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RCB-81-111

1981 March 27

Dr. M. Silberberg  
Nuclear Regulatory Commission  
1717 H Street  
WASHINGTON, D.C.  
U.S.A.

Dear Mel:

I enclose our comments on "Technical Bases for Estimating Fission Product Behavior During LWR Accidents". Owing to the very short time available, I was unable to circulate the draft to a wider range of people and we have therefore restricted our comments to our immediate area of knowledge - iodine chemistry. I have attached our comments on chapter 5. Our own draft document on iodine behaviour has been passed on to the authors of chapter 5.

Once again, thank you for inviting our participation; we expect this to lead to future collaboration with colleagues in U.S. laboratories.

Sincerely yours,

D.F. Torgerson, Head  
Research Chemistry Branch

DFT/mm

Encl.

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## IODINE BEHAVIOR REVIEW

### A. General Comments

1. We are impressed with the thorough job done by the authors on such short notice. We stress that our comments are intended, if possible, to strengthen the document and are not meant to criticize what has been done.
2. If time permits, we would ask the authors to check their predictions against the calculations in the draft AECL-6812 so that errors in either document can be changed as appropriate. If desired, AECL-6812 can be quoted or used to strengthen any of the iodine chemistry arguments.
3. In general, the role of oxidation potential is not addressed sufficiently. The authors have let the iodine reactions considered set the oxidation potential, whereas in the "real" case, the oxidation potential of water will be set by external factors (e.g., the partial pressure of oxygen in the containment building) owing to the low iodine concentrations.
4. There is no indication in the text (i.e., Appendix C) whether the data base used is internally consistent. When doing thermodynamic calculations, this check is important. It was difficult to evaluate the data base owing to the lack of information. However, it would appear that 15 - 20 year old data were used in several cases. Accepted values of Gibbs energies for some iodine species have changed considerably over the past few years and more rigorous values are contained in the CODATA tables. In general, we have found that values taken from text books or general handbooks ought not to be trusted. We refer the authors to Appendix B of AECL-6812.

### B. Specific Comments

Page 14, Paragraph 7

The 2nd line should read "will exist predominantly as the stable ionic ".

Page 5.5

For information, we note that both experiments and calculations in our laboratory indicate that  $I_2$  does not react with water vapor up to  $110^\circ C$ . According to M. Kabat,  $HOI$  (g) may not be stable at  $T > 200^\circ C$ .

### Section 5.3: Aqueous Iodine Chemistry

Page 5.13, Paragraph 2

For information only, it is our understanding that the iodate/iodide ratio depends on depth in the ocean. Near the surface, oxidizing conditions prevail and iodate predominates. At lower depths, iodide becomes more stable owing to the lower oxidation potentials.

Page 5.13, Paragraph 4

pH is a function of temperature; e.g., a neutral solution at  $25^\circ C$  is  $pH = 7$ , but if the neutral solution is heated to  $100^\circ C$ , the pH drops to  $\sim 6.2$ . A more realistic range of pH values under accident conditions allowing for a wide temperature range would be 6 - 11. If the solution is not buffered, or does not contain base, the pH at  $25^\circ C$  could drop to 5.5 owing to absorption of  $CO_2$  from the air.

Page 5.14, Paragraph 2

Re: sum of equilibrium concentrations of iodine species. Other iodine solution species such as  $HIO_3$  (aq) can be more abundant than  $I_2$  (aq) at these low total iodine concentrations depending on conditions. In general, under basic conditions, we find that  $HIO_3$  (aq) exceeds  $I_2$  (aq) in the range  $10^{-9}$  to  $10^{-6}$  mol  $dm^{-3}$  total iodine and  $P_{O_2} = 10^{-6}$  atm. At higher oxidation potentials,  $IO_3^-$  and  $HIO_3$  (aq) are the dominant species. More details are contained in the draft document AECL-6812.

Page 5.15, Paragraphs 1 and 2

The oxidation rate of  $I^-$  is pH-dependent and is only appreciable at very acidic pH's (e.g., 1).

Page 5.16, Paragraph 3 and Table 5.4

Reaction 5.4 - The reaction rate depends on the second power of the HOI concentration, and build up of high HOI concentrations is not likely. Therefore, these high concentrations of HOI are probably very conservative.

Pages 5.19 and 5.20

It should be made clear that the pH's are at the temperatures indicated.

Page 5.22, Paragraph 1

There is a missing line(s).

Page 5.22, Paragraph 5

We suggest a change to "On the other hand, molecular species  $I_2$  and  $CH_3I$  (and possibly HOI) have appreciable vapor pressures.....". This avoids taking a definite stand on HOI which may or may not be significant in nuclear safety.

Page 5.23, Equation 5.7

Again, this equation may not contain all the relevant species in the aqueous phase. Since  $I^-$  and  $IO_3^-$  predominate, this will probably not change the results, but as noted previously, species such as  $HIO_2$  (aq) can be present in greater concentrations than  $I_2$  or HOI under certain conditions.

Page 5.23, Paragraph 2

References to Kabat should be 5.50 and 5.51.

Page 5.23, Paragraph 3, Figures 5.4, 5.5

We have calculated the volatility of HOI to be  $\sim 1/50$  that of  $I_2$  at  $25^\circ\text{C}$  and  $\sim 1/6$  at  $100^\circ\text{C}$ . Our preliminary experiments indicate that these could be upper limits. Therefore, the factor of  $1/2$  is extremely conservative. The partition coefficients also depend on the oxidation potential.

#### Appendix C6

It is stated that there are no known rate studies on reaction C6.3. We refer the authors to (1) Thomas et al., J. Inorg. Nucl. Chem. 42, 183 (1980) and (2) Juznic, Acta Chem. Acad. Sci. Hung. 104, 37 (1980), and to the references contained in these papers.