{8}	1.64^{7}

*At 72°C (boildown temperature).

TABLE VI

Viscosity versus Temperature of Supplemental Mixing Study Products

Temperature (°C)	Viscosity (centipoise)*				
	100:0	85:15	70:30	55:45	40:60
75	27	45	26	23	17
60	47	76	45	40	22
45	173	278	123	80	144
35	582[a]	876[a]	317	224	311
25	1705[b]	6410[c]	1446[b]	8830[c]	2212[b]
75**	27	30	24	21	--

* Brookfield LVT spindle viscometer, #2 spindle. All viscosities at 60 rpm except: (a) 30 rpm
(b) 12 rpm
(c) 3 rpm.

** Cooled sample from 75°C down to 25°C, then reheated to 75°C.

TABLE VII

Trailing Edge Settling Rates of Supplemental Mixing Study Products*

75°C

Time	100:0	Time	85:15**	Time	70:30	Time	55:45**	Time	40:60
0	100	0	100	0	100	0	100	0	100
7	97	3	84	5	99	10	100	7	100
12	95	9	69	13	95	28	87	13	86
16	92	16	61	21	90	33	84	21	78
20	89	27	43	32	84	38	80	40	49
26	84	32	40	39	78	54	69	51	36
31	81	39	40	56	70	60	65	65	32
39	74			75	60	68	61	89	32
45	69			104	49	87	52		
996	47			300	47	98	49		
						136	46		
7200	65	7200	56	5760	51	5760	46	5760	33

* Time in minutes, ratio of SWL:DSP. Different times due to when boildowns completed.

** Mixtures were "cloudy" for some time while heavier solids built up on bottom. Difficult to assess trailing edge settling rate.

TABLE VIII

Al/OH Concentrations of Supernatant from Supplemental Mixing Study Products

75°C

Component	Ratio (SWL:DSP) 100:0	85:15	70:30	55:45	40:60
Al (moles/Liter)	2.66	2.47	2.57	2.32	2.03
OH (moles/Liter)	6.30	6.20	6.45	6.35	6.40
Volume % Supernatant*	35	44	49	54	67

* Some supernatant removed for analysis; volume % solids may be slightly biased low.

TABLE IX

Al/OH Concentrations of Supernatant From Supplemental Mixing Study Products

37°C*

Component	Ratio (SWL:DSP) 100:0	85:15	70:30	55:45	40:60
Al (moles/Liter)	2.40	2.63	2.74	2.37	2.24
OH (moles/Liter)	7.85	7.55	7.25	7.40	7.25
Volume % Solids**	79	85	61	63	78

* Actual temperature was 35°C.

** Some supernatant removed for analysis; volume % solids may be slightly biased low.

Internal Letter

Rockwell International

Date October 21, 1983

No. 65453-83-268

TO: (Name, Organization, Internal Address)
D. M. Tulberg
Waste Management Process Tech. Unit
2750E/200 E

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky/H. R. Risenmay
Chemical Laboratory Unit
MO-037/200 W, 222S/200 W
3-1572, 3-3612

Subject: Laboratory Support for Decladding Supernatant/Salt Well Liquor Mixing

References:

1. Letter, 65411-83-092, D. M. Tulberg to M. T. Jansky, "Decladding Supernate-Salt Well Liquor Mixing Study", April 21, 1983.
2. Letter, 65453-83-175, M. T. Jansky/H. R. Risenmay to D. M. Tulberg, "Laboratory Results from the Waste Mixing Study", June 24, 1983.
3. Letter, 65411-83-164, D. M. Tulberg to M. T. Jansky, "Supplemental DSP-SWL Mixing Study", August 15, 1983.
4. Letter 65453-83-234, M. T. Jansky/H. R. Risenmay to D. M. Tulberg, "Supplemental Mixing Study Data", September 7, 1983.
5. Cost Account Plan, WX43 Flowsheet Development, K. G. Carothers, CAM, September 21, 1983.
6. DSI, D. M. Tulberg to M. T. Jansky, June 17, 1983.

The storage of future PUREX-generated waste streams, specifically decladding supernatant liquor (DSP), will require mixing the DSP with existing waste. One scenario is to mix the DSP with salt well liquor (SWL). Data were requested (ref. 1) to determine the impact of mixing DSP and SWL in various ratios. The data were compiled and issued as an internal letter (ref. 2). Additional data were requested to verify the developed processing parameters of DSP/SWL mixtures. The request is discussed in ref. 3, with ref. 4 a compilation of the supplemental data. As per the October 21, 1983, milestone (ref. 5), a "letter report on all lab work supporting DSP-SWL mixing flowsheet" needs to be issued. The purpose of this letter is to provide the peripheral data required for completion of the milestone. Specific data are discussed below.

As mentioned in ref. 4, aliquots of each product from the supplemental study boildowns were stored at 37°C in graduated cylinders for an extended period of time. The supernatants were analyzed after 27 days. However, the extremely low values of aluminum and hydroxide indicate that water intrusion had diluted the samples. Therefore, product aliquots that had been stored at 68°C were transferred to the 37°C bath and stored for four days. Analyses of the supernatants are shown in Table I. Additionally, the data provided in Tables II and III are miscellaneous data you requested for comparison studies (ref. 6).

Rockwell International

The data appear to offer general trends. Specifically, the presence of complexants decreases the equilibrium concentration of hydroxide. Also, equilibrium concentrations of hydroxide approach 8M. An interesting observation, too, is that the presence of potassium (due to the addition of DSP to SWL) "inhibits" the sulfate solubility. Note that in Table III, the only time sulfate was detected was when no DSP was added to the SWL. This phenomenon (sulfate solubility depression) was consistent throughout the study.

This letter satisfies the October 21, 1983 milestone. Please call if you have questions or comments, or require any additional follow-up work. All archived samples pertaining to the mixing study will be discarded October 31, 1983 unless you have specific requirements for them.

M. T. Jansky
Chemist, Senior

H. R. Risenmay
Chemist

MTJ/HRR/pjm

cc: J. S. Buckingham JSB
K. G. Carothers
D. L. Herting
J. H. Lawler
L. H. Rodgers
D. G. Wilkins
File Code: WX
Process Aids

TABLE I

SUPERNATANT ANALYSES OF STORED* SUPPLEMENTAL PRODUCTS

Component	Ratio (SWL:DSP) 100:0	85:15	70:30	55:45	40:60
Al (moles/Liter)	1.16	1.08	1.19	1.08	1.29
OH (moles/Liter)	7.84	7.49	7.91	7.66	7.47

*Products stored at 68°C for 42 days, subsequently transferred to a 37°C environment and stored for 4 days, after which aliquots of the supernatants were analyzed for Al/OH content.

TABLE II

PHOSPHATE AND SULFATE CONCENTRATION OF SWL:DSP SUPERNATANTS*

Mixture			Concentration	
Ratio	% WVR	T (°C)	PO_4^{-3}(M)	SO_4^{-2}(M)
85:15	50	35	0.008	**
85:15	50	60	0.041	**
85:15	DSSF	35	0.017	**
85:15	DSSF	60	0.016	**
70:30	50	35	0.012	**
70:30	50	60	0.040	**
70:30	DSSF	35	0.016	**
70:30	DSSF	60	0.017	**

*See Reference 2, Letter #65453-83-175.

**Below Detection Limits.

TABLE III

ANALYSES OF SPECIFIC SWL:DSP MIXTURES*

Mixture			Concentration		
Ratio	% WVR	T (°C)	PO_4^{-3}(M)	SO_4^{-2}(M)	CO_3^{-2}(M)
100:0	DSSF	55	0.077	0.029	0.11
85:15	DSS	65	0.021	**	0.11
40:60	DSSF	45	0.012	**	0.095
40:60	DSS	75	0.027	**	0.12

*See Reference 2, Letter #65453-83-175.

**Below Detection Limits.

744

Internal Letter

Rockwell International

Date: September 9, 1983

No. 65453-83-231

TO: (Name, Organization, Internal Address)
- N. W. Kirch
- Process Engineering
- 271-B/300B/200 E

FROM: (Name, Organization, Internal Address, Phone)
- M. T. Jansky, H.R. Kisenmay
- Chemical Laboratory Unit
- 222S/MO-037/200 W
- 3-1571

Subject: Laboratory Results from Neutralized Zirflex Acid Waste (NZAW) Study

Reference: Document, #SD-RE-DTP-012, M.T. Jansky, "Laboratory Plan to Examine Dilution of Neutralized Zirflex Acid Waste (NZAW)", May 27, 1983.

PUREX processing of spent fuel rods, clad with zirconium, will produce zirflex acid waste (ZAW). The ZAW will be neutralized, producing neutralized ZAW (NZAW). The NZAW will be transferred to storage tanks to allow radiolytic decay of some of the high heat-producing elements in the waste. The waste will be mixed during storage using airlift circulators, to reduce the possibility of "bumping" or formation of hot spots in the tank.

The operation of the airlift circulators requires a minimum liquid volume of 650,000 gallons. The present scenario is to start with water in the tanks to allow the circulators to be working while the initial NZAW is being added. However, the addition of the NZAW, which contains dissolved aluminum and precipitated iron and chrome hydroxides, may precipitate the aluminum as gibbsite [$Al(OH)_3$]. The additional solids may interfere with airlift circulator operations. Laboratory results indicate that no problems should be encountered when the NZAW is diluted with either water or dilute caustic in the ranges examined. Laboratory details are discussed below.

The Waste Management Process Technology Unit (WMPTU) requested that the Chemical Laboratory Unit (CLU) provide the following data:

a) Determine the volume of solids produced during dilution of NZAW in water,

b) Determine the effects of using sodium hydroxide (NaOH) as the diluent.

One objective of the study was to determine the effects of dilution during the initial storage cycle of NZAW. A second objective was to determine if deliterious effects may be reduced by using a caustic

Rockwell International

solution as the diluent rather than water. The expectation was that as the NZAW to water ratio increased, the volume of solids would also increase, to a point, then decrease as the precipitated gibbsite redissolved. Similar effects were anticipated and the NZAW to caustic ratio increased, but at lower ratios.

Contrary to expectations, the volume of solids continued to increase as the relative dilution decreased. This was attributed to not agitating the mixtures during equilibration. The aluminum probably supersaturated, which caused the constant increase in solids volume. However, no problems occurred even after the supersaturation was relieved. Therefore, no problems are anticipated should the current scenario be followed. Specific laboratory details are discussed below.

Synthetic ZAW was prepared with composition as found in Table 1. Half of the ZAW was neutralized with 19 M NaOH to 1 Molar free hydroxide (NZAWA). The other half of the ZAW was neutralized to a hoped for 0.72 M free hydroxide (NZAWB). Upon analysis, the NZAWA was found to be 1.08 M free hydroxide and 0.679 M aluminum. The NZAWB was 0.796 M free hydroxide and 0.694 M aluminum.

The NZAWA solution was warmed to 50°C and added to 65°C water in 100 mL graduated cylinders, such that the ratio of NZAW to water was as shown in Table 2. These cylinders were marked with the letter H, to designate water dilution.

The NZAWB solution was warmed to 50°C and added to 65°C 0.45 M NaOH in 100 mL graduated cylinders, such that ratio of NZAWB to 0.45 M NaOH was as shown in Table 3. These cylinders were marked with the letter N, for NaOH dilution.

All solutions were made in triplicate, sealed with rubber stoppers with pressure relief valves, and wrapped with Teflon® tape around the stopper. The solutions were stored in 98°C ovens. The H1 and N1 series of cylinders were periodically sampled for analysis of aluminum and hydroxide, and the volume of solids was recorded for each one. After two weeks time, the volume of solids stabilized on all but the 10 H1 cylinder. Analytical results for aluminum showed that all but 8N1, 9N1, and 10 H1 cylinders were either stable or below detection limits imposed by the sample size. Hydroxide values were too erratic to be used in the study.

Rockwell International

The viscosity of the solutions in the H1 and N1 series of cylinders was then taken at 90°C. A Brookfield Viscometer was used, turning a #2 spindle at 60 rpm. The contents of the cylinder were poured into a jacketed beaker held at 90°C. The viscosities found are shown in Table 4. As the solutions were agitated to breakup the solids (so that the viscosity could be run) a large increase in volume of solids was generally encountered. This may suggest that the solutions were supersaturated because of no agitation.

The solids in the graduated cylinders were very hard and uneven, being deposited on the sides of the cylinders and on the bottom in lumps. It was very difficult to estimate the volume percent solids. The solids were scraped from the sides and crushed on the bottom with a glass rod. This agitation caused the percipitation of new solids.

The N2 and H2 series of cylinders were used to simulate what happens as new waste is added to the tanks. The ratios of NZAW used were to simulate different metric tons of uranium (MTU) processed. The contents of the cylinders were poured into a jacketed beaker held at 90°C and new quantities of NZAW were added to the beaker to jump the ratio of NZAWA/H_2O or NZAWB/0.45 M NaOH to that of the next cylinder in the series. In all instances, large amounts of white flocculent solids were formed as the NZAW was added. The largest volume of solids was found in the H series during the jump from 2,000 MTU to 2,500 MTU where the solution was so thick a magnetic stirrer could not stir the mass of solids. A glass stirring rod was used to thoroughly stir the mixture. The H series had the largest volume of new solids formed in the jump from 1,500 MTU to 2,000 MTU.

Settled solids volumes versus MTUs after 14 days of settling, are shown in Figure 1 and Table 5 for the water dilutions. Figure 2 and Table 5 contain similar data pertaining to caustic dilution. The Figures and Tables include data pertaining to relief of supersaturation, for comparative purposes. The analyses indicate that, except for in the cylinders representing 3,000 MTU, virtually all of the aluminum precipiated.

The third series of cylinders were used to determine if solids would redissolve when contacted with caustic. The contents of the H3 and N3 series were poured into a jacketed beaker at 90°C and titrated with 19 M NaOH. Caustic was added such that the hydroxide concentration would not exceed 0.72 M. Even after two weeks of 98°C, no solids appeared to dissolve.

Rockwell International

There was no cylinder in the N series that represented 2,500 MTU. Therefore, it is difficult to tell if the use of 0.45 M NaOH performed as expected or if little or no effect will be found by using caustic rather than water to fill the waste tank. In almost every case where the source amount of MTUs are represented in both the H and N series, the volume of solids appear to be essentially the same when the jump is made. After sitting in an oven for a week, the solids coalesce or dissolve. The series diluted with water appear, in most cases, to have fewer solids than those diluted with caustic. The volume of solids is shown in Table 6 and Figures 3 and 4.

Also found in Table 6 is the volume of NZAW added to make the jump in ratio of NZAWA/H_2O or NZAWB/0.45 M caustic. These values, expressed as milliliters, are also the percent of cylinder volume added. They range from a low of 2.1% to a high of 85.5% NZAW added. In the field the additions of NZAW will only be about 5,000 gallons at a time, or about 0.77% or less as the tank fills. The rapidity of the coalescing or dissolving of solids formed during the addition oif NZAW to the tank would suggest that the solids generated would not be a problem to proper operation of the airlift circulators.

The data indicate that no problem should arise should the present operating scenario be followed, i.e., addition of NZAW to essentilly water. The use of caustic as a diluent does not appear to reduce the volume of solids generated during dilution when compared to water.

Please call if you would like any follow-up work or if you have any questions or comments.

M. T. Jansky
Senior Chemist

MTJ for HRR
H. R. Risenmay
Chemist

MTJ:HRR:gij

Attachments

cc: J.F. Albaugh
D.G Baide
J.S. Buckingham JSB
K.G. Carothers
M.I. Fineman
D.L. Herting
L.H. Rodgers
D.G. Wilkins
Process Aids
File: WX63G

L 748

Table 1. COMPOSITION OF SYNTHETIC ZIRFLEX ACID WASTE (ZAW)

Compound	Concentration (Moles/Liter)
$Cr(NO_3)_3 \cdot 9H_2O$	0.018
$Fe(NO_3)_3 \cdot 9H_2O$	0.09
$Al(NO_3)_3 \cdot 9H_2O$	0.99
$NaNO_3$	0.20
HF	0.21
HNO_3	0.94
H_2SO_4	0.08

Table 2. DILUTION OF NZAWA WITH H_2O

Cylinder #	MTU	mLs H_2O	mLs NZAWA*	NZAWA/H_2O
1H1, 1H2, 1H3	500	84.7	15.3	0.18
2H1, 2H2, 2H3	1,000	73.5	26.5	0.36
3H1, 3H2, 3H3	1,500	64.1	35.9	0.56
4H1, 4H2, 4H3	1,600	61.7	38.3	0.62
5H1, 5H2, 5H3	1,700	59.2	40.8	0.69
6H1, 6H2, 6H3	1,800	56.8	43.2	0.76
7H1, 7H2, 7H3	2,000	52.1	47.9	0.92
8H1, 8H2, 8H3	2,500	40	60	1.50
9H1, 9H2, 9H3	3,000	28.1	71.9	2.56
10H1, 10H2, 10H3	4,500	0	161 mls reduced to 100	--

*NZAWA neutralized to 1 M excess free hydroxide.

TABLE 3. DILUTIONS OF NZAWB WITH 0.45 M NaOH

Cylinder #	MTU	mLs 0.45 MNaOH	mLs NZAWB*	NZAWB/0.45 M NaOH
1N1, 1N2, 1N3	500	84.7	15.3	0.18
2N1, 2N2, 2N3	700	80	20	0.25
3N1, 3N2, 3N3	800	77.5	22.5	0.29
4N1, 4N2, 4N3	900	75.1	24.9	0.33
5N1, 5N2, 5N3	1,000	73.5	26.5	0.36
6N1, 6N2, 6N3	1,500	64.1	35.9	0.56
7N1, 7N2, 7N3	2,000	52.1	47.9	0.92
8N1, 8N2, 8N3	3,000	28.1	71.9	2.56
9N1, 9N2, 9N3	4,500	0	162 mls reduced to 100 mls	--

*NZAWB neutralized to 0.72 M excess free hydroxide.

TABLE 4. VISCOSITY VERSUS MTU, 90°C

MTU	Viscosity (cps)
Water Dilution	
500	2
1,000	3
1,500	4
1,600	3
1,700	3
1,800	5
2,000	5
2,500	5
3,000	8
4,500	8
NaOH Dilution	
500	2
700	3
800	3
900	2
1,000	3
1,500	4
2,000	5
3,000	5
4,500	10

TABLE 5. VOLUME PERCENT SETTLED SOLIDS

WATER DILUTION

MTU	Time 14 Days	After Viscosity	After NZAW Add'n*
500	1	3	
1,000	3	5	11
1,500	7	7	56
1,600	7	8	32
1,700	7	8	37
1,800	6	7	40
2,000	9	9	75
2,500	10	10	96
3,000	12	11	29
4,500	15	39	

NaOH DILUTION

500	1	3	
700	1	3	26
800	1	4	17
900	2	4	23
1,000	3	4	11
1,500	2	5	47
2,000	6	8	67
3,000	10	25	24
4,500	8	41	

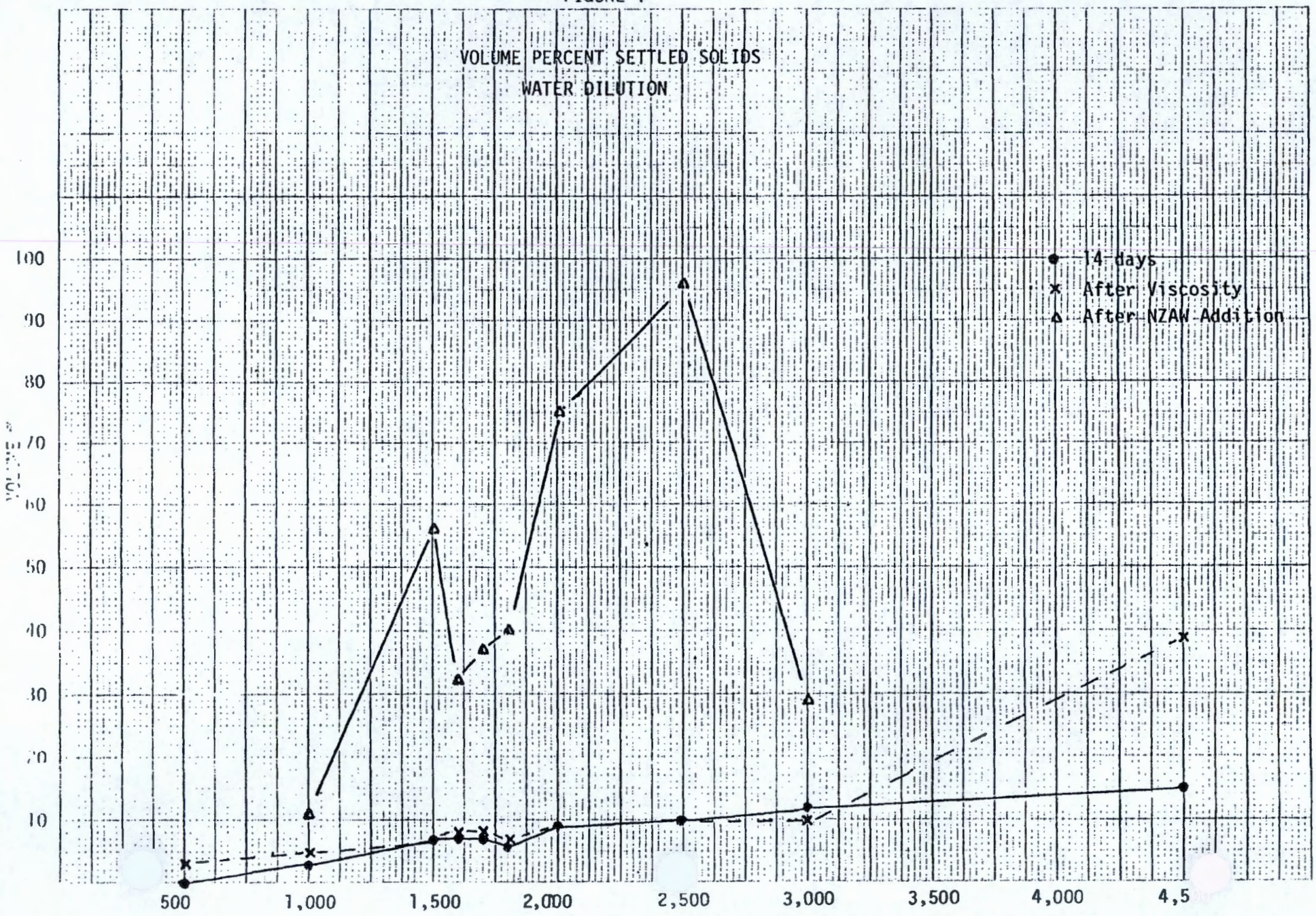
*NZAW added to "jump" to next MTU concentration, i.e., from 500 to 1,000 MTU. See text.

TABLE 6. VOLUME PERCENT SETTLED SOLIDS AFTER NZAW ADDITION

MTU	Time (Days) 0	5	8	NZAW Added (mLs)
WATER DILUTION				
1,000	11	13	13	15.2
1,500	56	18	17	14.7
1,600	32	20	18	3.8
1,700	37	28	26	4.3
1,800	40	32	29	4.2
2,000	75	21	17	9.1
2,500	96	46	20	30.2
3,000	29	25	27	42.2
NaOH DILUTION				
700	26	16	15	5.9
800	17	11	9	3.2
900	23	10	7	3.1
1,000	11	6	5	2.1
1,500	47	36	27	14.7
2,000	67	48	35	23.1
3,000	24	28	27	85.5

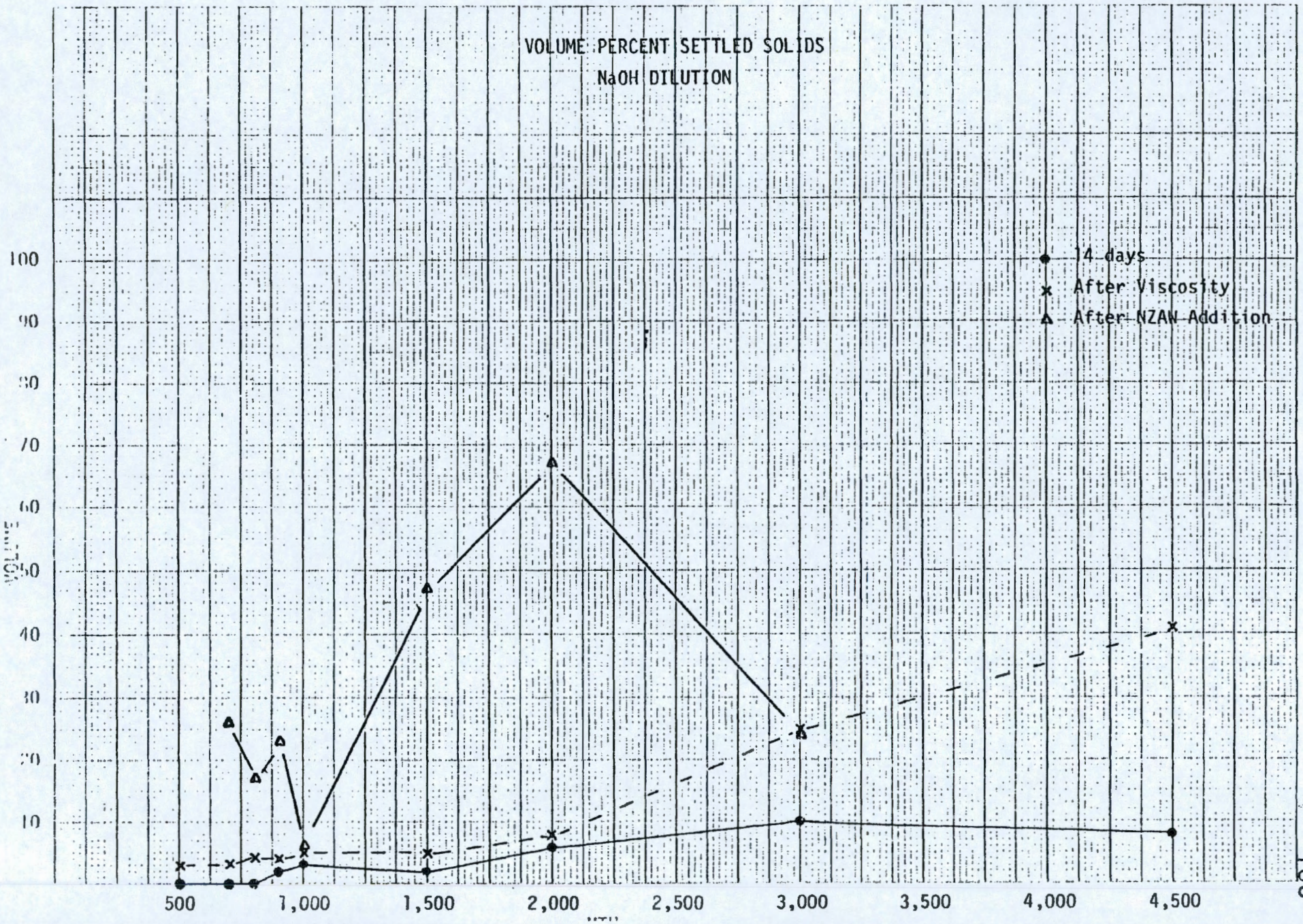
K+E 10 X 10 TO ½ INCH 7 X 10 INCHES KEUFFEL & ESSER CO. MADE IN U.S.A.
46 1320

FIGURE 1



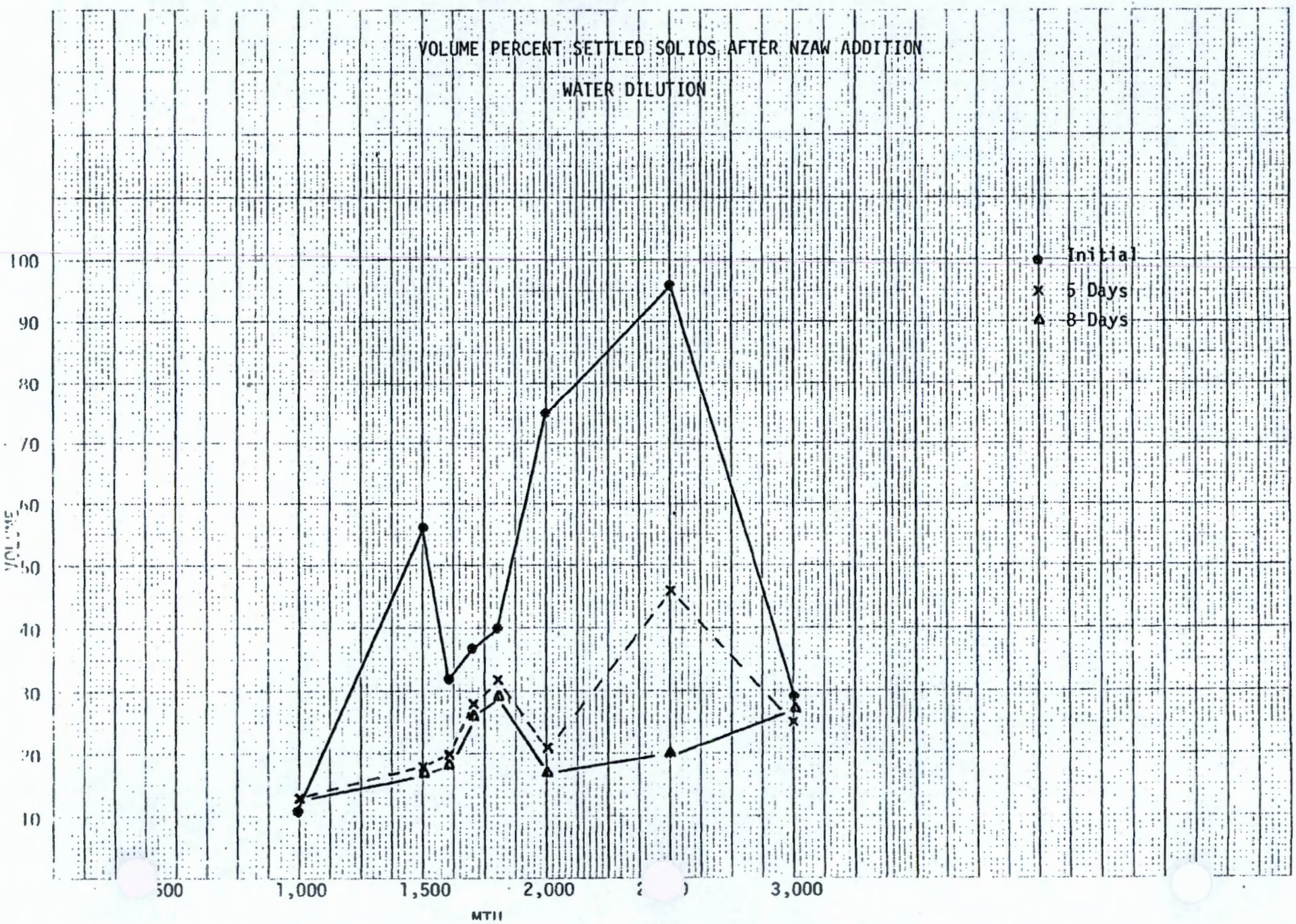
K+E 10 X 10 TO 1/2 INCH 7 X 10 INCHES KEUFFEL & ESSER CO. MADE IN U.S.A.

FIGURE 2



K+E 10 X 10 TO ½ INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

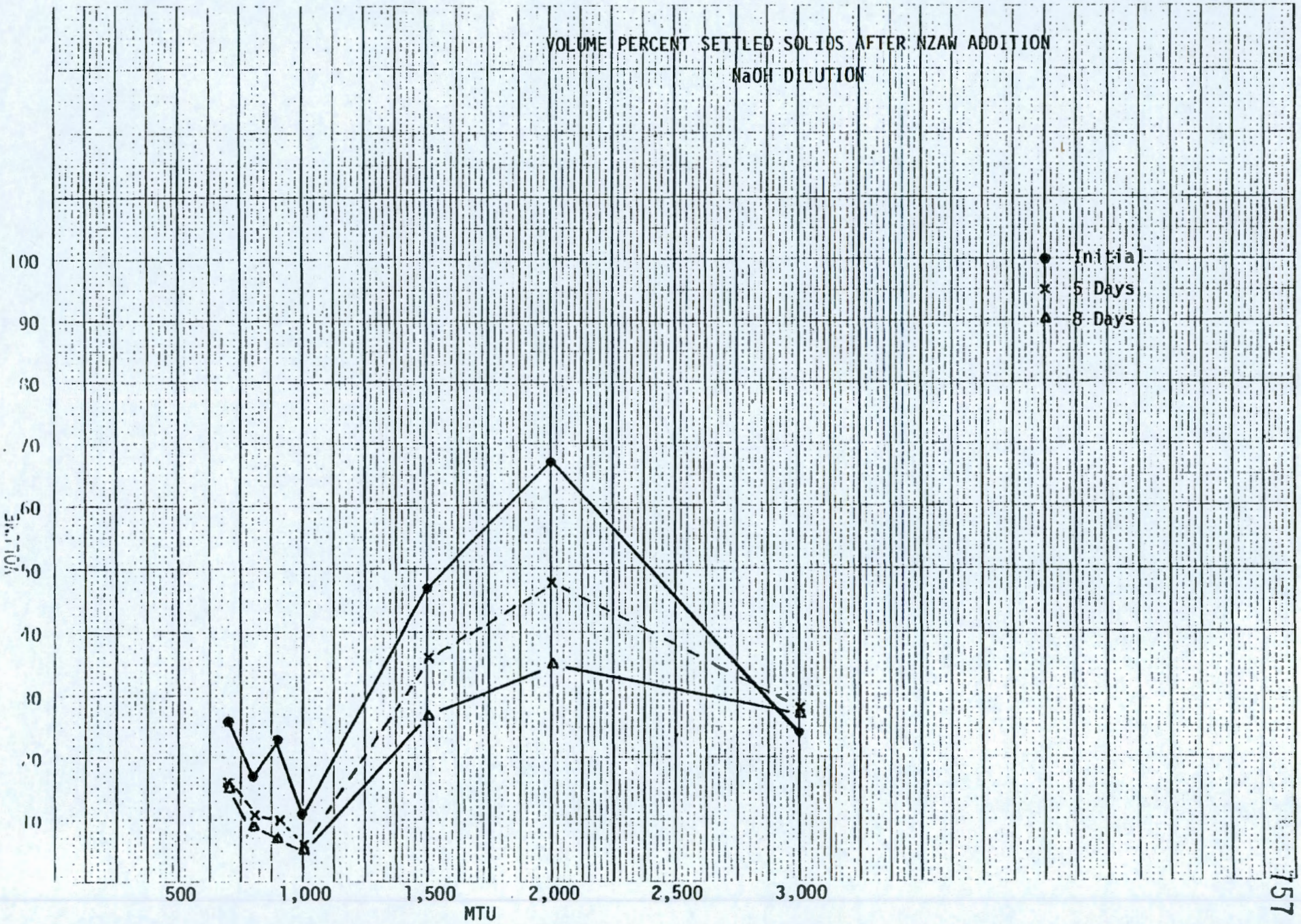
FIGURE 3



K+E 10 X 10 TO ½ INCH KEUFFEL & ESSER CO. MADE IN U.S.A.

46 1320

FIGURE 4



758

Internal Letter

Rockwell International

Date. February 22, 1983

No. 65453-83-048

TO: (Name, Organization, Internal Address)

- D. E. Tulberg
- Waste Mgt. Process Tech. Unit
- 2750E/200 East

FROM: (Name, Organization, Internal Address, Phone)

- B. D. Bullough
- Separations Process Development Unit
- 202-S/200 West
- 3-2967

Subject: Boiling Point of Neutralized Decladding Sludge

Two samples of neutralized decladding sludge were taken, and their boiling points determined. Samples labeled "pre-interface" and "interface" were used. Pre-interfacial solution is primarily supernatant liquid with approximately 30% very fine, slowly settling solids; interfacial solution is nearly all solids, of a heavier nature with an almost creamy texture. The pH of both samples was about 13.7.

Boiling occurs in a range of about two degrees Celcius, with steady, full boiling approximately two degrees higher than the onset of boiling. Temperatures were determined using three thermometers and an average taken. Variation between thermometers was not greater than 0.5°C. Pre-interfacial liquid full boil occurred at 99°C, while interface liquid boiling takes place at 97.5°C.

Bruce D. Bullough

B. D. Bullough
Engineer

BDB/naj

cc:

J. S. Buckingham
K. G. Carothers
D. E. Gana
M. T. Jansky
G. W. Reddick, Jr.
L. H. Rodgers
[redacted]
Letterbook

Internal Letter

Rockwell International

Date August 12, 1983

No 65453-83-197

TO: (Name, Organization, Internal Address)

M. I. Fineman
Process Design Department
2750E/200 E

FROM: (Name, Organization, Internal Address, Phone)

M. T. Jansky
Chem. Lab. Unit
MO-037/200 W
3-1571

Subject: Analysis of "Iron Oxide" Sludge

Reference: Letter, 65411-83-138, M. I. Fineman to M. T. Jansky, "Iron Oxide Sample Study", June 24, 1983

The Chemical Laboratory Unit (CLU) received a brown sludge sample from you recently. As per your reference letter, CLU examined various properties of the sludge. The purpose of this letter is to provide you with our findings.

Leading Edge Settling Rates of Solids in Water Medium

A representative aliquot of the sludge was tested for leading edge settling rates in water. When the sludge was added to water (in a graduated cylinder), the leading edge immediately went through the water. It took less than a second for solids to go through a column of water six inches high and one inch in diameter. There was some particulate lagging in the water, as the mixture appeared brown for several minutes.

Characterization of Iron Oxide

An aliquot of the sludge was dried for 24 hours and submitted for x-ray analysis. The results of the analysis indicate that the major components of the sludge are strontium carbonate ($SrCO_3$) and sodium sesquicarbonate. Iron oxide is a minor constituent, and is present in the form of magnetite (Fe_3O_4). Other minor constituents are strontium/ aluminum compounds.

Waters of Hydration

The iron component, Fe_3O_4, forms as the anhydrous crystal. The sodium sesquicarbonate is the dihydrate:

$$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O.$$

Rockwell International

Particle Size

The sludge was determined to contain particles with a weighted mean diameter of 29 micrometers. The particle size distribution (PSD) was determined using a HIAC particle counter.

Particle Density

The density of the particles was determined using two methods. One method was to calculate the density by "backing out" both weight and volume of interstitial liquor and water from a sludge sample. This method yielded an average particle density of 2.39 g/cc. The second method, displacement of an inert organic liquid by dried sludge, gave a density of 2.45 g/cc.

No additional tests were requested. Please call if you have questions or comments.

M. T. Jansky
Senior Chemist

MTJ:gij

cc: J. S. Buckingham JSB
K. G. Carothers
D. L. Herting
L. H. Rodgers
D. M. Tulberg
D. G. Wilkins
[redacted]
File Code: WX63G
Letterbook

Internal Letter

Rockwell International

Date: August 15, 1983

No: 65453-83-204

TO: (Name, Organization, Internal Address)
L. H. Rodgers
Program Engineering
2750E/A222/200 E

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Chemical Laboratory Unit
MO-037/200 W
3-1571

Subject: Irradiation of Synthetic Iron Hydroxide Sludge

The Waste Management Process Technology Unit (WMPTU) has expressed an interest in determining the effects of radiation on synthetic iron hyroxide sludge. Iron hydroxide [$Fe(OH)_3$] is produced during the neutralization of zirflex acid waste (ZAW). The extent of radiation exposure is on the order of one million rad (10^6R).

The Chemical Laboratory Unit (CLU) has some $Fe(OH)_3$ that may be used for this purpose. The best way to achieve sufficient (and accurate) amounts of radiation is to send the sample to Pacific Northwest Laboratory (PNL) and Earl Martin, for Cobalt-60 irradiation.

We propose to send five identical samples to PNL. Each sample will be irradiated for a different period of time to achieve different radiation doses (specifically 10^2R, 10^3R, 10^4R, 10^5R, 10^6R). Each sample will be examined to determine:

a) Does radiation convert the hydroxide to the oxide?

b) What form is the oxide (Fe_3O_4 vs. Fe_2O_3)?

c) Can information about the conversion kinetics be obtained?

As mentioned before, the irradiation would best be done at the PNL facility, and would cost $500. I have submitted a work order to cover the costs. The samples would then be returned to Rockwell, for x-ray analysis and scanning electron microscope (SEM) dispersive x-ray analysis. The capability for the SEM analysis should be in place by the end of September. Funding is necessary for two manweeks to follow the project and provide SEM analyses.

Please call me if this proposal meets with your approval. I will arrange sample transfers and analyses when we get the go-ahead.

M. T. Jansky
Senior Chemist

MTJ:gij

cc: D. S. Buckingham
K. G. Carothers
D. L. Herting
N. W. Kirch
J. H. Lawler
D. G. Wilkins
Process Aids
File: WX63G

762

Internal Letter

Rockwell International

Date. August 23, 1983

No. 65453-83-217

TO: (Name, Organization, Internal Address)
. J. H. L. Lawler
. Process Design
. 2750E/D228/200 East

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Chemical Laboratory
. 222-S/MO-037/200 West
. 3-1571

Subject: . Irradiation of Iron Hydroxide Sludge

Ref: Letter, #65453-83-204, dated August 15, 1983, M. T. Jansky to L. H. Rodgers, "Irradiation of Synthetic Iron Hydroxide Sludge"

The referenced letter discussed plans for irradiating synthetic iron hydroxide sludge. The amount of radiation was to be at five levels: 10^2-10^5R. The various amounts were discussed and agreed upon verbally.

Now, as per your phone call of August 19, the levels have been changed. The new levels are: 10^4R, 10^5R, 10^6R, 10^7R, and 10^8R. The higher doses of radiation will necessitate additional time for the work to be completed, with only minimal additional cost.

I shall keep you appraised of the progress of this project. Please call if you have additional comments or questions.

M T Jansky

M. T. Jansky
Senior Chemist

MTJ/naj

cc:

J. S. Buckingham JSB
K. G. Carothers
D. L. Herting
N. W. Kirch
L. H. Rodgers
D. G. Wilkins

[redacted]

File Code: WX63G
Letterbook

Internal Letter

Rockwell International

Date November 9, 1983

No 65453-83-285

TO: (Name, Organization, Internal Address)
N. W. Kirch
Process Design
2750E/A227/200E

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Chemical Laboratory Unit
222S/MO-037/200W
3-1571

Subject Irradiation of Synthetic Iron and Chrome Hydroxide Sludge

References

1. Letter, #65453-83-204, M. T. Jansky to L. H. Rodgers, "Irradiation of Synthetic Iron Hydroxide Sludge", August 15, 1983.

2. Letter, #65453-83-231, M. T. Jansky/H. R. Risenmay to N. W. Kirch, "Laboratory Results from Neutralized Zirflex Acid Waste (NZAW) Study", September 5, 1983.

As stated in Reference 1, the Waste Management Process Technology Unit (WMPTU) was interested in determining the effects of radiation on iron hydroxide sludge. The sludge is produced when zirflex acid waste (ZAW) is neutralized, producing neutralized ZAW (NZAW). The sludge, containing precipitated iron and chrome hydroxides, may be readily suspended with efficient mixing. However, conversion of the hydroxide to a denser, more crystalline oxide could create potential problems with air-lift circulator operations. The Chemical Laboratory Unit (CLU) has examined potential changes in synthetic NZAW hydroxide sludge due to irradiation of the sludge. No significant changes were observed when the synthetic sludge was irradiated up to 10^8 rad. The purpose of this letter is to document the iron hydroxide irradiation study, which satisfies the November 11, 1983, WX milestone. The study is discussed below.

Reference 2 discusses a study in which NZAW was prepared. The iron and chrome hydroxide sludge was removed from the ZAW that was neutralized to 1 molar excess hydroxide. The sludge was saved for this study. The sludge contained residual liquor, which included dissolved aluminum. Five aliquots of the sludge were irradiated, each at a different level, utilizing a Cobalt-60 radiation source. The five levels were initially requested to be 10^2-10^6 rad (Reference 1). However, WMPTU verbally requested that the irradiation levels be changed to 10^4-10^8 rad. A sixth aliquot was not subjected to irradiation, but used as a control.

After irradiation, the five test samples and the control were examined for structural (i.e., crystalline) changes. Specifically, CLU was looking for conversion of the original hydroxides to the oxides. To that end, the samples were examined utilizing x-ray diffraction (Analytical Laboratories) and photomicroscopy (Dan Herting, CLU).

The data indicate that irradiation of the synthetic iron and chrome hydroxide sludge did not cause significant changes in the sludge. The x-ray diffraction patterns for all six samples were virtually identical. Gibbsite [$Al(OH)_3$] was identified, because of its strong crystalline x-ray pattern. The remainder of the material was amorphous. The x-ray

764

Rockwell International

data were confirmed by photomicroscopy. No differences were seen between the six samples. In each, a minor amount of anisotropic material was present (gibbsite is anisotropic). The bulk of the material was isotropic, which amorphous substances are.

It should be pointed out that a synthetic sludge was used in this study. Actual tank sludge contains different chemicals and different radiation sources. Additionally, temperature differences may cause changes not observed in this study. However, for this experiment, no changes were observed.

This letter satisfies the November 11, 1983 WX milestone. Please call if you have any questions, comments, or desire follow-up work.

M. T. Jansky
Senior Chemist

MTJ/rr

cc: J. S. Buckingham JSB
K. G. Carothers
D. L. Herting
J. H. Lawler
L. H. Rodgers
D. M. Tulberg
File Code WX
Process Aids

Internal Letter

Rockwell International

Date: November 21, 1983

No. 65453-83-291

TO: (Name, Organization, Internal Address)
N. W. Kirch
Process Design
2750E/A227/200E

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky
Chemical Laboratory Unit
222S/MO-037/200W
3-1571

Subject: Sulfate Solubility in Aging Waste

References

1. Letter, #65411-83-105, N. W. Kirch to K. G. Carothers, "Sulfate Precipitation in Aging Waste", April 29, 1983.

2. Letter, #65411-82-175, M. T. Jansky/K. J. Patterson to J. H. Lawler, "Summary of Laboratory Study of 5 Molar Sodium Limit Rule", May 14, 1982.

Sulfate ions are present in PUREX neutralized high level waste (NHW). As the aging waste concentrates, solids will precipitate. The precipitation of sulfate solids, primarily sodium sulfate ($Na_2SO_4 \cdot xH_2O$) may produce dense solids. These solids may cause deliterious effects during airlift circulator operations. The Waste Management Process Technology Unit (WMPTU) used a computer program to determine the saturation point of sulfate in synthetic NHW [Ref. 1]. The computer program (ECES) indicated that sodium sulfate would precipitate at approximately 0.35 molar (M) sulfate, with a corresponding sodium concentration of approximately 6.44M. Earlier laboratory work [Ref. 2] indicated that at 6.5M sodium, a great deal of precipitation occurred in synthetic NHW. The purpose of this letter is to briefly outline a laboratory study to verify that sodium sulfate precipitates when synthetic NHW is ~6.5M sodium. Details are discussed below.

Synthetic zirflex acid waste (ZAW) will be prepared according to the "recipe" in Table I. Concentrated sodium hydroxide (19M) will be added such that the "free" hydroxide concentration will be 1M. The resulting mixture will be filtered to remove precipitated iron and chrome hydroxides. The filtrate will be analyzed to get exact values for sodium, sulfate, and fluoride. The filtrate will then be subjected to batch boildowns. The boildowns will be conducted at atmospheric pressure. Aliquots will intermittently be removed during concentration, and examined utilizing photomicroscopy. An observation of sulfate crystals will be indication of sulfate solubility limits. Concentrations will be calculated based on additive volumes, and verified by chemical analyses. All work should be completed by December 16, 1983, meeting the WX milestone.

Please indicate your approval of this study by returning a copy of the letter, initialled by both you and your manager to me as soon as possible. Experimentation will commence upon receipt of the intialled letter.

M. T. Jansky
Senior Chemist

MTJ/rr

cc: R.B. Bendixsen, J.S. Buckingham JSB, K.G. Carothers ____, D.L. Herting, J.H. Lawler, D.W. Lindsey, G.W. Reddick, H.R. Risenmay, D.A. Reynolds, L.H. Rodgers, D.G. Wilkins, R.D. Wojtasek, J.C. Womack, [redacted], File: WX

TABLE I

RECIPE FOR SYNTHETIC ZIRFLEX ACID WASTE

Compound	Concentration (M)
HF	0.21
H_2SO_4	0.08
HNO_3	0.94
$Cr(NO_3)_3 \cdot 9H_2O$	0.018
$Al(NO_3)_3 \cdot 9H_2O$	0.99
$Fe(NO_3)_3 \cdot 9H_2O$	0.09
$NaNO_3$	0.20

Internal Letter

Rockwell International

Date November 23, 1983

No. 65452-83-296

TO: (Name, Organization, Internal Address)
. N. W. Kirch NWK
. Process Design
. 2750E/A227/200E

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky
. Chemical Laboratory Unit
. 222S/MO-037/200W
. 3-1571

Subject . Feed Make-Up for Sulfate Solubility Study

Reference: Letter, #65453-83-291, M. T. Jansky to N. W. Kirch, "Sulfate Solubility in Aging Waste", November 21, 1983.

The referenced letter discussed a laboratory study to determine sodium sulfate solubility. The letter contained an attachment which was the proposed feed recipe (Table I). The feed was based on 6 percent fuels. Apparently, the composition of the feed was not representative of planned PUREX output. Therefore, the Waste Management Process Technology Unit (WMPTU) provided the Chemical Laboratory Unit (CLU) with the data shown in Table II. The Table II data are most noticeably different from Table I in the sulfate concentration. Therefore, the proposed feed has been adjusted to include the greater amount of sulfate. The new proposed feed is shown in Table III.

Please signify your approval of the study and feed by initialling this letter, having your manager also initial it, and returning it to me. Work will commence upon receipt of the initialled letter.

MT Jansky

M. T. Jansky
Senior Chemist

MTJ/rr

Attachments

cc: R. B. Bendixsen
J. S. Buckingham JSB
K. G. Carothers KGC
D. L. Herting
J. H. Lawler
D. W. Lindsey
G. W. Reddick
H. R. Risenmay
D. A. Reynolds
L. H. Rodgers
D. M. Tulberg
D. W. Wilkins
R. D. Wojtasek
J. C. Womack
[redacted]
File Code WX

TABLE I

RECIPE FOR SYNTHETIC ZIRFLEX ACID WASTE

Compound	Concentration (M)
HF	0.21
H_2SO_4	0.08
HNO_3	0.94
$Cr(NO_3)_3 \cdot 9H_2O$	0.018
$Al(NO_3)_3 \cdot 9H_2O$	0.99
$Fe(NO_3)_3 \cdot 9H_2O$	0.09
$NaNO_3$	0.20

TABLE II

ZAW FROM PROCESSING NPR FUEL
IRRADIATED TO YIELD 12% PLUTONIUM-240

Volume: 180 gal ZAW/MTU

Flow (average): 4.3 l/m @ 9.08 MTU/d

Ion	Concentration (M)	Range (M)
H^+	0.95	0.7 - 1.5
Al^{+3}	0.78	0.6 - 1.0
Fe^{+3}	0.16	0.1 - 0.2
Cr^{+3}	0.015	
Ni^{+2}	0.007	
Na^+	0.21	0.16 - 0.25
SO_4^{-2}	0.33	0.26 - 0.41
F^-	0.14	0.04 - 0.3
$NO_3 + NO_2^-$	Balance of anions ~3M	
U	0.03 gm/L	0.01 - 0.1 gm/L
Pu	4×10^{-4} gm/L	1×10^{-4} - 0.03 gm/L
^{237}Np	0.05 gm/L	
^{241}Am	0.006 gm/L for 1 yr. aged	
	0.04 gm/L for 10 yr. aged	

TK-F16 NaOH - 56 gal 19M NaOH/MTU processed
(consumption)

TK-F16 NaOH - 1.3 l/m @ 9.08 MTU/processing rate
Flow (average)

TABLE III

RECIPE FOR SYNTHETIC ZIRFLEX ACID WASTE

Compound	Concentration (M)
HF	0.15
H_2SO_4	0.33
HNO_3	0.70
$Cr(NO_3)_3 \cdot 9H_2O$	0.018
$Al(NO_3)_3 \cdot 9H_2O$	0.80
$Fe(NO_3)_3 \cdot 9H_2O$	0.10
$NaNO_3$	0.20

Internal Letter

Rockwell International

Date December 14, 1983

No. 65453-83-306

TO: (Name, Organization, Internal Address)
. N. W. Kirch
. Process Design
. 2750E/A-200/200 E

FROM: (Name, Organization, Internal Address, Phone)
. M. T. Jansky/H. R. Risenmay
. Chemical Laboratory Unit
. MO-037/200 W
. 3-1571, 3-3612

Subject: . Sulfate Precipitation in Aging Waste

References:
1. Letter, #65411-83-105, N.W. Kirch to K.G. Carothers, "Sulfate Precipitation in Aging Waste", April 29, 1983.
2. Letter, #65453-83-291, M.T. Jansky to N.W. Kirch, "Sulfate Solubility in Aging Waste", November 21, 1983.
3. Letter, #65453-83-296, M.T. Jansky to N.W. Kirch, "Feed Make-Up for Sulfate Solubility Study", November 23, 1983.

Sulfate ions are present in PUREX neutralized high level waste (NHW). As the aging waste concentrates, solids will precipitate. The precipitation of dense sulfate solids may interfere with airlift circulator operations. The Waste Management Process Technology Unit (WMPTU) utilized a computer program to determine the saturation point of sodium sulfate in the NHW matrix (reference 1). A laboratory "plan" was proposed by the Chemical Laboratory Unit (CLU) to verify computer calculations (ref. 2). Conflicting information as to the NHW composition led to "standardization" of the feed, as stated in ref. 3.

All laboratory work indicates that sulfate precipitates even without concentrating the synthetic feeds. The filtered feed (ref. 3), upon reflux, had sulfate precipitating in less than four hours. In fact, at room temperature sulfate dropped out within four days. The sulfate/sodium concentrations were 0.16 M/5.9 M in the freshly prepared filtered feed. Note that when the feed was taken to boiling and concentrated immediately, sulfate dropped out at 7% waste volume reduction (WVR). The CLU also examined the initially proposed feed (ref. 2), for the same phenomenon. Microscopic analysis indicated similar effects.

Sulfate precipitation in aging waste is a more complex problem than initially addressed. The data indicate that sulfate solubility is much lower than as believed from computer analysis (ref. 1). This fact (lower sulfate solubility) needs to be addressed by WMPTU. Perhaps no additional information is needed. However, if additional experimentation is necessary, several additional parameters would need to be examined. Specifically, kinetics, temperature effects, and matrix effects. A statistically designed experiment would be the most advantageous manner to incorporate the parameters into the study.

772

Rockwell International

This letter satisfies the December 16, 1983, WX milestone. Please contact CLU when you have reached a decision regarding additional experimenation.

M. T. Jansky
Senior Chemist

H. R. Risenmay
Chemist

MTJ:HRR:gij

cc: R. B. Bendixsen
J. S. Buckingham JSB
K. G. Carothers
D. L. Herting
J. H. Lawler
D. W. Lindsey
G. W. Reddick
D. A. Reynolds
L. H. Rodgers
D. G. Wilkins
R. D. Wojtasek
[redacted]
File: WX

Internal Letter

Rockwell International 773

Date February 22, 1983

No. 65453-83-050

TO: (Name, Organization, Interne Address)
D. E. Kurath
Waste Mgt. Process Tech. Unit
2750E/200E

FROM: (Name, Organization, Interne Address, Phone)
B. D. Bullough
Separations Process Development Unit
202-S/200 West
3-2967

Subject: Ever-Tite® Quick-Connect Fittings for Jet Pump Use

As requested, an investigation was performed to obtain information on the use of Ever-Tite® quick-connects in jet pump assemblies. These fittings may be used to more effectively change out failed jets/jet bodies or lengthen salt well pumping systems. The test facility consisted of a 1-1/4" quick connect fitting installed vertically in a line with a relatively constant 30-35 ft of H_2O pressure.

Several attempts were made to jam the male and female ends of the fitting together, or otherwise connect or disconnect the parts to render them not fully operable. It was determined that the sections cannot be installed in any but the desired configuration. Disconnection occurs readily if the locking "arms" of the female section are fully disengaged; it isn't important whether the arms are disengaged sequentially or simultaneously, from this standpoint.

Because no internal check-valves are present in this type of quick-connect, splashing or spraying of upheld water while disconnecting the fittings may present a problem. Minimum spraying was noted when disengaging the locking arms sequentially; squirting water was noted to travel three to four feet in the direction of the locking arm opposite the last one disengaged.

One caution which must be presented is the possibility of leakage around the metal on metal interface of the mating parts. Although the "faces" of each fitting are machined to fit tightly, some slow leakage and possibly even depressurization of the system may be encountered.

Bruce D. Bullough

B. D. Bullough
Engineer

BDB/naj

cc:

D. E. Bowers
J. S. Buckingham
K. G. Carothers
J. D. Keck
L. H. Rodgers
R. A. Van Meter
Letterbook

774

Internal Letter

Rockwell International

Date June 15, 1983

No. 65453-83-173

TO: (Name, Organization, Internal Address)
- G. D. Campbell
- Waste Management Process Group
- 2750E/206/200 E

FROM: (Name, Organization, Internal Address, Phone)
- D. L. Herting/K. J. Patterson
- Chemical Laboratory Proc. Dev. Unit
- MO-037/200 W
- 3-2532

Subject: Magnesium Hydroxide Neutralization Scouting Study

A brief scouting study has been completed on the neutralization of Zirlfex decladding waste using magnesium hydroxide, $Mg(OH)_2$. The primary goal of the study was to determine whether the Mg:Zr mole ratio has an effect on the volume of solids precipitated during neutralization. The results, as plotted in Figure 1, show that the Mg:Zr ratio does have a large effect. However, by interpreting the data in another way, the effect can be ascribed entirely or in part to changes in the "concentration" of the $Mg(OH)_2$-H_2O slurry. Experimental details and additional observations follow.

Each neutralization began with the $Mg(OH)_2$-H_2O slurry at room temperature in a round-bottom flask, and 160 ml of Zirflex decladding waste (0.395 M Zr) at 50°C in a dropping funnel. The Zirflex solution was added to the flask at a rate of about 30 mL/min. The final temperature was brought to 70°C by gentle heating, then the solution was cooled. Samples of the product slurry were transferred to graduated cylinders for settling tests, and to centrifuge cones. The centrifuged solids were analyzed for percent water.

Conditions used for the eight runs are shown in Table 1. Runs 1-6 differed in Mg:Zr mole ratio and in the "concentration" of the $Mg(OH)_2$-H_2O slurry. Runs 4, 7, and 8 differed only in the slurry "concentration". Results for all eight runs are shown in Table 2. It was surprizing that solid volumes as low as 9-11% were observed. In previous laboratory studies, volumes ranged from about 20% to 30%.

Figure 1 shows the volume percent settled solids and the supernatant liquid pH plotted against the Mg:Zr mole ratio for the first six runs. Since the volume of water used to slurry the $Mg(OH)_2$ was held constant for these runs, the slurry "concentration" varied. Therefore, runs 7 and 8 were done at the same Mg:Zr mole ratio as run 4, but at different slurry "concentrations". The effect on the volume percent settled solids was dramatic. Therefore, extreme caution must be exercised in interpreting the results from runs 1-6. Please keep in mind that this was a brief scouting study for an as-yet undefined task. More detailed and carefully planned studies will be needed to resolve some of the questions about this chemical system.

Rockwell International

Equations 1 and 2 represent possible routes for the neutralization reaction. Note that $(NH_4)_2ZrF_6$ and NH_4F are present in the decladding waste at about equal concentrations, so they can be treated on an equi-molar basis in the equations. Note, too, that the product $Zr(OH)_4$ could as well be written $ZrO(OH)_2$, or as the polymer:

```
  OH    OH    OH
  |     |     |
-Zr-O-Zr-O-Zr-O-
  |     |     |
  OH    OH    OH
```

without changing the Mg:Zr mole ratios in the equations. To balance equation 1, a mole ratio (Mg:Zr) of 3.5 is required. To balance equation 2, a ratio of 1.5 would be sufficient.

$$(NH_4)_2ZrF_6 + NH_4F + Mg(OH)_2 \rightarrow Zr(OH)_4 + MgF_2 + NH_3 + H_2O \qquad \text{(equation 1)}$$

$$(NH_4)_2ZrF_6 + NH_4F + Mg(OH)_2 \rightarrow MgZrF_6 + MgF_2 + NH_3 + H_2O \qquad \text{(equation 2)}$$

After each run, the supernatant solution was tested for unreacted Zr by adding NaOH. Only in run 1 did additional solids form. Since run 2 contained no Zr in the supernatant solution, equation 2 may be operating. At higher Mg:Zr ratios, equation 1 takes over. This conclusion is supported, at least by implication, by microscope studies. Solids from each run were examined under a polarizing microscope. In the first two runs, the solids were mainly small needles with moderate anisotropy. In the other runs, the solids were round, or "potato-shaped", and appeared to exhibit a bimodal size distribution in most cases. For the runs giving low volume percent solids, the bimodal distribution favored the larger particles. For runs 6-8, the smaller particles were more numerous. None of the three types of crystals (needles, large "potatoes", and small "potatoes") can be identified at the present level of study.

Even though positive identification is not possible as yet, some conclusions can be inferred. Since the Zr is completely precipitated in run 2, the needles are very likely some Mg-Zr double fluoride salt, possibly $MgZrF_6$.

Rockwell International

Run 3 solids contained no needles, but there was insufficient $Mg(OH)_2$ to drive equation 1 to completion. The implication is that $MgZrF_6$ is unstable in the presence of excess $Mg(OH)_2$, and forms intermediate Zr-OH-F compounds, perhaps like $Zr(OH)_2F_2$ or any of several polymers. (Incidentally, the total weight of solids from run 3 must be a mistake).

At any rate, one fact is assured by the microp studies - that the Mg:Zr ratio does have an effect on the type of solids produced. An important question remains: Can a slurry of $MgZrF_6$ solids be considered "neutralized" for tank farm purposes if the solids react with excess caustic?

Please call if you have any questions or answers.

Daniel Herting

D. L. Herting

DLH:gij

cc: J. N. Appel
J. S. Buckingham
M. T. Jansky
J. H. Lawler
D. A. Reynolds
L. H. Rodgers
D. M. Tulberg
[redacted]
File Code: WB

Table 1. Neutralization Conditions[a]

Run #	Weight $Mg(OH)_2$	Mg:Zr Mol Ratio	Volume H_2O[b]	Complete Precip.
1	3.73	1.0	35	no
2	7.46	2.0	35	yes
3	11.19	3.0	35	yes
4	14.92	4.0	35	yes
5	18.66	5.1	35	yes
6	22.39	6.1	35	yes
7	14.92	4.0	25	yes
8	14.92	4.0	45	yes

[a]All eight runs with 160 mL Zirflex waste.
[b]Volume of H_2O used in $Mg(OH)_2$-H_2O slurry.

Table 2. Results of Neutralization Experiments

Run #	Mg:Zr Ratio	Vol. % Settled Solids	Total wt. Dry Solids[a]	Supernate pH
1	1.0	24	10	7.2
2	2.0	28	18	8.7
3	3.0	11	8	8.5
4	4.0	11	24	9.5
5	5.1	9	21	9.8
6	6.1	24	35	9.4
7	4.0	17	26	9.6
8	4.0	31	26	9.3

[a]Theoretical total weight dry solids would be 23.8g for final products $Zr(OH)_4 + MgF_2$, 18.4g for final products $MgZrF_6 + MgF_2$.

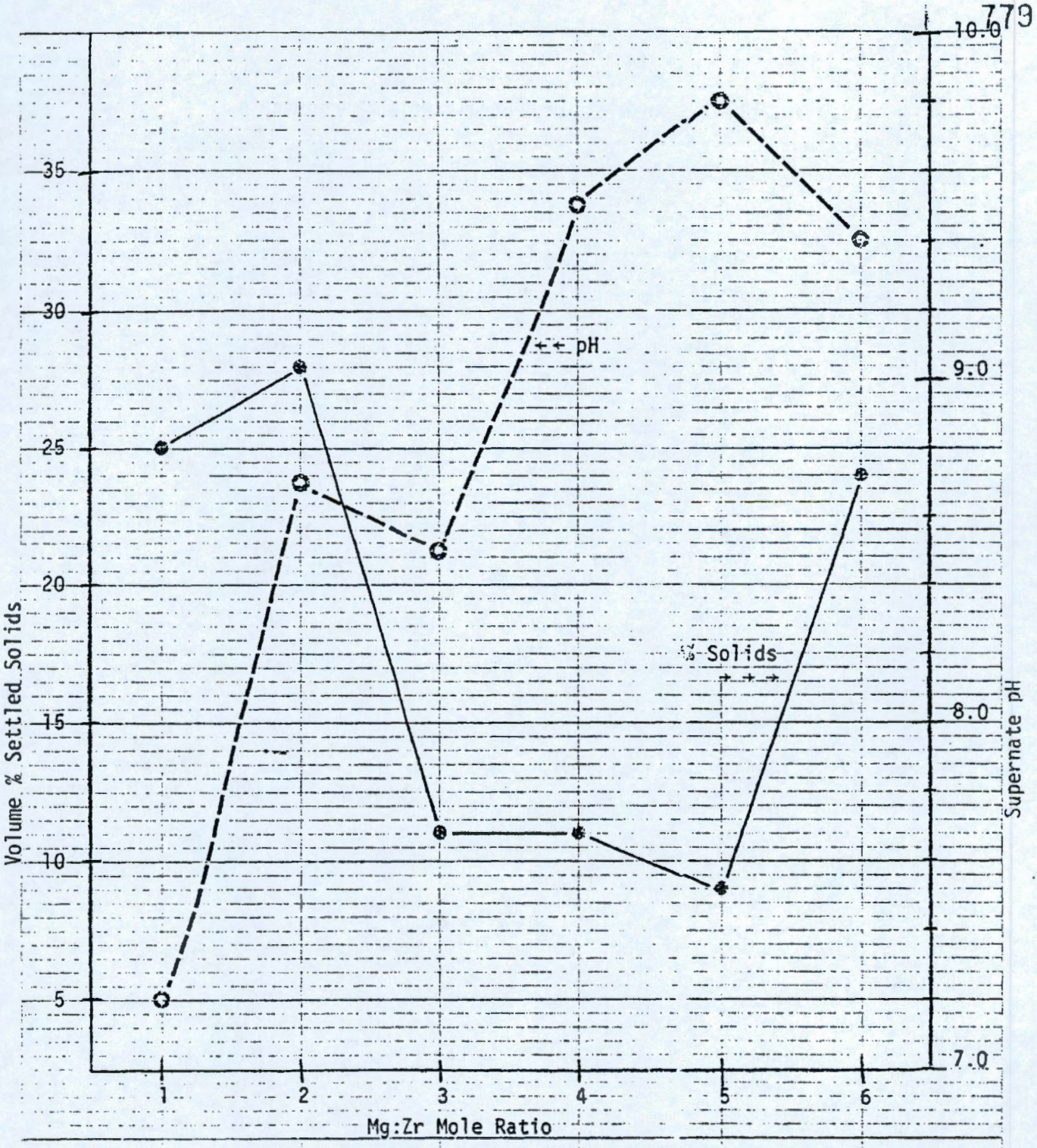


Figure 1. Volume percent settled solids (● — ●) and pH of supernatant solution (O — O) vs. Mg:Zr mole ratio for Zirflex decladding waste neutralized with $Mg(OH)_2$.

46 0700

780

Internal Letter

Rockwell International

Date: August 9, 1983

No: 65453-83-199

TO: (Name, Organization, Internal Address)

G. D. Campbell
Waste Management Process Group
2750E/A206/200E

FROM: (Name, Organization, Internal Address, Phone)

D. L. Herting/K. J. Patterson
Chemical Laboratory Unit
222S, MO-037/200 W
3-2532

Subject: Stability of Decladding Waste Solids in Excess Caustic

Reference: Letter, #65453-83-173, D.L. Herting and K.J. Patterson to G.D. Campbell "Magnesium Hydroxide Neutralization Scouting Study", June 15, 1983.

When decladding waste from the PUREX dissolver is neutralized with $Mg(OH)_2$, the pH of the resulting supernatant solution is about 9-10. Before transferring the neutralized waste from PUREX to Tank Farms, it will be mixed with metathesis waste, which is roughly 1.7 M in KOH and 0.83 M in KF. An experiment has been carried out in the laboratory to determine whether the added KOH from the metathesis waste would have any effect on the decladding waste solids. The results indicate that the KOH/KF addition causes a slight decrease in the actual volume of solids, and a large decrease in volume percent solids due to the increase in total volume. Analyses of supernatant solutions suggest that there is some interaction between the solids and the added KOH. Details of the experiment and results follow.

Experimental

In the first experiment, 15.3 g of $Mg(OH)_2$ and 22.0 g H_2O (total volume = 30 mL; 0.51 kg $Mg(OH)_2$ per liter slurry) were mixed in a round bottom flask, and 333 mL Zirflex decladding was added, slowly and with stirring. (Concentration of Zr in decladding waste = 0.395 M; Mg:Zr mole Ratio = 2:1) The neutralized slurry was divided into two portions, and each was transferred to a 250 mL graduated cylinder. After 24 hours, 45.5 mL KOH/KF solution (1.6 M KOH, 0.83 M KF) was added to the cylinder containing 205 mL of slurry.

In the second experiment, 38.5 g ($Mg(OH)_2$ and 57.0g H_2O (total volume = 76 mL; 0.51 kg $Mg(OH)_2$ per liter slurry) were mixed, and 333 mL decladding waste was added. (Mg:Zr mole ratio = 5:1). The neutralized slurry was divided into two portions, and each was transferred to a 250 mL graduated cylinder. After 24 hours, 45.5 g of KOH/KF solution was added to the cylinder which contained 185 mL of slurry.

Results

In the first experiment, the volume percent settled solids in the "control" was very high-88%. This reflects the combination of low Mg:Zr mole ratio with a poor choice of $Mg(OH)_2$ slurry concentration, i.e., the amount of H_2O added to the $Mg(OH)_2$ (see reference). The pH of the supernatant was 9.2. The other cylinder had 180 mL solids before adding KOH/KF.

Rockwell International

After adding the KOH/KF, the volume of solids dropped to 167 mL after one day, 160.5 mL after three days, and 144 mL after seven days. The pH of the supernatant was 9.8 - much less than the expected value. Simple dilution of the KOH from 45.5 mL to about 250 mL (the highest possible dilution factor) would give a pH of 13.5. The low pH together with the steadily decreasing volume of solids (while the control volume was stable) indicates that a reaction probably occurred between the solids and the added KOH/KF.

In the second experiment, the volume percent solids in the control was 44.5% after one day and 43.8% after seven days. Again, the volume of solids is much higher than the 9% obtained in the reference study at this mole ratio. In that study, the $Mg(OH)_2:H_2O$ weight ratio in the starting slurry was 0.53; in the present study, the ratio is 0.68 as requested. In our opinion, a laboratory study of the relationship between volume of solids and $Mg(OH)_2:H_2O$ ratio is crucial to any engineering planning on magnesium hydroxide neutralization.

In the other cylinder, the volume of solids after one day was 85.0 mL (45.9%). After adding the KOH/KF, the volume was 84.0 mL (37.2%) one day after mixing, and 81.5 mL (36.0%) after seven days. The pH of the supernatant was 12.5, compared to 10.6 for the control. Again, straight dilution of the KOH would lead to a hydroxide concentration of about 0.3 M, or a pH of 13.5. The much more modest shrinkage in solids volume than at the lower Mg:Zr mole ratio, together with the smaller suppression in the supernatant pH, points to a smaller amount of interaction between solids and KOH/KF at the 5:1 mole ratio.

Both supernatants from the second experiment were titrated with standard HCl. The control had a total caustic content of 0.69 M (almost entirely NH_4OH). The other supernatant (with added KOH/KF) had a total caustic content of 0.68 M (NH_4OH + KOH). Both supernatants were highly buffered at pH 9, due to the ammonia. The KOH/KF supernatant was also buffered at pH 3.5, due to the KF. It is not possible to determine from the titrations how much of the total hydroxide is from NH_4OH and from KOH individually. Both titrations are shown in Figure 1.

The data on volumes of solid for these experiments are summarized in Table 1. Please call if you have any questions.

Dave Herting

D. L. Herting
Senior Chemist

K. J. Patterson

K. J. Patterson
Parachemist

DLH:KJP:gij

cc: J. N. Appel, J. S. Buckingham, M. T. Jansky, J. H. Lawler, D. A. Reynolds, L. H. Rodgers, D. M. Tulberg, D. G. Wilkins, [redacted], File:WB Letterbook

TABLE 1. DATA SUMMARY FOR KOH/KF ADDITION EXPERIMENTS

Sample	Day	Solids Volume	Vol. %	Supernatant pH
1A Control	1*	104.0	88.1	
	7*	104.0	88.1	9.2
1B	1*	180.0	88.1	
+KOH/KF	1**	167.0	67.3	
	3**	160.5	64.6	
	7**	144.0	57.9	9.8
2A Control	1*	93.5	44.5	
	7*	92.0	43.8	10.6
2B	1*	85.0	45.9	
+KOH/KF	1**	84.0	37.2	
	7**	81.5	36.0	12.5

* Days after neutralization
**Days after adding KOH/KF

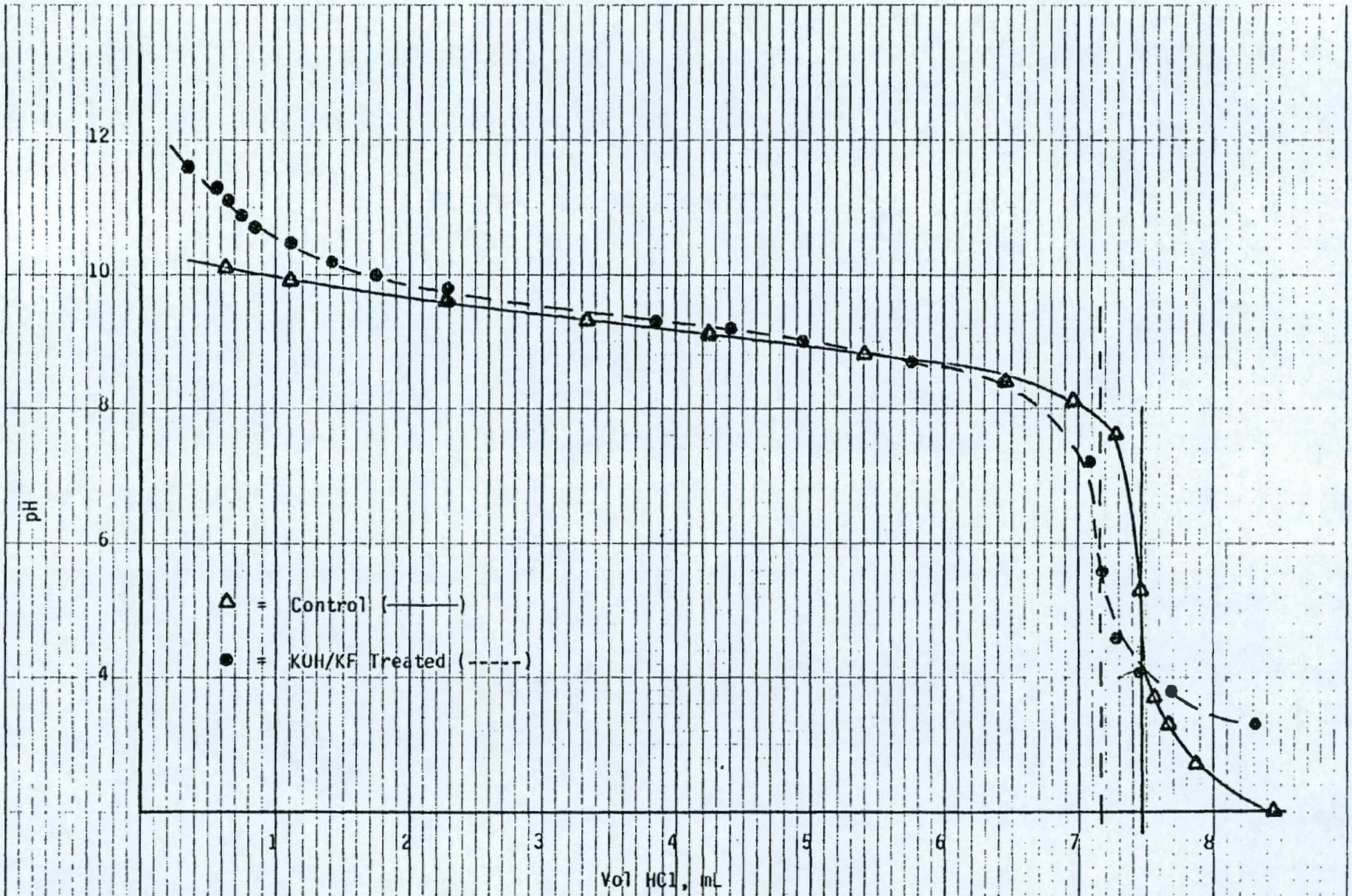


Figure 1. Titration of Supernatants from Experiment #2 with HCl

K+E 10 X 10 TO THE INCH • 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.
46 0700

784

Internal Letter

Rockwell International

Date September 12, 1983

No. 65453-83-236

TO: (Name, Organization, Internal Address)
D. A. Reynolds
Waste Management Process Tech. Unit
2750E/200 E

FROM: (Name, Organization, Internal Address, Phone)
D. L. Herting
Chemical Laboratory Unit
MO-037/200 W
3-2532

Subject: Thermal Stability of $NaNO_3$ and $NaNO_2$

During Phase Diagram studies on sodium aluminate solubility, the question arose as to whether the sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$) concentrations remained stable during the long (four weeks) equilibration periods. In a recently completed experiment, both $NaNO_3$ and $NaNO_2$ were shown to be thermally stable at 100°C in synthetic waste liquors for at least six weeks.. Six solutions stored at 100°C were analyzed at t = 0, 1, 2, 3, and 6 weeks. In no case was the change in concentration larger than the measurement uncertainty (see Table 1). Experimental details follow.

Six synthetic waste solutions were prepared with the approximate concentrations shown in Table 2. A direct (undiluted) sample was taken from each solution, and submitted to Analytical Laboratories (AL) for nitrate and nitrite analyses. The results of the analyses (Table 1) are very consistent from week to week, and also match the make-up concentrations (Table 2) very well. This is a tribute to the accuracy and consistency provided by AL during the Solubility Phase Diagram project.

The only problem encountered during this experiment was the slow (1-3 weeks) formation of a precipitate in solutions 4, 5, and 6. Those were the only solutions that contained complexants, and were also the three solutions having the highest NaOH concentrations. The compositions of all six solutions were designed so that all components would remain unsaturated, even at room temperature. Efforts are underway to determine the identity of the precipitate. Under the polarizing microscope, the solid appears as crystalline prisms, which don't match any of the familiar crystal patterns previously identified. Physical separation of the crystals is being attempted, and chemical tests will be performed to identify the compound.

D. L. Herting
Senior Chemist

DLH:gij

cc: J. S. Buckingham JSB
G. Burch
K. G. Carothers
W. W. Schulz

~~Process Aids~~
File: WB

Attachments

Table 1. Concentrations (in Molarity) of Solutions as a Function of Time

Nitrate

t =	0	1	2	3	6 (weeks)
1	2.90	3.06	2.96	3.04	2.86
2	2.96	2.98	2.88	2.89	2.82
3	2.48	2.56	2.62	2.58	2.59
4	2.32	2.32	2.47	2.41	2.40
5	2.36	2.27	2.34	2.30	2.30
6	2.40	2.33	2.34	2.36	2.30

Nitrite

t =	0	1	2	3	6 (weeks)
1	2.84	2.63	2.71	2.64	2.66
2	2.74	2.70	2.74	2.68	2.68
3	2.60	2.56	2.56	2.54	2.55
4	2.54	2.47	2.59	2.44	2.46
5	2.62	2.40	2.48	2.44	2.47
6	2.50	2.48	2.44	2.42	2.40

Table 2. Compositions of Synthetic Waste Solutions
(Concentrations in Molarity)

Component	Solution # 1	2	3	4	5	6
$NaAlO_2$	1.13	1.13	1.13	1.13	1.13	1.13
NaOH	2.91	2.91	3.69	4.08	4.08	4.08
$NaNO_3$	3.00	3.00	2.60	2.50	2.40	2.40
$NaNO_2$	2.80	2.80	2.70	2.60	2.60	2.60
Na_4 EDTA	-	-	-	0.04	0.04	0.04
Na_3 Citrate	-	-	-	0.07	0.07	0.07
TOC (g/L)	-	-	-	10	10	10

Internal Letter

Rockwell International

787

Date March 1, 1983

No. 65453-83-054

TO: (Name, Organization, Internal Address)
.D. A. Reynolds
.Process Design
.2750E/A110/200E

FROM: (Name, Organization, Internal Address, Phone)
. D. L. Herting
. Separations Process Development Unit
. 222-S/MO-037/200W
. 3-2532

Subject: .Return of the Missing Hydroxide

Refs: (1) Letter, #65453-82-168, D. L. Herting to D. A. Reynolds, "Search for the Missing Hydroxide", dated May 10, 1982

(2) Letter, #65453-82-282, D. L. Herting to D. A. Reynolds, "Sodium Aluminate Chemistry, Literature Review", dated August 12, 1982

Early in 1982, analysis of data from evaporator process runs led to the observation that sodium hydroxide (NaOH) seemed to be disappearing from concentrated waste liquors. The disappearance seemed to be associated with precipitation of sodium aluminate ($NaAlO_2 \cdot xH_2O$). Because this chemistry needed to be understood before attempting to do a solubility phase diagram for waste liquors, a laboratory study was undertaken. (See Reference 1). The results of that study show that NaOH does not disappear at all from solution when $NaAlO_2 \cdot xH_2O$ precipitates. Experimental details and a discussion of results follows.

One liter of solution at 50°C was prepared with the approximate composition: NaOH=4M, $NaAlO_2 \cdot 2H_2O$=2.5M, $NaNO_3$=2.5M, $NaNO_2$=2.5M. The solution was divided into four 250 mL portions (A, B, C and D). After a dilution was prepared for analysis, solution A was transferred to a 50°C shaking water bath. To solution B was added 20g (0.5 mole) NaOH, and the solution was then transferred to the water bath (after preparing a sample for analysis). Solutions C and D were treated in the same way as B, with 40g (1.0 mole) NaOH added to C and 60g (1.5 moles) to D.

All of the Al/OH analyses for this study were performed in our laboratory by Evan Jenson (a chemist on loan from Westinghouse). The instrument used for the analyses was a new thermotitrator loaned to us by Analytical Laboratories (AL). Analyses of solutions A-D are shown in Tables 1 and 2. The results are very interesting in a couple of ways. In Table 1, the very good agreement between calculated and found concentrations shows that the NaOH added to solutions B-D behaves in a perfectly predictable way. In particular, there is no evidence for formation of an $Al(OH)_6^{3-}$ ion. (See Reference 2). The agreement also lends a good deal of faith to the analytical method, and provides a solid foundation for interpreting later results.

When NaOH was added to solutions B-D, the volumes increased slightly, as expected. The volume increase is responsible for the steady decrease in aluminate molarity seen in Table 1 (reading down a column). It also accounts for the fact that the hydroxide molarity increases by less than 2M increments. The concentration of aluminate measured in molarity should be inde-

Rockwell International

pendent of volume changes, and Table 2 shows that this is true. In addition, the molality of NaOH should increase by a constant increment, as can also be seen in Table 2.

By adding NaOH to solutions B-D, it was hoped that these solutions would become supersaturated in sodium aluminate (Figure 1), and eventually precipitate $NaAlO_2 \cdot xH_2O$ crystals. Solution A was intended to be a "stable" solution, i.e., to be unsaturated in sodium aluminate. Each week, aliquots of the solutions were removed from the shaker bath, filtered, diluted, and analyzed. Results are shown in Table 3 and in Figure 2.

Solutions A and B remained clear (i.e., formed no significant solids) throughout the course of the experiment (4 weeks). Even though solution B was almost certainly supersaturated, all efforts to induce crystallization were unsuccessful. The analyses of both solutions show a general drift toward the origin (Figure 2), indicative of dilution. Since the flasks were immersed in water, and the chemical potential of water in the solutions was relatively low, that is not a surprising finding. However, the problem has been minimized for the current Phase Diagram study by replacing the PMP (polymethylpentene) flasks with FEP (fluorinated ethylene propylene) flasks.

Solutions C and D precipitated sodium aluminate, as can be seen clearly in Figure 2. As the aluminate precipitated, the volume of remaining solution decreased somewhat, resulting in slightly higher NaOH concentrations, which are also evident in Figure 2. (The effect of dilution in these solutions is to make the increase in hydroxide concentration less noticeable). Qualitatively, therefore, the effect of sodium aluminate precipitation on sodium hydroxide is perfectly straightforward. Had there been no gradual dilution of the solutions, calculations could be sufficiently quantitative to identify the hydration state of the aluminate precipitate, but that is not possible with the data at hand.

Please call if you have any questions or comments.

Dave L. Herting

D. L. Herting
Senior Chemist

DLH/naj

cc:

R. B. Bendixsen, J. S. Buckingham, K. G. Carothers, P. J. Certa, M. I. Fineman
M. T. Jansky, L. H. Rodgers, D. G. Wilkins, Letterbook, File: WB, [redacted]

Table 1. Concentrations (in Molarity) of Aluminate and Hydroxide in Freshly-Prepared Solutions at 50°C.

Sol'n #	Al		OH	
	Calc*	Found	Calc*	Found
A	*	2.85	*	4.25
B	2.76	2.77	6.10	5.95
C	2.66	2.64	7.83	7.83
D	2.58	2.59	9.44	9.36

* "Found" value for Solution A used to calculate values for B-D, using the total solution weights and SpG's to calculate final volumes of B-D; details of calculations available on request.

Table 2. Concentrations (in Molality#) of Aluminate and Hydroxide in Freshly-Prepared Solutions at 50°C.

Sol'n #	Al		OH	
	Calc*	Found	Calc*	Found
A	*	4.42	*	6.59
B	4.42	4.44	9.78	9.54
C	4.42	4.37	12.99	12.97
D	4.42	4.43	16.15	16.01

Molality = moles solute per kilogram solvent (H_2O).

* "Found" value for solution A used to calculate values for B-D; details of calculations available on request.

Table 3. Aluminate/Hydroxide Concentrations (in Molarity) as a Function of Time

Aluminate

Week	A	B	C	D
0	2.85	2.77	2.64	2.59
1	2.72	2.68	1.88	0.82
2	2.63	2.62	0.96	0.56
3	2.64	2.46	0.94	0.48*
4	2.64	2.50	1.04	0.60

Hydroxide

Week	A	B	C	D
0	4.25	5.95	7.83	9.36
1	4.16	5.82	7.82	10.22
2	4.21	5.98	8.32	10.41
3	3.96	5.50	7.82	8.76*
4	4.04	5.76	8.00	10.32

* Dilution error in preparing sample for analysis.

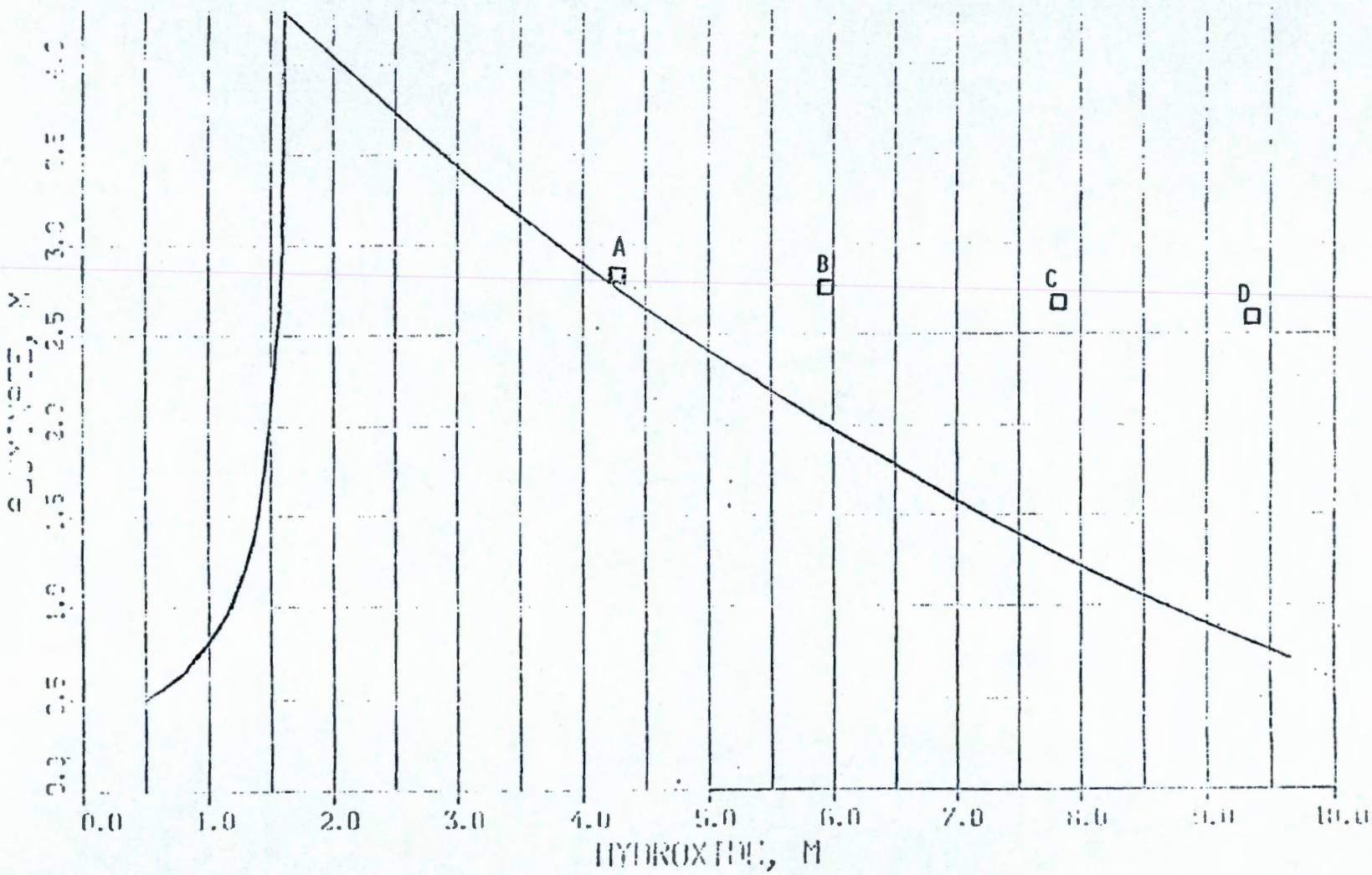


Figure 1. Concentrations (in Molarity) of Aluminate and Hydroxide in Freshly-Prepared Solutions at 50°C.

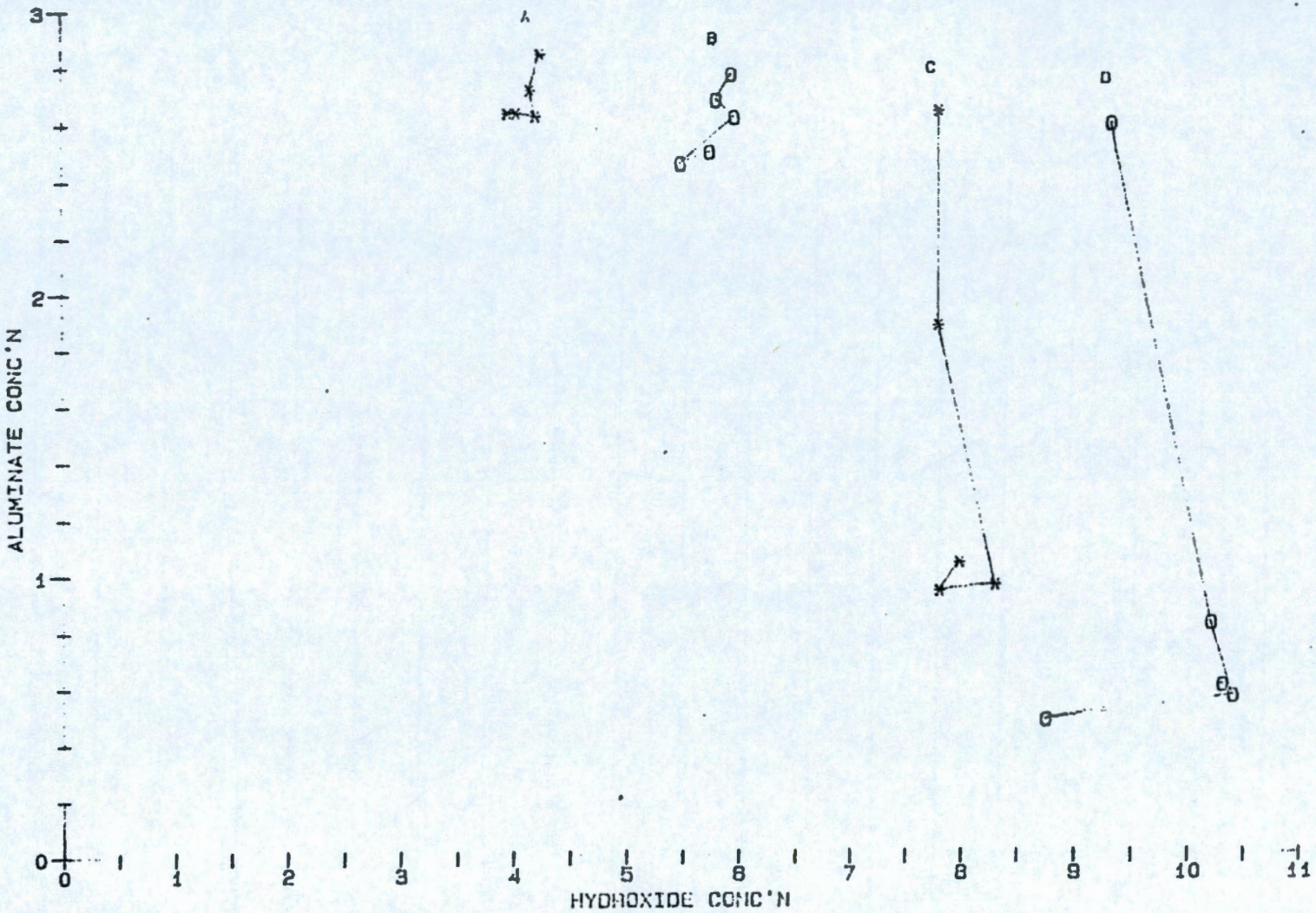


Figure 2. Concentrations (in Molarity) of Solutions A-D at t=0, 1, 2, 3, and 4 weeks.

TABLE I

COMPOSITION OF SYNTHETIC DSS SLURRY

Component	Concentration (Moles/Liter)
$NaAlO_2$	3.78
NaOH	7.70
$NaNO_3$	3.78
$NaNO_2$	4.86
$Fe(NO_3)_3 \cdot 9H_2O$	0.01

TABLE II

CHARACTERIZATION OF INITIAL DSS MIXTURES

Parameter	Value		
	Control	HEDTA*	Glycolic
Sp.G.[a]	1.73	1.76	1.73
Viscosity (cps)[a,b]	145	195	135
Al (M)	3.65	5.00 (3.75)	3.79
OH (M)	4.28	5.09 (4.00)	4.31
NO_2 (M)	4.69	5.29 (4.74)	4.78
NO_3 (M)	4.22	4.56 (3.59)	3.92
TOC (g/L)	**	18.85 (20.68)	1.84
HEDTA (M)	NA	UA	NA
% H_2O	23.7	24.1	23.8

[a]Measured at approximately 100°C.

[b]60 RPM, #2 spindle, Brookfield LVT spindle viscometer.

*See text for discussion of values in parentheses.

**Below detection limits.

NA-not applicable.

UA-unavailable.

TABLE III

COMPOSITION OF GASES IN CONTROL, VOLUME %

Date ---	9/19	9/20	9/21	9/26	9/30	10/03	10/04
H_2							
O_2	22	21	21	18	19.8	17.3	
N_2	80.0	80.0	71.5	68.0	73.0	65.5	
CO_2	--	--	--	--	--	--	
N_2O	--	--	--	--	--	--	
NO	--	--	--	--	--	--	
NH_3	--	--	--	0.2	--	2.10	2.45
NO_2	--	--		--		>0.85	0.52
TOTAL	102.2	101.0	92.5	86.2	92.8	85.0	

TABLE IV

COMPOSITION OF GASES IN HEDTA, VOLUME %

Date --	9/19	9/20	9/21	9/26	9/30	10/03	10/04
H_2	15.5	14	12.25	7.5	7.5	6.5	
O_2	7.0	7.0	5.75	4.25	5.0	4.5	
N_2	61.0	61.5	57.5	55.0	71.5	66.0	
CO_2	--	--	--	--	--	--	
N_2O	12.5	12	11.5	8	7.5	5	
NO	--	--	0.5	1	0.5	0.5	
NH_3	--	--	--	4.41	2.40	5.45	9.77
NO_2	0.08	0.19	0.03	0.06		0.88	0.44
TOTAL	96	94.7	87.5	80.2	94.4	88.8	10.21

TABLE V

COMPOSITION OF GASES IN GLYCOLIC, VOLUME %

Date --	9/19	9/20	9/21	9/26	9/30	10/03	10/04
H_2	32	23.75	15.5	3	~1	<<1	
O_2	7.5	9.75	9.25	14.0	17.3	18.75	
N_2	49.0	55	53.5	64.5	71.0	73.0	
CO_2	--	--	--	--	--	--	
N_2O	10.15	10.0	9.0	3.5	7	2.5	
NO	--	--	--	--	--	--	
NH_3	--	--	--	0.73	--	2.2	
NO_2	0.07	--			0.18	0.26	0.15
TOTAL	98.6	98.5	87	85.7	95	98.4	

TABLE VI

MASS SPECTROSCOPY DATA FOR DSS-GENERATED GASES

	Concentration (Volume %)			
Component	Air	Control	HEDTA	Glycolic
H_2	< 0.01	<0.01	2.77	0.01
O_2	21.2	21.2	14.8	21.2
N_2	77.8	77.6	79.6	77.8
CO_2	0.07	0.04	<0.1	0.09
N_2O	--	--	1.74	--
NO_x*	--	--	0.20	--
NH_3	--	--	--	∿0.02**
Ar	0.95	0.95	0.87	0.95
He	<0.01	<0.01	<0.01	<0.01
CH_4	<0.01	<0.01	<0.01	<0.01
CO	<0.10	<0.10	<0.1	<0.1

*NO_x as NO + NO_2.

**Confirmed using IR spectroscopy.

TABLE VII

ANALYSES OF FINAL DSS PRODUCT

Component	Concentration		
	Control	HEDTA*	Glycolic
Sp.G.	1.65	1.49	1.66
Al (M)	3.79	2.43 (3.47)	3.36
OH (M)	4.24	2.59 (3.53)	4.08
NO_2 (M)	4.51	3.07 (3.66)	4.31
NO_3 (M)	4.01	2.32 (3.16)	3.60
TOC (g/L)	**	13.40 (13.07)	2.16
HEDTA (M)	NA	(a)	NA

*See text for explanation of values in parentheses.
**Below detection limits.
NA-not applicable.
(a)-not available

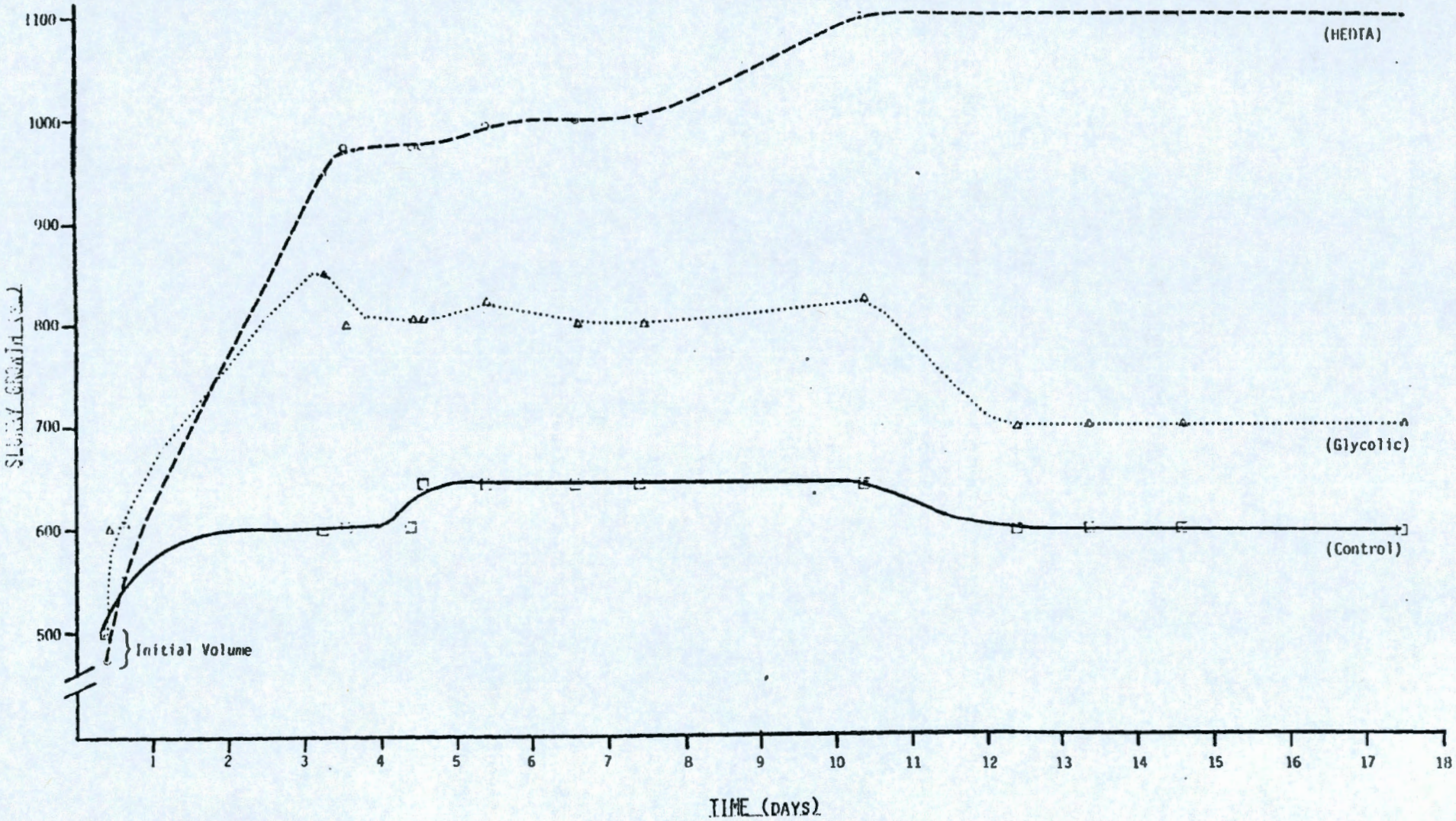


FIGURE 2. GROWTH vs. TIME AT 100°C

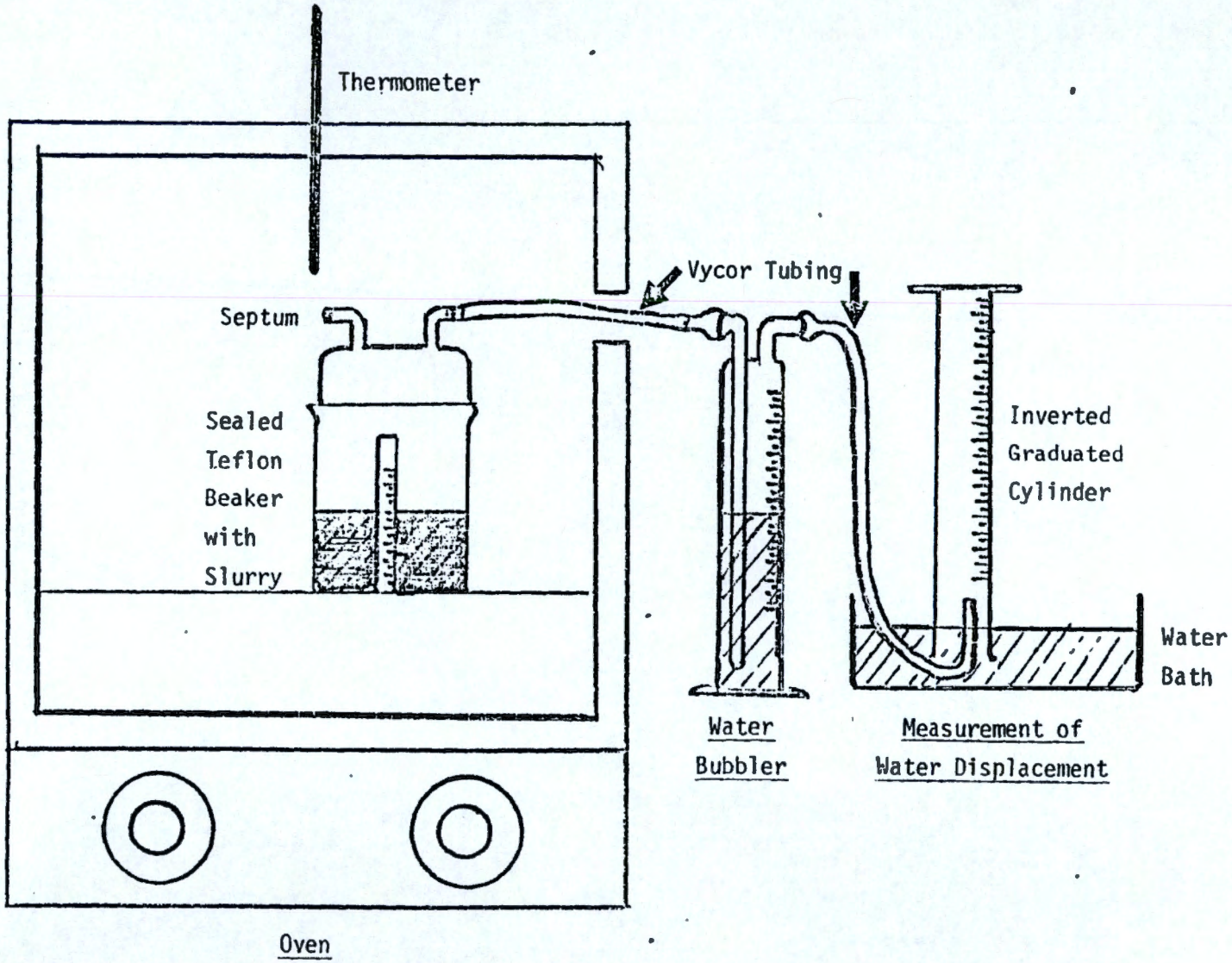


FIGURE APPARATUS

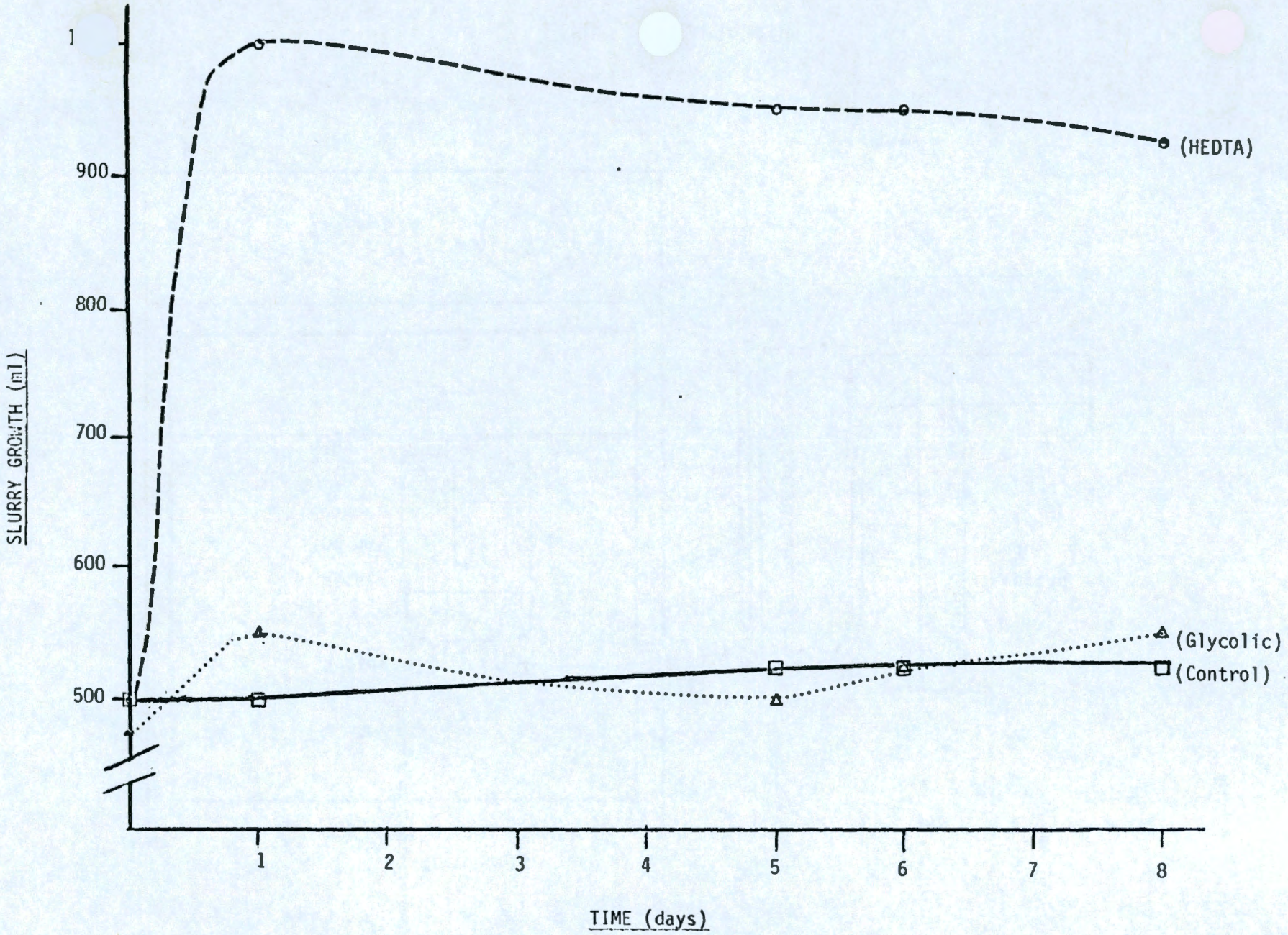


FIGURE 3. GROWTH vs. TIME UPON REHEATING TO 120°C

808

Internal Letter

Rockwell International

Date. November 7, 1983

No .65453-83-281

TO: (Name, Organization, Internal Address)
.R. B. Bendixsen
.Process Engineering
.2750E/A110/200E

FROM: (Name, Organization, Internal Address, Phone)
.M. T. Jansky
.Chemical Laboratory Unit
.222S/MO-037/200W
.3-1571

Subject: .Laboratory Study for Evaluating Water Soluble Oil Use

References

1. Letter, #65950-83-1544, R. B. Bendixsen to J. S. Buckingham, "Employee Suggestion #96215, Using Water Soluble Oil In Pits", October 11, 1983.

2. Letter, #65450-83-175, M. T. Jansky/H. R. Risenmay to D. M. Tulberg, "Laboratory Results From The Waste Mixing Study", June 24, 1983.

The letter of Reference 1 offers a suggestion for spraying water soluble oil in a contaminated pit to hold down loose contamination. Prior to the oil's use, it must be evaluated for possible deleterious effects when the oil is mixed with "typical" evaporator feeds and processed. The purpose of this letter is to briefly discuss a laboratory plan to investigate those effects.

Synthetic decladding supernatant liquor and salt well liquor will be the feeds examined. The synthetic decladding supernatant will be obtained from the Engineering laboratory, while the salt well liquor will be prepared in the Chemical laboratory. Specific compositions of the feeds are based on earlier work (Reference 2) and are shown in the attached Table. The feeds will be subjected to laboratory-scale batch boil downs and examined for: waste volume reduction (WVR) parameters [i.e., maximum WVR, P/T data, foaming and nucleation effects], crystallization phenomena, and product slurry growth. Duplicate boil downs will be made on the feeds containing 80 ppm water soluble oil, and the resulting data compared. A sample of the oil has already been received by the Chemical laboratory.

These experiments should be completed and data available by November 23, 1983. A letter report would follow. Please indicate your agreement of this laboratory plan by having you and your manager initial a copy of this letter and returning it to me. Work will commence upon receipt of the initialed letter.

M T Jansky

M. T. Jansky
Chemist, Senior

MTJ/rr

Attachment

cc: J.F. Albaugh, J.S. Buckingham JSB K.G. Carothers, D.L. Herting, D.W. Lindsey, H.R. Risenmay, L.H. Rodgers, R.D. Wojtasek, File Code WB, Process Aids

TABLE

COMPOSITION OF SYNTHETIC FEEDS FOR

WATER SOLUBLE OIL STUDY

Component	Concentration (M) Decladding Supernatant	Salt Well Liquor
Al	-	0.81
OH	0.80	1.70
NO_2	0.0165	1.08
NO_3	0.0202	1.57
CO_3	0.0154	0.117
PO_4	-	0.0297
SO_4	-	0.0147
K	0.388	-
Na	1.00	5.73

810

Internal Letter

Rockwell International

Date November 30, 1983

No 65453-83-300

TO: (Name, Organization, Internal Address)
R. B. Bendixsen
Process Engineering
2750E/200 E

FROM: (Name, Organization, Internal Address, Phone)
M. T. Jansky/H. R. Risenmay
Chemical Laboratory Unit
MO-037/222S/200 W
3-1572, 3-3612

Subject Laboratory Testing of Water Soluble Oil

References: 1. Letter, #65950-83-1544, R.B. Bendixsen to J.S. Buckingham, "Employee Suggestion #96215, Using Water Soluble Oil in Pits", October 11, 1983.

2. Letter, #65453-83-281, M.T. Jansky to R.B. Bendixsen, "Laboratory Study for Evaluating Water Soluble Oil Use", November 7, 1983

The letter of Reference 1 offers a suggestion for spraying water soluble oil in a contaminated pit to hold down loose contamination. Reference 2 discussed a brief laboratory study to evaluate the feasibility of using the oil. The Chemical Laboratory Unit (CLU) has completed the testing as discussed in Reference 2. The purpose of this letter is to summarize the results of the study, and to provide Process Engineering with the data.

Two feeds were prepared as discussed in Reference 2. A third feed was prepared by mixing salt well liquor (SWL) and decladding supernatant (DSP) in a 57:43 ratio. The particular ratio was chosen based on a probable mixing scenario. Batch boildowns were conducted on each feed. Separate aliquots of the feeds were spiked with water soluble oil and also concentrated. All feeds (with and without oil) were concentrated to a 58 percent waste volume reduction (WVR). Pressure versus temperature data were gathered during the boildowns, and are shown in Tables I - III. No significant changes occurred when the feeds were spiked with the oil and concentrated. Other relevant data were also gathered, and are shown in Table IV as product summation.

The data show that, up to approximately 80-90 parts per million (ppm), the water soluble oil does not affect the boildown of the synthetic wastes. The data pertaining to the products are not so clean cut. A short study such as this makes it difficult to determine causes for different product behavior, i.e., crystal habit, agglomeration, etc. Each feed appears to behave in its own unique fasion. The significantly lower volume percent solids in the SWL/oil mixture is beneficial, whereas DSP is just the opposite. No change was experienced with the SWL:DSP mixture.

The use of the oil for control of contamination is a viable suggestion. Probably no deliterious effects would occur if the oil/waste mixtures were to be processed in the evaporator. It would be interesting to examine

Rockwell International

surface effects due to the presence/lack of the oil, but additional time would be necessary for that study. The CLU would entertain any thoughts you have about persuing this suggestion. Please call if you have questions, comments, or interest in further work.

M. T. Jansky
Senior Chemist

H. R. Risenmay
Chemist

MTJ:HRR:gij

attachments

cc: J. F. Albaugh
J. S. Buckingham JSB
K. G. Carothers
M. I. Fineman
D. W. Lindsey
L. H. Rodgers
R. D. Wojtasek
[redacted]
File: WB

TABLE I

WVR VERSUS TEMPERATURE OF SWL ± OIL

WVR (%)	Pressure (torr)	Temperature °C w/o oil	Temperature °C w/oil*
0	40	40.0	40.0
	60	47.2	47.2
	80	52.8	52.8
5	60	47.8	47.4
10	40	41.0	40.8
	60	48.2	47.8
	80	53.8	53.6
15	60	48.8	48.4
20	40		41.8
	60		49.2
	80		54.8
25	60	49.6	49.8
30	40	43.2	43.4
	60	50.8	50.6
	80	56.6	56.4
35	60	51.6	51.6
40	40	45.6	45.6
	60	52.6	53.2
	80	58.4	58.8
45	60	54.2	54.8
50	40	49.2	49.6
	60	56.4	57.0
	80	62.2	62.8
55	60	59.2	59.6
58	40	43.8	53.6
	60**	61.4	61.6
	80	67.0	67.6

*91 ppm oil.
**Nucleation, sharply defined.

TABLE II

WVR VERSUS TEMPERATURE OF DSP ± OIL

WVR (%)	Pressure (torr)	Temperature °C w/o oil	Temperature °C w/oil*
0	40	36.2	36.2
	60	43.4	43.6
	80	48.8	49.2
5	60	43.6	43.6
10	40	36.4	--
	60	43.6	43.6
	80	49.2	--
15	60	43.6	43.6
20	40	36.2	36.2
	60**	43.6	43.6
	80	48.8	49.2
25	60	43.6	43.6
30	40		
	60	43.6	43.6
	80	--	--
35	60	43.6	43.8
40	40	36.6	36.4
	60	43.8	43.8
	80	49.2	49.4
45	60	43.8	43.8
50	40	36.8	37.2
	60	44.0	44.2
	80	49.6	49.8
55	60	44.2	44.4
58	40	37.2	37.4
	60	44.4	44.6
	80	49.8	50.0

*86 ppm oil.
**Nucleation, small amount of solids, cloudy.

TABLE III

WVR VERSUS TEMPERATURE OF MIXTURE ± OIL

(Mixture of 57:43/SWL:DSP)

		Temperature °C	
WVR (%)	Pressure (torr)	w/o oil	w/oil*
0	40	37.8	37.8
	60	45.4	45.2
	80	50.8	50.0
5	60	45.8	45.6
10	40	38.4	38.4
	60	46.0	45.8
	80	51.6	51.2
15	60	42.6	46.0
20	40	39.2	38.8
	60	46.4	46.2
	80	52.0	51.8
25	60	46.6	46.6
30	40	39.6	39.8
	60**	46.8	46.8
	80	52.4	52.4
35	60	47.0	47.6
40	40	40.4	40.8
	60	47.8	48.0
	80	53.2	53.6
45	60	48.6	48.8
50	40	42.2	42.6
	60	49.4	49.8
	80	55.2	55.4
55	60	50.6	50.8
58	40	44.4	44.6
	60	51.6	52.0
	80	57.2	57.8

*78 ppm oil.
**Nucleation.

TABLE IV

PRODUCT SUMMATION

	SWL		DSP		57:43 Mixture	
	without	with	without	with	without	with
Nucleation point (WVR) (60 torr)	58	58	20	20	30	30
Precipitate	mostly "feathery" aluminate some nitrate	aluminate cubes	NaF	NaF	NaF	NaF
Vol. % settled solids • immediately	46	6	7	13	10	10
• 9 days (80°C)	18[a]	NC*	NC	NC	NC[b]	NC[c]
• growth	0	0	0	0	0	0
SpG Feed	1.2564		1.0675		0.9157	
ppm Oil in Feed		91		86		78

*NC = no change.

[a]Crystal habit appears to be changing. Feathers converting to fuzz. Nitrate crust precipitated.

[b]Slight precipitation

[c]Solids relatively easy to suspend, compared to all other test product mixtures.

816

Internal Letter

Rockwell International

Date November 29, 1983

No. 65950-83-1662

TO: (Name, Organization, Internal Address)
W. A. McCullough
Facilities & Industrial
Engineering
2750E/D171/200E

FROM: (Name, Organization, Internal Address, Phone)
R. B. Bendixsen
Tank Farm & Evaporator
Process Control
2750E/A110/200E
3-1018

Subject:

Employee Suggestion 96215 - Water Soluble Oil

Reference: a) Letter, October 11, 1983, R. B. Bendixsen to J. S. Buckingham, "Employee Suggestion 96215, Using Water Soluble Oil in Pits"

b) Letter, November 7, 1983, M. T. Jansky to R. B. Bendixsen, "Laboratory Study for Evaluating Water Soluble Oil Use"

c) Letter, November 1983, M. T. Jansky to R. B. Bendixsen, "Laboratory Testing of Water Soluble Oil"

Employee Suggestion 96215 recommends spraying an open pump/valve pit during a windy day with a water soluble oil to hold down loose contamination and prevent airborne contamination. The oil is a Union Oil 76, soluble cutting oil No. 10, Rockwell Stock No. 12-8620-040. The effects of small quantities of the oil on waste solutions in tank farms was requested (reference a), a test plan was written (reference b), and the test results (reference c) indicate no measurable effect on crystallization waste volume reduction or slurry growth. The laboratory testing used simulated evaporator feeds of both decladding waste and saltwell liquor at an 80-ppm oil concentration. The 80-ppm concentration is higher than the maximum oil concentration expected and represents 80 gallons of soluble oil distributed in one million gallons of waste. Therefore, Process Engineering gives approval for use of the soluble oil for spraying in tank farm pump/valve pits.

R. B. Bendixsen, Engineer
Tank Farm & Evaporator
Process Control

RBB:bjb

cc: J. F. Albaugh
[redacted]
K. G. Carothers
M. T. Jansky
D. W. Lindsey
M. C. Teats
D. G. Wilkins

Interoffice Letter

Rockwell International

817

Date: May 31, 1983

No. 65453-83-155

TO: (Name, Organization, Internal Address)
J. J. Goldin
Program Engineering
2750E/A228/200 East

FROM: (Name, Organization, Internal Address, Phone)
D. R. Bratzel
Separations Process Development Unit
222-S/MO-037/200 West
3-1228

Subject: WG Monthly Report, May 1983

Radiotracer laboratory experiments to evaluate the effects of the complexant citrate on neutralization of synthetic B-Plant high-level waste have been completed. Results from these studies will assist in providing information on neutralization problems due to the presence of complexants, chemical composition and physical data of sludge feed, and sludge wash requirements for the B-Plant Waste Immobilization Annex (BWIA).

Neutralization of high-level B-Plant waste containing citrate as a buffering-complexing agent requires the addition of caustic to >pH13 to precipitate solids. Addition of hydrogen peroxide under reflux digestion conditions to destroy the complexant citrate results in acid destruction and solids precipitation at approximately pH8.

Radiotracer experiments to evaluate the effects of the complexants citrate, EDTA, and HEDTA on the neutralization of synthetic high-level B-Plant waste are shown in Table 1. Decontamination factor (DF) results for the neutralization of buffered ZAW containing 10% molar excess citrate are shown in Table 2. Results indicate citrate plays a more significant role in complexing americium (the primary actinide in aged waste) than plutonium or strontium. Preliminary results from citrate destruction by the addition of hydrogen peroxide suggest americium and plutonium are complexed in the supernatant to a greater extent after citrate destruction than when no citrate destruction is performed. Additional laboratory tests are needed to verify results, however. Chemical factors which may increase actinide complexation in citrate destruction tests include:

Breakdown of primary complexants by peroxide addition may form more powerful secondary organic complexing agents.

Carbonate (from the breakdown of citrate by peroxide) has been shown to complex plutonium at high pH's.

Upcoming work will include radiotracer experiments on synthetic high-level B-Plant waste complexed with citrate (20% molar excess), EDTA, and HEDTA.

D. R. Bratzel

D. R. Bratzel
Chemist

DRB/naj

cc: (W/Attachments)

J. S. Buckingham, K. M. Hodgson, M. J. Kupfer, K. J. Patterson, W. W. Schulz, A. H. Smith, R. J. Thompson, D. L. Uhl, W. G. Wilkins, File: W[redacted] Letterbook

Table 1

Laboratory Studies in Support of BWIA

Sludge Wash Studies

Chemical Waste Characterization and Physical Data for Battelle

Neutralization Studies:

Citrate

Citrate/Complexant Destruction

$^{239}Pu/^{85}Sr/^{241}Am$/Citrate

$^{239}Pu/^{85}Sr/^{241}Am$/Citrate/Complexant Destruction

Citrate-EDTA-HEDTA

Citrate-EDTA-HEDTA/Complexant Destruction

$^{239}Pu/^{85}Sr/^{241}Am$/Citrate-EDTA-HEDTA

$^{239}Pu/^{85}Sr/^{241}Am$/Citrate-EDTA-HEDTA/Complexant Destruction

$^{239}Pu/^{85}Sr/^{241}Am$/No Complexant (Base Case Comparison)

Table 2

NEUTRALIZATION OF CITRATE COMPLEXED HIGH-LEVEL B-PLANT WASTE

Radionuclide	Buffered ZAW (pH4.5) Spike Concentration[1]	Decontamination Factor (DF)
	Complexant	
^{239}Pu	1.48×10^7 dpm/L	160
^{85}Sr	2060 uCi/L	102
^{241}Am	384 uCi/L	37
	Complexant Destruction	
^{239}Pu	1.47×10^7 dpm/L	50
^{85}Sr	2050 uCi/L	114
^{241}Am	1320 uCi/L	10

[1]Analytically determined by counting methods.

820

Internal Letter

Rockwell International

Date June 27, 1983

No. 65453-83-176

TO: (Name, Organization, Internal Address)
J. J. Goldin
Program Engineering
2750E/A228/200 East

FROM: (Name, Organization, Internal Address, Phone)
D. R. Bratzel
Chemical Laboratory
222-S/MO-037/200 West
3-1228

Subject: WG Monthly Report, June 1983

Ref: (1) Letter, #65470-80-064, dated May 30, 1980, W. I. Winters to M. M. Beary, "Effects of Oxygen and H_2O_2 on Oxidation of NO_2^- and EDTA"

Discussion of Laboratory Results

Radiotracer laboratory experiments to examine the feasibility of peroxide destruction of the complexants citrate (10% excess), and citrate (20% molar excess)-EDTA (0.33M)-HEDTA (0.66M) in B-Plant waste are continuing. Results from these studies will assist in providing information on neutralization problems due to the presence of complexants, chemical composition and physical data of sludge feed, and sludge wash requirements for the B-Plant Waste Immobilization Annex (BWIA).

Radiotracer experiments to evaluate the effects of the complexants citrate (10% and 20% molar excess), EDTA (0.33M), and HEDTA (0.66M) are shown in Table 1. Decontamination factor results for the neutralization of buffered ZAW containing citrate (10% molar excess) and citrate (20% molar excess)-EDTA (0.33M)-HEDTA (0.66M) are shown in Tables 2 and 3, respectively. In addition, decontamination factors for neutralized ZAW containing no complexants are included in each table for comparison purposes. The DF results in Tables 2 and 3 indicate that EDTA and HEDTA are much stronger complexants then citrate.

Decontamination factor results for peroxide destruction studies on synthetic ZAW complexed with 10% molar excess citrate and sodium carbonate to pH 4.5 suggest americium and plutonium are complexed in the supernatant to a greater extent after citrate destruction than when no peroxide destruction is performed (Table 2). Averaged DF's from two experimental runs decreased from 29.5 to 13.5 for ^{241}Am and from 375 to 52 for ^{239}Pu after addition of peroxide. Peroxide destruction conditions included a 15:1 molar ratio of peroxide to citrate under boiling reflux conditions. Since peroxide also consumes acid under these conditions, the pH of the waste increased from pH 4.5 to pH 9 during peroxide addition resulting in solids precipitation at approximately pH 8. No attempt was made to control the pH or free acid concentration $[H^+]$ during peroxide addition in the citrate complexed tests.

Peroxide addition to ZAW complexed with citrate (20% molar excess)-EDTA (0.33M)-HEDTA (0.66M) was performed under controlled conditions at pH 2 to eliminate certain potential factors which may influence increased actinide solubility in peroxide destruction tests. Results (Table 3) show decontamination factors did not appreciably change when peroxide was added at a controlled pH of 2 (pH was controlled by addition of 6M HNO_3). In addition, neutralization to >pH 13 was required to precipitate solids.

Rockwell International

Various factors which can potentially influence the effectiveness of reducing actinide solubility by peroxide destruction of complexants, have been proposed. These proposed factors include:

- Effect of temperature - If added to boiling waste, it is possible that the H_2O_2 is destroyed instantaneously before kinetics favor organic complexant destruction
- pH at which peroxide destruction is performed. Earlier work by W. I. Winters (Reference 1) indicated that peroxide destruction of organics is most effective at low pH; e.g., pH 1-2
- Degradation of primary organic to form a more powerful secondary organic complexant
- Formation of inorganic species which promote actinide complexation, e. g., carbonate, peroxide
- Peroxide to complexant molar ratio of addition

Future Work

Tests to determine the effects of the various factors described above, will be performed. Of primary concern in peroxide destruction tests at high temperatures is the possibility of instantaneous peroxide destruction upon addition to boiling ZAW before kinetics favor organic complexant destruction. Peroxide destruction experiments on citrate complexed ZAW will be conducted at low temperatures to evaluate this possibility.

In order to fully understand and identify the factor(s) affecting increased solubility of the actinides americium and plutonium when peroxide is added to destroy complexants, a fraction factorial study has been designed by the Statistics Team (PDG). The factorial study consists of (18) experimental runs. Experimental parameters to be examined include citrate, carbonate, peroxide ratio, and the pH at which destruction is performed.

Since each complexant or combination of complexants present in high-level B-Plant waste will behave differently, tests will be started concurrent with the factorial study to examine neutralization effects and peroxide destruction of additional complexants. In addition to citrate, EDTA, and HEDTA, other complexants identified include hydroxyacetic acid and gluconic acid.

822

Rockwell International

J. J. Goldin
Page 3
June 27, 1983

D. R. Bratzel
Chemist

DRB/naj

Attachments

cc:

J. S. Buckingham JSB
K. M. Hodgson
M. J. Kupfer
K. J. Patterson
W. W. Schulz
A. H. Smith
R. J. Thompson
D. L. Uhl
R. A. Watrous
D. G. Wilkins
[redacted]
File: WG
Letterbook

Table 1

Laboratory Studies in Support of BWIA

Sludge Wash Studies

Chemical Waste Characterization and Physical Data for Battelle

Neutralization Studies:

Citrate

Citrate/Complexant Destruction

$^{239}Pu/^{85}Sr/^{241}Am$/Citrate

$^{239}Pu/^{85}Sr/^{241}Am$/Citrate/Complexant Destruction

Citrate-EDTA-HEDTA

Citrate-EDTA-HEDTA/Complexant Destruction (Controlled pH)

$^{239}Pu/^{241}Am$/Citrate-EDTA-HEDTA

$^{239}Pu/^{241}Am$/Citrate-EDTA-HEDTA/Complexant Destruction(Cont. pH)

$^{239}Pu/^{241}Am$/No Complexant (Base Case Comparison)

Table 2

NEUTRALIZATION OF CITRATE COMPLEXED HIGH-LEVEL B-PLANT WASTE

Radionuclide	Buffered ZAW (pH4.5) Spike Concentration[1]	Decontamination Factor[2]
	No Citrate	
^{241}Am	430 µCi/L	>2100
^{239}Pu	1.48×10^{10} dpm/L	>8000
	Citrate (10% Molar Excess)	
^{241}Am	384 µCi/L	37
	401 µCi/L	22
^{239}Pu	1.48×10^{7} dpm/L	160
	1.54×10^{7} dpm/L	597
^{85}Sr	2960 µCi/L	102
	Citrate Destruction[3]	
^{241}Am	1320 µCi/L	10
	475 µCi/L	17
^{239}Pu	1.47×10^{7} dpm/L	50
	1.55×10^{7} dpm/L	54
^{85}Sr	2050 µCi/L	114

[1]Analytically determined by counting methods

[2]Determined by the activity in the buffered waste at pH 4.5 divided by the activity in the neutralized supernatant at pH 13

[3]Peroxide addition started at pH 4.5 and ended at pH 9

Table 3

NEUTRALIZATION OF CITRATE-EDTA-HEDTA COMPLEXED HIGH-LEVEL B-PLANT WASTE

Radionuclide	Buffered ZAW Spike Concentration[1]	Decontamination Factor[2]
	No Citrate-EDTA-HEDTA	
^{241}Am	430 µCi/L	>2100
^{239}Pu	1.48×10^{10} dpm/L	>8000
	Citrate (20% Molar Excess), EDTA (0.33M), HEDTA (0.66M)	
^{241}Am	484 µCi/L	1.5
^{239}Pu	1.83×10^{7} dpm/L	7.9
	Peroxide Destruction of Citrate-EDTA-HEDTA[3]	
^{241}Am	293 µCi/L	4.0
^{239}Pu	1.52×10^{7} dpm/L	4.4

[1]Analytically determined by counting methods

[2]Determined by the activity in the buffered acid waste divided by the activity in the neutralized supernatant at pH 13

[3]Peroxide addition performed at pH 2

826

Internal Letter

Rockwell International

Date August 1, 1983

No. 65453-83-193

TO: Name Organization (Interna Address)
K. M. Hodgson
Advanced Concepts Group
2704E/16/200 E

FROM: Name Organization (Interna Address Phone
D. R. Bratzel
Chemical Lab. Process Dev. Unit
MO-037/200 W
3-1228

Subject WG Monthly Report, July 1983

References: 1) Letter, #65453-83-176, D. R. Bratzel to J. J. Goldin, "WG Monthly Report, June 1983" June 27, 1983.

2) Letter, #65450-83-133, M. J. Kupfer to J. J. Goldin, "WG Monthly Report, May 1983" May 31, 1983.

3) Schulz, W. W., "Decontamination of Hanford Plutonium Reclamation Facility Salt Waste Solution", RHO-SA-23, Rockwell Hanford Operations, June 1978.

4) Schulz, W. W., "Removal of Radionuclides from Hanford Defense Waste Solutions", RHO-SA-51, Rockwell Hanford Operations, January 1980.

5) Strachan, D. M. and W. W. Schulz, "Removal of Radionuclides from Water-Soluble Fraction of Hanford Nuclear Defense Waste", RHO-SA-145, Rockwell Hanford Operations, February 1980.

Laboratory studies are in progress to evaluate destruction of the complexant citrate in synthetic B-Plant high-level waste by addition of peroxide. This work is in support of the B-Plant Immobilization Pilot Plant (BIPP) in which transuranic (TRU) sludge waste will be vitrified for subsequent repository storage and non-TRU/low-level supernatant will be immobilized for shallow land disposal.

Citrate Destruction

A combined complexant destruction-precipitation-ion exchange process for removing americium from synthetic high-level B-Plant acid waste complexed with citrate (0.48 M) has been demonstrated. A normalized decontamination factor (DF*) of >3280 was determined for ^{241}Am. A DF of 3600 for ^{241}Am must be obtained in complexant destruction studies to reach non-TRU supernatant limits (<100 nCi/g total alpha activity). This process involves:

- Multiple additions of 30% hydrogen peroxide under controlled pH conditions followed by variable temperature digestion periods to partially destroy the complexant citrate.

*Decontamination Factor, DF = (Radionuclide Activity in the Acid Waste Feed)/(Radionuclide Activity in the Neutralized Supernatant)

Rockwell International

- Addition of NaOH to a one mole caustic excess to precipitate metal hyroxides (predominately iron) which act as a scavenging agent for americium.

- Addition of the inorganic ion exchange material sodium titanate [$Na(Ti_2O_5H)$] in powdered form (40 to 140 mesh) for the sorption of complexed americium to make a non-transuranic (<100 nCi/g) supernatant.

- The neutralized waste can then be centrifuged-filtered to separate the TRU sludge. After washing the sludge to remove sulfate, the sludge can be vitrified for subsequent repository storage. The low-level non-TRU supernatant waste can be immobilized for shallow land disposal.

Preliminary Complexant Destruction Studies

Preliminary scouting studies to evaluate the effects of the complexants citrate (10% and 20% molar excess), EDTA (0.33 M), and HEDTA (0.66 M) were reported in Reference 1. Previously reported scouting studies are shown in Table 1. Decontamination factor results for the neutralization of buffered ZAW containing citrate (10% molar excess) and citrate (20% molar excess)-EDTA(0.33 M)-HEDTA (0.66 M) are reported in Tables 2 and 3, respectively. For comparison purposes, decontamination factors for neutralized ZAW containing no complexants are included.

Decontamination factors and total organic carbon (TOC) values are updated in Tables 2 and 3 as normalized values to correct for dilution effects by neutralization and peroxide addition. Decontamination factors are normalized to the original ZAW volume while TOC values are normalized to the buffered ZAW volume (includes sodium citrate and sodium carbonate additions to buffer to pH 4.5). Normalized values provide a means of direct comparison between experimental runs, simulate process conditions more closely since added caustic and peroxide volume under actual process conditions can be reduced by concentration, and represent the lowest attainable DF or "worst case" conditions.

Scouting study results from citrate destruction by peroxide addition indicate americium and plutonium are complexed in the supernatant to a greater extent after peroxide addition than when no peroxide is added to destroy citrate. Further laboratory work indicates residual organic carbon is most likely responsible for actinide complexation after peroxide addition and neutralization. Neither oxalate (a suspected degradation product of citrate) or peroxide was found to cause actinide complexation after peroxide addition and neutralization.

Rockwell International

Total Organic Carbon Results

Preliminary TOC results indicate incomplete citrate destruction occurs after multiple peroxide additions and variable digestion period. With an initial TOC concentration [TOC] of 35 grams carbon per liter (gC/L) in buffered ZAW, the [TOC] was decreased to 26 gC/L after batch addition of 30% hydrogen peroxide (15 moles peroxide per mole citrate) and a 24 hour digestion period at 20°C. After a 4 hour digestion period under boiling-reflux conditions (105°C), a second addition was performed by continuously metering in peroxide (20 moles peroxide per mole citrate) over a two hour period and refluxing (105°C) for four hours. The final normalized supernatant [TOC] was 10 gC/L. After neutralization to one mole excess caustic, americium was still complexed in the supernatant rather than scavenged by iron hyroxide in the sludge.

Sodium Titanate Addition

After multiple additions of peroxide and precipitation of metal hydroxides from synthetic ZAW, the majority of americium is still complexed in the supernatant. Upon neutralization by the addition of NaOH, the scavenging effects of iron hyroxide in the presence of residual organic carbon yields a DF of <30 which is considerably lower than the required DF (>3600) to meet non-TRU (<100 nCi/g) supernatant limits.

To remove complexed americium from the neutralized waste, the inorganic ion exchanger sodium titanate [$Na(Ti_2O_5H)$] was added in powdered form (40-140 mesh). Sodium titanate has exhibited superior properties for the sorption of actinides (americium and plutonium), fission product rare earths, ^{90}Ar, and other $\geq$ +2 multivalent cationic radionuclides from Hanford waste types containing no organic complexants (References 3-5). Addition of sodium titanate to neutralized waste (after peroxide destruction) for the sorption of americium from complexed supernatant has been demonstrated in the laboratory to meet non-TRU supernatant limits. A normalized DF of >3280 was achieved after a 72 hour contact period.

Since sorption of americium is an ion exchange process, the DF is dependent on the contact time. Americium distribution ratios (K_d*) were calculated for a single experimental run and are reported in Table 4.

$$*Am\ K_d = \frac{\text{Waste Volume } (Am_I - Am_F)}{\text{Wt. Titanate Sorbent(G)}.Am_F}$$

Am_I and Am_F are the initial and final equilibrium ^{241}Am concentrations in the supernatant.

Rockwell International

Distribution ratios for complexed waste (>8090) are considerably lower and require a longer contact time (72 hours) than K_d's for other Hanford wastes (10^5 to 10^8) containing no organic complexants (Reference 3). This difference most likely reflects the complexant ability of the residual organic carbon.

Although passage of neutralized supernatant through column beds of sodium titanate would probably be more efficient for actinide removal, it is preferable to carry out actinide sorption by direct addition of sodium titanate powder to minimize operation steps. In addition, disposal of the spent sodium titanate in the column is avoided.

Oxalate Destruction

It is suspected that oxalate may be a degradation product of EDTA, HEDTA, and citrate. Laboratory results show that americium can be precipitated-scavenged from synthetic high-level B-Plant acid waste complexed with oxalate (0.6 M) after peroxide destruction. After continuous addition of 30% hydrogen peroxide to boiling ZAW and a four hour reflux period, NaOH was added to a one mole caustic excess to precipitate the scavenging agent iron hydroxide. A normalized DF of >9050 was determined for ^{241}Am after neutralization. No addition of sodium titanate was needed as required in citrate destruction studies.

Future Work

For the upcoming month, laboratory studies will focus on decreasing TOC concentrations by peroxide destruction to meet TOC sludge requirements. Studies are currently in progress to optimize the citrate destruction temperature (20°, 50°, 75°, and 105°C). In addition, catalyst-oxidizers (manganous ion and permanganate) will be evaluated. Lab studies will also be conducted on the addition of precipitation-scavenger agents (ferric and ferrous ion).

Rockwell International

Overall, a significant amount of additional laboratory work is required to study and optimize sodium titanate sorption, complexation and sorption of other nuclides (plutonium and strontium), alternative actinide scavenging technology, and destruction of additional complexants (EDTA, HEDTA, oxalate, hydroyacetate, and gluconate).

D. R. Bratzel

D. R. Bratzel
Chemist

DRB:gij

attachments

cc: D. L. Burt
J. S. Buckingham
W. R. Dworzak
J. J. Goldin
J. O. Honeyman
M. J. Kupfer
K. J. Patterson
W. W. Schulz
A. H. Smith
C. R. Stroup
R. J. Thompson
D. L. Uhl
R. A. Watrous
D. G. Wilkins
Process Aids
File: WG
Letterbook

Table 1

Laboratory Scouting Studies in Support of BIPP

Sludge Wash Studies

Chemical Waste Characterization and Physical Data for Battelle

Neutralization Studies:

Citrate

Citrate/Complexant Destruction

$^{239}Pu/^{85}Sr/^{241}Am$/Citrate

$^{239}Pu/^{85}Sr/^{241}Am$/Citrate/Complexant Destruction

Citrate-EDTA-HEDTA

Citrate-EDTA-HEDTA/Complexant Destruction (Controlled pH)

$^{239}Pu/^{241}Am$/Citrate-EDTA-HEDTA

$^{239}Pu/^{241}Am$/Citrate-EDTA-HEDTA/Complexant Destruction(Cont. pH)

$^{239}Pu/^{241}Am$/No Complexant (Base Case Comparison)

Table 2

NEUTRALIZATION OF CITRATE COMPLEXED HIGH-LEVEL B-PLANT WASTE

Radionuclide	Normalized DF
No Citrate	
^{241}Am	>1630 >16,300
^{239}Pu	11,000
Citrate (10% Molar Excess)	
^{241}Am	30.7 20.0
^{239}Pu	264 314
^{85}Sr	93.0
Citrate Destruction[1]	
^{241}Am	5.8 9.6
^{239}Pu	28.9 32.1
^{85}Sr	65.2
Citrate Destruction (Controlled pH[2])	
^{241}Am	8.9
Peroxide Addition (No Citrate)	
^{241}Am	>4680
Citrate Destruction (Multiple Peroxide Additon) + Titanate	
^{241}Am	>3280

[1]Peroxide addition started at pH 4.5 and ended at pH 9

[2]Peroxide addition controlled at pH2 by simultaneous addition of HNO_3

Table 3

NEUTRALIZATION OF CITRATE-EDTA-HEDTA COMPLEXED HIGH-LEVEL B-PLANT WASTE

Radionuclide	Normalized DF
No Citrate-EDTA-HEDTA	
^{241}Am	>1630
	>16,300
^{239}Pu	11,000
Citrate (20% Molar Excess), EDTA (0.33M), HEDTA (0.66M)	
^{241}Am	1.2
^{239}Pu	7.2
Peroxide Destruction of Citrate-EDTA-HEDTA[1]	
^{241}Am	2.7
^{239}Pu	2.3

[1]Peroxide addition performed at pH 2

Table 4

Americium Decontamination Factors and Distribution Ratios
For Sodium Titanate Addition to Synthetic ZAW*

Contact Time, hrs.	^{241}Am Normalized Decontamination Factor, DF	^{241}Am Distribution Ratio
0.3	19.1	32
0.5	25.4	62
1.0	34.8	110
2.0	47.8	170
5.7	90.2	370
22.0	478	2200
72.0	>3280	>8090

*Experimental Conditions:
ZAW buffered to pH 4.5 by addition of sodium citrate and sodium oxalate.
Two peroxide additions under variable conditions
Neutralized to one mole excess OH^-
Sodium titanate powder added to NBAW.

Internal Letter

Rockwell International

Date August 31, 1983

No. 65453-83-227

TO: (Name, Organization, Internal Address)
- K.R. Shah
- Advanced Projects
- 2704E/200 E

FROM: (Name, Organization, Internal Address, Phone)
- D.R. Bratzel
- Chemical Lab. Unit
- MO-037/200 W
- 3-1228

Subject: WG Monthly Report, August 1983

Reference: Letter, #65453-83-193, D.R. Bratzel to K.M. Hodgson, "WG Monthly Report, July 1983" August 1, 1983.

The presence of citrate in B-Plant high-level waste complexes the actinides americium and plutonium and prevents metal hydroxides from scavenging the complexed actinides in neutralized waste. Laboratory studies to optimize destruction of the complexant citrate in synthetic B-Plant high-level waste by peroxide addition are continuing. This work is in support of the B-Plant Immobilization Pilot Plant (BIPP) in which transuranic sludge will be vitrified for subsequent repository storage and non-TRU/low-level supernatant will be immobilized for shallow land disposal.

Laboratory studies conducted during the past month have focused on optimizing citrate destruction conditions (temperature, pH, and peroxide to citrate ratio) in order to optimize the complexant destruction efficiency and decrease the amount of sodium titanate required to sorb complexed actinides from neutralized waste.

Excess Peroxide Addition

It was previously reported (Reference) that partial destruction of the complexant citrate by addition of a 20:1 mole ratio of peroxide to citrate followed by addition of the inorganic ion exchanger sodium titanate [$Na(Ti_2O_5H)$] is successful in sorbing americium and plutonium to reach nontransuranic supernatant limits (<100nCi/g total alpha activity). Laboratory results during the past month indicate that by adding an excess concentration of peroxide to destroy the complexant citrate, addition of the inorganic exchanger sodium titanate is not required to meet non-TRU supernatant limits. A summary of peroxide destruction results is reported in Table 1.

Rockwell International

Using optimized citrate destruction conditions (peroxide addition conducted at pH1 and 70°C) and a peroxide to citrate mole ratio of 50:1, the total organic carbon concentration [TOC] was reduced from approximately 37 grams carbon per liter (gC/L) to 1.5gC/L. After neutralization to one mole excess caustic, the normalized ^{241}Am decontamination factor was >58,300. An ^{241}Am DF of >3600 is required to reach non-TRU supernatant limits.

Addition of a 50:1 peroxide to citrate ratio increases the neutralized waste volume by apoproximately 800% over the original ZAW volume. Volume increases of this amount would require further waste concentration for process feasibility. Additional laboratory studies are planned to optimize the peroxide to citrate mole ratio and to establish tradeoff criteria between the peroxide volume, sodium titanate quantity, and final neutralized waste volume to achieve complexant destruction and non-TRU supernatant limits.

pH Effects

Acid waste is treated by addition of sodium citrate and sodium carbonate to buffer the waste to pH 4.5 prior to strontium removal by solvent extraction in the B-Plant process. Continuous addition of hydrogen peroxide to buffered ZAW is accompanied by an increase in pH. This is most likely attributed to generation of hydroxide from destruction of the organic complexant citrate. Laboratory tests indicate that addition of a peroxide to citrate mole ratio of 20:1 results in a pH increase from pH4.5 to pH9.5.

In order to optimize citrate destruction efficiency by peroxide addition, laboratory studies were conducted by controlling the pH during peroxide addition to synthetic ZAW containing the complexant citrate (0.48M). Studies were conducted under controlled conditions by maintaining the buffered acid waste at pH 1, 2, 3, and 4.5 during peroxide addition by simultaneous addition of 6M HNO_3. An experimental run was also conducted at pH4.5 without controlling the pH during peroxide addition.

Rockwell International

Laboratory results are reported in Table 2. Results indicate total organic carbon destruction is increased by decreasing the pH during peroxide addition. Total organic carbon concentration [TOC] was decreased from 30gC/L to 1.3gC/L at pH1 using a peroxide to citrate mole ratio of 20:1 under boiling-reflux conditions. Comparison of results between the final total organic carbon concentration and citrate concentration indicate that at least half of the final total organic carbon concentration remaining after peroxide addition is some other organic complex than citrate.

There were also numerous pH effects noted during pH studies. Rapid addition of peroxide to boiling ZAW containing organic complexants causes excess frothing to occur. Frothing is reduced by keeping the waste below pH2 during peroxide addition. Peroxide addition to synthetic acid waste with a pH greater than three results in solids precipitation accompanied by instantaneous pH changes by as much as two pH units. Upon solids precipitation, the frothing effect is significantly enhanced. It is therefore recommended that citrate destruction be conducted at less than pH2 to optimize TOC destruction and to decrease solids precipitation, rapid pH changes, and the frothing effect.

Temperature Optimization

Experimental studies are in progress to evaluate the effects of digestion temperature on citrate destruction efficiency. Completed studies were conducted by adding a peroxide to citrate mole ratio of 20:1 to synthetic buffered ZAW containing 0.48M citrate. Peroxide addition-digestion was controlled at 20°, 50°, 75°, and boiling-reflux. No attempt was made to control the pH during peroxide addition. Waste solutions from the 20°, 50°, and 75° runs were digested at the respective peroxide addition temperatures from 24 to 72-hours. A 4-hour boiling-reflux period immediately followed the digestion period to kill the residual peroxide.

Rockwell International

Results indicate peroxide destruction efficiency increases as the peroxide addition-digestion temperature increases. In addition, it was found that addition of large volumes of peroxide was difficult to control at temperatures less than 95°C in order to avoid exothermic peroxide reactions. Exothermic peroxide reactions can occur at lower digestion temperatures upon increasing the temperature after the digestion period. This indicates incomplete reaction of the peroxide. Further studies have indicated exothermic peroxide reactions can be avoided at lower peroxide addition-digestion temperatures by controlling the acid waste at a pH of less than 2 during peroxide addition. Addition of peroxide to acid waste at higher temperatures (>95°C) prevents exothermic peroxide reactions from occuring. This is most likely due to an increase in the reaction kinetics between peroxide and citrate and also by rapid catalytic destruction of the peroxide due to metal cations in the acid waste. It is recommended that citrate destruction be performed at greater than 95°C to increase citrate destruction efficiency and to avoid exothermic peroxide reactions.

D.R. Bratzel

D. R. Bratzel
Chemist

DRB:gij

cc:
D.L. Burt
J.S. Buckingham JSB
W.R. Dworzak
J.J. Goldin
R.N. Gurley
K.M. Hodgson
J.O. Honeyman
M.J. Kupfer
K.J. Patterson
W.W. Schulz
A.H. Smith
C.R. Stroup
R.J. Thompson
D.L. Uhl
R.A. Watrous
D.G. Wilkins
B.A. Wolfe
[redacted]
File: WG
Letterbook

Table 1. Peroxide Destruction Tests

Experimental Parameters	Normalized ^{241}Am Df
Titanate	1500
H_2O_2 (20:1)	9
H_2O_2 (20:1) + Titanate	> 3300
H_2O_2 (50:1)	>58,300

Conditions:
Synthetic ZAW (citrate complexed)
H_2O_2 addition at $\leq$ pH2

Table 2. Effects of pH on Citrate Destruction in Synthetic ZAW by Addition of Hydrogen Peroxide

pH	[TOC],gC/L Initial	[TOC],gC/L Final	[Citrate],N Initial	[Citrate],N Final	$[CO_3^{=}]$,M Initial	$[CO_3^{=}]$,M Final
1	29.4	1.4	0.4	0.002	2.3×10^{-3}	1.7×10^{-3}
2	32.0	2.4	0.4	0.009	2.2×10^{-3}	1.5×10^{-3}
3	34.0	I*	0.5	0.07	1.8×10^{-3}	4.6×10^{-4}
4.5 (controlled)	35.0	6.6	0.5	0.04	4.2×10^{-4}	8.5×10^{-4}
4.5 (Variable)	36.0	5.1	0.5	0.03	1.6×10^{-3}	4.9×10^{-2}

*I=Incomplete Analysis

Internal Letter

Rockwell International

841

Date November 1, 1983

No. 65453-83-274

TO: (Name, Organization, Internal Address)
K. R. Shah
Waste Management Process
W/E-13, 300 Area

FROM: (Name, Organization, Internal Address, Phone)
D. R. Bratzel
Chemical Laboratory
222S/MO-037/200W
3-1228

Subject: Proposed FY84 Laboratory Studies for BIPP Feed Preparation

Refs:
1. Letter, #65450-83-264, September 27, 1983, D. R. Bratzel, M. J. Kupfer, C. R. Reichmuth to K. R. Shah, "Waste Preparation Requirements for Waste Feed to BIPP - Progress Report on FY-83 Laboratory Tests", Rockwell Hanford Operations

2. Letter, #65453-83-006, July 5, 1983, D. G. Shepard to C. R. Reichmuth, "High Pressure Centrifuge Wash Study Report", Rockwell Hanford Operations

3. Letter, #65455-83-057, M. J. Schliebe and J. D. Moore to J. P. Sloughter, "Selection of Equipment for Processing Sludge from Neutralized Current Acid Waste (NCAW) and Double-Shell Tank Slurry (DSS)", Rockwell Hanford Operations

Reference 1 is a draft report on laboratory and pilot-scale studies completed in FY83 to determine feed preparation requirements to the B-Plant Immobilization Pilot Plant (BIPP). A general statement of proposed FY84 laboratory studies is outlined for your review. The studies include sludge washing of neutralized current acid waste (NCAW) and complexant destruction studies to be completed on B-Plant acid waste (BAW). After FY84 laboratory studies are fully defined, a detailed laboratory test plan will be issued by December 1, 1983. Priority will be placed on completing sludge washing studies.

SLUDGE WASHING STUDIES

Laboratory Scale

Laboratory sludge washing studies completed to date have indicated problems may exist in the detection limit of low concentrations of sulfate from dissolved sludge. Laboratory sludge washing studies are in progress to spike known concentrations of sulfate in washed sludge from NBAW and in sludge from NCAW containing no sulfate to determine sulfate detection limits and possible analytical problems associated with current methodology used by Battelle (inductively coupled plasma spectroscopy using a vacuum detector for sulfur analysis).

Rockwell International

Also in progress are sludge washing studies on product from the pilot-scale centrifuge wash study (Ref. 2). Washed sludge from this study will also be used for sulfate spike studies to determine the sulfate detection limit.

Additional sludge wash laboratory studies will include neutralized product from pilot-scale enhanced sugar denitration. Lab studies will include base case neutralization experiments on bottoms from pilot-scale enhanced sugar denitration studies to determine the complexing effects of residual organic carbon compounds resulting from sucrose breakdown (10gC/L) and also to determine the total organic carbon content in the sludge after repeated sludge washings.

Laboratory studies are required to determine the chemical composition and physical properties of NCAW (both neutralized supernatant and slurry) for use by PNL. These studies are currently being defined by Don Larson (PNL) and will be incorporated into the laboratory test plan.

Pilot Scale

Additional pilot-scale tests are required to optimize solid-bowl centrifuge operation for initial supernatant-sludge separation and sludge washing. Based on Ref. 3 which recommends proposed equipment to use for BIPP feed preparation, pilot-scale studies are recommended to test inertial filters for centrate polishing.

COMPLEXANT DESTRUCTION LABORATORY STUDIES

Citrate Destruction

Laboratory optimization studies for the destruction of the complexant citrate by addition of peroxide are approximately 80% complete. Optimized parameters for citrate destruction have been proposed (Ref. 1).

Additional laboratory studies for citrate destruction include optimization of the peroxide to citrate mole ratio and laboratory studies to establish trade-off criteria between peroxide volume, titanate quantity, and total waste volume. By addition of the inorganic ion exchanger sodium titanate to neutralized waste to sorb complexed radionuclides from residual citrate and degradation products in the supernatant, a smaller volume of peroxide is required for complexant destruction and the neutralized waste volume is decreased.

Rockwell International

EDTA-HEDTA Destruction

Preliminary laboratory studies have been completed for destruction of the complexants EDTA-HEDTA by peroxide addition. Results indicate optimized parameters developed for citrate destruction are not adequate to obtain the required americium decontamination factor (^{244}Am>DF 3600) for EDTA-HEDTA destruction to obtain a non-TRU supernatant (<100nCi/g) upon neutralization. Addition of the inorganic ion exchanger sodium titanate appeared to have no effect on sorption of americium in the presence of residual EDTA-HEDTA degradation products.

Laboratory studies to be completed for destruction of the complexants EDTA-HEDTA include optimization of the peroxide to EDTA-HEDTA mole ratio and additional sodium titanate sorption studies.

Oxalate Destruction

Preliminary studies indicate the complexant oxalate is easily destroyed by peroxide addition parameters developed for citrate destruction. A limited number of studies are required to optimize the final peroxide to oxalate mole ratio.

Reaction Kinetics Studies

Detailed laboratory studies are recommended to determine the reaction kinetics of peroxide destruction of primary complexants over the range of possible process conditions.

Sodium Titanate Sorption

Additional laboratory tests are required to study the feasibility of addition of the inorganic ion exchanger sodium titanate to neutralized acid waste, specifically, to develop tradeoff criteria between peroxide volume, titanate quantity, and total waste volume. In addition, laboratory studies have been recommended to study the feasibility of in-situ generation of sodium titanate to reduce the cost of direct sodium titanate addition to neutralized waste.

Rockwell International

K. R. Shah
Page 4
November 1, 1983

Please call if you have any questions or comments.

JS Buckingham for

D. R. Bratzel
Chemist

DRB/pjm

cc: J. S. Buckingham
L. L. Buckley
D. A. Dodd
W. R. Dworzak
L. A. Gale
R. N. Gurley
K. M. Hodgson
M. J. Kupfer
F. D. Nankani
W. W. Schulz
J. P. Sloughter
R. J. Thompson
D. L. Uhl
D. G. Wilkins
B. A. Wolfe