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Scientific Notebook No. 303: Spent Fuel  
Dissolution Studies (01/21/1999 through  
03/14/2007)

CENTER FOR NUCLEAR WASTE  
REGULATORY ANALYSES



CNWRA  
CONTROLLED  
COPY 303

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CNWRA

x 6084

OPR 01/21/1999

January 13, + 21, 1999

Initial Entry (PRW 3/14/07)

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Title: Spent fuel dissolution studies

Title: ~~TRANSPORT THROUGH DEFECTIVE WASTE PACKAGE~~ 01/21/1999

Oswaldo Pensado

Objective:

Document studies toward the development of spent fuel dissolution models to be incorporated or relevant to the development of the TPA code

Charge numbers: 20.01402.571, 20.01402.761

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OPM

## Secondary task: Validation of formula

Objective: In the module descriptions and user's guide of the TOTAL-SYSTEM PERFORMANCE ASSESSMENT (TPA) VERSION 3.2 CODE, page 4-64,

the following equation is used for the spent fuel dissolution rate:

$$(1) \quad r = r_0 e^{-343/RT} \quad R \text{ in } \text{kJ mol}^{-1} \text{K}^{-1} \quad (4-59)$$

$$r_0 \in [1.4 \times 10^4, 5.5 \times 10^4] \text{ mg m}^{-2} \text{ d}^{-1}$$

The objective of this secondary task is to validate the above formula based on the references given in the document.

[1] Gray, W.J. 1992. Dissolution of spent fuel. Presentation to Nuclear Waste Technical Review Board Meeting, October 14-16, Las Vegas, Nevada. Richland, WA: Pacific Northwest Laboratory

[2] Gray, W.J., H.R. Lesder, S.A. Steward. 1992. Parametric Study of LWR Spent Fuel Dissolution Kinetics. Journal of Nuclear Materials 190: 46-52

[3] Gray, W.J., and C.N. Wilson. 1995. Spent Fuel Dissolution Studies FY 1991 to 1994. PNL-10540. Richland, WA: Pacific Northwest National Laboratory

Statement presumably found in [3]: "In the presence of Si and Ca ions, the dissolution rate decreases about 100 times"

Statement presumably in [1]: "The dissolution rate in the batch tests (under immersion) is about 10 times lower than that in flow-through tests."

Equation [4-59] is presumably developed from data in [3] and [2].

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[3] page 1.3

"Previous dissolution tests with unirradiated  $\text{UO}_2$  (Wilson and Gray 1990a) showed that dissolution rates in dilute  $\text{NaHCO}_3$  solution were greatly depressed when Si was added as dissolved silicic acid. Dissolved Ca also depressed the dissolution rate, but appeared to have less effect than Si."

The reference cited is

Wilson, C.N., and W.J. Gray. 1990. "Effects of Water Composition on the Dissolution Rate of  $\text{UO}_2$  under oxidizing conditions." In High Level Radioactive Waste Management, Vol. 2, pp. 1431-1436 American Nuclear Society, Inc., La Grange Park, Illinois.

Page 4.12

The dissolution rates under high-flow-rate conditions are not much higher (factor of 10 or less) than those reported near-static conditions, which are more representative of expected repository conditions.

Page 4.13

Wilson and Gray (1990b) showed that the addition of Si and Ca to bicarbonate solution could reduce the dissolution rate of unirradiated  $\text{UO}_2$  up to at least 100 times.

References:

Wilson C.N., and W.J. Gray. 1990b. "Measurement of Soluble Muclide Dissolution Rates from Spent Fuel." Sci. Basis for Nuclear Waste Management XIV, Vol. 176 eds. V.M. Oversky and P.W. Brown, p.p. 489-498. Materials Research Society, Pittsburgh Pennsylvania

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Page 4.3, equation (4.1)

$$\log R = 9.310 + 0.142 \log [CO_2] - 16.7 \log P_{O_2} + 0.140 \log [H] - 2130/T + 6.81 \log T \cdot \log P_{O_2}$$

$$[CO_2] \sim M$$

$$P_{O_2} \sim O_2 \text{ overpressure in atm}$$

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$$R = 10^{9.31} [CO_2]^{0.142} P_{O_2}^{-16.7} [H]^{0.14} 10^{-2130/T} (T P_{O_2})^{6.81}$$

$$R = 2.042 \times 10^9 [CO_2]^{0.142} T^{6.81} P_{O_2}^{-16.7} [H]^{0.14} e^{-2130/T}$$

$$\frac{\ln 10 \cdot 2130}{T} = \frac{40777.73 \text{ J mol}^{-1} \text{ K}^{-1}}{RT} \quad R = 8.31434 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$R = 2.042 \times 10^9 [CO_2]^{0.142} T^{6.81} P_{O_2}^{-9.89} [H]^{0.14} e^{-\frac{40777.73}{RT}}$$

Assume  $T = 298.15 \text{ K}$

$$R = 2.042 \times 10^9 \times 7.0942 \times 10^{16} \times 7.177 \times 10^{-8} [CO_2]^{0.142} P_{O_2}^{-9.89} [H]^{0.14}$$

$$R = 1.039 \times 10^{19} [CO_2]^{0.142} P_{O_2}^{-9.89} [H]^{0.14}$$

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$$R = 10^{9.31} [CO_2]^{0.142} P_{O_2}^{-16.7} [H]^{0.14} 10^{-2130/T} 10^{6.81 \log T \log P_{O_2}}$$

$$R = 10^{9.31} (6.457 \times 10^6)^{\log T \log P_{O_2}} [CO_2]^{0.142} P_{O_2}^{-16.7} [H]^{0.14} 10^{-2130/T}$$

$$10^{-2130/T} = e^{-\frac{40777.73 \text{ J mol}^{-1} \text{ K}^{-1}}{RT}} \quad R = 8.31434 \text{ J mol}^{-1} \text{ K}^{-1}$$

Assume  $T = 298$

$$R = 10^{9.31} (70.7 \times 10^{15})^{\log P_{O_2}} [CO_2]^{0.142} P_{O_2}^{-16.7} [H]^{0.14} 7.11 \times 10^{-8}$$

$$R = 145.33 (70.7 \times 10^{15})^{\log P_{O_2}} [CO_2]^{0.142} P_{O_2}^{-16.7} [H]^{0.14}$$

$$\text{If } P_{O_2} \rightarrow 0, R \rightarrow 0$$

$$\text{If } P_{O_2} \rightarrow 1, R \rightarrow 145.33 [CO_2]^{0.142} [H]^{0.14}$$

Figures A.71 and A.72 indeed show that Ca and Si containing substances decrease the dissolution rate.

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### High Level Radioactive Waste Management

Vol 2, pp. 1431 - 1436

American Nuclear Society Inc. La Grange Park, Illinois

Gives evidence that Si and Ca effectively reduce the rate of  $UO_2$  dissolution. No measurement of mass fluxes is made, since no measurement of surfaces is made.

Going back to the analysis of  $r = r_0 e^{-34.3/RT}$

$$r_0 \in [1.4 \times 10^4, 5.5 \times 10^4] \text{ mg m}^{-2} \text{ d}^{-1}$$

at 298K  $r = r_0 \times 9.7 \times 10^{-7} \approx 10^{-6} r_0$

$$r \in [1.4 \times 10^{-2}, 5.5 \times 10^{-2}] \text{ mg m}^{-2} \text{ d}^{-1}$$

at 358  $r = r_0 \times 9.9 \times 10^{-6} \approx 10^{-5} r_0$

$$r \in [1.4 \times 10^{-1}, 5.5 \times 10^{-1}] \text{ mg m}^{-2} \text{ d}^{-1}$$

The above rates of dissolution are quite small. They can be accomplished only if the  $P_{O_2}$  (overpressure) is lesser than  $10^{-6}$  atm.

See figure A.64 in Spent Fuel Dissolution Studies FY 1991 to 1994

PNL-10540 UC-802, W.J. Gray and C.N. Wilson.

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### Measurement of Soluble Nuclide Dissolution Rates from Spent Fuel

C.N. Wilson and W.J. Gray

Mat. Res. Soc. Symp. Proc. Vol. 176, 1990 Materials Research Society

It shows that Si and Ca have an important effect on dissolution rates; however, no correlation between rate and temperature is provided.

Tao M. Ahn presentation at Workshop on Alternative Models and Interpretations for the Waste Form Degradation and Radionuclide Mobilization Expert Elicitation (WFFEE) Project. December 15-16, 1997. San Francisco CA

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Gives reference to

Zwahlen diffusion models for release through pin holes [Zwahlen, et al, 1980]

$$f = \pi r^2 D / (l V)$$

f: fractional release

r: radius of a single equivalent hole

l: length of a single equivalent hole

D: diffusivity

V: volume

Observed dissolution rate of primary phase of spent fuel

at 25°C / 9 mg/m<sup>2</sup>-d in J-13 well water  
72 mg/m<sup>2</sup>-d in carbonate water

at 90°C / 77 mg/m<sup>2</sup>-d in J-13 well water

Assume  $r = r_0 e^{-\frac{B}{T}}$

$$9 = r_0 e^{-\frac{B}{298}}$$

$$r_0 = \frac{9}{e^{-\frac{B}{298}}}$$

$$77 = \left( \frac{9}{e^{-\frac{B}{298}}} \right) e^{-\frac{B}{363}} = 9 e^{-\left(\frac{B}{363} - \frac{B}{298}\right)} = 9 e^{-B\left(\frac{1}{363} - \frac{1}{298}\right)}$$

$$\frac{77}{9} = e^{B\left(\frac{1}{298} - \frac{1}{363}\right)} \Rightarrow B = \frac{1}{\frac{1}{298} - \frac{1}{363}} \ln\left(\frac{77}{9}\right) = 3572.3728$$

$$r = r_0 e^{-\frac{3572.37}{T}}$$

$$r_0 = \frac{9}{e^{-\frac{3572.37}{298}}} = 1.5 \times 10^6$$

$$\text{Activation energy} = 3572.37 \times R = 29701.9 \text{ J mol}^{-1}$$

This activation energy coincides with some other reported elsewhere. For example

in W. J. Gray, H. R. Linder and S. A. Steward, Parametric Study of LWR spent fuel dissolution kinetics, Journal of Nuclear Materials

190 (1992) 46-52, North Holland, the following correlation is provided:

(cont P. 7)

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$$\log R_1 = 7.45 + 0.258 \log [C] + 0.142 \log [H^+] - 1550/T$$

The activation energy is found as

$$10^{-1550/T} = e^{-\log_{10} 10 \frac{1550}{T}} = e^{-\frac{29.673}{RT}} \approx e^{-\frac{29673 \text{ J mol}^{-1}}{RT}}$$

The activation energies are comparable.

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Spent Fuel Dissolution Studies FY 1991 to 1994

W. J. Gray and C. N. Nilson

Composition of J-13 Well Water, Table 2.4

Ca 13 mg/L  $\approx 3.2 \times 10^{-4} \text{ M}$

Si 30 mg/L

HCO<sub>3</sub> 126 mg/L

pH 8.4

Figure A.42 shows that the average dissolution rate is of the order of 2.5 mg m<sup>2</sup> d<sup>-1</sup>, U<sub>2</sub> = 0.2 atm, T = 22°C, Series-3 Archive

Specimen  $\rightarrow$  spent fuel stored for 4 years

Figure A.71, Solution composition (designated as BCS in Table 3.2)

Ca 10 mg/L

Si 32 mg/L

HCO<sub>3</sub> 102 mg/L

pH 8.4  $\pm$  0.2

Figure A.71, Average dissolution rate: 0.06 mg m<sup>2</sup> d<sup>-1</sup> (BCS composition)

Figure A.72, Average dissolution rate: 0.01 mg m<sup>2</sup> d<sup>-1</sup> (BCS composition)

We believe that such tests were carried out at room temperature and

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at 0.2 atm of O<sub>2</sub>.

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Table 3.1: Test #2, T = 25°C [CO<sub>3</sub>] = 2 x 10<sup>-3</sup> P<sub>O<sub>2</sub></sub> = 20%

pH = 10 U Diss Rate = 2.42 mg m<sup>-2</sup> d<sup>-1</sup>

Figure A.20 summarizes results for this test.

Comments: The experiments whose results are summarized as Figures A.20 and A.42 were carried out under similar conditions (room temperature, 20% P<sub>O<sub>2</sub></sub>, similar [CO<sub>3</sub>]) and both rates are of the order of 2.4 mg m<sup>-2</sup> d<sup>-1</sup> ± 0.1

Note that J-13 contains Ca and Si in comparable amount as the experiment whose results are displayed in Figures A.71 and A.72. However the U dissolution rates with J-13 as solution (Figure A.42) are two orders of magnitude larger than those in Figures A.71 and A.72 (2.5 mg m<sup>-2</sup> d<sup>-1</sup> versus 0.01-0.06 mg m<sup>-2</sup> d<sup>-1</sup>). It must be acknowledged that the testing fuel in both experiments did not have the same history, and this may be a reason for the variation.

Page 4.3, equation (4.1)

$$R = 10^{9.31} (6.457 \times 10^6)^{\log T \log P_{O_2}} [CO_3]^{0.142} P_{O_2}^{-16.7} [H^+]^{0.14} 10^{-2150/T}$$

Assume T = 298 K, P<sub>O<sub>2</sub></sub> = 0.2, [H<sup>+</sup>] = 10<sup>-8.4</sup>, [CO<sub>3</sub>] = 2 x 10<sup>-3</sup>

$$R = 3.152 \text{ mg m}^{-2} \text{ d}^{-1}$$

which is quite comparable to 2.4 mg m<sup>-2</sup> d<sup>-1</sup> found experimentally.

On the other hand, using Equation (1) in W.J. Gray et al. Journal of Nuclear Materials 170 (1992) 46-52, North-Holland

$$\log_{10} R_1 = 7.45 + 0.258 \log [CO_3] + 0.142 \log [H^+] - 1550/T$$

one obtains R<sub>1</sub> = 2.288 mg m<sup>-2</sup> d<sup>-1</sup> which is closer to the experimental

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value.

Conclusions:

The experiment associated with Figure A.42 is not consistent with the notion that Ca and Si reduce the rate of dissolution. It must be acknowledged, however, that the fuel sample has been stored for 4 years before the test. A different sample history may be associated with a variation in the dissolution rate.

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The average dissolution rate (at BCS composition) in Figure A.71 is 0.06 mg m<sup>-2</sup> d<sup>-1</sup> (roughly). The average dissolution rate at BCS composition in Figure A.72 is roughly 0.01 mg m<sup>-2</sup> d<sup>-1</sup>.

The formula  $r = k_0 e^{-34.3/RT}$ ,  $1.4 \times 10^4 < k_0 < 5.5 \times 10^4$  predicts  $1.4 \times 10^{-2} < r < 5.5 \times 10^{-2} \text{ mg m}^{-2} \text{ d}^{-1}$ , which is consistent with the average dissolution values in Figures A.71 and A.72.

We have not found data at a different temperature, with solutions including Ca and Si, allowing for the validation of Equation (4-59).

Equation (4-59) does not reflect the P<sub>O<sub>2</sub></sub> nor [H<sup>+</sup>] dependence of the SF dissolution rate. The hypotheses behind its derivation must be clearly stated.

Figure A.31 shows that oxidized spent fuel dissolves faster than unoxidized SF, for more than a factor of 100.

2/25/99

OPJ

Teleconference with Tae Anh

$$r = r_0 e^{-\frac{34.3 \text{ kJ/mol}}{RT}} \quad (1)$$

Anh says there has been some consensus around.

The model seems to apply to a bathtub situation.

Tae said that he used a factor (arbitrary) of 1/100 in one collection of data.

Tae stated that he can't support the activation energy of 34.3 kJ/mol! Limited database to support it.

Gustavo requested to state clearly the steps taken to deduct an equation such as equation (1).

Chemistry of the environment → needs to be defined. Corrosion products must be taken into account → suggested by Gustavo.

Tae Anh says that Equation (1) depends only on the temperature because of the limited database. However, equation (1) was explained to be consistent with the database! The activation energy seems to have developed by "Model 1," which is the model that shows dependence on pH,  $P_{O_2}$ .

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OPJ

Comments sent to Tae Anh on 01/28/1999

#### TOTAL-SYSTEM PERFORMANCE ASSESSMENT (TPA) VERSION 3.2 CODE: MODULE DESCRIPTIONS AND USER'S GUIDE

On page 4-64 it is mentioned that the spent fuel (SF) dissolution rate ( $\text{mg m}^{-2} \text{d}^{-1}$ ) can be described by

$$r = r_0 e^{-\frac{34.3 \text{ kJ/mol}}{RT}} \quad (4-59)$$

where  $1.4 \times 10^4 \text{ mg m}^{-2} \text{d}^{-1} < r_0 < 5.5 \times 10^4 \text{ mg m}^{-2} \text{d}^{-1}$  and  $R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1}$ . It is argued that Equation (4-59) takes into account the fact that SF dissolution rates are greatly decreased by the presence of Si and Ca. Gray and Wilson provided experimental evidence supporting this effect of Si and Ca.<sup>1</sup> On the other hand, Gray and Wilson have shown that there exists a strong dependence between the SF dissolution rate, the oxygen overpressure, and pH, which is not included in Equation (4-59). The hypotheses to derive Equation (4-59) and the range for  $r_0$  must be clearly stated.

Equation (4.1) in Reference 1 [Defined as Equation (4-58) in the TPA Version 3.2 Code] has an activation energy of  $41 \text{ kJ mol}^{-1}$ . Gray et al.<sup>2</sup> published a different correlation [Equation (1) in Reference 2] with an activation energy of  $30 \text{ kJ/mol}$ . The activation energy in Equation (4-59) lies between these two values, but it is not clear how it was obtained. The method must be explained.

We found that dissolution rates computed with Equation (4-59) are reasonable if extra assumptions are made. For example, the experiments summarized as Figures A.71 and A.72 in Reference 1 indicate average dissolution rates of  $0.06$  and  $0.01 \text{ mg m}^{-2} \text{d}^{-1}$ , respectively, for solutions containing  $10 \text{ mg/L}$  of Ca,  $32 \text{ mg/L}$  of Si,  $102 \text{ mg/L}$  of  $\text{HCO}_3$ , and pH 8.4. We presume that these experiments were carried out at room temperature with an oxygen pressure of  $0.2 \text{ atm}$ . Substitution of  $T = 295 \text{ K}$  in Equation (4-59) yields

$$1.18 \times 10^{-2} \text{ mg m}^{-2} \text{d}^{-1} < r < 4.65 \times 10^{-2} \text{ mg m}^{-2} \text{d}^{-1}$$

which is comparable with the average dissolution rates in Figures A.71 and A.72, in solutions containing Ca and Si. No other experimental data were found allowing for additional validation of Equation (4-59).

Figure A.42 in Reference 1 indicates that the average SF dissolution rate in J-13 well water is roughly  $2.5 \text{ mg m}^{-2} \text{d}^{-1}$ . According to Table 2.4 in Reference 1, the J-13 well water used in the test contained  $13 \text{ mg/L}$  of Ca,  $30 \text{ mg/L}$  of Si and  $126 \text{ mg/L}$  of  $\text{HCO}_3$ , with pH 8.4. Therefore, the experimental conditions are comparable with those described above, but the dissolution rates differ by two orders of magnitude. A possible reason may be the different fuels used for testing (in the case of the J-13 well water test, the SF was stored 4 years before testing). Nonetheless, these data needs to be reconciled with Equation (4-59). The test with J-13 well water does not support the statement that the presence Ca and Si reduces the dissolution rate by two orders of magnitude. For example, the average dissolution rate of Test 9 (Figure A.20 in Reference 1) is  $2.42 \text{ mg m}^{-2} \text{d}^{-1}$ . The  $\text{CO}_3$  concentration, oxygen overpressure, and temperature ( $2 \times 10^{-3} \text{ M}$ ,  $0.2$

<sup>1</sup> Gray, W. J., and Wilson, C. N. 1995. Spent Fuel Dissolution Studies FY 1991 to 1994. PNL-10540. Richland, WA: Pacific Northwest National Laboratory.

<sup>2</sup> Gray, W. J., Leider, H. R., and Steward, S. A. Journal of Nuclear Materials 190 (1992) 46-52 North Holland.



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QFJ

Continuation from page 11

QFJ

atm, and 295 K, respectively) were comparable to those of the J-13 well water test. The tests differed in the pH (8.4 versus 10) and the content of Si and Ca. The average dissolution rates are similar, raising the issue of whether or not Si and Ca content is relevant. These rates are consistent with rates computed via Equation (4.1) in Reference 1 and Equation (1) in Reference 2 (see Table below). These equations presume that Si and Ca are not present in the solution. Additional experimental support of the effect of Ca and Si on the SF dissolution rate is necessary to justify a rate expression such as Equation (4-59).

pH	SF dissolution rate Equation (4.1), Reference 1 mg m <sup>-2</sup> d <sup>-1</sup>	SF dissolution rate Equation (1), Reference 2 mg m <sup>-2</sup> d <sup>-1</sup>
8.4	2.8	2.03
10	1.67	1.2

T = 295 K, [CO<sub>3</sub>] = 2 × 10<sup>-3</sup> M, P<sub>O<sub>2</sub></sub> = 0.2 atm.

QFJ

6/18/99

QFJ

Tae Ahn forwarded the following answer concerning the activation energy.

From the paper

W.J. Gray, H.R. Leider, and S.A. Steward, Parametric Study of LWR spent fuel dissolution kinetics, *J. of Nuclear Materials*, Vol 190 (1992) p. 46-52

In Table 2 it is seen that by changing the temperature from 23 °C to 75 °C the dissolution rate changes by a factor of 3. Ahn proposed, as an upper bound (conservative approach) that by changing the temperature from 23 °C to 85 °C the dissolution rate changes, at most, by a factor of 10. This is just a conservative approach. Thus, the activation energy can be computed as

$$r = r_0 e^{-\frac{\Delta E}{RT}}$$

$$r(298) = r_0 e^{-\frac{\Delta E}{R(298)}}$$

$$r(358) = r_0 e^{-\frac{\Delta E}{R(358)}} = 10 r_0 e^{-\frac{\Delta E}{R(298)}}$$

$$e^{-\frac{\Delta E}{R} \left( \frac{1}{358} - \frac{1}{298} \right)} = 10$$

$$-\frac{\Delta E}{R} \left( \frac{1}{358} - \frac{1}{298} \right) = \ln 10$$

$$\Delta E = \frac{R \ln 10}{\frac{1}{298} - \frac{1}{358}} = 34040 \text{ J mol}^{-1} = 34 \text{ kJ mol}^{-1}$$

This activation energy is consistent with other literature data, as explained in page 11.

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Reference: Waste Management, Vol. 14, No. 5, pp 393-408 (1994)

Tae M. Ahn, Long-term  $C14$  Source Term for a High-level Waste Repository.

On the b-note for TABLE 3, p. 402, the following is said:

"Approximately 3.4 and 21.3 times the dissolution rates increased by raising temperature from 23-75°C in  $2 \times 10^{-2}$  and  $2 \times 10^{-4}$  M carbonate/bicarbonate solutions, respectively, without minor pH corrections."

The factor 10 in page 13 lies between 3.4 and 21.3.

It is a representative factor, but it is not conservative.

The author reports, under the "Flow-through Tests" column, on

Table 3:

$$\text{Uranium} \rightarrow (0.3 \sim 1.2) \times 10^{-6} \text{ g/day}$$

$$(0.3 \sim 1.2) \times 10^{-3} \text{ mg d}^{-1}$$

According to the a) note, the above rate corresponds to a surface area of  $205 \text{ cm}^2 = 2.05 \times 10^{-2} \text{ m}^2$ . Thus, the dissolution

$$\text{flux is } J_{\text{uranium}} \rightarrow (0.3 \sim 1.2) \times 4.88 \times 10^{-2} \text{ mg d}^{-1} \text{ m}^{-2}$$

$$J_{\text{U}} \rightarrow (1.5 \sim 5.86) \times 10^{-2} \text{ mg d}^{-1} \text{ m}^{-2}$$

It is claimed that the above dissolution flux range was

reported in: Gray, W.J. Dissolution testings of spent fuel.

Presentation to Nuclear Waste Technical Review Board Meeting

Pacific Northwest Laboratory, October 14-16, Las Vegas NV (1992)

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I have reviewed this Gray's reference, and the fluxes there reported are much higher than  $5.9 \times 10^{-2} \text{ mg d}^{-1} \text{ m}^{-2}$ . Dissolution fluxes of the order of  $10 \text{ mg m}^{-2} \text{ d}^{-1}$  were reported in Gray's presentation.

The steady-state fluxes are usually of the order of  $1 \text{ mg m}^{-2} \text{ d}^{-1}$ .

The rates (or fluxes) reported by Gray in his presentation correspond to experiments performed in carbonate/bicarbonate solutions. Experiments including Ca or Si to measure dissolution fluxes were not carried out. Gray reported an experiment where it was suggested that the addition of Ca and/or Si reduces the U concentration in the solution. One may conclude that the dissolution flux is reduced by the presence of Ca/Si. Since the U concentration is decreased by a factor of roughly 100, apparently T. Ahn concluded that the dissolution flux must be reduced by a factor of  $\sim 100$ .

If the dissolution fluxes in Ahn's paper are multiplied by 100 one gets:  $(1.5 \sim 5.86) \text{ mg d}^{-1} \text{ m}^{-2}$

This range is consistent with the data presented by Gray at the Technical Review Board Meeting.

Assuming T. Ahn is right, and that the results in Gray's presentation are at 25°C, then

$$r = (1.5 \sim 5.86) \times 10^{-2} \text{ mg d}^{-1} \text{ m}^{-2} = r_0 e^{-\frac{34040 \text{ J mol}^{-1}}{R(298 \text{ K})}}$$

$$\text{then } r_0 = (1.5 \sim 5.86) \times 10^{-2} \times 923061 \text{ mg m}^{-2} \text{ d}^{-1}$$

$$r_0 = (1.4 \sim 5.5) \times 10^4 \text{ mg m}^{-2} \text{ d}^{-1}$$

This is exactly the range reported in the TPA Code 3.2 User's Manual

6/23/99 APY

In summary  
the activation energy, suggested by T. Ahn, of  
 $-84.3 \text{ kJ mol}^{-1}$

is reasonable. It is consistent with results by Gray. It was derived by assuming that the dissolution rate increases by a factor of 10 when the temperature changes from  $25^\circ\text{C}$  to  $85^\circ\text{C}$ . This factor is a conservative estimate based on the 1992 Gray's paper in the Journal of Nuclear Materials. However, in T. Ahn's 1994 paper (Waste Management), dissolution rates in  $2 \times 10^{-4} \text{ M}$  carbonate/bicarbonate solutions are reported to increase by a factor of 21.3 when the temperature changes from  $23^\circ\text{C}$  to  $75^\circ\text{C}$ . Apparently this is reported in the Gray's paper mentioned above.

With respect to the TPA formula  $r = r_0 e^{\frac{-84.3 \times 10^3 \text{ J mol}^{-1}}{RT}}$   
and the range  $1.4 \times 10^4 \text{ mg m}^{-2} \text{ d}^{-1} \leq r_0 \leq 5.5 \times 10^4 \text{ mg m}^{-2} \text{ d}^{-1}$   
(reported in the TPA code 3.2 user's manual), the range in  $r_0$  seems to have been deduced from data presented by Gray in the 1992 NWTRB Meeting, but scaled by an arbitrary factor of  $\frac{1}{100}$ . The  $\frac{1}{100}$  factor was proposed by T. Ahn to account for the effect of Ca and Si on the dissolution rate.

It is important to mention that although the experimental data suggests that Ca and Si affect the dissolution rate, the results are non-conclusive. Second, the experimental data presented by Gray was not necessarily comprehensive.

9/22/99

APY

Effects of Water Composition on the Dissolution Rate of  $\text{UO}_2$   
under oxidizing conditions

C.N. Wilson and W.J. Gray

High Level Radioactive Waste Management

Vol. 2, pp. 1431-1436

American Nuclear Society, Inc. La Grange Park, Illinois

- Ca and Si seem to decrease the dissolution rate
- Authors suggest that this is due to precipitated Ca and Si products on the surface that act as kinetic barriers.
- Ca and Si are not solubility limiting phases - assumed by authors
- Flow-through experiments
- Unirradiated  $\text{UO}_2$

Actinide-bearing Secondary phases have low solubility  $\rightarrow$  U, Pu, Np and Am are solubility-controlled.

long-lived soluble radionuclides  $\rightarrow$   $^{99}\text{Tc}$ ,  $^{135}\text{Cs}$ ,  $^{14}\text{C}$  and  $^{129}\text{I}$   
 $\rightarrow$  controlled by the degradation and dissolution rates of the fuel.

In static experiments, it reached a steady-state concentration of 700 ng/ml of J-13 water.

Decrease in the  $\text{U}$  concentration by the addition of Ca and Si to  $\text{NaHCO}_3$  solutions are interpreted by postulating the presence of a layer of Ca and Si on the spent fuel, thus decreasing its dissolution rate. However, the layer of Ca and Si is present in deionized water, but the dissolution rates are quite high. Therefore, the Ca and Si



9/22/99

QF1

is not always protective. The authors believe that Ca and Si does not have any impact on the U solubility, but they do not give convincing arguments.

I do believe that the solubility problem is worthwhile to be investigated. <sup>For OPR</sup> ~~For~~ example, the increase in the concentration when using deionized water, may be attributed to an increase in the solubility.

Delivered to QA records on 5/9/00

4/2/2001

QF2

A paper has been submitted for presentation to the American Ceramic Society. Authors: Yi-Ming Pan, Vijay Jain, and Osvaldo Pensado. Title: Dissolution Kinetics of High-Level Waste Glasses and Application to Performance Assessment Studies.

To be submitted for publication in the Ceramic Transactions for the Symposium on Waste Management Science and Technology in the Ceramic and Nuclear Industries (paper B4C-02-2001)

Annual Meeting of the American Ceramic Society. Indianapolis, Indiana April 22-25, 2001.

The paper includes computations of the TPA code. The TPA code was modified by incorporation of an equation for glass dissolution. Modifications were implemented into the module release.f. The modifications were tested and compared to computations done in excel. One-hundred percent agreement was achieved, and it was considered that modifications to release.f were verified.

Yi-Ming Pan recorded his experimental data in Scientific Notebook 3/4.

All analyses are recorded in "readme" files in the attached electronic files. The objective of the computations is explained in the draft paper, also available in electronic form.

4/2/2001 *OPJ*

Computations <sup>and plots</sup> are documented in the file plots2.xls.  
The support mathematica file comp.nb is also provided.

Parameters, inventories, and appropriate references are available in the file Inventory.xls.

All <sup>TPA</sup> computations were completed in Vulcan. Relevant input and output files are attached in electronic form in the file Vulcan.zip

The modified versions of the TPA code are available in the files TPA41eGlass.zip and TPA2Glass2.zip.

The former file has implemented the glass dissolution rate equation adopted by the DOE, and parameters consistent with Si and B release observations. TPA2Glass2.zip contains parameters suggested by Yi-Ming Pan and his experiments. "Readme" files in the zip files contain more details.

4/2/2001 *OPJ*

4/3/2001

Turned in to QA records on 4/3/2001  
Here are the contents of the attached CD

*OPJ*

Name	Size	Type	Modified	Attributes
Abstract Submission 111300.txt	1KB	TXT File	3/16/01 10:28 AM	A
acers paper B4C-02-2001.wpd	685KB	Corel Word...	4/3/01 3:36 PM	A
ACSabstract_2001.wpd	7KB	Corel Word...	11/6/00 11:55 AM	A
bc41e.zip	7,583KB	WinZip File	4/2/01 9:43 AM	A
comp.nb	50KB	Mathematic...	4/2/01 9:33 AM	A
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DeltaT.txt	9KB	TXT File	2/8/01 4:01 PM	A
GlassDissolution.wpd	36KB	Corel Word...	4/3/01 10:06 AM	A
GlassPlots.doc	77KB	Microsoft W...	3/22/01 9:06 PM	A
HandComp.xls	415KB	Microsoft E...	4/2/01 10:09 AM	A
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nuclides.dat.xls	53KB	Microsoft E...	2/16/01 5:30 PM	A
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Vulcan.zip	5,596KB	WinZip File	4/2/01 9:43 AM	A
Yi-Ming glass dissolution parameters_rev1...	68KB	Corel Word...	3/7/01 6:14 PM	A
Yi-Ming Revised glass dissolution paramet...	1KB	TXT File	3/2/01 10:04 AM	A

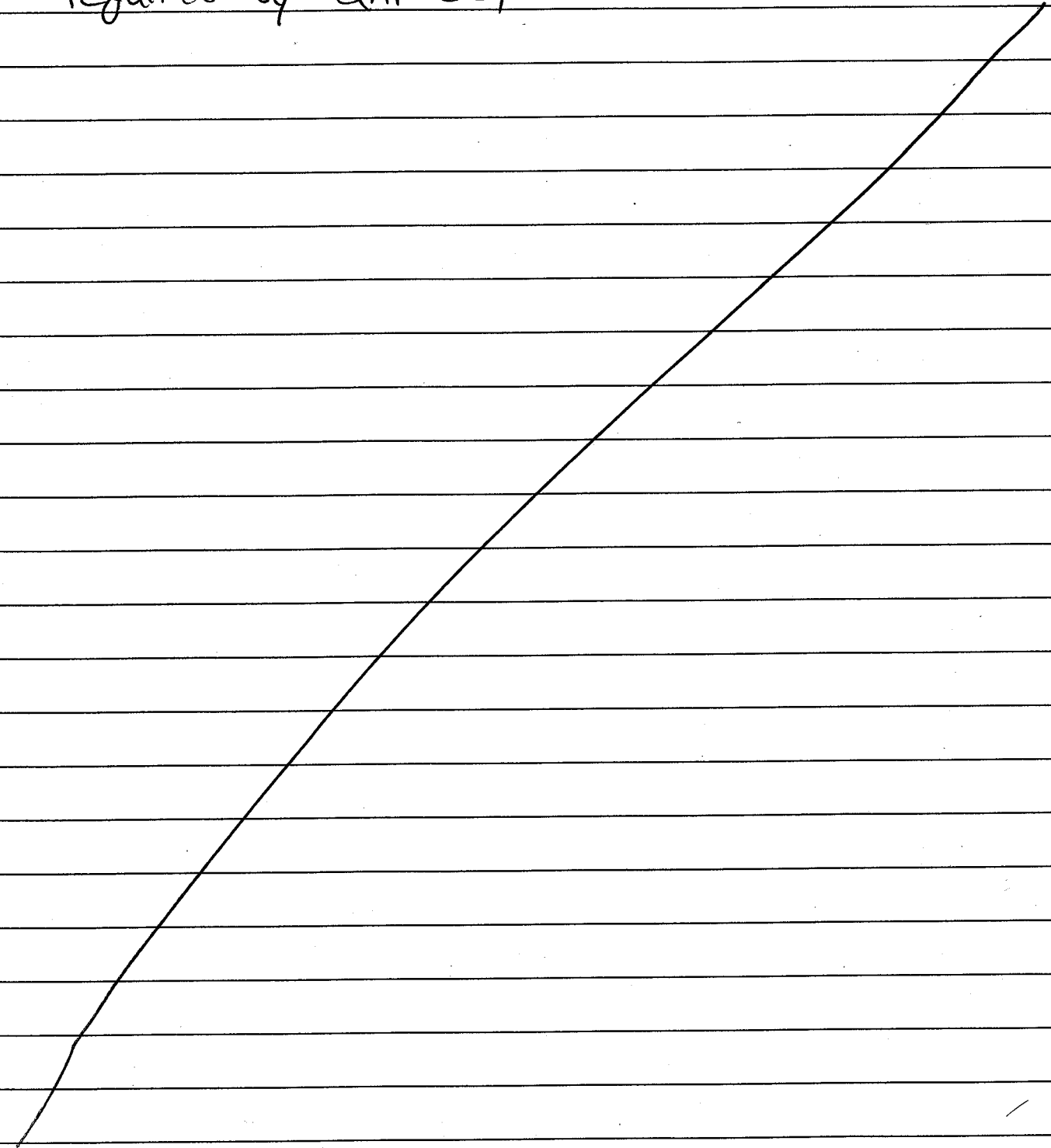
*OPJ*

Submitted to QA records on 4/3/2001

3/14/2007

Manager Review per QAP-001, conducted by James Winterle, 3/14/2007 JRW  
manager, PA Group.

- Contrary to statement on preceding page, this notebook was submitted for records on 9/28/2006
- see following two pages for review check lists required by QAP-001



### GEOSCIENCES AND ENGINEERING DIVISION

JRW

#### SCIENTIFIC NOTEBOOK REVIEW CHECKLIST RECORD

Scientific Notebook No.: 303 Project Numbers: 06002.01.352

Accomplished

- JRW 1. Initial entries per QAP-001
- JRW 2. Dating of entries
- JRW 3. Corrections (crossed out, one line through w/initials/date)
- JRW 4. No White out used
- JRW 5. Page number visible on copy or original notebook
- JRW 6. In process entries per QAP-001
- JRW 7. Figure information present
- JRW 8. Text readable
- JRW 9. Copyrighted material is identified N/A
- JRW 10. Permanent ink or type only
- JRW 11. Signing of entries (not required on each page)
- JRW 12. Electronic media in the scientific notebook properly labeled N/A
- JRW 13. NRC Supplementary Scientific Notebook Questions are addressed. see following page

Any discrepancies must be resolved before notebook closeout.

I have reviewed this scientific notebook and find it in agreement with QAP-001.

JRW  
Manager's Signature

3/14/07  
Date

Attach this completed form to the last page of the notebook.