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Abstract

The pH calculations of Polestar Applied Technology for containment water in the Perry Plant were evaluated at Oak Ridge National Laboratory (ORNL) by both calculated and measured values. The technique used in the pH calculations by Polestar should not be used at higher borate concentrations without modifications to include additional borate species.

1. Introduction

This evaluation is based on material transmitted by Stephen LaVie, of the Nuclear Regulatory Commission (NRC) staff, on July 9, 1998. The information is a calculation that was carried out by Polestar to determine pH values for the Perry containment water pool. It consists of a set of assumptions and four types of calculations related to pH. The information for each of the four types of calculations is presented in the form of a brief description of what is being calculated, the assumptions used in the calculation, and a table of calculated values. In one case, the table headings are not labeled so it was difficult to discern what was listed.

One important assumption not listed is that the water pool is well mixed so that fission products, radiolysis products, and pH control chemicals are at equilibrium and uniform throughout. Also, the means and timing for introducing the pH control chemical are not given.

2. Evaluation of Calculational Techniques

A) Calculation of OH^- or H^+ in Water Pool as a Function of Time

These calculations combined the formation of nitric acid, HNO_3, with fission product cesium. It was assumed that 90% of the cesium was in the form of cesium hydroxide. The radiolysis model referenced another Polestar report, but was not given in this calculation. The pH was not calculated

in this part of the analysis, but a table indicated that the water pool became acidic between 10 and 20 days after accident initiation, based on fission product cesium and HNO_3 alone. It should be noted that the technique employed in the calculation involved negative concentrations. In some cases this technique can give correct numerical values, but it obviously has no physical reality. An independent evaluation of HNO_3 production is provided in Section 4.

B) Calculation of HCl in Water Pool as a Function of Time

The concentration of hydrochloric acid, HCl, in the water pool as a result of the radiation degradation of Hypalon cable jacketing was described. The HCl concentration given for 30 days after accident initiation was 9.9×10^{-4} mol/L. An independent evaluation of HCl production is provided in Section 4.

C) Calculation of H^+ Added to the Pool

In this section the concentrations of hydroxide, sometimes with negative values, were summed with the concentrations of HCl to obtain an overall hydrogen ion concentration. As noted, this is algebraically, but not physically, correct.

D) Calculation of pH of the Water Pool

The pH calculations were based on the equilibrium constant for the dissociation of boric acid. This approach is valid for dilute solutions. In this case the pH control chemical, sodium pentaborate, had a concentration of 8.4×10^{-4} mol/L. However, in borate solutions at concentrations ≥ 0.1 mol/L, as sometimes occur in containment water pools, this calculational method is inaccurate because of borate species that are not accounted for by the single equilibrium constant. The temperature for the calculated pH was not given. Based on the value of the equilibrium constant used, it corresponds to 20–25 °C.

The pH calculational method for the concentration of sodium pentaborate appears to be valid, but it should not serve as the basis for extrapolation or calculations at higher concentrations or temperatures. Because of variations in the distribution of borate species with concentration and temperature, it is possible to have a lower pH at higher borate concentrations. The reported pH values varied from 8.6 initially to 8.0 after 30 days.

3. Determination of pH in the Perry Containment Water Pool

Solutions of sodium pentaborate act as pH buffers. This means that the addition of acid causes only a small decrease in pH. At some point with acid addition, the buffer capacity is exceeded and a large decrease in pH can be observed for a relatively small addition of acid. It is helpful to know the limit of the buffering capacity of the pH control chemicals in containment water pools so as to avoid conditions where a large decrease in pH occurs.

The supplier of sodium pentaborate does not have any data on pH or on the variation of pH with acid addition. Since no measured data were available, we prepared a set of sodium pentaborate solutions and measured the pH at 25 °C and also measured the pH as acid was titrated into the samples. The initial solution contained 8.4×10^{-4} mol/L sodium pentaborate. (This was based on 5236 lb of $Na_2O{\cdot}5\ B_2O_3{\cdot}10\ H_2O$ in 4.81×10^6 L of containment water, as given in the Polestar document.)

Figures 1 and 2 show pH readings as a function of acid addition. These plots were scaled to 4.81×10^6 L to correspond to the Perry containment. Eight samples, four of which were titrated with 0.1 *M* HNO_3 and four of which were titrated with 0.01 *M* HNO_3, were tested. The initial pH measured was 8.5 to 8.6. This is consistent with the Polestar calculation. The Polestar calculation also gave a pH of 8.0 at 30 days. The acid addition, by Polestar calculation, was $\sim 4 \times 10^3$ mol. The measured values confirm the pH at this acid addition. The plots in Figs. 1 and 2 show that the buffer capacity would be exceeded with the addition of $\sim 7 \times 10^3$ mol of acid. The data used to prepare Figs. 1 and 2 are listed in Table 1.

4. Independent Recalculation of Acid Additions and pH

Uncertainties in the Polestar terminology led us to perform additional calculations to verify the predictions of acid formation and pH. The assumptions used in this process are described in the paragraphs that follow.

1. Containment inventories were calculated for the fission product groups Xe-Kr, I-Br, Cs-Rb, and Te-Se-Sb, following exactly the release rates described by Polestar (including assumption of 105% power).

2. Dose rates per unit mass (MeV/s·g) for each element group were those used in earlier NRC calculations for the AP-600 [1,2].
3. Fission products were apportioned to water and airspace as described by Polestar: 87% in water, 13% in airspace (except noble gases, for which 100% remained in airspace).
4. The total dose rates to water and air were determined by combining inventories from assumptions 1 and 3 with the specific dose rates from assumption 2.
5. For species distribution, 5% of the iodine was assumed to be HI and the balance CsI. Cesium not apportioned as CsI was assumed to be CsOH.
6. Polestar data for containment: 2.9×10^4 lb Hypalon, 4.81×10^6 L water, 5236 lb sodium pentaborate.
7. Both sodium pentaborate and water are present initially.
8. The HCl generation was calculated from the procedure described in Ref. 3.
9. The HNO_3 generation was calculated from the model in Ref. 4. This model is based on the absorption of radiation by water. An evaluation of HNO_3 generation from absorption by gas and the reason for its rejection are provided in Appendix A.
10. The containment operates at a constant temperature of 25 °C (77 °F).

The inventories of acids and bases can be determined on the basis of these ten assumptions.

Upon dissolution in water, sodium pentaborate hydrolyzes to form base and boric acid as follows:

$$Na_2O \cdot 5B_2O_3 \cdot 10H_2O + 6H_2O \rightarrow 2NaOH + 10H_3BO_3.$$

The Perry Plant contains 4029 mol of borate buffer; hence, the water consumed by the hydrolysis reaction is 6×4029 mol, or 444 L. This amount is negligible as compared with the total water inventory, 4.81×10^6 L. When dissolved, the initial constituents in water are (assuming a density of 0.981 kg/L) 0.001708 *m* NaOH and 0.008542 *m* H_3BO_3.

The initial pH is calculated by assuming that no other constituents are in the solution.

Using assumptions 1–4, energy deposition rates to both air and water can be calculated. These are shown in Fig. 3. Note the rate of increase at 0.5 h — due to the increase in fission product source rates — and the peak at 2 h — the end of fission product releases. The gradual decline after 2 h is due to the reduction of fission product inventory as the result of radioactive decay.

Following assumptions 8 and 9 and using the energy deposition rates in Fig. 3, the generation of containment acids can then be computed (see Fig. 4 and Table 2). The total acid generated at 30 days is about 2250 mol, roughly half that of the Polestar calculation. The discrepancy is likely because Polestar tailored the HCl generation from Hypalon specifically to the Perry Plant, resulting in about twice the generation rates for HCl. The current analysis assumes the generic model of Ref. 4. In addition, the current analysis considers the reduction in energy deposition rate over time for a given mass of each fission product group. If such an effect was also considered by Polestar, it has not been described.

The pH of containment water is determined by considering all the additions to the water. Acids (listed in Table 2) include radiolytically generated HCl and HNO_3, as well as a small amount of HI. The only base is CsOH, which is added within the first 2 h. The sodium pentaborate buffer is assumed to be present initially in the water. The method and timing are not indicated by Polestar.

At each time in Table 2, the total additions are used as input to a pH model calculation. This model computes pH by calculating chemical equilibrium and is described in Ref. 5. The resulting values, which are shown in the final column of Table 2, are reasonably consistent with Polestar results. With only buffer solution, the initial pH is 8.58. However, the pH increases to 8.63 as fission products are added. The subsequent decline due to acid additions reaches a final value of 8.48 at 30 days, which is somewhat higher than the Polestar result, undoubtedly due to the lower amount of acid generated.

5. Summary

The pH calculations of Polestar for Perry containment water were evaluated at ORNL by both calculations and measured values. The technique used in the Polestar calculations should not be used at higher borate concentrations without modifications to include additional borate species.

In the document that was evaluated in this study, there was no justification for the unstated assumption that the 4.81×10^6 L of containment water was well mixed, uniform, and at equilibrium. No information was included relative to how or when the pH control chemical would be introduced, and no data were available on other water pools. Our calculated and measured values were in agreement with Polestar results.

Table 1. Titration of sodium pentaborate solution. 8.4×10^{-4} mol/L

0.1 *M* nitric acid: first set of titrations		0.01 *M* nitric acid: second set of titrations	
Mol acid scaled to Perry containment	pH reading	Mol acid scaled to Perry containment	pH reading
0	8.51	0	8.64
1828	8.46	904	8.54
3944	8.25	1794	8.44
5916	7.92	2694	8.33
8129	4.1	3593	8.18
		4262	8.05
0	8.51	4935	7.87
2261	8.46	5368	7.73
4425	8.12	6041	7.33
6638	7.64	6263	7.12
8658	3.63	6460	6.88
		6926	6.28
0	8.51	7989	3.90
2309	8.36	9620	3.39
4521	8.15		
6734	7.61	0	8.61
8850	3.15	1000	8.50
		2232	8.37
0	8.66	3439	8.20
2116	8.49	4570	7.99
4233	8.24	5248	7.79
6542	7.17	5695	7.58
8562	4.06	6147	7.29
9716	3.59	6595	6.68
		7278	4.65
		9620	3.33
		0	8.61
		981	8.52
		1847	8.43
		2261	8.33
		3131	8.21
		4021	8.06
		5166	7.92
		5849	7.68
		6282	7.46
		6936	6.83
		8047	4.25
		9620	3.48
		0	8.56
		803	8.54
		1481	8.48
		2126	8.42
		2828	8.33
		3502	8.26
		4185	8.15
		4858	8.02
		5503	7.88
		6195	7.62
		6878	7.15
		7090	6.86
		7773	5.18
		8494	3.88
		9168	3.59

Table 2. Additions to water and pH in the Perry containment pool at important accident sequence time intervals

	Cumulative additions to water (mol)				Totals ($m \times 10^3$)		Calc.
Time (h)	HCl	HNO_3	HI	CsOH	Acid	Base[a]	pH
0	0	0	0	0	0	1.708	8.58
1	8.4	2.2	2	407	0.003	1.794	8.61
2	39.1	8.3	4.6	868	0.011	1.892	8.63
5	133	26	4.6	868	0.035	1.892	8.63
12	268	54	4.6	868	0.069	1.892	8.62
24	425	91	4.6	868	0.11	1.892	8.60
72	767	187	4.6	868	0.203	1.892	8.58
240	1317	348	4.6	868	0.354	1.892	8.53
480	1623	448	4.6	868	0.44	1.892	8.50
720	1745	503	4.6	868	0.477	1.892	8.48

[a]Includes 0.001708 *m* NaOH, contributed from sodium pentaborate; remainder is CsOH.

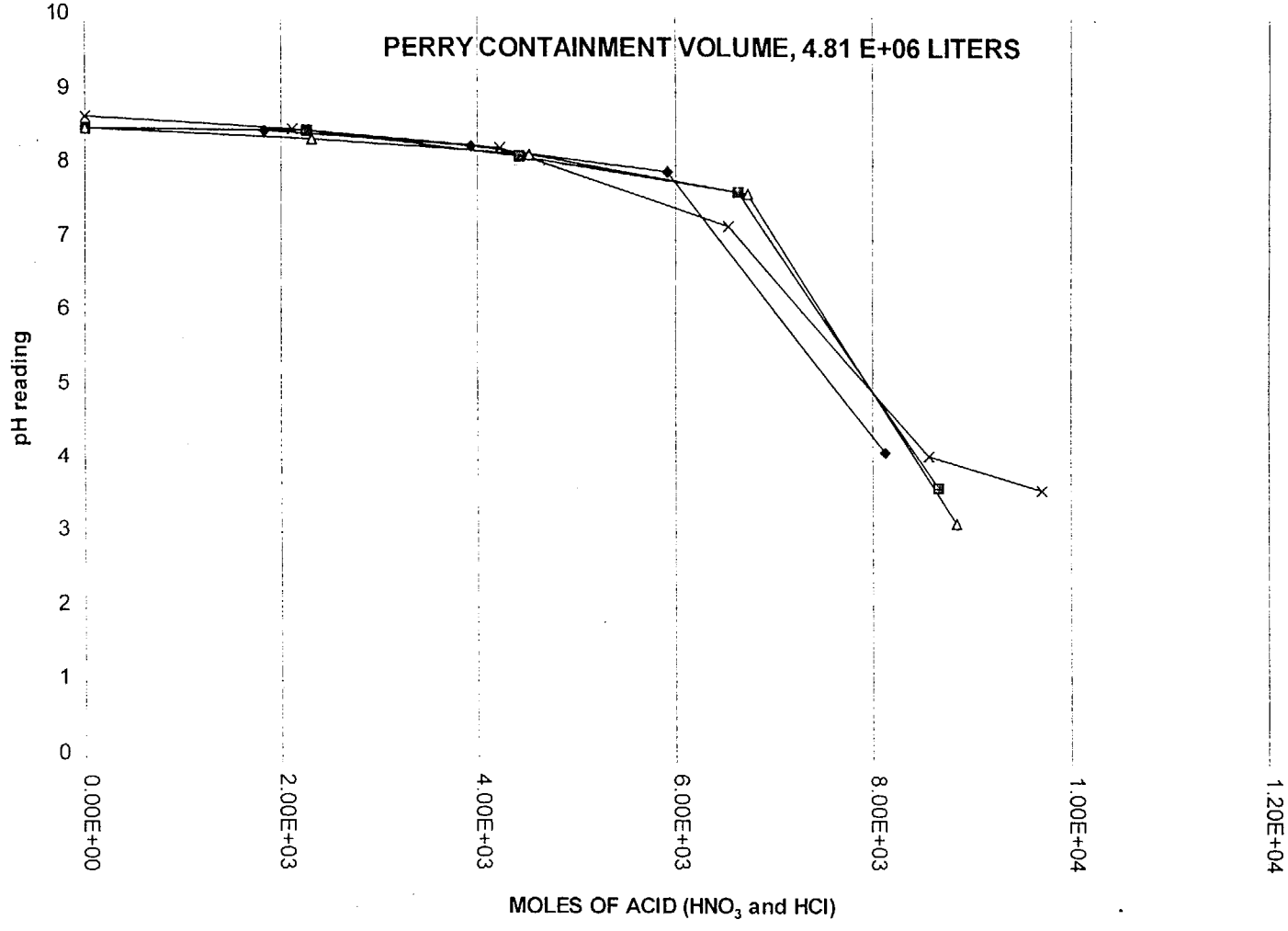

Fig. 1. Results obtained by titration with 0.1 M HNO_3.

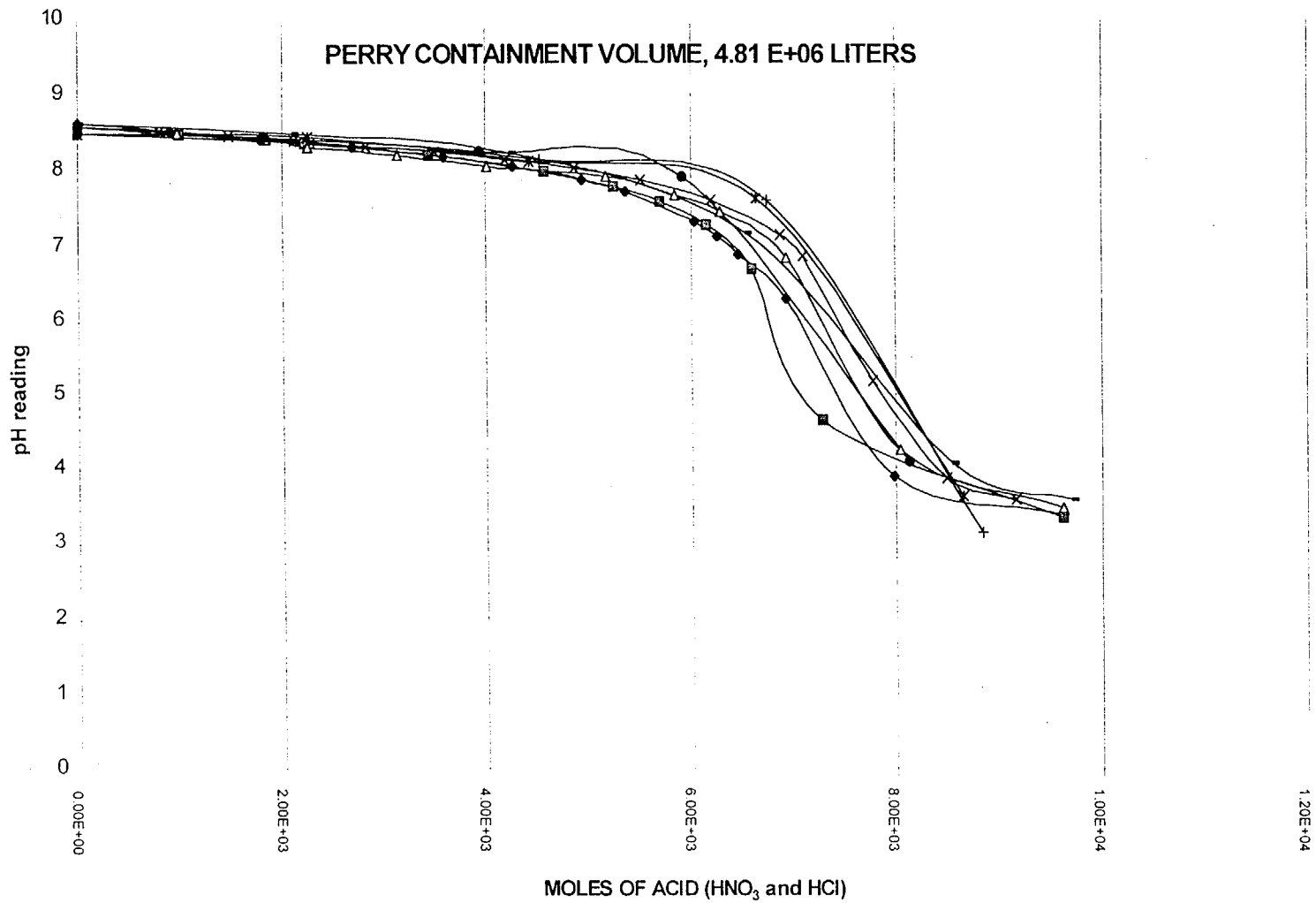

Fig. 2. Results obtained by titration with 0.01 *M* HNO_3.

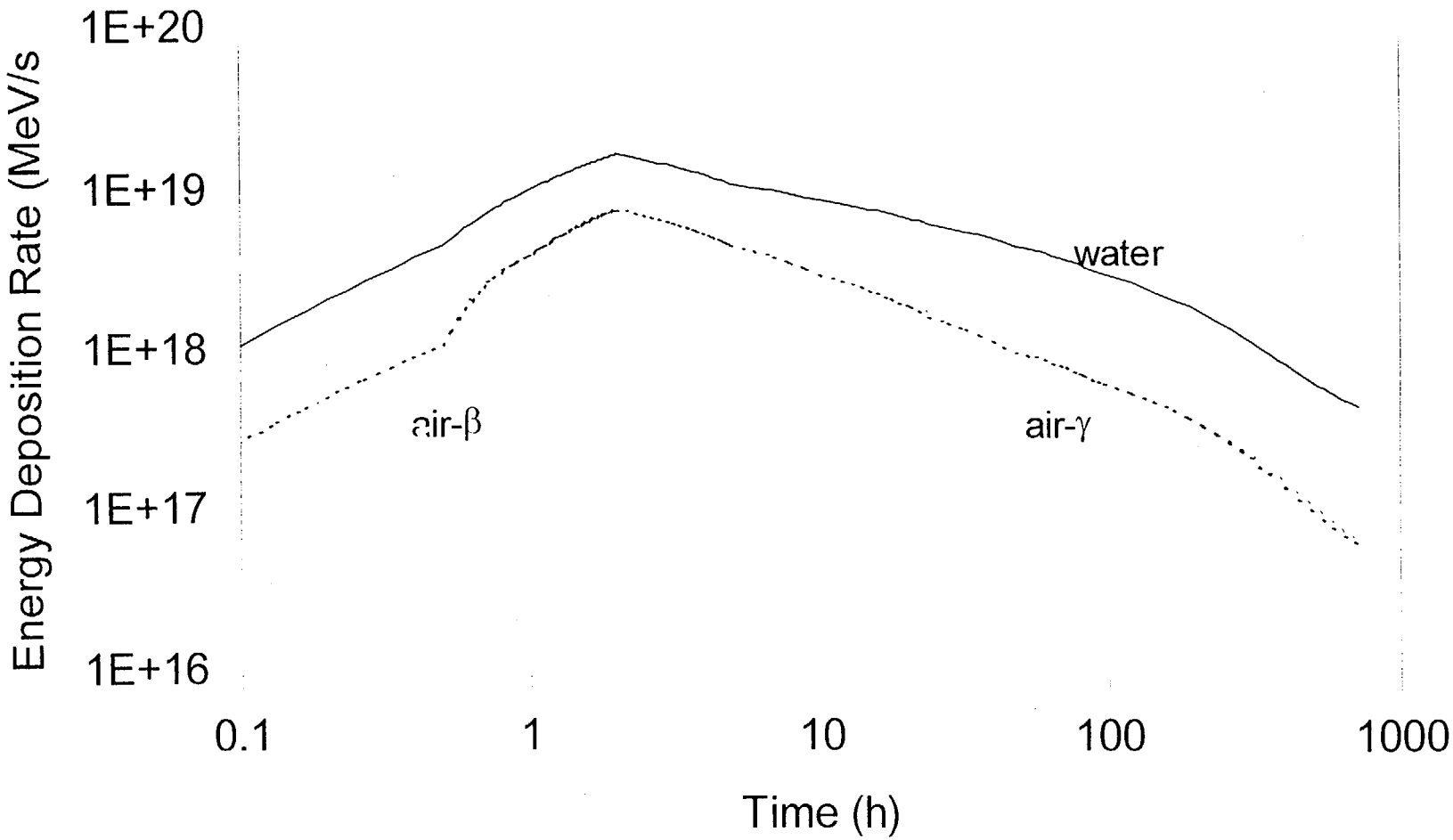

Fig. 3. Energy deposition rates due to fission product decay.

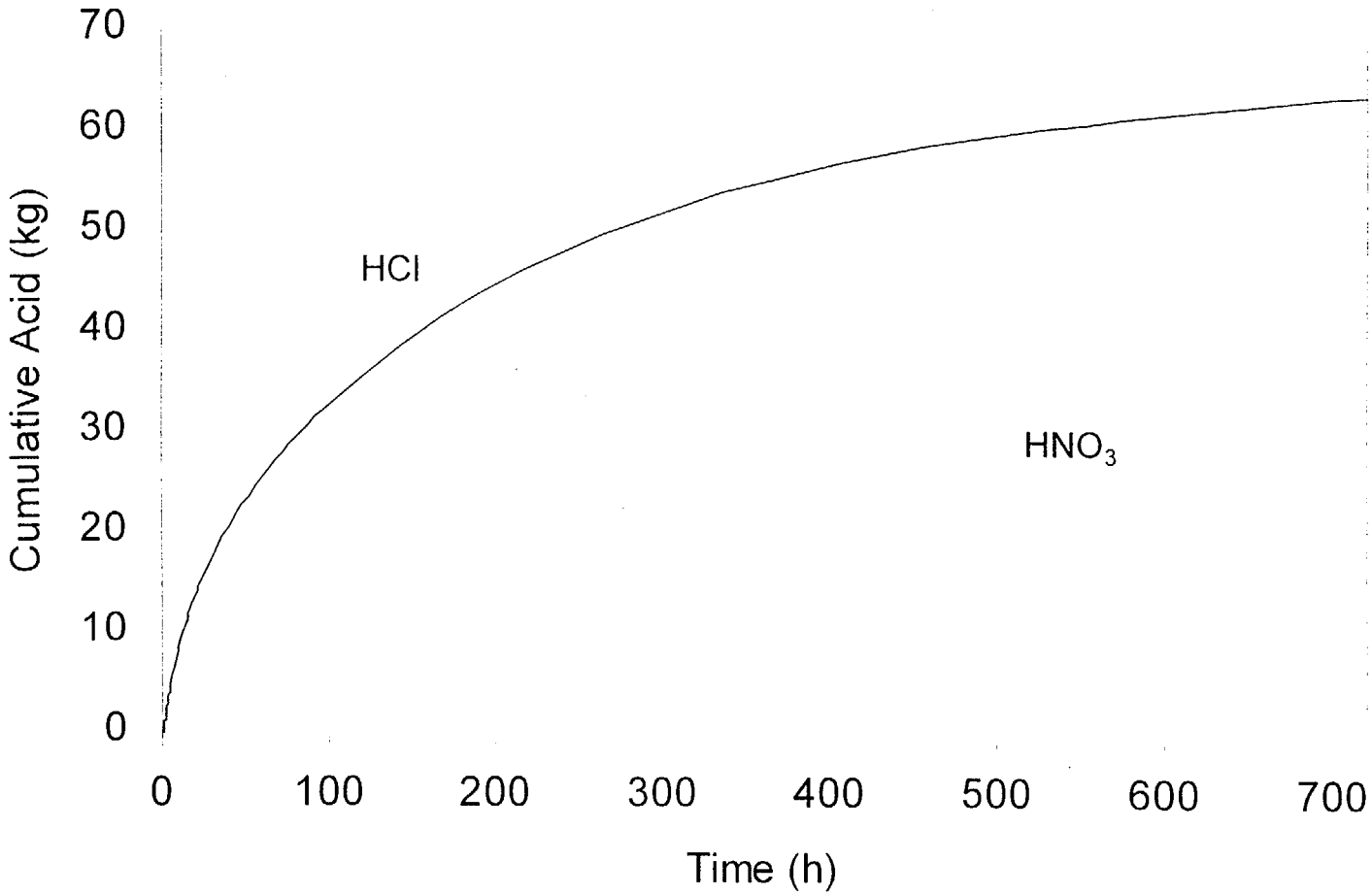

Fig. 4. Radiolytically generated acids in containment.

References

1. E. C. Beahm, C. F. Weber, and T. A. Dillow, "Technical Assistance in Review of Source Term–Related Issues of Advanced Reactors," NUREG/CR-6408 (ORNL/TM-13144), Oak Ridge National Laboratory, Oak Ridge, TN (September 1998).

2. C. F. Weber and E. C. Beahm, "Iodine Volatility and pH Control in the AP-600 Reactor," NUREG/CR-6599 (ORNL/TM-13555), Oak Ridge National Laboratory, Oak Ridge, TN (September 1998).

3. E. C. Beahm et al., "Iodine Evolution and pH Control," NUREG/CR-5950 (ORNL/TM-12242), Oak Ridge National Laboratory, Oak Ridge, TN (1992).

4. C. F. Weber et al., "Models of Iodine Behavior in Reactor Containments," ORNL/TM-12202, Oak Ridge National Laboratory, Oak Ridge, TN (1992).

5. C. F. Weber and E. C. Beahm, "Calculation of pH and Iodine Volatility Under Reactor Accident Conditions," Draft Letter Report to Jason Schaperow (October 1998).

APPENDIX A

ALTERNATIVE CALCULATION OF NITRIC ACID GENERATION

Appendix A
Alternative Calculation of Nitric Acid Generation

Some researchers have suggested a radiation dose to the containment atmosphere as the proper driving force for HNO_3 generation. It is, of course, beyond the scope of this work to debate the appropriate model or chemical mechanism. In the Perry accident, most of the fission products end up in water (except for noble gases), which suggests that a formation mechanism using an air dose may generate considerably less HNO_3. In fact, the analysis below demonstrates that this is the case.

To evaluate, we use the model of Burns et al. [1], which can be restated as

$$n_1(t) = 2n_0 \left[1 - \exp(-1.45 \times 10^{-5}\, G\dot{D}t)\right], \tag{1}$$

where $n_1(t)$ = initial inventory of HNO_3 at time t (mol),

n_0 = initial inventory of N_2 (mol),

G = g-value of HNO_3 in moist air = 1.0 (molecules/100 eV),

$\dot{D}$ = dose rate to containment atmosphere (Mrad/h),

t = time (h).

We consider only beta radiation since a negligible amount of gamma radiation should be absorbed by the gas itself; all beta radiation is assumed to be absorbed. The Perry accident produces a peak dose rate of 0.0073 Mrad/h at 2 h, although it is above 0.001 Mrad/h for about 4 days. Using Equation (1), an inventory of about 73 mol HNO_3 has been generated after 30 days. This is nearly an order of magnitude lower than the amount generated using a water dose. Hence, the latter is preferred since it is conservative, regardless of the true formation mechanism.

Reference

1. W. G. Burns et al., "Radiation Effects and the Leach Rates of Vitrified Radioactive Waste," *Nature* **295**, 130–132 (1982).

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