

Annual and Quarterly Progress Report  
**Enhanced Control of PWR Primary Coolant Water Chemistry Using Selective Separation  
Systems for Recovery and Recycle of Enriched Boric Acid**

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Annual Progress Report

Reporting Period, 15 September 2004-15 September 2005

Quarterly Progress Report

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## **Project Overview**

The objective of this project is to develop systems that will allow for increased nuclear energy production through the use of enriched fuels. The developed systems will allow for the efficient and selective recover of selected isotopes that are additives (B-10, Li-7) to power water reactors' primary coolant chemistry for suppression of corrosion attack on reactor materials.

The economics of operating existing and advanced pressurized water reactors (PWR) clearly identify that increasing nuclear fuel enrichment will produce more energy. To operate within the nuclear reactor safety requirements, the concentration of natural boric acid used as a flux chemical shim would have to be increased. Enriched boric acid (B-10) has a greater cross section than natural boric acid and is favored over natural boric acid because of primary side water corrosion cracking issue associated with the increased requirement for higher lithium hydroxide (Li-7) concentrations to maintain operational pH with increased natural boric acid concentration. However, the cost of producing and using enriched isotopes such as B-10 and Li-7 requires a means to cost-effectively recover and reuse them.

Under the NERI category of fundamental chemistry under fundamental science we propose work to develop and field test polymeric sequestering systems designed to efficiently and selectively recover enriched boric acid/lithium hydroxide from the primary coolant water of reactors. These advanced separation materials will reduce the cost of operating existing and advanced light water reactor systems by improving the chemical control of the primary reactor coolant. Contaminants present in the coolant system will be characterized as to their interference potential with the selective recovery of enriched boric acid (B-10) and lithium hydroxide (Li-7), and counter measures to mitigate their interferences will be developed. The cost benefits result in greater energy production per reactor unit, reduced operational radiation exposure, and protection from accelerated corrosion of critical core components.

Another important aspect of this project is the close cooperation between a university and a national laboratory. The partner laboratories at UNLV and UC Berkeley provide students for the project. Through the LANL partner, students can have additional experience performing research in a DOE setting. This will provide a unique and constructive opportunity for developing quality graduate students with experience and expertise in handling actinides. Our ability to produce experienced actinide scientists is currently restricted by the dearth of radiochemistry and nuclear research at universities. Regardless of all else, future researchers must be trained and educated if the United States is to maintain a leadership role in nuclear technology. This project provides such an opportunity.

### **Year 3: Progress on milestones to date**

Task 10: Process modeling (n,p energy, LANL, UNLV, UC Berkeley)

Model results based on reactor testing

Milestones: Utilize project experimental and site data for modeling B and radionuclide removal

The model is complete and will be utilized to compare calculations with reactor studies. The model was varied from initial considerations to include different binding modes and variation in speciation calculations. Experimental spectroscopy data was used to determine the appropriate speciation for use in the model. A manuscript on the modeling considerations was prepared.

Task 12: Evaluation of results and mitigation (LANL, UNLV, UC Berkeley)

Milestones: Determine the overall utility of the B separation method

Analysis of the process model has been performed. The analysis is based on data collected from the reactor study.

### **Results from Current Quarter (15 July 05 -15 September 05)**

An overview of the results from UC Berkeley is presented in Appendix 1. It was found that boric acid readily forms what are essentially covalent bonds with alcohol functionalities through the displacement of the boron hydroxyl group. Based on the equilibrium constants reported, reagents having two sets of phenolic hydroxyl groups generally form much more stable borate complexes than those of alcohols. It is anticipated that boric acid complexation by these ligands will occur at the neutral conditions present in reactor coolant water. Solution thermodynamic studies with other ions have demonstrated that substituting various amide substituents can affect the overall stability of the resultant complex by changing the charge of the net complex.

The LANL team member examined the role of salts and temperature in extractions (Appendix 2). It was shown that 0.1 M NaCl salt addition to PEI/100 ppm BA solution had the effect of quenching the ion-pairing between the borate anion and the weak anion exchange sites of the PEI polymer. It was not known if salt addition could have some unanticipated effect on borate ester formation, which could bias the previous borate ester/borate ion-pairing ratio estimate. In previously reported salt-suppression studies, where complete ion-pairing suppression was observed for PEI, used 0.1 M NaCl with the 1/4-1,2-diol-PEI and 100 ppm B. The previously reported results may see only a small bias in the salt suppression value. We had not anticipated the large observed changes that accompanies the addition of 1 M neutral salt Easy and straightforward reversal of boron binding is a very important factor for recycling <sup>10</sup>B-enriched BA in the nuclear power industry. Temperature reversal of boron binding is more amenable to nuclear power applications than the more often reported acid or base stripping. The facility of 1,2-diol-PEI polymers to perform as temperature-reversible boron chelators was investigated for the 2/3 functionalized PEI polymer, the polymer that according to the <sup>11</sup>B-NMR studies appears to give the optimum level of boron binding. Consequently, the water-soluble polymers proposed in this study for BA recovery are expect to perform efficiently with regard to reversible boron binding as well. There are several approaches to addressing the Sb contamination problem. One is the selective back stripping of the B from the water-soluble polymers, leaving the Sb on the polymers. Once the soluble polymer is loaded with Sb to some predetermined level the polymer concentrate could be discarded as radioactive waste and be replaced with fresh polymer for binding more boric acid. Since we are focusing on thermal stripping as the mode of boric acid recovery, we need to determine if there is any selectivity in thermal stripping between boric acid and Sb. A decontamination factor (DF) defined as (Initial Feed count- Permeate count)/Permeate count for both the first treatment step and the thermal treatment step. The Sb-122 along with the spiked Sb-125 were concentrated in the Polymer Filtration process and the permeate gave material near the detection limit. The Sb is expected to form complex esters similar to the boric acid esters or possibility some of these species are absorbed to particular matter and are ultrafiltered and concentrated.

### **Results from 3<sup>rd</sup> Quarter (15 March 05- 15 July 05)**

The manuscript on boron modeling was completed. The UCB Chemistry team continued to study the structural characteristics of optimized ligand system for complexing boronic acid, determining complex formation of boric acid/borate with polyalcohols. It was found that boric acid readily forms covalent bonds with alcohol functionalities through the displacement of the boron hydroxyl group. The LANL laboratory team continued efforts in synthesis and B binding. The diol-PEI polymer is shown to be a very promising material for boron recovery.

## Results from 2<sup>nd</sup> Quarter (15 December 04-15 March 05)

The UCB-Nuclear Engineering Department and UNLV partner has produced a first draft of a manuscript on the separation modeling. The manuscript presents the development of the polymer for enriched boron recovery and models its behavior over a range of conditions. The description and utility of the developed model in explore the range of boron recovery under a variety of possible reactor coolant water conditions are explored.

The UCB-Chemistry Department partner continued to investigate the solid state and solution behavior of simple borate salts in which the boron atom was attached to bidentate aromatic ligands. Due to the low solubility of the alkyl substituted terephthalamide ligands, a series of substituted terephthalamides and terephthalic acids have been investigated that feature water solubilizing subunits. The synthesis of a series of terephthalamide borate ester complexes for structural and solution studies was also performed. Complex formation of boric acid/borate with polyalcohol featuring vicinally positioned hydroxyl groups has been extensively studied in the literature. Boric acid readily forms covalent bonds with alcohol functionalities through the displacement of the boron hydroxyl group. Kinetic and thermodynamic parameters on the interaction of these ligands with boron are under investigation.

The LANL partner is performing experiments evaluating the utility of the ligands and polymers under a variety of conditions. Five water-soluble polymers and PEI are being evaluated for their ability to extract boron at ~20°C and release it at a higher temperature. Thermal desorption will be used to recover the boron from the polymer in the recovery system. All the polymers exhibit a temperature dependence on release. Comparisons are made to determine the most effective polymer for boron recovery and the required temperature.

## Results from 1<sup>st</sup> Quarter (15 September 04-15 December 04)

Finalization of the complexation model was performed by UC Berkeley, Department of Nuclear Engineering and UNLV. The model adjustments from ion pairing and ionic strength have shown to result in improvements.

The Los Alamos group performed research on complexation, and process modeling. The targeting Sb ions with Sb-specific ligands was performed. This included the testing of the alpha hydroxy carboxylate ligand for Sb binding and the initial preparation of a solid Sb-binding material. Process modeling studies were performed based on results from the previous quarter. A schematic design for the polymer filtration process for the recovery of boron has been developed.

The n,p energy partner developed research plans and performed experiments on boron removal at a commercial reactor. The results will be used for further analysis of the capacity of the polymers to selectively separate boron. The behavior of the polymers with <sup>51</sup>Cr, <sup>54</sup>Mn, <sup>58,60</sup>Co, <sup>110m</sup>Ag, <sup>122,125</sup>Sb, and <sup>131,133</sup>I was also examined. The collected data is not presented.

## Year 2 Task Results

Task 1: Thermodynamic Modeling

Milestone: Finalize thermodynamic modeling of B interaction with ligands

Matlab is now the modeling platform. Deviations between modeling and experiments were noted in very low boron concentration. In the range of boron in the filtration system the model accurately describes the boron removal.

Task 2: Develop and prepare polymers

Milestone: Synthesis of improved ligands based on initial results

Based on B coordination with the examined ligands, improvements in the ligands and their degree of functionalization were investigated. A wide series of ligands were developed.

Task 3: Characterization of polymers

Milestones: Spectroscopically characterize synthesized ligands from Task 2

Synthesized ligands were characterized by nuclear magnetic resonance and x-ray diffraction, permitting a molecular level evaluation of the complexants.

Task 4: Binding Studies

Milestones: Comparison of B binding with literature

The complexation constants for the interaction of the examined ligands with B have been evaluated by titration and spectroscopy. The results will be compared with literature data to quantify the affinity of B for the examined ligands. A number of complexation constants have been evaluated with potentiometric titration and  $^{11}\text{B}$  NMR spectroscopy.

Task 5: Selectivity study of polymers

Milestones: Determine B selectivity

Using data from the 1<sup>st</sup> reactor study the extraction of radionuclides in the coolant water was examined. The polyol polymers developed for boron recovery appear to have a substantial extraction coefficient for antimony. If the radionuclides extracted with the boron are removed during the thermal stripping cycle with the boron, the net effect would be to increase the  $^{58}\text{Co}$  and  $^{125}\text{Sb}$  concentrations over tenfold. All of the polymers showed some degree of affinity for cobalt with the exception of PEI-DP.

Task 7: Simulant process development

Milestones: Prepare and test simulant

Los Alamos has prepared experiments with Sb to address issues raised in previous reactor studies.

Task 9: Second Reactor Site Testing

Milestones: Perform 2<sup>nd</sup> reactor test

n,p energy has options of performing studies at Turkey Point on 26 September 2004 and at Palisades on 19 September 2004. This is contingent upon funding. The dates for the shutdown of these reactors has been postponed until later this year, at which time n,p energy will perform the proposed studies.

Task 10: Process modeling

Milestones: Utilize project experimental and site data for modeling B and radionuclide removal

Initial process modeling efforts using Ft. Calhoun data have been performed

## **Year 1 Task Results**

Task 1: Thermodynamic Modeling

The existing boron/polymer chemical speciation model has been expanded to include polyborate ion paired species. In order to model behavior of the polymer filtration chemical system, it is necessary to make assumptions as to the actual chemical species involved.

Task 2: Develop and prepare polymers, Task 3: Characterization of polymers, Task 4: Binding Studies

Terephthalamide (TAM) functionalized polyethylenimine (PEI) was prepared for use in the on site industrial investigations. Previous work found terephthalamide ligands to be useful in the separation of actinide metal ions in polymer filtration when incorporated into water soluble chelating polymers, such as PEI. Current work is moving on to examine the boron and boric acid binding of a variety of catecholamide (CAM), terephthalamide (TAM), and hydroxypyridinone (HOPO) ligands.

Model compound studies were completed using simple primary (1°), secondary (2°) and tertiary (3°) nitrogen-containing compounds. The reactions were followed by NMR and selected peaks were integrated to determine the loss of starting material and gain of product. The synthesis of the last polymer of the series, the triol, was performed. The material was characterized by H and C-NMR and verified to be the target polymer. An extraction series was performed, with the extraction order for B found to be triol > diol > monol. Ion-pairing suppression studies were performed in an attempt to get an estimate of the ratio of ion pairing to diol ester formation. At 0.1 M ionic strength the monol was essentially suppressed while the diol retained 28% of its original 79% binding.

#### Task 6: Analytical Methods Development

Analytical methods for B and other selected elements were developed.

#### Task 8: First Reactor Site Testing

Flow sheet development and training for the 1<sup>st</sup> reactor test was performed.

**Appendix 1**  
**NERI Quarterly report**  
**15-July-05 to 15-September 05**  
**UC Berkeley Contribution Project Milestones**

Task 2: Developed and prepared polymers

Milestone: Synthesis of improved ligands based on initial results

Based on B coordination with the examined ligands, improvements in the ligands and their degree of functionalization were investigated. A wide series of ligands were developed.

Task 3: Characterization of polymers

Milestones: Spectroscopically characterize synthesized ligands from Task 2

Synthesized ligands were characterized by nuclear magnetic resonance and x-ray diffraction, permitting a molecular level evaluation of the complexants.

Task 4: Binding Studies

Milestones: Comparison of B binding with literature

The complexation constants for the interaction of the examined ligands with B have been evaluated by titration and spectroscopy. The results have been compared with literature data to quantify the affinity of B for the examined ligands. A number of complexation constants have been evaluated with potentiometric titration and  $^{11}\text{B}$  NMR spectroscopy.

**Summary of results from collaboration:**

Boric acid readily forms what are essentially covalent bonds with alcohol functionalities through the displacement of the boron hydroxyl group. Based on the equilibrium constants reported, reagents having two sets of phenolic hydroxyl groups generally form much more stable borate complexes than those of alcohols. It is anticipated that boric acid complexation by these ligands will occur at the neutral conditions present in reactor coolant water. Solution thermodynamic studies with other ions have demonstrated that substituting various amide substituents can affect the overall stability of the resultant complex by changing the charge of the net complex.

This project was to develop and evaluate a series of chelating agents that are effective for the removal of boric acid from the primary coolant water of reactors. The UC Berkeley team has focused on the synthesis of a series of boron complexes, under Tasks 2-4. The hypothesis is that catecholamides, terephthalamides, and hydroxypyridinonates will be more effective and feature higher binding constants than simple sugars with vicinal diols when supported to water soluble PEI. Using a number of synthetic chemical steps, a series of novel boron chelating compounds, and their resulting borate esters, have been synthesized.

These ligands are capable of binding a range of ions and can be easily altered to affect complexation and solubility properties. Potentiometric and spectrophotometric titrations and  $^{11}\text{B}$ -NMR spectroscopy have been used as to study the structure, solution thermodynamics and kinetics of borate complexes. The structural characteristics, kinetics, and solution thermodynamics of these systems have been investigated at various conditions. The solution behavior of these species has been investigated and the formation constants have been used by the UCB-Nuclear Engineering team in modeling efforts.

**Appendix 2**  
**NERI Quarterly report**  
**15-July-05 to 15-September 05**  
**NERI Quarterly report**  
**15 July 05 to 15 September 05**  
**Boron Removal**  
**LANL**

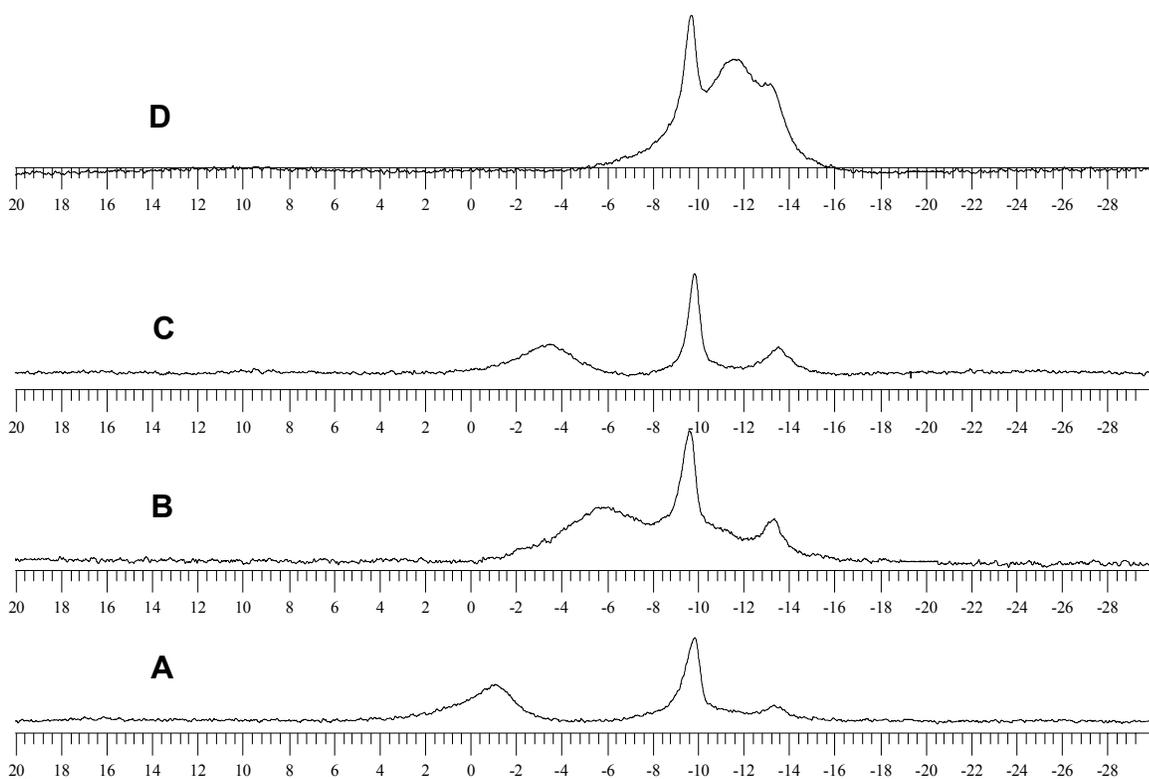
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### **Completion of Salt Suppression Studies**

We showed in a previously published paper that 0.1 M NaCl salt addition to PEI/100 ppm BA solution had the effect of quenching the ion-pairing between the borate anion and the weak anion exchange sites of the PEI polymer. Addition of 0.1 M NaCl to ¼-1,2-diol-PEI/100 ppm BA solution quenched borate ion-pairing and allowed for an estimate of ion-pairing to borate ester ratio. However, it was not known if salt addition could have some unanticipated effect on borate ester formation, which could bias the previous borate ester/borate ion-pairing ratio estimate. Thus, we examined by <sup>11</sup>B-NMR the influence of adding a neutral D<sub>2</sub>O solution of salt (NaCl) to the 2/3 and the 3/3-1,2-diol-PEI polymers in the presence of BA. Solutions containing 1 M in NaCl and 600 ppm boron were analyzed by <sup>11</sup>B NMR and compared with their counterpart ones without NaCl. Surprisingly, the addition of NaCl resulted in very large increases in pD, and, as a consequence, in large chemical shifts of the BA/borate peak (Figure 11). For instance, the pD for the 2/3-PEI changed from 7.83 to 9.54 when salt was added to the solution. The same effect was observed for the fully functionalized PEI, where pD changed from 7.52 to 9.02. A similar pD increase was also observed when 1 M NaCl was added to 0.0775 M PEI. A possible explanation for the salt effect on pD values could be the displacement of hydroxyl groups from the cationic sites on the polymer backbone by chloride. This would release hydroxyl groups into the solution and thus increase pD. Another explanation for the pD increase could be a shift in the BA/borate equilibrium due to a displacement of borate anions from the ion pair by chloride. At this point, we have no clear evidence to support either conjecture. Furthermore, the monoester and diester concentration showed a decrease with salt addition. It changed from 53.5% to about 44% for the 2/3-PEI, and from 48% to about 36% for the 3/3-PEI. Thus, it appears that higher salt concentrations and/or pD values have promoted more borate formation at the expense of monoester and diester formation.

The previously reported salt-suppression studies, where complete ion-pairing suppression was observed for PEI, used 0.1 M NaCl with the ¼-1,2-diol-PEI and 100 ppm B. Under these conditions only a small pD change was observed upon 0.1 M salt addition (pH 9.14 to 9.62). Thus, the previously reported results may see only a small bias in the salt suppression value. But, these newer <sup>11</sup>B-NMR results do corroborate the much smaller borate ester value observed for the 0.5 M NaCl salt suppression conditions reported in our first paper. It was these initial observations of the variable numbers in the previously reported salt-suppression studies that stimulated the salt studies using <sup>11</sup>B-NMR to observe directly any effects on the ester formation. We had not anticipated the large observed pD changes that accompanies the addition of 1 M neutral salt. Thus, NMR analysis

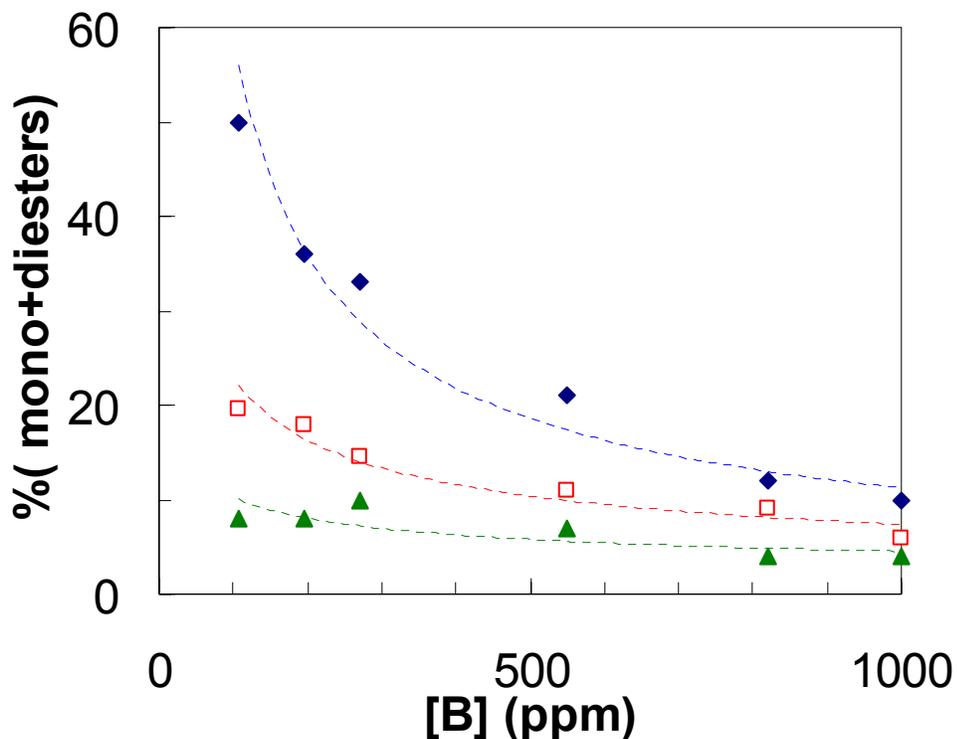
is a much better method for directly measuring borate ester formation, than salt-suppression extractive techniques.



$^{11}\text{B}$  NMR spectra for (A) 3/3 diol 600 ppmB, (B) 3/3 diol 600 ppm and 1M NaCl, (C) 1/3 diol 600 ppm B, (D) 1/3 diol 600 ppm and 1M NaCl.

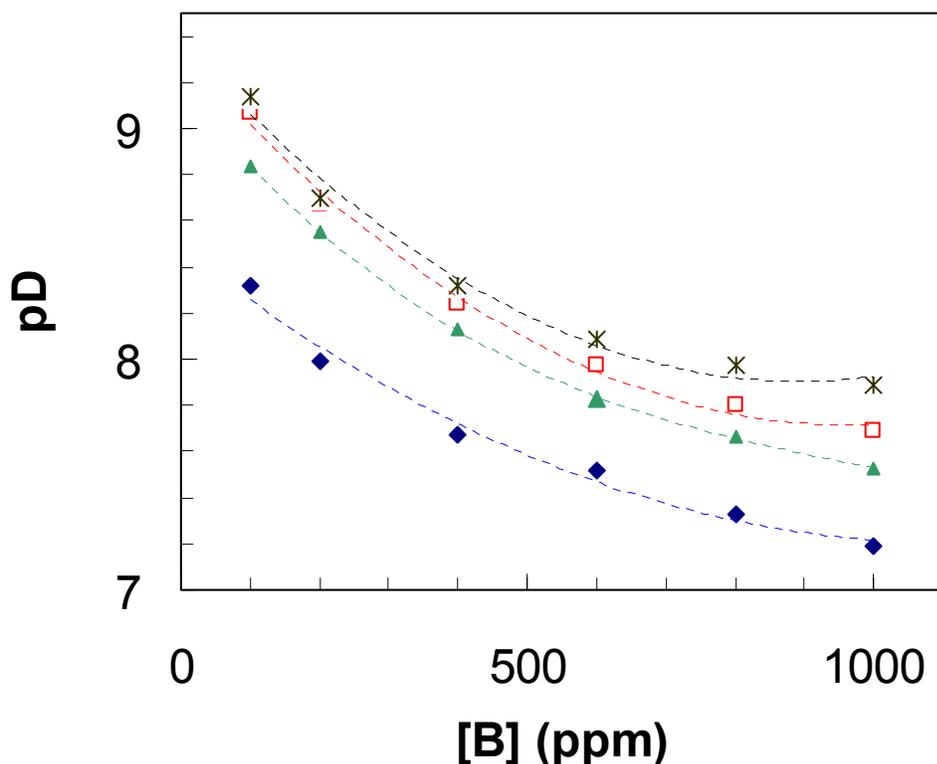
### Variable Temperature Studies

Easy and straightforward reversal of boron binding is a very important factor for recycling  $^{10}\text{B}$ -enriched BA in the nuclear power industry. Temperature reversal of boron binding is more amenable to nuclear power applications than the more often reported acid or base stripping. The facility of 1,2-diol-PEI polymers to perform as temperature-reversible boron chelators was investigated for the 2/3 functionalized PEI polymer, the polymer that according to the  $^{11}\text{B}$ -NMR studies appears to give the optimum level of boron binding. This sample was prepared with 1%w/v polymer concentration and for boron concentrations ranging from 1000 to 100 ppm.  $^{11}\text{B}$  NMR spectra data obtained from 25 to 65°C are summarized below. These results indicate that an increase in temperature to 65°C suppresses most borate ester formation for all boron concentrations. In addition, binding of borates with anion exchange resins through ion pairing has been reported to decrease as temperature rises. Consequently, the water-soluble polymers proposed in this study for BA recovery are expect to perform efficiently with regard to reversible boron binding as well.



Relative abundance of mono- and diester for 2/3-PEI versus boron concentration at various temperatures: (◆) 25 °C, (□) 45 °C, and (▲) 65 °C.

The question arises as to why the 2/3-1,2-diol-PEI binds better than the 3/3-1,2-diol-PEI when the fully-functionalized polymer has more overall binding sites on a molar basis than the 2/3 functionalized polymer. We surmise that the answer is a balance between pD values and number of binding sites. The 1/3-1,2-diol-PEI is the most basic of the polymers acting under all boron concentrations to give the highest overall solution pD. Borate ester formation is pH dependent with a maximum ranging from approximately pH 8 to 9. But, the 1/3 functionalized polymer has the smallest number of binding sites, which limits the amount of binding possible. The solutions are in the best pH range for borate ester formation but are limited and overall show the lowest amount of borate ester formation. In contrast, the fully functionalized polymer has the most number of diol sites, many of them preorganized to give the high-binding borate diesters. But the 3/3-diol-1,2-diol-PEI polymer is the least basic and at all B concentrations the solutions give the lowest overall pD values mostly below pD 8. Thus the pD values are in a range where borate ester formation is not as favorable, even though on a molar basis there are more diol sites available. That leaves the 2/3-2,3-diol-PEI with the intermediate number of binding sites, but its pD range is only slightly lower than for the 1/3 functionalized polymer; almost every pD value is in the range of 8 to 9, a favorable range for borate ester formation. Thus, the balance between pD and number of binding sites are the circumstances that allow the 2/3-functionalized polymer to be the overall best performer.



pD values obtained for PEI and its 1,2-diol-PEI polymers as a function of boron concentration: 0.077 M (\*) PEI, (□) 1/3-PEI, (▲) 2/3-PEI and (◆) 3/3-PEI.

A second manuscript summarizing all the PEI-1,2-diol NMR studies was submitted and we are awaiting acceptance for publication. The summary abstract is as follows:

#### ABSTRACT

Three water-soluble polymers incorporating increasing levels of linear 1,2-diol attached to polyethylenimine (PEI) backbone were synthesized, characterized by  $^1\text{H}$  NMR/ $^{13}\text{C}$  NMR, and investigated for their ability to bind boric acid (BA).  $^{11}\text{B}$  NMR spectroscopy showed that BA interacted with the polymeric 1,2-diols by forming borate monoester and borate diesters in the boron concentration range of 100 to 1000 ppm and at 0.0775 M polymer. Borate monoester species predominated for low functionalization levels (33% of the PEI amines functionalized), whereas borate diester species was prevalent for the higher functionalized polymers (66 to 100% of the PEI amines functionalized) at room temperature. One hundred percent of the BA was bound as a mixture of borate mono- and diesters at 100-ppm boron for all the polymers synthesized. The overall best performer based on total borate ester formation was 2/3-1,2-diol-PEI. Borate ion concentration was measured from the  $^{11}\text{B}$  NMR chemical shift of the BA/borate peak between 0 ppm (all BA) and  $-17.7$  ppm (all borate ion) in the presence of the 1, 2-diol-PEI polymers. The order of borate ion generation was pD dependent and followed the order 1/3-1,2-diol-PEI > 2/3-1,2-diol-PEI > 3/3-1,2-diol-PEI. Ion-pairing capabilities of the weak anion exchange sites in the PEI backbone for the functionalized polymers were estimated to have 3 to 10 times more ion-pairing sites than borate ions, giving rise to the potential to have all the borate in solution ion-paired with

the 1,2-diol-PEI polymers. Variable temperature  $^{11}\text{B}$  NMR data showed that borate ester formation was dramatically reduced to 10% at 65°C. Thus, polyethylenimine polymers, as the ones investigated in this work, are reasonable candidates for the selective recovery and recycle of boric acid.

### Sb Extraction/Stripping

As reported earlier, there are several approaches to addressing the Sb contamination problem. One is the selective back stripping of the B from the water-soluble polymers, leaving the Sb on the polymers. Once the soluble polymer is loaded with Sb to some predetermined level the polymer concentrate could be discarded as radioactive waste and be replaced with fresh polymer for binding more boric acid. Since we are focusing on thermal stripping as the mode of boric acid recovery, we need to determine if there is any selectivity in thermal stripping between boric acid and Sb. The best way to determine if the dilute solution species of Sb in the power plants can be removed is to do live tests at the power plants.

Previous plant studies showed that Sb was strongly bound or absorbed onto the water-soluble polymer even in the presence of high concentrations of BA (1000 to 2000 ppm B range, 15 Sept 03 to 15 Dec 03, Quarterly report). What was not known was if Sb would thermally strip as does boric acid. New power plant studies have been done and the results are now summarized. The experiments entailed adding 2/3 PEI-1,2-diol to coolant water to make 2100 mL of a 0.5wt% polymer solution containing approximately 1349 ppm B. Extra Sb-125 spike solution (20 mL of Sb(III), oxidation state adjusted with KI) was added to assure there was plenty of antimony present for analysis purposes. An aliquot (12 mL) was removed from the feed at the start to determine isotopics as shown in Table 1. The system was concentrated by ultrafiltration using a 10,000 MWCO hollow fiber membrane with a cycle flow rate of 600 mL/min and a membrane flux rate of 50 to 60 mL/min, which gave a backpressure of approximately 50 psig. The system temperature was 30°C. When the permeate reached 1500 mL, the process was stopped and the permeate and concentrate analyzed for isotopics (Table 1).

The concentrate (346 mL, 3.33% polymer) was diluted with DI water (343 mL) to give 690 mL (1.66% polymer and enough volume to load the system) of the new feed, which was then thermally stripped at 82°C. The stripping system was again a 10,000 MWCO hollow fiber membrane using a cycle flow rate of 600 mL/min and a membrane flux rate of 50 to 60 mL/min, which gave a backpressure of 10 psig (the solution viscosity is greatly reduced at 80°C). The final permeate volume was 430 mL and concentrate volume was 260 mL. Samples were removed for isotopic analysis and the results are also shown in Table 1.

A decontamination factor (DF) defined as (Initial Feed count- Permeate count)/Permeate count is given in Table 1 for both the first treatment step and the thermal treatment step. From the results summarized in Table 1 it can be seen that Sb-122 along with the spiked Sb-125 were concentrated in the Polymer Filtration process and the permeate gave material near the detection limit. Then the solutions were thermally stripped at 82°C the Sb does not strip. Concentration was observed for all the other isotopes found in reactor coolant water. As reported earlier in the previous power plant studies, it appears that some of these other isotopes exist as particulates that can be concentrated by simple ultrafiltration (e.g. 15 Sept 03 to 15 Dec 03 Quarterly report, Fe, Co, Ln were concentrated, but Sb and Mn are not concentrated at all by UF). Thus it appears that it is possible to concentrate BA along with all contaminating isotopes that cause a problem in reactant cooling water and then selectively recover the boric acid. Though the exact mechanism is not known for each isotope as we do not know all the speciation for them, it is possible to guess at their

speciation and to make a mechanistic guess as to how they are being removed. Some of them could be removed as by ion-pairing through the weak cationic site on the polymeric backbone. But we might expect those to be removed with thermal stripping. Some could form nitrogen complexes as might be expected for the cobalt species, silver species and perhaps even the chromium species. And the Sb is expected to form complex esters similar to the boric acid esters. Another possibility is that some of these species are absorbed to particular matter and are ultrafiltered and concentrated. From past blanks from other power plant studies this was not observed to occur for Sb species.

Table. Summary results of extraction and stripping of nuclear power reactor coolant water isotopics with 0.5% 2/3-PEI-1,2-Diol using ultrafiltration at 30°C. The activities are given in  $\mu\text{Ci/mL}$ . (DF defined as (feed - permeate/permeate) counts)

Solutions	Sb-122 *E-05	Sb-125 *E-05	Co-58 *E-04	Co-60 *E-04	Cr-51 *E-04	Mn-54 *E-04	Ag-110m *E-04	I-131 *E-05	I-133 *E-04
Initial Feed	13.6	60.5	7.38	1.80	9.28	1.11	2.02	2.21	3.37
Permeate	1.56	2.05	2.23	0.24	----	0.46	----	0.52	0.83
Concentrate	44.0	322	16.9	5.02	27.0	2.42	7.66	5.22	9.88
Treatment DF	7.7	29	2.3	6.5	----	1.4	-----	3.3	3.1
Stripping Feed	22.0	161	8.44	2.51	13.5	1.21	3.83	2.61	4.94
Permeate	1.13	2.13	1.36	0.06	-----	0.22	----	0.60	0.92
Concentrate	106	691	23.2	6.61	41.3	3.00	7.59	13.6	22.3
Strip DF	16.1	74.6	5.2	40.8	----	4.5	-----	3.4	4.3

#### Tartrate Ligands

As reported previously we have prepared a cyclic diol ligand and have been characterizing it by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR and comparing the structure to a model compound of similar structure. The product appears to be the desired material. We were unable to complete the testing at this time due to ICP instrumentation breakdown, which will not be repaired until late December.

#### Engineering studies.

Again these studies could not be completed because of ICP instrumentation failure.