LETTER REPORT

To: C. P. McGinnis

Subject of Document: FY 1999 Saltcake Dissolution Workshop

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LETTER REPORT

ORNL/TM-1999/113

FY 1999 Saltcake Dissolution Workshop

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Letter Report presented to the
Pretreatment Technical Integration Manager of the Tank Focus Area
Office of Science and Technology
U.S. Department of Energy

in fulfillment of Milestone C-2 of TTP OR16WT41

June 30, 1999

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PROGRAMMATIC OVERVIEW

During the FY 1998 Saltcake Dissolution Workshop, participants identified nine tasks to be performed prior to the FY 1999 workshop. Discussions during the workshop indicated that significant progress was made in each area. The workshop focused on the strengths and weaknesses of the Environmental Simulation Program (ESP). In addition, the ESP predictions for the Tank SY-101 remediation and the ESP validation efforts were evaluated. Finally, the need for a broader user base was identified.

At the request of the Tank Waste Remediation System (TWRS), the ESP model was successfully utilized to predict the effects of Hanford tank farm operations such as waste transfers and water dilutions. The ESP model was originally developed to predict the compositions of solutions from off gas scrubbers. Therefore, the original database for the ESP model was designed for use with solutions with low ionic strengths. However, the Hanford tanks contain waste with very high ionic strengths. TWRS and Tank Focus Area (TFA) staff members have measured the solubilities of key components at high ionic strengths. The results from these studies were used to develop the Hanford database for the ESP model so the model could more accurately predict the compositions of Hanford waste streams with high ionic streams. The OLI Corporation, which developed the ESP model, has now incorporated most of the Hanford database into its standard ESP database. Another deficiency of the ESP model involves the lack of detailed documentation. Most new users of the ESP model normally encounter several obstacles. Therefore, TWRS management has proposed the development of an ESP user guide based on the

experiences of TWRS and TFA researchers. The objective of the user guide is to make the ESP model more user friendly for the Hanford process engineers.

The saltcake dissolution experiments at Hanford and the SOLGAS calculations at Oak Ridge are critically in the validation of the ESP model. Due to the high costs associated with the experiments with actual waste, the TWRS would prefer to use the ESP model to predict the effects of most tank farm operations. A comparison of the SOLGAS and ESP calculations indicated that the models were not in good agreement at most of the hydroxide concentration. The SOLGAS model uses the Gibbs free energy of formation to determine the solubilities of the chemical constituents while the ESP uses the KFIT subroutine. The agreement between the ESP and SOLGAS predictions improved when the ESP calculations were based on thermodynamic functions. TFA researchers will contact OLI Corporation to determine the experimental results needed to improve the fit. In addition, a high ionic strength model, which was developed by Moonis Ally of Oak Ridge National Laboratory, will be used to validate the ESP model.

One of the new points of emphasis involves the need for the TFA researchers to work with a wider range of users at the Hanford site. Most of the previous TFA and users interactions involved the engineering group, which is responsible for the initial remediation of Tank SY-101. A list of other potential users in the areas of process engineering, tank farm operations, and retrieval was developed. Meetings between the TFA researchers and these potential customers will be held over the next several months.

AGENDA

SALTCAKE DISSOLUTION WORKSHOP

Wyndham Garden Hotel in Knoxville, TN

May 18–19, 1999

Tuesday, May 18, 1999

8:00 a.m.	***Introduction***
	(Ed Beahm, Phil McGinnis, and Randy Kirkbride)
8:30 a.m.	***Review of Saltcake Dissolution Workshop Held May 5, 1998***
	(Jeff Lindner, Randy Kirkbride, and Ed Beahm)
9:30 a.m.	***Break***
9:45 a.m.	***Saltcake Dissolution Tests and Modeling***
	(Dan Herting and Becky Toghiani)
11:45 a.m.	***Lunch***
12:45 a.m.	***ESP Calculations of Tank SY-101***
	(Jeff Lindner and Becky Toghiani)
2:45 p.m.	***Break***
3:00 p.m.	***ESP Validation Issues and Test Case Benchmarks for Different ESP Versions***
	(Becky Toghiani, Jeff Lindner, Ed Beahm, and Graham MacLean)

Tuesday, May 18, 1999

3:30 p.m. ***Experimental Tests at Mississippi State***

(Jeff Lindner and Becky Toghiani)

4:30 p.m. ***Approaches to Validation at High Ionic Strengths and Consistency of Activity Coefficients***

(Moonis Ally, Ed Beahm, and Becky Toghiani)

7:00 p.m. ***Tutorial on ESP***

(Becky Toghiani and Jeff Lindner)

Wednesday, May 19, 1999

8:00 a.m. ***Conclusion of ESP Validation Issues – Comparison Calculations of ESP and SOLGAS***

(Ed Beahm and Becky Toghiani)

8:45 a.m. ***Saltcake Dissolution Program Outlook and Administration***

(Phil McGinnis)

10:00 a.m. ***Break***

10:15 a.m. ***Workshop Highlights and Path Forward***

(Workshop Participants)

LIST OF PARTICIPANTS

Name	Organization
Moonis Ally	Oak Ridge National Laboratory
Ed Beahm	Oak Ridge National Laboratory
Brian Bowsher	AEA Technology
Craig Barfield	Mississippi State University
Jim Henslaw	AEA Technology
Dan Herting	Numatec Hanford Corporation
Albert Hu	Lockheed Martin Hanford Corporation
Rodney Hunt	Oak Ridge National Laboratory
Randy Kirkbride	Numatec Hanford Corporation
Jeff Lindner	Mississippi State University
Graham MacLean	Numatec Hanford Corporation
Phil McGinnis	Oak Ridge National Laboratory
Mong Eng Tan	Mississippi State University
Becky Toghiani	Mississippi State University
George Vandegriff	Argonne National Laboratory
Jack Watson	Oak Ridge National Laboratory
Chuck Weber	Oak Ridge National Laboratory
Tim Welch	Oak Ridge National Laboratory

KEY POINTS

Introduction

Phil McGinnis

- The new cross site transfer line at Hanford cost $50,000,000.
- The Savannah River Site spent $4,000,000 to remove the aluminosilicate plug from the 242-16H evaporator gravity drain line.
- Due to the high costs associated with pipeline plugs and limited tank availability, the Tank Focus Area is currently scheduled to fund three related research tasks for FY 2000. These tasks are Saltcake Dissolution, Prevention of Solids, and Pipeline Plugs and Recovery.

Randy Kirkbride

- The latest version of the Tank Waste Remediation System's Operations and Utilization Plan (TWRSO&UP) is now available.
- The Hanford Tank Waste Operations Simulator (HTWOS) is the primary model used by TWRS personnel. The HTWOS model is used to predict the effects of the waste transfer and to determine if the new waste meets the contract specification.
- At the moment, TWRS is more concern with physical constraints such space and equipment availability than waste compatibility.
- The HTWOS is evaluating several processing scenarios, which could form the new baseline for the Tri Party Agreement.
- The Environmental Simulation Program (ESP) is used to determine if the proposed transfer will cause a problem based on the chemistries of the wastes.

- Experimental studies are performed to determine the effects of dilution and viscosities of the resulting solutions.
- It is expected that the ESP model will reduce the number of process tests. A process test on a single tank cost approximately $240,000.
- BNFL is now expected to use the same processing facility for both phases of the contract.
- The decision on sludge treatment will be made by the Department of Energy after BNFL conducts limited experimental tests on water washes and caustic leaches.

Review of Saltcake Dissolution Workshop Held May 5, 1998

Ed Beahm

- When ESP results are reported, it is necessary to include the options and database used in the calculations.
- During FY 1998 and FY 1999, the initial remediation of Tank SY-101 became a high priority.
- Future characterization efforts need to determine the chemical form of the solids.
- The ESP model uses a single species of sodium aluminate, which is probably not adequate.

Saltcake Dissolution Tests and Modeling

Dan Herting

- The saltcake sample from Tank S-102 was almost pure sodium nitrate, and it contained very little water.
- The dissolution results at 25 and 50°C were comparable.

- The saltcake sample from Tank A-101 contains the sodium sulfate carbonate double salt.
- Polarized light microscopy can be used to identify the solids that remain after the dissolution process.
- In the test with the Tank A-101 sample, the undissolved solids were primarily sodium carbonate.
- A plug occurred during the column test with saltcake from Tank BY-102.

Becky Toghiani

- Key inputs into the ESP model include input composition, water concentration, and density.
- The two methods of charge reconciliation are dominant ion and user choice.
- Mississippi State University researchers are using the user choice method, which permits the addition of hydroxide.
- The selection of the user choice method improved the BY-102 simulation. The initial simulation results had a noticeable differences between the predicted nitrate concentration and the experimental value.
- The new BY-102 predictions disagree with the experimental total inorganic carbon (TIC) results. Efforts to improve the predictions, which included the exclusion of dawsonite, were not successful.
- The A-101 and S-102 simulations are using hydroxide for charge reconciliation and excluding dawsonite.
- The initial predictions for S-102 and the experimental results are in good agreement.

- For Tank A-101, the predictions for the fluoride concentrations disagree with the experimental results. Discrepancies also occur with the liquid density.
- ESP can make qualitative predictions of the major anions in Tank A-101.
- Approximately 70% of the centrifuged solids is liquid.

ESP Calculations of Tank SY-101

Jeff Lindner

- The ESP model will not accounted for trapped gases or morphology.
- Version 6.0 of the ESP model required a revised database for nitrate.
- The SY-101 predictions are in good agreement for the major salts.
- The best basis inventory is not necessarily up to date, and portions of the inventory are based on educated guesses.
- An adjusted inventory based on waste transfers can be found in appendix C of the TWRSO&UP.
- The crust in Tank SY-101 was divided into three layers based on gas void fraction. The top layer of crust includes ambient gases while the other two layers contain only gases from the tank.
- Predictions were based on dissolution of the top layer first. A Hanford committee recommended dissolution of the bottom layer first.
- Hanford engineers needs to verify that the TFA researcher's assumptions are reasonable.

ESP Validation Issues and Test Case Benchmarks for Different ESP Versions

Becky Toghiani

- Test cases are needed to ensure that new versions of the ESP model produce comparable results to the earlier versions. If the results are not comparable, then reason for the differences must be identified.
- Nominations for the test cases include the test results by Person, the saltcake results by Dan Herting, the simulations of transfers for Tank SY-101, and an evaluation of key compounds, which are known to effect the processing conditions.
- The test cases should be able to segregate the effects.
- The key species for process control must be identified. In addition, parameters for safe processing must be determined.
- These options will be explored during a future teleconference call on saltcake dissolution.

Experimental Tests at Mississippi State

Jeff Lindner

- A polarizing light microscope, an ion chromatograph, a fluoride selective electrode, and a conductance meter will be used.
- An experimental system will be built for isopiestic measurements.

Craig Barfield

- The solubility of the sodium, fluoride, and phosphate system will be measures at 1 and 3 M sodium hydroxide and at 25, 35, and 50°C.
- The cloud point measurements were hampered by the very small fluoride crystals.

Mong Eng Tan

- In the isopiestic experiments, solvent activity is a function of temperature so precise thermal measurement is needed.
- A concern over the use of glass was raised.

Approaches to Validation at High Ionic Strengths and Consistency of Activity Coefficients

Moonis Ally

- The activities of salts and waster and solid phase equilibria can be calculated through the application of the general properties of solutions to extensions of the Stokes-Robinson application of the Brunauer-Emmett-Teller (BET) adsorption isotherm.
- The Oak Ridge model is very good for concentrated solutions, which are similar to the Hanford wastes, but it should not be used with mixed hydrates or dilution solutions.
- This model uses the results from isopiestic measurements.
- The Oak Ridge model should be used to independently validate the extrapolation of the EPS model to high ionic strenghth.

Tutorial on ESP

Jeff Lindner and Becky Toghiani

- Water analyzer module is used to reconcile charge balance, pH, and density, and the module generates a molecular stream.
- The experimental data from Hanford is in Excel spreadsheet.

- A review of the chemical species selected for use in the ESP calculations for Hanford indicated that modifications to chromium, uranium, aluminum, and hydroxide are required. In particular, the experimental results provides the concentration of free hydroxide while the ESP model requires the total hydroxide concentration.
- The solid densities from the ESP model are not correct.

Conclusions of ESP Validation Issues - Comparison Calculations of ESP and SOLGAS

Ed Beahm

- At 1 M hydroxide, the SOLGAS and ESP predictions for fluoride and phosphate are in good agreement.
- At 3 and 5 M hydroxide, the ESP results for fluoride and phosphate were below the uncertainiity for the SOLGAS calculations.
- At 0 M hydroxide, the ESP predictions were at the high end of the SOLGAS uncertainities.
- The SOLGAS model uses the Gibbs free energy of formation to determine the solubilities of the chemical constituents while the ESP uses the KFIT subroutine.
- The agreement between the ESP and SOLGAS predictions improved when the ESP calculations were based on thermodynamic functions.
- TFA researchers will contact OLI Corporation to determine the experimental results needed to improve the fit.

Saltcake Dissolution Program Outlook and Administration

Phil McGinnis

- A review of the FY 2000 workscope is currently underway.
- Workscopes will be discussed in the next teleconference on saltcake dissolution.
- The Feed Preparation task consists on three segments, which include solids formation, feed stability, and dynamics during settling.
- The Department of Energy has requested a review of all technologies, which have been supplied to Hanford. The review will take place during the first week of June, and the TFA efforts on saltcake dissolution will be presented.

Workshop Highlights and Path Forward

Rodney Hunt

- See next section on Action Items

Randy Kirkbride

- Improvements to the ESP model and databases are needed to avoid excess conservativeness during operations.
- The ESP model will be used as a tool for process engineers to set the parameters for tank farm operations.
- OLI Corporation needs to expand capabilities of the ESP model. In particular, the number of species and solids should be increased.
- The TFA researchers and users need to work together to identify future tests and their benefits.

- Future tests should be tied to an actual waste stream or used to evaluate a proposed tank farm process.
- The ESP predictions should include the composition of the final feed, which was used in the calculations.

ACTION ITEMS

Saltcake Dissolution Team

- Integration between the two pretreatment tasks (Saltcake Dissolution and Feed Preparation) and the retrieval task (Pipeline Plugs) tasks is required.
- The TFA researchers need to work more closely with the process engineers. The TFA products must be in a format, which can be easily used by the process engineers.
- The rationale for the choice of the chemical forms must be developed.
- When additional characterization information on a Hanford waste is needed for the modeling effort, the user should be contacted so the user can make the appropriate request to the Characterization Organization.
- The database for the double salts should be improved.
- Input for the user guide on the ESP model and for the test cases to validate new version of the ESP model was requested by TWRS personnel.
- Future ESP results should include the composition of the final feed, the database, and the options used.
- Users should verify if key assumptions in the TFA research are reasonable.

Mississippi State University

- The experimental results on hydroxide concentrations must be converted to free hydroxide concentration for the ESP model.
- After the modification on hydroxide concentration is made, then the dominant ion method should be reevaluated for charge reconciliation.
- ORNL staff members should be consulted on the isopiestic measurements.
- OLI Corporation should be contacted about potential ESP model upgrades such as the number of species and additions to the database.

Numatec Hanford Corporation

- The cause of the plug during the column test should be determined.

Oak Ridge National Laboratory

- The Oak Ridge model will be used to independently validate the extrapolation of the EPS model to high ionic strength.

APPENDIX A

Oak Ridge National Laboratory Presentations

Saltcake Dissolution Workshop

May 18 and 19, 1999

Wyndham Garden Hotel
Knoxville, Tennessee

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WORKSHOP

An intensive educational program for a small group of people that emphasizes participation in problem solving.

SALTCAKE DISSOLUTION WORKSHOP

Wyndham Garden Hotel
208 Market Place Lane
Knoxville, Tennessee 37922
Telephone: (423) 531-1900

May 18–19, 1999

AGENDA

Tuesday, May 18, 1999

8:00 a.m.	***Introduction*** **Ed Beahm, Phil McGinnis, Randy Kirkbride**
8:30 a.m.	***Review of Saltcake Dissolution Workshop Held May 5, 1998*** **Jeff Lindner, Randy Kirkbride, Ed Beahm**
9:30 a.m.	***Break***
9:45 a.m.	***Saltcake Dissolution Tests and Modeling*** **Dan Herting, Becky Toghiani**
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3:00 p.m.	***ESP Validation Issues*** ***Test Case Benchmarks for Different Versions of ESP*** **Becky Toghiani, Jeff Lindner, Ed Beahm, Graham MacLean**
3:30 p.m.	***Experimental Tests at Mississippi State*** **Jeff Lindner, Becky Toghiani**
4:30 p.m.	***Approaches to Validation at High Ionic Strengths and Consistency of Activity Coefficients*** **Ed Beahm, Becky Toghiani**
	Evening Tutorial on ESP **Becky Toghiani, Graham MacLean, Jeff Lindner**

Wednesday, May 19, 1999

7:00 a.m.	***AEA Review Team Breakfast*** **George Vandegrift, Jack Watson, Becky Toghiani, Dan Herting, Joe Westsik, Phil McGinnis**
8:00 a.m.	***Conclusion of ESP Validation Issues – Comparison Calculations of ESP and SOLGAS*** **Ed Beahm, Becky Toghiani**
8:45 a.m.	***Saltcake Dissolution Program Outlook and Administration*** **Phil McGinnis**
10:00 a.m.	***Break***
10:15 a.m.	***Workshop Highlights and Path Forward*** **Saltcake Team, TFA, Randy Kirkbride**

REVIEW OF WASTE PRECIPITATION/DISSOLUTION STUDIES PROGRAM AEA TECHNOLOGY

Chairman: Joe Westsik

12:30 p.m.	***Introduction*** **Phil McGinnis**
12:45 p.m.	***Program Overview*** **Brian Bowsher and AEA Team**
1:15 p.m.	***Dissolution of Alumina With Silica*** **30–45 Minute Presentation: AEA Team** **45 Minutes–1 Hour: Questions and Discussion**
2:45 p.m.	***Break***
3:00 p.m.	***Precipitation Studies*** **30–45 Minute Presentation on Results and Plans: AEA Team** **45 Minutes–1 Hour: Questions and Discussion**
4:30 p.m.	***Summary and Reevaluation of Goals*** **AEA Team, Review Committee, Randy Kirkbride**

REVIEW OF SALTCAKE DISSOLUTION WORKSHOP HELD MAY 5, 1998

Topics

- Hanford Requirements
- Tank SY-101 Level Increase Problem
- ESP Model Validation
- TFA Program Status

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REVIEW OF SALTCAKE DISSOLUTION WORKSHOP HELD MAY 5, 1998

Hanford Requirements

1. Use ESP to simulate Dan Herting's lab tests with B-106, BY-102, and BY-106 waste samples.

2. Use ESP to simulate SY-101 and SY-103 waste behavior.

3. Obtain solubility data for the sodium-fluoride and sodium-fluoride sulfate systems.

4. Validate ESP predictions for sodium-fluoride-phosphate and sodium-carbonate-sulfate.

5. Improve the accuracy of the existing data or modeling. Part of this improvement would be helping us understand if there are problems with ESP that we need to be aware of and if there are other chemical systems or interactions that we need to understand.

REVIEW OF SALTCAKE DISSOLUTION WORKSHOP HELD MAY 5, 1998

Tank SY-101 Level Increase

Thermodynamic modeling of potential remedies:

- Addition of water or caustic solution
- Removal of water
- Dissolving crust.

REVIEW OF SALTCAKE DISSOLUTION WORKSHOP HELD MAY 5, 1998

ESP Model Validation

- Concerns about program consistency in using different options and data bases.
- ESP results should include options used and data banks.
- An understanding of mixing and the combination of heat transfer, chemical reaction, and heat of dissolution in ESP would enhance modeling.

REVIEW OF SALTCAKE DISSOLUTION WORKSHOP HELD MAY 5, 1998

Scorecard

Task	Status
Saltcake dissolution tests.	
Modeling of saltcake dissolution tests.	
Experimental solubility data sodium fluoride, sodium fluoride sulfate.	
Improve accuracy of ESP data and modeling.	
Identify problems or cautions in using ESP.	
Solubility Modeling: sodium fluoride-sulfate,	
sodium aluminate,	
comparison calculations with ESP and SOLGAS on sodium phosphate fluoride system.	
Improve communication in the Saltcake Dissolution Program within the team and outreaching to others.	

Table 1. Gibbs Energies of Formation and their uncertainties

	Gibbs Energy of Formation (μ^0/RT)	
Solid	Nominal	Uncertainty
TSP	–1926.923	±0.5
NaF	–219.391	±0.2
DS	–3512.445	±1.0

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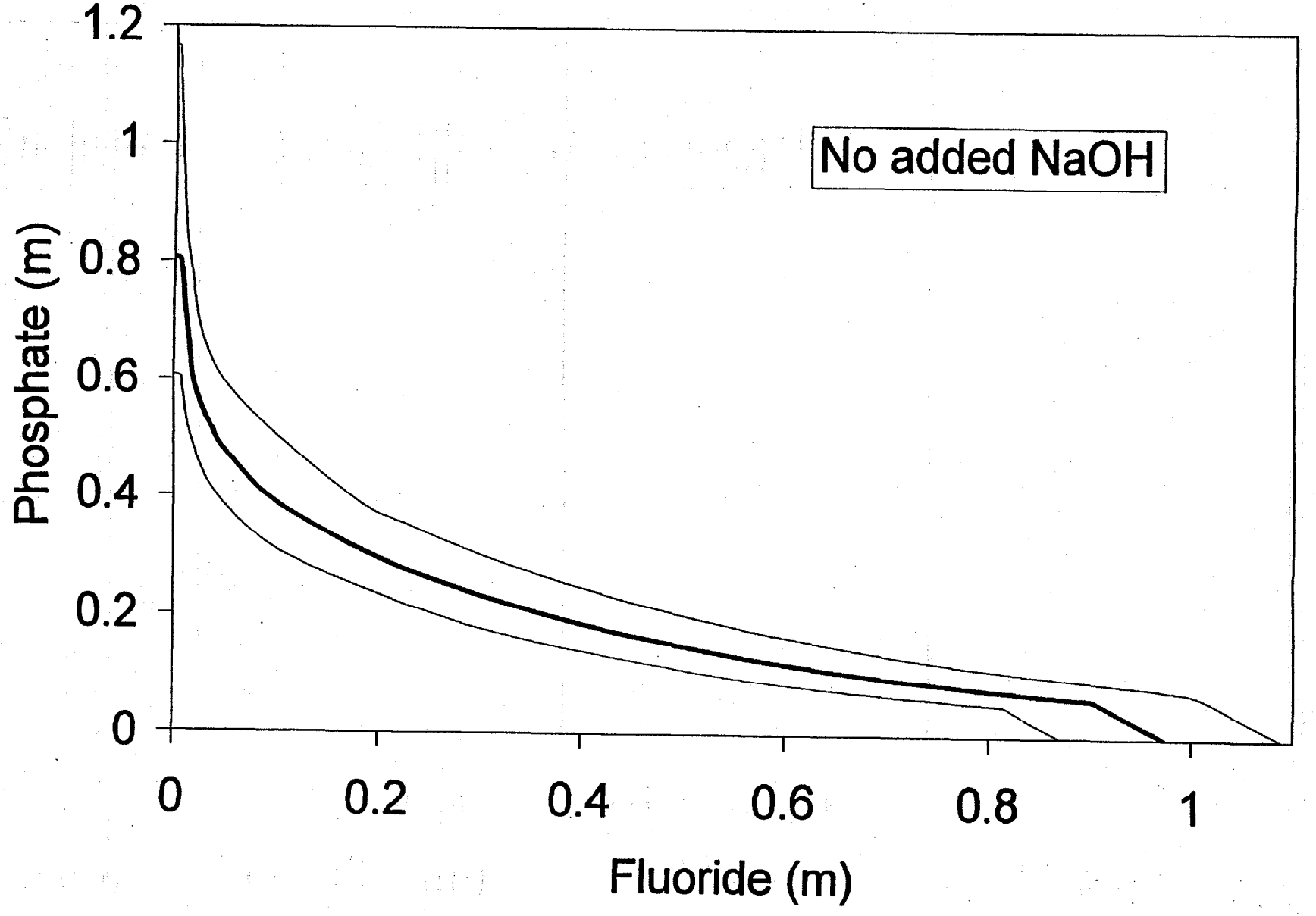

Fig. 1. Uncertainty region – no added NaOH at 25 °C.

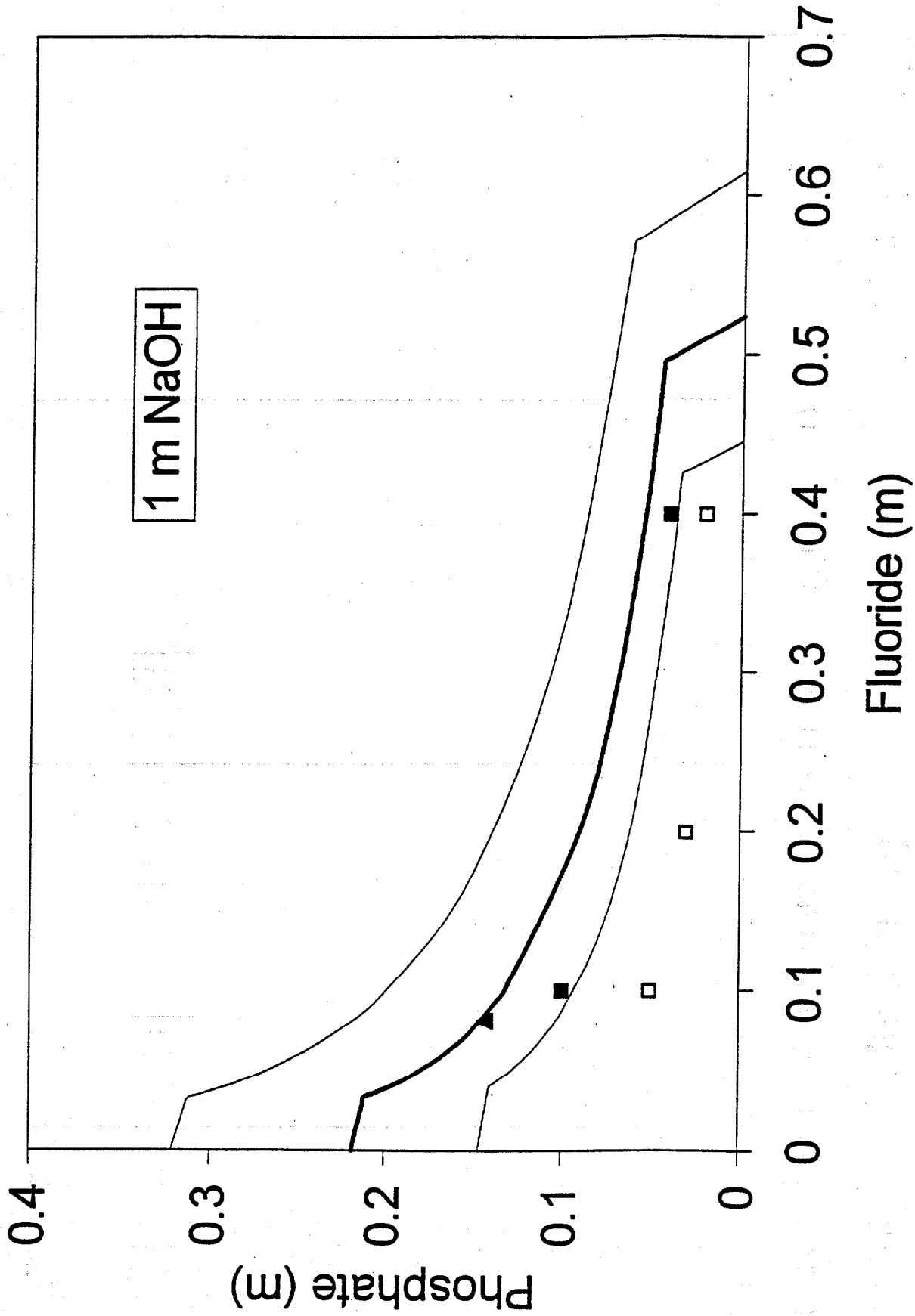

Fig. 2. Uncertainty region – 1 *m* NaOH at 25°C.

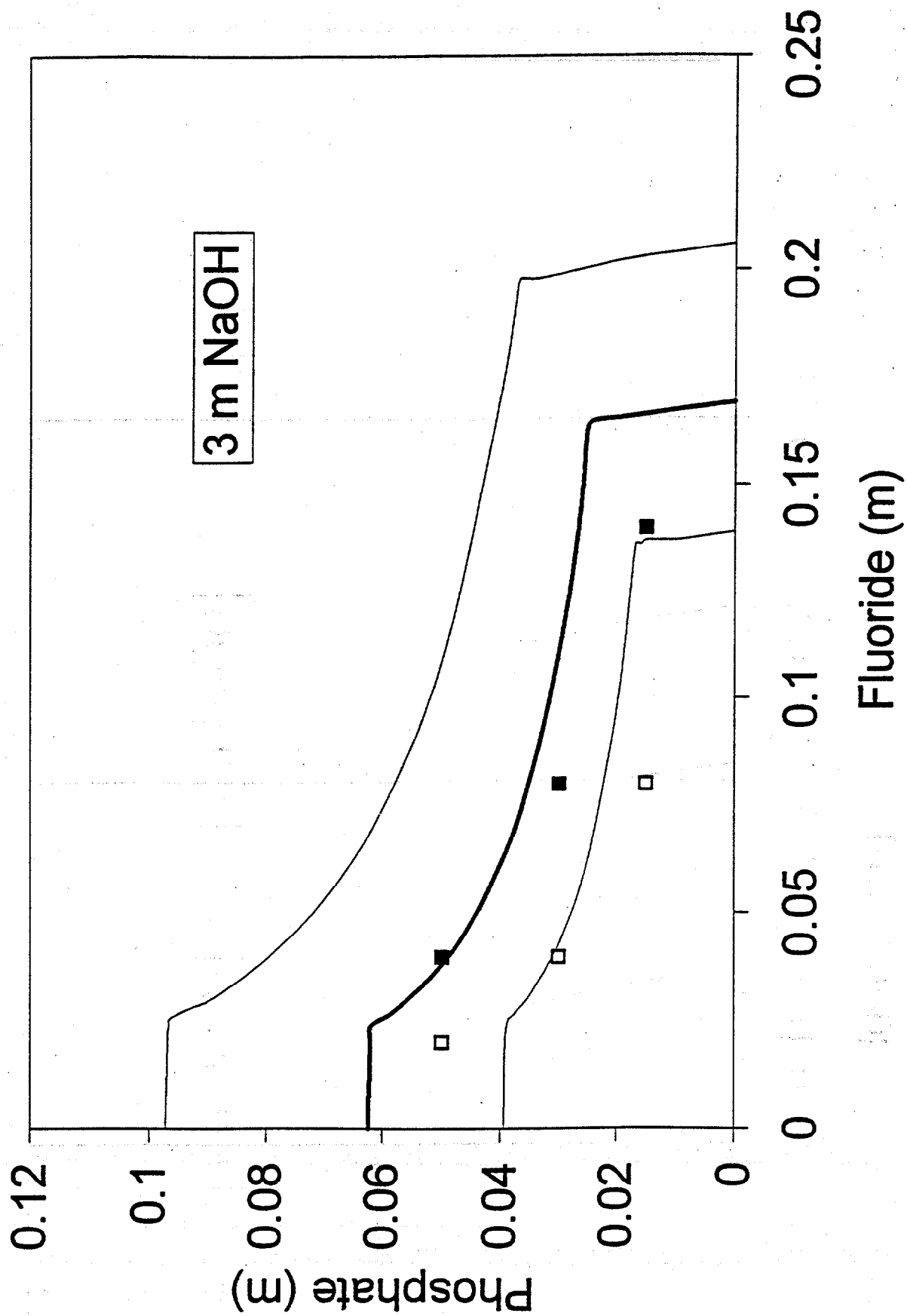

Fig. 3. Uncertainty region – 3 *m* NaOH at 25°C.

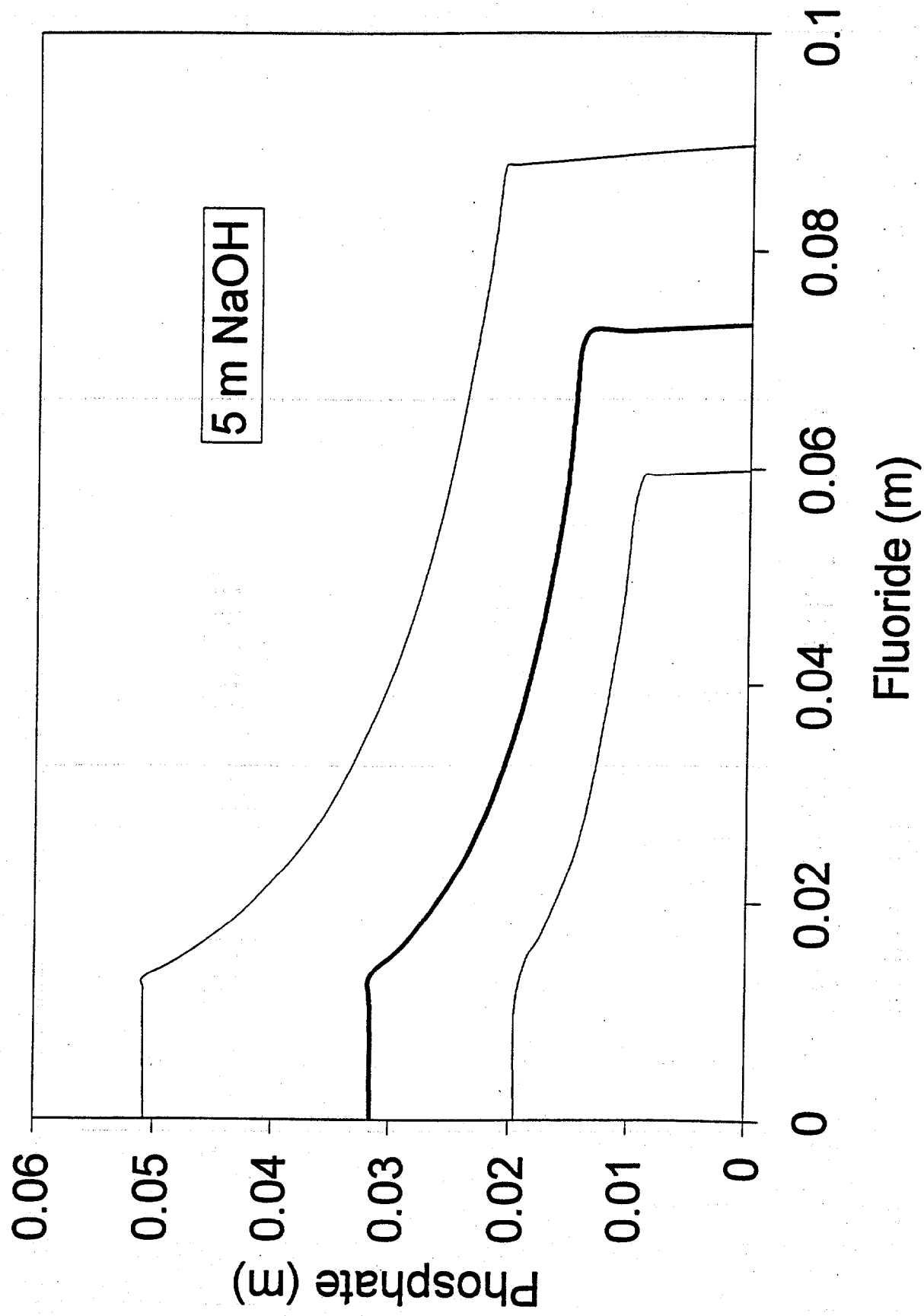

Fig. 4. Uncertainty region – 5 *m* NaOH at 25°C.

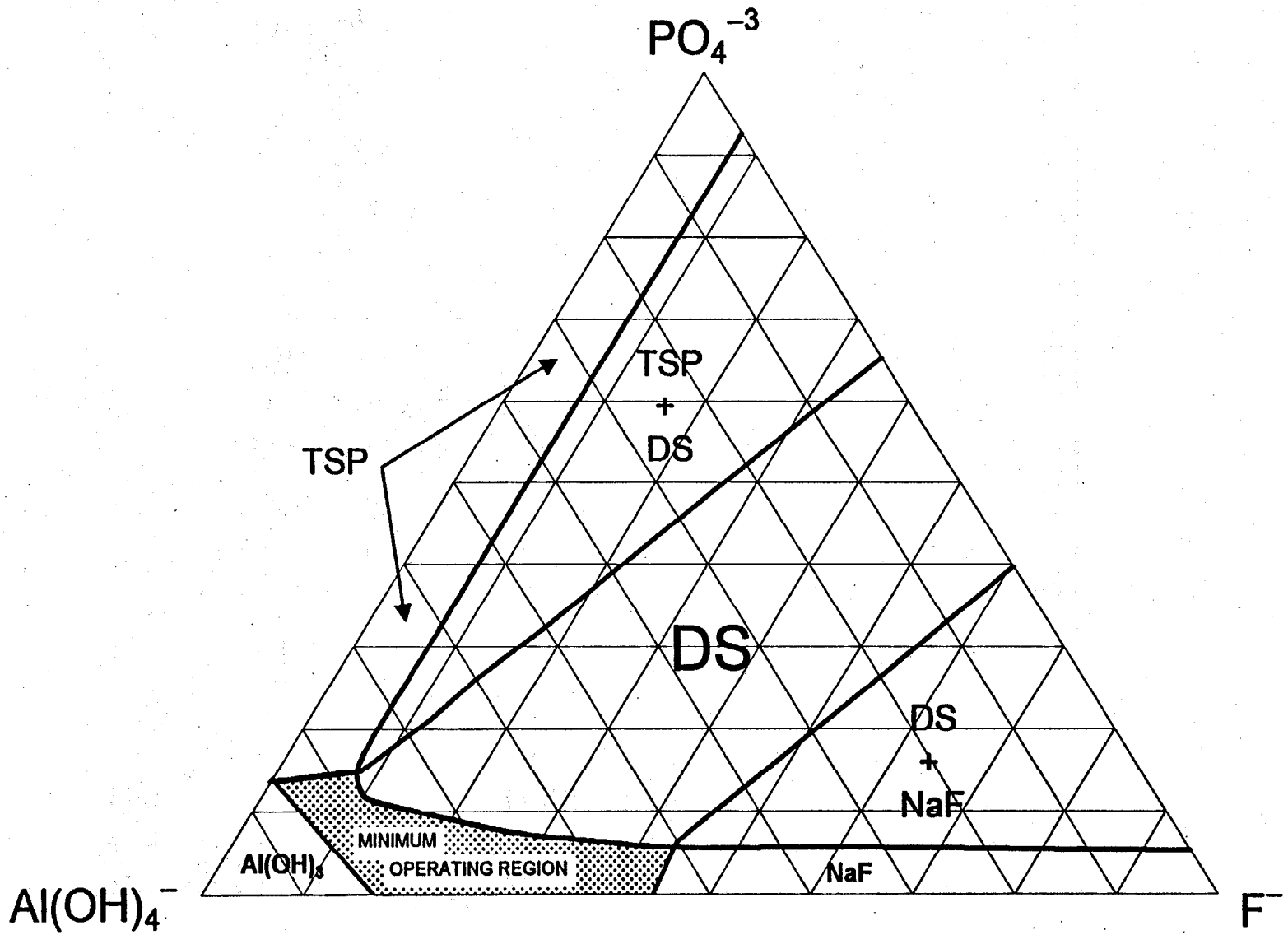

Fig. 5. Minimum operating region: 3.0 *m* NaOH at 25°C, $N_{PO_4} + N_F + N_{Al} = 0.3$ *m*.

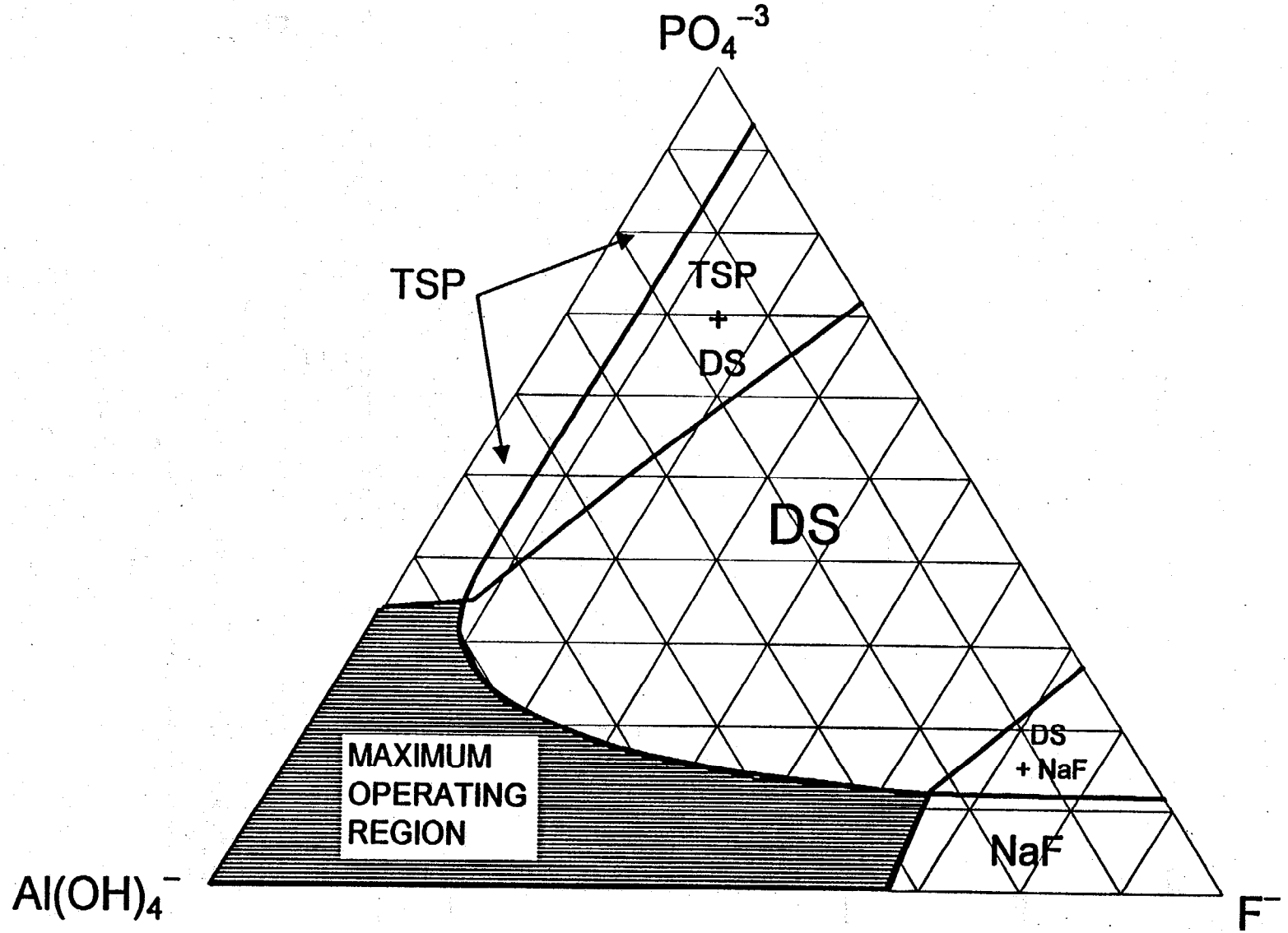

Fig. 6. Minimum operating region: 3.0 *m* NaOH at 25°C, $N_{PO_4} + N_F + N_{Al} = 0.3$ *m*.

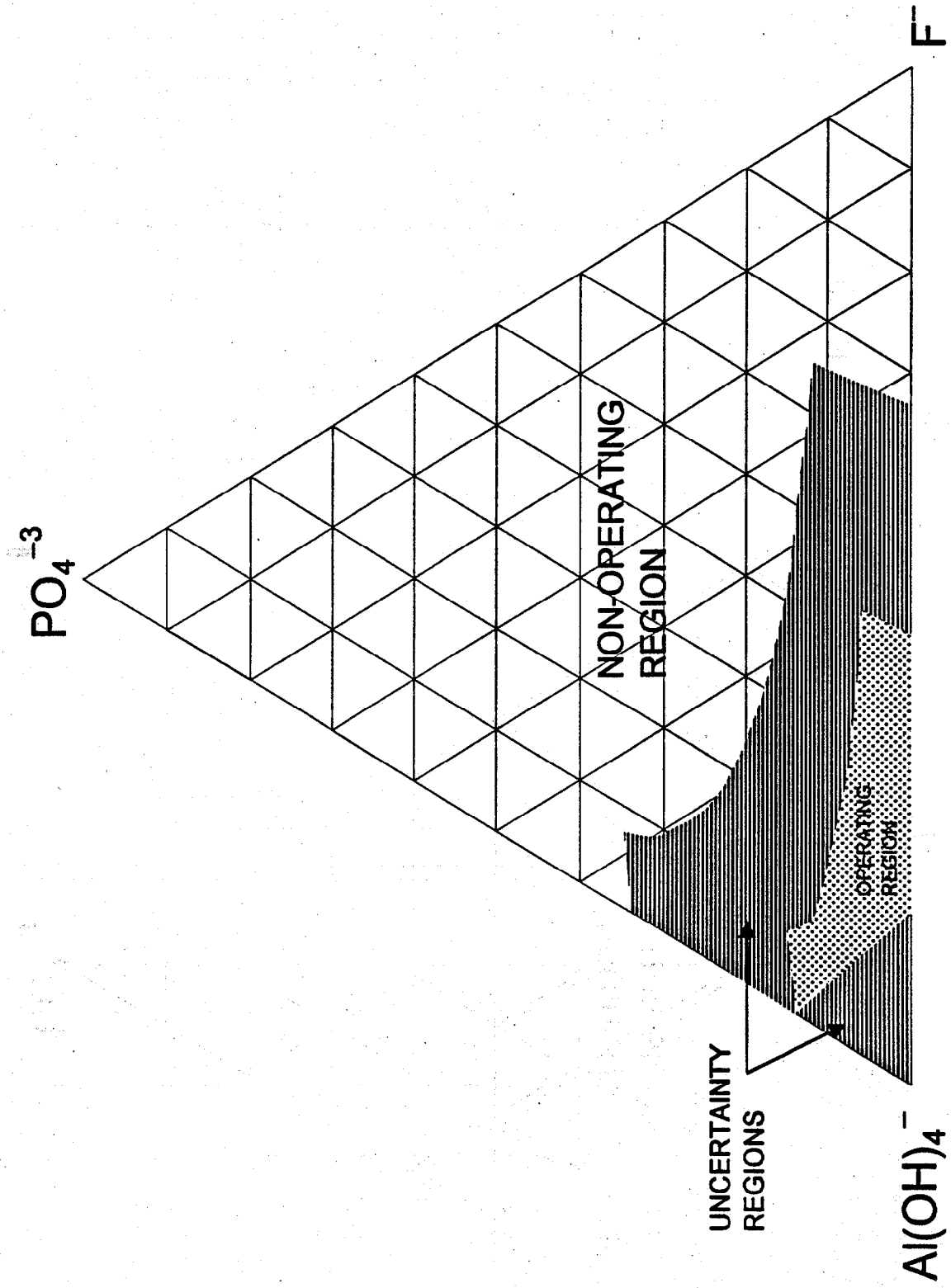

Fig. 7. Uncertainty regions: 3.0 *m* NaOH at 25°C, $N_{PO_4} + N_F + N_{Al} = 0.3$ *m*.

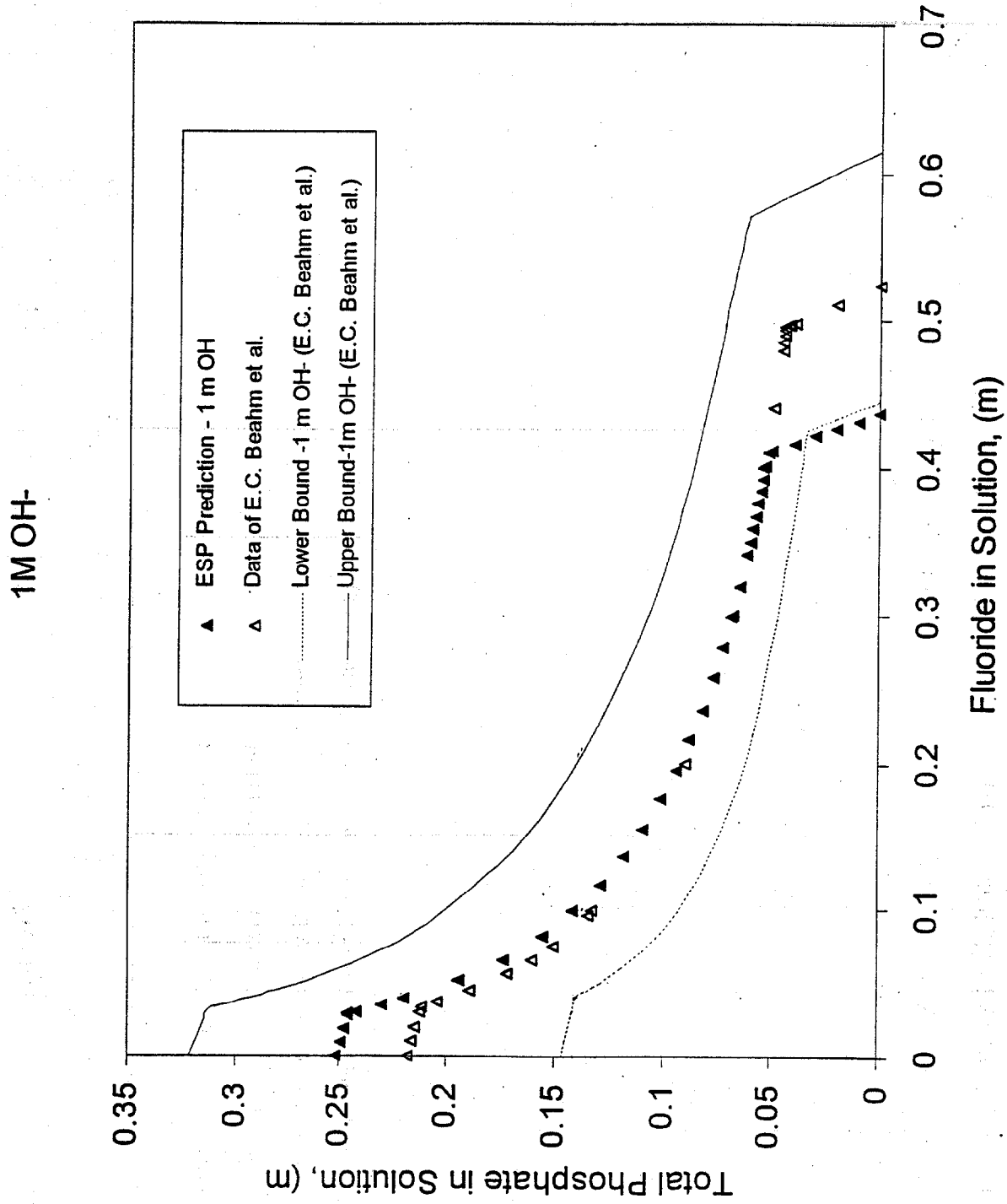

Fig. 8. Comparison calculations ESP and SOLGAS 1 *m* NaOH at 25°C.

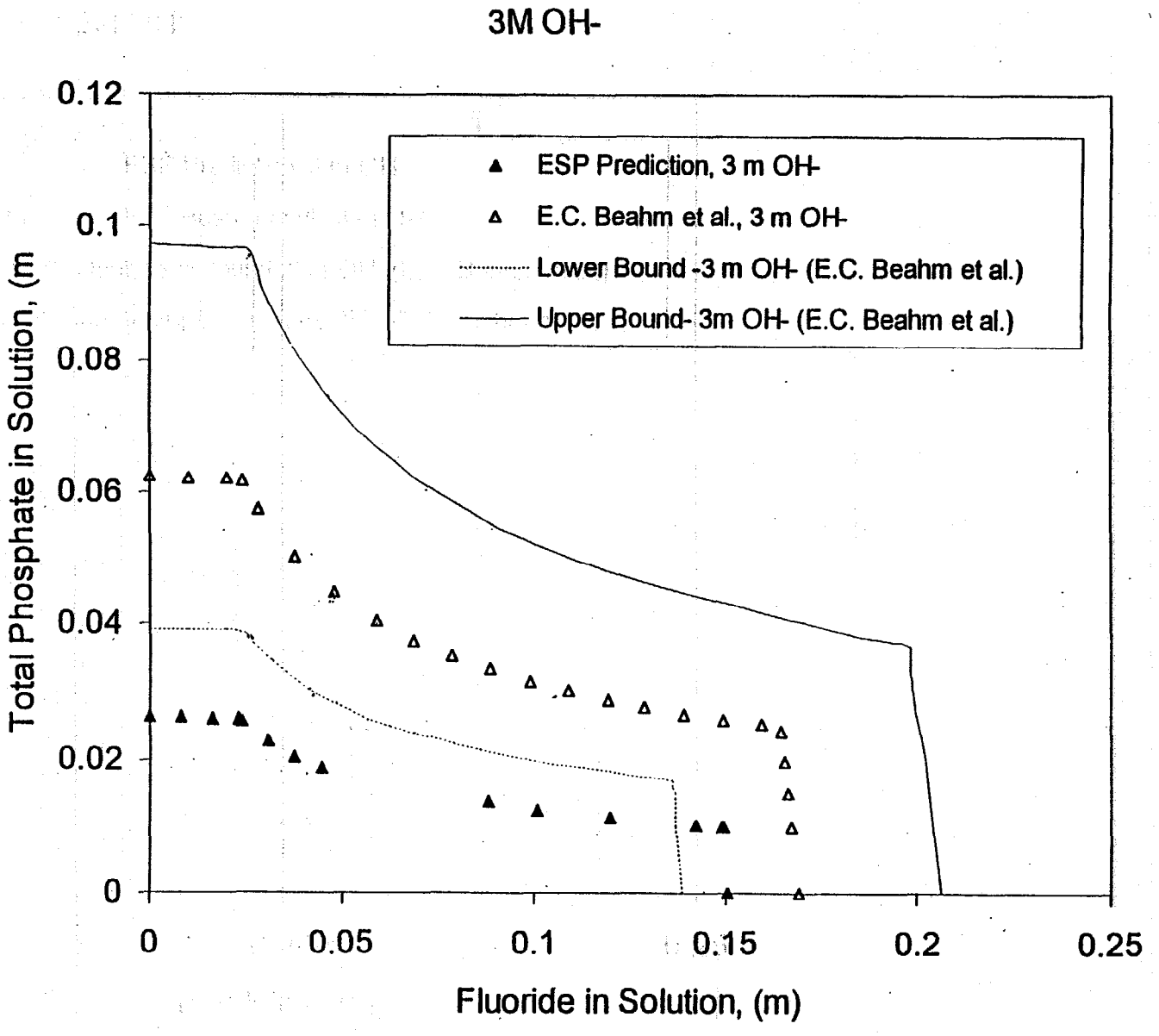

Fig. 9. Comparison calculations ESP and SOLGAS 3 *m* NaOH at 25°C.

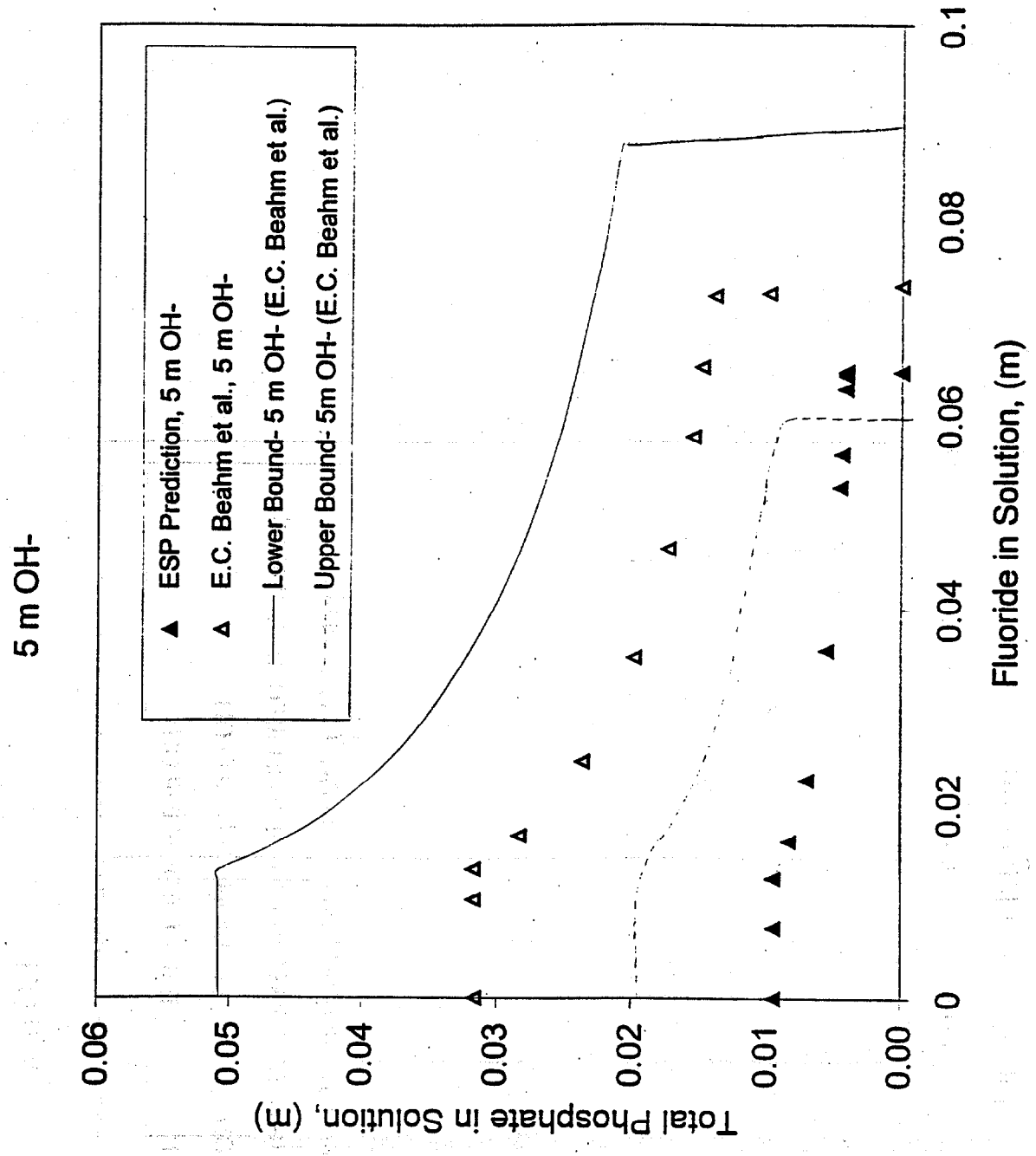

Fig. 10. Comparison calculations ESP and SOLGAS 5 *m* NaOH at 25°C.

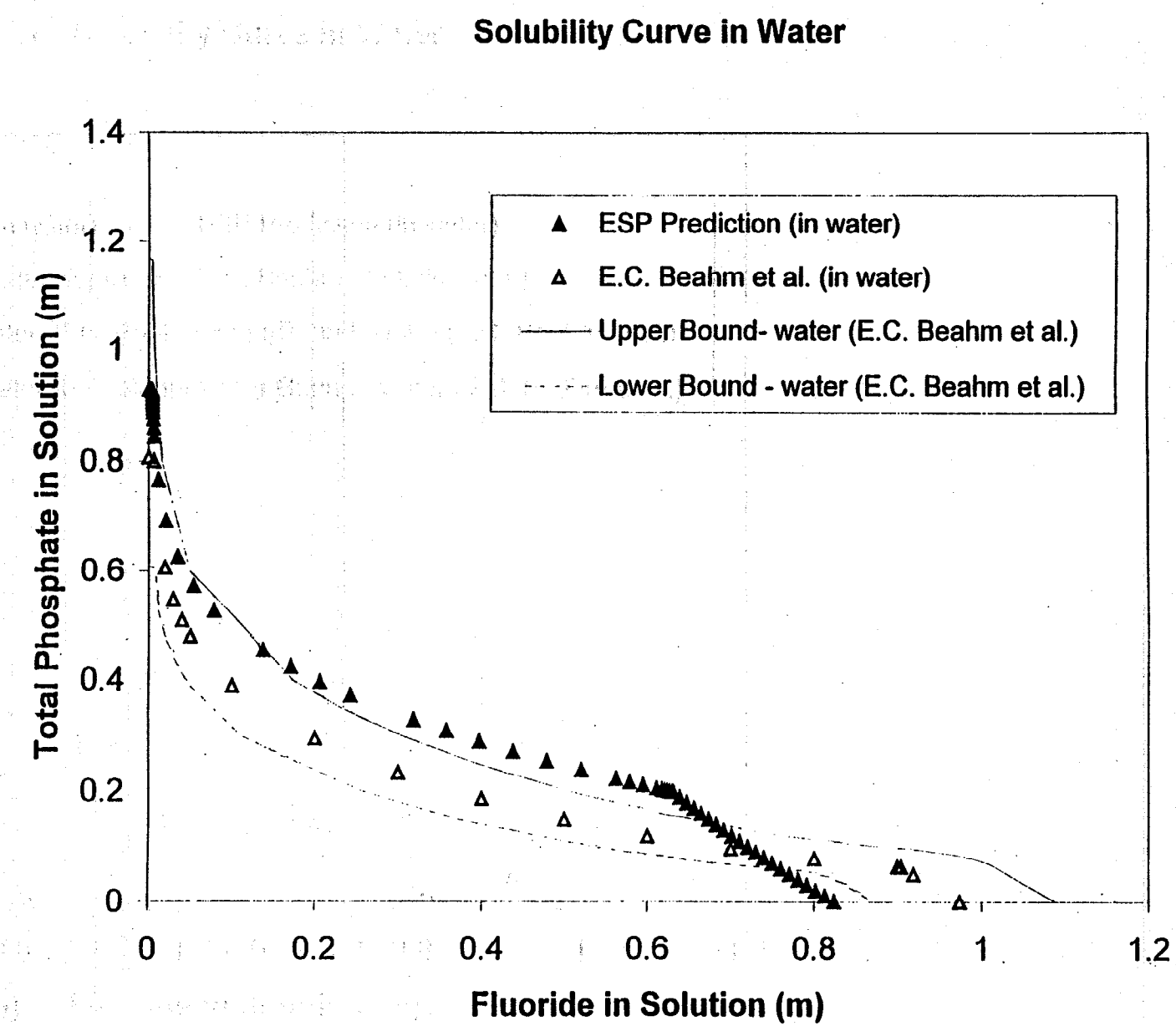

Fig. 11. Comparison calculations ESP and SOLGAS water at 25°C.

Gibbs-Duhem Equation

$$x_1 \, d \ln a_1 + x_2 \, d \ln a_2 + x_3 \, d \ln a_3 + \ldots = 0$$

(at constant pressure and temperature where x's are mole fractions and a's are activities)

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Ionic Strength

$$I = \frac{1}{2} \sum m_i z_i^2$$

where I is ionic strength, m_i are molalities, and z_i are ion charges.

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APPENDIX B

Mississippi State University Presentations

Saltcake Dissolution Tests and Modeling

Simulation of Dissolution Tests

- Current Efforts
  - Dissolution tests for A-101 and S-102
  - Revised Simulation of BY-102
- Modeling of dissolution experiments
  - Water as diluent
  - 25°C, 50°C
  - 0 to 500% diluent by weight (1000 gsaltcake + 1000 g diluent = 100% dilution by weight)

Lessons Learned Thus Far

- Importance of Input Composition
  - verification of molecular stream composition
  - density
- Method of Charge Reconciliation
- Tuning of pH
- Manual Selection of Solids
- Modeling of 50°C Experiments

Importance of Input Composition

- Cation/Anion concentrations supplied to Water Analyzer. Also supplied are water concentration and experimental density
- Molecular stream generated by Water Analyzer
  - contains proper amounts of various cations/anions and water
  - verify with inter-/intra-phase equilibria determination (ESP)/reconstruction of cation/anion contributions

Method of Charge Reconciliation

- Number of methods available in Water Analyzer - two are:
  - Dominant Ion - cation/anion with highest concentration identified; net charge evaluated; if net charge positive, dominant anion is added to balance charge.
  - User Choice - user specifies which cation/anion should be added - this species is added until the net charge is zero.
- Impact of choice depends on degree of charge imbalance

Revised Simulation of BY-102

- Simulation results reported in FY98 report
  - noticeable difference between predicted nitrate concentration and experimental value
- Why the discrepancy between experimental $[NO_3^-]$ and predicted $[NO_3^-]$?
  - Identified choice of charge reconciliation method as root cause for discrepancy

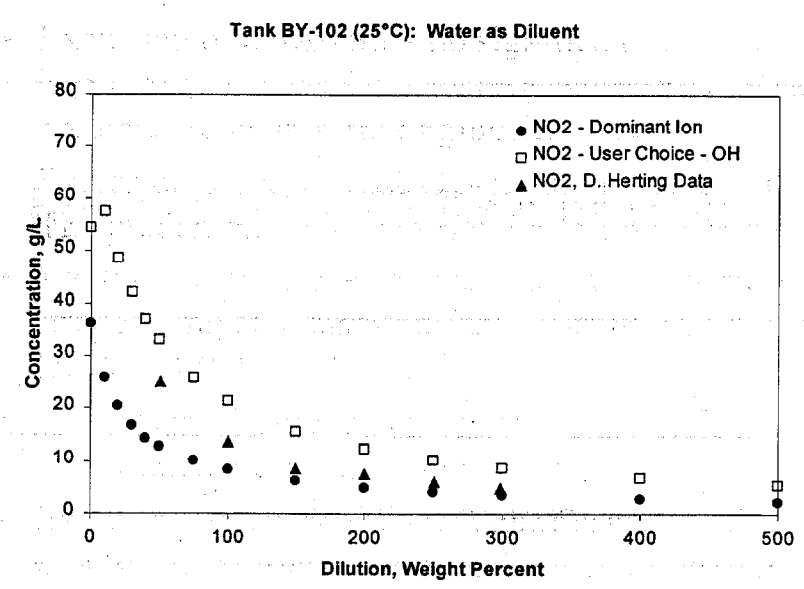
- BY-102: laboratory data exhibited significant charge imbalance (net positive charge)
- Dominant anion was nitrate
- Significant amount of nitrate was added within Water Analyzer to balance charge
- Negatively impacted ESP predictions of dissolution experiments

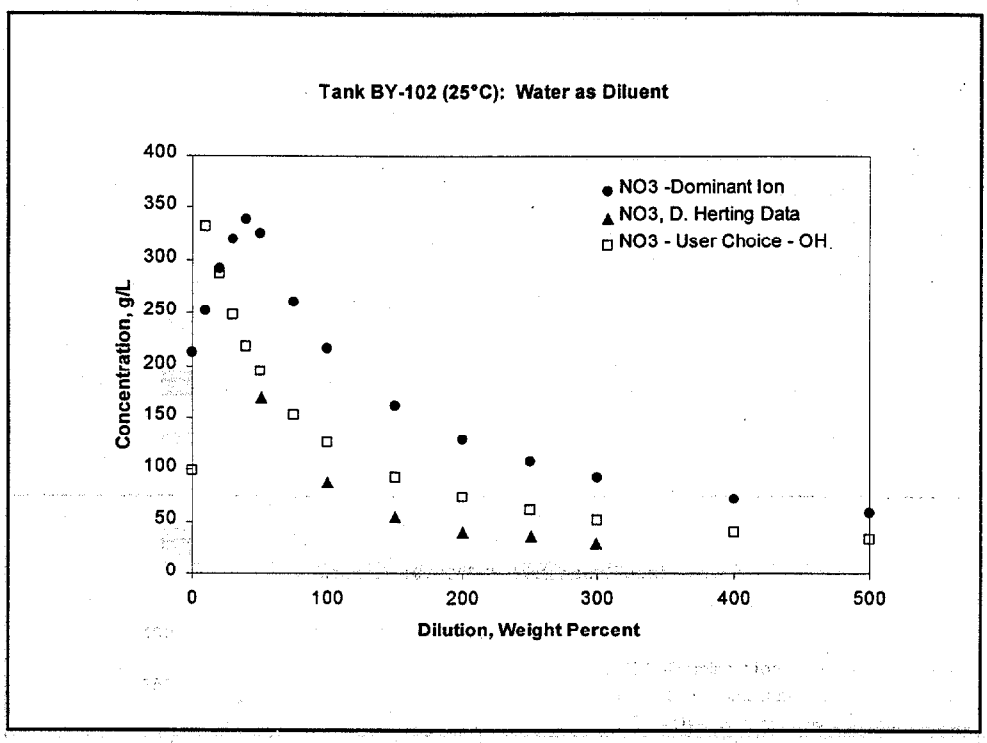
Revised BY-102 Simulation Results

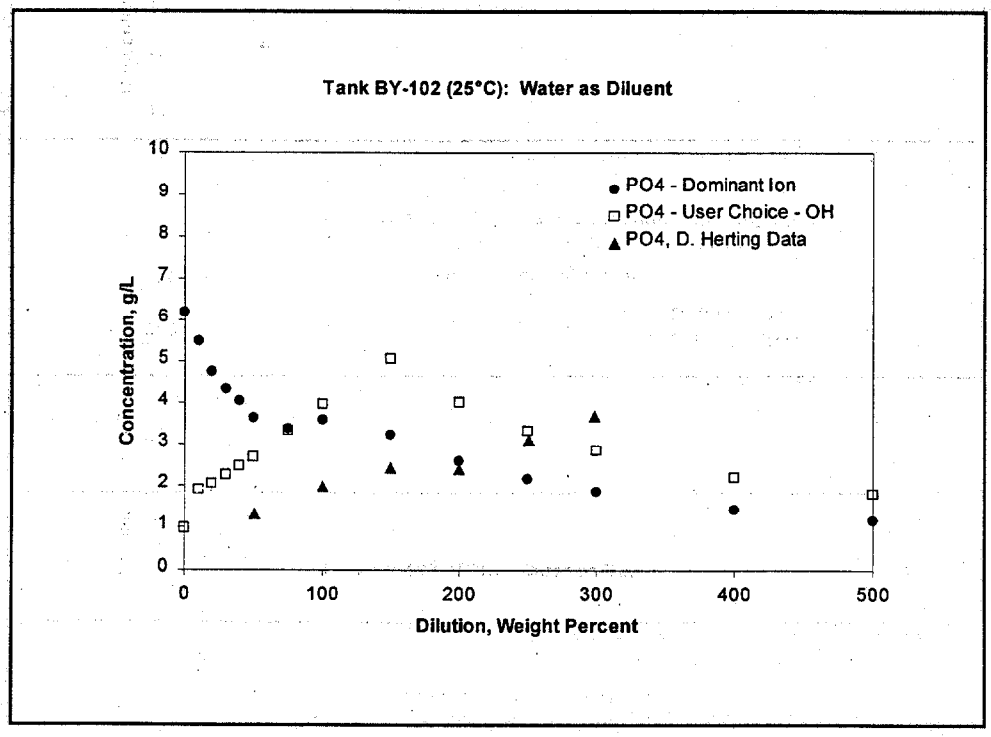
- User Choice - [OH^-] adjusted to balance charge
- Improved agreement between predicted and simulation results - general trends exhibited by experimental data mirrored by simulation predictions

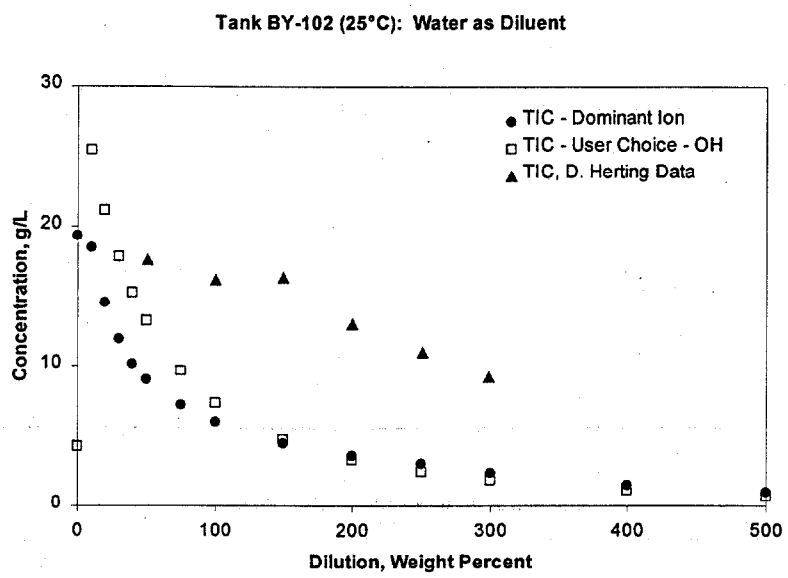
Revised BY-102 Results (cont.)

- V 6.0 - new solid species predicted at low ionic strengths/high levels of dilution - dawsonite [$NaAlCO_3(OH)_2$]
- Disagreement noted between experimental TIC and predicted concentrations
- Exclusion of dawsonite - no significant improvement in prediction of TIC - Al present is predicted to be in form of gibbsite
- Exclusion of $Na_6(SO_4)_2CO_3$ - no improvement in TIC prediction




Tank BY-102 (25°C): Water as Diluent
NO3 -Dominant Ion
NO3, D. Herting Data
NO3 - User Choice - OH
Concentration, g/L
Dilution, Weight Percent
0
50
100
150
200
250
300
350
400
0
100
200
300
400
500


Tank BY-102 (25°C): Water as Diluent
PO4 - Dominant Ion
PO4 - User Choice - OH
PO4, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500



A101/S102 Preliminary Results

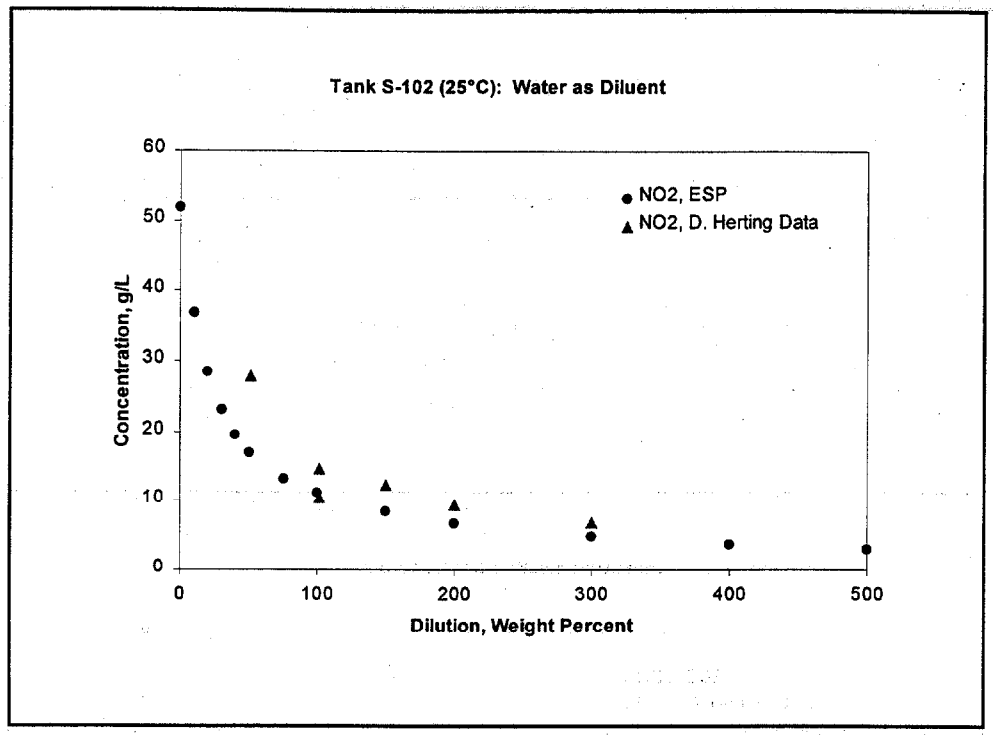
- Experimental results recently available for dissolution tests and composite determination by total sequential dissolution
- Preliminary simulations -
  - reconciliation with OH^-
  - exclusion of dawsonite
  - pH adjusted to approximate given $[OH^-]$

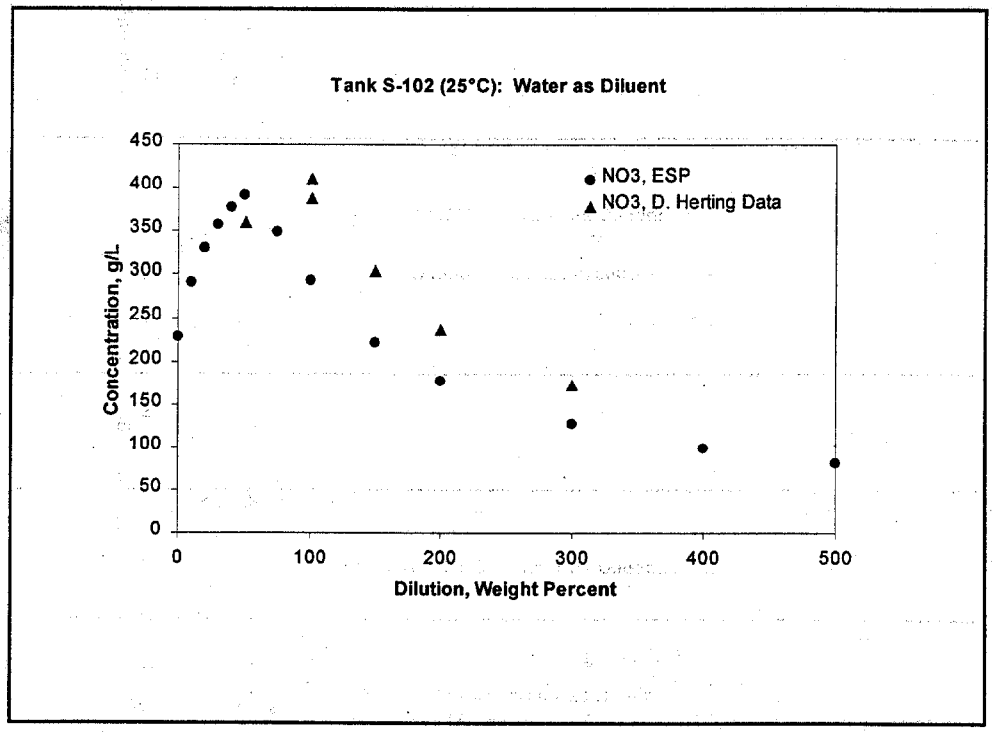
Composition of S-102

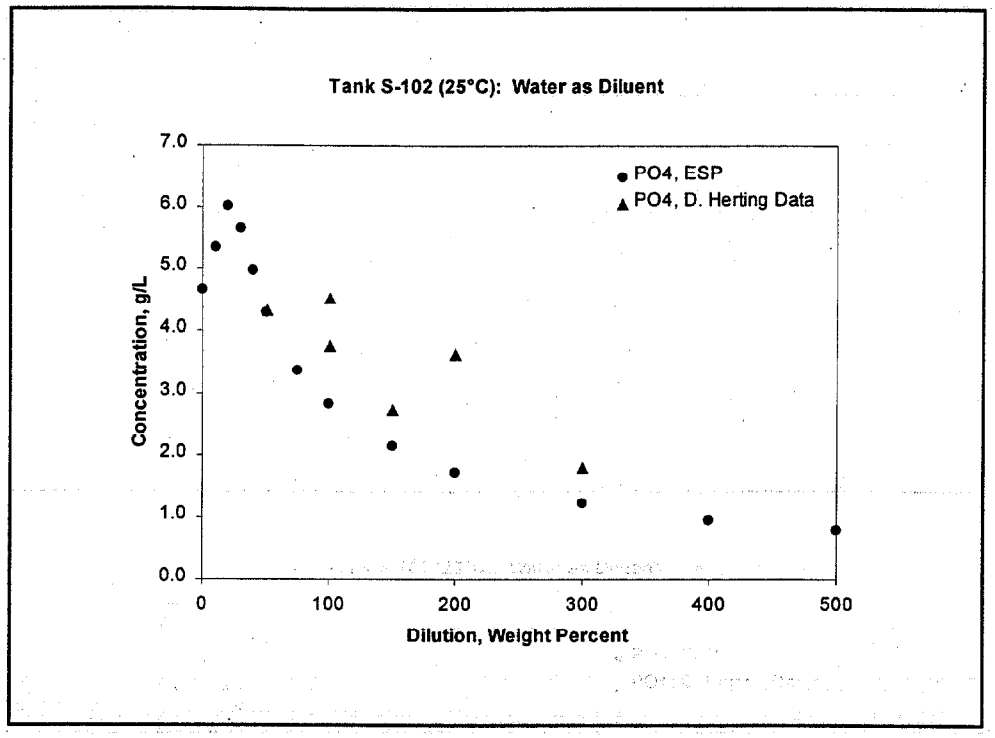
S-102 - Previously Reported			S-102 - from Total Seq. Diss.		
	wt.%	mg/L		wt.%	mg/L
Al	1.36	24578	Al	0.671204	10454
Ca	0.051	922	Ca	0	0
Cl	0.35	6325	Cl	0.164821	2567
CO3	2.6	46988	CO3	2.94609	45884
Cr	0.27	4880	Cr	0.123016	1916
F	0.03	542	F	0.01682	262
Fe	0.092	1663	Fe	0	0
K	0.085	1536	K	0.068809	1072
Na	19	343376	Na	22.99416	358123
NO2	3.35	60543	NO2	2.042801	31816
NO3	30.2	545787	NO3	53.71661	836610
OH	4	72290	OH	0.423119	6590
Ox	0.75	13554	Ox	0.174254	2714
PO4	4.41	79699	PO4	0.519862	8097
SO4	0.895	16175	SO4	0.320513	4992
Si	0.053	958	Si	0.026119	407
TOC	0.35	6325	TOC	0.168635	2626
U	0.2	3614	U	0	0
H2O	22.7	410244	H2O	5	77873
SpG	1.64		SpG	1.392	

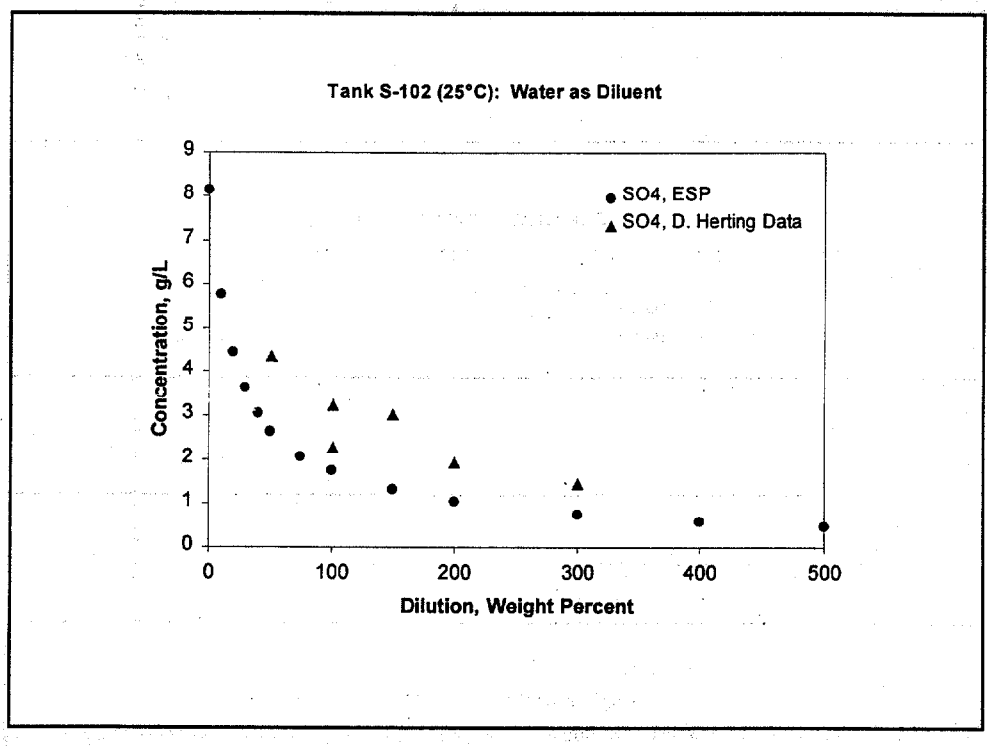
ESP Simulation Results
25°C
1000 g Saltcake Simulant Feed (from Water Analyzer results)
Private NaNO3 Database Used
S-102
Experimental Results from D. Herting
Diluent Added -Pure Water
Charge Reconciliation with OH-

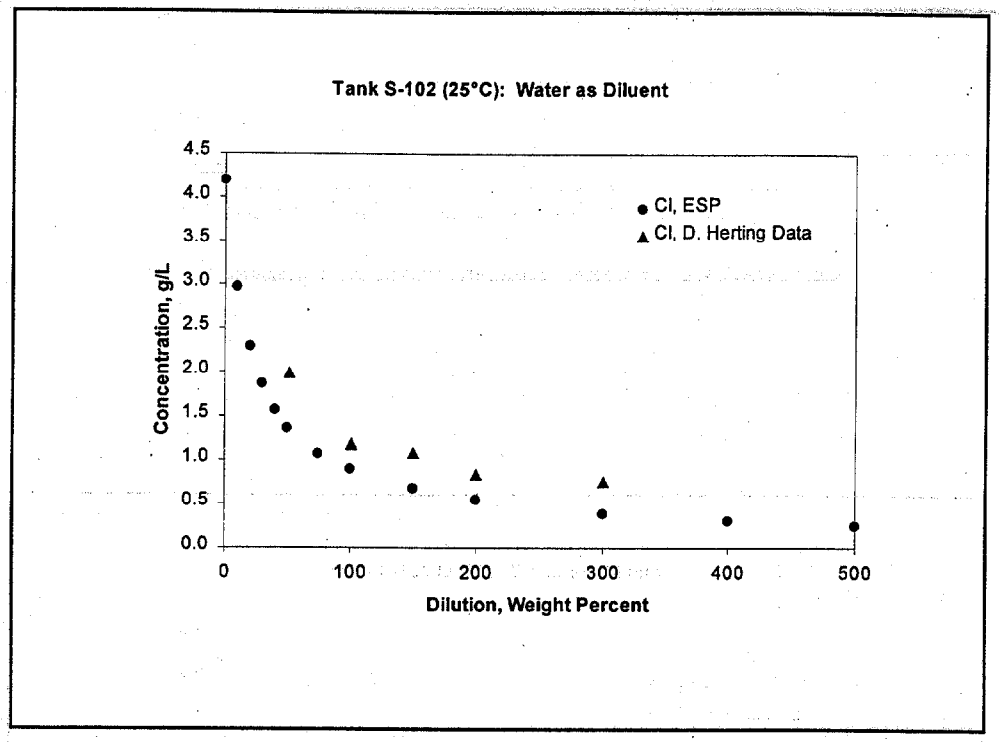
	EXP	ESP	EXP	ESP	EXP	ESP	EXP	ESP	EXP	ESP
% Dilution	51	50	101	100	150	150	200	200	300	300
SpG (g/ml)	1.392	1.417	1.377	1.309	1.273	1.235	1.231	1.190	1.165	1.137
pH		14.6		14.2		13.8		13.6		13.4
Ionic Strength		12.0		7.9		5.6		4.4		3.0
Concentrations in g/L										
TIC	6.71	4.87	4.17	3.21	3.51	2.43	2.47	1.95	1.59	1.39
F		2.61		1.72		1.30		1.05		0.75
Cl	1.99	1.36	1.17	0.90	1.08	0.68	0.84	0.54	0.76	0.39
NO_2	27.90	16.87	14.70	11.14	12.30	8.41	9.46	6.75	6.87	4.83
NO_3	359.00	391.38	410.50	292.90	304.00	221.22	237.00	177.52	173.00	127.11
PO_4	4.32	4.29	4.51	2.83	2.75	2.14	3.63	1.72	1.80	1.23
SO_4	4.36	2.65	3.23	1.75	3.04	1.32	1.94	1.06	1.46	0.76
C_2O_4		0.34		0.70	0.66	0.72	1.00	0.58	0.65	0.41

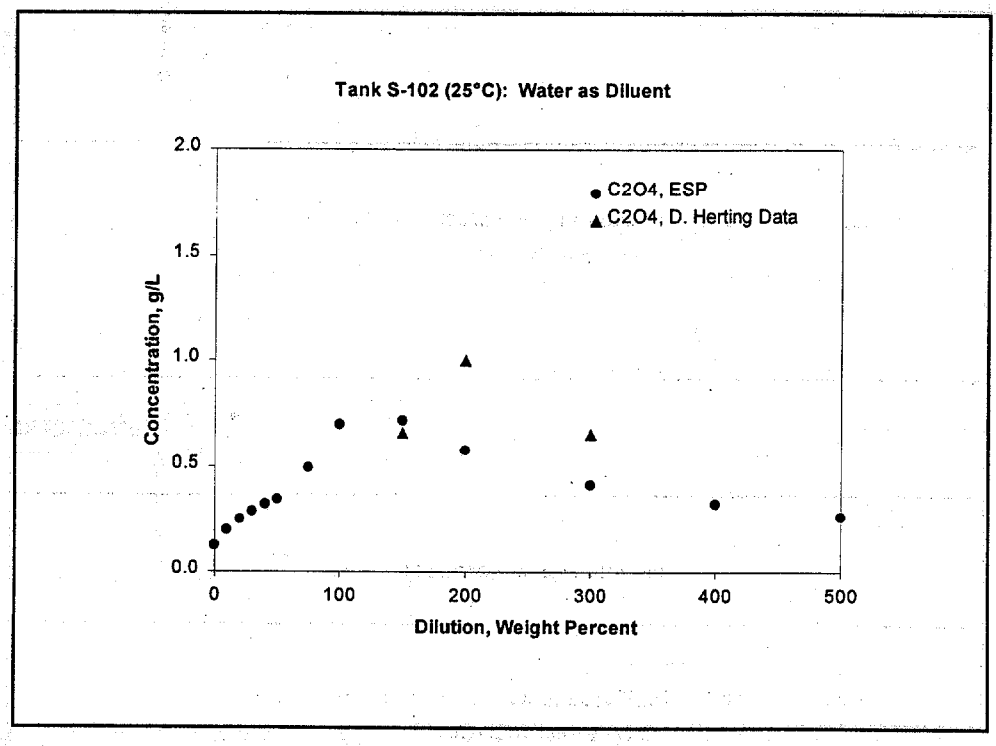

Tank S-102 (25°C): Water as Diluent
NO2, ESP
NO2, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
10
20
30
40
50
60
0
100
200
300
400
500

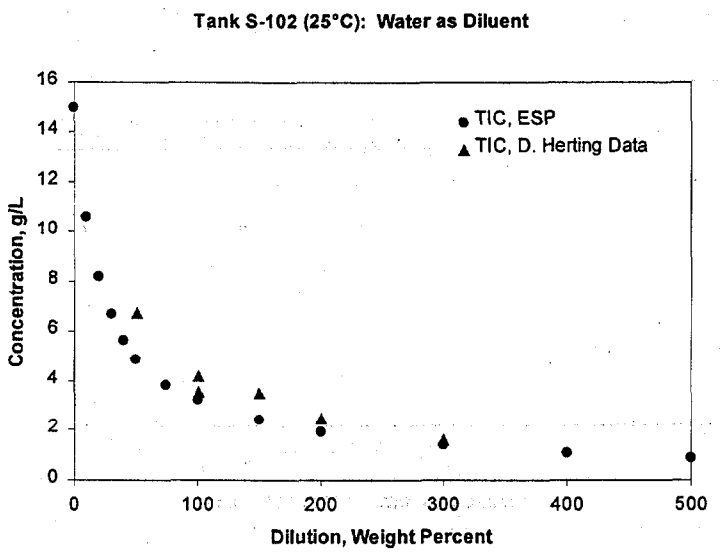

Tank S-102 (25°C): Water as Diluent
NO3, ESP
NO3, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
50
100
150
200
250
300
350
400
450
0
100
200
300
400
500


Tank S-102 (25°C): Water as Diluent
PO4, ESP
PO4, D. Herting Data
Concentration, g/L
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
100
200
300
400
500
Dilution, Weight Percent


Tank S-102 (25°C): Water as Diluent
SO4, ESP
SO4, D. Herting Data
Concentration, g/L
9
8
7
6
5
4
3
2
1
0
0
100
200
300
400
500
Dilution, Weight Percent

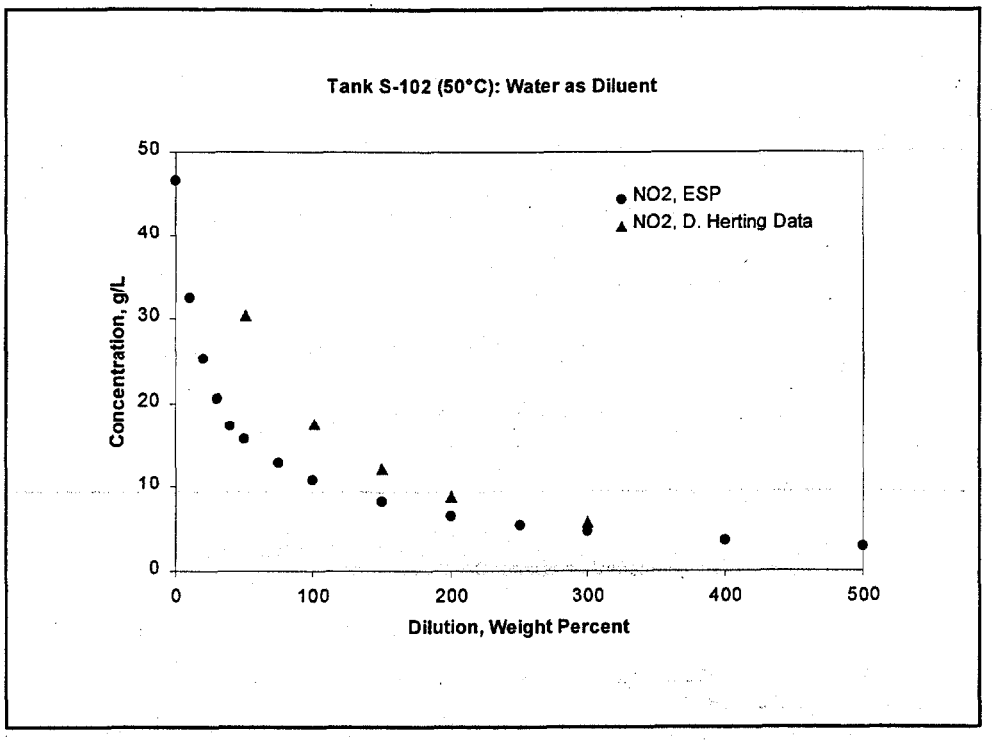

Tank S-102 (25°C): Water as Diluent
Cl, ESP
Cl, D. Herting Data
Concentration, g/L
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
Dilution, Weight Percent

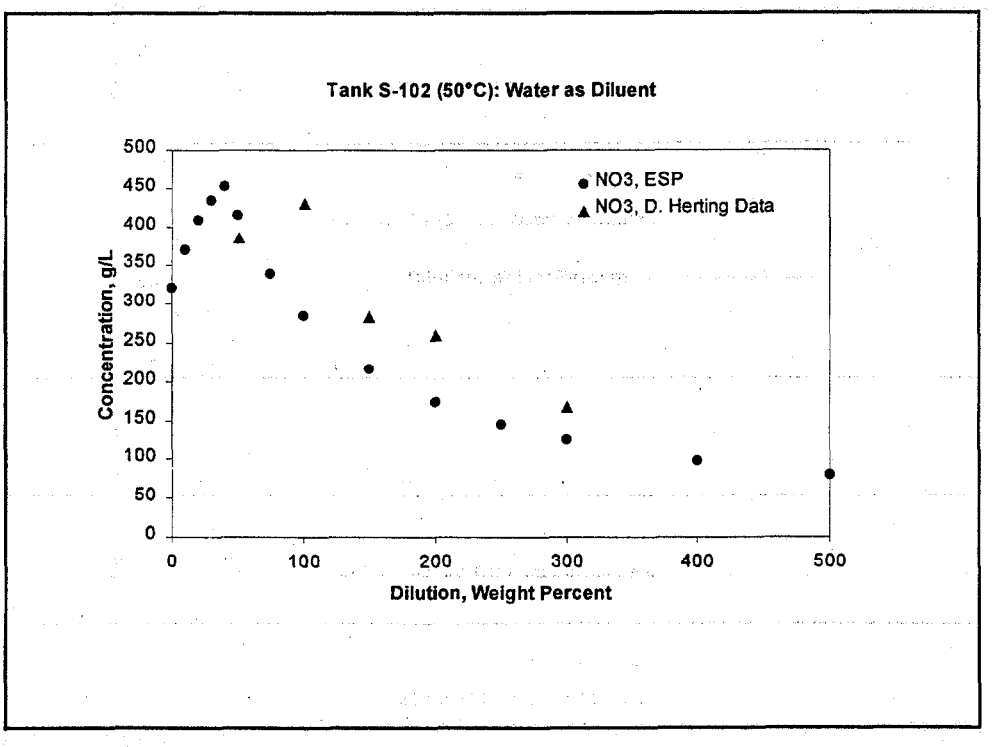

Tank S-102 (25°C): Water as Diluent
C2O4, ESP
C2O4, D. Herting Data
Concentration, g/L
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
Dilution, Weight Percent

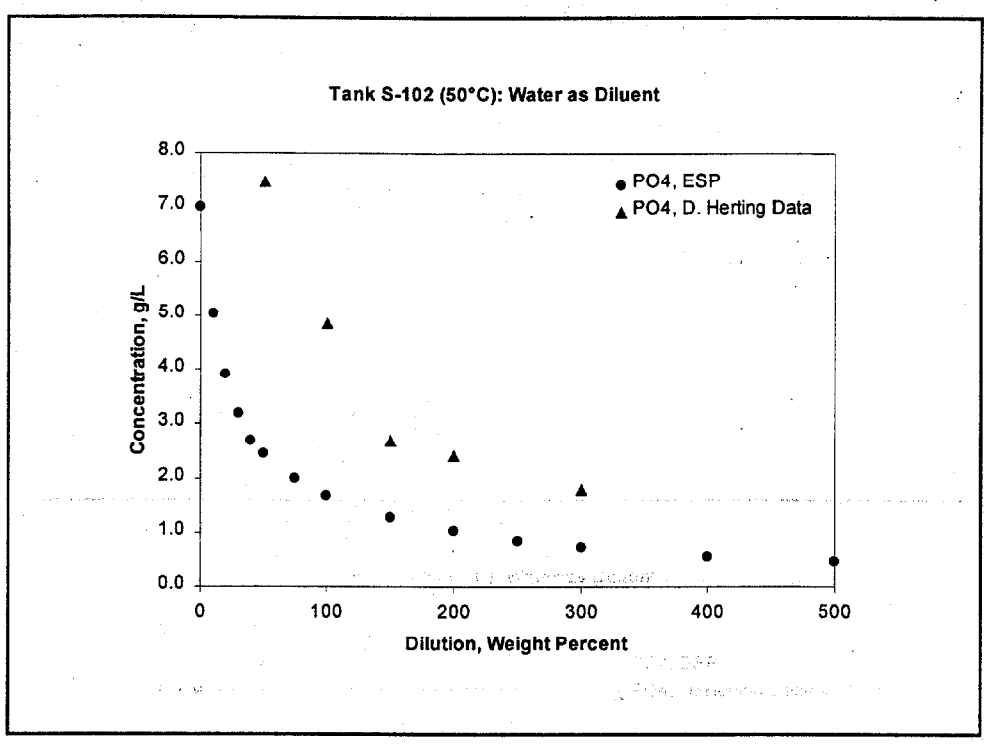


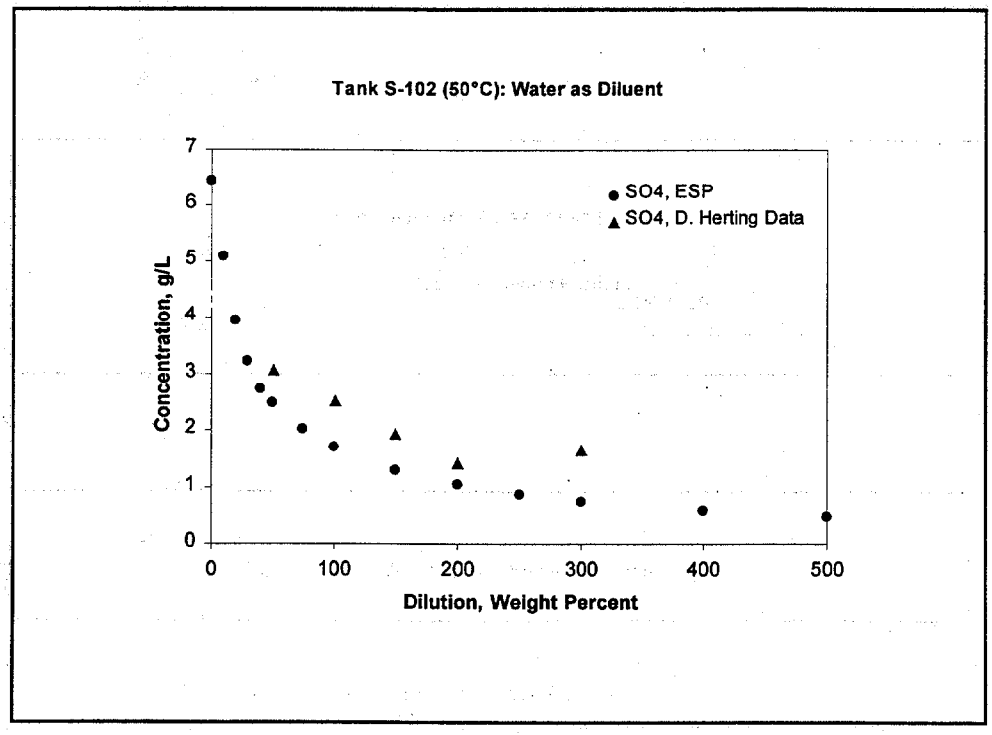
ESP Simulation Results
50°C
1000 g Saltcake Simulant Feed (from Water Analyzer results)
Private NaNO3 Database Used
S-102
Experimental Data from Dan Herting
Diluent Added -Pure Water
Charge Reconciliation with OH-

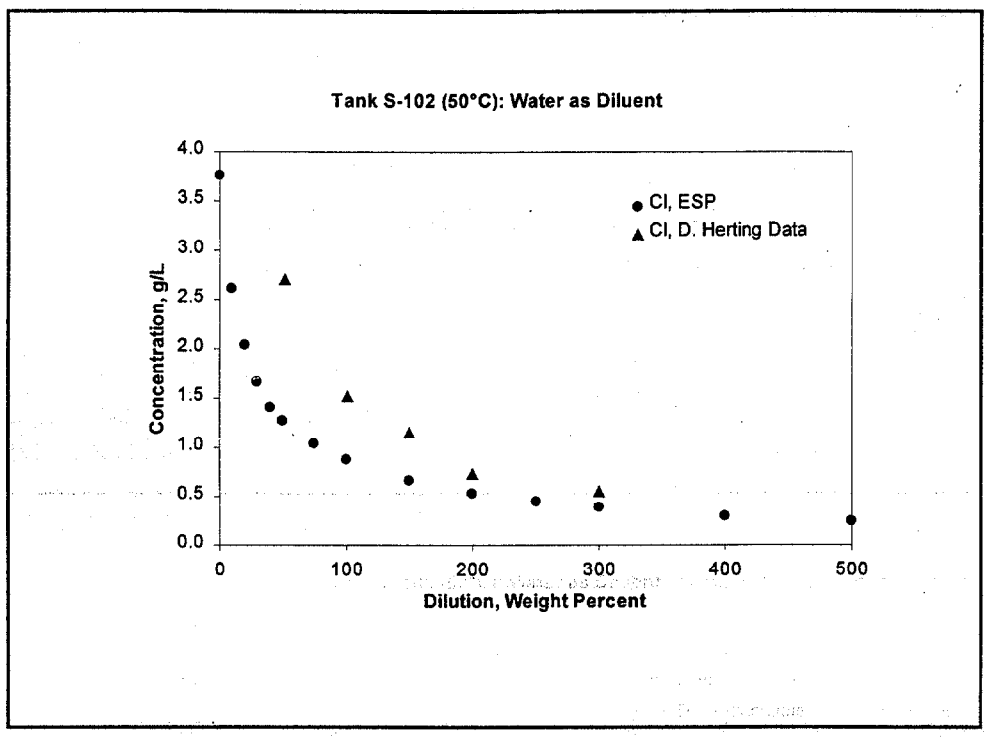
	EXP	ESP	EXP	ESP	EXP	ESP	EXP	ESP	EXP	ESP
% Dilution	51	50	101	100	150	150	200	200	300	300
SpG (g/ml)	1.493	1.392	1.381	1.276	1.285	1.210	1.232	1.169	1.154	1.120
pH		13.8		13.3		13.0		12.8		12.6
Ionic Strength		13.2		7.9		5.7		4.4		3.1
Concentrations in g/L										
TIC	7.29	4.55	3.11	3.13	2.97	2.37	1.67	1.91	1.75	1.37
F		2.44		1.68		1.27		1.02		0.74
Cl	2.71	1.27	1.52	0.87	1.15	0.86	0.74	0.53	0.55	0.38
NO_2	30.40	15.78	17.60	10.84	12.20	8.22	8.90	6.62	5.90	4.76
NO_3	385.00	414.96	431.00	284.91	283.00	216.14	260.00	174.02	168.00	125.04
PO_4	7.47	2.44	4.84	1.68	2.70	1.27	2.42	1.02	1.79	0.74
SO_4	4.36	2.48	2.52	1.70	1.94	1.29	1.41	1.04	1.64	0.75
C_2O_4	-	0.42	0.76	0.92	1.12	0.70	1.03	0.56	0.89	0.41

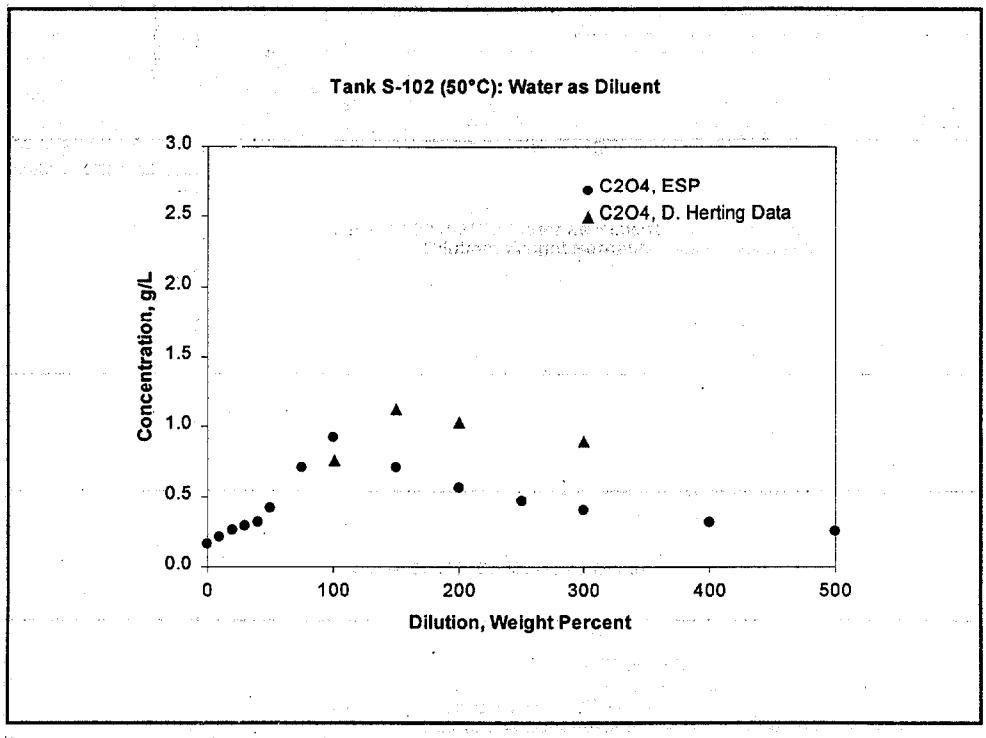

Tank S-102 (50°C): Water as Diluent
NO2, ESP
NO2, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
10
20
30
40
50
0
100
200
300
400
500

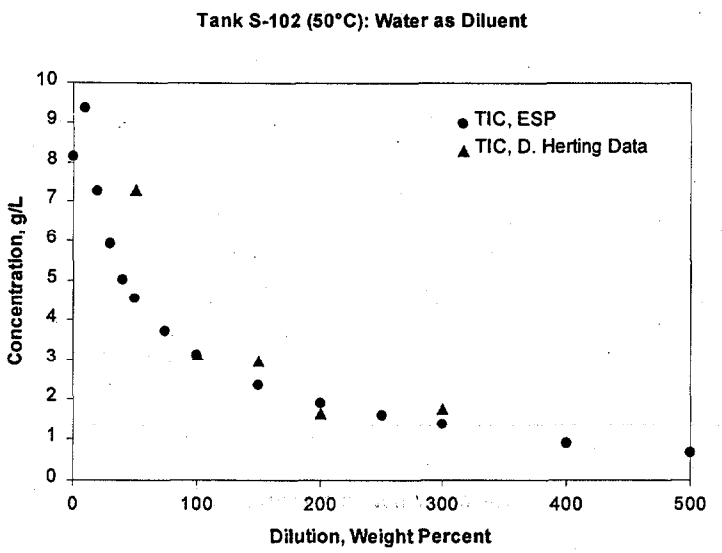

Tank S-102 (50°C): Water as Diluent
NO3, ESP
NO3, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
50
100
150
200
250
300
350
400
450
500
0
100
200
300
400
500


Tank S-102 (50°C): Water as Diluent
PO4, ESP
PO4, D. Herting Data
Concentration, g/L
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
100
200
300
400
500
Dilution, Weight Percent


Tank S-102 (50°C): Water as Diluent
SO4, ESP
SO4, D. Herting Data
Concentration, g/L
7
6
5
4
3
2
1
0
0
100
200
300
400
500
Dilution, Weight Percent


Tank S-102 (50°C): Water as Diluent
Cl, ESP
Cl, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500


Tank S-102 (50°C): Water as Diluent
C2O4, ESP
C2O4, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500

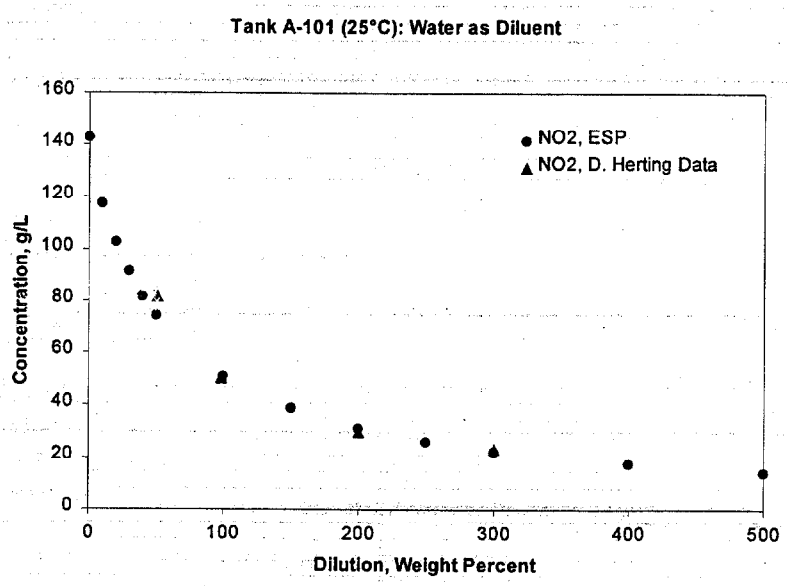


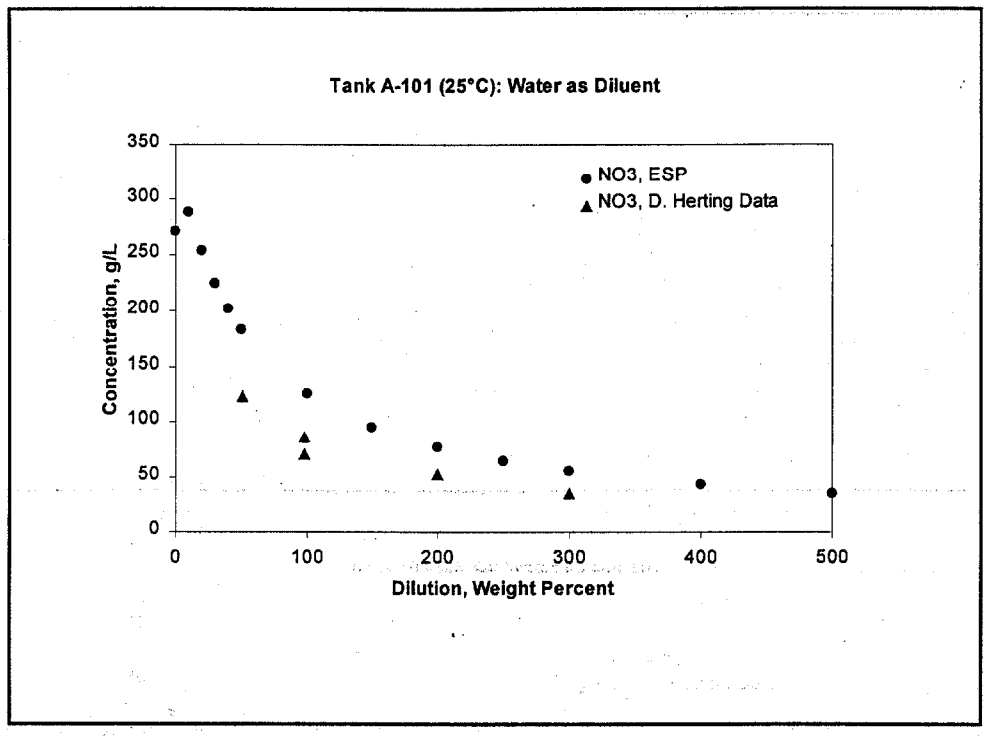
Composition of A-101

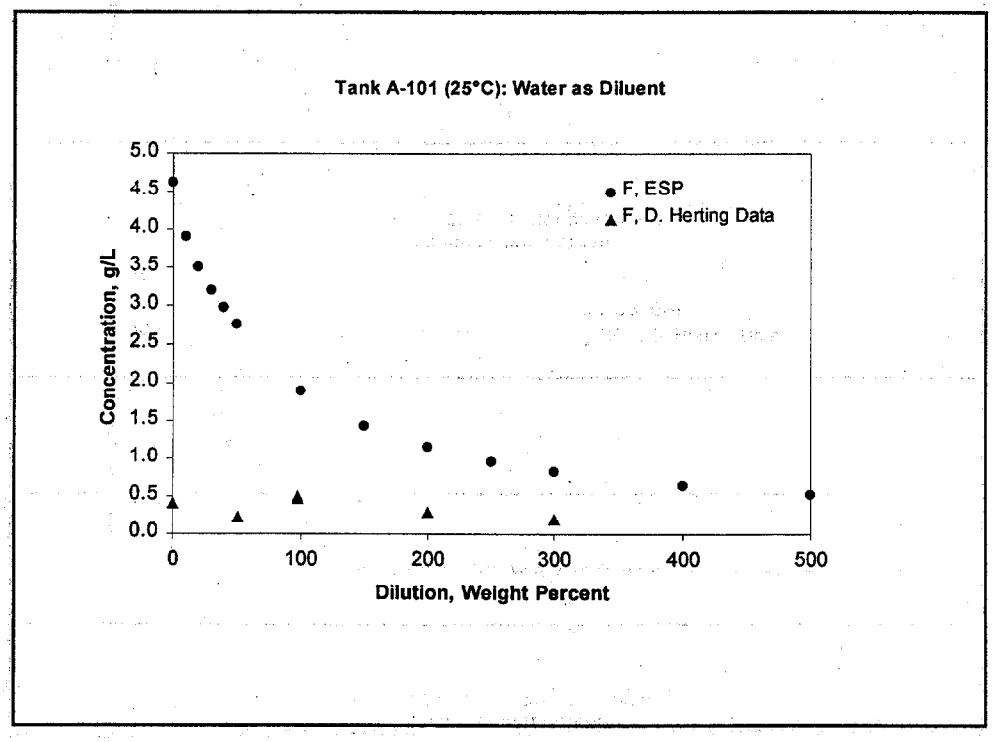
A-101- Previously Reported			A-101 - from Total Seq. Diss.		
	wt.%	mg/L		wt.%	mg/L
Al	2.47	40467	Al	2.39216	40559
Ca	0.023	377	Ca	0.008078	137
Cl	0.39	6389	Cl	0.410284	6956
CO3	5	81916	CO3	9.036525	153215
Cr	0.18	2949	Cr	0.171638	2910
F	0.048	786	F	0.069103	1172
Fe	0.034	557	Fe	0.014469	245
K	0.052	852	K	0.312523	5299
Na	20.6	337495	Na	21.20087	359462
NO2	8.22	134670	NO2	7.428487	125951
NO3	20.3	332580	NO3	12.60358	213695
OH	3	49150	OH	2.097762	35568
Ox	1.03	16875	Ox	1.347261	22843
PO4	0.65	10649	PO4	0.377013	6392
SO4	1.27	20807	SO4	2.437621	41330
Si	0.037	606	Si	0.026912	456
TOC	0.48	7864	TOC	0.367435	6230
U	0.039	639	U	0.034274	581
H2O	37.5	614372	H2O	31.2	528998
SpG	1.66		SpG	1.552	

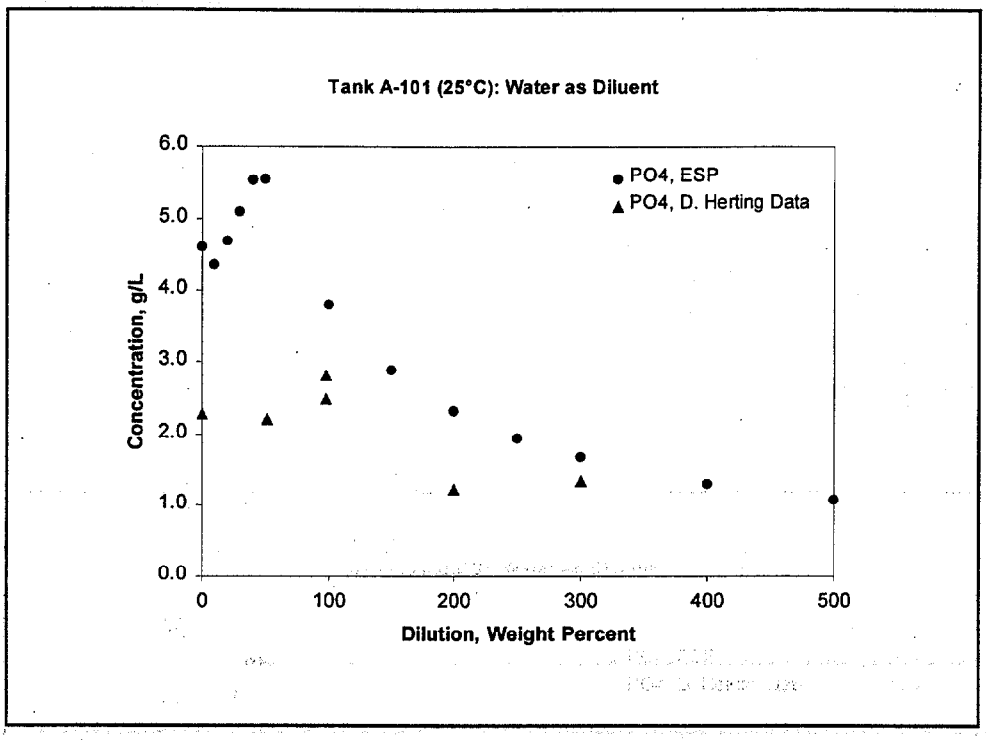
ESP Simulation Results
25°C
1000 g Saltcake Simulant Feed (from Water Analyzer results)
Private NaNO3 Database Used
A-101
Experimental Data from Dan Herting
Diluent Added -Pure Water
Charge Reconciliation with OH-

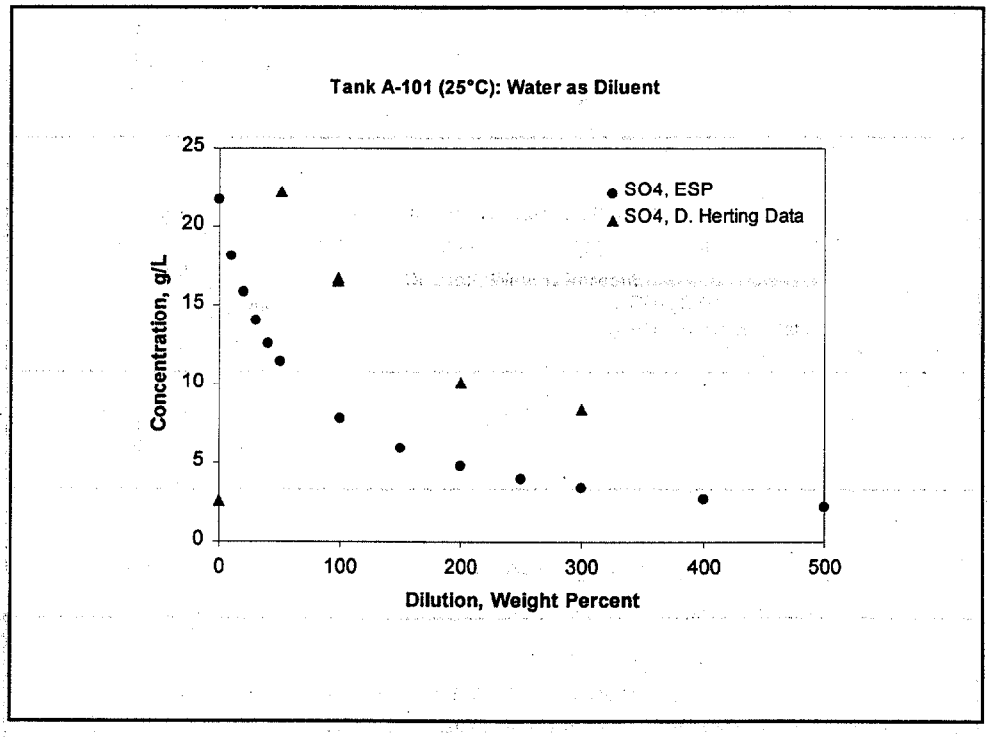
	EXP	ESP	EXP	ESP	EXP	ESP	EXP	ESP	EXP	ESP
% Dilution	0	0	51	50	98	100	200	200	299	300
SpG (g/ml)	1.552	1.514	1.452	1.320	1.348	1.223	1.246	1.140	1.158	1.103
pH		14.5		13.7		13.3		12.9		12.7
Ionic Strength		18.5		9.0		5.8		3.4		2.4
Concentrations in g/L										
TIC	1.24	17.3462	13.33	9.019136	11.50	6.172991	7.52	3.772245	5.25	2.714155
F	0.401	4.62	0.222	2.75	0.50	1.88	0.29	1.15	0.193	0.83
Cl		6.76	4.39	3.52	2.59	2.41	1.55	1.47	1.36	1.06
NO_2		142.59	81.5	74.14	50.60	50.74	29.70	31.01	23.5	22.31
NO_3		271.54	122.5	183.09	85.40	125.31	52.45	76.58	35.2	55.10
PO_4	2.28	4.60	2.2	5.54	2.80	3.79	1.23	2.32	1.34	1.67
SO_4	2.62	21.70	22.2	11.45	16.50	7.64	10.10	4.79	8.44	3.45
C_2O_4		0.19		0.71	0.34	1.33	0.97	2.56	2.86	2.80

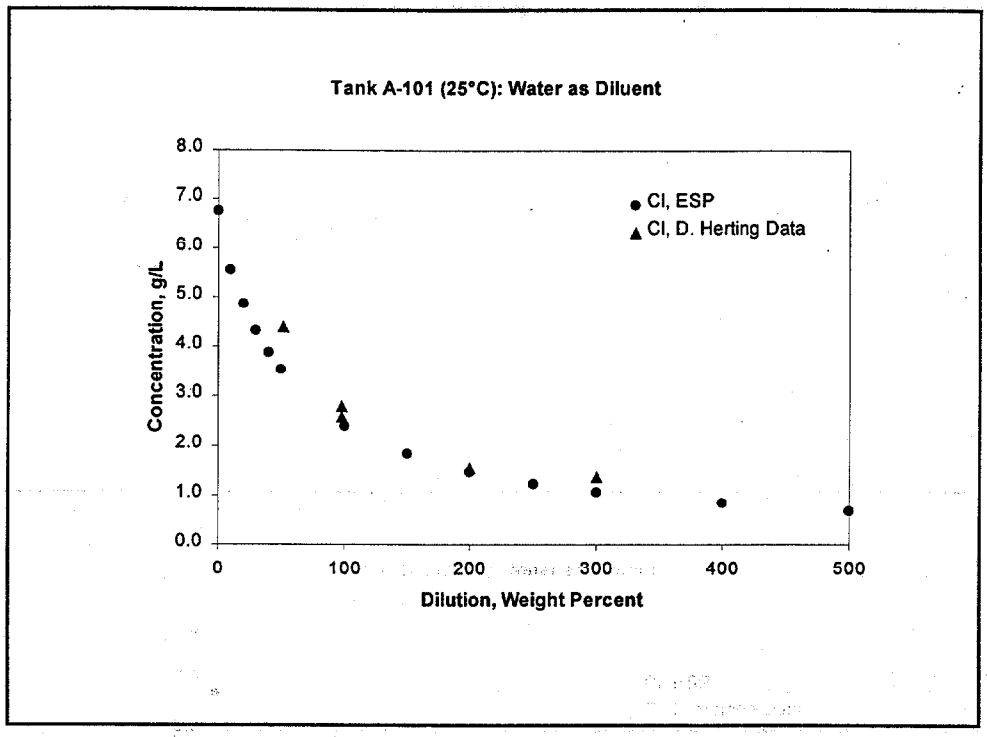


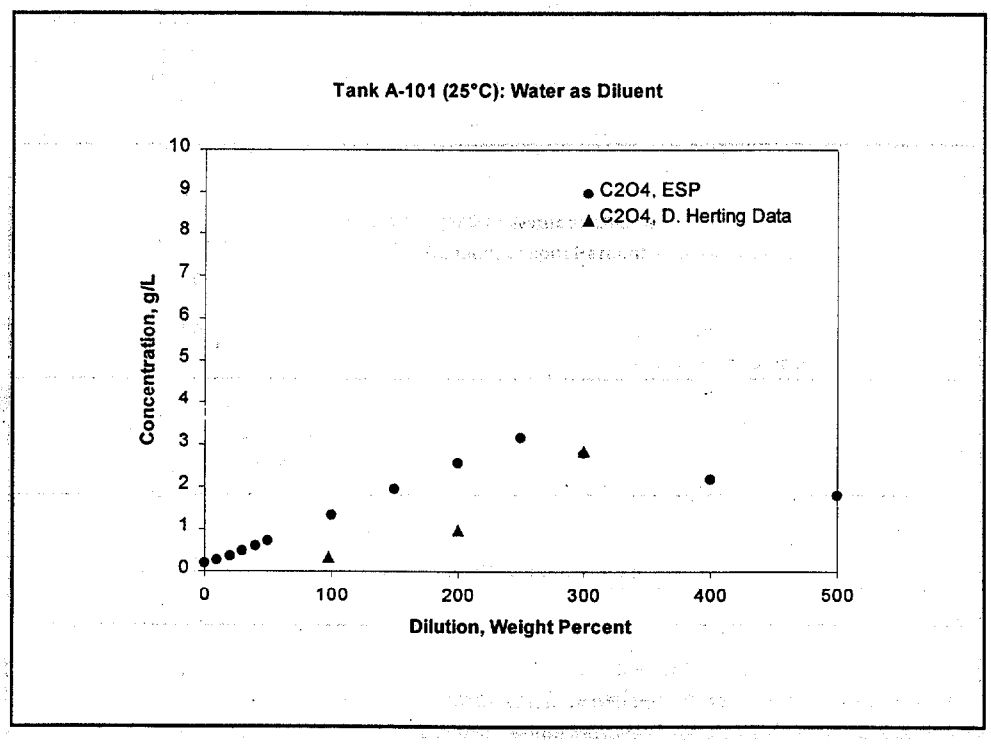

Tank A-101 (25°C): Water as Diluent
NO3, ESP
NO3, D. Herting Data
Concentration, g/L
350
300
250
200
150
100
50
0
0
100
200
300
400
500
Dilution, Weight Percent

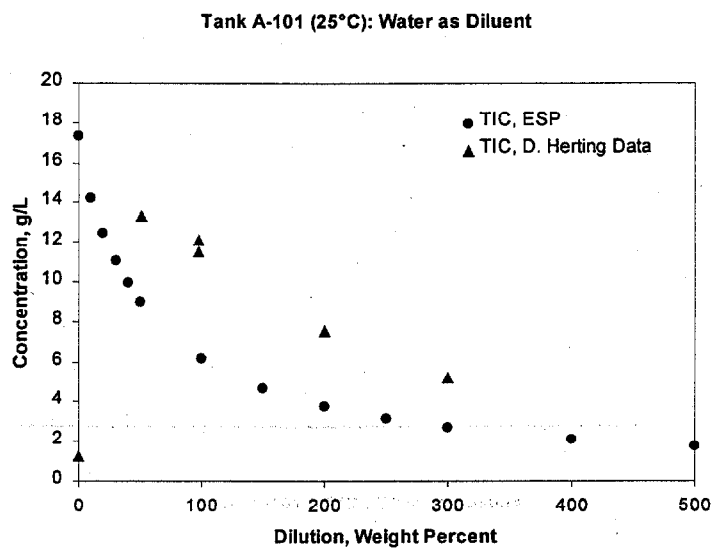

Tank A-101 (25°C): Water as Diluent
F, ESP
F, D. Herting Data
Concentration, g/L
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
Dilution, Weight Percent


Tank A-101 (25°C): Water as Diluent
PO4, ESP
PO4, D. Herting Data
Concentration, g/L
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
100
200
300
400
500
Dilution, Weight Percent


Tank A-101 (25°C): Water as Diluent
SO4, ESP
SO4, D. Herting Data
Concentration, g/L
25
20
15
10
5
0
0
100
200
300
400
500
Dilution, Weight Percent

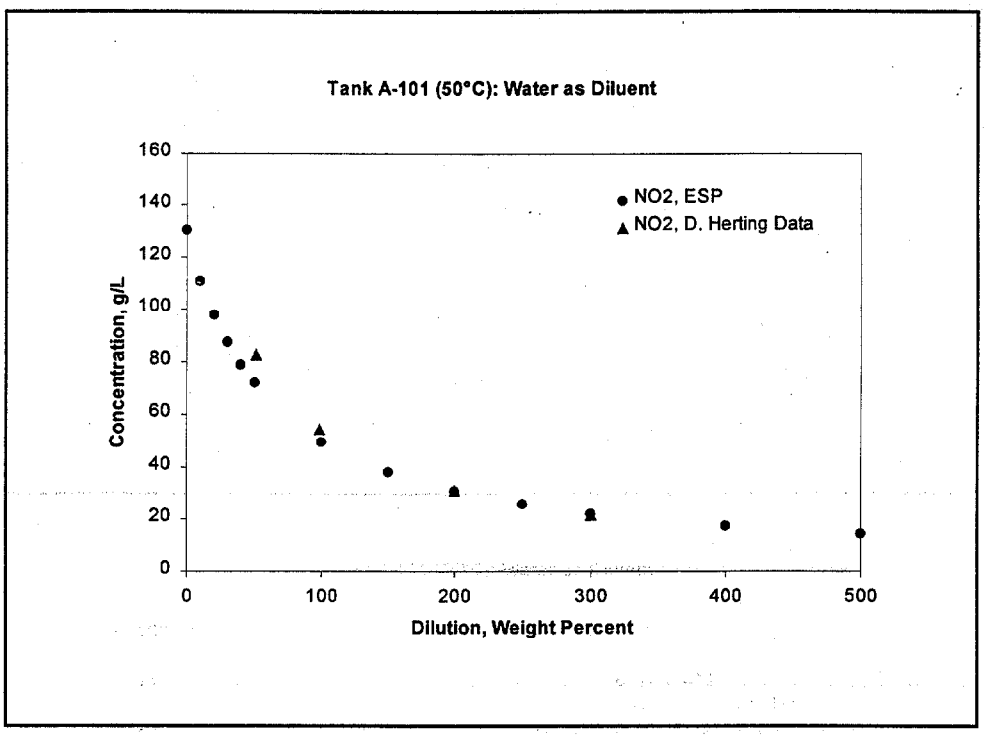

Tank A-101 (25°C): Water as Diluent
Cl, ESP
Cl, D. Herting Data
Concentration, g/L
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
100
200
300
400
500
Dilution, Weight Percent

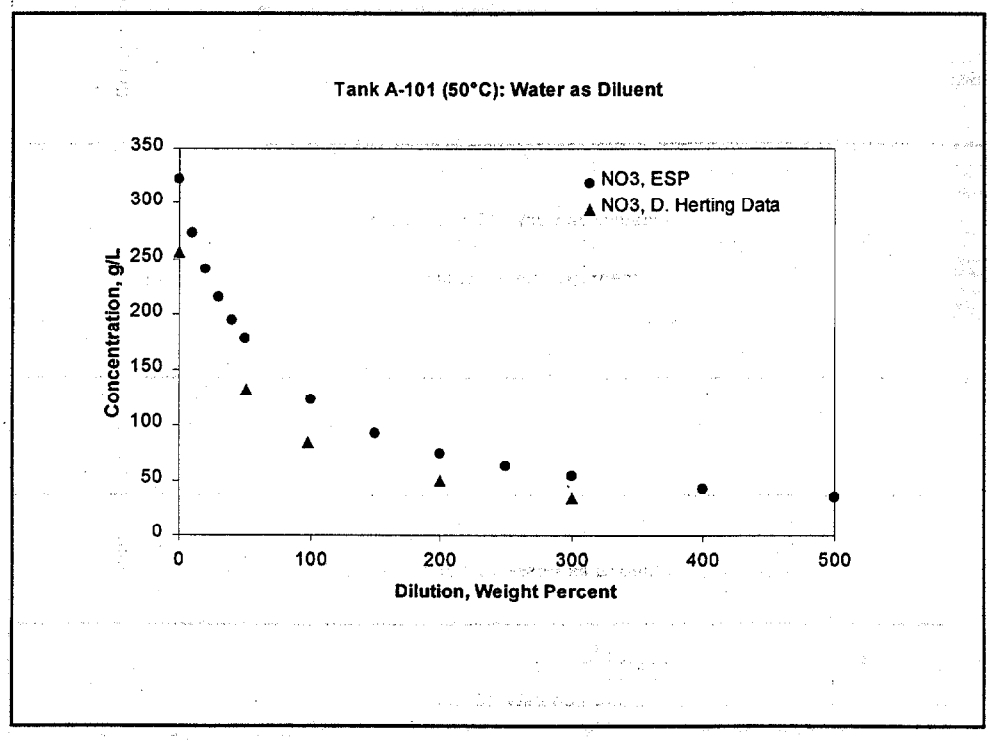

Tank A-101 (25°C): Water as Diluent
C2O4, ESP
C2O4, D. Herting Data
Concentration, g/L
10
9
8
7
6
5
4
3
2
1
0
0
100
200
300
400
500
Dilution, Weight Percent

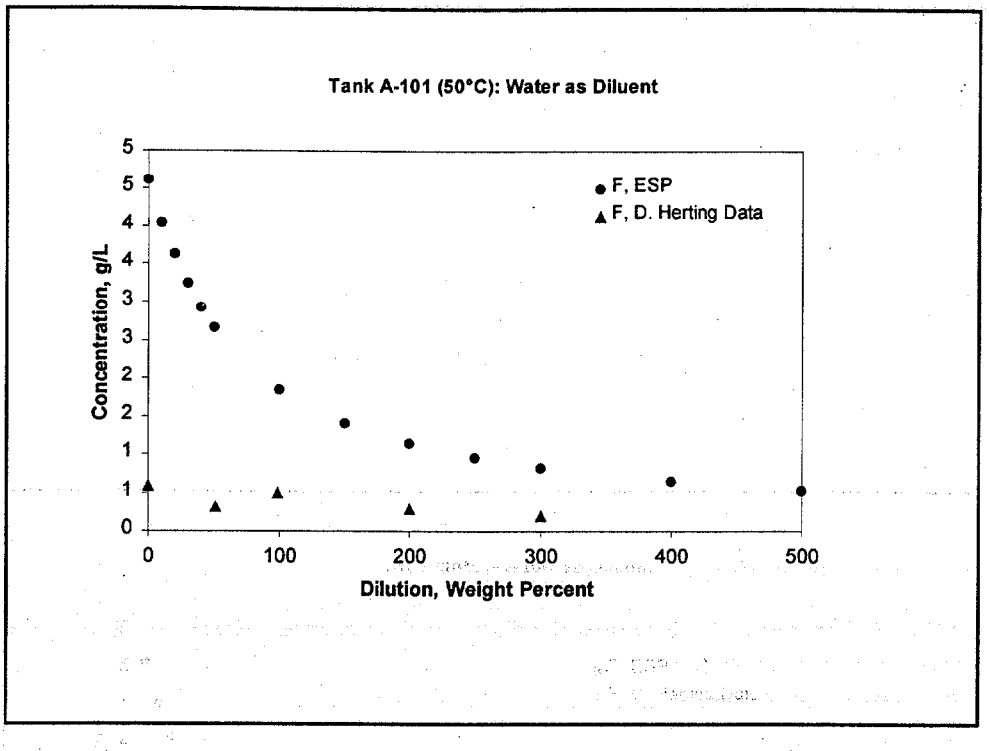


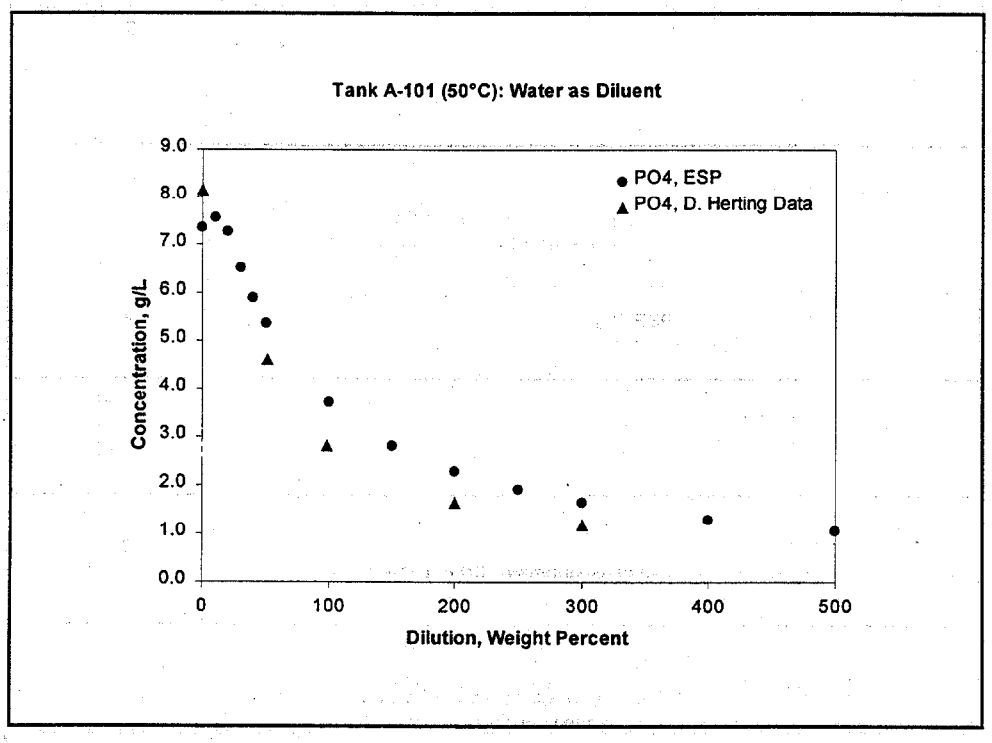
ESP Simulation Results
50°C
1000 g Saltcake Simulant Feed (from Water Analyzer results)
Private NaNO3 Database Used
A-101
Experimental Data from Don Herting
Diluent Added -Pure Water
Charge Reconciliation with OH-

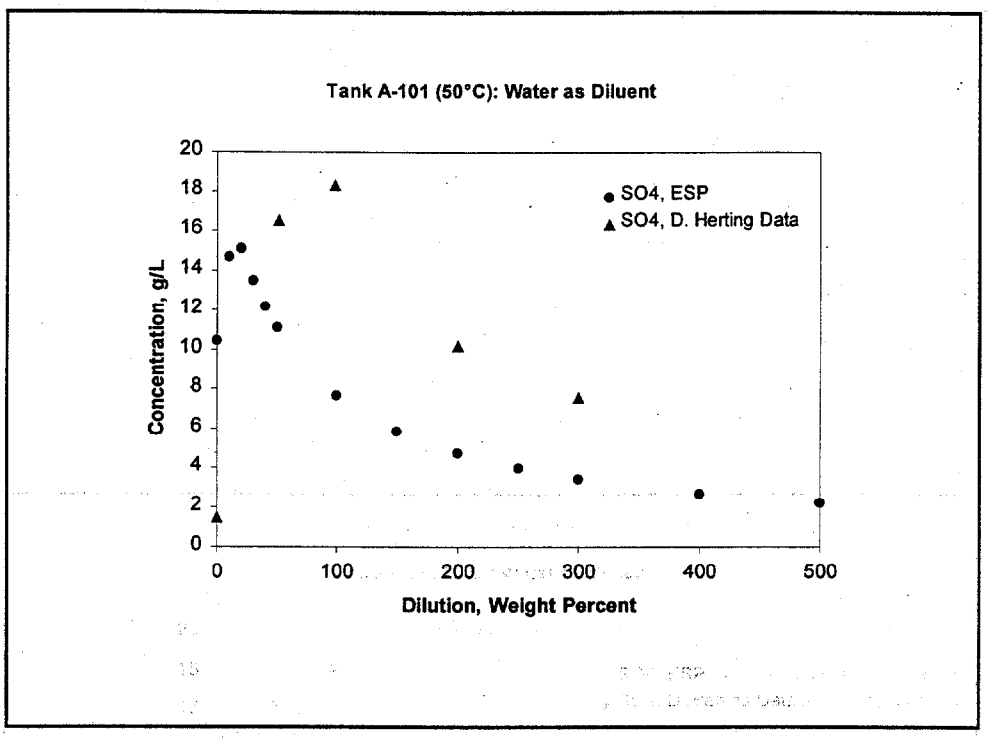
	EXP	ESP	EXP	ESP	EXP	ESP	EXP	ESP	EXP	ESP
% Dilution	0	0	51	50	98	100	200	200	300	300
SpG (g/ml)	1.63	1.443	1.372	1.281	1.321	1.197	1.208	1.123	1.141	1.087
pH		13.5		12.8		12.5		12.1		11.9
Ionic Strength		18.9		9.1		5.9		3.5		2.5
Concentrations in g/L										
TIC	2.02	11.36	11.90	8.74	12.20	6.03	7.15	3.71	5.28	2.68
F	0.60	4.60	0.32	2.67	0.49	1.84	0.29	1.13	0.20	0.82
Cl	9.64	6.19	4.54	3.41	2.94	2.35	1.75	1.45	1.20	1.04
NO_2	173.00	130.38	82.50	71.81	54.50	49.57	30.90	30.48	21.30	21.99
NO_3	256.00	321.97	132.00	177.35	84.95	122.41	50.00	75.27	34.20	54.31
PO_4	8.15	7.37	4.60	5.36	2.81	3.70	1.64	2.28	1.18	1.64
SO_4	1.45	10.44	16.50	11.10	18.30	7.66	10.20	4.71	7.54	3.40
C_2O_4	1.31	0.24		1.03	0.56	1.99	2.32	3.82	3.74	2.76

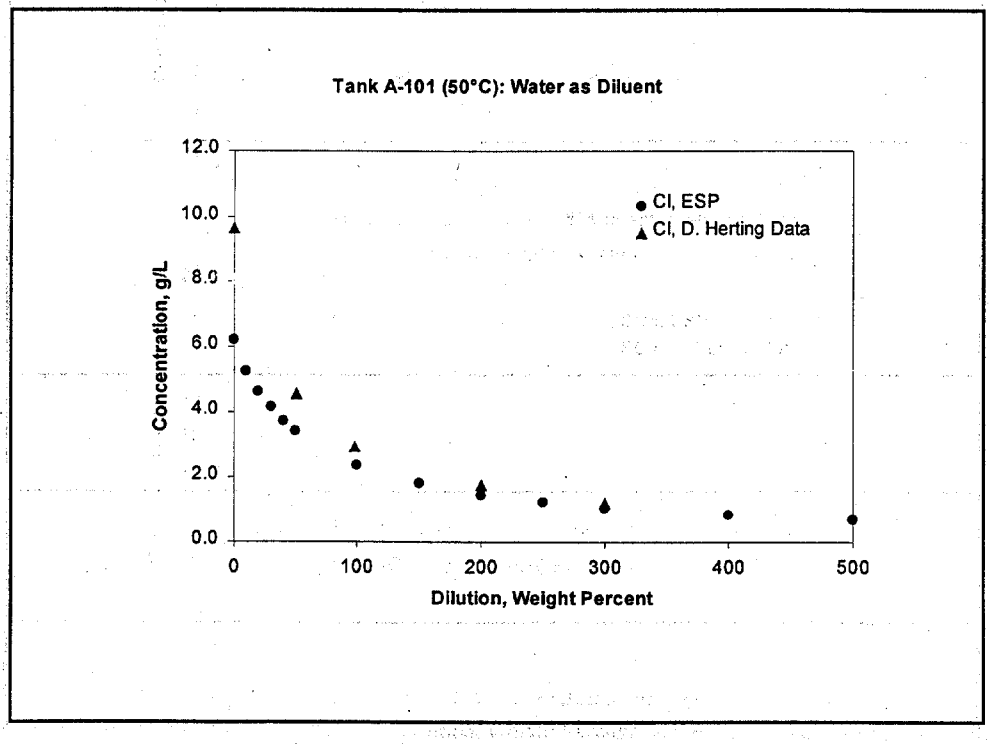

Tank A-101 (50°C): Water as Diluent
NO2, ESP
NO2, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
20
40
60
80
100
120
140
160
0
100
200
300
400
500

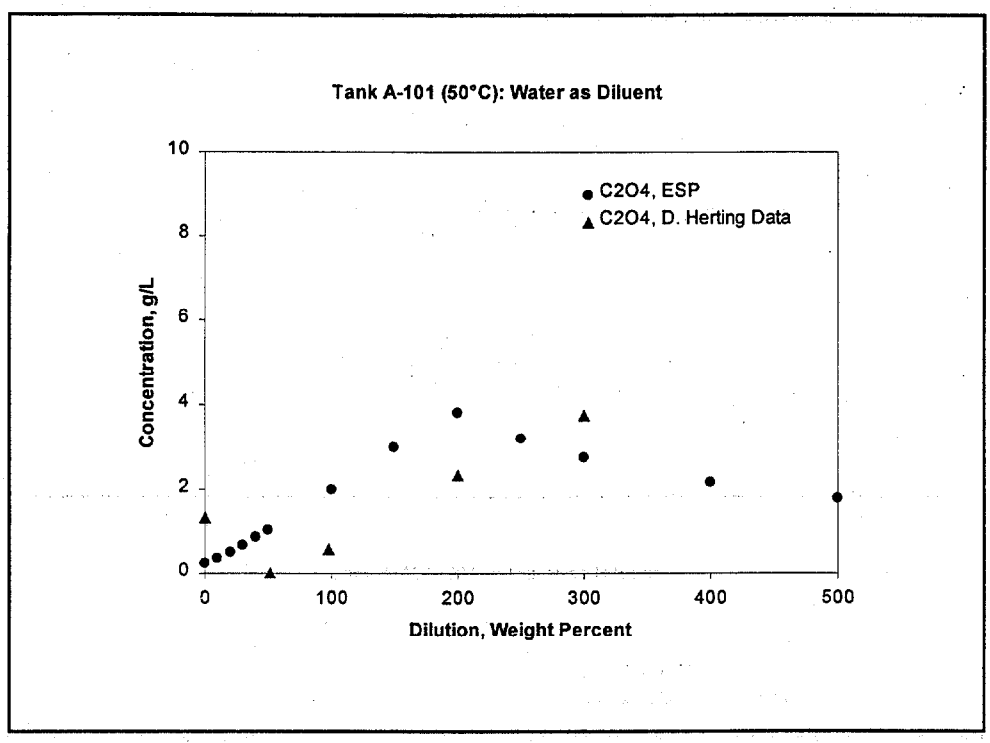

Tank A-101 (50°C): Water as Diluent
NO3, ESP
NO3, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
50
100
150
200
250
300
350
0
100
200
300
400
500

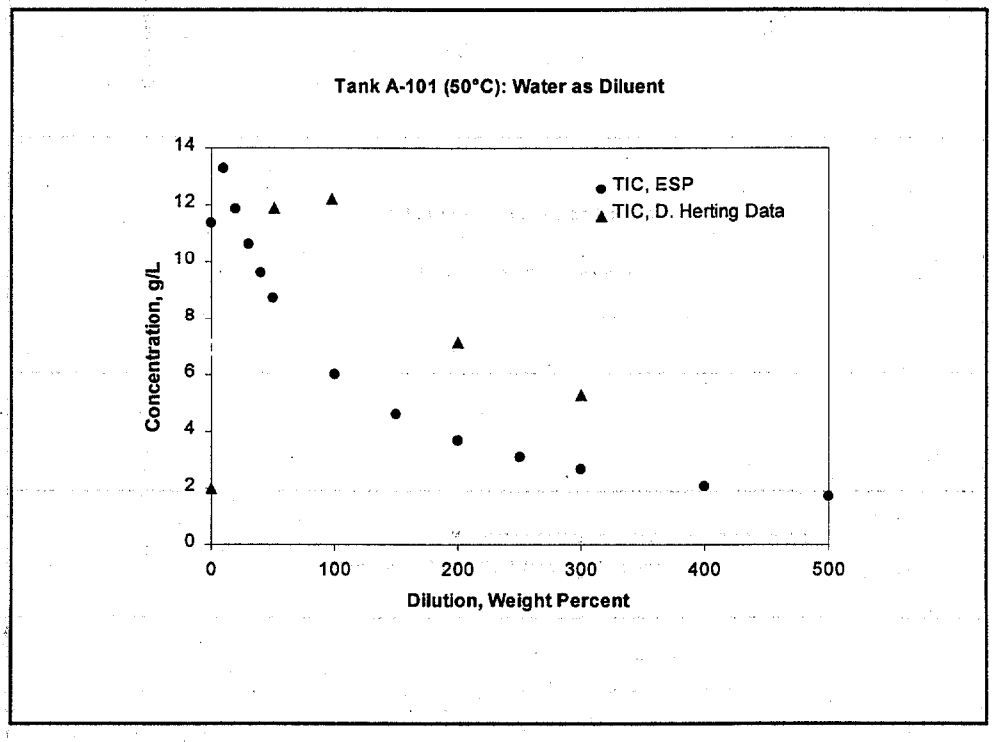

Tank A-101 (50°C): Water as Diluent
F, ESP
F, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
1
1
2
2
3
3
4
4
5
5
0
100
200
300
400
500


Tank A-101 (50°C): Water as Diluent
PO4, ESP
PO4, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
0
100
200
300
400
500


Tank A-101 (50°C): Water as Diluent
SO4, ESP
SO4, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
2
4
6
8
10
12
14
16
18
20
0
100
200
300
400
500


Tank A-101 (50°C): Water as Diluent
Cl, ESP
Cl, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0.0
2.0
4.0
6.0
8.0
10.0
12.0
0
100
200
300
400
500


Tank A-101 (50°C): Water as Diluent
C2O4, ESP
C2O4, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
2
4
6
8
10
0
100
200
300
400
500


Tank A-101 (50°C): Water as Diluent
TIC, ESP
TIC, D. Herting Data
Concentration, g/L
Dilution, Weight Percent
0
2
4
6
8
10
12
14
0
100
200
300
400
500

Summary of S102/A101 Simulation Results

- Noticeable differences between preliminary composite composition and that obtained from TSD
- Qualitative prediction of major anions
- Discrepancies in predicted liquid phase density and experimental value warrant further investigation
- S102 - behavior dominated by presence of $NaNO_3$ (~53% by weight of composite sample)

Path Forward

- Fine tuning of pH, density in Water Analyzer to improve ESP predictions for A101 and S102
- Examine impact of user-supplied density on molecular stream composition
- Use of ESP to simulate BY-102 column test

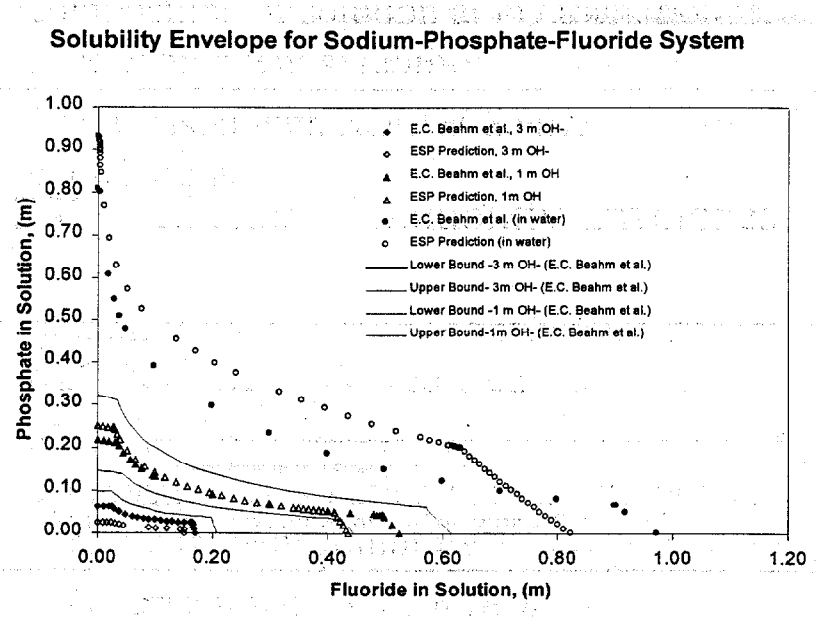
Comparison Studies

Objective - Comparison Studies

- To compare solubility envelopes predicted by ESP with those generated by SOLGASMIX
- To examine influence of uncertainties in ΔG_f on predicted solubility
- Focus on NaF-Na_3PO_4-H_2O system, including $Na_7F(PO_4)_2.19H_2O$

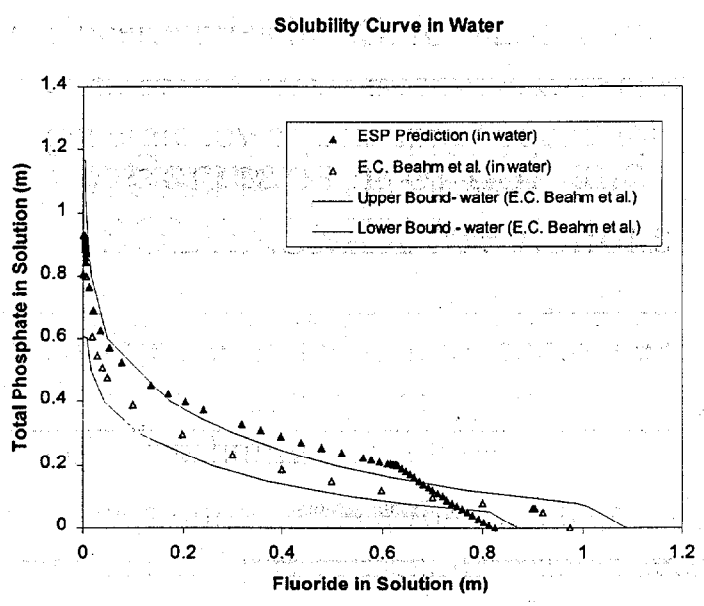
ESP Prediction of Solubility Envelopes

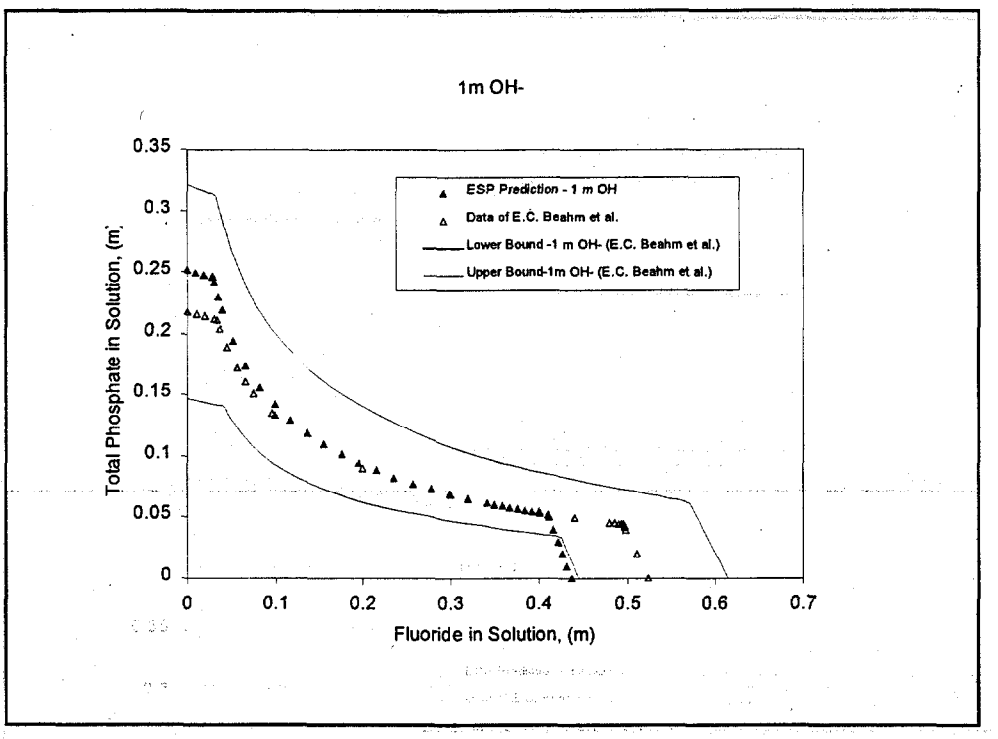
- Solubility for various initial compositions of NaF, Na_3PO_4, H_2O predicted
- Identification of solid phase(s) present, composition of solution at invariant points, pure component solubility
- Comparison with SOLGASMIX calculations

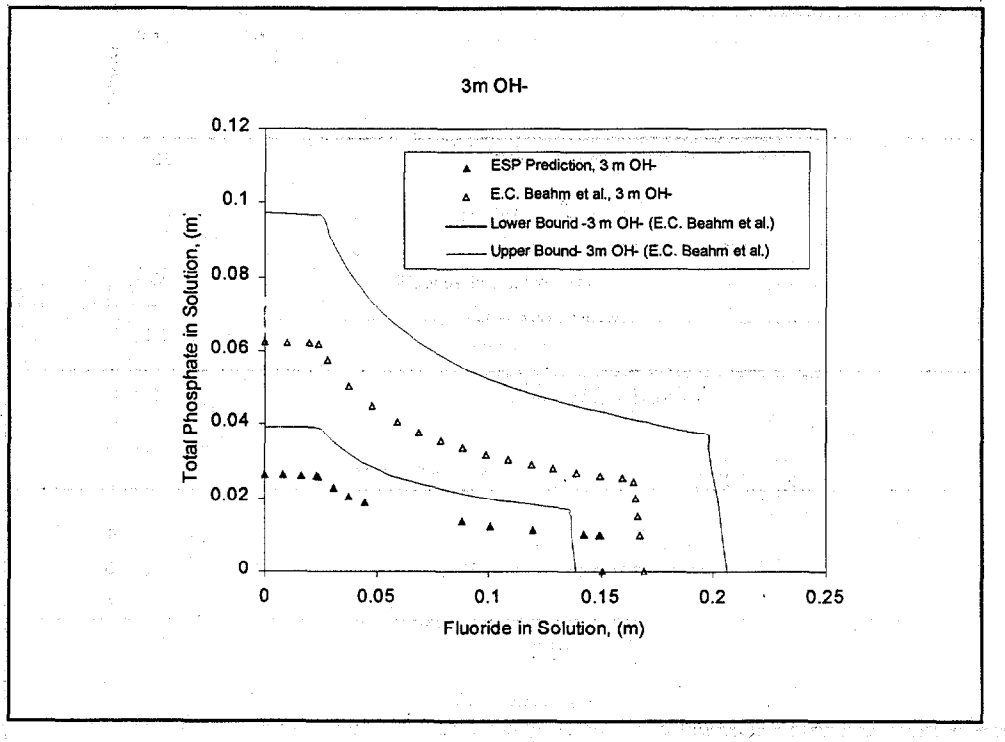


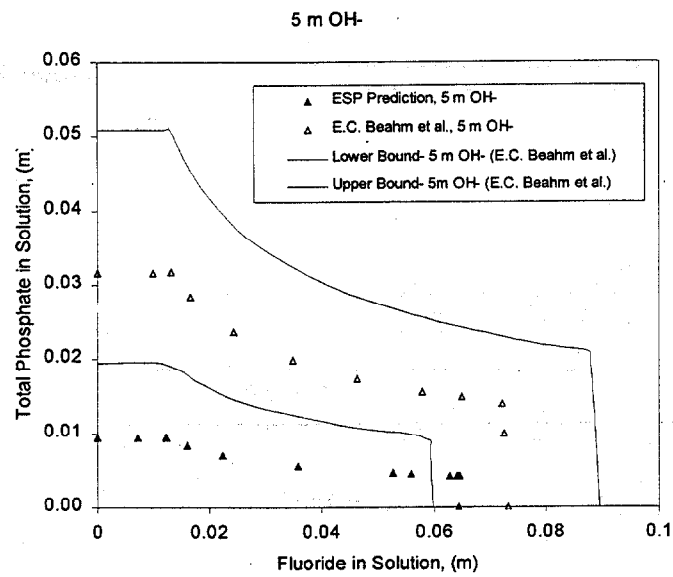
Comparison of ESP and SOLGASMIX Predictions

- Differences noted in pure component solubility, solution composition at invariant points, solubility envelope
- Uncertainties in ΔG_f for various species estimated by E.C. Beahm et al. - used to generate lower and upper bound for SOLGASMIX predictions




1m OH-
ESP Prediction - 1 m OH
Data of E.C. Beahm et al.
Lower Bound -1 m OH- (E.C. Beahm et al.)
Upper Bound-1m OH- (E.C. Beahm et al.)
Total Phosphate in Solution, (m)
Fluoride in Solution, (m)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7


3m OH-
ESP Prediction, 3 m OH-
E.C. Beahm et al., 3 m OH-
Lower Bound -3 m OH- (E.C. Beahm et al.)
Upper Bound- 3m OH- (E.C. Beahm et al.)
Total Phosphate in Solution, (m)
Fluoride in Solution, (m)
0.12
0.1
0.08
0.06
0.04
0.02
0
0
0.05
0.1
0.15
0.2
0.25



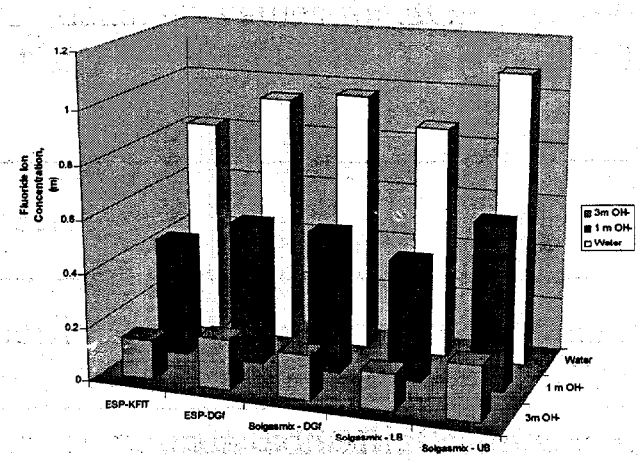
ESP Evaluation

- KFIT used to predict solubility within ESP
  - expression for solubility as a function of temperature
  - coefficients determined by fitting of available experimental data by OLI Systems, Inc.
- ΔG_f, although provided in database, not used for prediction of solubility UNLESS KFIT expression is not available

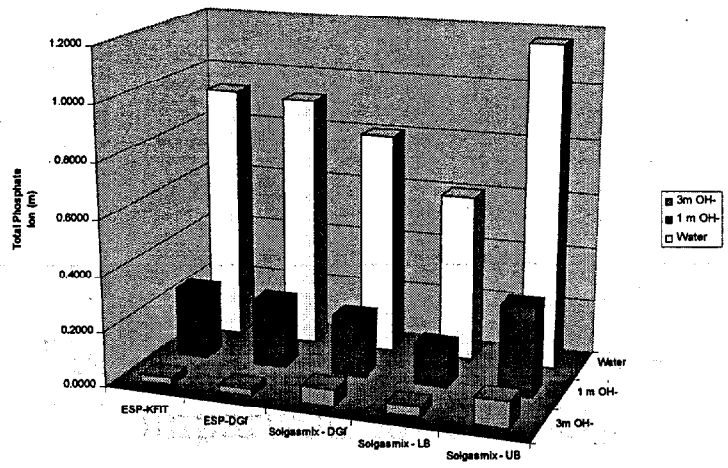
Revision of ESP Prediction

- OLI supplied database entries for relevant species
- Private database generated with KFIT coefficients zeroed out for solid phase of each relevant species
- Pure component solubility estimated using OLI database values for ΔG_f

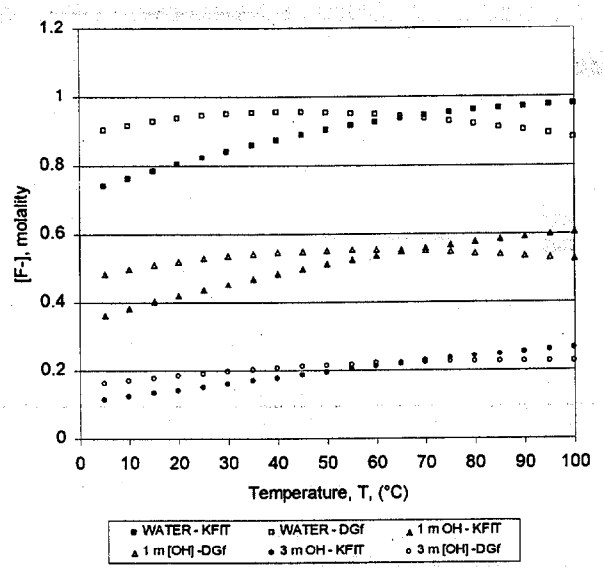
Pure Component Solubility - Comparison for NaF



Pure Component Solubility - Comparison for Na_3PO_4



- Pure component solubility predicted by ESP using database ΔG_f values - comparable to those from SOLGASMIX
- Significant differences in pure component solubility between ESP- ΔG_f and ESP-KFIT for NaF; for Na_3PO_4, differences minimal
- Temperature sweep of solubility for NaF performed to compare ESP- ΔG_f and ESP-KFIT predictions



ESP-ΔG_f versus ESP-KFIT

- As [OH^-] increases, curvature of solubility envelope changes significantly
- ΔG_f predictions - display troublesome behavior as temperature increases - perhaps due to inaccuracies in specific heat information in the database - warrants closer look
- For low temperature range (5 to 55°C), ESP-KFIT predicts lower solubility than ESP-ΔG_f; difference strong function of [OH^-]

Conclusions

- Best to use KFIT when available in ESP, due to uncertainties in specific heat information
- More information on experimental data used to determine KFIT parameters and on how the parameters are determined should be solicited from OLI Systems. Will allow for maximum input into database entries for critical species at Hanford.

APPENDIX C

Numatec Hanford Corporation Presentations

LOCKHEED MARTIN

TWRSO&UP
Revision 1

R. A. (Randy) Kirkbride

May 7, 1999

LOCKHEED MARTIN

TWRSO&UP Team Members

Team Lead - Randy Kirkbride

LAW Feed Staging - Jaiduk Jo

HLW Feed Staging - Tom Crawford/Ted Hohl

SST Retrieval - Dexter Penwell

Waste Inventory Characterization - Linda Fergestrom

Characterization Data Needs - John Baldwin

HTWOS Model - Gail Allen/Rick Wittman

Process Flowsheet - Ron Orme

LOCKHEED MARTIN

TWRSO&UP, Rev.1

- *Purpose*
- *Scope Overview*
- *Key Findings*
- *LAW Staging*
- *HLW Staging*
- *Meeting Waste Feed Specifications*
- *HLW Source Tanks*
- *Project Impacts*
- *SST Retrieval*
- *Risk-Based SST Retrieval*
- *Sampling Needs*
- *Waste Inventory Characterization*
- *Flowsheet*
- *TRWSO&UP Document Key Elements*

LOCKHEED MARTIN

Purpose

- *Engineering analysis for the "Retrieval baseline"*
- *Supports privatization under RL program and budget guidance*
- *Cases represent logical extensions of the program baseline*
- *Investigate alternatives that potentially improve the baseline*
- *Baseline guidance drives work*
- *Primary analysis tool for baseline improvements*

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Scope Overview

- ***Several processing scenarios were analyzed***
- ***Confirm PHMC ability to meet the BNFL Inc. contract***
  - Schedule, Feed quantities, and Feed compositions
- ***Determine feasibility of meeting Tri-Party Agreement SST retrieval milestones***
- ***Assess the impact of different options within the contract boundaries***

LOCKHEED MARTIN

Scope Overview (cont)

- ***Case 0 – Tri-Party Agreement Compliant Baseline***
  - Complies with current TPA milestones (SST retrieval by 2018)
- ***Case 1 - Accelerated BNFL Inc. Extension***
  - Complies with MYWP update guidance (does not include BNFL optimization results)
  - Phase 1 start dates (per BNFL IMP)
  - Phase 2 start dates (FY 2012)
  - Nominal processing rates (including BNFL ramp ups)
- ***Case 3 - Project Planning***
  - BNFL Inc. provides new tanks
  - BNFL Inc. processes Envelope B first
  - LAW feed is staged from AN Farm only
  - AP Farm is available for other uses

LOCKHEED MARTIN

Key Findings

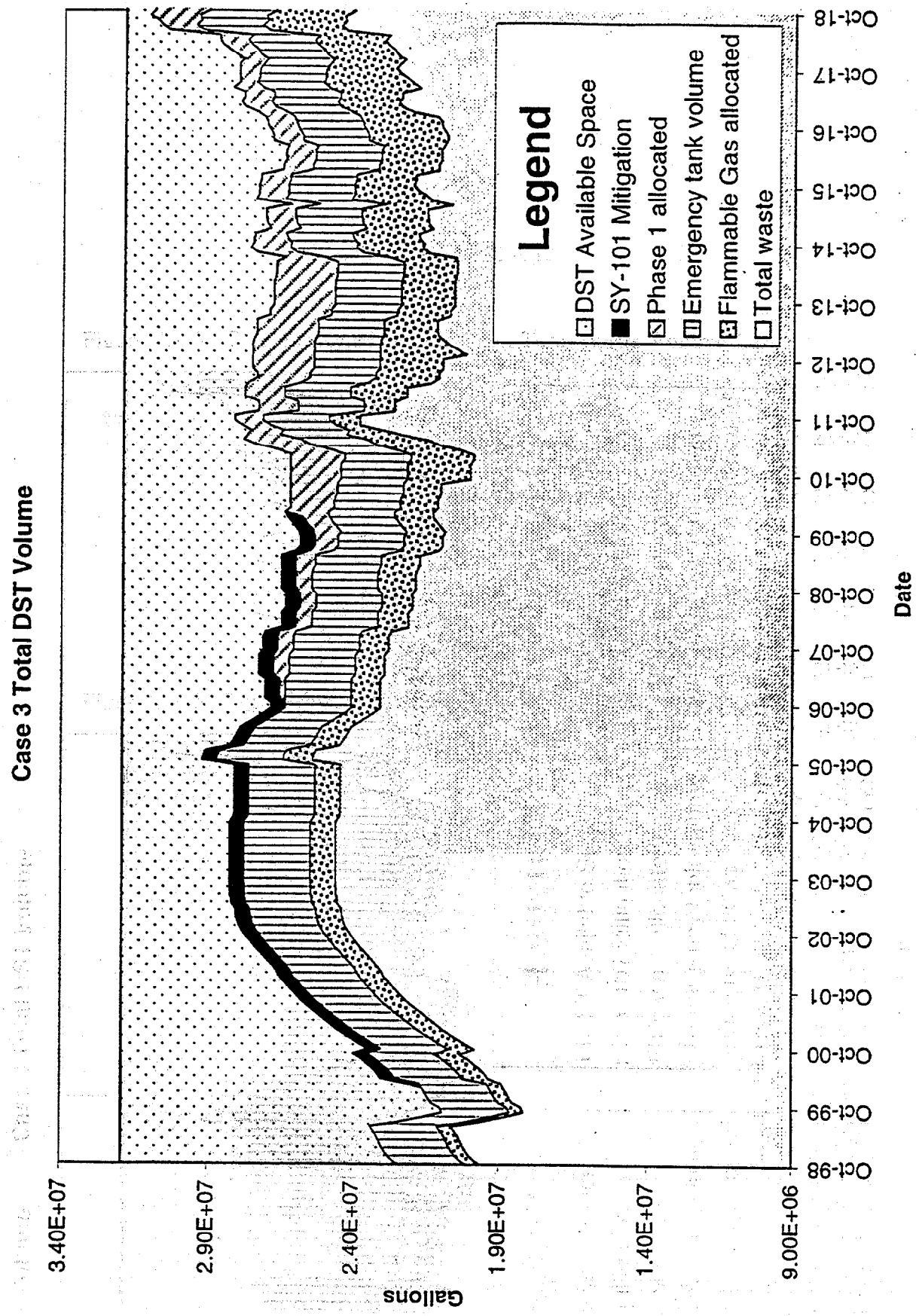
- ***Accelerated BNFL Extension (Case 1)***
  - Viable feed delivery
  - Does not exceed the double-shell tank (DST) tank space available
  - DST space is fully allocated and may not support complete retrieval of 241- SY- 101 for safety mitigation prior to startup of LAW treatment facilities
- ***Project Planning (Case 3)***
  - Viable feed delivery
  - Provides wider margin for PHMC waste storage needs
  - No apparent cost penalty for PHMC

LOCKHEED MARTIN

Key Findings (cont)

- ***Tri-Party Agreement Compliant Case 0***
  - Requires impracticably high and unprecedented SST retrieval and processing rates in Phase 2
  - Original dates based on 30 year mission starting in 1988 and completing SST retrieval by 2018
  - Tank space is not available

Figure 3.1-5. Total Projected Double-Shell Tank Waste Volume Case 3.



LOCKHEED MARTIN

LAW Staging

- *Sufficient LAW waste exists to provide contracted feed quantities*
- *Staged waste projected to meet feed specifications*

LOCKHEED MARTIN

HLW Staging

- *Privatization contract changes have largest impact on HLW feed staging plans*
- *Contract changes include the following:*
  - BNFL Inc. now responsible for HLW pretreatment
  - HLW feed quantity basis has changed
  - HLW feed specifications were revised
  - Requirement added that liquids associated with HLW solids need to meet LAW feed specifications for envelopes A, B, or C.
- *Two additional HLW source tanks identified to provide enough HLW feed*
- *Blending tank wastes increases WOL*

Table 3.1-2. Summary Feed Staging Schedule Case 3.

Delivered feed				Approximate timing[a]			
Envelope	Feed source (static date)	Batch	Units	Staging tank (intermediate tank)	Start retrieval[b]	Begin staging[c]	Start delivery[d]
C	241-AN-107 (static)	1	652	241-AN-106	5/2005	5/2005	10/2005
A	241-AN-104 (static)	2 3	532 566[f]	241-AN-101 241-AN-104	9/2006 10/2007	11/2006 10/2007	1/2008 9/2008
C	241-AN-102 (static)	4 5	548 532	241-AN-106 241-AN-101	8/2007 1/2008	8/2007 1/2008	6/2009 2/2010
A	241-AN-105 (static)	6 7	519 534	241-AN-104 241-AN-105	6/2008 9/2008	8/2008 9/2008	4/2010 2/2011
A	241-SY-101 (static)	8 9	421 306	241-AN-106 (241-AP-106) 241AN-101 (241-SY-102)	3/2010 9/2010	3/2010 9/2010	8/2011 1/2012
A	241-AN-103 (static)	10 11	548 701	241-AN-105 241-AN-103	12/2010 4/2011	2/2011 4/2011	4/2012 11/2012
B[e]	241-AZ-101/ 241-AZ-102	12	637	BNFL	NA	NA	6/2013
A	241-AW-101 (static)	13 14	515 516	241-AN-106 241-AN-101	8/2011 6/2012	10/2011 6/2012	1/2014 6/2014
C	241-AW-104	15	475	241-AN-105	8/2013	8/2013	1/2015
C	241-AP-105 (SWL)[g]	16 17	574 574	241-AN-106 241-AN-101	2/2014 7/2014	2/2014 7/2014	6/2015 12/2015
C	241-AP-104 (SWL)[g]	18 19	499 499	241-AN-105 241-AN-106	1/2015 6/2015	1/2015 6/2015	7/2016 12/2016
C	241-AP-101 (SWL)[g]	20 21	513 513	241-AN-101 241-AN-105	2/2016 7/2016	2/2016 7/2016	7/2017 11/2017

NA = Not applicable

[a]All dates are based on the operating scenario and are subject to change within the contract and ICD limits.

[b]The Start Retrieval date applies to the source tank and includes the 60 days allocated for controlled degassing of waste in the watch-list tanks.

[c]The Begin Staging is when feed for this batch is first transferred into the intermediate feed staging tanks.

[d]Start delivery date to Private Contractor

[e]Pretreated supernate waste from 241-AZ-101 and 241-AZ-102 will be treated as Envelope A waste.

[f]Decantation of the supernatant liquid from tank 241-AN-104 leaves settled solids that are high in sulfate. Retrieval of all the waste in this tank as a slurry should alleviate the high sulfate problem.

[g]SWL – salt well liquor..

The DST processing sequences for Case 3 are shown in Section 3.1.1.5. The waste transfers and certain precedence relationships directly needed to implement the LAW portion of the operating scenario are shown on the schedule. The full set of transfers are included in Appendix H, Table H-3.

Case 3 offers an improved approach to management of tank space over Case 1. A Private Contractor's tank (instead of tank 241-AP-106) is used for feed staging, adding much needed tank space. Furthermore, pretreated Envelope B waste would not be returned to PHMC/DOE and processed as Envelope A waste after sulfate was removed. Moreover, the entrained solid will be stored at the BNFL Inc. facility. This option will utilize tanks 241-AN-101 and 241-AN-106 as feed staging tanks rather than tanks 241-AP-102 and 241-AP-104.

3.2.1 Results and Conclusions

The following section presents the results and conclusions for the HLW feed staging plans in Cases 3, 6b and 1. Case 3 represents the baseline for planning purposes.

3.2.1.1 Case 3

3.2.1.1.1 Operating Scenario - Case 3. The baseline HLW operating scenario refers to the waste transfers and other operational activities needed to deliver HLW feed to BNFL Inc. The major bases and assumptions governing this operating scenario are discussed in Appendix A. The operating scenario is summarized in Table 3.2-1.

Table 3.2-1. Summary Feed Staging Schedule – Case 3.

Available feed			Approximate timing[a]				
Batch Group	Source tanks	Staging tank	Start retrieval[b]	Begin staging[c]	First batch ready	Batch	Batch delivered[e]
1	AZ-101	AZ-101	-	10/2003	1/2004	1	10/2004
						6	6/2006
2	AZ-102	AZ-102	-	7/2005	10/2005	7	6/2006
						12	10/2006
3	AY-102/C-106 AW-103 (20%)	AY-102	1/2006	1/2006	5/2006	13	4/2007
						18	1/2009
4	AY-101 AW-103 (30%)	AY-101	10/2007	10/2007	2/2008	19	2/2009
						26	4/2011
5	SY-102 AW-103 (40%)	AZ-101	4/2010	10/2010	1/2011	27	7/2011
						32	3/2014
Phase 1B-Prime HLW Feed							
6	C-104 (50%) AW-105 (50%)	AZ-102	2/2009	7/2011	7/2013	33	7/2014
						39	10/2015
7	C-104 (50%) AW-105 (50%)	AY-101	3/2013	3/2013	7/2013	40	12/2015
						47	6/2017
8	C-102 (50%) AW-105 (50%)	AZ-101	3/2014	3/2015	7/2016	48	7/2017
						53	10/2018
9	C-102 (50%) AW-105 (50%)	AY-102	3/2016	3/2016	7/2016	54	12/2018
						59	4/2020

[a]All dates are based on the operating scenario and are subject to change within the contract and ICD limits. The dates listed assume projected retrieval efficiencies, which are found in Appendix A. Since 100% retrieval would deliver more feed than is expected, dates could be later than shown except for the 1st and 13th batches which are fixed by contract dates.

[b]The Start Retrieval date applies to the earliest source tank listed in a batch group. Retrieval schedules for each source tank are provided in the Mission Summary Diagram – Case 3, Appendix I.

[c]The Begin Staging date is when feed for a batch is first transferred into the HLW feed staging tank.

[d]The Batch Ready date (static date) includes the 114-day limit in the proposed feed delivery protocol, where applicable.

[e]First and last delivery dates for specific batch group to Private Contractor (BNFL Inc. pretreatment feed receipt tanks).

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HLW Staging (cont)

- *Addition of 30 percent more feed material does not increase overall glass production*
- *Currently identified HLW source tanks provide just enough sludge to produce 600 canisters required by the contract*
- *Recommend adding or substituting HLW source tanks for C-102 and C-104*
- *Evaluating alternative or additional HLW source tanks*

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HLW Staging (cont)

- *HLW batches not fully comply with current specifications even when source tanks are blended*
- *Proposed blends just outside HLW feed specification limits*
- *Liquids associated with sludges are further out-of-specification*
- *Specification compliance issues do not drive vendor costs or viability*
- *Specification compliance issues resolved by adjusting envelopes to match available feed.*

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Meeting Waste Feed Specifications

- *May require revision of contract or feed batch adjustment for both HLW and LAW feed batches*
- *Discrepancies can be accommodated with contract modifications*
- *Discrepancies do not pose technical threat to privatization flowsheet viability*

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HLW Source Tanks

- *Identified source tanks provide the minimum 600 canisters required by Phase 1 contract*
- *Blending HLW feeds increases waste oxide loading and therefore increases the amount of waste processed.*
- *Revised inventory estimates indicate 241-C-104 inventory reductions*
- *Alternate feeds can be blended and used in place of C-102 and C-104*
  - AW-103, SY-102, and AY-101
- *Option provides sufficient feed (over 800 canisters) and frees additional DST space.*

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Project Impacts

- ***WFD schedules for HLW and LAW support continuous BNFL Inc. operations for Cases 1 and 3 at Phase 1 rates***
- ***Current suite of tank farm project scopes and schedules support Case 1***
- ***Case 3 can be adopted if projects are realigned***
  - Project capital costs appear to be off setting
  - Adjustment in LAW source tanks, new transfer routes, and new transfer pit can be added to current projects without technical complications

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SST Retrieval

- ***Privatization contract changes impacted SST retrieval plans***
- ***Delay in starting HLW and LAW processing reduces available DST space***
- ***No DST space available to retrieve tanks beyond C-106 demonstration***
- ***LAW processing needed to free up space for SST retrieval***
- ***Delays do not allow any SST retrieval interim target milestones to be met***

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SST Retrieval (cont)

- *BNFL Extension (Case 1)*
- *HLW glass production rate adequate to complete by 2026 TPA milestone*
  - Average of 7.2 MT/day; design capacity of 12 MT/day
  - 2012 Phase 2 start date
  - Glass volume estimated by PNNL glass properties model

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Risk-Based SST Retrieval

- ***Phase 1 Portions of Case 1 or 3 coupled with Phase 2 risk-based SST retrieval sequence***
- ***Case 1***
  - Can complete by 2026 by ramping up to higher processing capacities
    - 120 MT/day LAW and 12 MT/day HLW
  - Assumes Phase 2 start date of FY 2012 (based on MYWA update guidance)
  - Mission completion is limited by processing rates not retrieval rates
- ***Case 3***
  - Completes by 2041
    - Peak capacity, ~60 MT/day LAW and ~6 MT/day HLW
  - Phase 2 start date of FY 2018

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Sampling Needs

- *Minimal sampling is required to complete to meet Phase 1B Waste Feed Delivery needs*
- *Sampling needed for 4 tanks; AZ-101, AZ-102, C-106 (in AY-102) and C-102*
- *Phase 1 tank sampling (except AZ-101) completion expected by end of CY 1999*
- *Phase 1 Testing and analysis completion expected by end of 2000*
- *Revision of source tank list will require review of Characterization data needs and may require additional sampling*

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Waste Inventory Characterization

- ***Existing plans and flowsheets updated with:***
  - Tank-by-tank BBI data (as of October 1, 1998)
  - Most recent water wash data for each tank
  - Caustic wash data applied to HLW feed calculations
  - Additional data and data manipulation needed to supplement BBI data for HTWOS model
- ***Additional work included:***
  - Partitioning wastes into water-soluble and water-insoluble phases
  - Accounting for waste transfers not included in BBI
  - Adding data for BNFL contract analytes not in BBI

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Flowsheet

- *Content and volume of IHLW and ILAW in reasonable agreement with expectations*
- *First use of tank specific inventory data and new set of water solubility data with HTWOS model*

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TWRSO&UP Document Key Elements

- *Phase 1 Low-Activity Waste (LAW) Feed Staging Plans*
- *Phase 1 High-Level Waste (HLW) Feed Staging Plans*
- *Phase 2 SST Retrieval Sequence--Section 4.3*
- *Process Flowsheet Summary Basis for Phase 1 and 2*
- *Hanford Tank Waste Operating Simulator Model Description*
- *Constraints, Requirements, and Assumptions*
- *Tank Characterization and Inventory Description*

Overview of Key Findings

- *The BNFL Extension (Case 1) is viable from a feed delivery standpoint and does not exceed the double-shell tank (DST) tank space available. However the space is fully allocated and may not support complete retrieval of 241-SY-101 for safety mitigation prior to startup of LAW treatment facilities.*

- *A new scenario (Case 3) has been identified which offers additional tank space, avoids vendor returns, avoids some Phase 1 capital project costs, and improves the reliability of waste feed delivery in Phase 1. Key elements of this scenario are:*
  - *BNFL Inc. provides new tanks such that no feed or solids are returned*
  - *BNFL Inc. processes envelope B first such that DST storage is not required*
  - *LAW feed is staged from AN Farm only – simplified interface*
  - *AP farm is available to "store" salt well liquor and 241-SY-101 safety mitigation wastes – and "stage" backup LAW feed (same wastes)*

  This case is also viable and provides a wider margin for PHMC storage needs with no apparent cost penalty for the PHMC.

- *The Tri-Party Agreement compliant Case 0 requires impractically high and unprecedented retrieval and processing rates in order to meet the Tri-Party Agreement SST end dates. The original dates were based on a 30 year mission in 1988 and was envisioned to complete SST retrieval by 2018.*

- *The available waste won't meet all the criteria in the new feed specifications. The out-of-specification analytes should not represent any technical challenge in processing the waste and only minor modifications to the contract feed specifications will be required to correct the specification compliance problem.*

- *HLW source tanks have been identified to provide a contingency margin above the minimum of 600 canisters required by the Phase 1 contract. Blending feeds from 241-AW-103, 241-SY-102, 241-AP-102, and 241-AY-101 reduces life-cycle cost, improves the reliability of feed delivery and frees additional DST space.*

- *The current suite of projects are aligned to support case 1. If Case 3 is adopted, projects will require additional realignment to support privatization. Costs are approximately off setting.*

- *The Phase 1 portions of Case 1 or 6b coupled with a new risk-based SST retrieval sequence for Phase 2 can be completed by 2028 by ramping up to higher processing capacities provided by BNFL Inc. (120 MT/day LAW and 12 MT/day HLW). This assumes a Phase 2 start date of 2012 based on the MYWP update guidance.*

Hanford Contributors FY 1999

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FY99 TASKS

Task A - Batch Dissolution (A-101, S-102)

90% complete

Task B - Column Dissolution (BY-102)

30% complete

Task C - Solids Characterization (BY-102)

50% complete

Task D - Feed Stability (tanks TBD)

5% complete

Task A - Batch Dissolution

- Tanks A-101 & S-102
  - A-101: mixed salts; wet; "upside down"
  - S-102: high nitrate; dry
- Sequential Dissolution (ESP Input)
- Series Dissolution (ESP Output)

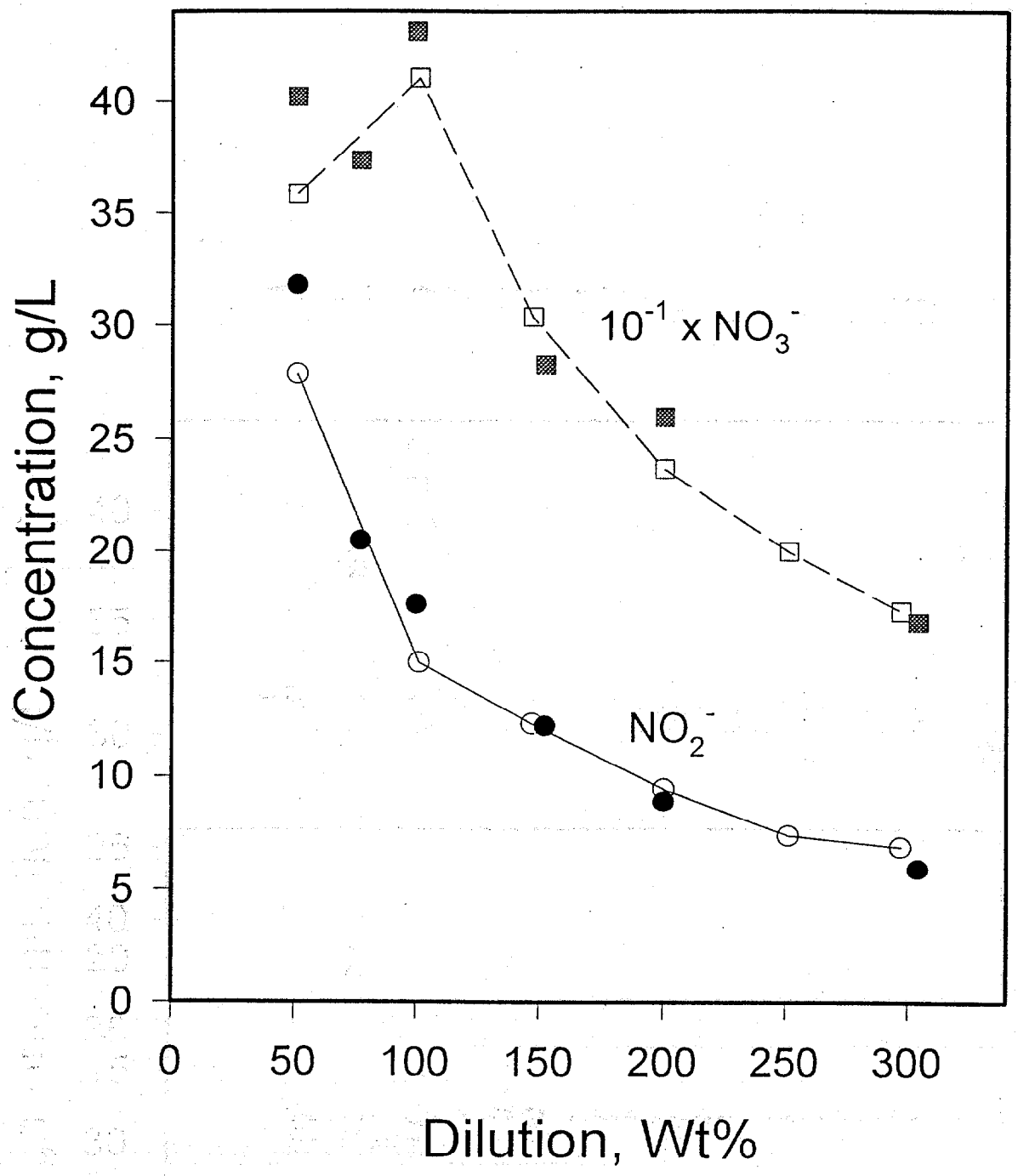
Sequential Dissolution (ESP Input)

- Mix 60 g Saltcake & 60 g H_2O
- Centrifuge; analyze Wash #1
- Add 60 g H2O to Undissolved Solids
- Mix, centrifuge, analyze Wash #2
- Analyze Undissolved Solids
- Calculate Overall Composition

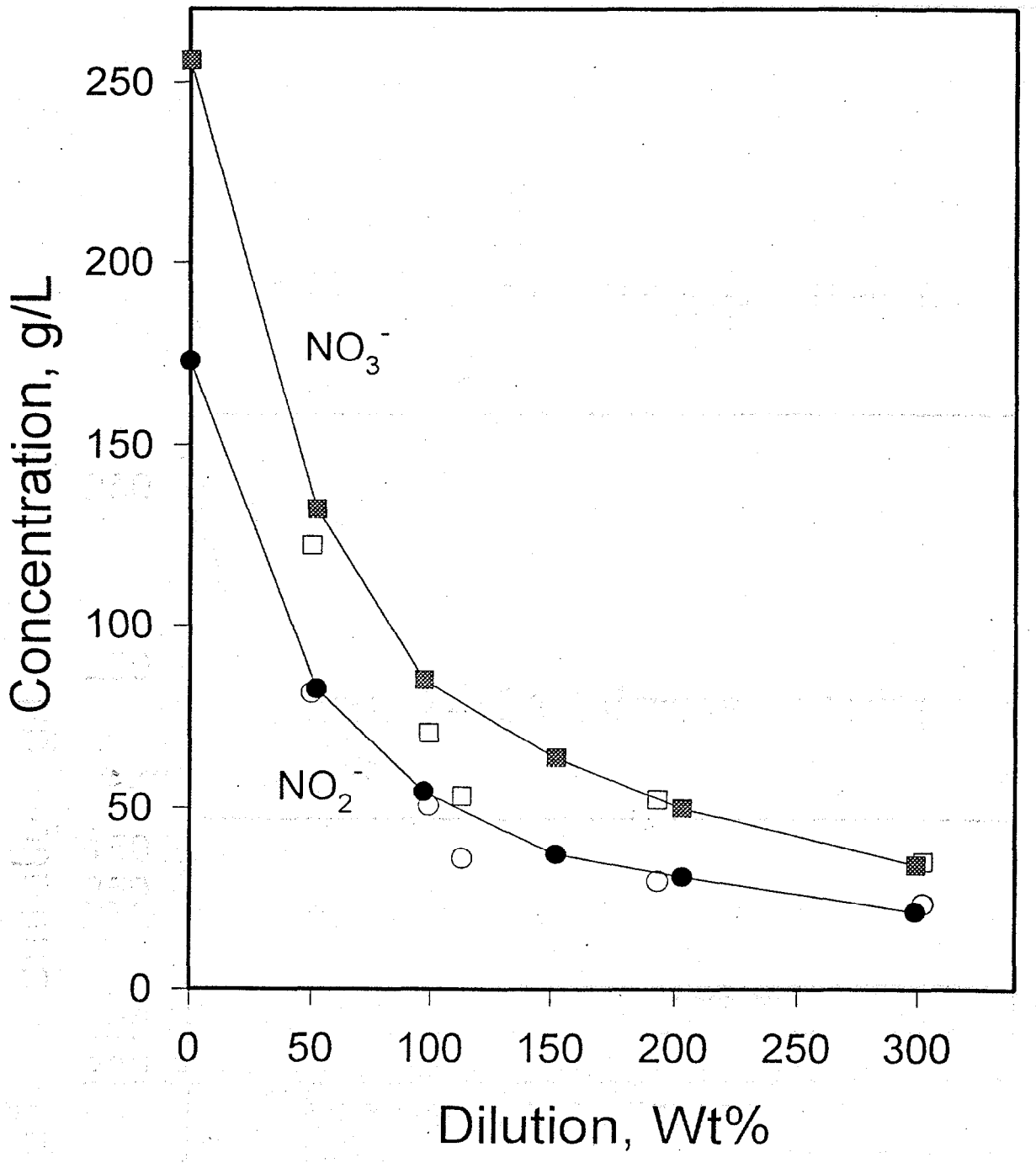
Series Dissolution (ESP Output)

- Add Saltcake to each of 6 cones
- Add different amount of H_2O to each cone
  - dilution range 0% to 300% by weight
- Mix, centrifuge, analyze supernate

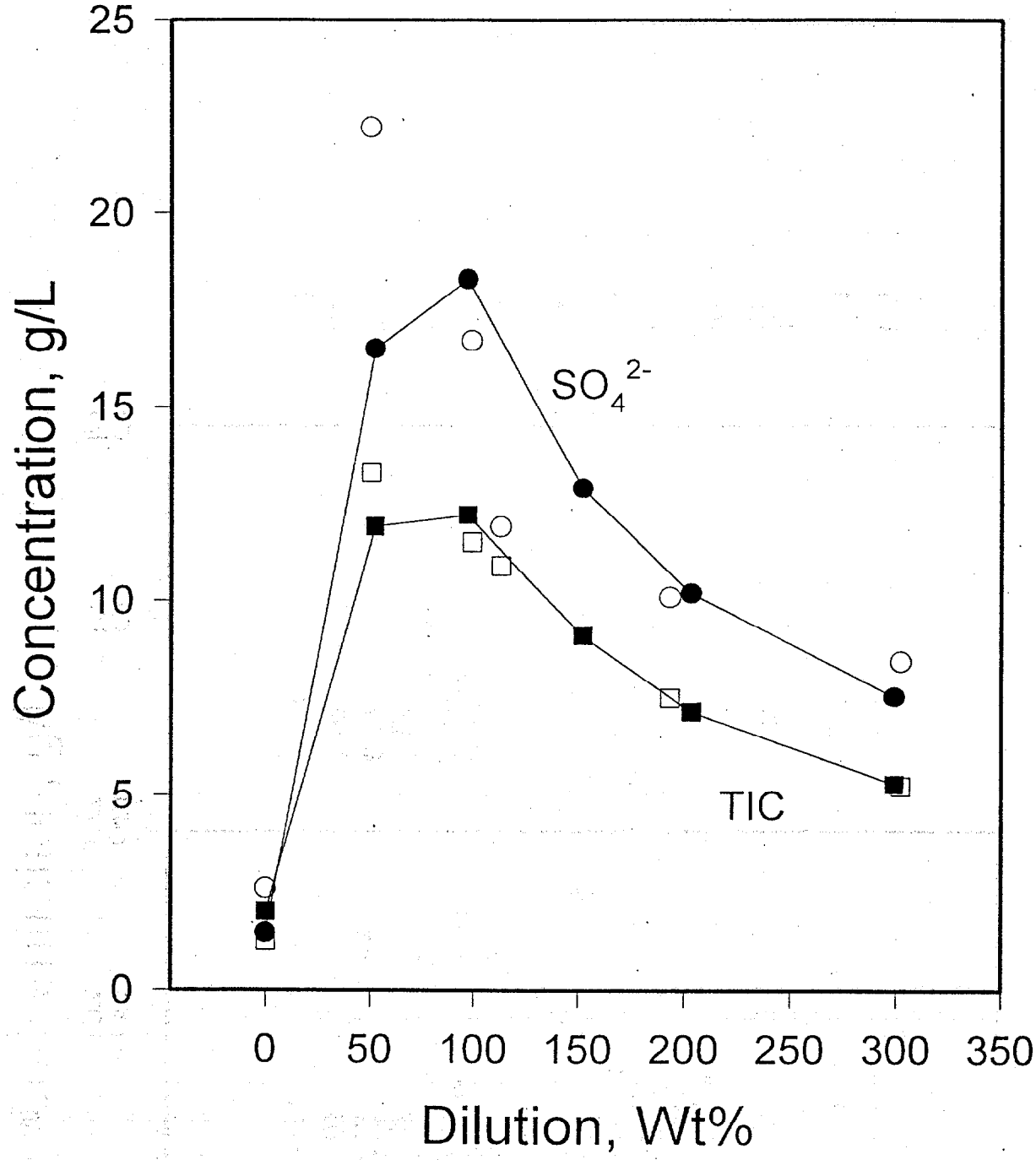
Tank S-102 Nitrate, Nitrite

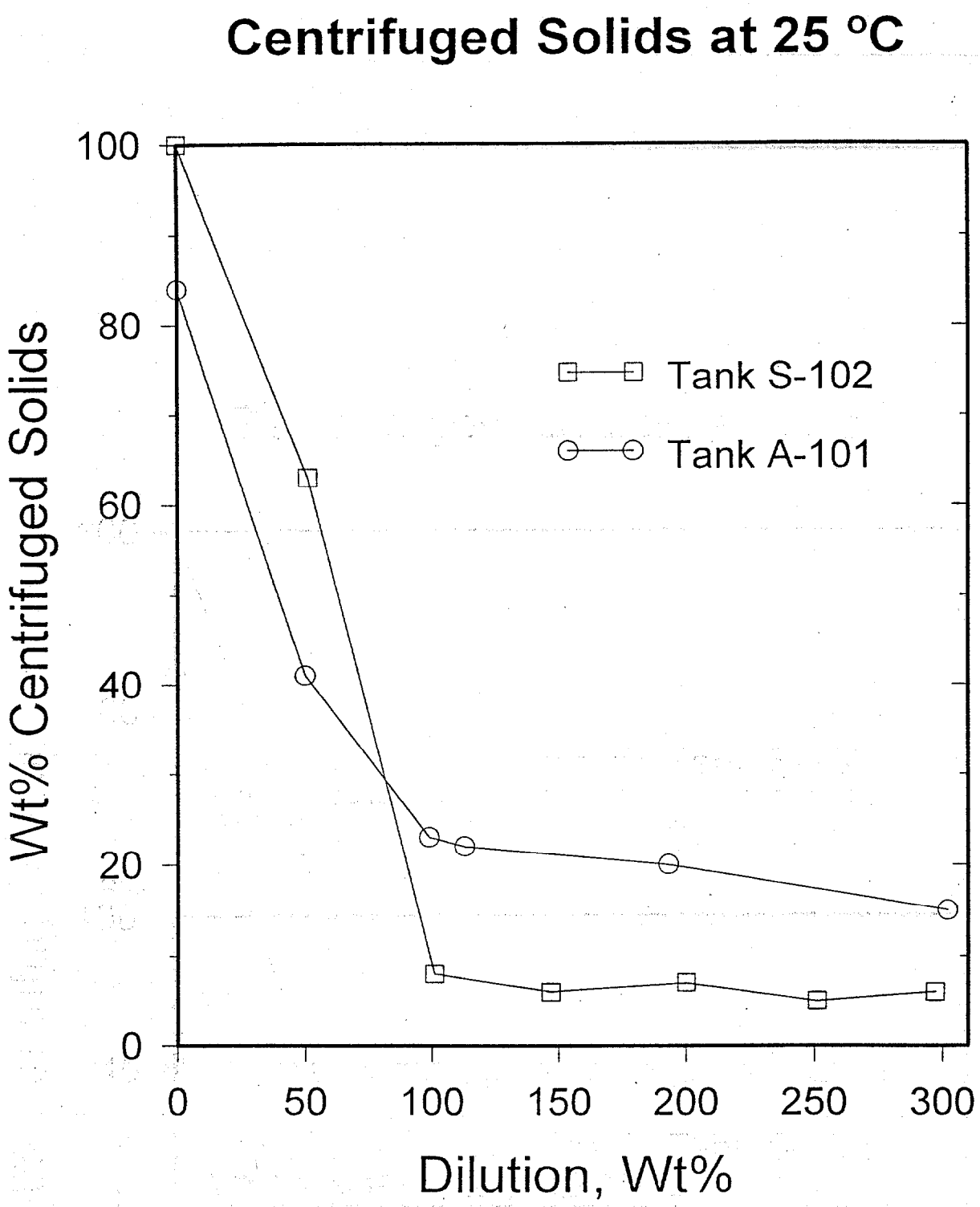


Tank A-101 Nitrate, Nitrite



Tank A-101 Sulfate, TIC




Centrifuged Solids at 25 °C
Wt% Centrifuged Solids
100
80
60
40
20
0
0
50
100
150
200
250
300
Dilution, Wt%
Tank S-102
Tank A-101

Task B - Column Dissolution (BY-102)

- Model in-situ saltcake retrieval
- Match flow rate to tank
  - (~ 0.15 mL/cm^2·hr)
- Sample effluent vs. time
- Model with ESP?
- Video

Task C - Solids Characterization
Tank BY-102 (from FY'98)

- Need driven by ESP
- Sample divided into wash fractions
  - eight solids
  - three liquids
- Three solids analysis techniques
  - PLM (complete)
  - SEM/EDS (25% complete)
  - XRD (first sample ran last week!!!)

BY-102 Wash Fractions

- Undissolved Solids
  - untreated
  - after 1st water wash
  - after 3rd water wash
- Recrystallized Solids
  - from 1st water wash (2 crops)
  - from 2nd water wash
  - from 3rd water wash (2 crops)
- Liquids
  - 1st, 2nd, 3rd water washes