



# GSI-191 Chemical Effects Testing

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Dominion Resources and AECL  
October 11, 2007

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## Agenda

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- *Introductions* *Dominion/NRC*
- *Purpose* *K. Basehore-Dominion*
- *Chemical effects assessment and testing approach* *D. Guzonas - AECL*
- *Conclusions* *K. Basehore-Dominion*
- *Q&A* *Dominion/NRC*
- *Other Issues* *K. Basehore-Dominion*

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## ***Purpose***

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**To provide the Dominion-AECL approach for chemical effects assessment and testing for resolving GSI-191 concerns for:**

- **Millstone Power Station Units 2 and 3**
- **North Anna Power Station Units 1 and 2**
- **Surry Power Station Units 1 and 2**

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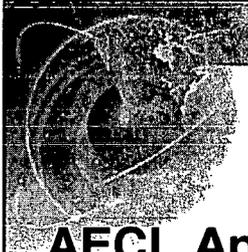
## ***AECL Presentation***

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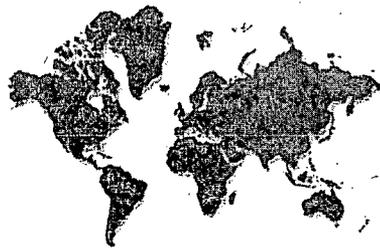
- **David Guzonas - AECL**

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## **AECL Approach to Chemical Effects – Assessment and Bench-top Testing**



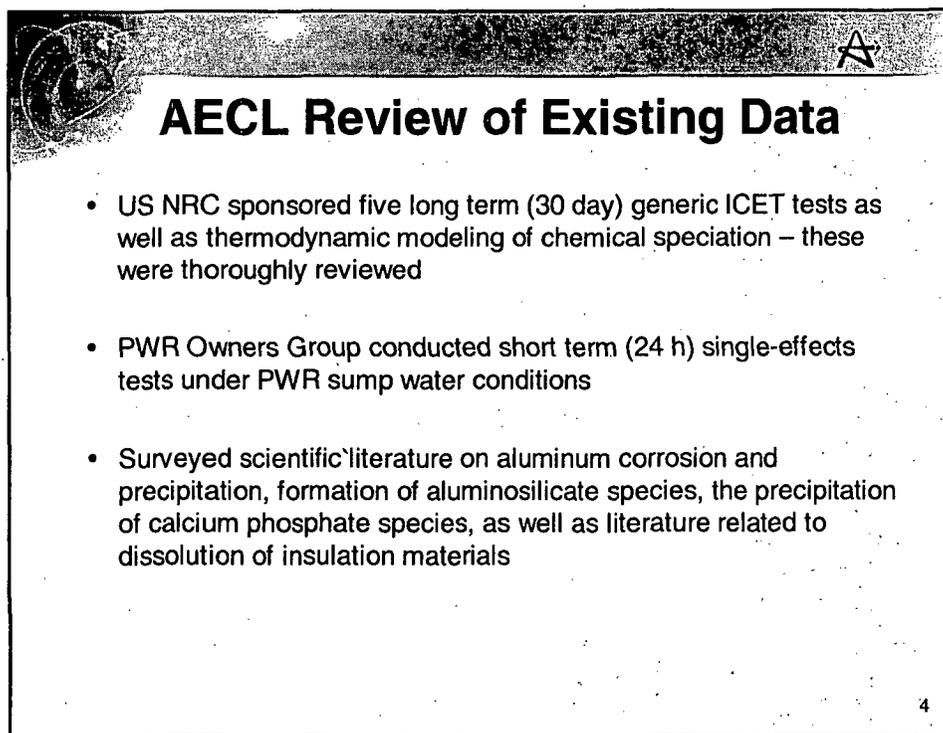
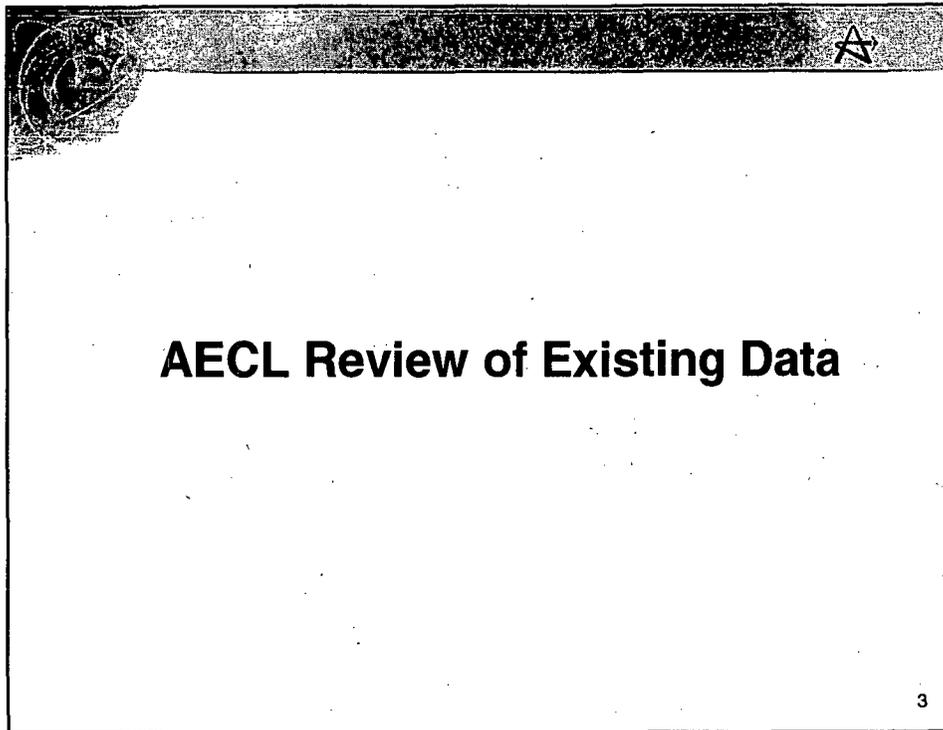
 **AECL EACL**



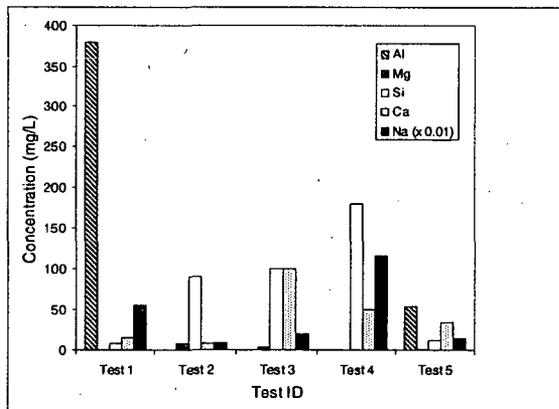
### **Outline**

- Review of Existing Data
- Aluminosilicate Formation
- Methodology for Release Calculations
- Precipitation
- Detailed Calculations

2



## Concentrations of major species measured in solution in ICET Tests 1-5



Data for [Na] divided by 100 to facilitate comparison

5

## Percentage Weight Loss(-) or Gain of Submerged Al Coupons after 30 days

Coupon Location	Test Number				
	Fibreglass			Cal-sil/Fibreglass	
	1	2	5	3	4
	pH 10, no TSP	pH 7, TSP	pH 8.5, borax	pH 7, TSP	pH 10, no TSP
submerged	-25%	-0.2%	-2.9%	0.15%	0%
unsubmerged	0.48%	0.1%	0.1%	0.1%	0.15%

6

## Summary of Chemical Phases Identified during the ICET TESTS

Test ID	Deposit	Formula
ICET 1	tincalconite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$
	borax	$\text{Na}_2\text{B}_4\text{O}_7(\text{OH})_4 \cdot 8\text{H}_2\text{O}$
	unknown	Compound containing Al, B, Na, $\text{CO}_3^{2-}$
	unknown	Compound containing Na, B, Al
ICET 2	calcium phosphate (hydroxyapatite?)	$\text{Ca}_5(\text{PO}_4)_3\text{OH?}$
ICET 3	tobermorite	$\text{Ca}_{2.25}(\text{Si}_3\text{O}_{7.5}(\text{OH})_{1.5})(\text{H}_2\text{O})$
	calcite	$\text{CaCO}_3$
	sodium calcium hydrogen carbonate phosphate hydrate	$(\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot \text{H}_2\text{O} \cdot \text{NaHCO}_3 \cdot \text{H}_2\text{O})$
	lithium calcium hydrogen carbonate phosphate hydrate	$(\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot \text{H}_2\text{O} \cdot \text{Li}_2\text{CO}_3 \cdot \text{H}_2\text{O})$
	calcium phosphate (hydroxyapatite?)	$\text{Ca}_5(\text{PO}_4)_3\text{OH?}$
ICET 4	tobermorite	$\text{Ca}_{2.25}(\text{Si}_3\text{O}_{7.5}(\text{OH})_{1.5})(\text{H}_2\text{O})$
	calcite	$\text{CaCO}_3$
ICET 5	unknown	Compounds containing O, Na, Al, C, Ca Mg and Si

7

## Concentration of Selected Elements in Water Samples taken from the ICET Tests

Test ID	pH	Maximum concentration in water samples (mg/L)										
		B	Al	Fe	Ni	Cu	Zn	Mg	Si	Ca	Na	P
Test 1	10 (no TSP)	3120	380	Nr	nr	1.2	1.8	nr	8.5	15	5500	nr
Test 2	7 (TSP)	2800	bd	bd	bd	bd	10	8	90	8	900	nr
Test 3	7 (TSP)	2550	0.1	0.4	nr	0.2	0.1	3.5	100	100	2000	0.7
Test 4	10 (no TSP)	3390	bd (5.5)	bd	nr	0.3	bd (0.3)	bd	180	50	11500	nr
Test 5	8.5 (borax)	2860	54	bd	nr	0.9	0.8	1	12	34	1400	nr

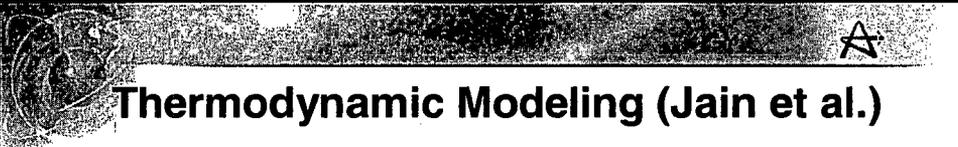
8



## Thermodynamic Modeling (Jain et al.)

- Preliminary modeling, carried out before first ICET results were available, used input values from peer-reviewed literature (corrosion/dissolution rates) and ICET test plan (surfaces areas, water composition)
- Assumed system was in thermodynamic equilibrium
  - no kinetic information was included
  - Most oversaturated phase allowed to precipitate
- Reactions limited to those materials used in ICET tests and excluded the uptake of CO<sub>2</sub> from air

9



## Thermodynamic Modeling (Jain et al.)

- At pH 10, various amounts of silicate species were predicted to form over time;
  - CaSiO<sub>3</sub>
  - Ca<sub>2</sub>Mg<sub>5</sub>Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>
  - Zn<sub>2</sub>SiO<sub>4</sub>
  - SiO<sub>2</sub>
  - NaAlSi<sub>3</sub>O<sub>8</sub>
  - Fe<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>
  - Ca<sub>3</sub>FeSi<sub>3</sub>O<sub>12</sub>
  - ZnFe<sub>2</sub>O<sub>4</sub>
- However, silicate phases not observed to form in ICET tests
  - while these silicates are the thermodynamically stable phases, their formation is kinetically slow
  - Simulations repeated with formation of silicates suppressed

10



## Thermodynamic Modeling (Jain et al.)

- Revised simulations for ICET Test 1 gave reasonable predictions of aluminum and calcium concentrations in solution for the first 720 h
  - after this time the model overpredicted the concentrations
  - attributed to the passivation of the surfaces
- Model also overpredicted the concentration of Si in solution at all times
- Model also predicted the formation of  $\text{Fe}(\text{OH})_2$  after 148 h and  $\text{Zn}(\text{OH})_2$  after 32 h

11



## Major Results of Review

1. The ICET tests clearly show that, at the pH values studied, aluminum corrosion can give rise to the formation of an aluminum-bearing precipitate
  - a. The data show that:
    1. Boric acid significantly increases the corrosion rate of aluminum
    2. Aluminum corrosion may be inhibited by species present in the sump environment (e.g., phosphates, silicates)
    3. The precipitate formed included boron, which affects the mass or flocculation properties of aluminum-bearing precipitate formed. In particular, boron increases the "solubility" of aluminum hydroxides
2. For the surface areas of materials used in these tests, only low concentrations of iron, nickel, magnesium and zinc dissolved into the simulated sump water, and these species did not lead to the formation of detectable amounts of precipitates

12



## Major Results of Review

3. Silicon and calcium can be released into the sump solutions from dissolution of fibreglass and cal-sil
  - a. If TSP is present, precipitates containing calcium and phosphate, or calcium, phosphate and carbonate, can form. In the absence of TSP, the calcium and silicon do not lead to the formation of detectable chemical precipitates
  - b. Release of calcium from fibreglass is much lower than that from cal-sil
4. Bare concrete is not a significant source of calcium in solution under these conditions
5. Thermodynamic modeling alone cannot properly predict the identity or quantities of precipitates formed under PWR sump conditions; kinetic factors are very important

13



## Major Results of Review

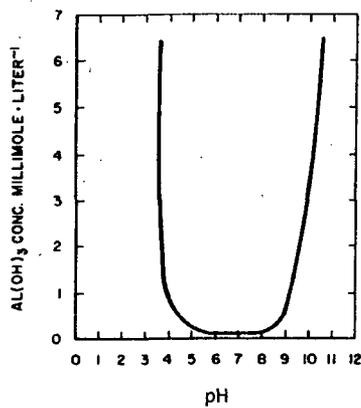
6. Based on AECL's assessment of available data, no evidence of direct chemical effects from paint debris
  - However, radiolysis of organic compounds leaching from paints and coatings will lead to the formation of carbonate species, which will lower the pH of the sump solution
7. While WCAP-16530 suggests that sodium aluminum silicate is a possible precipitate, a review of the literature on the thermodynamics and kinetics of aluminosilicate formation suggests that this is unlikely under PWR post-LOCA sump water conditions

14

## Aluminosilicate Formation

15

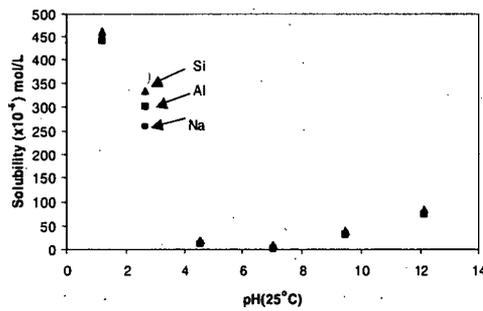
## Solubility of $\text{Al}(\text{OH})_3$



- Amphoteric
  - Aluminium hydroxide precipitation favoured in the pH range 4 to 9
- Above pH 9 and low Al concentrations, dominant species in solution is  $\text{Al}(\text{OH})_4^-$
- Wefers, K and Bell, G.M. [1972]. Oxides and Hydroxides of Aluminium. Technical Paper no. 19, Alcoa Research Laboratories

16

## Solubility of Nepheline Glass, $\text{NaAlSiO}_4$



- In alkaline solutions, a high pH generally increases the solubility of aluminosilicates
- In acidic solutions, increasing acid concentration destroys the framework of aluminosilicates and increases the solubility
- Near neutral pH, nepheline has the lowest solubility; this behavior is also observed from the solubility data for jadeite and albite glasses [Hamilton, J.P., Brantley, S.L., Pantano, C.G., Criscenti, L.J. and Kubicki, J.D. [2001]. Dissolution of Nepheline, Jadeite, and Albite Glasses: Toward Better Models for Aluminosilicate Dissolution. *Geochimica et Cosmochimica Acta*, 65, 3683].

17

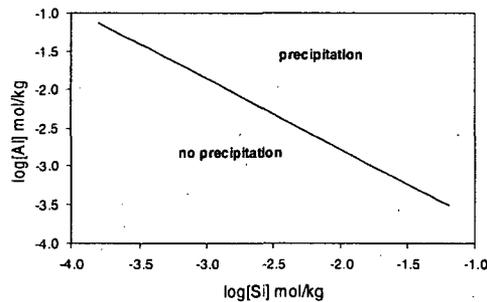
## Aluminosilicate Formation

- In the pH range 6.8 to 9.3 at 25°C, the major dissolved silicon species is  $\text{H}_4\text{SiO}_4$
- When aluminium and silicon species are both present in aqueous solution, polymerization of aluminium and silicon similar to the polymerization of silicon species can occur to form various aluminosilicates
- Depending on Al/Si ratio and solution pH, aluminosilicates such as feldspars, nepheline and zeolites can be produced in which the molar ratio of Al/Si ranges from 0 to 1

18



## Precipitation Zone of Sodium Aluminosilicate at 25°C and 0.89 M Hydroxide



- pH higher than ICET tests
- however, dependence of solubility of aluminosilicate is weak at  $\text{pH} < 1\text{M}$
- Relatively low [Si] and [Al] and low weak alkali concentration make sodium aluminosilicate precipitation unlikely

Park, H. and Englezos, P [2001]. Precipitation Conditions of Aluminosilicate Scales in the Recovery Cycle of Kraft Pulp Mills. *Pulp & Paper Canada*, 102, 20.

19



## Aluminosilicate Formation - Conclusions

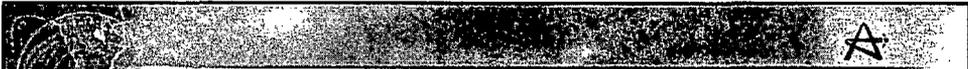
- Based on a review of the effects of pH, temperature, and Al and Si concentrations on the solubility and precipitation of aluminosilicates, it is concluded that:
  - Amorphous phases (which have much higher solubilities than crystalline phases) are generally the precursors in aluminosilicate precipitation
  - Increasing temperature increases the solubility but decreases the induction time
  - High pH increases the solubility but decreases the induction time to precipitate sodium aluminosilicates
  - High supersaturation ratio decreases the induction time for precipitation
  - The relatively low Si and Al concentrations and low alkali concentration means it is unlikely that sodium aluminosilicates would precipitate under sump water conditions

20



## Methodology for Release Calculations

21



## Release Calculations

- Basic methodology outlined in WCAP-16530 used to calculate mass of aluminum released
- Rather than use WCAP-16530 release equation, data from WCAP-16530 and other sources used to develop release equations

22

## Selected Corrosion Rate Data for Aluminum

Solution Composition	Temperature(°C)	Corrosion rate (g/m <sup>2</sup> h)	Reference
0.28 M(3000ppm) B+0.15 M NaOH (3450 ppm Na)	55	0.35-0.61	Griess and Bacarella [1969]
	100	14.0-18.0	
Not described	90	23.9	Nhyogi et al. [1982]
pH =9.2 with NaOH, borated	90	1.45	Pilppo et al [1997]
pH =10 with NaOH, borated		0.012	
Borated alkaline containment water at pH 10	60	0.986	
	90	1.89	Jain et al., [2006]
	110	2.21	
pH 10 with NaOH	60	0.06	ASM [1999]
ICET Test 1 Data	60	0.73	Dallman et al. [2005a]
WCAP-16530 data			Lane et al. [2006]
pH 4	88	0.56	
pH 8	88	2.68	
pH 12	88	60.1	
pH 4	130	5.4	
pH 8	130	23.7	
pH 12	130	200	
WCAP-7153A data			Bell et al. [1975]
pH 7	99	0.078	
pH 8	99	2.2	
pH 9	99	12.96	
pH 10	99	365	

23

## Al Corrosion Data

- pH, temperature and time dependencies of the corrosion rates evaluated separately and then combined at the end
- Allows better comparison with existing literature data on aluminum corrosion

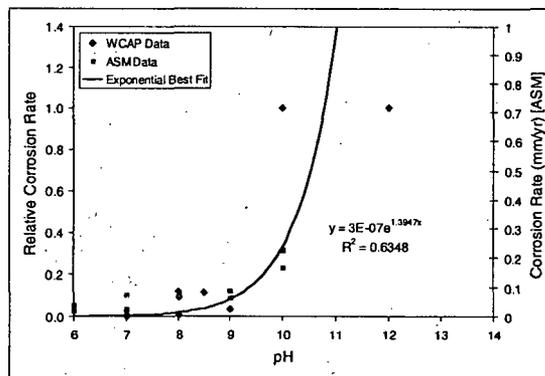
24

## pH Dependence

- Three data sets used to assess pH dependence:
  - ICET data from Tests 1, 3 and 5
  - data from WCAP-16530 at 88°C
  - data from WCAP-16530 at 130°C
- Data normalized such that the largest corrosion rate in each data set was set to unity

25

## pH Dependence



Also shown are data for the pH dependence of the aluminum corrosion rate in non-borated water [ASM, 1999]

26

## pH Dependence

- All data show a similar trend of increasing corrosion as a function of pH
  - similar to that observed in the absence of boric acid
- Increase in corrosion rate mirrors the increase in solubility of aluminum hydroxides

27

## pH Dependence

- Exponential function used to fit the three data sets measured in borated water
- Exponential dependence of Al corrosion rate on pH reported in some studies
  - Shatalov, A.Y. Doklady Akad Naak, 86, 775, 1952.
  - McKee, A.B.; Brown, R.H., Corrosion, 3, 595, 1948.
  - Vujicic, V.; Lovrecek, B., Surf. Technol. 25, 49, 1985.
- Function used to fit the data:

$$\text{Corrosion Rate (pH)} = 3 \times 10^{-7} \cdot \exp(1.3947 \cdot \text{pH})$$

28




## Temperature Dependence

- Similar approach used to develop expression for temperature dependence
- Rates of chemical reactions typically exhibit Arrhenius behavior, e.g.:

$$\text{Corrosion Rate (T)} = A \cdot \exp(-E/k \cdot T)$$

- E = activation energy for the reaction
- A = frequency factor
- T = temperature in K
- k = Boltzmann's constant

- Plot of corrosion rate vs 1/T should show exponential behavior

29




## Temperature Dependence

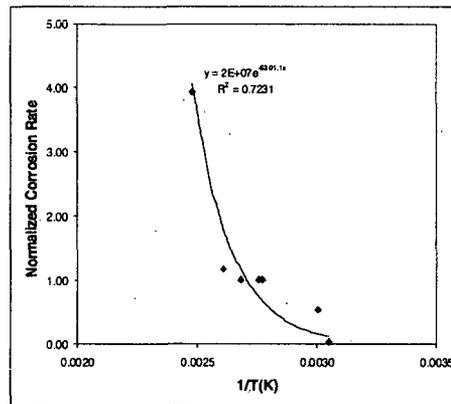
- Data sets with values at more than one temperature plotted as normalized (at 90°C) corrosion rate vs 1/T
  - Reasonable fit observed
- Resulting temperature dependence:

$$\text{Corrosion Rate (T)} = 2 \times 10^7 \cdot \exp(-6301,1 \cdot T^{-1})$$

scaled to pass through average corrosion rate at 90°C

30

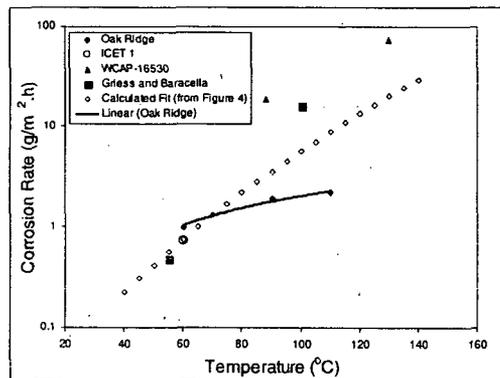
## Temperature Dependence



31

## Final Scaling Corrosion Rate vs Temperature at pH 10

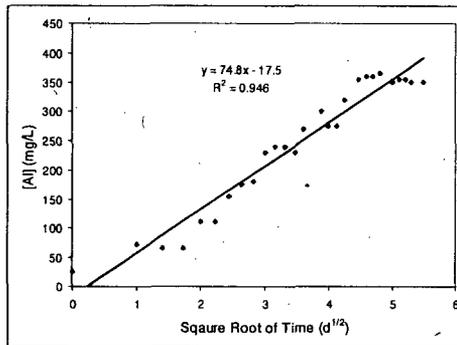
Fit scaled to pass through the average corrosion rate at 90°C.  
Data used in fit plus average corrosion rate from ICET Test 1



32

## Al Release Rate

- Time dependence of Al release rate
  - only the same as the Al corrosion rate if all the Al released by the corrosion process enters the solution



- Corrosion rates often exhibit a parabolic behavior

$$\text{Rate} = a \cdot t^{1/2}$$

- Solid line is a linear least squares fit to the data

33

## Al Release Rate

- Release rate decreases with increasing exposure time
  - Data reasonably well described by:

$$\text{Aluminum Release} = a \cdot t^{1/2}$$

- Differentiating wrt time gives instantaneous Al release rate
  - decreased by a factor of 20 over 30 days
- Using a single value for Al release rate obtained from short duration testing therefore excessively conservative when used to calculate aluminum release over long periods

34



## Inhibitory Effects

- Weight changes of Al coupons in ICET Tests 1 and 4 were significantly different
  - both tests used NaOH to adjust the pH to the same target value (pH = 10); average pH in ICET Test 1 was only 0.4 pH units lower than that in ICET Test 4
- High [Al], which increased with experimental time, was measured in solution in Test 1
  - only trace concentrations of Al present in ICET Test 4 solutions
- Attributed to the presence of silicate species from cal-sil
- Additional experiments by the PWROG confirmed the inhibitory effect of silicates and phosphates on aluminum corrosion

35



## Al Release Calculations - Assumptions

1. Maximum temperatures of sump and spray water used
  2. Maximum pH values used during corrosion calculations
  3. No credit taken for inhibitory effects (silicate, phosphate, etc) on Al corrosion
  4. No credit for presence of pre-existing oxide films on Al surfaces
  5. All Al released by corrosion enters the solution
  6. No credit taken for effect of oxygen in the sump water.
  7. No credit taken for decrease in corrosion rate as a factor of exposure time resulting from development of passive film
- Assumptions build a significant conservatism into Al release calculations
  - Believed that Al release into sump water significantly overestimated (as much as 2-3 orders of magnitude)

36



## Precipitation

37



## Solubility of Aluminium Hydroxide

- “Solubility” refers to the mass of a substance dissolved in a given amount of solvent to form a saturated solution at a given temperature and pressure
- Major factors affect solubility of a substance
  - Temperature – generally, as T increases, solubility increases
  - Solution pH can increase or decrease the solubility
  - Ionic strength increases the solubility
  - Common ions decrease the solubility
- An equilibrium property – the kinetics of formation can be very important in determining the phases that form and the time required for their formation

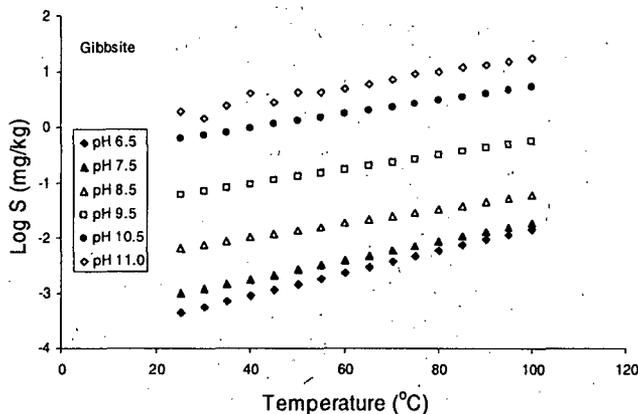
38

## Solubility of Aluminum Hydroxides

- Aluminum can form various hydroxides in weak acidic and alkaline aqueous solutions: gibbsite, boehmite, bayerite and diaspore
  - Solubilities of all of these species are similar
- Gibbsite is the thermodynamically most stable phase and the less stable phases can be transformed to gibbsite
- Amorphous aluminum hydroxide has much higher solubility than crystalline aluminum hydroxides and can form in highly supersaturated aluminum solutions

39

## Solubility of Gibbsite



- Solubility increases with increasing pH and T
- Strong function of pH and weak function of T

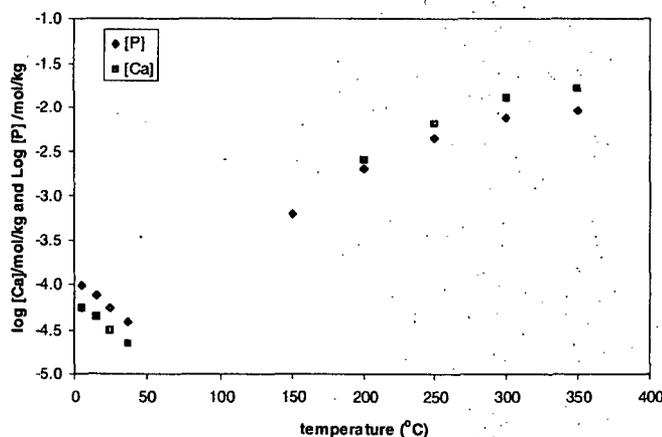
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## Solubility of Calcium Phosphates

- Calcium and phosphate forms various low solubility salts:
  - Hydroxyapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$
  - Whitlockite,  $\beta\text{-Ca}_3(\text{PO}_4)_2$
  - Octacalcium phosphate,  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$
  - Monetite,  $\text{CaHPO}_4$ , and
  - Brushite,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
  - Amorphous calcium phosphate
- Dissolution generally is not congruent (i.e., composition of the solution and solid are different) and accurate solubility data are hard to obtain
- Hydroxyapatite is the least soluble in water above pH 4 and thermodynamically most stable

41

## Solubility of Hydroxyapatite



42



## Detailed Calculations

43



## Calculations

- Information provided by Dominion:
  - Estimated Al surface areas
  - Materials present in containment
  - Post-LOCA temperature evolution of the sump water and containment air or spray water
  - Minimum and maximum pH values for the sump water and spray water at each time interval.
    - To be conservative, the maximum pH value was chosen for the calculation of the aluminum corrosion rates, since the aluminum corrosion rates are higher at higher pH values.
  - Sump water volume

44

## Calculations

- Al corrosion rate at each temperature and pH evaluated using the corrosion data presented earlier:

$$\text{CORROSION RATE (T)} = 9.2 \times 2 \times 10^7 \times \text{EXP}(-6301.1 \times (1/\text{TEMPERATURE (K)}))$$

and

$$\text{CORROSION RATE (pH)} = 3 \times 10^{-7} \times \text{exp}(1.3947 \times \text{pH})$$

- Overall corrosion rate at given temperature and pH calculated using:

$$\text{CORROSION RATE} = \text{CORROSION RATE (T)} \times \text{CORROSION RATE (pH)}$$

45

## Calculations

- Average corrosion rate over time interval calculated assuming a linear change in corrosion rate over interval
- Al release calculated using:

$$\text{Al RELEASE OVER INTERVAL} = \text{CORROSION RATE} \times \text{INTERVAL LENGTH} \times \text{Al SURFACE AREA}$$

- Total Al release over time segment and cumulative Al release since time = 0 also calculated

46



## Bench Top Testing

- Purpose is to confirm the conservative nature of assumptions on precipitate formation
- Tests will be carried out to determine the concentrations at which aluminum hydroxide will precipitate under representative conditions (pH, temperature, ionic strength)
- If required, bench top testing will also be performed to determine the optimum method for preparation of precipitates for reduced scale testing
  - Assess issues related to storage, aging



## Summary

- AECL's chemical effects calculations are based on a thorough assessment of the existing literature
- Based on this assessment, aluminum hydroxide and calcium phosphate were the only possible precipitates considered in this analysis *precipitates*
- While the spreadsheet from WCAP-16530 was not used for the calculations of the concentrations of species released into solution, the methodology developed by AECL is believed to be very conservative
  - A number of conservative assumptions were made during the release calculations

## Conclusions

- AECL chemical effects assessment is consistent with WCAP-16530 but uses more realistic plant operating conditions
- Significant conservatism is maintained in the determination of chemical precipitants as well as in the overall chemical assessment approach
- Confirmatory bench-top testing will be performed to validate assessment results
- Based on bench-top testing results, head-loss testing will be performed if deemed necessary
- Should head-loss testing be required, it would not be completed prior to the 1st quarter of 2008

*criteria -  
no participants  
no head loss study*

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## GSI-191 Chemical Effects Assessment

### Questions?

- Travel Time Arrangements
- reconcile approaches between methodologies

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***Other GSI-191 Topics***

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