ARGONNE NATIONAL LABORATORY

Chemical Effects/Head Loss Testing

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THE UNIVERSITY OF CHICAGO

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Chemical Effects/Head Loss Testing

- Objectives
  - Evaluate head loss associated with chemical by-products observed during the integrated chemical effects testing (ICET).
  - Understand how relevant changes within the environment affect chemical by-product formation, physical characteristics, and any associated head loss.
- Motivation
  - Program needed to explore implications of some chemical by-products observed during ICET.
  - Little information exists on head loss associated with chemical by-products.

Background

- NRC and the nuclear industry jointly developed an ICET program to determine if chemical reaction products can form in representative PWR post-LOCA containment sump environments.
- Chemical effects head loss test program developed and conducted by Argonne National Laboratory (ANL)
  - Intended to determine the potential for chemical products observed in ICET program to contribute to head loss
  - Intended to examine a broader range of conditions than examined in ICET
  - Simulate chemical products rather than perform integrated tests
    - *Critical questions: Do we have the right products? Do we have the right amounts?*
  - Critical parameter to characterize head loss is mass of chemical product & debris / area of screens

Regulatory Applications

- Research supports GL 2004-02 resolution.
- Information is used to evaluate licensee submittals and to inform the auditing process.
- The test data is being used specifically to evaluate the treatise of chemical effects in plant specific environments.

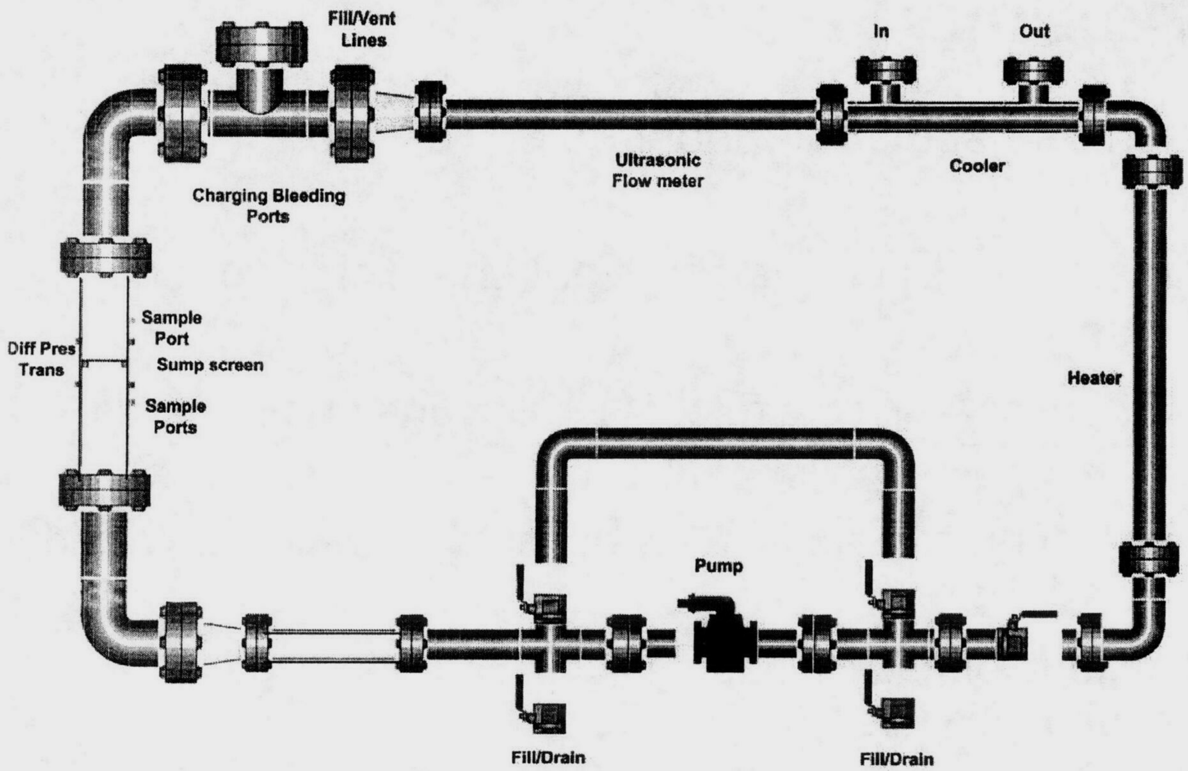
Testing Program

- Head Loss Tests for trisodium phosphate (TSP) buffered environments *(representative environments for ICET- 2 and 3)*:
  - Initial tests identify important variables that affect the amount of calcium phosphate that can form in TSP-buffered environments containing dissolved calcium.
  - Additional tests examine effect of important post-LOCA environmental variables on the pressure drop across debris beds created by various mixtures of cal–sil, fibrous insulation, and calcium phosphate precipitates.
  - Dissolution Tests: Investigate the effect on dissolved calcium formation over a range of simulated containment pool conditions.
  - Settling Tests: Measure expected settling rate of precipitates.

Ongoing Work

- NUKON/cal-sil benchmark testing without chemical products for comparison with historical and ongoing testing programs.
- Examine head loss from chemical products in sodium hydroxide buffered environments *(representative environments for ICET- 1 and 4)*.
- Examine head loss from chemical products in sodium tetraborate environments *(representative environments for ICET- 5)*.
- Test Schedule
  - February: Benchmark testing.
  - February – March: Sodium hydroxide environment.
  - March: Sodium tetraborate environment.
  - April: Complete testing.
  - May – June: Analysis, reporting and documentation.

ANL Test Facility



Fluid volume is 4.2 ft^3. Diameter of screen is 6.5 in. At 0.1 ft/s, the transit time around the loop is about 4 minutes. For tests to date screen a perforated plate with a 51% flow area and staggered 3/16 in. holes.

Tests to date have been performed with a horizontal screen, but also can be run with a vertical screen

Loop can operate up to 180°F (LEXAN); 140°F (clear PVC)

- Head loss characterized by mass of chemical product & debris / area of screen. In ANL loop 1 g debris = 47.6 g/m^2

ICET–3 and Plant Conditions

- ICET-3 represents plants which use sodium triphosphate (TSP) for pH control after an accident
- Calcium phosphate precipitates seem to be the principal chemical product with potential to cause head loss
  - Dissolved calcium could arise from cal–sil, concrete, etc., although primary source in ICET–3 is cal–sil
  - Critical parameter for production of precipitate is mass of cal–sil/volume sump fluid; plants are now estimated to be < 1.5 g/l
  - ICET–3 cal–sil loading is 19 g/l, but for cal–sil loadings greater than ≈ 2g/l formation of precipitate is phosphate limited
  - Precipitate formation will proceed until either essentially all the phosphate or Ca is exhausted; kinetics of process may depend on rate of TSP addition

Initial Head Loss Tests

- First test was intended to simulate the conditions in ICET–3
- Second test was parametric and intended to examine the effect of a range of chemical product loadings.
- Test conditions
  - Initial environment: 2800 ppm B, 3 ppm LiOH, 4 g/L TSP, Temperature = 54°C
  - Screen loading: 0.71 kg/m^2 (15g) cal–sil; 0.71 kg/m^2 (15 g) NUKON
  - Flow rate = 0.1 ft/s
  - Establish debris bed, then add dissolved Ca as $CaCl_2$
    - *200 ppm (Estimated initial conditions in ICET–3)*
    - *10, 25, & 50 ppm (Parametric study of effect of dissolved Ca level)*

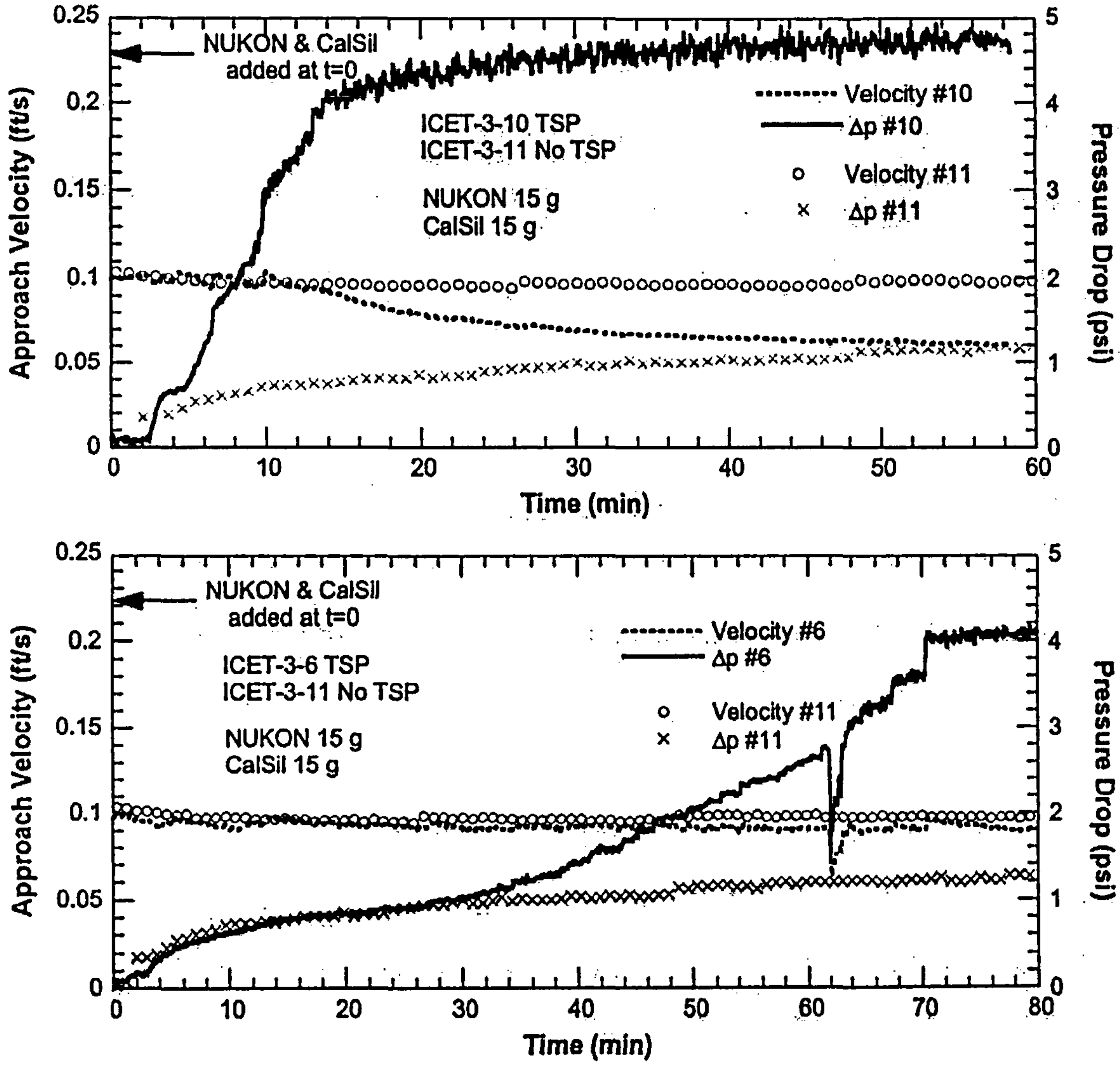
Results from Initial Head Loss Tests

- Calcium phosphate products generated in TSP-buffered environments contributed to test loop head loss.
  - Increased head loss for all dissolved Ca concentrations tested (down to 10 ppm).
  - Significant head loss for greater than 25 ppm of dissolved Ca.
  - Calcium phosphate may agglomerate at low fluid flow velocities.
- Separate dissolution tests showed that for the range of cal–sil concentrations examined (6 – 25 g/L) 200 ppm of dissolved Ca can form within 30 minutes in initially acidic (ph < 7) environments.
  - Additional dissolved Ca expected for longer times as cal–sil dissolution continues.

Additional Head Loss Tests for ICET-3

- Principal Test Variables
  - Degree of cal–sil dissolution that occurs prior to debris bed formation
    - *Depends on time to recirculation, transport time, and rate of TSP dissolution*
  - Relative arrival time of the precipitates and insulation debris at the test screen
  - NUKON and cal–sil screen loading
- Test Procedures
  - Baseline (no TSP) tests conducted to assess effect of precipitates compared with just physical debris
  - cal–sil and NUKON were presoaked in many tests at 60°C for 30 minutes to simulate time prior to recirculation. Represents minimum residence time for dissolution
    - *$CaCl_2$ used in some tests to represent very long dissolution times*
  - Various dissolved TSP fractional quantities initially added to either presoak or test loop; any remaining TSP was titrated in after forming the debris bed to simulate effects of various TSP dissolution rate scenarios

Head Loss Tests for ICET-3



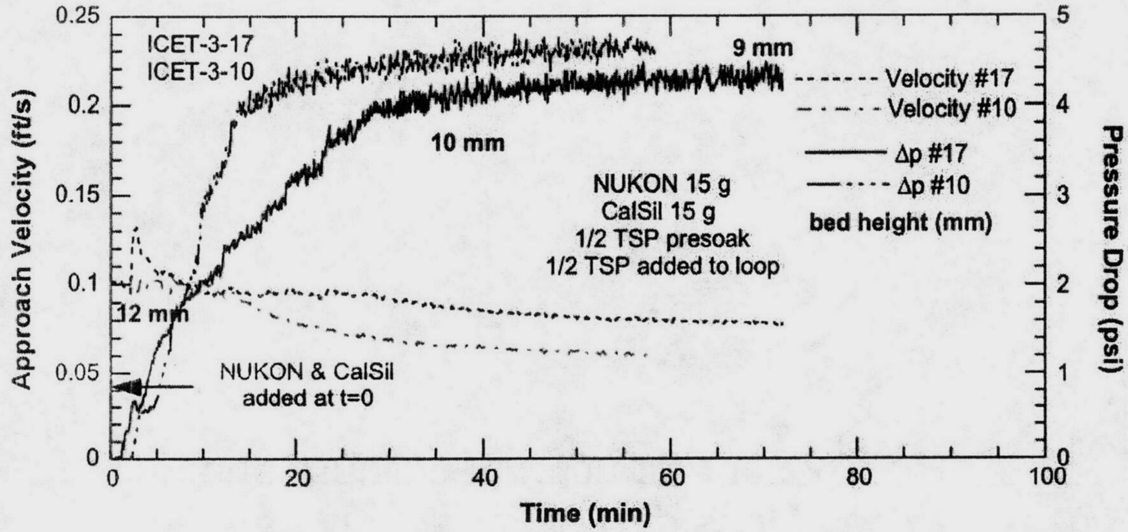
Test 10 ½ TSP in presoak
Test 6 No TSP in presoak
0.71 kg/m^2 (15 g) NUKON cal–sil

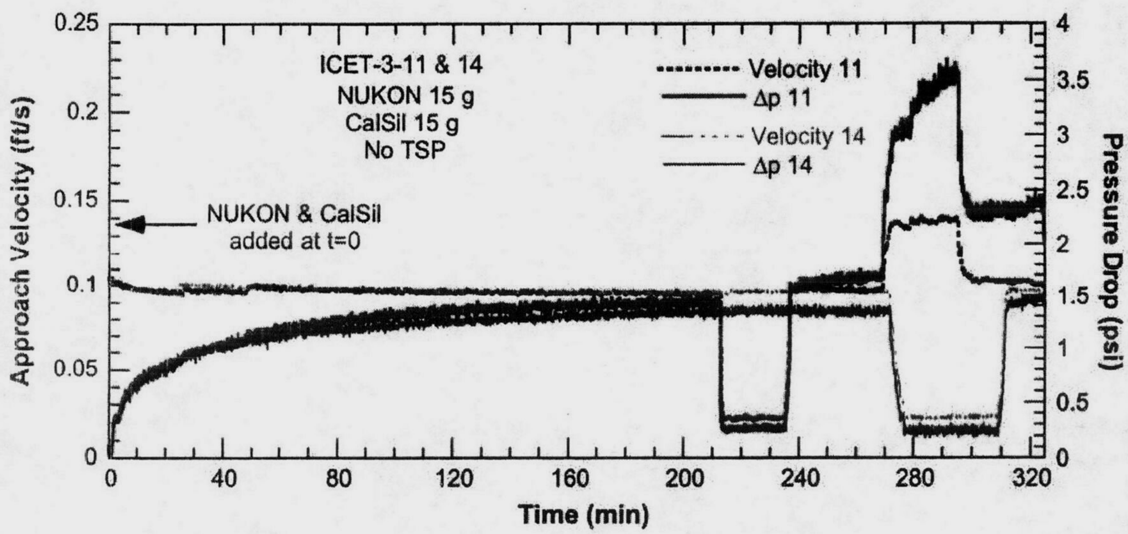
Test Results

Head losses with chemical products are greater than with an equivalent amount of cal–sil

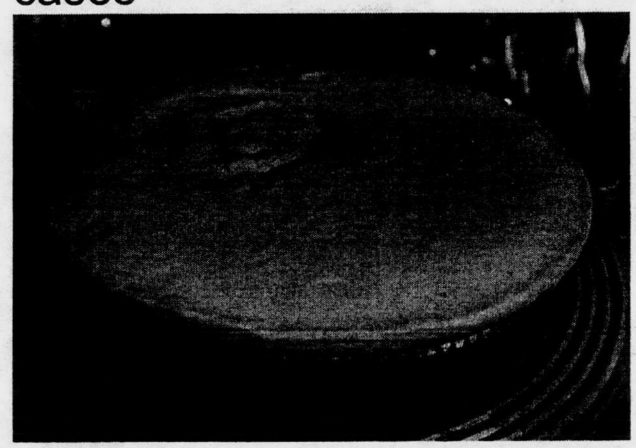
No significant difference in maximum head loss apparent whether significant dissolution occurred prior to formation of the debris bed, although rate of increase changes significantly

Head Loss Tests for ICET-3 (cont'd.)

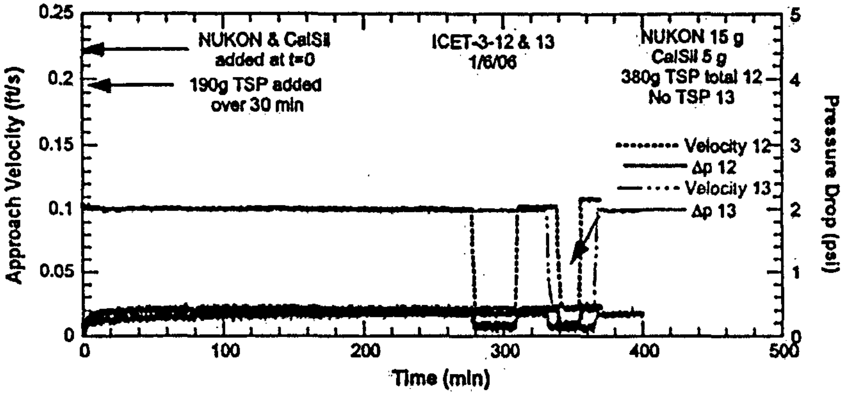


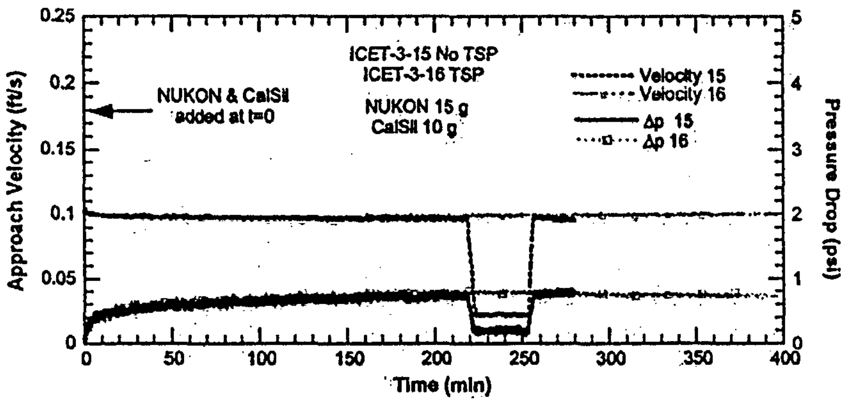


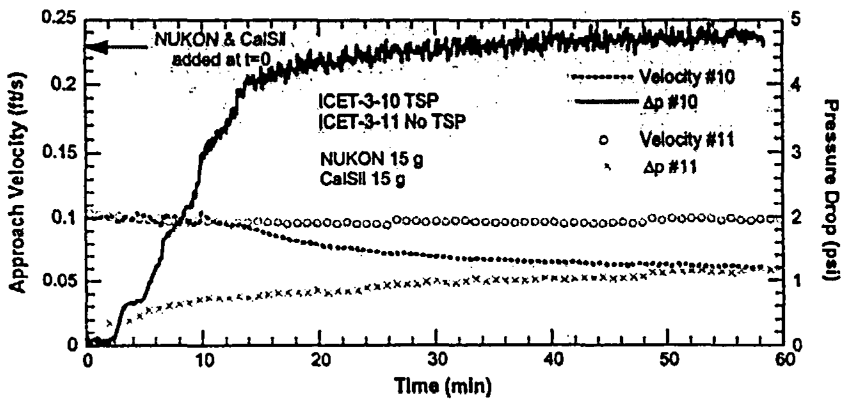
Replicate tests show reasonably good reproducibility in most cases



Head Loss Tests for ICET-3 (cont'd.)

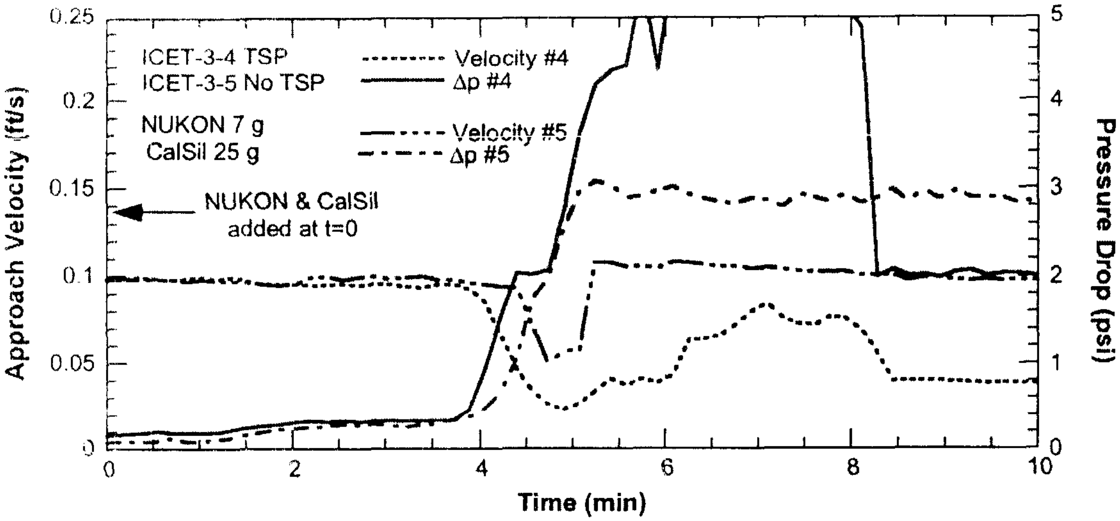


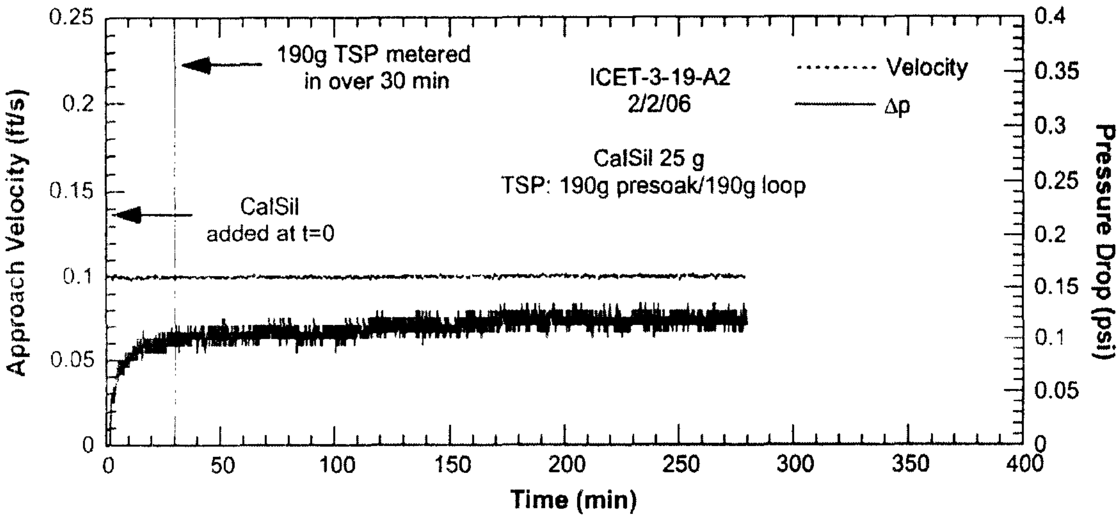




Relative contribution of calcium phosphate to head loss depends strongly on the debris loading

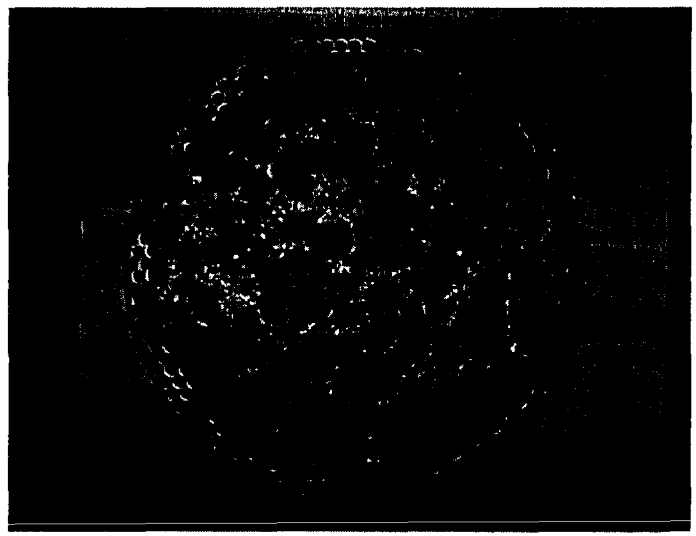
Head Loss Tests for ICET-3 (cont'd.)





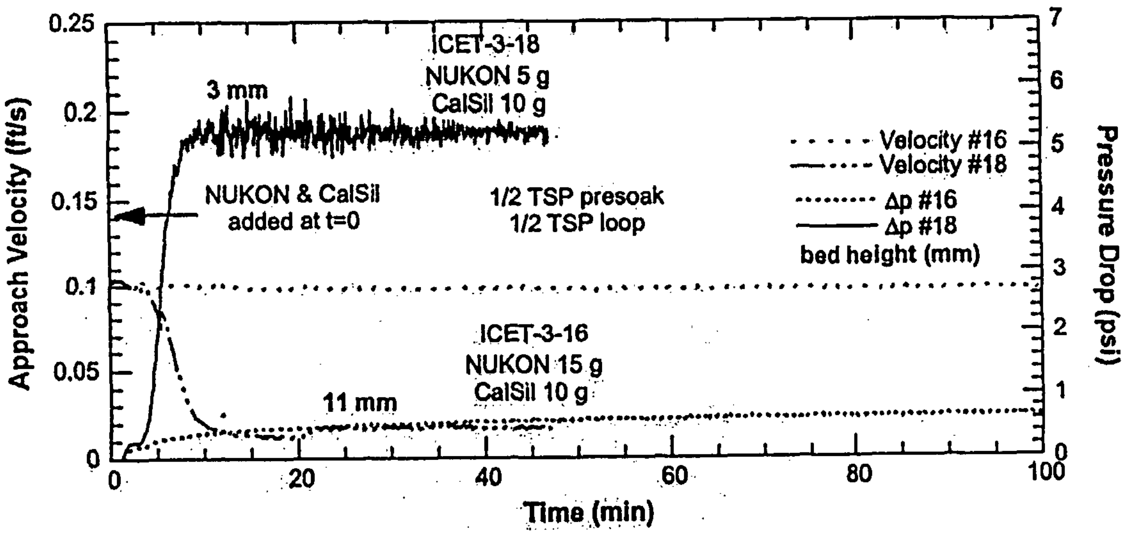
With NUKON 7g cal–sil 25 g head loss is significant with or without calcium phosphates

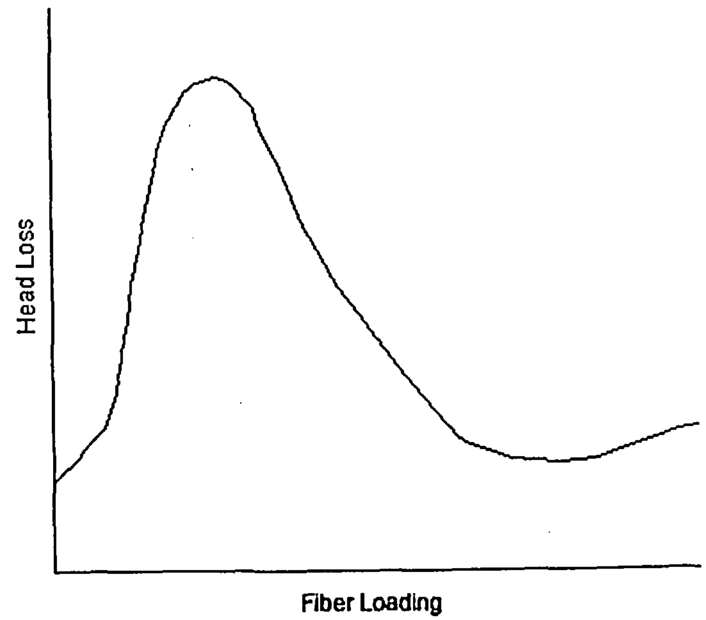
With cal–sil 25 g alone, flow through occurs over ≈10% and pressure drops are much smaller



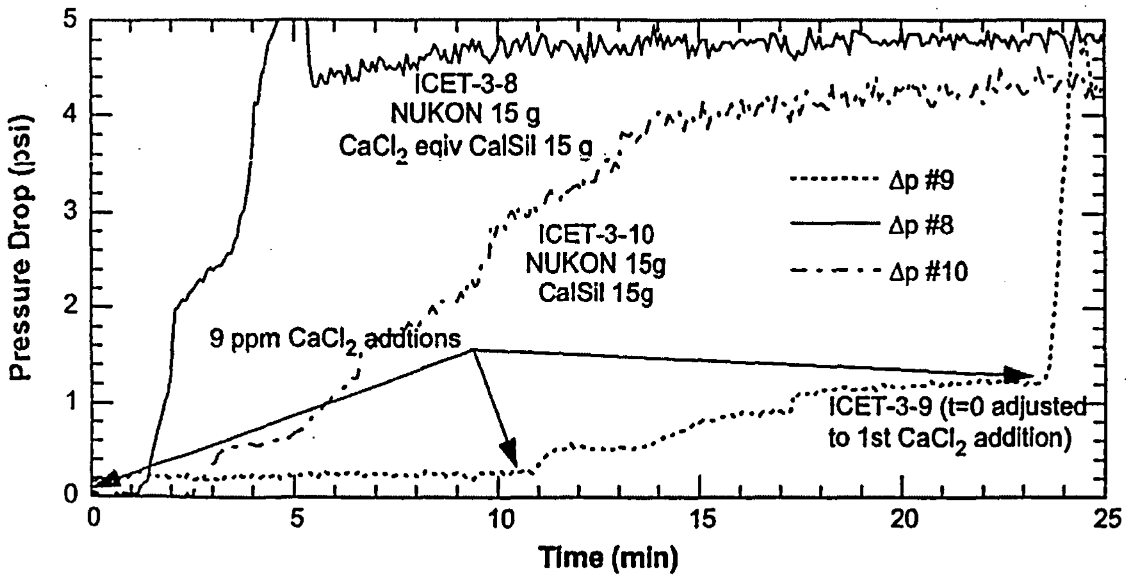
Head Loss Tests for ICET-3 (cont'd.)

For a given cal–sil loading, head loss can be highly nonlinear, non-monotonic function of fiber loading





Head Loss Tests for ICET-3 (cont'd.)

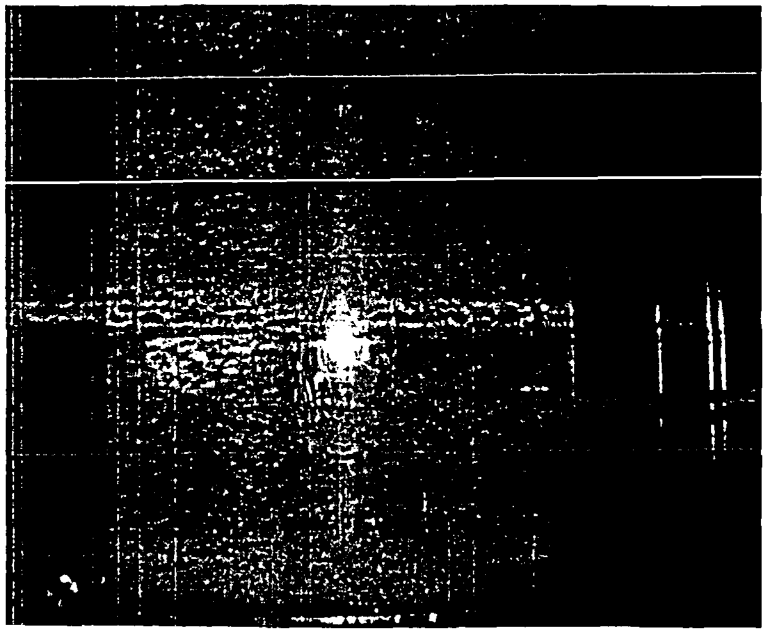


ICET-3-8 is bounding case for complete dissolution of cal–sil prior to formation of the debris bed. ICET-3-10 is minimum expected dissolution of cal–sil prior to bed formation.

Head Loss Test for ICET–1

- $Al(OH)_3$ emulsions seem to be the principal chemical product with potential to cause had loss
- ICET–1 test 1 was intended to determine head losses associated with the chemical products generated in ICET–1. $Al(NO_3)_3$ 9H2O additions were used to generate an $Al(OH)_3$ emulsion.
- Test was compromised by non-prototypical behavior during the Al additions A heavy "snowfall" was observed during the period of addition. "Snow" dissolved in a relatively few minutes.
  - Solution added over 4 minute period. Average concentration exiting control volume was correct, but obviously high local concentrations occurred

Head Loss Test for ICET–1 (cont.)



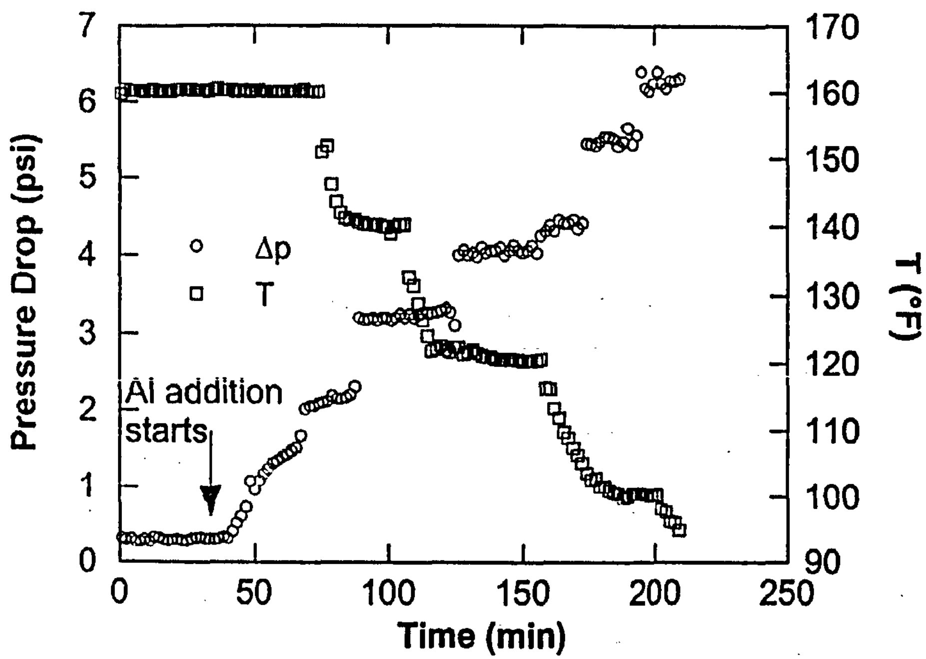
Initial snowfall as dissolved Al is added

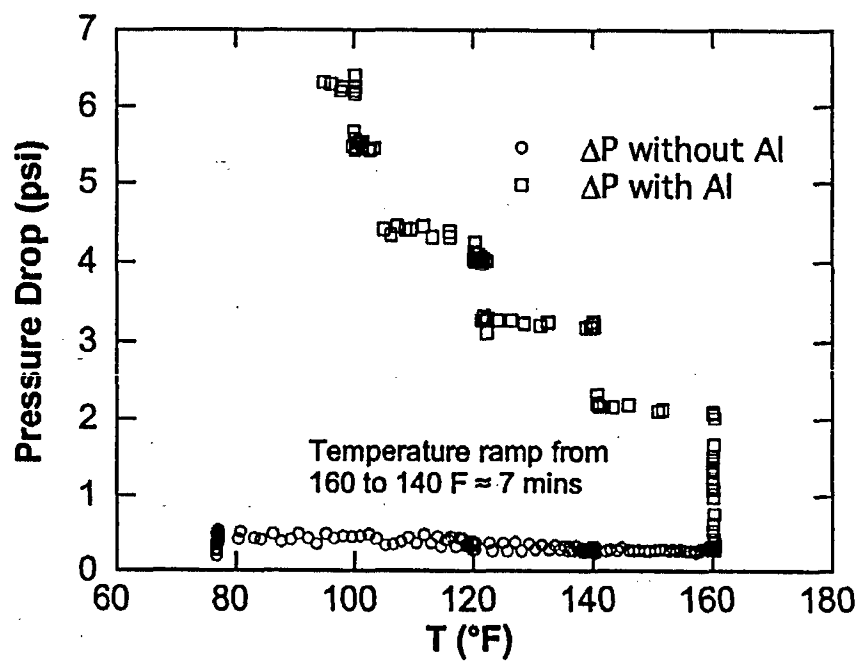
Head Loss Test for ICET–1 (cont.)

Bed at 160°F shortly after completion of Al additions

Bed at ≈110°F with increasing turbidity.

Head Loss Test for ICET–1 (cont.)





- Al additions resulted in large increases in pressure drop across a NUKON bed (15 g, approximately 11/16 in before the chemical additions).
  - Increases not associated with precipitate build up on the bed as in ICET-3 environments.
- As temperature dropped to ≈ 90°F, 0.1 ft/s velocity could not be maintained

Head Loss Test for ICET–1 (cont.)

- LEXAN components in the loop were severely damaged during the test. Numerous axial and circumferential cracks formed.
- Future testing in ICET–1 environments will require PVC test section, which restricts temperature to 140°F and better engineered system for Al additions
- Although test compromised, results certainly indicate significant head losses can be associated with ICET–1 chemical products for plants with high levels of dissolved Al.

Effect of nonisothermal histories for ICET-1

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

4 Loop

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

3 Loop

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Ice Condensor

Type	Al 30 days g/m^2	Al spray g/m^2
4 loop	836	30
3 loop	1395	29
Ice	441	3
ICET-1	878(439)	5

Plant Data ICET–1 environments

Plant	Plant Type	Al / vol. ft^2/ft^3	Al / vol. (Submerged)	Al / vol. (Spray)	1 day total ppm	30 day total ppm
T	B&W	0.29	0.003	0.29	65	80
U	CE	0.02	0.000	0.02	5	6
J	3 Loop	0.02	0.02	0.000	2	34
K	3 Loop	0.01	0.01	0.000	1	17
Q	4 Loop	0.05	0.003	0.051	13	20
BB	B&W	0.08	0.001	0.08	18	22
N	2 Loop	0.005	4.94e-05	0.005	1	1
JJ	4 Loop	0.12	0.001	0.12	27	33
S,KK,LL	B&W	1.91e-05	1.91e-05	0	0	0
R	CE	3.4	0.84	2.51	678	5026
O,P	2 Loop	0.02	0.002	0.02	5	15
RR	4 Loop	0.04	0.001	0.04	10	13
QQ	3 Loop	0.02	0.000	0.02	4	4
X	4 Loop	0.01	0.001	0.01	3	5
ICET–1		3.5	0.18	3.3	57	375

No deactivation of Al surfaces, except for ICET–1

Spray corrosion rates = 2* submerged, except for ICET–1 where the factor is 0.6

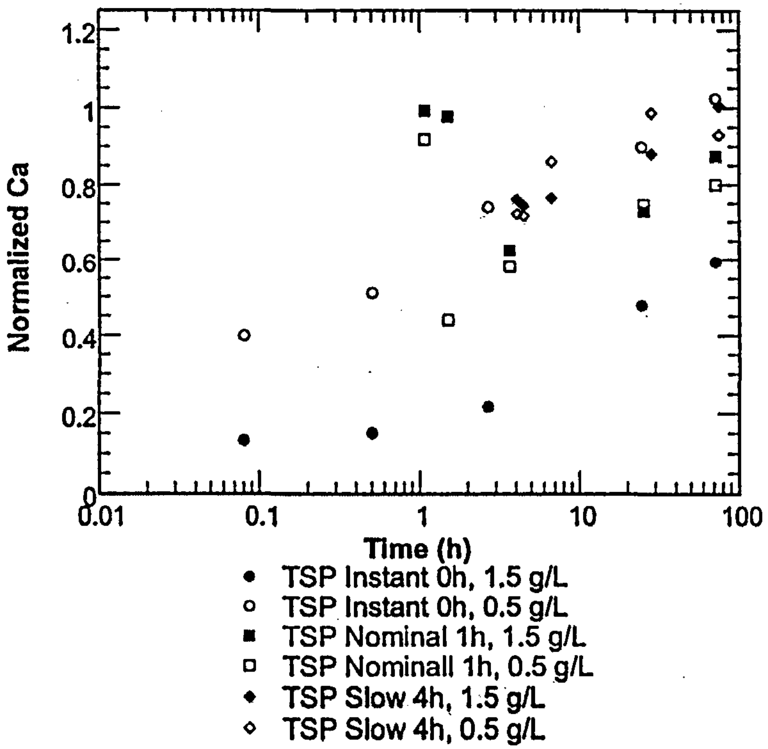
Sprays on for 4 h

No scaling for screen size

Cal–sil Dissolution Tests

- Initialize dissolution tests were for relatively high concentrations characteristic of ICET–3 test
  - Demonstrated that in boric acid environment at 60°C characteristic of sump and cal–sil solutions with ≥ 6 g/L dissolved Ca levels saturate at about 200 ppm in 15–20 minutes
  - Dissolution rate is pH dependent
  - Even without TSP additions, pH rises quickly due to ≈5% sodium silicate in cal–sil
- Follow–on tests at cal–sil concentrations more representative of those of interest 0.5 and 1.5 g/L
- Three different TSP addition histories
  - Add TSP before cal–sil addition (instantaneous dissolution of TSP).
  - Titrate TSP over 1 hr period into solution after cal–sil addition (nominal case).
  - Titrate TSP over 4 hr period into solution after cal–sil addition (very slow TSP addition).

Cal-sil Dissolution Tests Results



Cal–sil dissolution rate is not strongly dependent on the TSP dissolution rate or cal–sil concentration for realistic TSP dissolution histories.

Equivalent dissolved Ca exceeds 75 ppm in a few hours for cal-sil concentrations down to 0.5 g/L.

Settling Tests

Test Procedure

Performed in settling tower initially filled with B, LiOH, and TSP. $CaCl_2$ solution added

Solution stirred initially to provide uniform concentration.

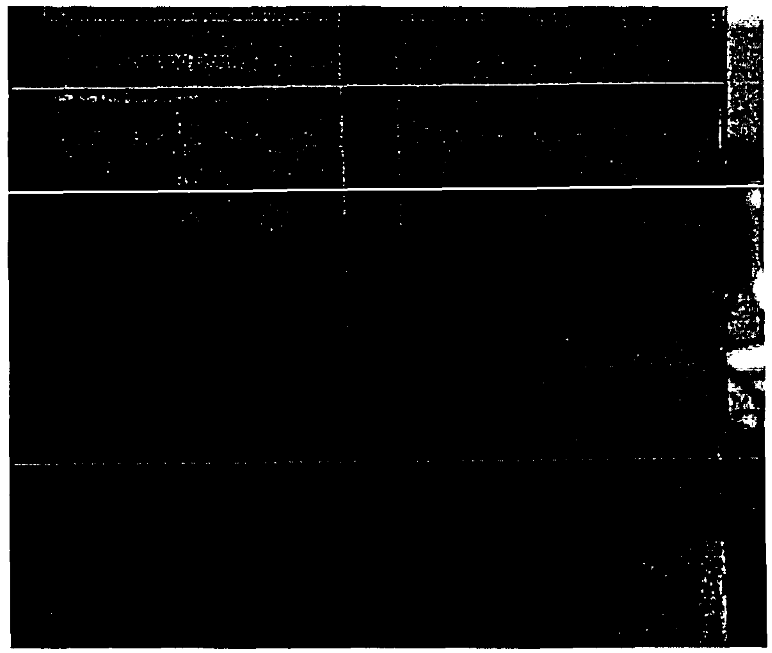
Periodic sampling to quantify settling.

Results

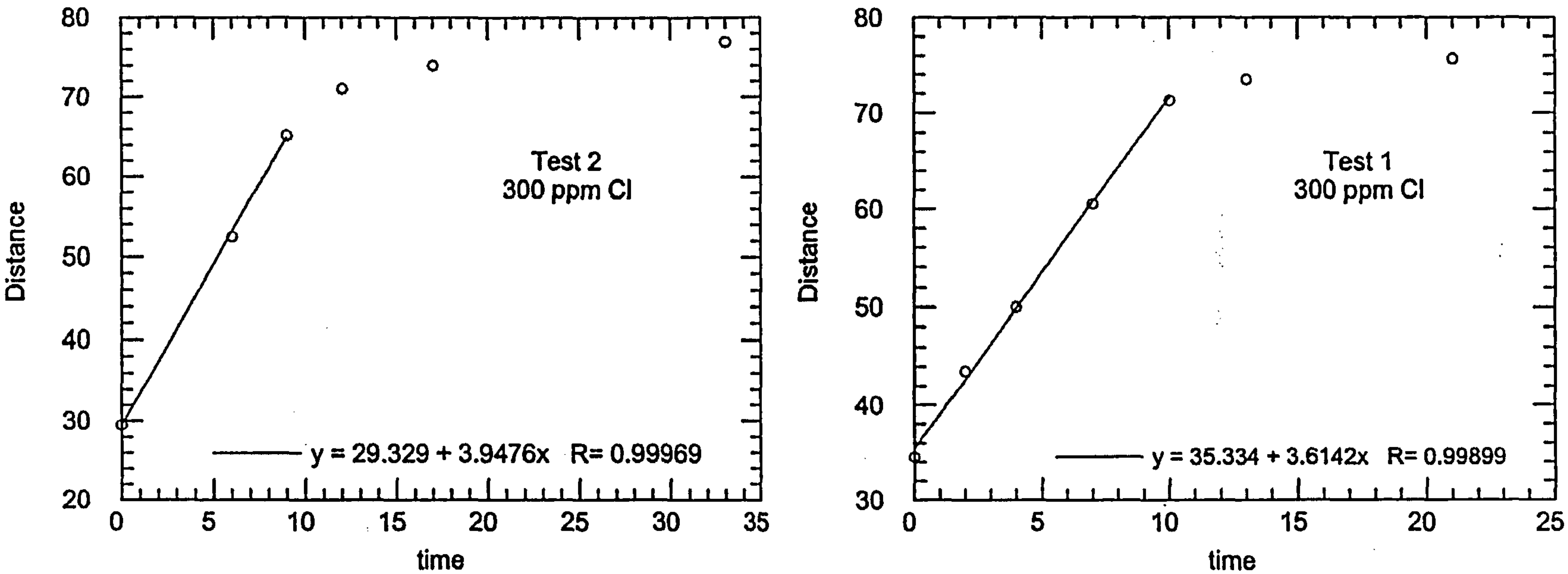
No agglomeration within column.

300 ppm dissolved Ca tests showed distinct "settling front" which removed about the product

75 ppm dissolved Ca showed no distinctive front. Solution slowly cleared.

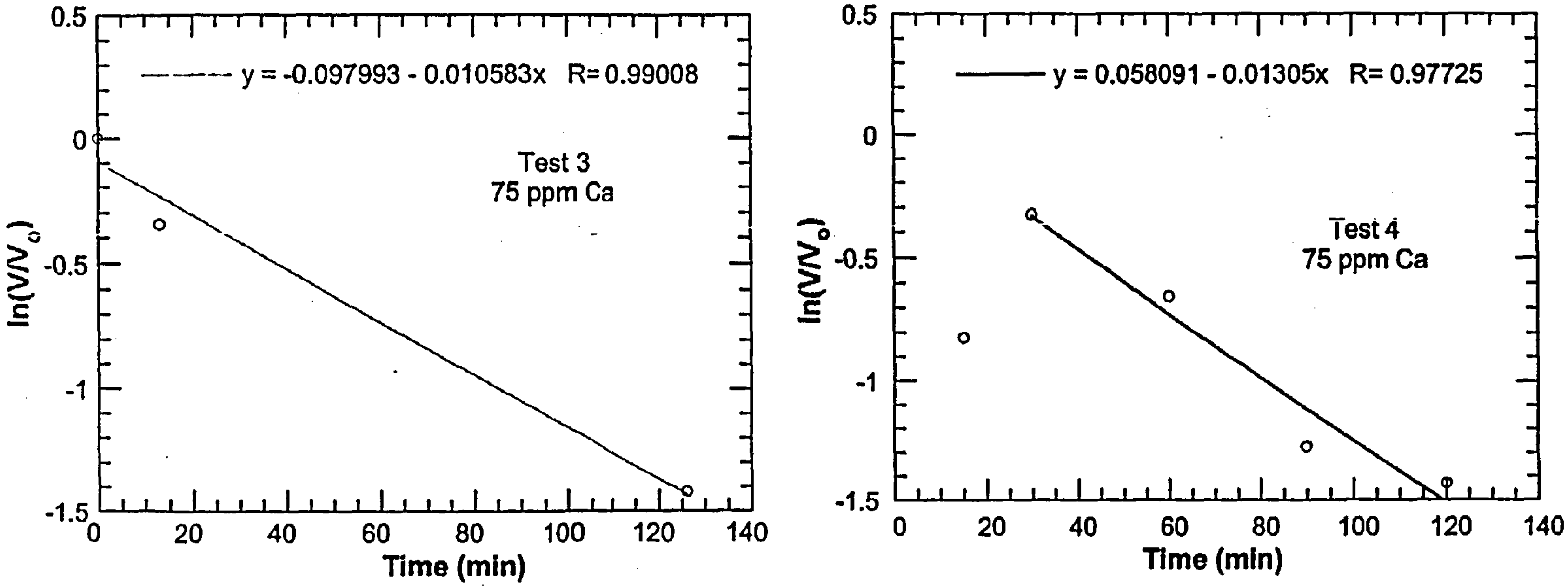


Settling Tests (cont'd)



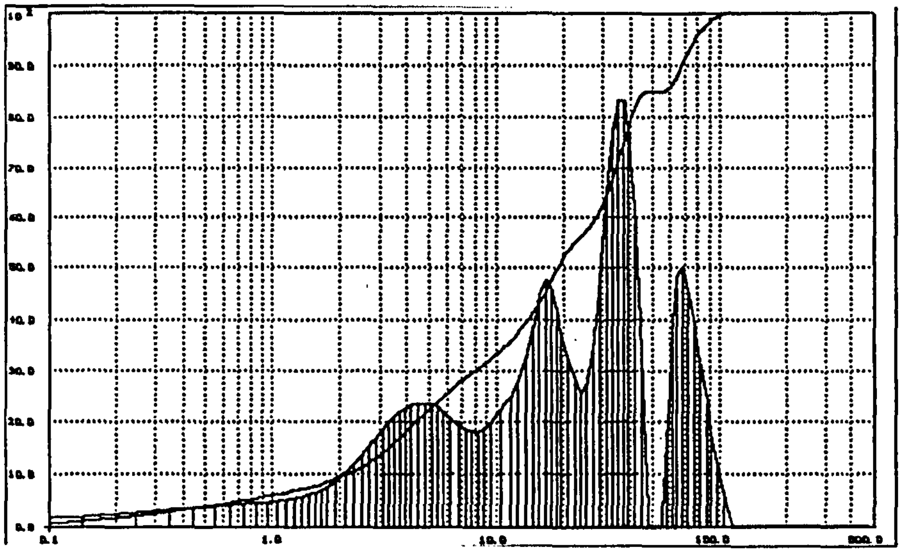
- Settling front in the two 300 ppm dissolved Ca settling tests moves at about 3.8 cm/min

Settling Tests (cont'd)



- Time constant for settling is about 82 minutes corresponding to a settling velocity of about 0.8 cm/min

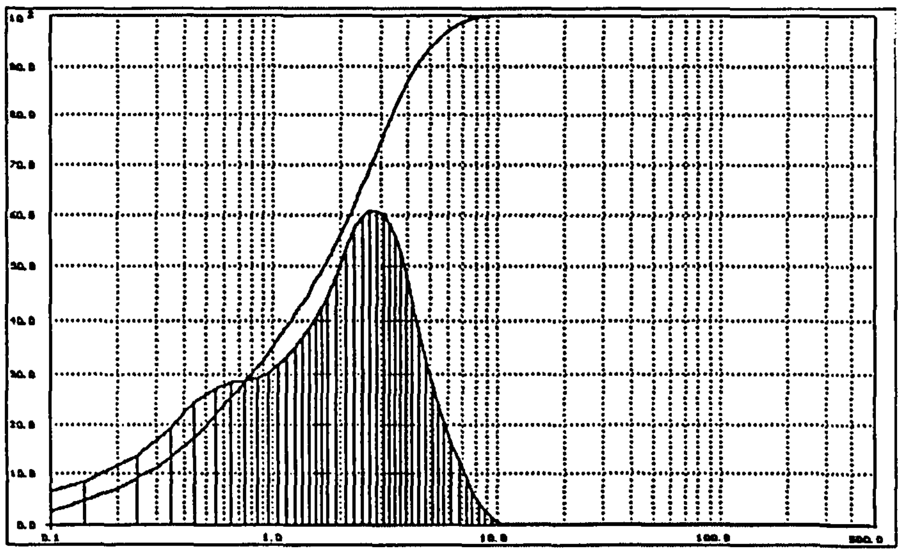
Characterization of particle size for ICET–1



ICET–1 simulation product

Particle size histogram and cumulative size distribution by laser granulometry without ultrasound deflocculation

Median particle size 18.6 µm

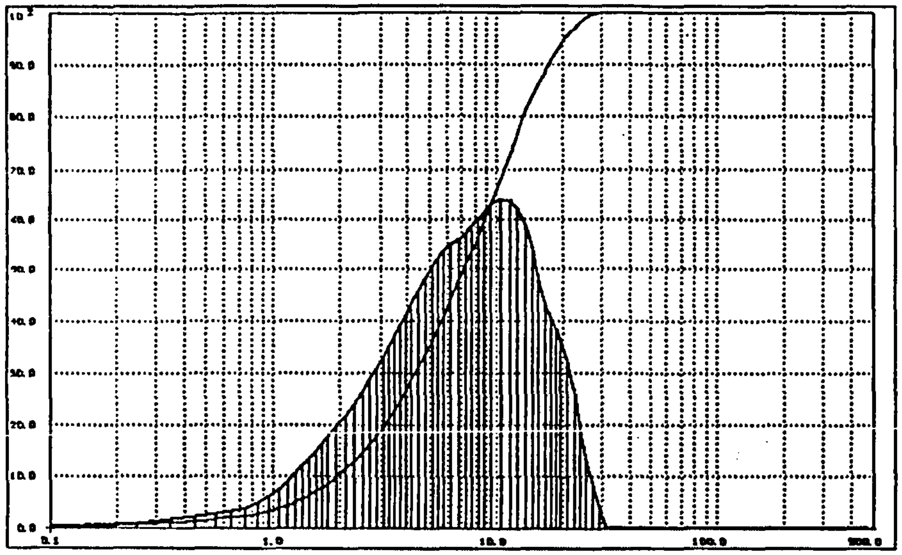


ICET–1 simulation product

Particle size histogram and cumulative size distribution with ultrasound deflocculation

Median particle size 1.7 µm

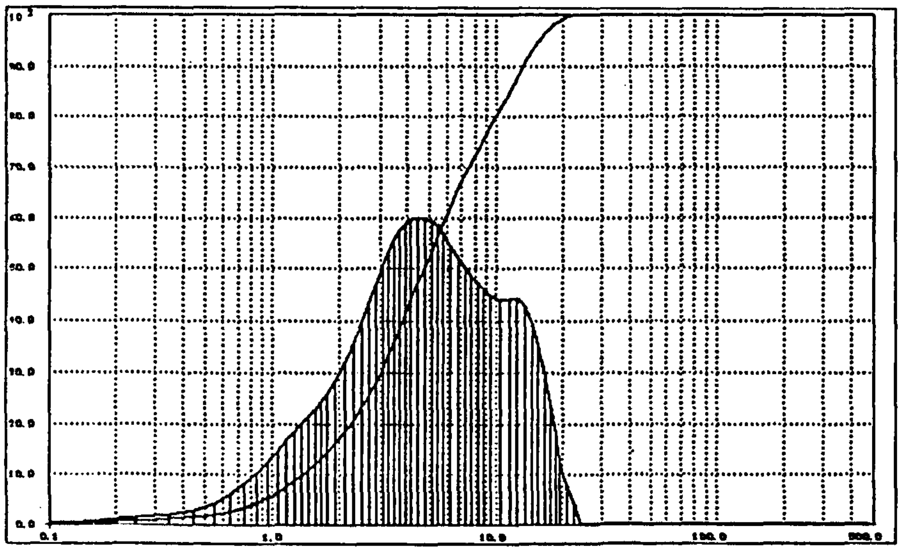
Characterization of particle size for ICET–3



ICET–3 simulation product

Particle size histogram and cumulative size distribution without ultrasound deflocculation

Median particle size 7.1 µm



ICET–3 simulation product

Particle size histogram and cumulative size distribution with ultrasound deflocculation

Median particle size 4.7 µm

Summary

- Head losses with chemical products are greater than with an equivalent amount of cal–sil
- No significant difference in maximum head loss apparent whether significant dissolution occurred prior to formation of the debris bed, although rate of increase changes significantly
- Relative contribution of calcium phosphate to head loss depends strongly on the debris loading
- For a given cal–sil loading, head loss can be highly nonlinear, non-monotonic function of fiber loading
- Cal–sil dissolution rate is not strongly dependent on the TSP dissolution rate or cal–sil concentration for realistic TSP dissolution histories and concentrations of interest.
- Equivalent dissolved Ca exceeds 75 ppm in a few hours for cal-sil concentrations down to 0.5 g/L

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Chemical Speciation Prediction: Technical Program and Results

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February 15, 2006

UNITED STATES NUCLEAR REGULATORY COMMISSION

Work Sponsored by
US Nuclear Regulatory Commission

Outline

- Project objectives
- Motivation
- Phased technical approach
- Results, analysis, and discussion
- Summary
- Plan for upcoming program
- Where to find more information

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Program Objectives

- Evaluate readily available analytical tools
- Assess ability of tools to predict chemical by-products in Integrated Chemical Effects Tests (ICET) environments
- Recommend suitable thermodynamic simulation code
- Evaluate applicability limits for plant-specific environments

Program Motivation

- ICET is only examining a few representative environments
- Need to understand plant variability
- Need to provide a tool to evaluate chemical by-products in individual plants

Phased Technical Approach

- Preliminary thermodynamic modeling using input values from the peer-reviewed literature (corrosion rates) and ICET Test Plan (exposed surface area, containment water composition)
- Pre-ICET thermodynamic modeling based on input values from Center for Nuclear Waste Regulatory Analyses (CNWRA) experimental corrosion data
- Post-ICET thermodynamic modeling based on input values from experimental corrosion data and on results from ICET

Thermodynamic Simulation Computer Codes

- Examples of aqueous chemistry modeling software
  - EQ3/6
  - Geochemist's Workbench®
  - PHREEQC
  - Stream Analyzer™
  - Environmental Simulation Program™
- Most simulations in this study performed using Stream Analyzer
  - Predicts conventional and redox reactions
  - Large multi-component systems
  - Ionic strength (0–30 molal)
  - Temperature (−50 to 300 °C)
  - Pressure (0–1500 bar)
  - Modeling of up to 250 solid phases

Assumptions for Thermodynamic Simulations

- System is in thermodynamic equilibrium
  - All reactions achieve equilibrium instantly
  - Exclude consideration of reaction kinetics
  - Rate of reaction is partly included by the use of experimental corrosion rates
  - Allow the most oversaturated phases (dominated by silicate minerals) to precipitate from solution
- Reacted materials limited to those used in ICET
  - Excluded paints and organics
- Exclude uptake of atmospheric CO_2

Modeling Inputs for Trial Simulations

- Select containment water composition
  - 2,800 ppm boric acid concentration
  - Selection of buffering agent
    - Trisodium phosphate ($pH_{initial}$=7)
    - NaOH ($pH_{initial}$=10)
    - Sodium borate ($pH_{initial}$=8.2)
- Calculate corrosion amount as a function of time based on corrosion rate of debris components
  - Metals: zinc, copper, aluminum, carbon steel
  - Insulation: Nukon, calcium silicate
  - Concrete

Thermodynamic Simulations Using Measured Corrosion Rates

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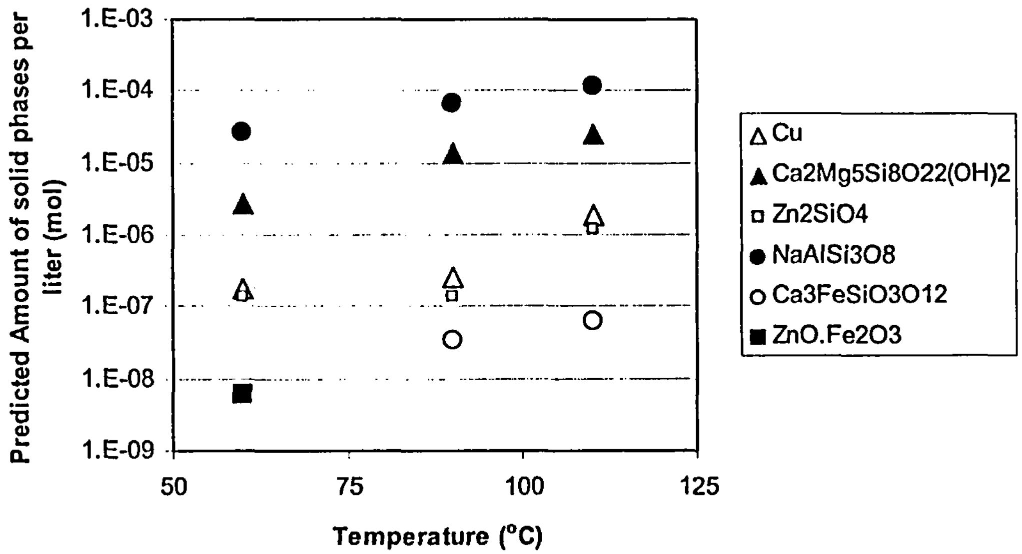
Pre-ICET Simulation Results Using Measured Corrosion Rates



Chemical evolution of pH 10 containment water as a function of temperature, pressure

- Greater amounts of various silicates predicted to form with increasing temperature
- Calculations indicate that over 99 percent of solid phases predicted in the pressurized system would be similar to the phases predicted in the non-pressurized system at a lower temperature
- Corrosion products from insulation and aluminum are the major contributors to secondary solid phases

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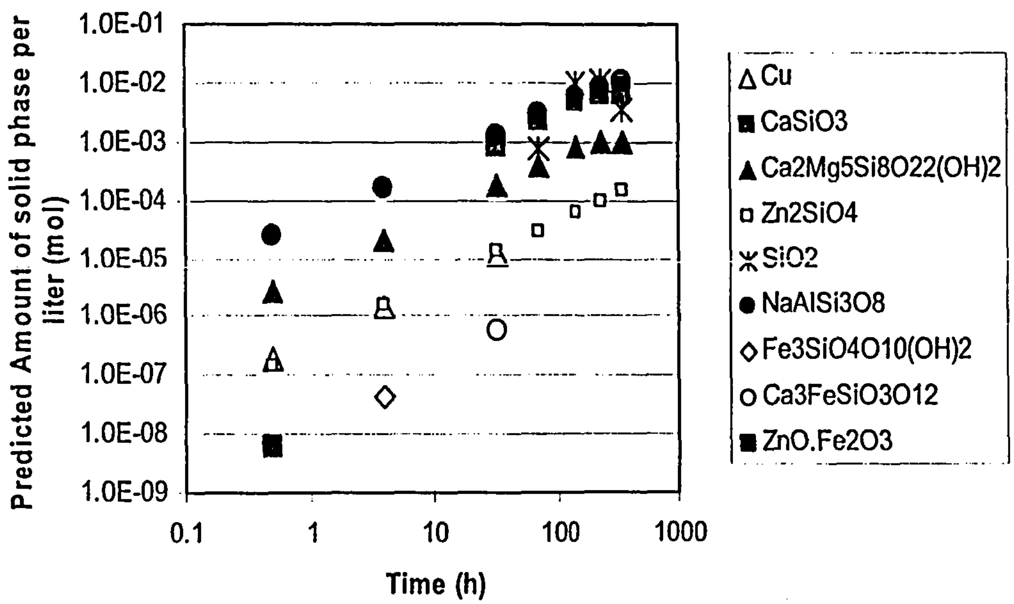
Pre-ICET Simulation Results Using Measured Corrosion Rates



Chemical evolution of pH 10 containment water as a function of time

- Greater amounts of various silicates predicted to form with increasing times
- Corrosion products from insulation and aluminum are major contributors to secondary solid phases

Simulations Based on Insights from ICET

- Silicate phases were not observed to form in ICET environments
  - Many precipitation and dissolution reactions are kinetically controlled at pressure-temperature-time conditions of the ICET experiments (i.e., Sluggish)
  - Silicates are thermodynamically stable phases; kinetically very sluggish
  - Suppressed formation of silicates in the modeling

- Aluminum hydroxide phase was not observed to form in ICET environments; aluminum oxyhydroxide phase was observed
  - Suppressed formation of aluminum hydroxide to allow formation of aluminum oxyhydroxide phase

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Description of Integrated Chemical Effects Tests

- Tests simulate five unique chemical environments
- Primary variables: pH (buffering agent) and insulation materials

Test Number	Buffering Agent	Insulation Material	Completion Date
1	**Sodium Hydroxide: pH ≈ 10**	**100% Fibrous (NUKON)**	**12/20/04**
2	Tri-sodium Phosphate: pH ≈ 7	100% Fibrous (NUKON)	3/7/05
3	**Tri-sodium Phosphate: pH ≈ 7**	**80% Particulate (CalSil) 20% Fibrous (NUKON)**	**5/5/05**
4	Sodium Hydroxide: pH ≈ 10	80% Particulate (CalSil) 20% Fibrous (NUKON)	6/23/05
5	Sodium Tetraborate: pH ≈ 8.2	100% Fibrous (NUKON)	8/25/05

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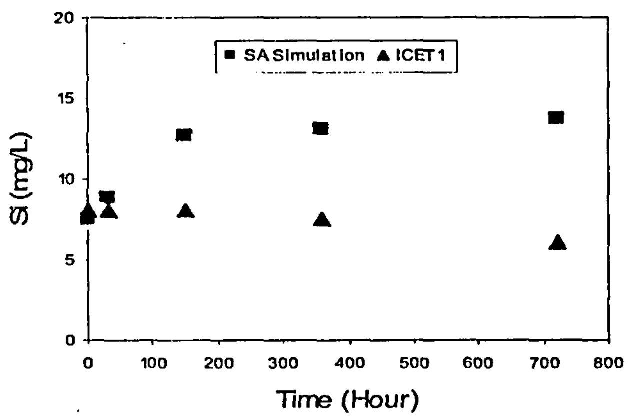
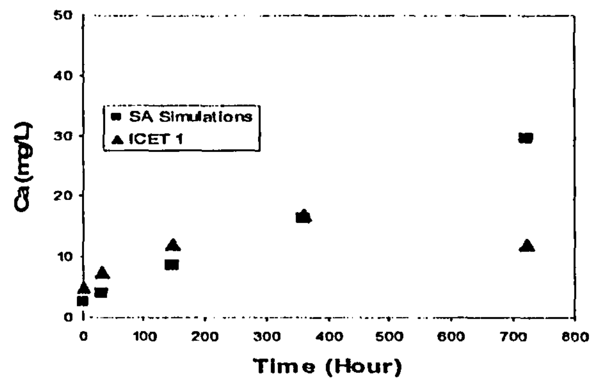
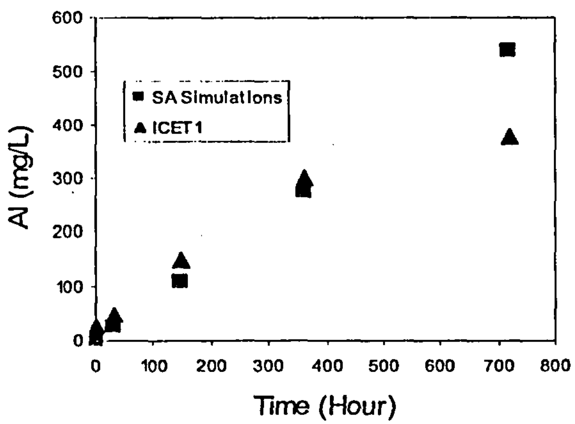
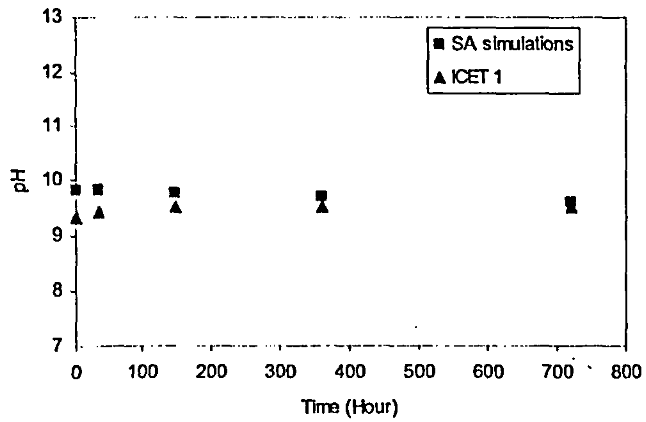
Post-ICET Simulation Results Based on ICET #1 Conditions (pH 10, Nukon)









Analysis of Simulation Results Compared to ICET #1 (pH 10, Nukon)

- Model predicts higher silicon concentration in solution
  - Concrete particulates are assumed to dissolve instantly
  - Silicon concentration well below saturation concentration in pH 10 containment water
- Model predicts higher concentrations for aluminum and calcium at 720 hours
  - Reactivity of the surfaces reduces with time
  - Formation of passive film or secondary phases on the surfaces
- Model predicts formation of solid phases
  - $Fe(OH)_2$ after 148 hours
  - $Zn(OH)_2$ after 32 hours

Summary of Simulation Results

ICET #	Simulation Results
1	Good correlation with major elements up to 360 hours. Simulation predicts higher concentration in solution at 720 hours.
2	Good correlation with major elements, except Ca, up to 360 hours. Simulation predicts Ca precipitation as phosphates.
3	Good correlation with major elements, except Ca, up to 360 hours. Simulation predicts higher concentration of Ca in solution after 96 hours.
4	Prediction did not correlate with ICET results because simulations inputs were based on separate corrosion measurements for CalSil insulation and Al. ICET data indicate strong synergetic effects between CalSil and Al corrosion.
5	Prediction did not correlate with ICET results because simulations inputs were based on corrosion measurements either at pH 10 or 7.

Summary

- Chemical evolution of representative sump waters evaluated as a function of temperature, pressure, and time
  - Calculations indicate that the phases predicted in the pressurized system would be similar to the phases predicted in the non-pressurized system at a lower temperature
  - Insulation and aluminum are major contributors to corrosion products
- Benchmarked thermodynamic simulations to ICET
  - ICET data indicate lack of formation of silicates and aluminum hydroxide in the containment water in a 30-day test
  - Revised thermodynamic modeling calculations indicate good correlation with ICET data for Tests 1, 2, and 3 up to 360 hours
  - Modeling results calculations tend to diverge after 360 hours and are attributed to
    - Selection of initial dissolution rate
    - Reduction in surface reactivity with time due to the formation of a passive layer
- Experimental data indicates strong synergetic effects between insulation and aluminum
- Combination of ICET, laboratory tests, and simulations provides insights into reactor-specific chemical effects

Plan for Upcoming Program

- Additional modeling based on ICET results
  - Include uptake of carbon dioxide
  - Limit precipitation of solid as indicated in ICET results
  - Simulate gradual evolution of ICET containment water chemistry
  - Use PHREEQC for these investigations
- Develop generalized modeling approach for other reactor-specific conditions

Additional Information

- NRC public web site
  www.nrc.gov/reactors/operating/ops-experience/pwr-sump-performance.html
- NUREG/CR – 6873. "Corrosion rate Measurements and Chemical Speciation of Corrosion Products using Thermodynamic Modeling of Debris Components to Support GSI-191"
- NUREG/CR – xxxx. "GSI-191 PWR Sump Screen Blockage Chemical Effects Tests — Thermodynamic Simulations" to be published (3rd Quarter 2006)

Backup Slides

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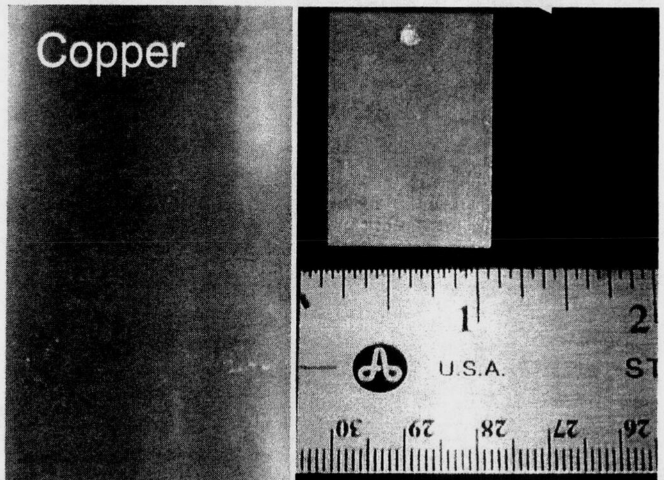
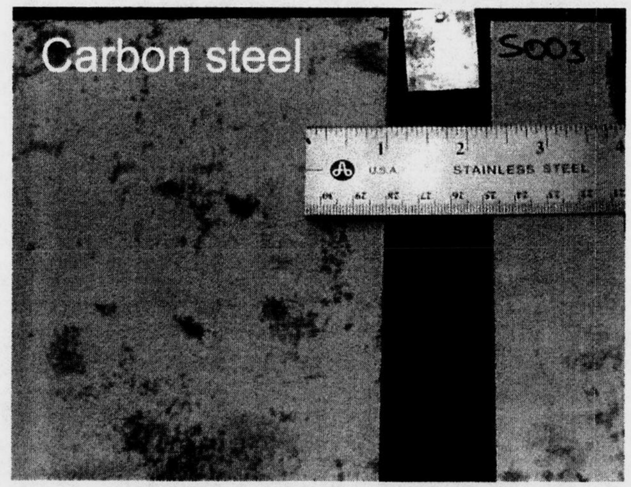
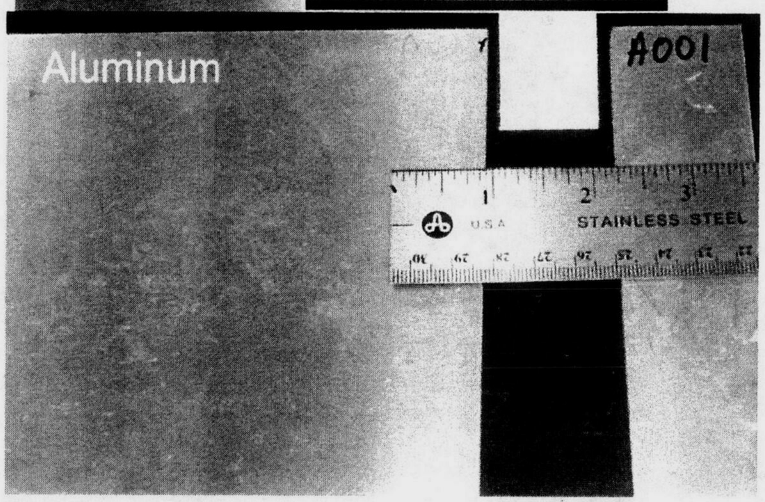
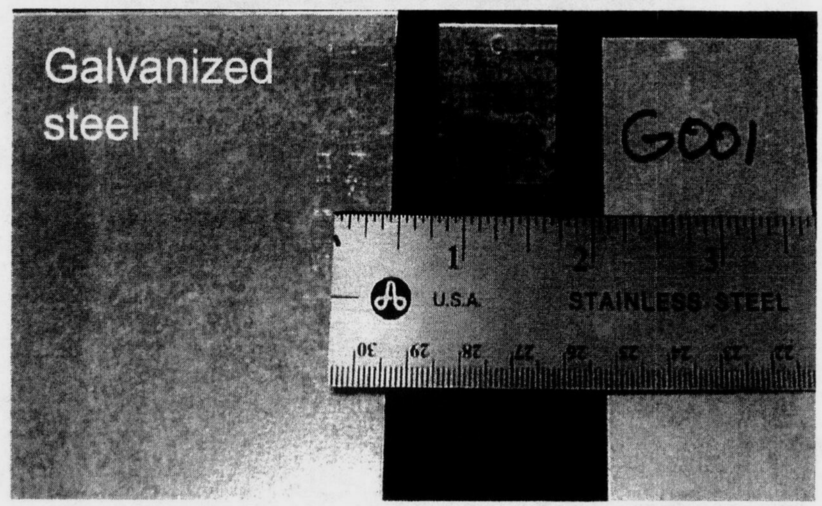
Debris Components: Metals









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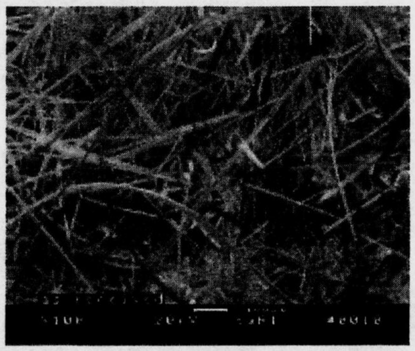
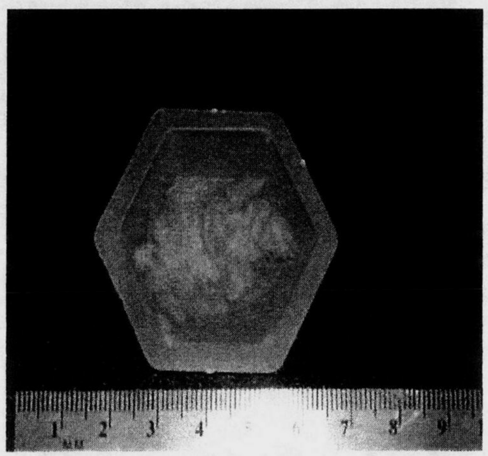
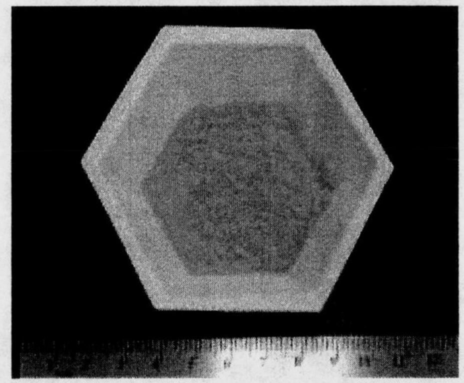
Debris Components: Insulation Samples

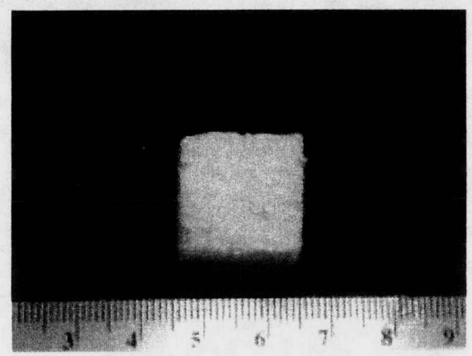
Nukon Fiber



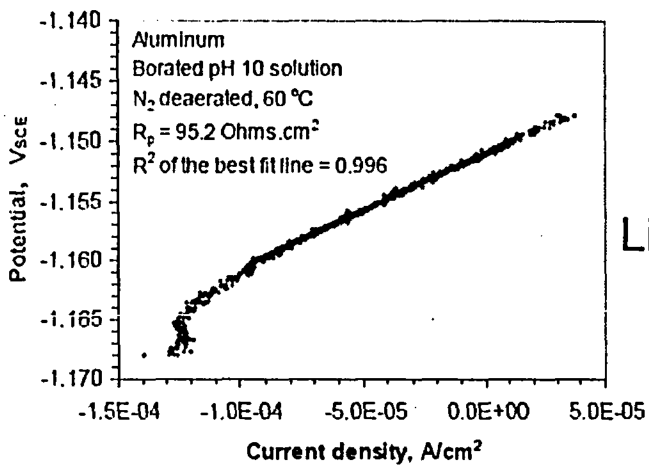


Calcium-Silicate

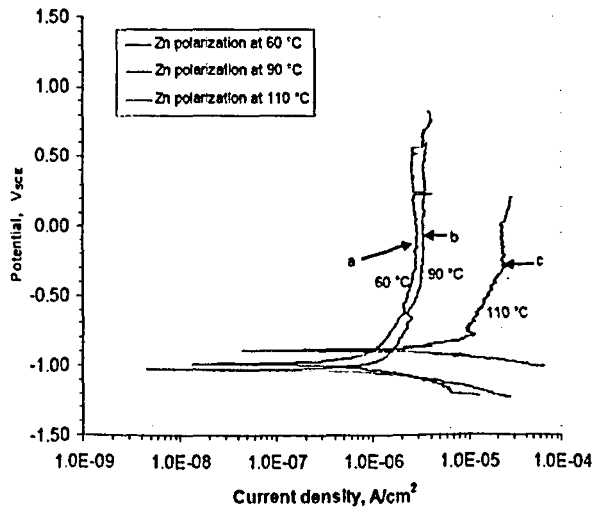




Experimental Results: Metal Corrosion Rates



Linear Polarization



Potentiodynamic Polarization

- Corrosion rates measured in borated alkaline containment water (pH 10)
- Linear polarization method for aluminum and copper
  - Significant noise for carbon steel and galvanized steel
- Potentiodynamic polarization method for carbon steel and galvanized steel

Corrosion Rates: Metals

Table 1. Measured Corrosion Rates for Aluminum, Carbon Steel, Copper, and Galvanized Steel (Zinc) in Borated Deaerated Alkaline Water at pH 10

Metals	Corrosion Rate [$g/m^2 \cdot h$ (mil/yr)]		
	Temperature 60 °C [140 °F]	Temperature 90 °C [194 °F]	Temperature 110 °C [230 °F]
Aluminum Density 2.70 g/cm^3 Equivalent weight 9.66 g/mol	0.986 [126]	1.89 [241]	2.20 [281]
Carbon Steel Density 7.84 g/cm^3 Equivalent weight 27.9 g/mol	1.35×10^{-2} [0.594]	2.95×10^{-2} [1.30]	8.21×10^{-2} [3.61]
Copper Density 8.96 g/cm^3 Equivalent weight 63.5 g/mol	4.78×10^{-3} [0.184]	5.19×10^{-2} [2.00]	9.91×10^{-2} [3.82]
Galvanized Steel (Zinc) Density 7.13 g/cm^3 Equivalent weight 32.7 g/mol	3.57×10^{-2} [1.73]	4.05×10^{-2} [1.96]	2.34×10^{-1} [11.4]
Measured Corrosion Rates for Carbon Steel in Borated Water at pH 7			
Carbon Steel	1.27×10^{-1} [5.59]	9.36×10^{-2} [4.12]	2.14×10^{-2} [0.944]

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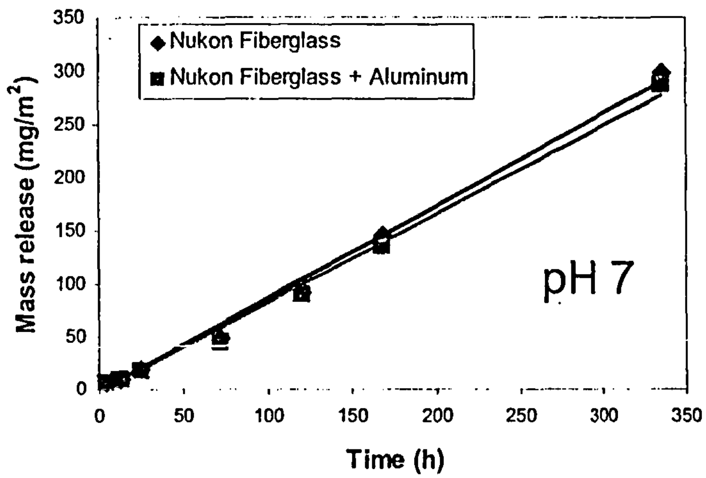
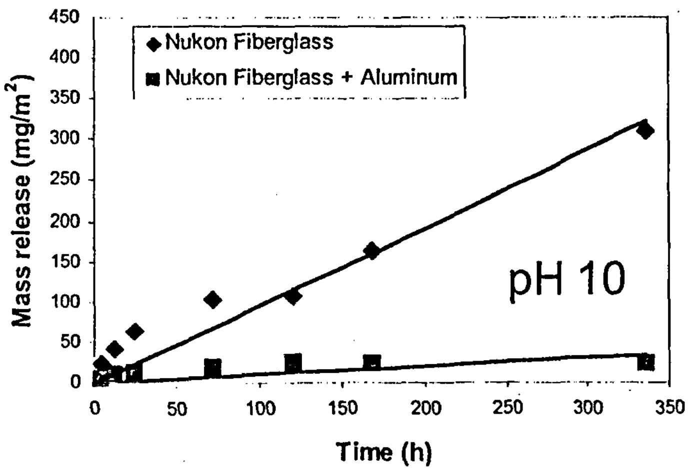
Experimental Results: Nukon Insulation Dissolution Rates





- Nukon dissolution rates measured in pH 10 and pH 7 containment waters with and without aluminum at 60 °C for 14 days
- ASTM C-1220 static leach rate test method
- At pH 7, presence of aluminum makes no difference in leaching behavior
  - Aluminum weight loss negligible
- At pH 10, presence of aluminum significantly inhibits dissolution of Nukon
  - Aluminum weight loss was approximately 40 percent after 336 hours

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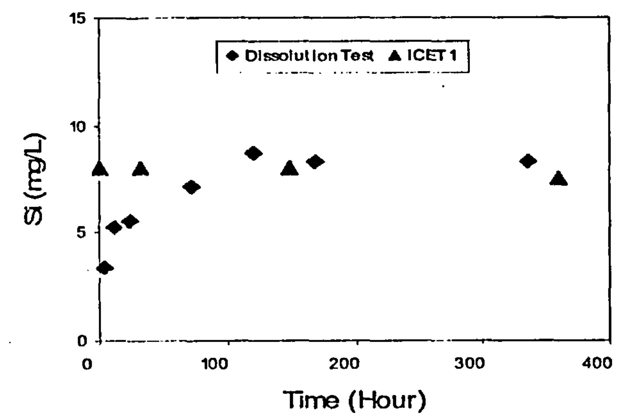
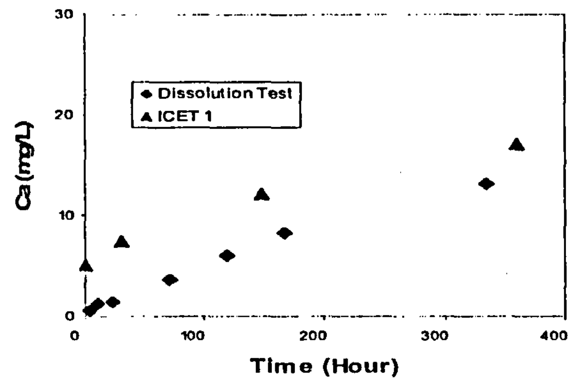
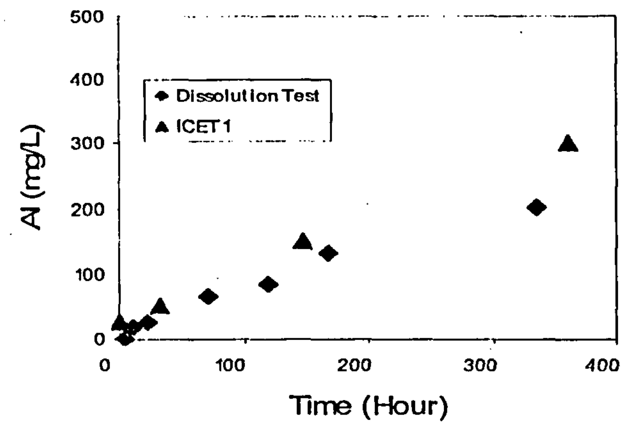
Results and Analysis: Comparison of Dissolution Data With ICET #1 Test Results







- Dissolution tests with Nukon and aluminum in pH 10 containment water at 60 °C indicate release of key elements similar to ICET #1 results
- Slightly higher calcium concentration in ICET #1 attributed to contribution from concrete

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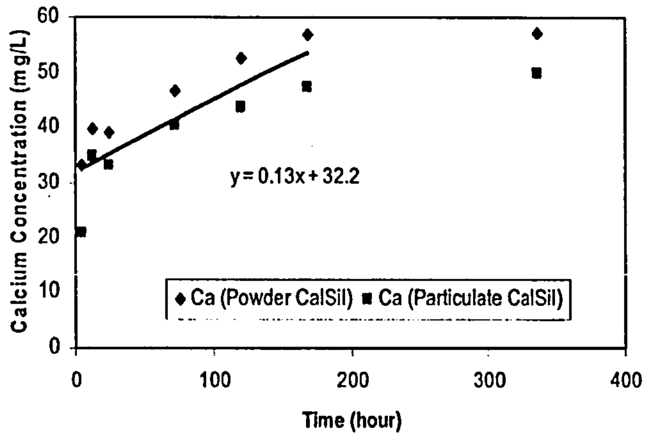
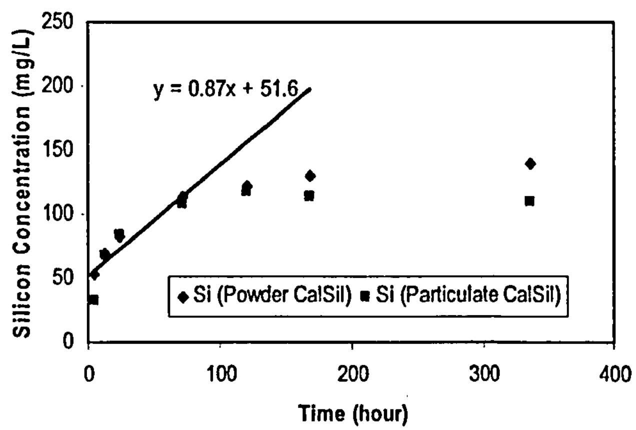
Results and Analyses: Calcium Silicate Insulation Dissolution, pH 10 Containment Water





- Calcium silicate dissolution rates measured in pH 10 and pH 7 containment waters at 60°C for 336 hours
  - Calcium silicate solid and powder samples
- ASTM C-1220 static leach rate test method
- Dissolution rate calculated using initial linear portion
- Incongruent release of calcium and silicon
  - Silicon release is much larger than calcium release
  - Calcium silicate insulation is expected to have similar molar ratio of silicon and calcium
  - Calcium silicate insulation chemical analysis indicates significantly lower silicon compared to calcium

Dissolution Rate: Insulation

Table 2. Summary of Dissolution Behavior of Insulation Materials in Borated Containment Water at 60 °C [140 °F]

Insulation	Test Conditions	Dissolution (mg/L)	Remarks
Nukon low-density glass fiber insulation	Trisodium phosphate, ph 7	0.79 × time	Linear increase with time. Used for estimating amount of Nukon for simulating ICET* #2.
Nukon low-density glass fiber insulation	Aluminum, trisodium phosphate, ph 7	0.76 × time	No effect of aluminum on Nukon dissolution.
Nukon low-density glass fiber insulation	Sodium hydroxide, pH 10	35 + 0.73 × time	Showed instantaneous release.
Nukon low-density glass fiber insulation	Aluminum, sodium hydroxide, pH 10	14 + 0.14 × time	Strong inhibitive effect of aluminum on Nukon dissolution. Maximum release 30 mg/L. Used for estimating amount of Nukon for simulating ICET #1.
Calcium silicate insulation (particulate)	Trisodium phosphate, pH 7	5.61 × P + 1.27 × time	Calcium silicate reaction with trisodium. phosphate. Used for estimating amount of Calcium silicate for simulating ICET #3.
Calcium silicate insulation (solid)	Trisodium phosphate, pH 7	5.61 × P + 3.02 × time	Behavior similar to calcium silicate particulate but higher calcium release.
Calcium silicate insulation (particulate/solid)	Sodium hydroxide, pH 10	Ca: 32.2 + 0.13 × time Si: 51.6 + 0.87 × time	Used for estimating calcium and silicon amount from calcium silicate for simulating ICET #4.

*ICET = Integrated Chemical Effects Test

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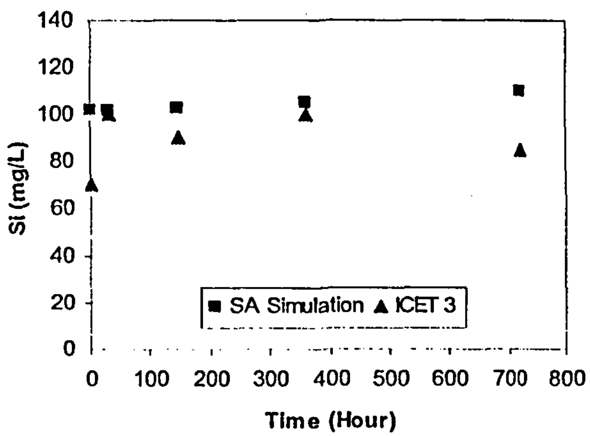
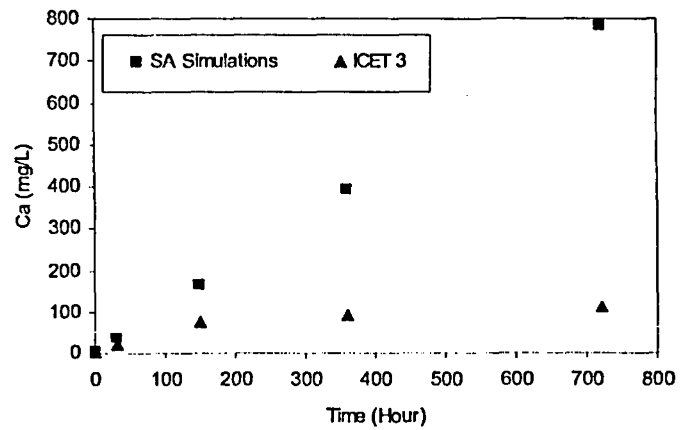
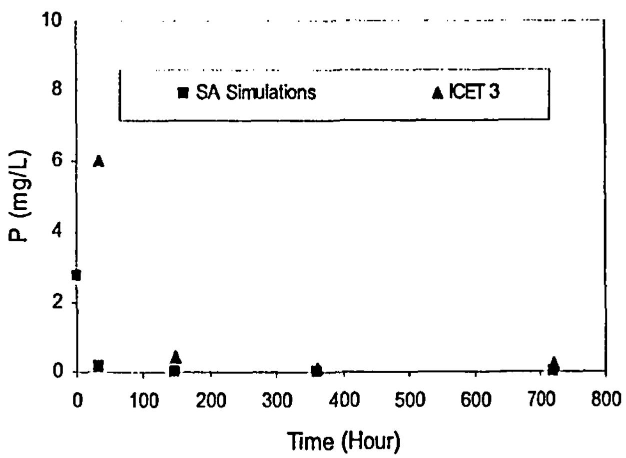
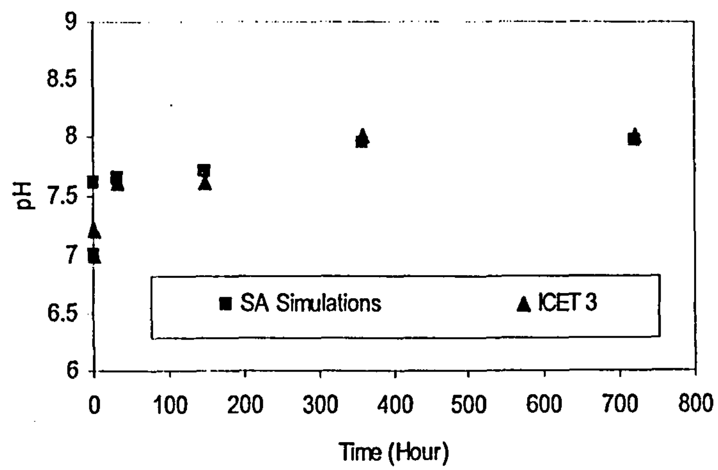
Results: Prediction of ICET #3 20% Nukon and 80% Calcium-Silicate pH 7 Containment Water









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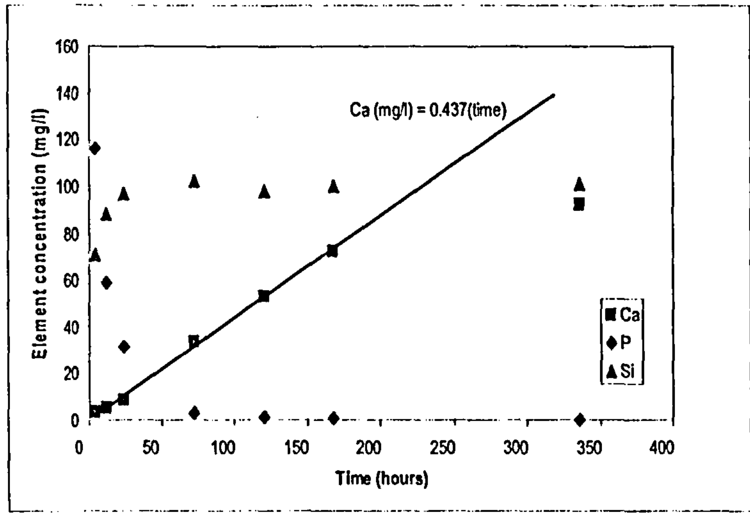
Summary: Prediction of ICET #3 20% Nukon and 80% Calcium-Silicate pH 7 Containment Water



- Approximately 95% of trisodium phosphate was completely consumed within 24 hours
  - Model assumes reaction between trisodium phosphate and calcium-silicate insulation occurs instantaneously
- Model predicts formation of solid phases
  - $Ca_3(PO_4)_2$ instantaneously
  - SiO_2 instantaneously
  - $Zn(OH)_2$ after 360 hours
- High calcium concentration in solution is attributed to the formation of calcium borate complexes

Integrated Chemical Effects Test (ICET) Research Program

Presented by

Dr. B. P. Jain, P.E.
Engineering Research Applications Branch
Division of Engineering Technology, RES

Bruce Letellier
Los Alamos National Laboratory

at
ACRS Thermal-Hydraulics Subcommittee Meeting
February 14-16, 2006

Contents

- ICET RECAP
- Objective & Regulatory Use
- ICET Test Plan
- Significant Research Findings
- Tests 4 and 5 Results
- Where to find more ICET information

ICET RECAP

- July 20, 2005 – Briefed ACRS T-H Subcommittee

  - **ICET Test Plan and Test Matrix**
  - **Test Loop and Test Operation**
  - **Results of Tests 1-3**

- Results of Final ICET Tests 4 and 5 are Presented Today

ICET Program Objectives

- Determine, characterize, and quantify the chemical reaction products that may develop in a PWR containment pool under a representative post- LOCA recirculation phase

- Determine and quantify any gelatinous material that could develop during post-LOCA circulation phase

Regulatory Use of ICET Findings

- **ICET research used by NRC in resolving GSI-191**
  - Support NRR review of licensee responses to Generic Letter 2004-02
  - Plans for chemical effects head loss testing at ANL

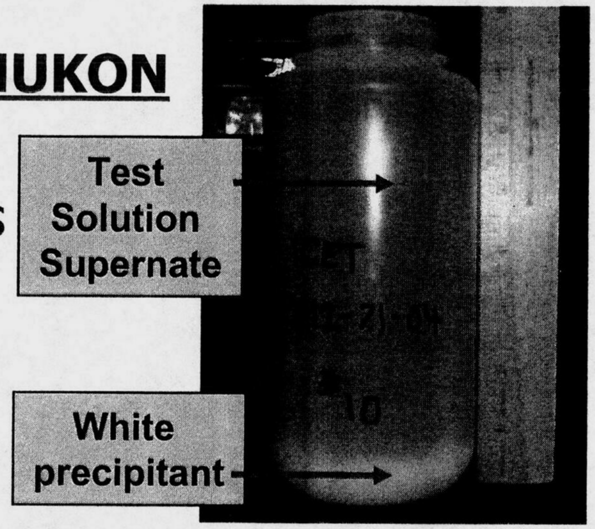
ICET Test Plan (30 day test)

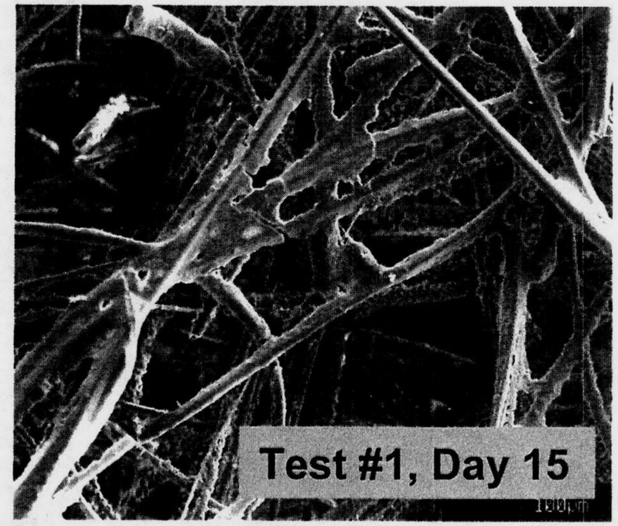
Test	Temp, C	Buffering Agent	Initial pH	Boron (ppm)	Comment
1	60	NaOH	10	2800	100% fiberglass insulation, high pH, NaOH concentration determined by pH
2	60	TSP	7	2800	100% fiberglass insulation, lower pH, TSP concentration determined by pH
3	60	TSP	7	2800	80% cal-sil/20% fiberglass insulation, lower pH, TSP concentration determined by pH
4	60	NaOH	10	2800	80% cal-sil/20% fiberglass insulation, high pH, NaOH concentration determined by pH
5	60	Sodium Tetraborate	8.0 – 8.5	2400	100% fiberglass insulation, pH determined by achieving target boron concentration.

Significant Research Findings: ICET

Test #1: NaOH & NUKON

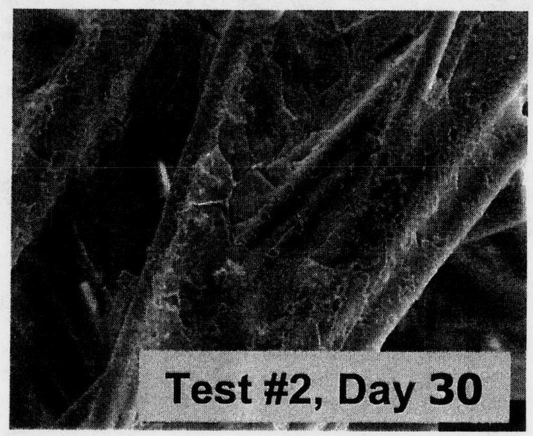
- White precipitate
- Insulation deposits





Test #2: TSP & NUKON

- Insulation deposits



Test 3 Gel-Like Material at Tank Bottom

J

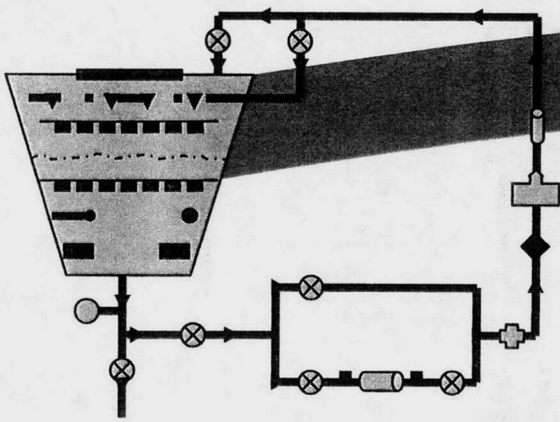
Integrated Chemical Effects Tests
Test Methodology

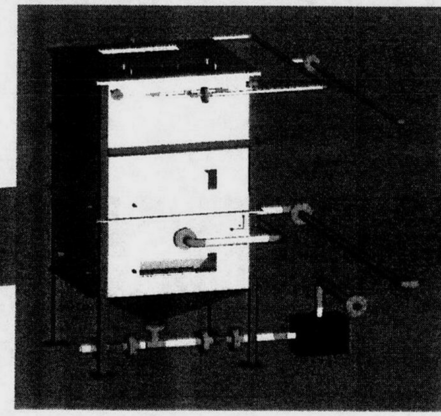
Bruce Letellier
Nuclear Design and Risk Analysis
Los Alamos National Laboratory

ICET Development Timeline

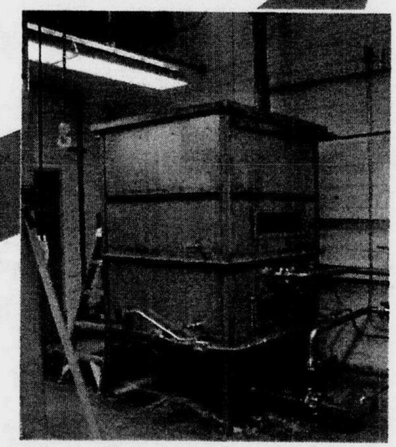
Los Alamos
NATIONAL LABORATORY
EST. 1943

Conceptual Design June 04

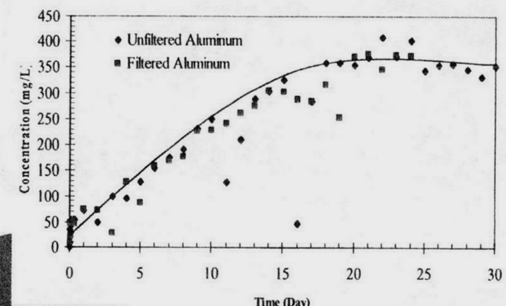




Structural Design and Fabrication July-Aug 04



Assembly and Shakedown
Sept-Oct 04

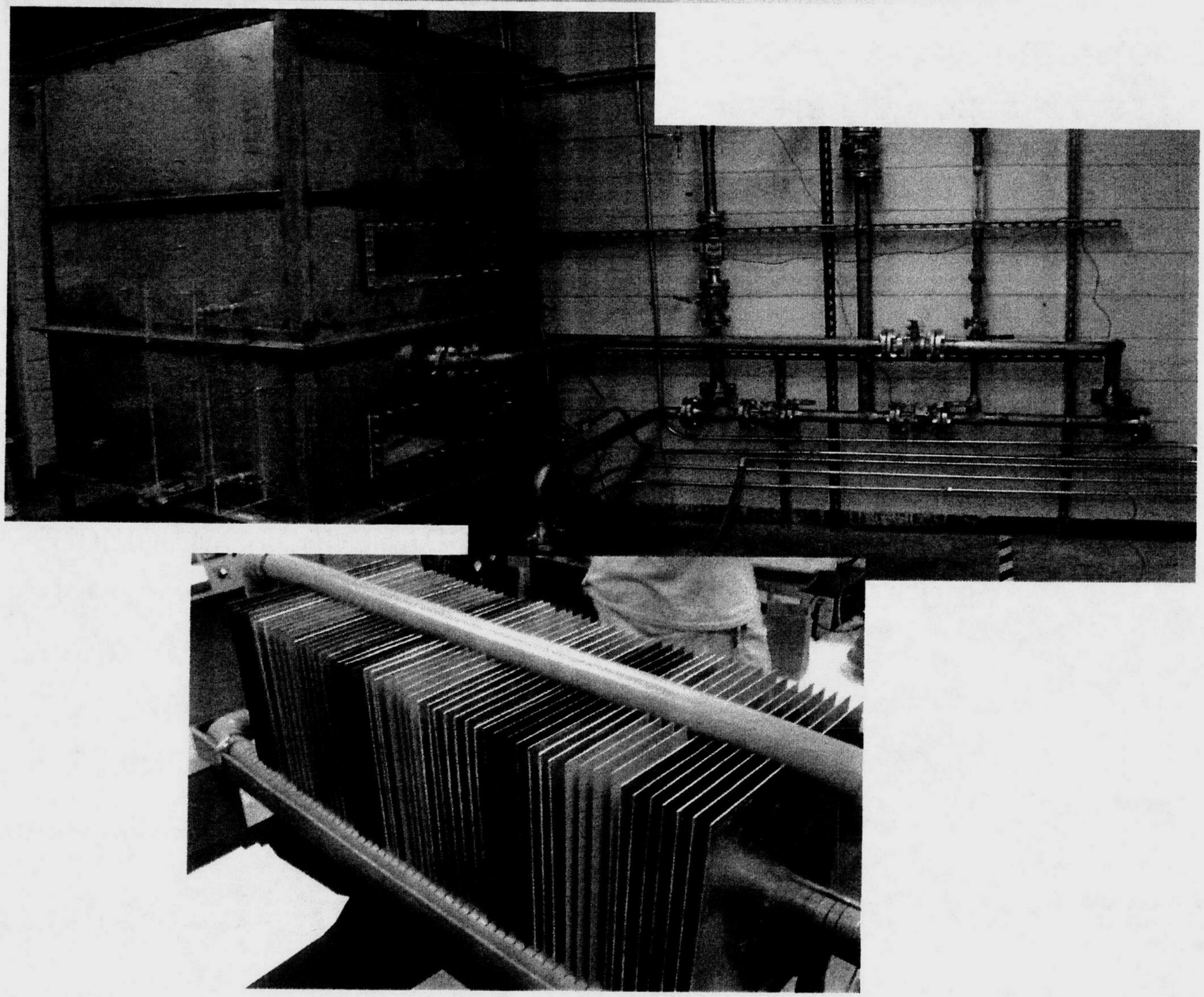


Test #1 Complete Dec 21, 04

Test 5
Complete
Aug 05

ICET Chemical Effects Tank

Los Alamos NATIONAL LABORATORY EST. 1943



Physical Attributes

Los Alamos NATIONAL LABORATORY EST.1943

- Stainless steel construction with CPVC spray distribution
- 250 gal of reverse-osmosis (RO) treated water
  - Approx 1/3 full up to lower flange
- Redundant 3.5 kW titanium jacketed heating elements
- One submerged coupon rack and six suspended coupon racks for 374 total coupons (including 1 submerged concrete slab)
- Polycarbonate view ports (1 below water, 1 above water, 1 in cover)
- External sight glass for water level
- External thermal insulation (~1.2 kW heat loss)
- Three thermocouple probes in pool (<1 °C variation, ~1 °C drop in piping)
- Automated data acquisition for pH, flow rate, and temperature
  - Paging system for offsite alarm, remote website monitoring access
- Emergency power generators, backup pump, duplicate data storage, valve isolation of diagnostic loop

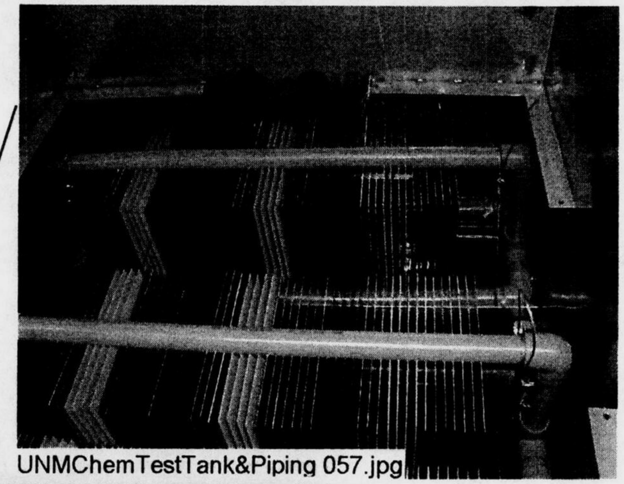
ICET Tank Operations

Los Alamos NATIONAL LABORATORY EST. 1943

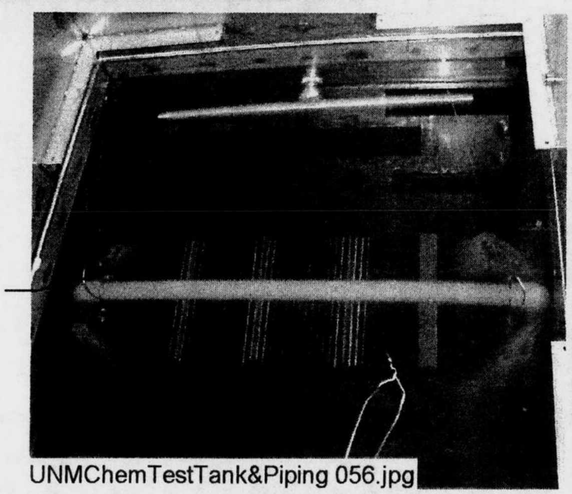

DSC02520.JPG

Gantry Loading of Coupon Racks

Upper Suspended Coupon Racks


UNMChemTestTank&Piping 057.jpg

Single Submerged Coupon Rack


UNMChemTestTank&Piping 056.jpg

DSC02539.JPG

Side View Port Above Water Line

ICET Parameter Summary

- ICET Tests # 1 – 5 have many common test parameters
  - Coupon racks: 373 metal (mixed type) + 1 concrete slab
  - Test temperature: 60°C (140°F)
  - Test pressure: ambient
  - Recirculation flow: 25 gpm
  - Flow velocity over submerged coupons: 0 – 3 cm/s
  - Boron concentration: 2800 ppm
  - HCl concentration: 100 mg/L
  - LiOH concentration: 0.7 ppm lithium
- Tests # 1 and # 4 add NaOH for a target pH of 10
- Tests # 2 and # 3 add trisodium phosphate for a target pH of 7
- Test # 5 combined 100 gal. of the standard solution with 150-gal. of 1.8% sodium tetraborate solution

Sample Types

- Fiberglass blankets
- Sacrificial fiberglass coupons
  - (high-flow, low-flow regions)
- Water samples
- Filter paper
  - High-volume and daily
- Visible precipitates
- Floor sediment
- Fiberglass drain column
- Metal coupons
- Post-test "sludge"
- Tank and pipe residue
- Clean Baselines
  - Fiberglass
  - Latent debris
  - Nylon mesh
  - Metal coupons

Supporting Diagnostics and Analyses

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- Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS)
- Environmental SEM
- Transmission Electron Microscopy (TEM)
- X-Ray Diffraction (XRD)
- X-Ray Fluorescence (XRF)
- Inductively Coupled Plasma (ICP) spectroscopy
- Total Organic Carbon (TOC)
- Carbonate analysis
- Shear-rate viscosity
- Optical microscopy

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Integrated Chemical Effects Tests
Survey of Results

Bruce Letellier
Nuclear Design and Risk Analysis
Los Alamos National Laboratory

ICET Test 4 General Observations

- **Day 1**: No deposits on coupon racks or insulation, most Cal-Sil had settled.
- Test Observations:
  - Excluding Day zero, tank clarity and color remained constant.
  - No corrosion products are apparent on the submerged coupons.
  - No obvious chemical by-products present in the tank.
  - No precipitates visible in water samples.
- Post-Test Observations.
  - Very little corrosion apparent on submerged specimens, in contrast to Test #1.
  - More corrosion evident of unsubmerged specimens than submerged specimens (especially Al and Zn).
  - Some apparent chemical by-products evident in insulation samples (webbing), but not as prevalent as in Test #1.

ICET Test 4 General Observations

- Less scale in tank after draining compared to Test #3.
- Insulation samples clearly visible in bags.

Test Chamber: Top View during Draining

ICET Test 5 General Observations

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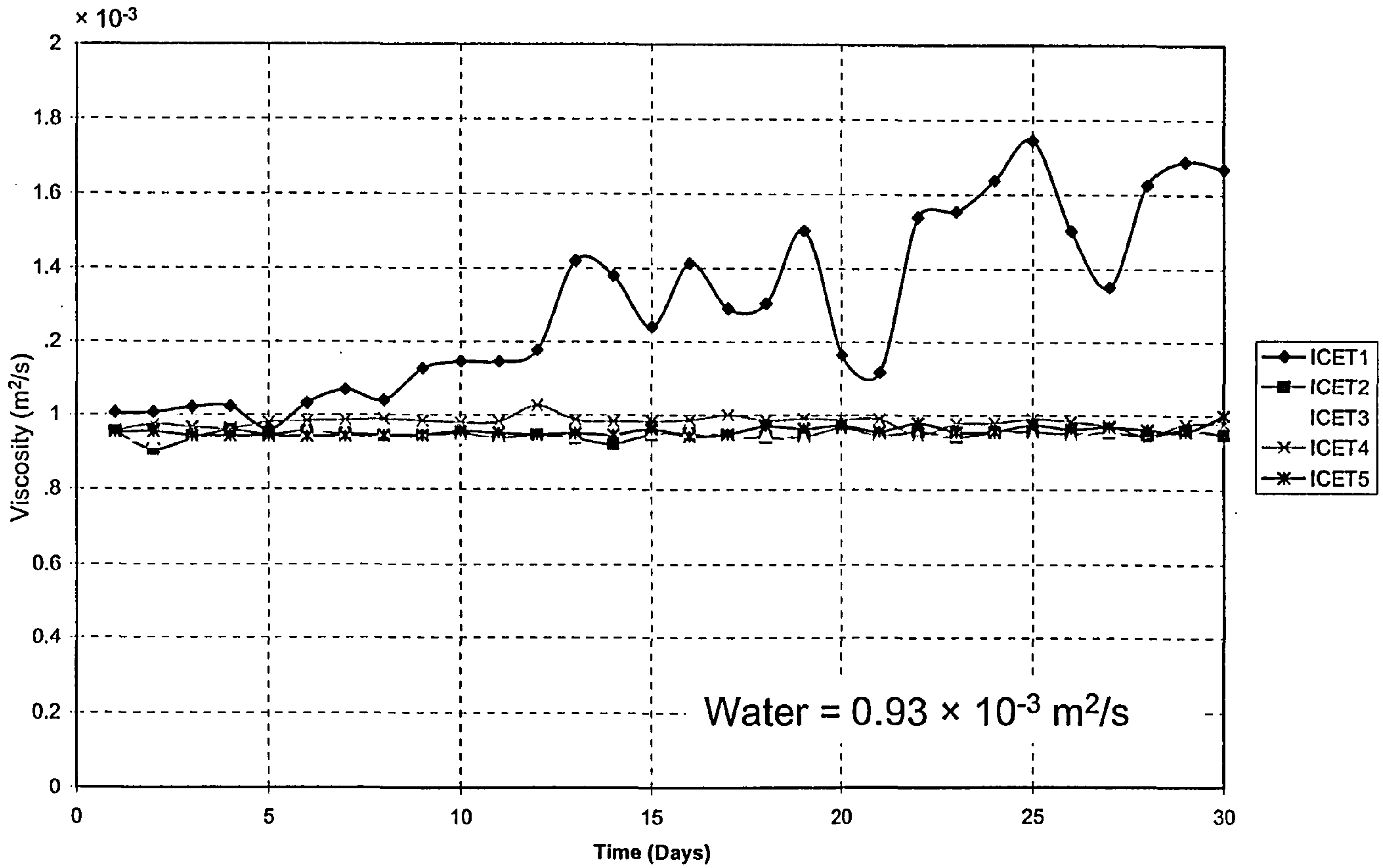
- pH
  - Before sprays, 6.48 kg boric acid, 10 kg borax, and 0.284 g lithium hydroxide were dissolved into the ICET tank for pH ~8.4 at 60 °C
  - During addition of HCl, pH dropped to 8.34. Continued decline to 8.21 over first 8 days of test
- Turbidity (60 °C)
  - 0.77 NTU before latent debris and concrete dust, 14.1 NTU after latent debris and concrete dust, declined to 12.4 after 4 hours, asymptotic decline to 0.97 NTU after 8 days
  - Remained turbid longer than other tests. Opposite side visible Day 6
  - Slight increase in 23 °C turbidity near end of test
- Hydrogen Generation
  - At or below 0.1% through Day 17, nondetect thereafter.

ICET Test 5 General Observations (cont.)

- Precipitates
  - Visible ppts in Day-8 sample (room temp) by Day-17
  - Visible ppts in Day-2 sample after many days at room temp. Wispy, easily suspended, 2-3 days for resettling
  - Visible ppts in post Day-30 solution when cooled 20 ^{o}C over 10 min.
- Kinematic Viscosity
  - No apparent trend at either 23 or 60 ^{o}C
- Metal corrosion
  - Relatively little discoloration and mass loss by comparison
  - Al had rough dull coating by Day 22 similar to IOZ coated steel
- Fiberglass Condition
  - Relatively clean with no visible external deposits and minor interior deposits found under SEM

Kinematic Viscosity (23°C)



Kinematic Viscosity (60°C)

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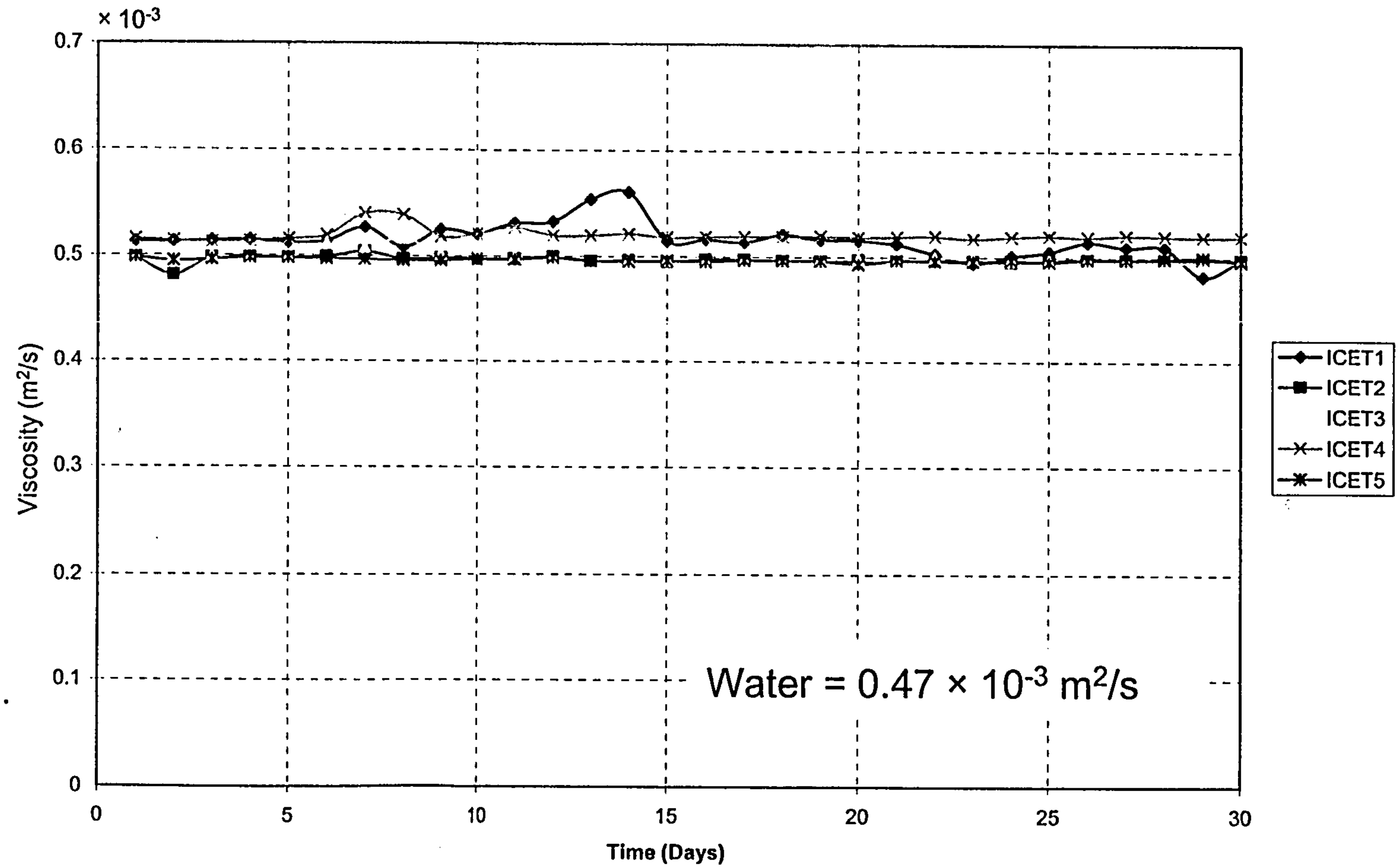
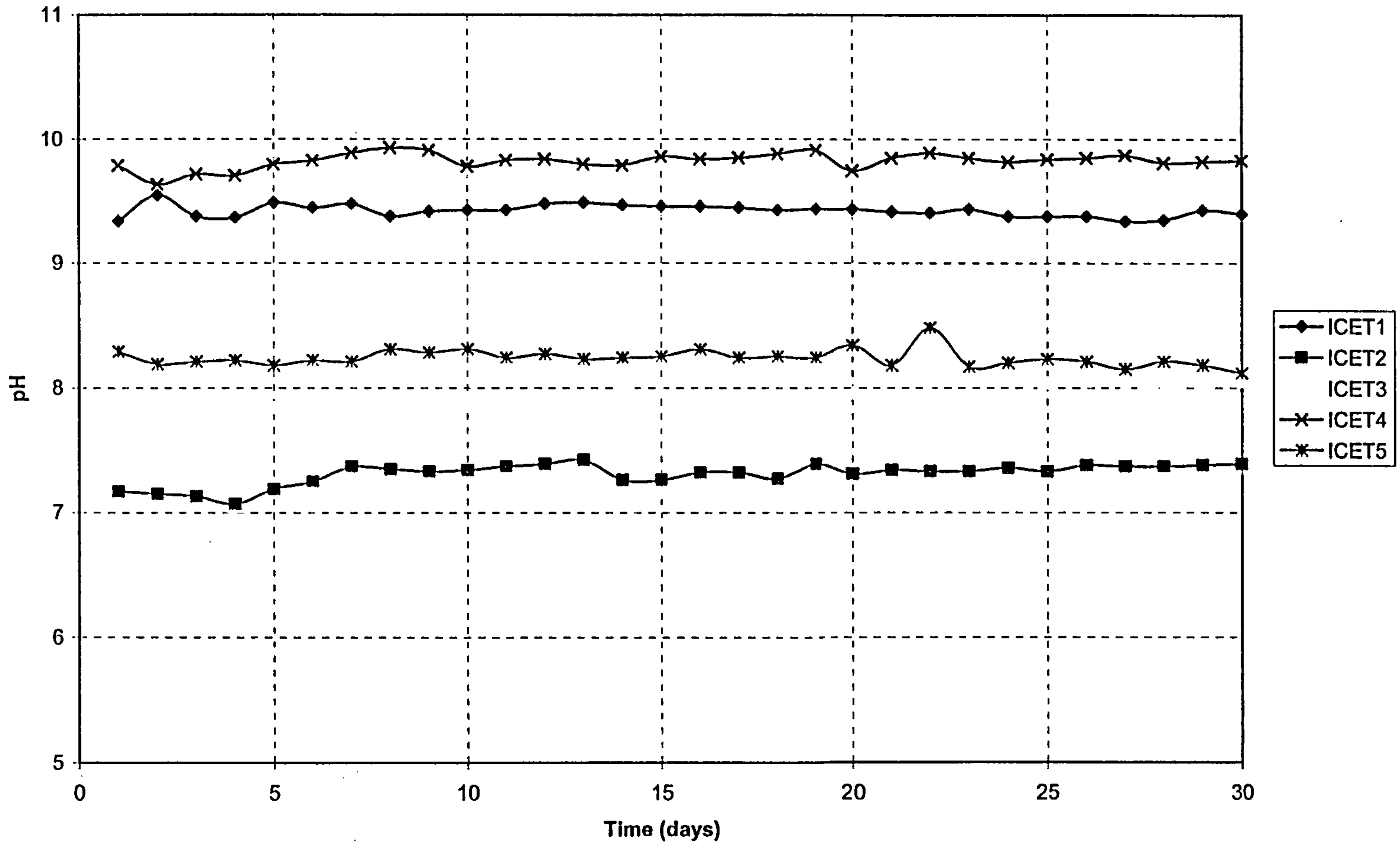


Benchtop pH



11
10
9
8
7
6
5
pH
0
5
10
15
20
25
30
Time (days)
ICET1
ICET2
ICET3
ICET4
ICET5

Total Suspended Solids

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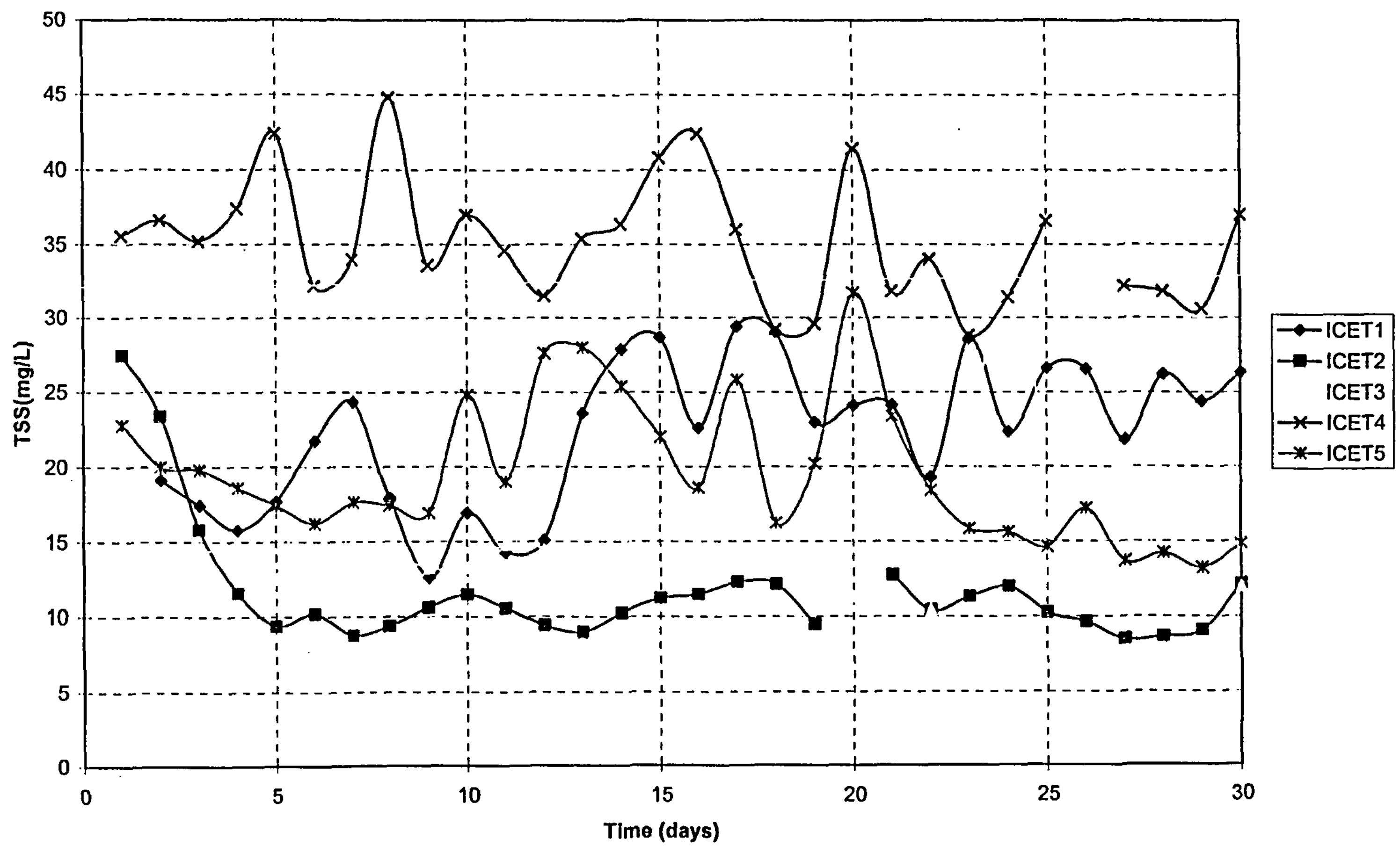
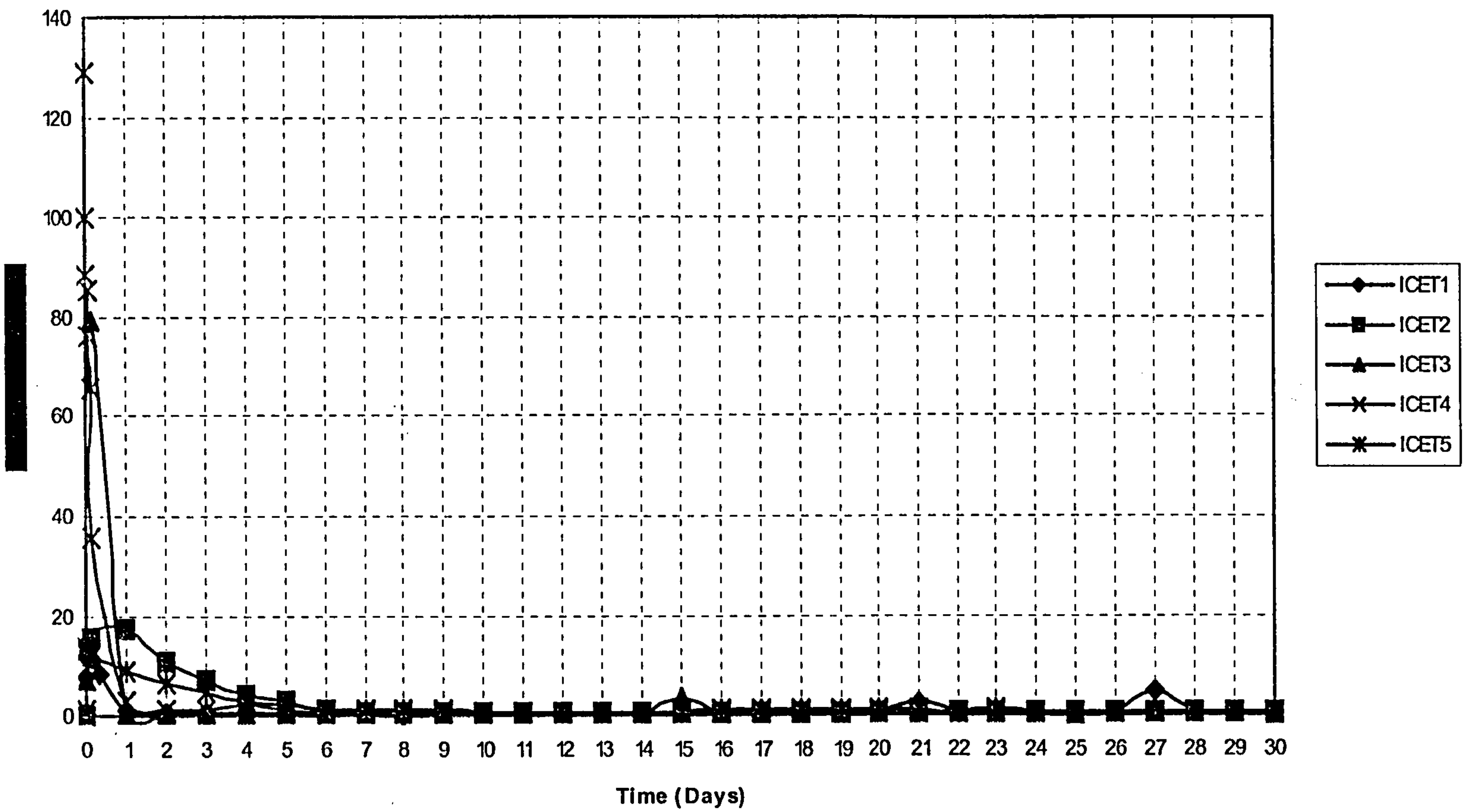
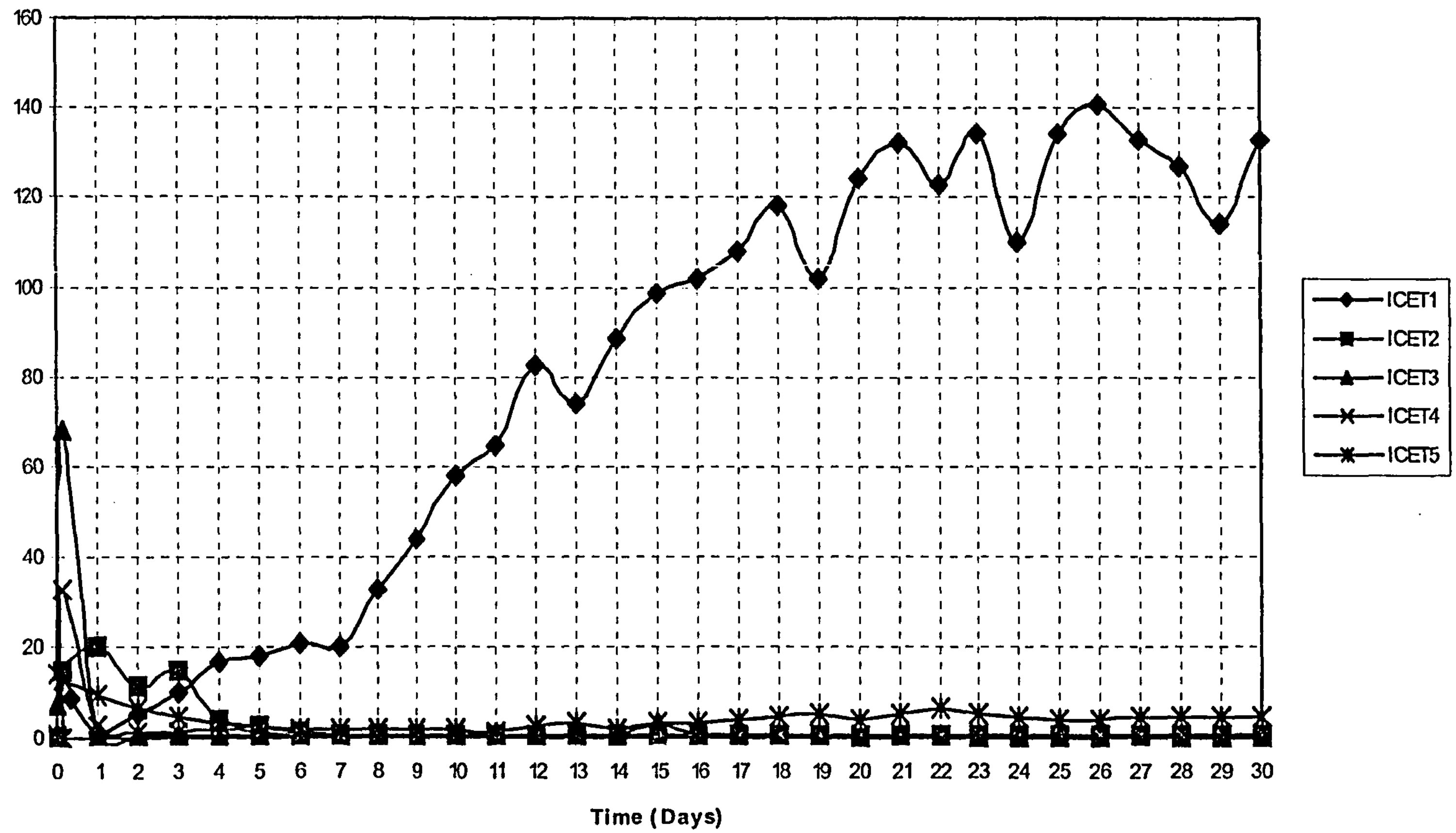


Turbidity (60°C)



Turbidity (25°C)



Hydrogen Generation

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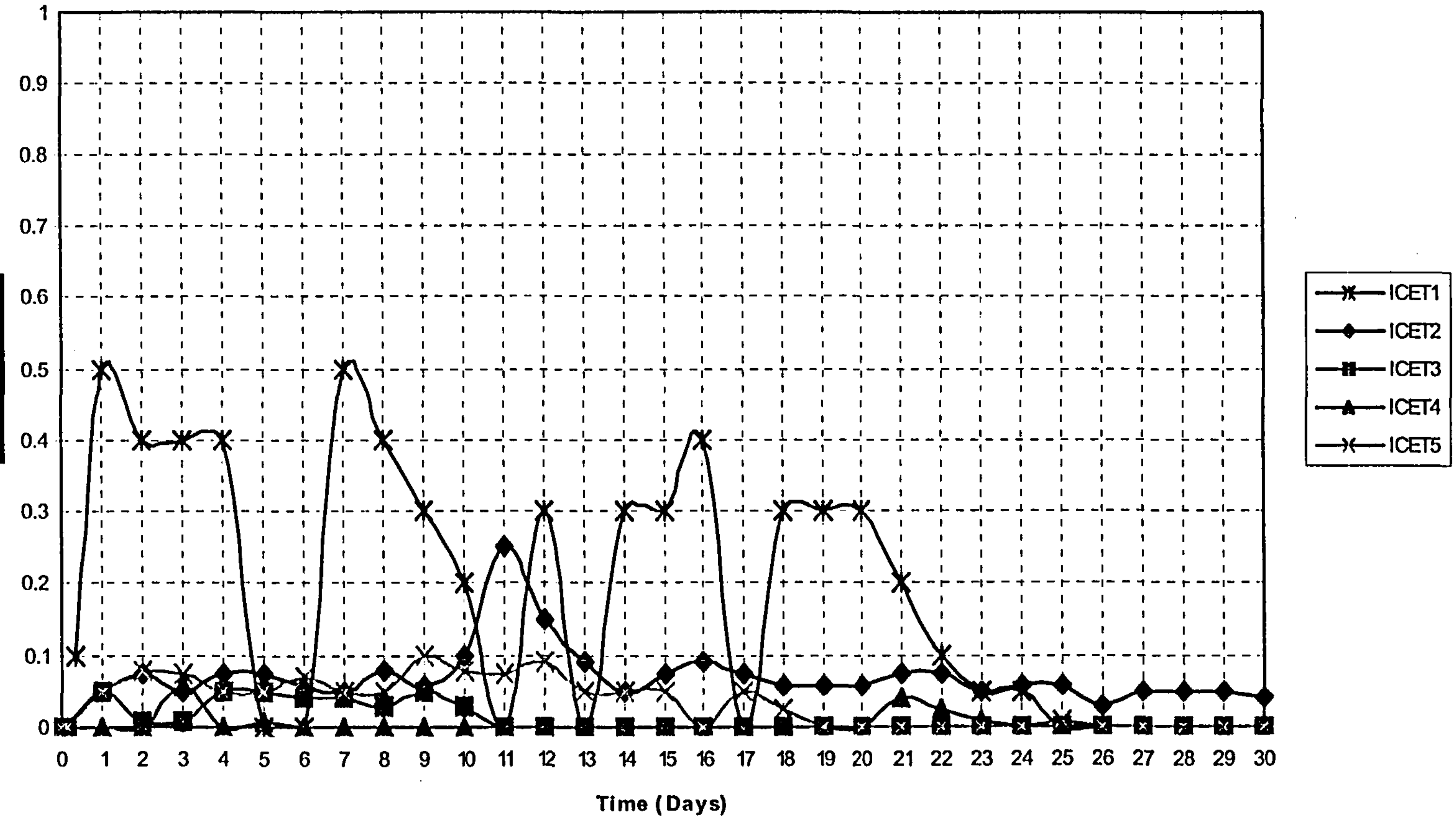
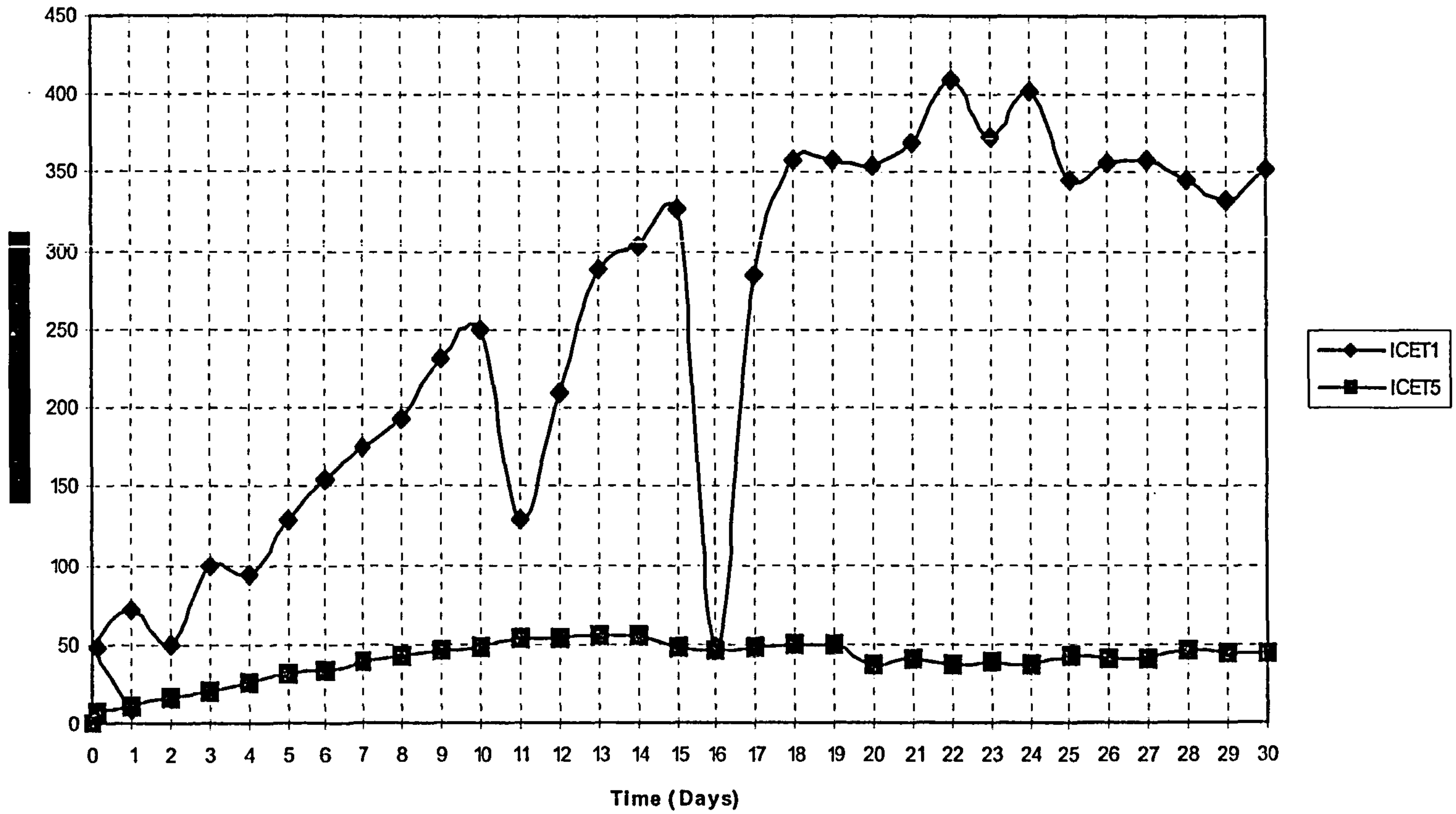
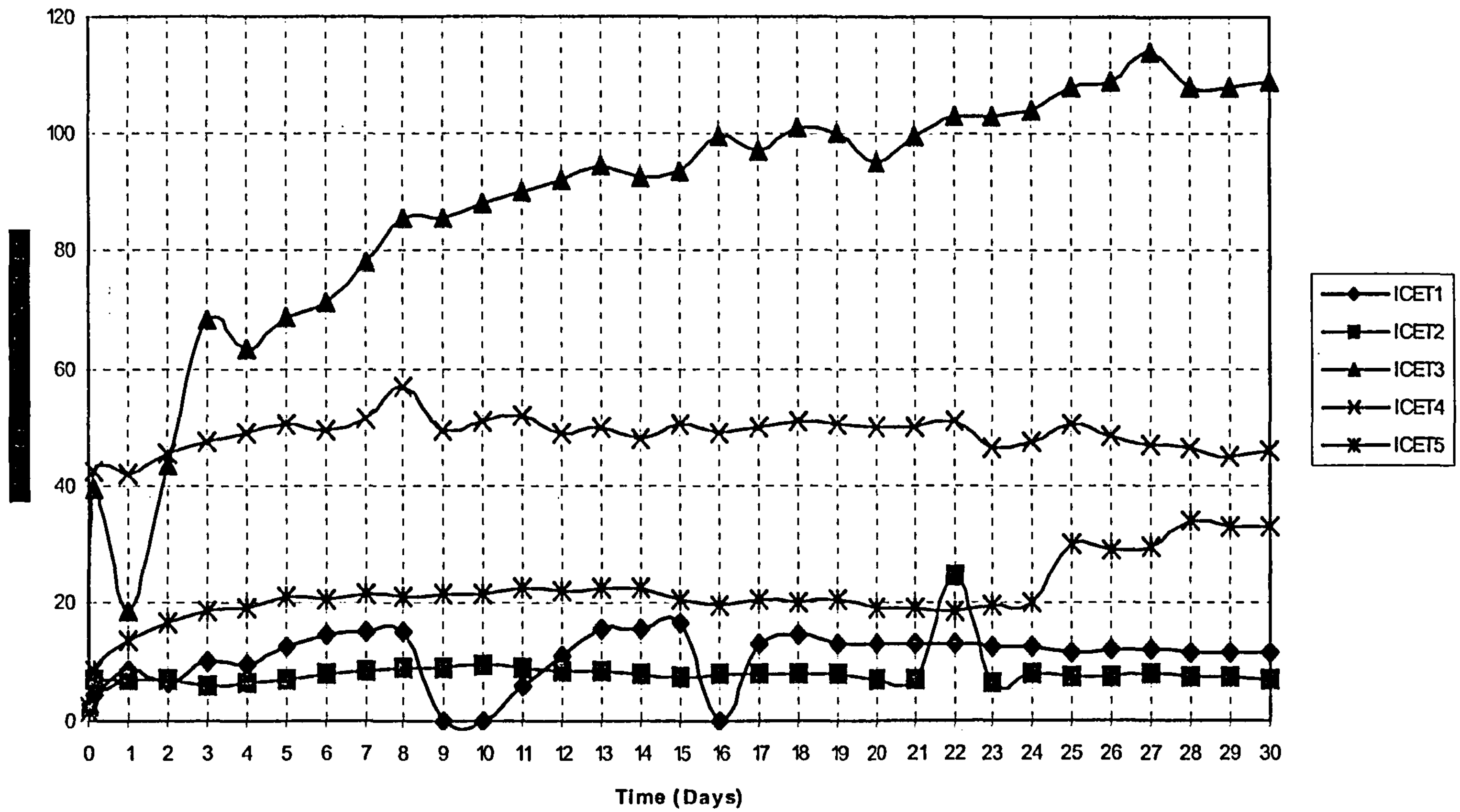


Unfiltered Aluminum Concentration



Unfiltered Calcium Concentration



Unfiltered Copper Concentration

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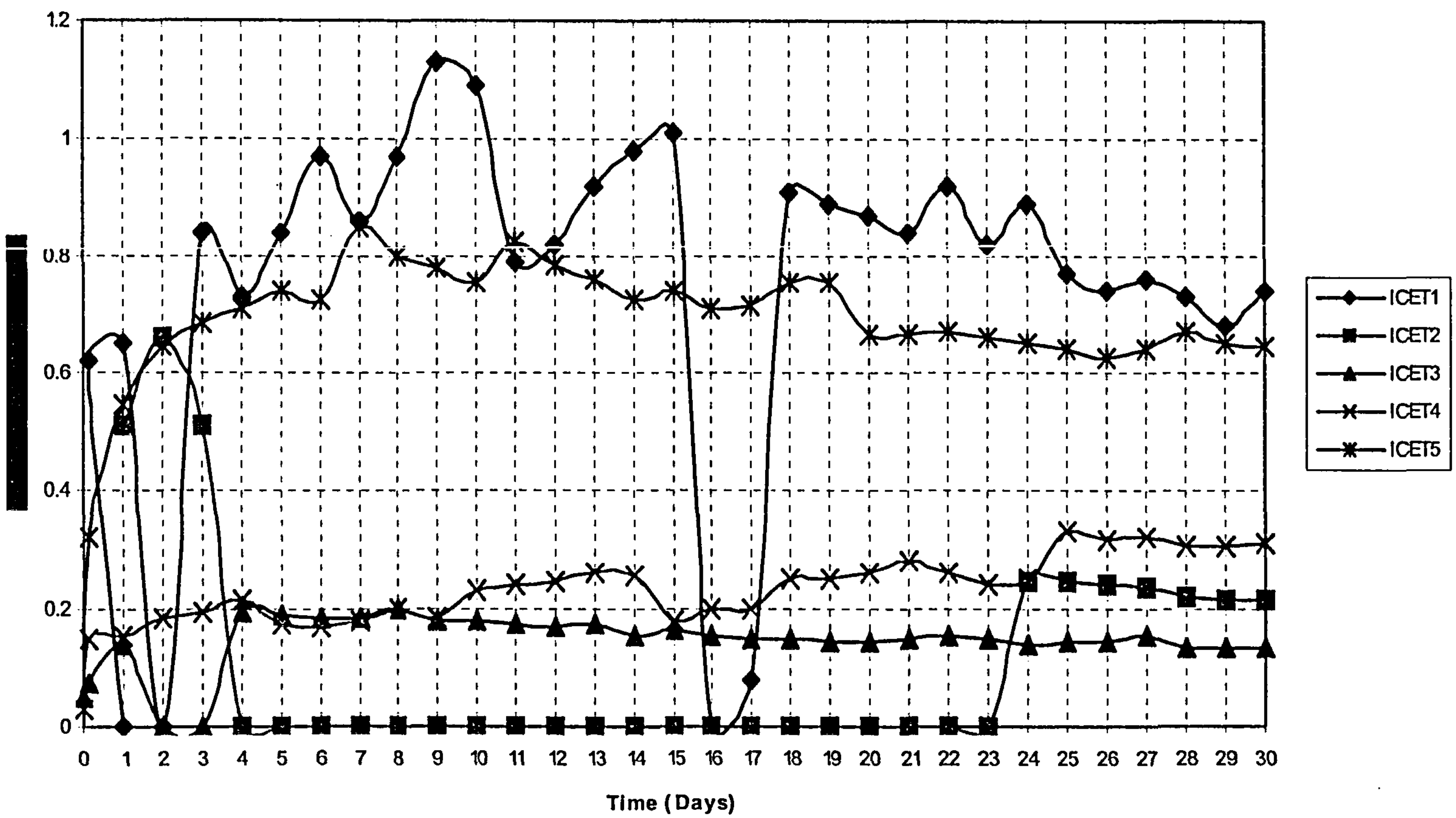

Unfiltered Silica Concentration

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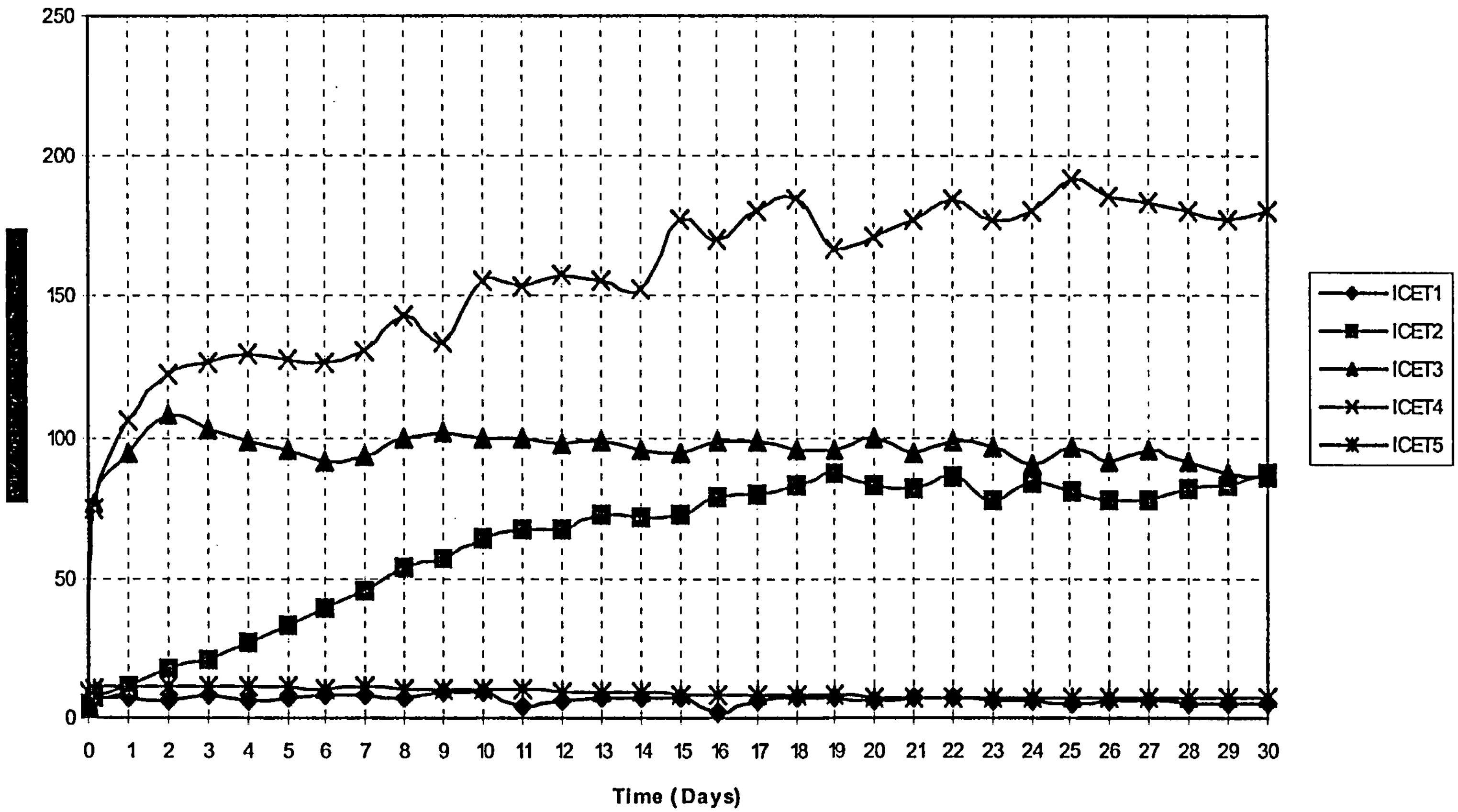

Unfiltered Sodium Concentration

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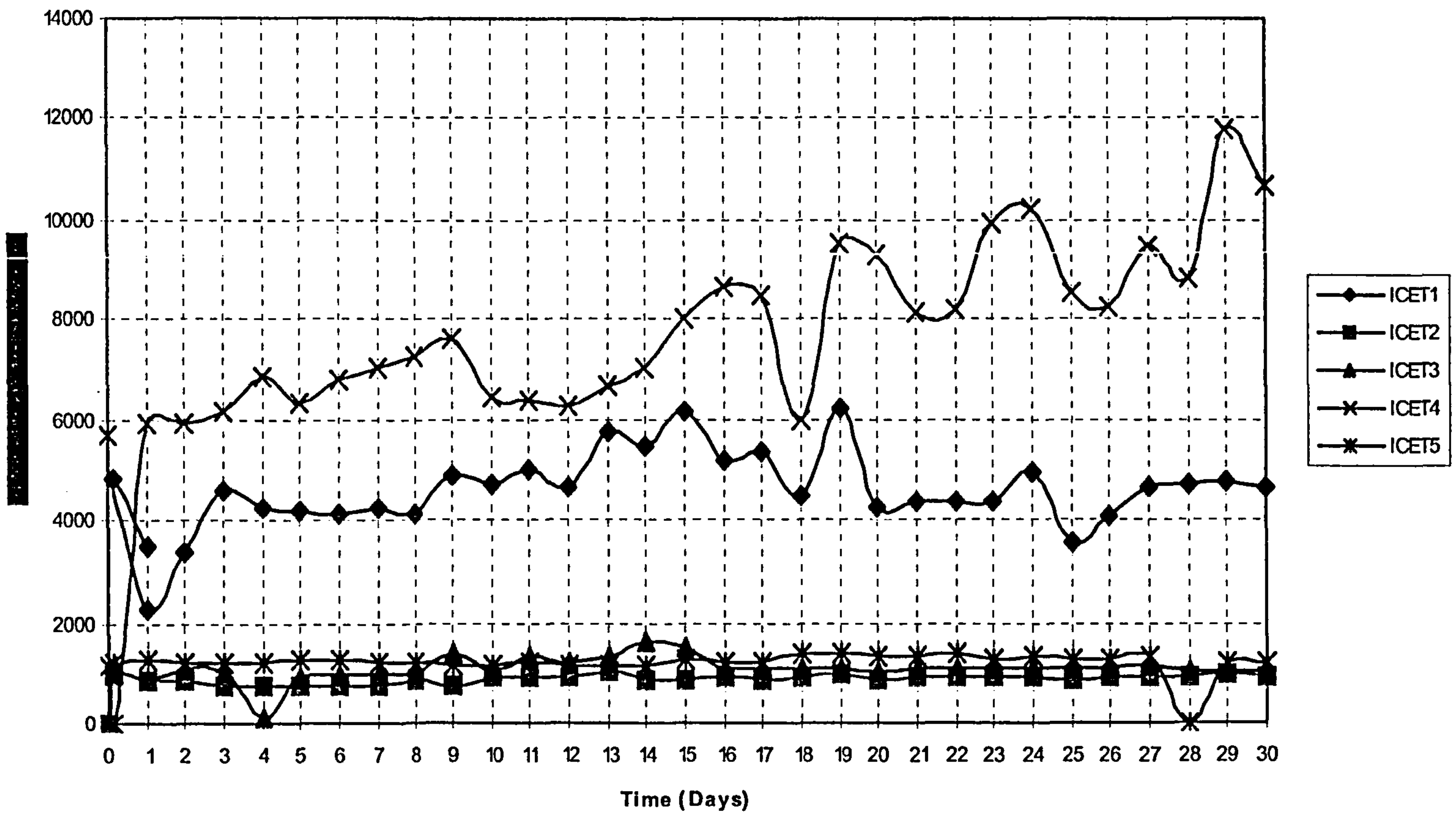

Unfiltered Magnesium Concen.

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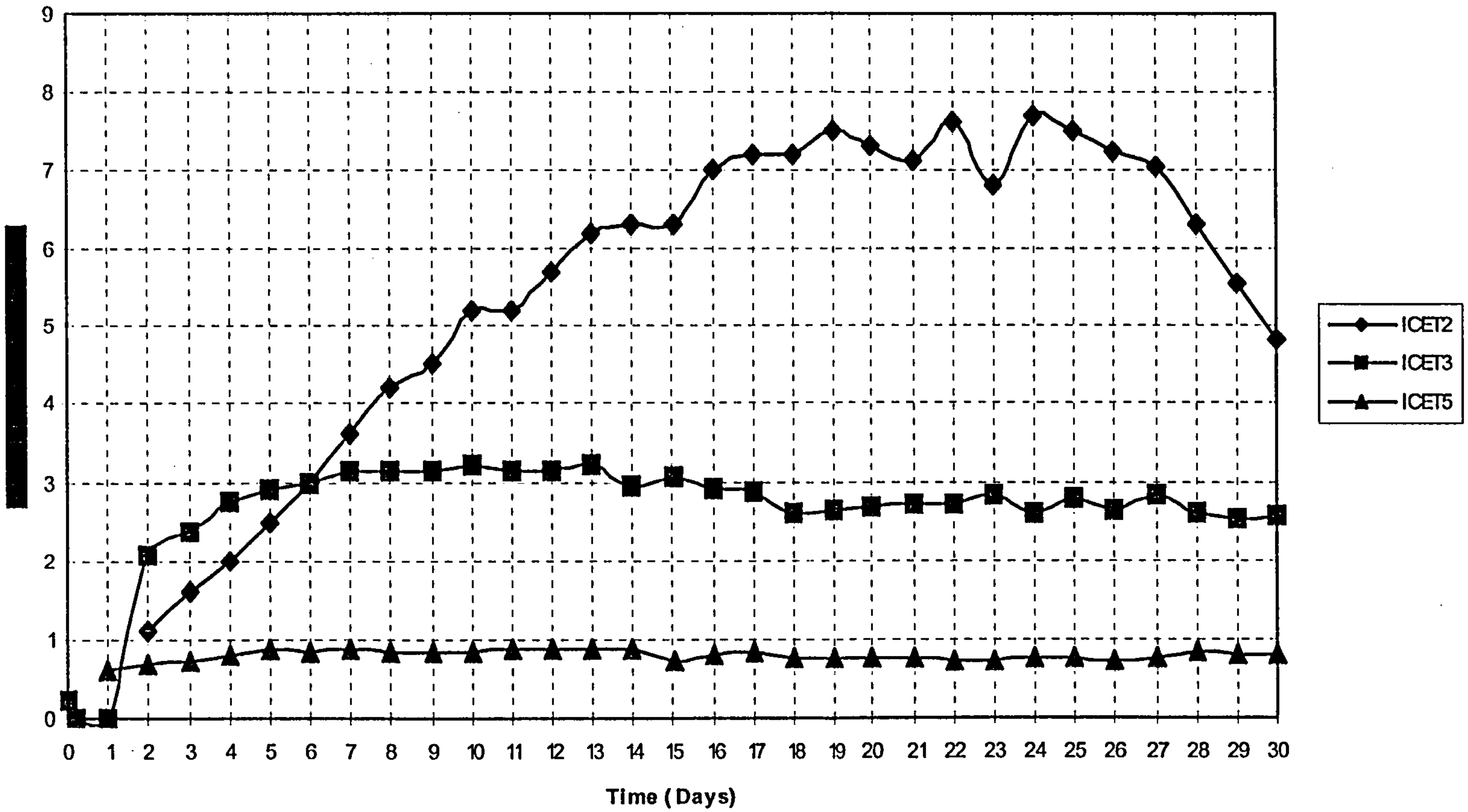

Additional Information on GSI-191/ICET

- NRC Public Web Site
  www.nrc.gov/reactors/operating/ops-experience/pwr-sump-performance.html
- Test Plan, Rev. 13 (ADAMS ML052100429)
- Test 1 Data Report (ADAMS ML051800488)
- Test 2 Data Report (ADAMS ML052770416)
- Test 3 Data Report (ADAMS ML053040533)
- Test 4 Data Report (ADAMS ML053350172)
- Test 5 Data Report (ADAMS ML053550433)
- Web Summary of All Five ICET Test Results and Implications (ADAMS ML052840114)
- Summary NUREG/CR – Available in 3rd Qt 2006

Backup Slides Follow

ICET Findings:
Test #3 Initial Observations

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- **Conditions:** pH ~7.1 with 80% Cal-Sil and 20% fibrous insulation.

- Turbidity
  - Initially, very high (> 200 NTU) right after Cal-Sil added into the tank.
  - Decreased to ~ 60 NTU just prior to initiating the spray phase.
  - After 30 minutes into the TSP injection phase, increased to > 200 NTU.
  - After TSP+HCL mixture was injected into the spray, turbidity came down to appr. 80 NTU at the conclusion of 4-hour spray phase.
  - Turbidity at 0.4 NTU after 24 hours.

- White Precipitant
  - After 30 minutes into TSP injection phase, white flocculent material was visible in fairly large quantities and in large particle sizes.
  - May be a calcium phosphate compound.
  - The white precipitant partially covers everything in the submerged region: insulation holders, coupon rack, tank bottom, etc.

ICET Test 3 General Observations

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- White Precipitate
  - **20 minutes into TSP injection**: White flocculent material was visible in fairly large quantities and in large particle sizes. Material entrained in chamber flow.
  - **3 hours**: Size of white material much smaller, but finer and denser.
  - **1 day**: White deposit observed on submerged stainless-steel insulation mesh and galvanized steel coupons.
  - **After testing**: White shiny substance (face cream texture) present in the top layer of sediment, on insulation sample bags, and other test chamber surfaces.
- Flow Meter
  - Stopped working on **Day 8**.
  - Inspection revealed scale and precipitation deposits on flow meter turbine.
  - After cleaning and reinstallation, flow meter operated without failure for remainder of test.
  - No additional deposits apparent at end of test.

Calcium Silicate Accumulation

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CalSil on Flowmeter Struts

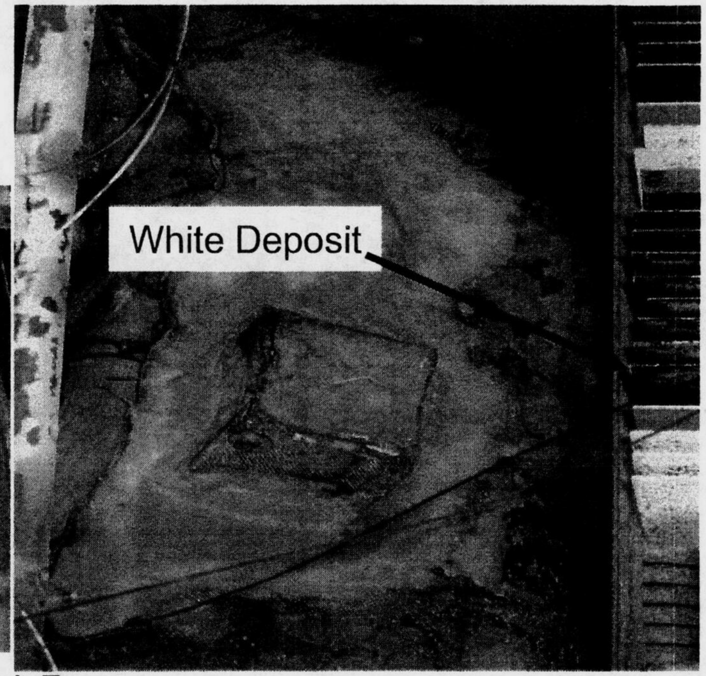
CalSil on Piping Walls

Clean Flowmeter Struts

ICET Test 3 General Observations

Los Alamos NATIONAL LABORATORY EST. 1943

Test Chamber: Top View after Draining



Overview of NRC-Sponsored Research Supporting GL2004-02 Resolution

Robert L. Tregoning
Office of Nuclear Regulatory Research

ACRS Subcommittee on Thermal-Hydraulic Phenomena
February 14 - 16, 2006

Objectives of Research Presentations

1. Discuss motivation, objective and goals for NRC-sponsored research initiatives supporting GL2004-02 resolution
2. Provide overview of associated technical areas for research and discuss interrelationships among programs
3. Discuss regulatory coordination and peer review
4. Provide status report for each research program
   - Outline objective, motivation, and intended regulatory use
   - Describe technical approach
   - Summarize important results, observations, and analysis conducted to-date
   - Provide plans and schedule for remaining work

General Research Philosophy

- **Motivation:** Recognized that research was necessary in important technical areas to reduce uncertainty associated with GL 2004-02 resolution
- **Broad Objectives**
  - Focus on technical areas having highest uncertainty (ACRS, staff, industry) and where generic evaluation provides the most impact
  - Conduct parametric and/or scoping studies to evaluate important variables over ranges of representative conditions
  - Interact with regulatory staff and industry to inform testing approach & conditions
- **Goals**
  - **Integrated Chemical Effects Testing (ICET) Program:** Provide basic technical knowledge to industry and staff on formation of chemical byproducts
  - **Other Programs**
    - Conduct confirmatory research for staff use in conducting an independent review and assessment of licensee GL 2004-02 evaluations
    - Make important results publicly available to inform ongoing industry activities

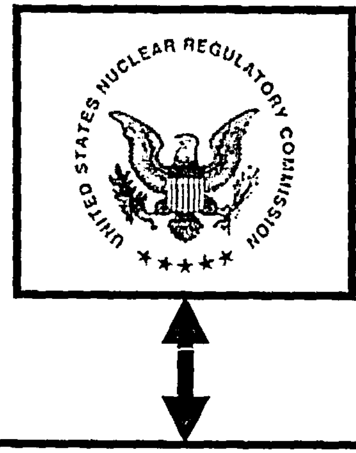
Technical Areas of Study

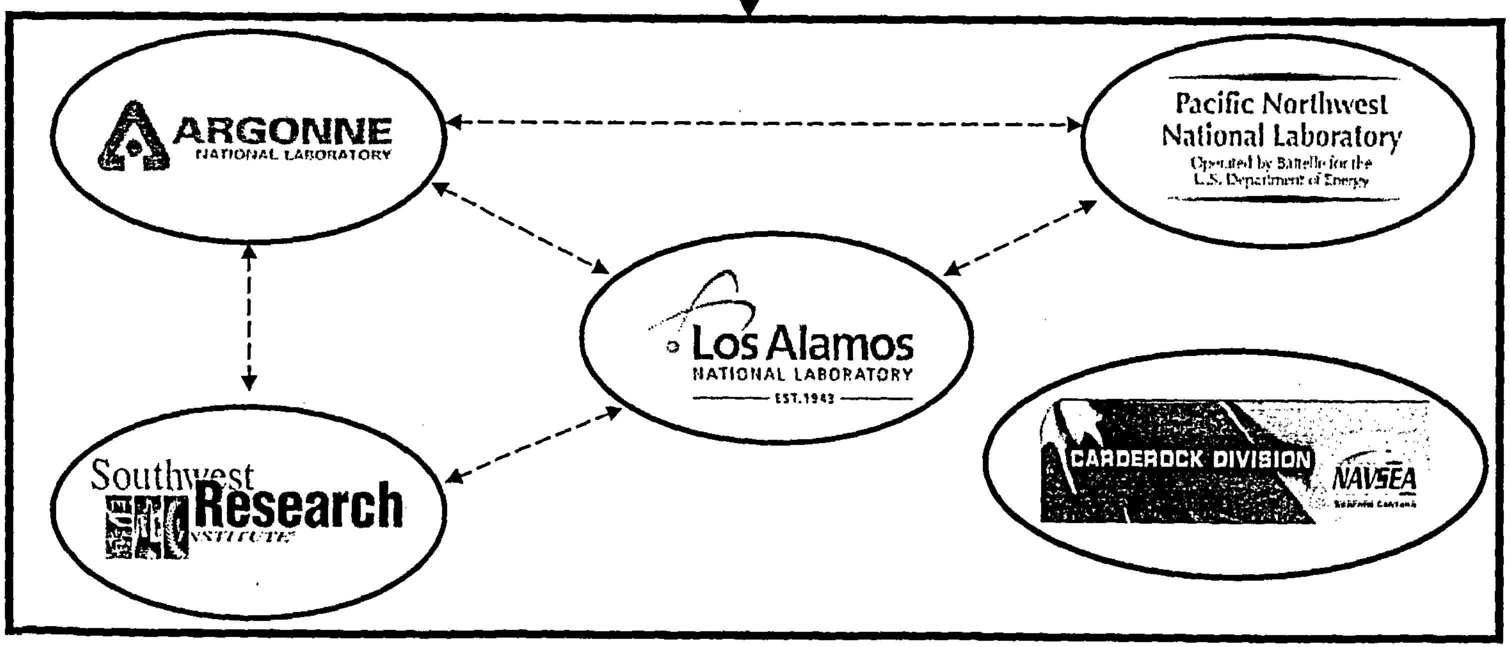
- **Chemical effects**: Determine potential for chemical by-product formation within containment pool environments. Characterize and predict by-products that form.
  - ICET: Los Alamos National Laboratory (LANL)
  - Chemical Speciation Prediction: Center for Nuclear Waste Regulatory Analyses (CNWRA) @ Southwest Research Institute
- **Head loss**: Confirmatory research on head losses associated with PWR containment materials with and without chemical effects
  - Chemical Effects Head Loss Testing: Argonne National Laboratory (ANL)
  - Particulate Head Loss Testing: Pacific Northwest National Laboratory (PNNL)
- **Downstream effects**: Confirmatory research on the effect of injected debris on HPSI throttle valve performance, LANL
- **Coatings transport**: Confirmatory research on the transportability of coating chips to the sump screen, Naval Surface Warfare Center (NSWC)

GL 2004-02 Research Team

Working Group

- Test Plan Development
- Test Coordination
- Review of Results





Regulatory Coordination and Peer Review

Regulatory Coordination

- NRR and RES contacts track research in each technical area
  - Plan test matrices
  - Resolve technical issues with laboratories
  - Communicate status and findings to internal staff and management
  - Assess regulatory implications

Peer Review

- Up to three layers depending on technical area
  - Layer 1: NRR and RES review
  - Layer 2: Research team review
  - Layer 3: External peer review
- External peer review provided for all activities related to chemical effects
  - Five members with diverse experience, affiliations, and expertise
  - Status: received preliminary feedback

External Peer Reviewers

Name	Affiliation	Areas of Technical Expertise
Wu Chen	Senior specialist at The Dow Chemical Co.	▪Fluid/particle separation ▪Industrial filtration processes
John Apps	Senior Scientist, Lawrence Berkeley National Laboratory	▪Geochemical modeling ▪Gel formation and characterization ▪Chemical speciation modeling ▪Nuclear waste isolation
Calvin Delegard	Pacific Northwest National Laboratory	▪Experimental testing and analysis ▪Analytical chemistry ▪Nuclear materials safeguards
Robert Litman	Independent consultant at Radiochemistry Laboratory Basics	▪Analytical chemistry ▪Metallic/corrosion processes ▪Nuclear industry experience
Digby Macdonald	Professor and Director of Center for Electrochemical Science and Technology at Penn State Univ.	▪Electrochemistry and thermodynamics Metallic/corrosion processes ▪Experimental testing and analysis

Important Messages

1. NRC's research is designed to provide some basic conceptual understanding about several important technical issues which impact ECCS functionality.
2. NRC's primary research role is to provide confirmatory information so the staff can independently evaluate whether licensees satisfy regulatory requirements.
3. Several important research findings will be discussed that should be considered in reaching an acceptable resolution of the technical issues raised in Generic Letter 2004-02.
4. Thorough understanding and consideration of plant-specific issues is required to assess the implications of research findings and develop acceptable resolution strategies.