

ATTACHMENT 1

RESPONSE TO REQUEST FOR ADDITIONAL INFORMATION REMOVAL OF TSP FROM PALISADES CONTAINMENT

EA-EC976-09, "Determine Post-LOCA Sodium Hydroxide Amount"

50 Pages Follow



Calculation Signature Sheet

Document Information

NMC Calculation (Doc) No: EA-EC976-09		Revision: 0
Title: Determine Post-LOCA Sodium Hydroxide Injection Amount		
Facility: <input type="checkbox"/> MT <input type="checkbox"/> PB <input type="checkbox"/> PI <input checked="" type="checkbox"/> PL <input type="checkbox"/> HU/FT		Unit: <input checked="" type="checkbox"/> 1 <input type="checkbox"/> 2
Safety Class: <input checked="" type="checkbox"/> SR <input type="checkbox"/> Aug Q <input type="checkbox"/> Non SR		
Special Codes: <input type="checkbox"/> Safeguards <input type="checkbox"/> Proprietary		
Calc Type (PassPort DOC-DESC-CODE): (if applicable, Palisades only)		

NOTE: Print and sign name in signature blocks, as required.

Major Revisions

EC Number: 976	<input type="checkbox"/> Vendor Calc
Vendor Name or Code:	Vendor Doc No:
Description of Revision: Initial Issue	
Prepared by: <i>J. Erickson</i>	Date: 6-23-06
Reviewed by: J. L. Voskuil	Date: 6-23-2006
Type of Review: <input checked="" type="checkbox"/> Design Verification <input type="checkbox"/> Tech Review <input type="checkbox"/> Vendor Acceptance	
Method Used (For DV Only): <input checked="" type="checkbox"/> Review <input type="checkbox"/> Alternate Calc <input type="checkbox"/> Test	
Approved by: <i>J. Depuy</i> FOR G.H. GORALSKI DS DEPUY	Date: 6-23-2006

Minor Revisions

EC No:	<input type="checkbox"/> Vendor Calc:
Minor Rev. No:	
Description of Change:	
Pages Affected:	
Prepared by:	Date:
Reviewed by:	Date:
Type of Review: <input type="checkbox"/> Design Verification <input type="checkbox"/> Tech Review <input type="checkbox"/> Vendor Acceptance	
Method Used (For DV Only): <input type="checkbox"/> Review <input type="checkbox"/> Alternate Calc <input type="checkbox"/> Test	
Approved by:	Date:

(continued on next page)



Calculation Signature Sheet

NOTE:

This table is used for data entry into the PassPort Controlled Documents Module, reference tables. If the calculation references and inputs are all listed in the calculation directly, then only the inputs and outputs need to be listed here. If the calculation invokes this form for the list of references and inputs, then list them all here. Only the input and output references need to be entered in PassPort.

Associated Document References:

#	Document Name	Document Number	Doc Revision	Control Doc and Doc Type (i.e. in Pass-Port) :	Type (input, output, general ref):
1	Containment Sump pH Control	EA-FC-949-01	4	<input checked="" type="checkbox"/> CALC	Input
2	NWT 731, "Effect of Sodium Hydroxide Additions on pH of Boric Acid Solutions At 25°C (77°F) and 139°C (283°F)", February 2006.			<input type="checkbox"/>	Input
3				<input type="checkbox"/>	
4				<input type="checkbox"/>	
5				<input type="checkbox"/>	

Add additional lines if needed.

Associated Equipment or System References:

#	Facility	Unit	System	Equipment Type	Equipment Number
1	N/A	N/A	N/A	N/A	N/A
2					

Add additional lines if needed.



Calculation Signature Sheet

Superseded Calculations

Facility	Calc Document Number	Title
N/A	N/A	N/A

Add additional lines if needed.

Purpose:

The passive post-LOCA containment sump pH control agent of tri-sodium phosphate baskets will be removed. In its place, sodium hydroxide will be injected into the sump in order to maintain the pH of the sump contents at a pH of 7.0 to 8.0. This analysis will determine the amount of 25% sodium hydroxide to be added in order to achieve this pH range.

Methodology:

The amount of sodium hydroxide to be injected will be determined through use of vendor-generated calculations. The vendor, NWT Corporation, has used the software "MULTEQ" for the pH calculations. MULTEQ was developed by EPRI and is common to the industry for various chemical solution- pH calculations.

Acceptance Criteria:

The acceptance criteria will result in a containment sump pH of 7.0 to 8.0.

Inputs:

- 1) Post-LOCA (Loss of Coolant Accident) sump pH must be at 7.0 to 8.0 (EA-FC-949-01).
- 2) Minimum expected containment sump boron concentration and mass is 1436 ppm boron, and 2,437,820 lbs of water solution (EA-FC-949-01).
- 3) Maximum expected containment sump boron concentration and mass is 2852 ppm boron, and 3,392,395 lbs of water solution (EA-FC-949-01).

References:

- 1) NWT Report 731, "Effect of Sodium Concentration on pH of Boric Acid Solutions At 25°C (77°F) and 139°C (283°F)", February 2006 (see attachment).
- 2) EA-FC-949-01, "Containment Sump pH Control Using Trisodium Phosphate", Revision 4.

Assumptions:

- 1) Containment sump sampling is not possible due to high radiation levels from the sample. This is a conservative assumption based upon the expected radioisotopes potentially released to the containment sump.
- 2) The designs inputs as defined in analysis EA-FC-949-01 remain current and acceptable. The water volumes used as inputs to this analysis are conservative.

Analysis:

The replacement of the tri-sodium phosphate (TSP) baskets has created the need for an alternative pH control agent. Sodium hydroxide has been selected as there is a reduced potential for chemical reactions that would impede or otherwise create containment sump recirculation flow restriction. The sodium hydroxide (NaOH) is to be procured in a 25% by weight concentration, and then transferred to the Radwaste Chemical Addition Skid, M-66. Following an accident, the NaOH will be pumped to the containment sump where it will raise the pH of the water- boric acid solution into the range of 7.0 to 8.0.

The consulting firm of NWT Corporation was contracted to determine the amount of NaOH needed to adjust pH to within this range. NWT used the industry-recognized software MULTEQ Version 2.2.4 with Database 1396 to perform the assessment. MULTEQ was developed by the Electric Power Research Institute (EPRI) for this type of assessments. As part of their work, NWT also verified the software results with a laboratory test. The complete assessment performed by NWT is documented in NWT Report 731, "Effect of Sodium Hydroxide Additions on pH of Boric Acid Solutions at 25 C (77F) and 139 C (283 F)", February 2006.

The analysis must consider the four possible bounding solution chemistries for the plausible LOCA scenarios. These are:

- 1) Minimum boron at pH 7.0
- 2) Minimum boron at pH 8.0
- 3) Maximum boron at pH 7.0
- 4) Maximum boron at pH 8.0

Therefore the analysis should select the required amount of NaOH to achieve the target pH for each of the four solutions. Given that assumption 1 makes sampling of the sump prohibitive, a single NaOH addition is highly desirable. A single addition makes the adjustment of pH much more reliable and requires no further assessment and/or additions.

The following data is extracted by interpolation of data in Table 4, "Effect of Sodium Concentration on pH of Boric Acid Solutions at 25°C (77°F)", of the NWT report. Table 4, which is reproduced below, determines the amount in gallons of 50% sodium hydroxide needed to create the desired pH.

	<u>Amount of 50% NaOH</u>
1) Minimum boron at pH 7.0	29
2) Minimum boron at pH 8.0	197
3) Maximum boron at pH 7.0	182
4) Maximum boron at pH 8.0	825

Table 4
Effect of Sodium Concentration on pH of Boric Acid Solutions at 25°C (77°F)

Boron = 1436 ppm			Boron = 2852 ppm		
Na, ppm	Volume, gal	pH @ 25°C	Na, ppm	Volume, gal	pH @ 25°C
0	0.0	4.85	0	0	4.48
10	6.7	6.35	20	19	5.92
15	10.0	6.53	50	46	6.33
20	13.3	6.66	100	93	6.66
30	20	6.84	200	185	7.01
40	27	6.97	300	278	7.24
50	33	7.08	450	417	7.49
75	50	7.27	500	464	7.56
100	67	7.41	700	649	7.81
125	83	7.52	1000	927	8.11
150	100	7.61			
200	133	7.77			
300	200	8.01			

As the above indicates, there is a sub-set of data for the minimum and maximum boron scenarios that allows for a single NaOH addition. For the minimum boron scenario the required range of NaOH is 29 to 197 gallons. For the maximum boron the required range is 182 to 825 gallons. Thus, the suggested 50% NaOH addition amount is 190 gallons. For a 25% by weight NaOH addition strength, the amounts increase by a factor of 2, so a 25% by weight NaOH addition strength would necessitate an addition amount of 380 gallons.

The analysis also considered the question of whether sump pH must be controlled within the range of 7.0 to 8.0 at temperatures greater than 25 C. It was determined that only 25 degrees C would be considered based upon the following:

- EEQ test solution analysis is performed at or near 25 degrees C, as accurate measurement of pH at elevated temperatures is not possible.
- Review of related regulatory documents failed to reveal clear direction as to whether pH at temperatures >25 degrees C need to be considered.
- NWT Report 731, Addendum 2, "Effect of Temperature and pH on Iodine Volatility" concludes that maintaining a pH of greater than 7.0 at 25 degrees C in a post-LOCA solution should maintain vapor phase iodine concentrations at solution temperatures up to 80 degrees C below levels that would be present if the solution was at 25 degrees C.

Conclusions:

This analysis determined that the amount of 25% sodium hydroxide required to bring the post-LOCA containment sump pH to within 7.0 to 8.0 is 380 gallons.

Attachments:

NWT Report 731, "Effect of Sodium Concentration on pH of Boric Acid Solutions at 25°C (77°F) and 139°C (283°F)", February 2006. (36 pages)

 <p>NMC Committed to Nuclear Excellence Fleet Modification Process</p>	<h2 style="margin: 0;">Design Review Checklist</h2>
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Document Number / Title: EA-EC976-09 / Determine Post-LOCA Sodium Hydroxide Injection Amount

Verifier's Name/ Discipline: JLVoskuil / Engineering Programs

DESIGN REVIEW CONSIDERATIONS:

	<u>Yes</u>	<u>No</u>	<u>N/A</u>
1. Were the inputs correctly selected and incorporated into design?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
2. Are assumptions necessary to perform the design activity adequately described and reasonable? Where necessary, are the assumptions identified for subsequent re-verifications when the detailed design activities are completed?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
3. Are the appropriate quality and quality assurance requirements specified?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
4. Are the applicable codes, standards, and regulatory requirements including issue and addends properly identified and are their requirements for design met?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
5. Have applicable construction and operating experience been considered?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
6. Have the design interface requirements been satisfied?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
7. Was an appropriate design method used?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
8. Is the output reasonable compared to inputs?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
9. Are the specified parts, equipment and processes suitable for the required application?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
10. Are the specified materials compatible with each other and the design environmental conditions to which the material will be exposed?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
11. Have adequate maintenance features and requirements been specified?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
12. Are accessibility and other design provisions adequate for performance of needed maintenance and repair?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
13. Has adequate accessibility been provided to perform the in-service inspection expected to be required during the plant life?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
14. Has the design properly considered radiation exposure to the public and plant personnel?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
15. Are the acceptance criteria incorporated in the design documents sufficient to allow verification that design requirements have been satisfactorily accomplished?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
16. Have adequate pre-operational, subsequent periodic test, and inspection requirements been appropriately specified, including acceptance criteria?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
17. Are adequate handling, storage, cleaning, and shipping requirements specified?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
18. Are adequate identification requirements specified?	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
19. Are requirements for record preparation, review, approval, and retention adequately specified?	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

COMMENTS: ☐ None

☒ Attached (Use Form QF-0528)

 <p>NMC Committed to Nuclear Excellence Fleet Modification Process</p>	<p align="center">Design Review Comment Form</p>
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Sheet 1 of 3.DOCUMENT NUMBER/ TITLE: EA-EC976-09 / Determine Post-LOCA Sodium Hydroxide Injection AmountREVISION: 0 DATE: 06/22/2006

ITEM #	REVIEWER'S COMMENTS	PREPARER'S RESOLUTION	REVIEWER'S DISPOSITION
1	See marked-up hard-copy of EA-EC976-09 for editorial comments and typos.	<i>No resolution needed.</i>	OK.
2	The QF-0549 form indicates this calculation is safety related. Palisades' TSP removal license amendment request dated March 20, 2006 clearly indicates on page 9 of 16 that the NaOH injection system is non-safety related. Is there a requirement that this calculation be classified as safety-related?	<i>This will be considered safety related as a conservative measure.</i>	OK.
3	The impact of other acid sources on sump pH has not been explicitly calculated. Iodine as hydriodic acid (HI), atmospheric species such as carbon dioxide (carbonic acid) and nitrogen (nitric acid), and cable insulation decomposition into hydrochloric acid can affect post-LOCA sump pH. NUREG/CR-5950 "Iodine Evolution and pH Control" indicates that in containments where no pH control chemicals are present, these other acids can determine pH. WCAP-15737 "Evaluation of the Effect of Non-Traditional Acid Formers on Post-Accident Containment Sump pH for CEOG Plants" indicates that the impact from the most important non-traditional acids, hydrochloric acid from cable insulation and nitric acid from air, are very minor (~0.1 units pH) and would not impact iodine re-evolution. In addition, the dose calculation supporting TSP removal (EA-EC-976-01) does not credit any sump pH control. No response required.	<i>No resolution needed.</i>	OK.

 Fleet Modification Process	Design Review Comment Form
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Sheet 2 of 3.
 DOCUMENT NUMBER/ TITLE: EA-EC976-09 / Determine Post-LOCA Sodium Hydroxide Injection Amount

 REVISION: 0 DATE: 06/22/2006

4	The quantity of NaOH is determined from data obtained at 25°C. Much higher sump temperatures are possible (e.g., near 139°C). The analysis provides a basis for the acceptability of only considering data at 25°C. This basis seems reasonable and avoids the situation where a single NaOH injection volume cannot be determined. In addition, the dose calculation supporting TSP removal (EA-EC-976-01) does not credit any sump pH control. No response required.	<i>No resolution needed.</i>	OK.
5	Input 1, Page 1: Note that a more fundamental reference for the requirement for control of post-LOCA sump pH to between 7 and 8: FSAR Section 14.22.2, which references EA-TAM-95-05,R0 that contains Assumption 4.19. No response required.	<i>No resolution needed.</i>	OK.
6	Reference 1, Page 1: The title of the NWT report should be "Effect of Sodium Hydroxide Additions on pH of Boric Acid Solutions At 25°C (77°F) and 139°C (283°F)". Also, consider citing Addendum 1 and Addendum 2 as well.	<i>Correction made to the EA.</i>	OK.
7	Analysis section, Page 2: The statement "Sodium hydroxide has been selected as there are no chemical reactions that would impede or otherwise create containment sump recirculation flow restriction." should be replace with "Sodium hydroxide has been selected as there is a reduced potential for chemical reactions that would impede or otherwise create containment sump recirculation flow restriction."	<i>Correction made to the EA.</i>	OK.
8	Analysis section, Page 2: The reference to MULTEQ appears to contain references to documents in the NWT report.	<i>No resolution needed.</i>	OK. <i>Correction made.</i>

 NMC Committed to Nuclear Excellence Fleet Modification Process	Design Review Comment Form
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Sheet 3 of 3.
 DOCUMENT NUMBER/ TITLE: EA-EC976-09 / Determine Post-LOCA Sodium Hydroxide Injection Amount

 REVISION: 0 DATE: 06/22/2006

9	Analysis section, Page 3: The statement indicating that for a 25% by weight NaOH solution, the amounts increase by a factor of 2 over a 50% by weight NaOH solution is true because the added water volume is negligible relative the sump water volume. No response required.	<i>No resolution needed.</i>	OK.
10	The use of industry-recognized software MULTEQ, in combination with independent verification by NWT with laboratory tests, provides sufficient confidence in the calculated results. No response required.	<i>No resolution needed.</i>	OK.
Reviewer: <u>J. L. Voskuil</u> Date: <u>6-23-06</u> JLVoskuil		Preparer: <u>JSErickson</u> Date: <u>6/23/06</u> JWThelath 6-23-06	

NWT 731
February 2006

**Effect of Sodium Hydroxide Additions on pH of Boric Acid Solutions
At 25°C (77°F) and 139°C (283°F)**


S. G. Sawochka

Technical Content Reviewed and Approved by


M. A. Leonard

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**NWT Report 731
February 2006**

Effect of Sodium Hydroxide Additions on pH of Boric Acid Solutions At 25°C (77°F) and 139°C (283°F)

S. G. Sawochka

Based on concerns about the role of tri-sodium phosphate (TSP) interactions with insulation material compounds, specifically the precipitation of calcium phosphate resulting in possible blockage of containment sump suction strainers, Palisades has decided to remove the TSP baskets from the containment building during the April 2006 refueling outage. The plan includes a temporary compensatory measure, i.e., prepare equipment/procedures to inject sodium hydroxide into the containment sump upon a containment recirculation scenario. The intent of the sodium hydroxide injection is to assure the pH of the containment liquid remains at 7.0 to 8.0 to reduce the evolution of radioactive iodines.

As part of the evaluation of this approach, estimates of the volume of 50 weight percent sodium hydroxide needed to give the desired pH range were developed. Two approaches were employed. First, the pH of boric acid solutions containing 1436 ppm boron and 2852 ppm boron was calculated as a function of the sodium concentration in the solutions. MULTEQ (1, 2, 3) Version 2.24 with Database 1396 was employed. Calculations were performed at temperatures of 25°C (77°F) and 139°C (283°F). The MULTEQ database thermodynamic constants have been expressed as a function of temperature with available data weighted to provide improved estimates at approximately 300°C. However, the code has a default option that allows best fit data at 25°C to also be



used for calculations. Although the normal range of code application is in the range of 150 to 300°C, only minimal error was expected at 139°C since this temperature is only 11°C outside the range normally specified for code application, and the boric acid equilibria relations were developed for the temperature range of 25 to 300°C by Baes and Mesmer (4).

Results of the calculations at 25°C are shown in Table 1 and Figure 1. Results at 139°C are shown in Table 2 and Figure 2.

Although the code construct and database have been thoroughly reviewed by a team of experts in the thermodynamic area, it was considered prudent to evaluate the effect of sodium additions to solutions containing the prior referenced boric concentrations in the laboratory at 25°C (77°F). Laboratory results are given in Table 3. They are compared to calculated values at 25°C in Figure 3. Agreement is reasonable. The boric acid solutions were prepared from a NIST traceable standard in high purity water (conductivity of <0.06 uS/cm). After establishing a nitrogen cover gas above the solution, the pH was measured as a function of sodium concentration using a Corning 530 pH meter. The meter was calibrated prior to the measurements using pH 4, 7 and 10 buffers. Laboratory data were not developed at 139°C (283°F) since a high pressure apparatus would have been required.

The design inputs used in the modification to install the TSP baskets in 1994 (EA-FC-949-01) are shown below:

Temperature range: 77 to 283°F (25 to 139°C)

Minimum boron

(2,437,820 lbs solution at 1436 ppm boron)

Maximum boron

(3,392,395 lbs solution at 2852 ppm boron)



The variation in pH of 1436 and 2852 boron concentration solutions at 25°C (77°F) as a function of the added volume of a 50 weight percent sodium hydroxide solution is shown in Figure 4 and Table 4. The relation of caustic solution volume and solution pH at 139°C (283°F) is shown in Figure 5 and Table 5. As shown, the volume required to achieve a given pH at 283°F is significantly greater than that required at 25°C (77°F). For example, to achieve a pH of 7.5 (0.5 units above neutral at 25°C) in the 1436 ppm boron solution at 25°C requires addition of approximately 80 gallons of caustic. At 139°C, the required volume to achieve a pH of 7.5 is approximately 570 gallons. However, to elevate the pH to ~6.35 at 139°C (0.5 units above neutral at 139°C) requires only 23 gallons since neutral pH at this temperature is 5.85.

The volume estimates were based on a specific gravity of 1.525 at 20°C for a 49.9 weight percent sodium hydroxide solution (5, 6). This corresponds to 47.6 lbs./ft³ or 6.36 lbs of NaOH per gallon of sodium hydroxide solution at 20°C. The effect of temperature on the specific gravity of pure water is on the order of 0.035% per °C in the range of 10 to 60°C.



References

1. Alexander, J. H., and Luu, L., "MULTEQ: Equilibrium of an Electrolytic Solution with Vapor-Liquid and Precipitation, Volume 1: User's Manual (Revision 1)," Electric Power Research Institute, May 1989 (NP-5561-CCM, Volume 1, Revision 1).
2. Alexander, J. H., and Luu, L., "MULTEQ: Equilibrium of an Electrolytic Solution with Vapor-Liquid and Precipitation, Volume 1: User's Manual (Revision 2)," Electric Power Research Institute, July 199 (NP-5561-CCML, Volume 1, Revision 2).
3. Alexander, J. H., and Luu, L., "MULTEQ: Equilibrium of an Electrolytic Solution with Vapor-Liquid and Precipitation, Volume 3: Theory Manual," Electric Power Research Institute, August 1992 (NP-5561-CCML, Volume 3).
4. Baes, C. F. Jr., and Mesmer R. E., The Hydrolysis of Cations, John Wiley & Sons, 1976.
5. Engineering Manual for the Amberlite Ion Exchange Resins, Rohm and Haas Company.
6. Water and Waste Treatment Data Book, U.S.Filter Corporation, 15th Printing, 1991.



Table 1
Effect of Sodium Concentration on pH of Boric Acid Solutions at 25°C (77°F)

Boron = 1436 ppm		Boron = 2852 ppm	
Na, ppm	pH @ 25°C	Na, ppm	pH @ 25°C
0	4.85	0	4.48
10	6.35	20	5.92
15	6.53	50	6.33
20	6.66	100	6.66
30	6.84	200	7.01
40	6.97	300	7.24
50	7.08	450	7.49
75	7.27	500	7.56
100	7.41	700	7.81
125	7.52	1000	8.11
150	7.61		
200	7.77		
300	8.01		



Table 2

Effect of Sodium Concentration on pH of Boric Acid Solutions at 139°C (283°F)

Boron = 1436 ppm		Boron = 2852 ppm	
Na, ppm	pH @ 139°C	Na, ppm	pH @ 139°C
0	4.83	0	4.56
10	6.04	50	5.65
20	6.23	100	6
40	6.4	300	6.23
75	6.55	700	6.46
150	6.71	1200	6.71
300	6.91	2000	7.22
500	7.11	2250	7.43
750	7.37	2500	7.71
1000	7.68	2750	8.05
1250	8.06		



Table 3
Effect of Sodium Concentration on pH of Boric Acid Solutions at 25°C
(Laboratory Results)

Boron = 1436 ppm		Boron = 2852 ppm	
Na, ppm	pH @ 25°C	Na, ppm	pH @ 25°C
23	6.63	46	6.26
46	6.95	92	6.59
69	7.13	138	6.79
92	7.27	184	6.94
115	7.38	230	7.06
138	7.48	276	7.16
161	7.56	322	7.25
184	7.64	368	7.33
207	7.71	414	7.41
230	7.76	460	7.48
253	7.81	506	7.54
276	7.86	552	7.6
299	7.91	598	7.66
322	7.95	644	7.71
345	8	690	7.76
368	8.04	736	7.81
391	8.07	782	7.86
414	8.11	828	7.9
		874	7.95
		920	7.99
		966	8.03
		1012	8.07
		1058	8.11



Table 4

Effect of Sodium Concentration on pH of Boric Acid Solutions at 25°C (77°F)

Boron = 1436 ppm			Boron = 2852 ppm		
Na, ppm	Volume, gal	pH @ 25°C	Na, ppm	Volume, gal	pH @ 25°C
0	0.0	4.85	0	0	4.48
10	6.7	6.35	20	19	5.92
15	10.0	6.53	50	46	6.33
20	13.3	6.66	100	93	6.66
30	20	6.84	200	185	7.01
40	27	6.97	300	278	7.24
50	33	7.08	450	417	7.49
75	50	7.27	500	464	7.56
100	67	7.41	700	649	7.81
125	83	7.52	1000	927	8.11
150	100	7.61			
200	133	7.77			
300	200	8.01			



Table 5
Effect of Sodium Concentration on pH of Boric Acid Solutions at 139°C (283°F)

Boron = 1436 ppm			Boron = 2852 ppm		
Na, ppm	Volume, gal	pH @ 139°C	Na, ppm	Volume, gal	pH @ 139°C
0	0	4.83	0	0	4.56
10	6.7	6.04	50	46	5.65
20	13.3	6.23	100	93	6
40	27	6.4	300	278	6.23
75	50	6.55	700	649	6.46
150	100	6.71	1200	1112	6.71
300	200	6.91	2000	1854	7.22
500	334	7.11	2250	2086	7.43
750	500	7.37	2500	2318	7.71
1000	667	7.68	2750	2549	8.05
1250	834	8.06			

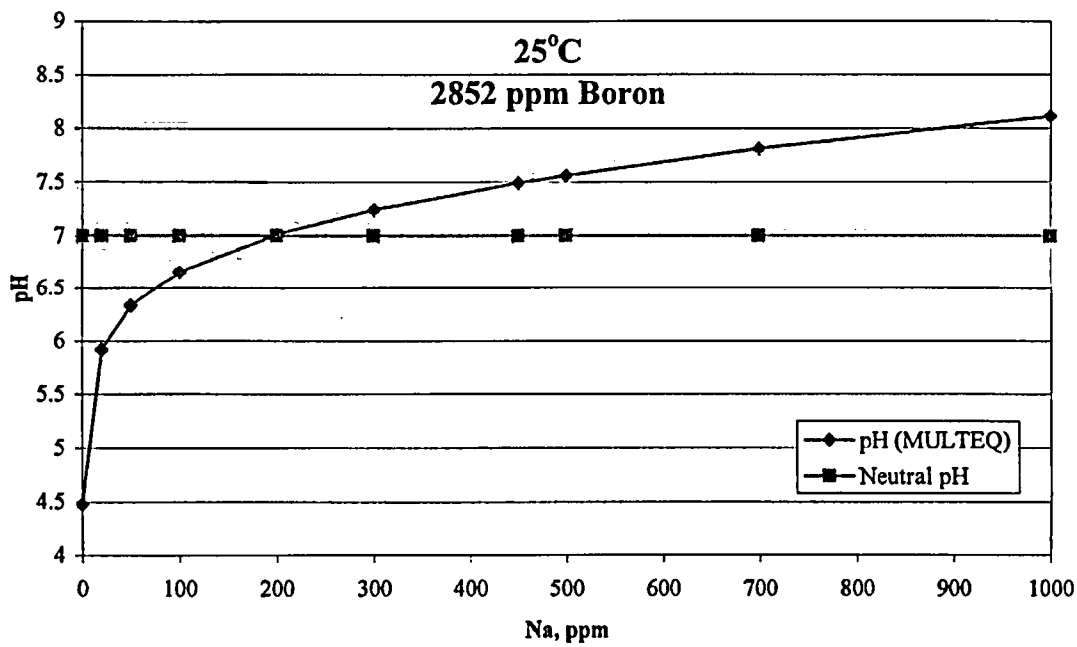
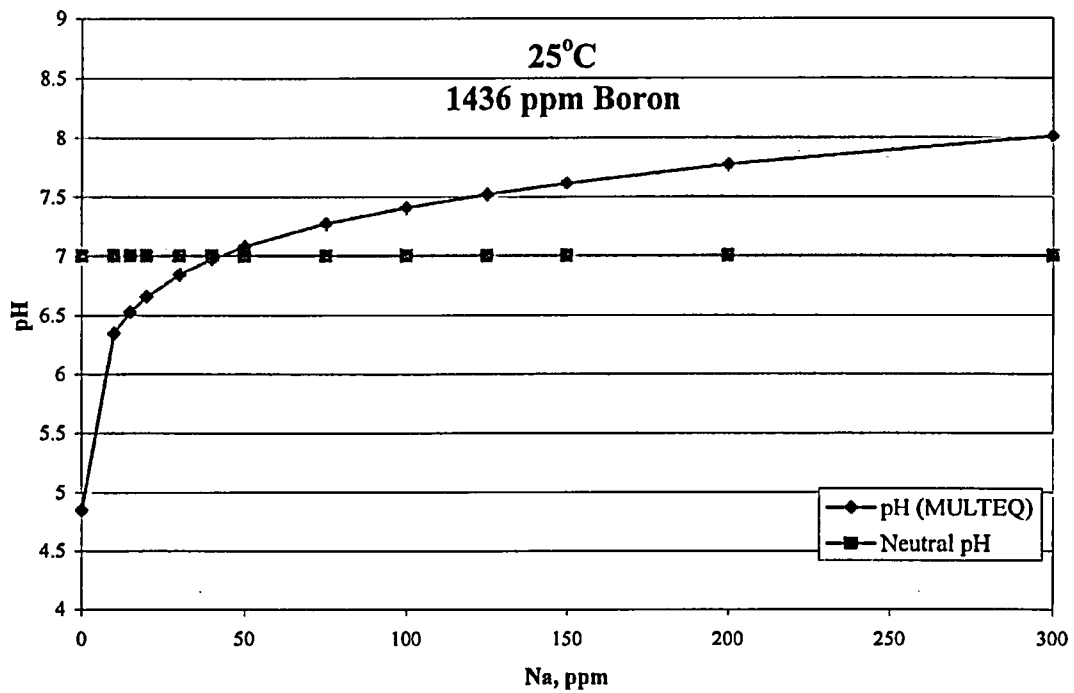


Figure 1 pH of Boric Acid/Sodium Hydroxide Solutions at 25°C
(MULTEQ 2.24; Database 1396)

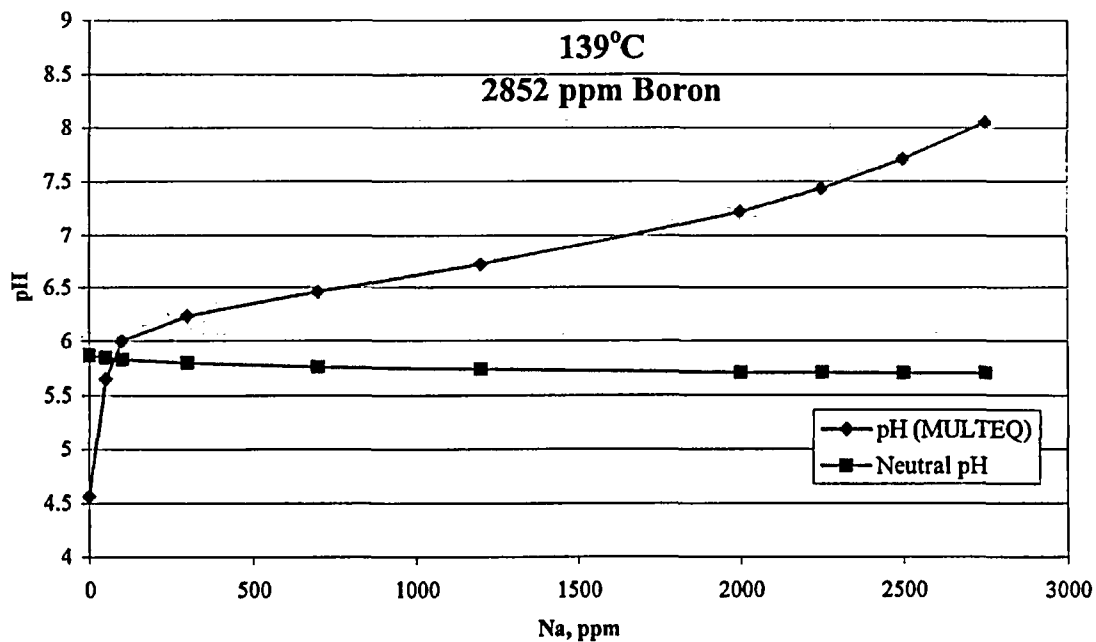
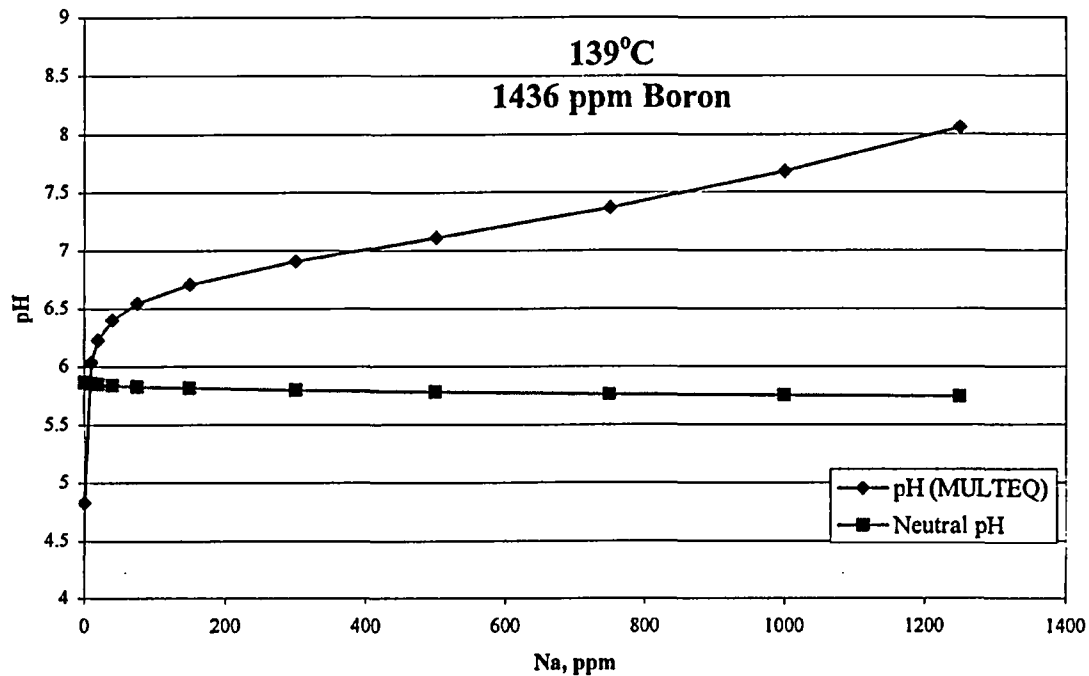


Figure 2 pH of Boric Acid/Sodium Hydroxide Solutions at 139°C
(MULTEQ 2.24; Database 1396)

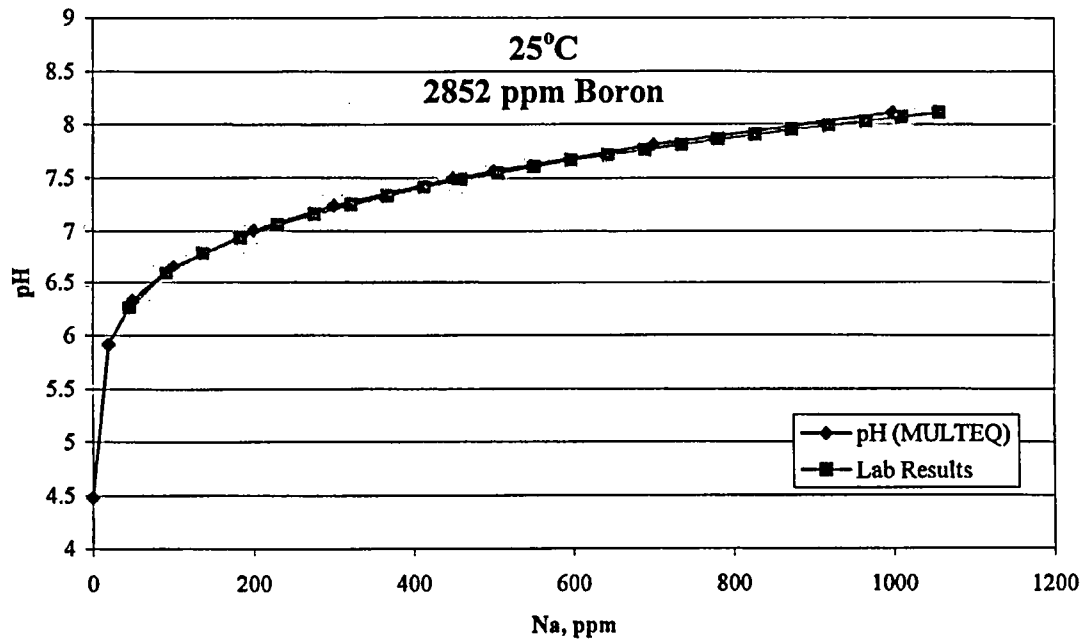
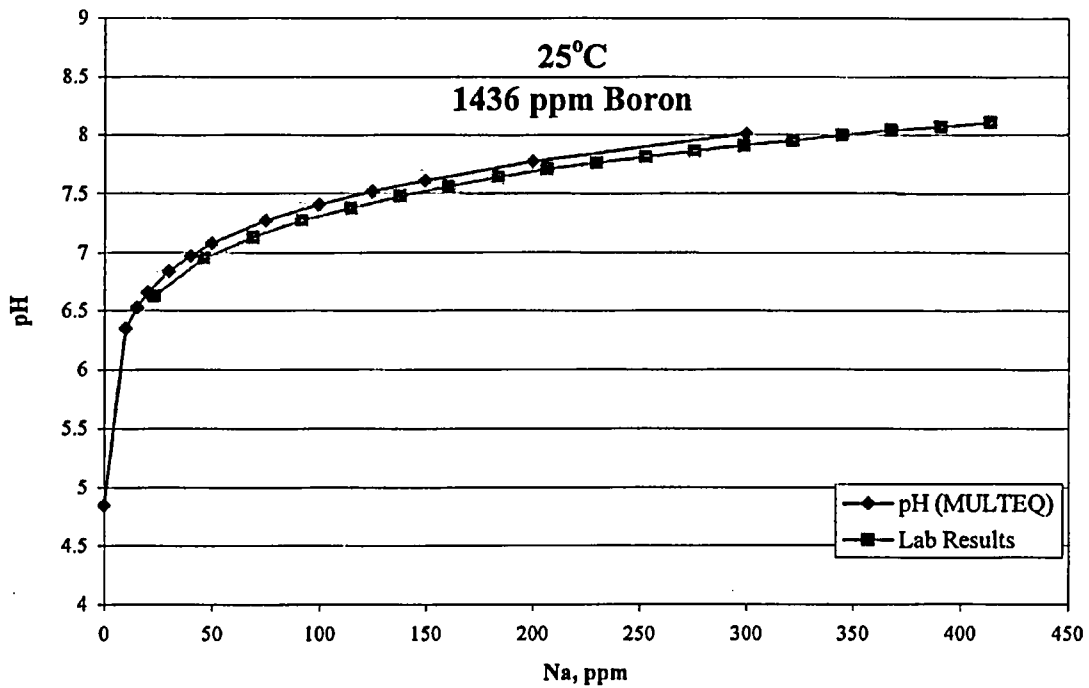


Figure 3 Comparison of Laboratory and Calculated pH results at 25°C

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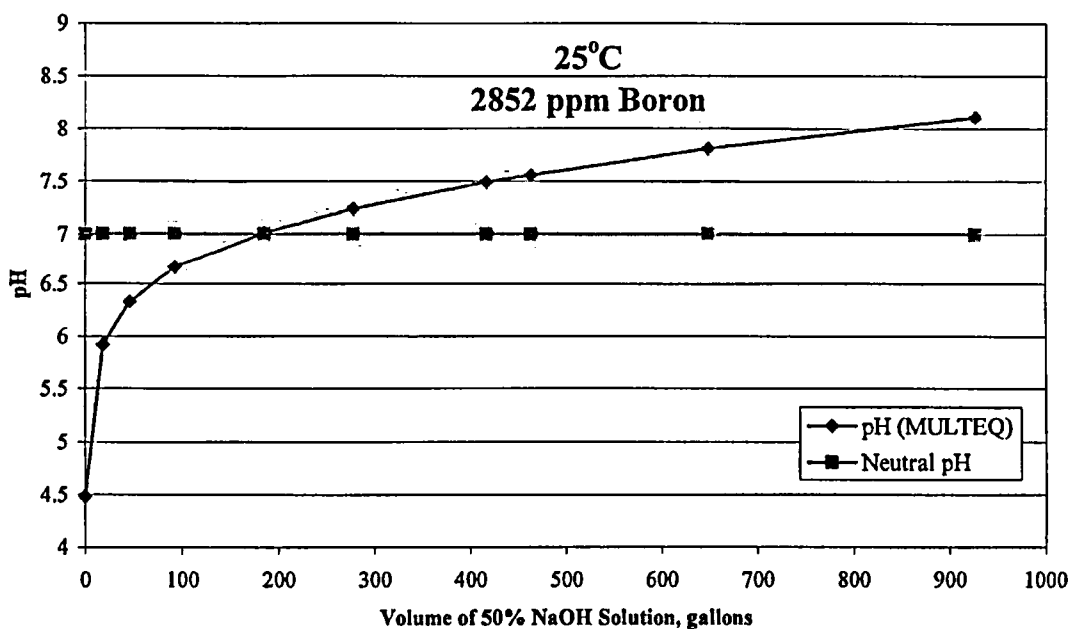
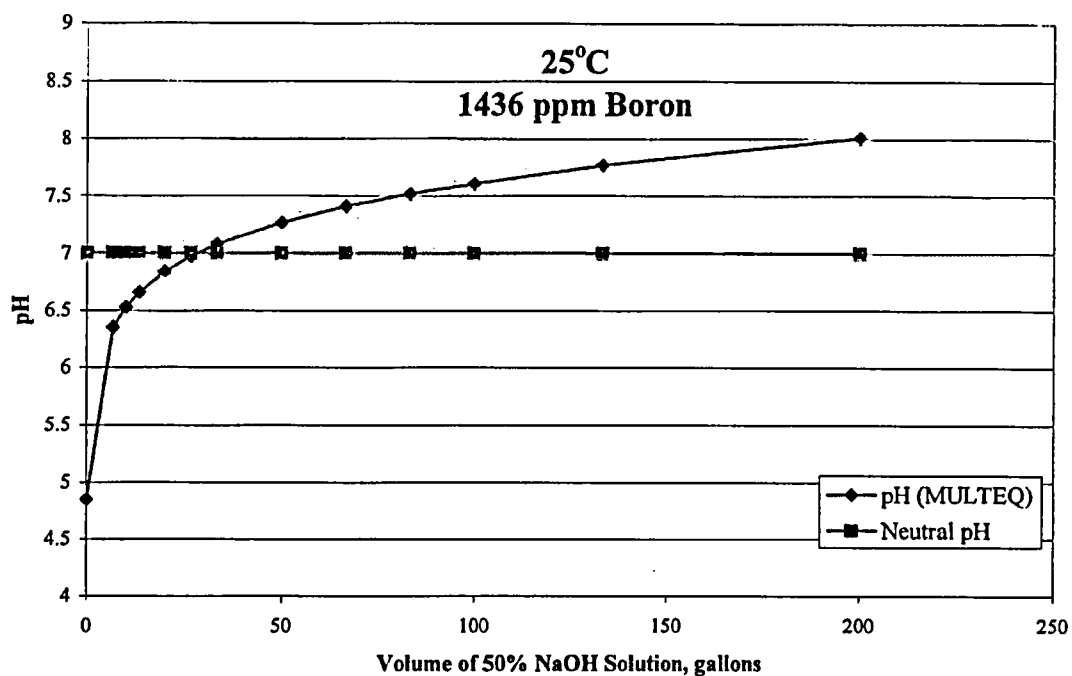


Figure 4 Variation of Boric Acid Solution pH at 25°C with Addition of 50% Weight Percent NaOH

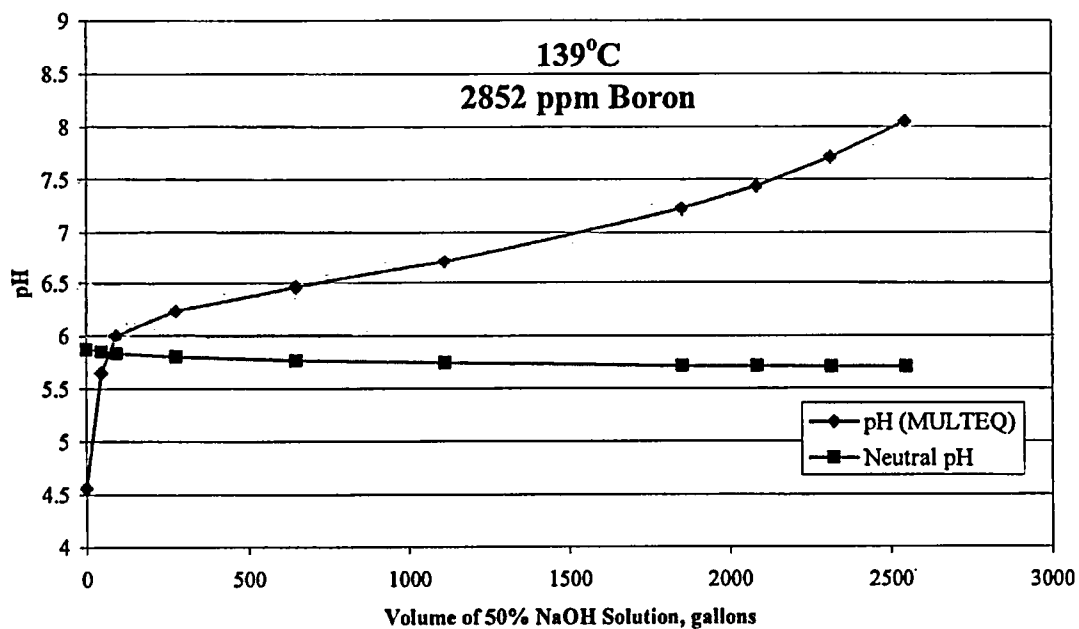
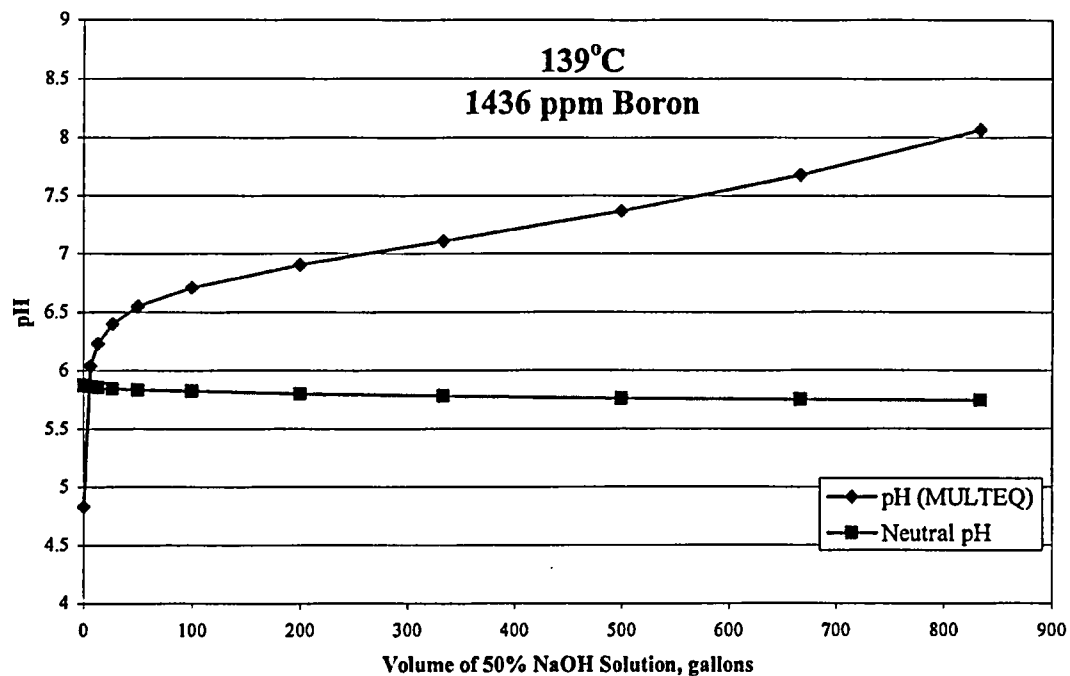


Figure 5 Variation of Boric Acid Solution pH at 139°C with Addition of 50% Weight Percent NaOH

NWT 731
Addendum 1
March 2006

**Effect of Sodium Hydroxide Additions on pH of Boric Acid Solutions
At 71°C (160°F)**



S. G. Sawochka

Technical Content Reviewed and Approved by



M. A. Leonard

Prepared for:

Palisades Nuclear Plant

Nuclear Management Company, LLC

P.O. P800869



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Effect of Sodium Hydroxide Additions on pH of Boric Acid Solutions
At 71°C (160°F)

S. G. Sawochka

Following the release of NWT 731, Palisades personnel have determined that containment sump pH control is not required until approximately two days following the LOCA initiation. At this time, the containment sump temperature has decreased to <160°F. As a result, the amount of 50% sodium hydroxide required to maintain the containment solution pH at 7.0 to 8.0 at 71°C (160°F) was calculated. Results of the calculations are shown in Table 1A and Figure 1A. The variation in pH of the 1436 and 2852 boron concentration solutions at 71°C (160°F) as a function of the added volume of a 50 weight percent sodium hydroxide solution is shown in Table 2A and Figure 2A. The amounts of sodium hydroxide required to achieve a containment solution pH of 7.0 at 25°C, 71°C and 139°C are given in Table 3A.

Table 1A
Effect of Sodium Concentration on pH of Boric Acid Solutions at 71°C (160°F)

Boron = 1436 ppm		Boron = 2852 ppm	
Na, ppm	pH @ 71°C	Na, ppm	pH @ 71°C
0	4.82	0	4.5
10	6.15	50	6.01
20	6.37	100	6.19
40	6.57	300	6.46
75	6.74	700	6.73
150	6.93	1200	7.00
300	7.14	2000	7.51
500	7.36	2250	7.73
750	7.63	2500	7.98
1000	7.93	2750	8.30
1250	8.29		

Table 2A
Effect of Sodium Concentration on pH of Boric Acid Solutions at 71°C (160°F)

Boron = 1436 ppm			Boron = 2852 ppm		
Na, ppm	Volume, gal	pH @ 71°C	Na, ppm	Volume, gal	pH @ 71°C
0	0	4.82	0	0	4.5
10	6.7	6.15	50	46	6.01
20	13.3	6.37	100	93	6.19
40	27	6.57	300	278	6.46
75	50	6.74	700	649	6.73
150	100	6.93	1200	1112	7.00
300	200	7.14	2000	1854	7.51
500	334	7.36	2250	2086	7.73
750	500	7.63	2500	2318	7.98
1000	667	7.93	2750	2549	8.30
1250	834	8.29			

Table 3A
Amount of Sodium Hydroxide Needed to Achieve pH 7.0

Temperature	Sodium Hydroxide, gal	
	Boron = 1436 ppm	Boron = 2852 ppm
25°C	29	185
71°C	127	1112
139°C	260	1576

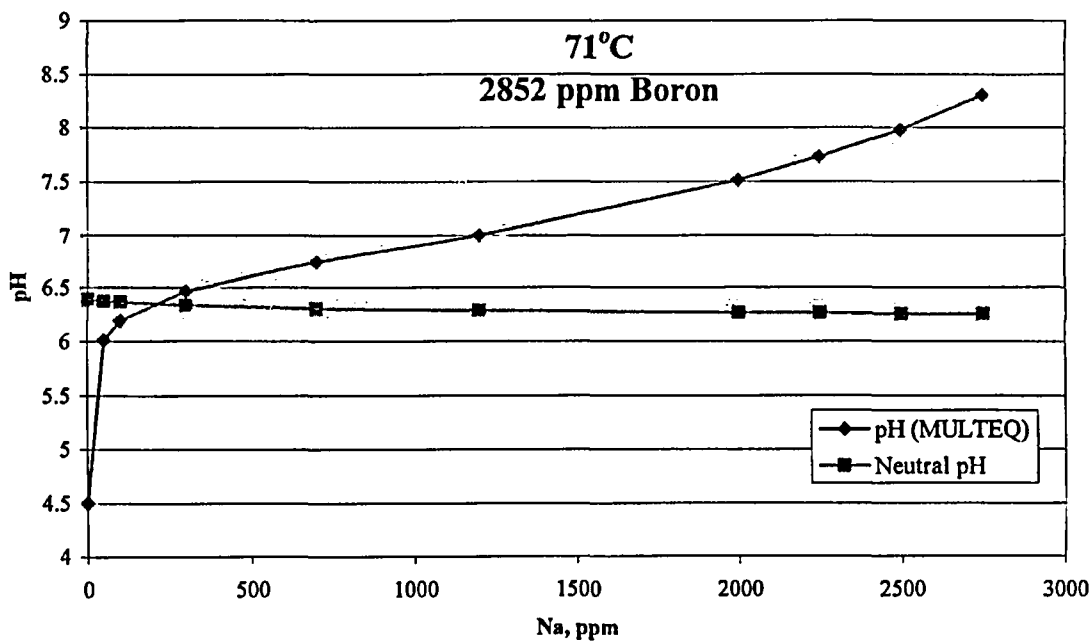
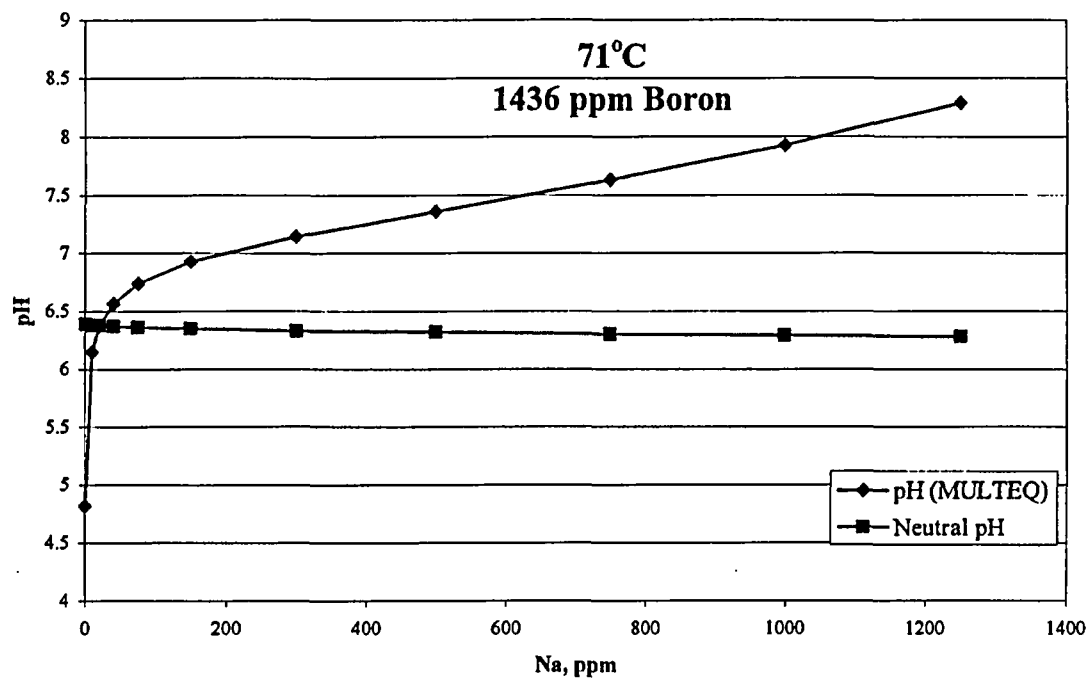


Figure 1A pH of Boric Acid/Sodium Hydroxide Solutions at 71°C
(MULTEQ 2.24; Database 1396)

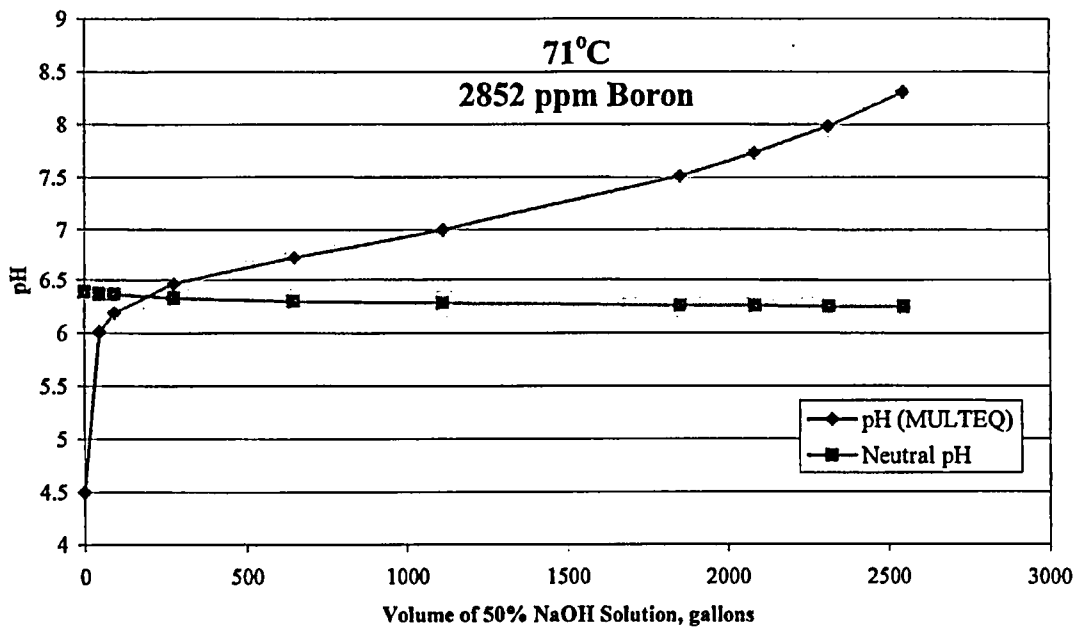
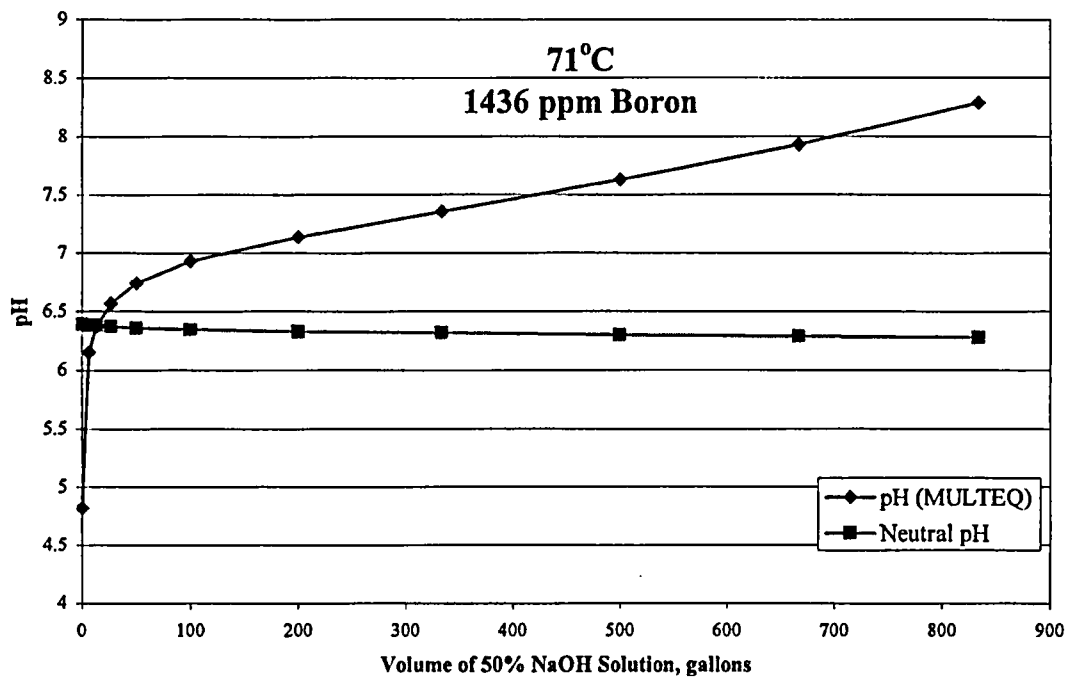


Figure 2A Variation of Boric Acid Solution pH at 71°C with Addition of 50% Weight Percent NaOH

NWT 731
Addendum 2
March 2006

Effect of Temperature and pH on Iodine Volatility




S. G. Sawochka



M. A. Leonard

Technical Content Reviewed and Approved by



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Effect of Temperature and pH on Iodine Volatility

**S. G. Sawochka
G. F. Palino
M. A. Leonard**

Background

A limited review of experimental data was performed to determine if a clear trend was present in results on the effect of pH and temperature on the volatility of iodine. The results for the effect of pH are consistent in two pertinent sources identified during the review (1, 2). Specifically, the volatility decreases as pH is increased. This is consistent with simplistic expectations based on the assumption that I_2 is the major volatile species and its fraction in solution decreases with an increase in pH. However, it is well known that 1) there are several major forms of iodine in solution, 2) that pH, oxidation potential and radiation fields impact on the relative quantities of these species and 3) that the volatilities of the species differ. For example, note that in the Reference 1 experiments, attempts were made to quantify the relative volatility of two unidentified species based on the ability to remove these species from the vapor phase on different media.

The effect of temperature is not as clear as that of pH. Reference 1 indicates a minimal effect of pH on iodine volatility at pH 7 whereas Reference 3 indicates an increase with temperature at approximately the same pH. In Reference 2, where the iodine solutions were exposed to radiation fields consistent with LOCA conditions, the effect of increasing temperature was to decrease iodine volatility.

Results

Results from Reference 1 were summarized by the investigators as follows:

"The objective of the program is to determine experimentally partition coefficients for radioiodine in water. Partition coefficients were measured as a function of iodine concentration, water temperature and pH. The results showed that partition coefficients were independent of concentration in the range encountered under normal operation of a nuclear power plant (10^{-8} to 10^{-5} mg/l). The effect of increasing pH was to increase the partition coefficient, (i.e. decrease the quantity of iodine in air). The reason was the fact that the fraction of the total iodine in water that was volatile decreased with increasing pH. "

"The effect of increasing temperature was to lower the partition coefficient. However, this tendency was offset to an extent dependent on pH, by a decrease in the fraction of iodine in water that was volatile. Chemical impurities in water appeared to have relatively little effect on iodine partitioning." (1)

The Reference 1 results were developed using fuel storage pool water from Commonwealth Edison's Dresden and Zion stations. Values of the partition coefficient at pH 5, 7 and 9 at 25°C, 50°C and 80°C are given in Table 1 and Figure 1. Distribution coefficient values are given in Figure 2. As shown, increasing pH increases the partition coefficient which reflects decreased iodine volatility (Figure 1). At pH 5 and 9, volatility increases (the distribution coefficient increases) as temperature is elevated. At pH 7, the effect of temperature on volatility is negligible.

In the Reference 2 investigation, tests were performed using CsI as a tracer to simulate the behavior of iodine in post LOCA borated solutions. Excerpts from the abstract of Reference 2 are given below:

"Radiolytic oxidation is considered to be the main mechanism for the formation of I_2 from aqueous CsI in the containment of a water cooled reactor after a loss of coolant accident (LOCA) in a PWR. Despite the amount of study over the last 60 years on the radiation chemistry of iodine, there has been no consistent set of experiments spanning a wide enough range of conditions to allow models to be verified with confidence."

"This paper describes the results from a set of experiments carried out in order to remedy this deficiency. In this work the rate of evolution of I_2 from sparged irradiated borate solutions containing CsI labeled with ^{131}I was measured on-line over a range of conditions. This work involved the measurement of the effects of pH, temperature, O_2 concentration, I concentration, phosphate concentration, dose-rate and impurities on the rate of evolution of I_2 . The range of conditions was chosen in order to span as closely as possible the range of conditions expected in a LOCA, but also to help to elucidate some of the mechanisms especially at high pH."

"The pH was found to be a very important factor in determining iodine volatility. Over the temperature range studied, the extent of oxidation decreased with increasing temperature but this was counteracted, to a greater or lesser extent, by the decrease in partition coefficient. The oxygen concentration was more important in solutions not containing phosphate. The fractional oxidation was not particularly dependent on iodide concentration but G_{I_2} was very dependent on. There was no effect of added impurities, Fe, Mn, Mo or organics although in separate work silver was found to have a very important effect."

"During attempts to interpret the data it was found that it was necessary to consider the iodine atom as a volatile species with a partition coefficient of 1.9 taken from thermodynamic data." (2)

As in the Reference 1 experiments, the effect of increasing pH was to reduce volatility (Figures 3A and B). At any given pH, the iodine volatility increased with increasing radiation field. A reduced volatility was observed as temperature was increased (Figures 4 and 5).

Results from Reference 3 were summarized by the investigator as follows:

"The equilibrium partition coefficients of iodine species between water and gas phase as a function of iodine concentration have been measured. At very low concentrations the partition coefficients have been determined to be ~7800 and ~1650 at 21 and 72°C, respectively. The results of chemical analyses for iodine species in both phases provide convincing evidence of the existence of hypoiodous acid (HIO) in both phases in low concentration experiments. The partition coefficient data are used to estimate the equilibrium constant and some thermodynamic properties of HIO." (3)

Summary

An increase in pH was indicated to decrease iodine volatility in both Reference 1 and 2. In Reference 1, the effect of increasing temperature from 25°C to 80°C on the iodine volatility (partition coefficient) was found to be negligible at pH 7. In Reference 2, the rate of iodine volatilization during purging of a pH 7 CsI solution decreased to negligible levels at 63°C and 73°C compared to that at 22°C (Figure 4). The fraction of iodine transferred to the vapor phase after 3 hours of purging a solution of boric acid at 70°C (158°F) was 70% compared to approximately 95% at 25°C (77°F) (Figure 5). This reflects reduced iodine volatility at temperatures up to 80°C compared to that at 25°C.

Since the Reference 2 studies were performed specifically to address post-LOCA iodine behavior, the reviewers consider the applicability of the Reference 2 investigations to the Palisades situation to be the most appropriate. On this basis, the reviewers conclude that establishing a sodium hydroxide design specification to assure a pH of 7 at 25°C in the post-LOCA solution should maintain vapor phase iodine concentrations at solution temperatures up to 80°C below levels that would be present if the solution was at 25°C. However, the extent of the review was limited, and results reported for different experimental conditions varied with respect to the effect of temperature.

References

1. Pelletier, C. A., Hemphill, R. T., "Nuclear Power Plant Related Iodine Partition Coefficients," Electric Power Research Institute, December 1979 (NP-1271)
2. Ashmore, C. B., Brown, D., Dickinson, S., Sims, H. E., "Measurements of the Radiolytic Oxidation of Aqueous CsI Using a Sparging Apparatus," Materials and Chemistry Group, AEA Techonology, 1998.
3. Lin, C. C., "Volatility of Iodine in Dilute Aqueous Solutions," J. Inv. Nucl. Chem., Volume 43, No. 12, pp 3229-3238, 1981.

Table 1
Partition and Distribution Coefficients for Iodine (1)

	pH=5		pH=7		pH=9	
Temp., °C	Partition Coefficient	Distribution Coefficient	Partition Coefficient	Distribution Coefficient	Partition Coefficient	Distribution Coefficient
25	4.80E+03	2.08E-04	4.40E+03	2.27E-04	8.30E+04	1.20E-05
50	2.00E+03	5.00E-04	3.50E+03	2.86E-04	4.00E+04	2.50E-05
80	1.40E+03	7.14E-04	4.90E+03	2.04E-04	2.50E+04	4.00E-05

Partition Coefficient $(\mu\text{Ci/ml})_l/(\mu\text{Ci/ml})_{\text{air}}$

Distribution Coefficient $(\mu\text{Ci/ml})_{\text{air}}/(\mu\text{Ci/ml})_l$

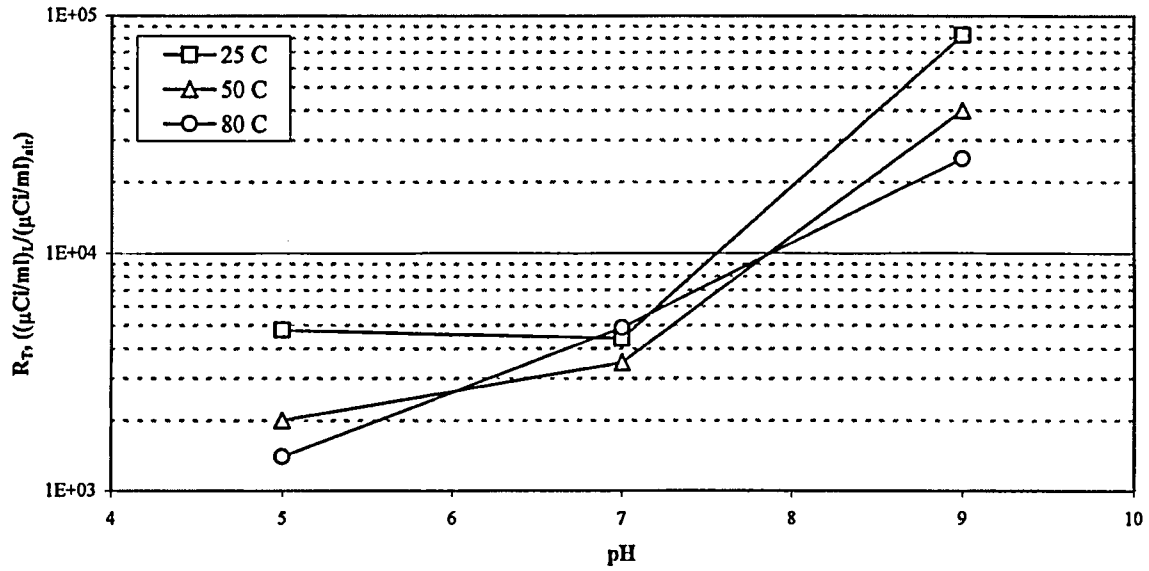


Figure 1 Effect of pH on the Partition Coefficient of Iodine from Fuel Pool Storage Water (1)

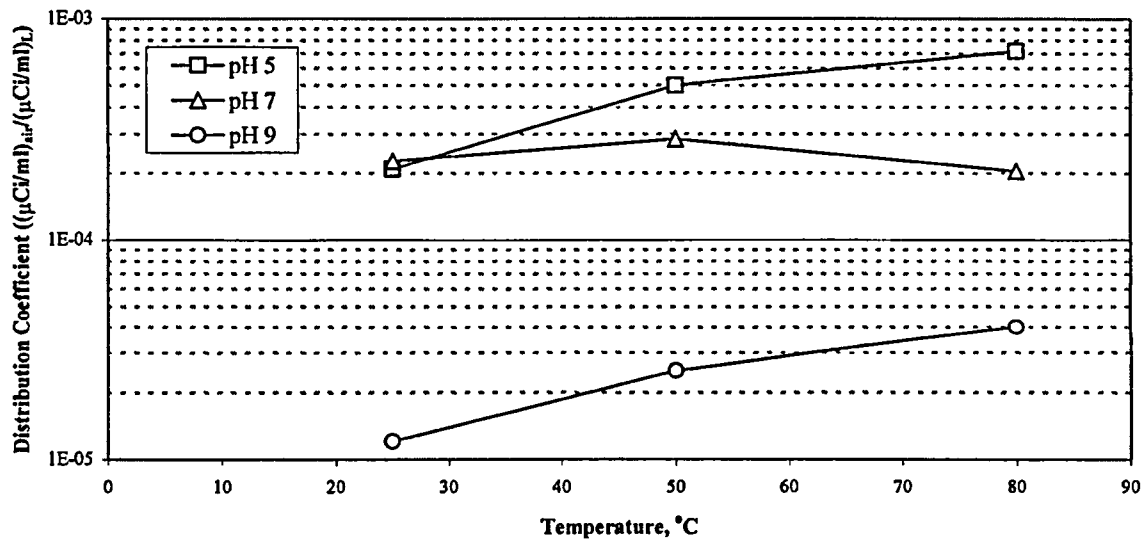


Figure 2 Effect of Temperature on the Distribution Coefficient of Iodine from Fuel Pool Storage Water (1)

Matt C:\Palisades\Partition Coeff

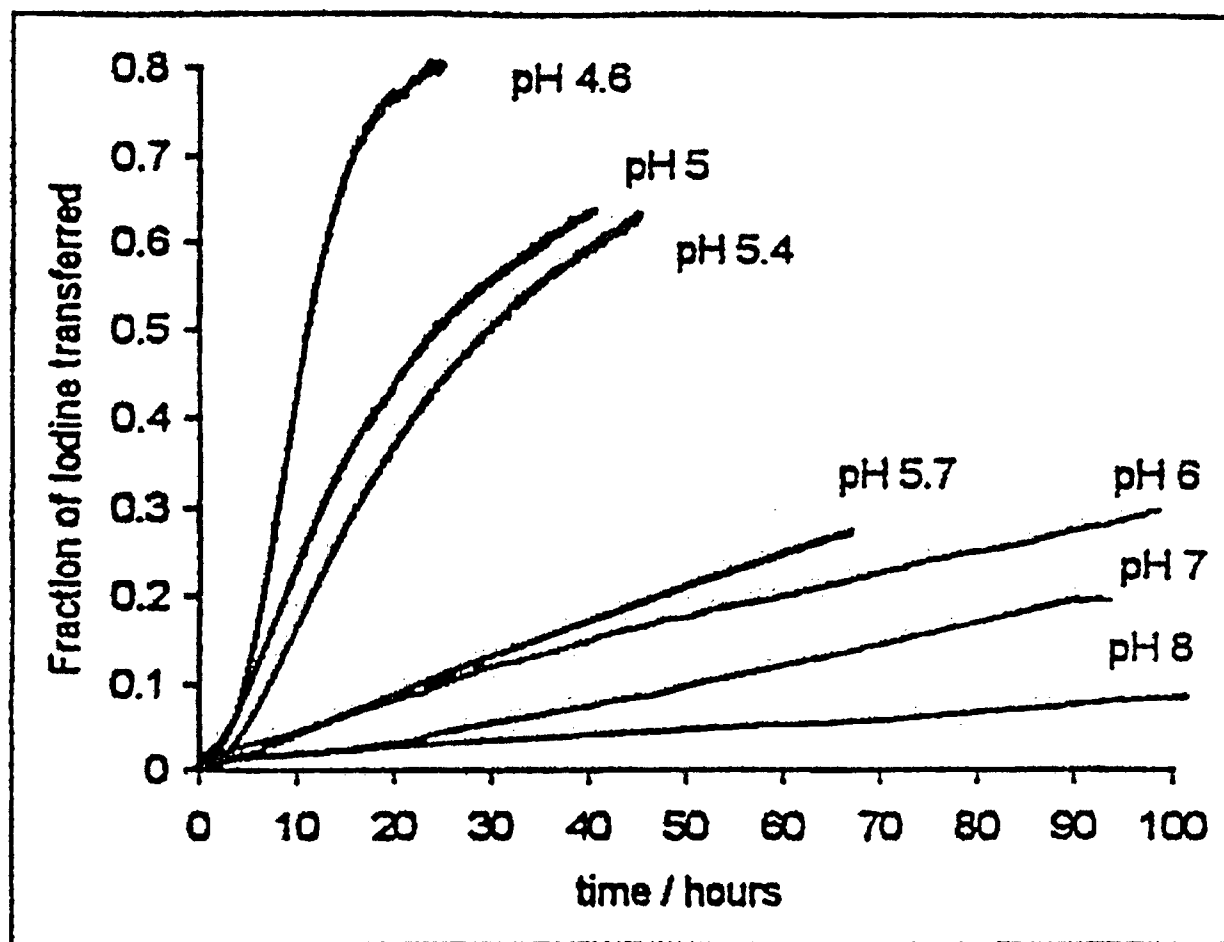


Figure 3A Effect of pH on iodine volatility (0.26 kGy hr^{-1} , $10^{-4} \text{ mol dm}^{-3} \text{ I}$)

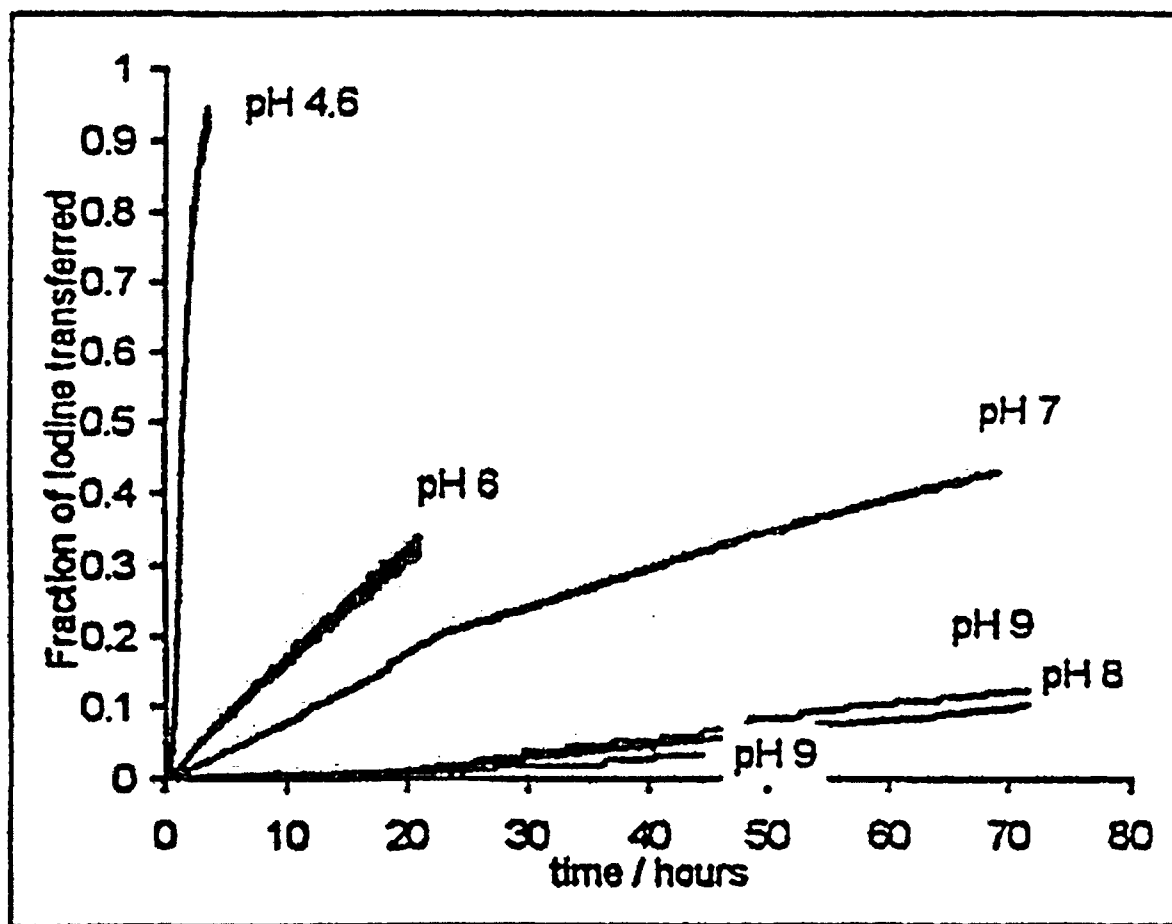


Figure 3B Effect of pH on iodine volatility (1.95 kGy hr^{-1} , $10^{-4} \text{ mol dm}^{-3} \text{ I}$)

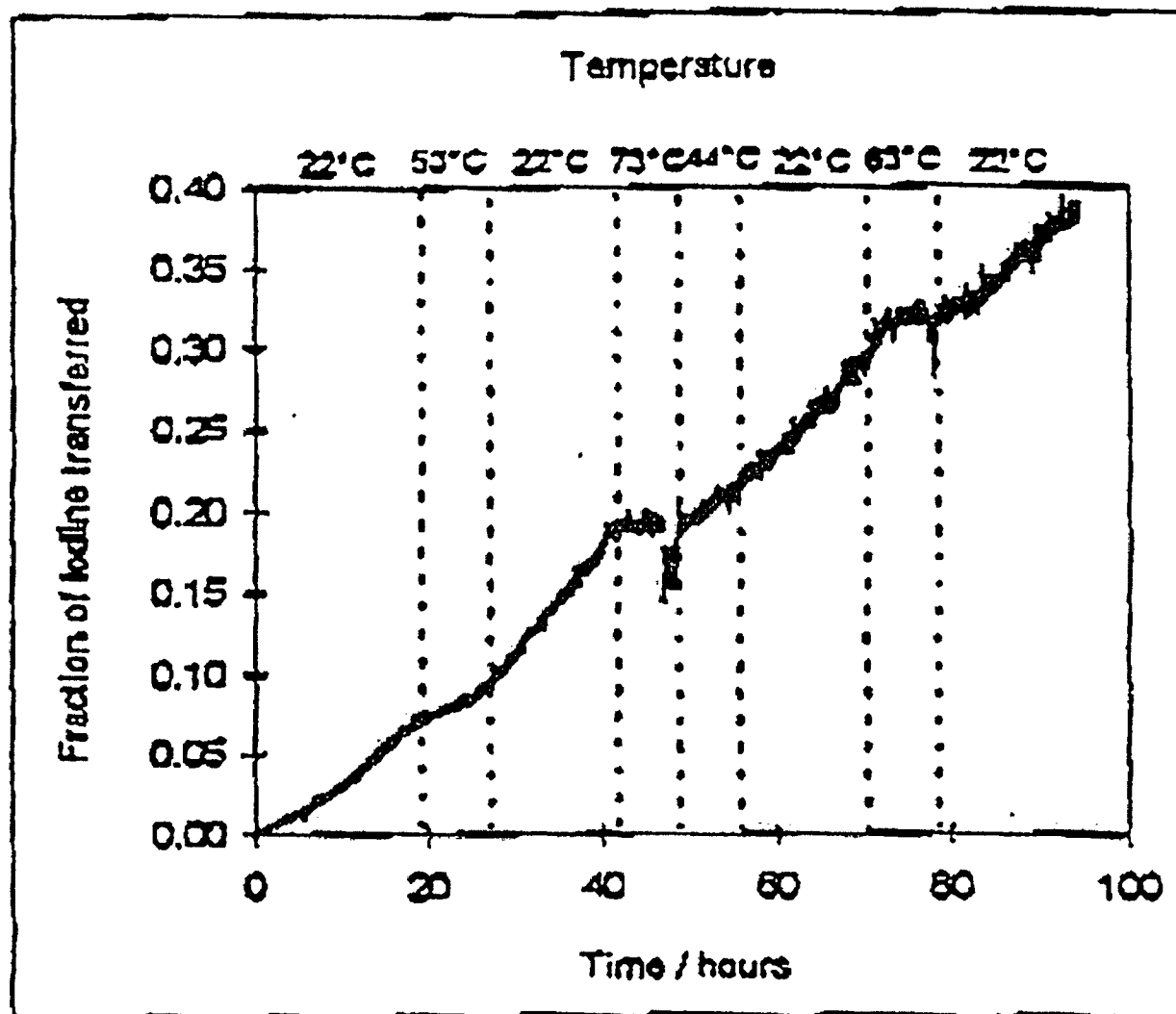


Figure 4 Effect of Temperature at pH 7
 (1.95 kGy hr⁻¹, 10⁻⁴ mol dm⁻³ I, 0.2 mol dm⁻³ H₃BO₃, 0.1 mol dm⁻³ Na₃PO₄)

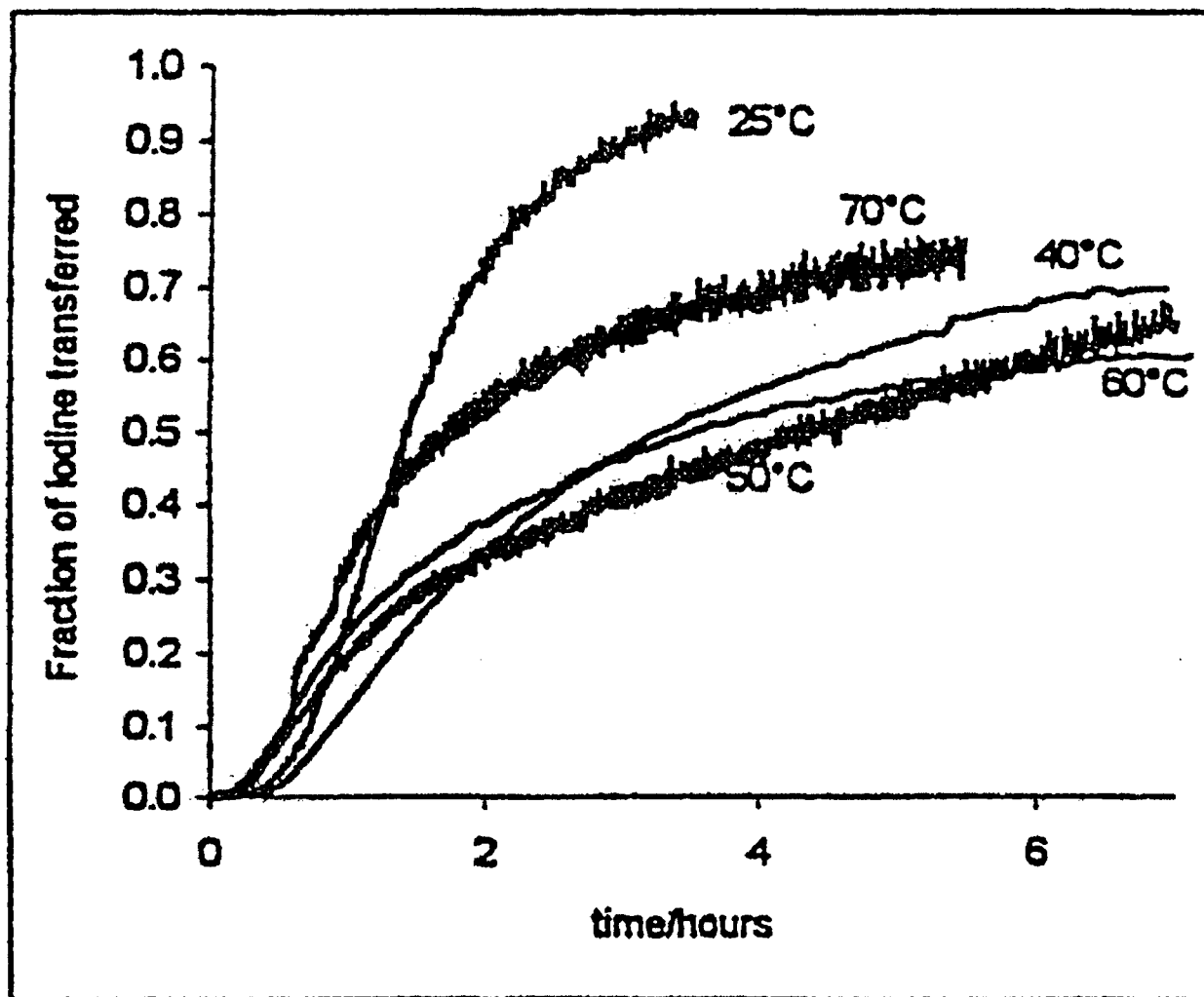


Figure 5 Effect of Temperature at pH 4.6
(1.95 kGy hr^{-1} , $10^{-4} \text{ mol dm}^{-3} \text{ I}$, $0.2 \text{ mol dm}^{-3} \text{ H}_3\text{BO}_3$)

DR. GERARD F. PALINO

B.S. Chemistry, San Jose State University (1963)

M.S. Physical Chemistry, Iowa State University (1965)

Ph.D. Physical Chemistry, Iowa State University (1968)

Postdoctoral Fellow, University of California, Irvine (1969)

Dr. Palino joined NWT in December 1979. Prior to that time (1974-1979), Dr. Palino was associated with the Chemical and Radiological Engineering Subsection of the General Electric Company, Nuclear Energy Division (GE), San Jose, California. While at GE, Dr. Palino was a program manager in radiological technology and for the EPRI/GE funded Boiling Water Reactor Radiation Assessment and Control program. Dr. Palino also participated in numerous programs involving radiological measurements including: N-16/N-13 recoil chemistry, transport and dosimetry in the BWR; modeling of fission product fuel releases; feedwater flow measurements; turbine performance tests; calibration and utilization of Ge(Li) pipe gamma scanning system; site N-16/C-15 measurement programs; site radiological measurements relative to Mark III containment. He also participated in the Commonwealth Edison/Department of Energy/GE Alternate Water Chemistry program; and in an EPRI funded gamma/neutron drywell and reactor cavity measurement program. Prior to joining GE, Dr. Palino taught courses in beginning chemistry, physical chemistry, radiochemistry, health physics, and nuclear instrumentation at San Jose State University (1971-1974), at the graduate college of the Federal University of Rio de Janeiro (1970), and at Harvey Mudd College (1969).

Since joining NWT, Dr. Palino's responsibilities have included technical management of numerous PWR primary and secondary system chemistry and BWR chemistry and radiation level assessment and control programs including evaluations of proposed methodologies for controlling shutdown radiation levels. He also has directed evaluations of reverse osmosis for PWR waste treatment, RO/UF for BWR waste volume reduction, and solid waste assay practices. Recent efforts have focused on developing and teaching training courses for BWR and PWR chemistry staffs, developing chemistry department manuals covering all BWR systems, performing PWR and BWR feedwater flowmeter tracer calibrations, quantifying PWR steam generator moisture carryover, and supporting turbine performance warranty demonstrations.

Dr. Palino is a member of the American Chemical Society and the American Association for the Advancement of Science.

DR. STEPHEN G. SAWOCHKA

B.S. Chemical Engineering, Purdue University, 1959

M.S. Chemical Engineering, Calif. Institute of Technology, 1960

PhD Chemical Engineering, University of Cincinnati, 1965

Dr. Sawochka currently is President of NWT Corporation which he co-founded in 1974. Previously he was Manager of Water Chemistry Development for the Atomic Power Equipment Department (APED) of the General Electric Company in San Jose, California. In this position, his responsibilities included formulation and execution of APED's development activities on feedwater and reactor water chemistry, water treatment, radioactive waste treatment, and sampling and analysis, and consultation in these areas for domestic and overseas plants. Prior to assuming this position, he was engaged primarily in the areas of two phase flow and heat transfer in BWR cores and in alkali metal space power systems.

At NWT, Dr. Sawochka has been involved primarily with consulting and research and development projects for electric power utilities and the Electric Power Research Institute (EPRI) in the fields of water chemistry, water treatment, radioactivity buildup, corrosion, and gaseous, liquid and solid radioactive waste treatment in BWR and PWR systems. He has been a member of the Guidelines Committees that developed the original and revised versions of the pressurized water reactor (PWR) secondary system chemistry guidelines, the boiling water reactor (BWR) chemistry guidelines and the PWR primary system chemistry guidelines. He also was the lead editor on the 2004 Condensate Polishing Guidelines.

Dr. Sawochka has technically directed and contributed to major EPRI and utility programs in areas such as PWR steam generator corrosion minimization by operating, design, and materials improvements, impact of chemistry on corrosion, effects of crevice flushing, correlation of steam generator chemistry and corrosion, and chemistry monitoring program adequacy. Major BWR activities have included evaluations of design/operating approaches for improving reactor water chemistry to reduce rates of intergranular cracking, fuel failures, and activity buildup. In addition, he routinely provides consulting support on critical problems to many utilities in areas such as the above.

Dr. Sawochka is a member of ANS and ASME and is a registered Professional Nuclear Engineer in the State of California. He has authored numerous publications on heat transfer, corrosion, water chemistry, and sampling and analysis.

MATTHEW LEONARD

B.S. Chemical Engineering, University of California at Davis, 2000

Since joining NWT in 2000, Mr. Leonard has participated in a variety of activities relative to impurity transport and corrosion in PWR and BWR systems. He has been involved primarily in crevice and surface solution chemistry, hideout return, corrosion product transport, and PWR fuel deposit modeling efforts. He has participated in several plant gamma scans and a feedwater flowrate/moisture carryover tracer evaluation. Mr. Leonard also has responsibility for test loop operation and sampler/ECP electrode fabrication.