Preliminary Results: Chemical Effects Modeling

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Presentation Outline

I. Model Objectives and Background

II. Input Parameters

III. Model Results:

- Effect of Temp & Pressure
- Effect of pH

IV. Initial Validation Efforts

V. Conclusions

Model Objectives & Background

- The OLI Systems developed Stream Analyzer (SA) and Environmental Simulation Programs (ESP) are being used to simulate typical post-LOCA water chemistries with representative corrosion products and leachates.
- They are being used as a guide to constrain the numerous parameters in preparation for the actual loop experiments.
- The OLI methodology provides an accurate prediction of multi-component aqueous systems over a wide range of [C] (0-30molal), temp (-50-300°C), & P (0-1500Bar).
- The OLI methodology has been previously validated by comparing calculated results with experimental data available in the literature, but, not for waters containing B.

Input Parameters

- Input parameters as stipulated in the GSI-191 Chemical Effects Test Plan: Characterization of Chemical and Corrosion Effects Potentially Occurring During a PWR LOCA - Revision 7.
- Corrosion product (Zn, Al, Cu, Fe, Ca, & Si) amounts equivalent to exposure to 30min at 150°C and scaled appropriately with water volume.
- Nukon fiberglass insulation composition, specific surface area (fiber surface area/volume), and leaching rates were obtained from Owens Corning.
- B = 2,000 ppm & NaOH additions for an initial pH of 7 (pH was varied with NaOH additions).

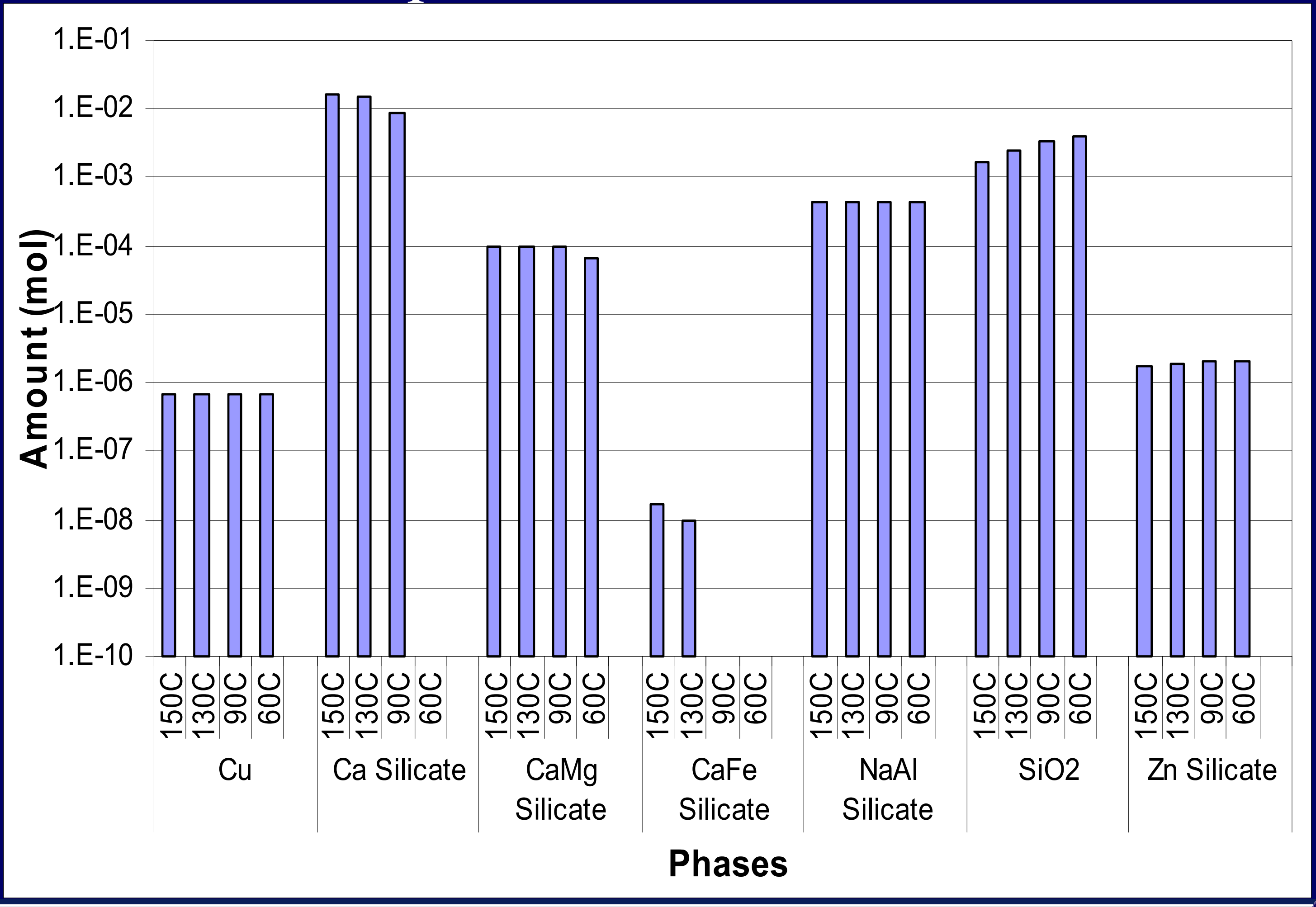
ESP & SA

Modeling Results

Effects of Temperature & Pressure

Results: Effects of Temp & Pressure

Precipitation of Solid Phases

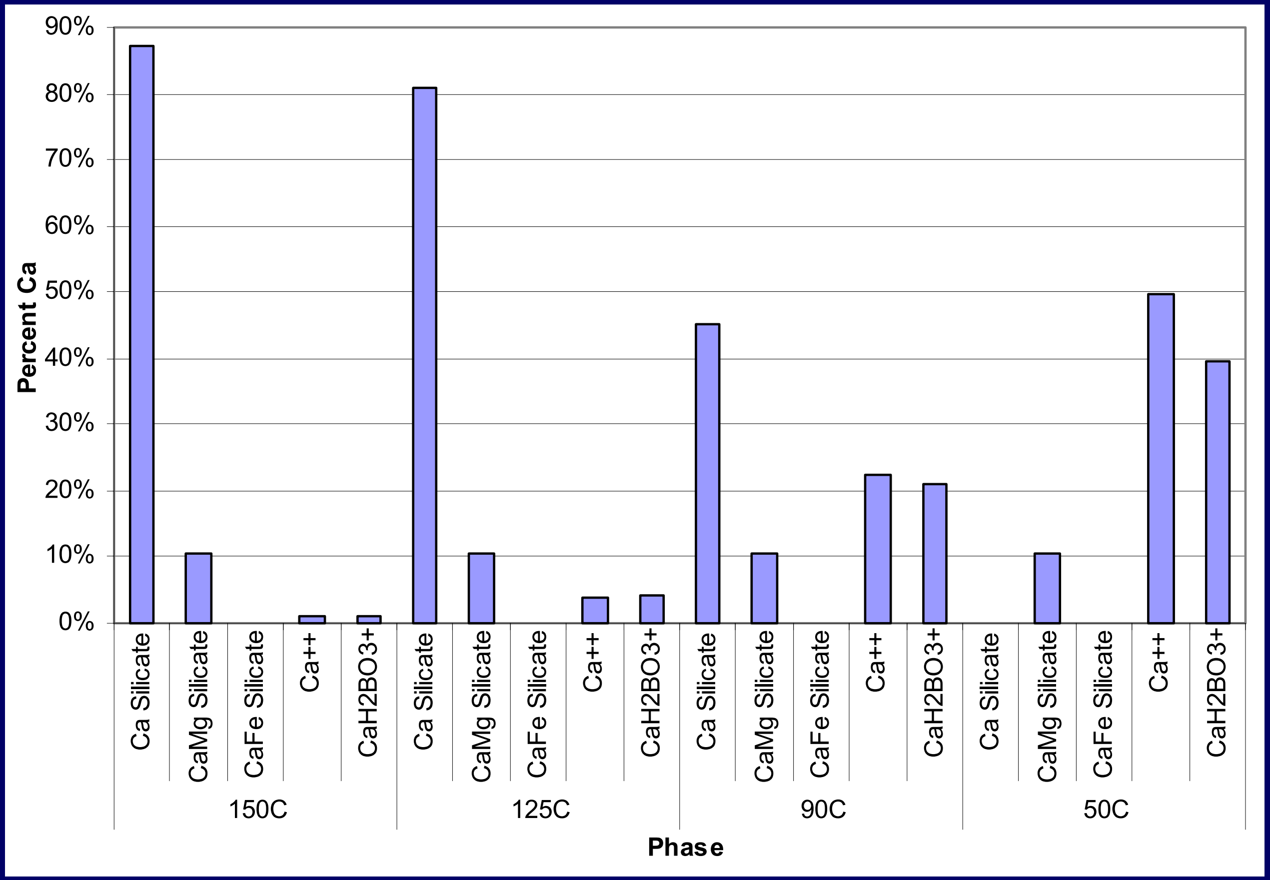


Results: Effects of Temp & Pressure

- A fixed amount of material corrosion products and insulation leachates were mixed at 150°C @ 5atm, 130°C @ 3atm, and 90°C and 60°C @ 1atm and then allowed to speciate.
- No phase changes were observed for Cu, Zn, and Al species.
  - Most of the Cu was present as Cu metal.
  - Most of the Zn was present as Zn_2SiO_4.
  - Most of the Al was present as sodium alumino silicate ($NaAlSi_3O_8$).
- Various silicates formed with greater amounts at lower temps.
  - SiO_2 solids increased from 1.7E-3 to 4.0E-3 mol from 150°C to 60°C.
  - $CaSiO_3$ solids decreased from 150°C to 90°C and dissolved at 60°C.
  - A slight decrease in calcium magnesium silicate observed at 60 C.
  - A very small quantity (1.0E-8 mol) of calcium iron silicate was formed at 130-150°C which dissolved in the solution at 60-90°C.
- $NaAlSi_3O_8$ formed and is widely known to form gel species.

Results: Effects of Temp & Pressure

Ca Distribution in Solids and Liquids



- $CaSO_3$ showed retrograde solubility.
- At high temps, the majority of Ca is present as $CaSiO_3$.
- At low temperatures, Ca is present as dissolved Ca^{++} & $CaH_2BO_3^+$ ions.
- At low temperatures, more SiO_2 ppt.

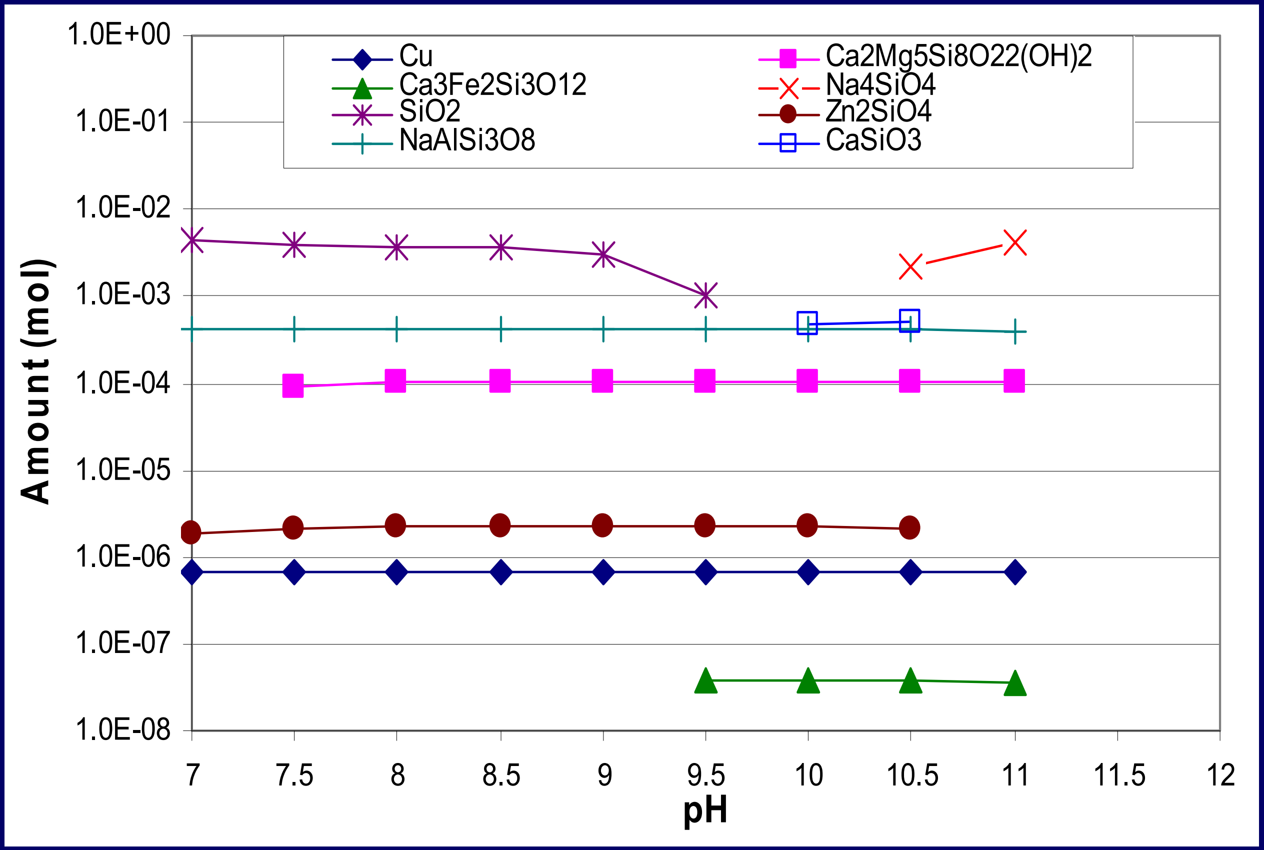
ESP & SA

Modeling Results

Effects of Temperature & pH

Results: Effects of Temp & pH

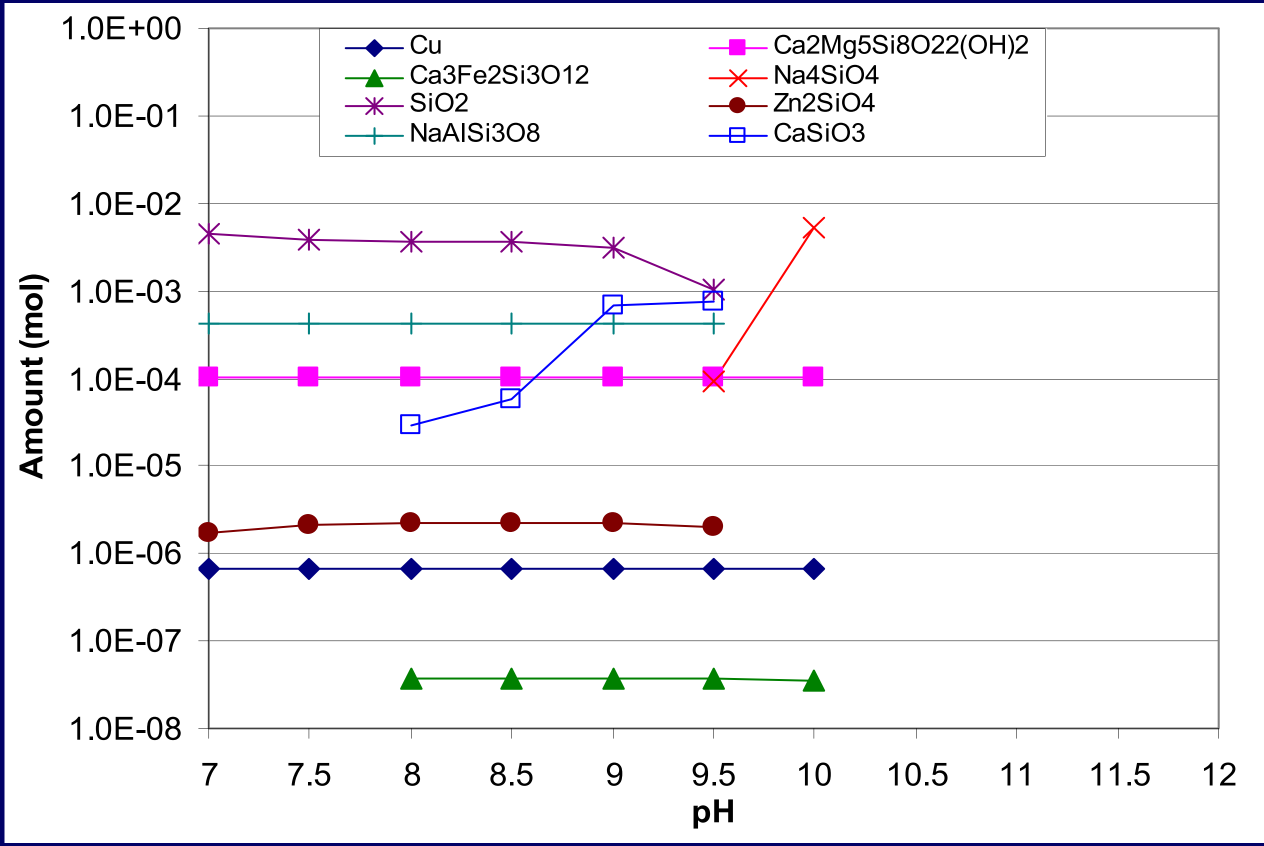
Effect of pH @ 60°C for Solid Phase Precipitation



- The pH was adjusted by the addition of NaOH.
- Significant changes in the formation of silicate phases were observed starting at the 9.5.
- In the pH range between 9 and 10, $CaSiO_3$ was formed at the expense of SiO_2 while Na_4SiO_4 precipitated at the expense of $CaSO_3$ at a pH greater than 10.5.

Results: Effects of Temp & pH

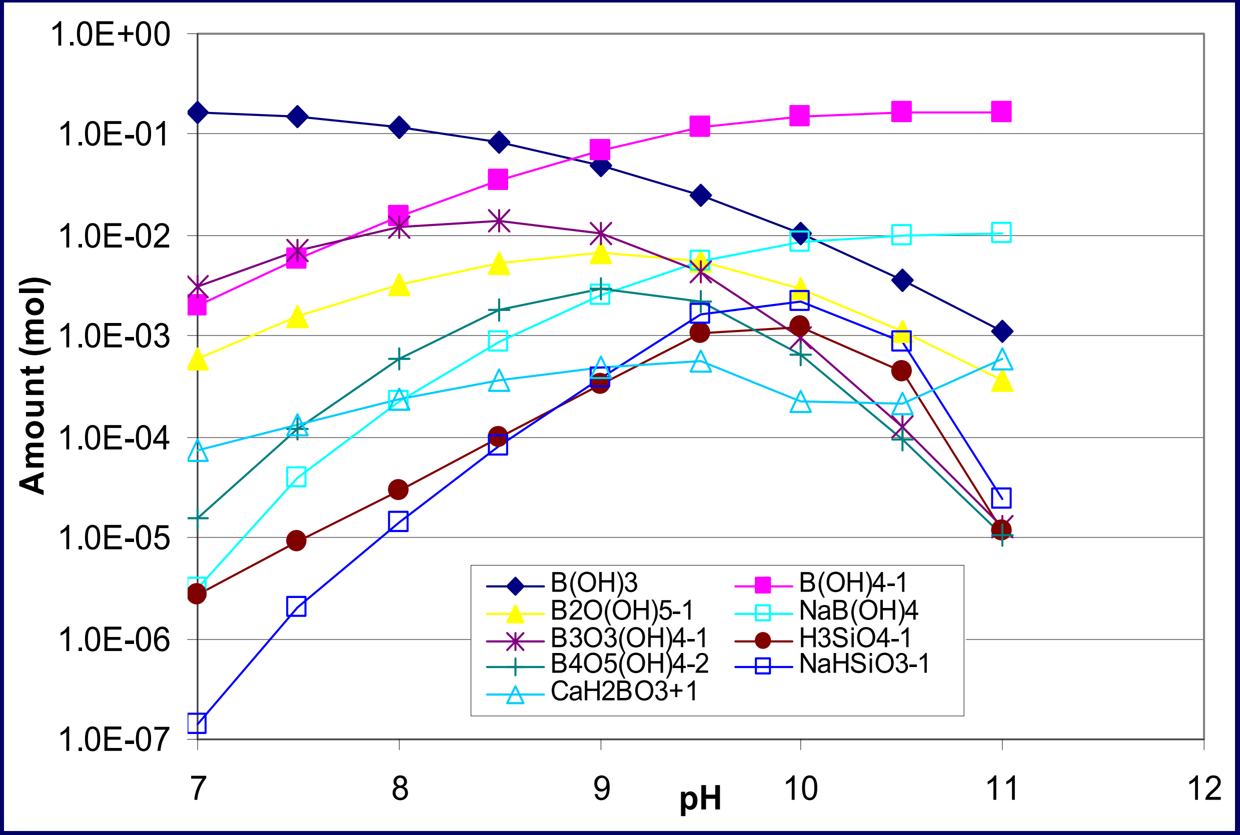
Effect of pH @ 130°C for Solid Phase Precipitation



- The pH was adjusted by the addition of NaOH.
- Simulation indicated that the precipitation of the same solids occurred at 130°C as found at 60°C.
- The formation of silicate solids moved to a lower pH at the higher temp.
- $CaSO_3$, CaFe silicates, and Na_4SiO_4 solids precipitated at a lower pH than at 60°C.

Results: Effects of Temp & pH

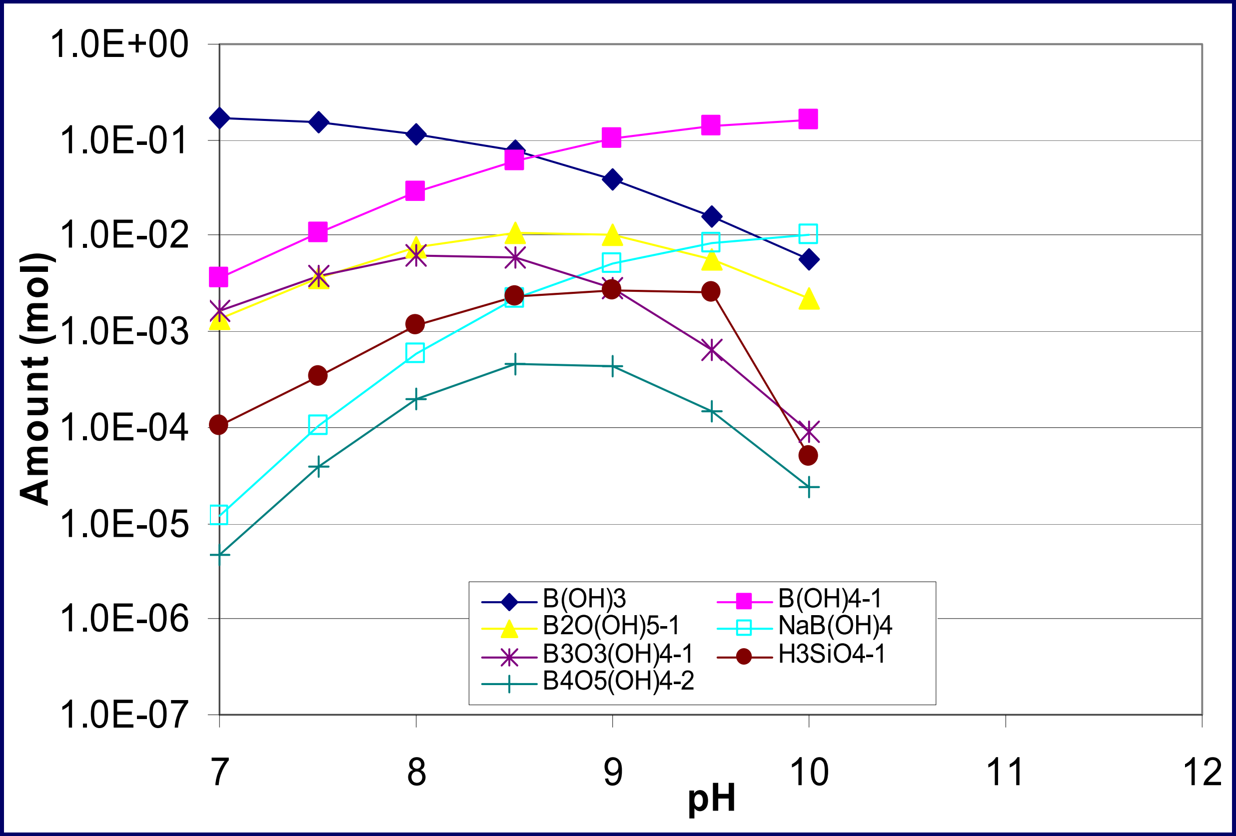
Effect of pH @ 60°C for Aqueous Phase Speciation



- The pH was adjusted by the addition of NaOH.
- Dominant aqueous phase at pH of 7 is $B(OH)_3$ which diminishes with increasing pH.
- At pH > 9, $B(OH)_4^{-1}$ becomes the dominating aqueous species.
- Additional aqueous species contributing the evolution of the pH in the solutions are shown.

Results: Effects of Temp & pH

Effect of pH @ 130°C for Aqueous Phase Speciation

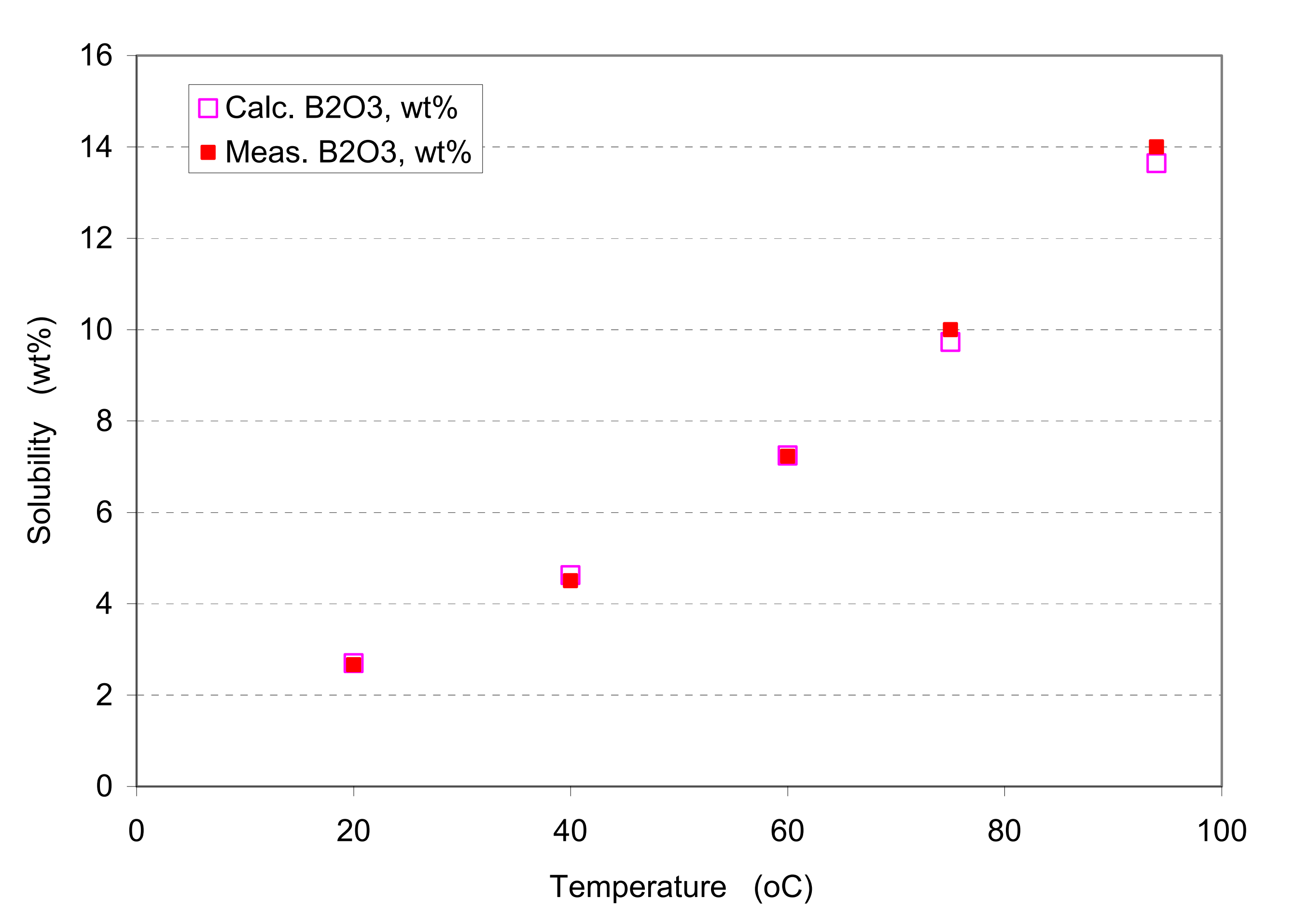


- The pH was adjusted by the addition of NaOH.
- The results indicate a similar trend b/w $B(OH)_3$ & $B(OH)_4^{-1}$ at 60°C and 130°C.
- Similar aqueous species and trends were found for the other species except for Ca^{++}, $CaH_2BO_3^+$, and $NaHSiO_3^-$

Initial
Validation Efforts
of
ESP and SA
in
Borated Waters

Validation Efforts from Literature Data

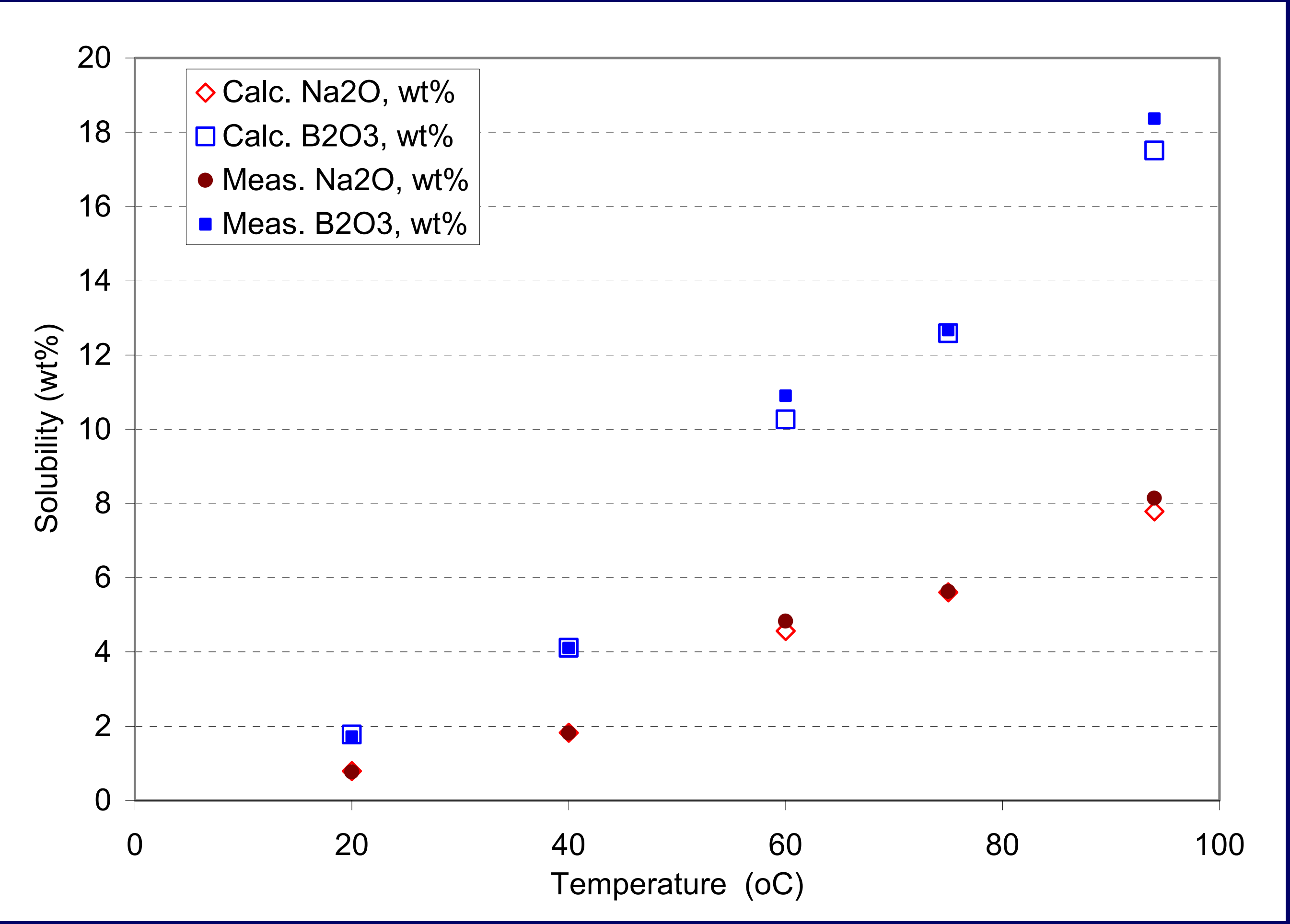
Solubility of Boric Acid [$B(OH)_3$] in Water



Experimental data from: N.P. Nies & R.W. Hulbert, “Solubility Isotherms in the System Sodium Oxide-Boric Oxide-Water,” J. Chem. Eng. Data 1967, 12(3), pp. 303-313.

Validation Efforts from Literature Data

Solubility of Borax [$Na_2B_4O_7$] in Water



Experimental data from: N.P. Nies & R.W. Hulbert, "Solubility Isotherms in the System Sodium Oxide-Boric Oxide-Water," J. Chem. Eng. Data 1967, 12(3), pp. 303-313.

Conclusions

- The chemical speciation of corrosion products and leachates was evaluated as a function of temperature and pressure (150°C-5atm, 130°C-3atm, & 90°C & 60°C-1atm) and temperature and pH (pH 7-12 at 60°C-1atm and 130°C-3atm).
- No temp effect was observed for Cu, Zn, and Al ppt solids.
- $NaAlSi_3O_8$ formed and is widely known to form gel species.
- Various silicates formed with greater amounts at lower temps.
- Retrograde solubility of some Ca species was observed, thus, the role of Ca could be important for a non-pressurized system.
- Both Nukon insulation fibers and concrete are a source for Ca.
- Preconditioning the solution with high temperature insoluble precipitates may be needed for a non-pressurized test facility.

Future Work

- Update inputs to values found in the Chemical Effects Test Plan: Characterization of Chemical and Corrosion Effects Potentially Occurring During a PWR LOCA - Revision 8.
- Additional work is needed to determine the solubility and kinetics of the Ca solid phase precipitation since preconditioning may be important.
- Further model validation is needed in borated waters and the anticipated and actual experimental test solutions.
- Continue literature survey on silicate formation:
  - Insoluble metal silicates when precipitated from aqueous solution are usually gelatinous and amorphous. In dilute solutions, precipitation occurs at a pH below which metal hydroxide would precipitate (Iler,1955).