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RADIOLYTIC HYDROGEN GENERATION IN SAVANNAH RIVER SITE (SRS) HIGH LEVEL WASTE TANKS – COMPARISON OF SRS AND HANFORD MODELING PREDICTIONS

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EXECUTIVE SUMMARY

In the high level waste tanks at the Savannah River Site (SRS), hydrogen is produced continuously by interaction of the radiation in the tank with water in the waste. Consequently, the vapor spaces of the tanks are purged to prevent the accumulation of H_2 and possible formation of a flammable mixture in a tank. Personnel at SRS have developed an empirical model to predict the rate of H_2 formation in a tank. The basis of this model is the prediction of the G value for H_2 production. This G value is the number of H_2 molecules produced per 100 eV of radiolytic energy absorbed by the waste. Based on experimental studies it was found that the G value for H_2 production from beta radiation and from gamma radiation were essentially equal. The G value for H_2 production from alpha radiation was somewhat higher. Thus, the model has two equations, one for beta/gamma radiation and one for alpha radiation. Experimental studies have also indicated that both G values are decreased by the presence of nitrate and nitrite ions in the waste. These are the main scavengers for the precursors of H_2 in the waste; thus the equations that were developed predict G values for hydrogen production as a function of the concentrations of these two ions in waste. Knowing the beta/gamma and alpha heat loads in the waste allows one to predict the total generation rate for hydrogen in a tank. With this prediction a ventilation rate can be established for each tank to ensure that a flammable mixture is not formed in the vapor space in a tank.

Recently personnel at Hanford have developed a slightly different model for predicting hydrogen G values. Their model includes the same precursor for H_2 as the SRS model but also includes an additional precursor not in the SRS model. Including the second precursor for H_2 leads to different empirical equations for predicting the G values for H_2 as a function of the nitrate and nitrite concentrations in the waste.

The difference in the two models has led to the questions of how different are the results predicted by the two models and which model predicts the more conservative (larger) G values. More conservative G values would predict higher H_2 generation rates that would require higher ventilation rates in the SRS tanks.

This report compares predictions based on the two models at various nitrate and nitrite concentrations in the SRS HLW tanks for both beta/gamma and for alpha radiation. It also compares predicted G values with those determined by actually measuring the H_2 production from four SRS HLW tanks (Tanks 32H, 35H, 39H, and 42H). Lastly, the H_2 generation rates predicted by the two models are compared for the 47 active SRS high level waste tanks using the most recent tank nitrate and nitrite concentrations and the beta/gamma and alpha heat loads for each tank.

The predictions of the models for total H_2 generation rates from the 47 active SRS waste were, for the most part, similar. For example, the predictions for both models applied to 25 tanks agreed within ±10% of each other. For the remaining 22 tanks, the SRS prediction was more conservative for 9 tanks (maximum 29% higher) and the Hanford prediction was more conservative for 13 tanks (maximum 19% higher).

When comparing G values predicted by the equations presuming only alpha radiation or only beta/gamma was present the results were somewhat different. The results of predictions for alpha radiation, at the 47 current nitrate and nitrite concentrations in the SRS tanks indicated that all the SRS predictions were higher (up to 30%) than the Hanford predictions and thus more conservative. For beta/gamma radiation the predictions for both models agreed to ±10% for 18 of the combinations, the Hanford model predicted higher values (11 up to 17%) for 25 of the concentrations considered, and the SRS model predicted higher G values for the remaining two combinations (12 and 17%).

For the four SRS tanks, where we compared measured G values to those predicted by the two different models, the results for two tanks (Tanks 35 and 39) were in good agreement with predictions from both models. For the other two tanks (Tanks 32 and 42) the predictions of both models were conservative. The predictions were 3 to 4X higher than the measured G values for H_2 production.

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BDGRE	Buoyant Displaced Gas Release Event
DNFSB	Defense Nuclear Facilities Safety Board
HLW	High Level Waste
SRS	Savannah River Site

1.0 INTRODUCTION AND BACKGROUND

Hydrogen gas is generated in Savannah River Site (SRS) high level waste (HLW) tanks by the alpha, beta and gamma radiolysis of water. Interactions of these radiations with the water molecules produce the precursors of the H_2. Production of hydrogen is a concern because of the possible formation of a flammable gas mixture in the vapor space of the tank. Currently models exist both at SRS and Hanford for predicting the rate of H_2 formation in order to prevent formation of a flammable mixture. In this report the results of these two predictive models applied to the SRS HLW tanks are compared.

The yield of H_2 from radiolysis of aqueous solutions is defined as the G-value for H_2 production and has the symbol $G(H_2)$. $G(H_2)$ is the number of H_2 molecules produced per 100 eV of energy absorbed. If the G value and the radiation dose rate are known, then the H_2 generation rate can be calculated. There is evidence from many laboratory studies that dissolved species in the water may react with the precursors of H_2 and decrease the value for $G(H_2)$.[1] In the HLW tanks both at SRS and Hanford, the two predominant species that scavenge the precursors of H_2 are nitrate and nitrite ions. At SRS an empirical model, which in this document we call the SRS model, was developed to predict the decrease in $G(H_2)$ as a function of nitrate and nitrite concentrations in the tanks.[2] The model is based on results of laboratory studies and has two predictive equations. One is applicable for alpha radiation and the other is applicable for beta/gamma radiation. This model is summarized in the next section. Recently researchers at the Radiation Laboratory of the University of Notre Dame have published evidence [3] for a mechanism for radiolytic hydrogen production that involves a precursor not considered in the SRS model. As a result, scientists at Hanford have developed a model, which we call the Hanford model, that leads to two predictive equations, one for alpha and one for beta/gamma, that are different from those in the SRS model. [4,5] This second model is also summarized below.

A recent inquiry from the Defense Nuclear Safety Facilities Board (DNFSB) to SRS personnel (See Appendix I for text of this inquiry) has questioned how different the results would be for predicted hydrogen generation rates in SRS HLW tanks if the Hanford model was used rather than the SRS model. A primary concern for the hydrogen generation rate predictions is whether one model or the other gives predictions that are much higher or much lower than the other model.

In this report, we compare values for $G(H_2)$ predicted by the two models based on recently reported NO_3^- and NO_2^- concentrations in the SRS HLW tanks. We also compare values for $G(H_2)$ that have actually been measured for four SRS HLW tanks to values for $G(H_2)$ predicted by the two models. Lastly, using the most recent heat loads for beta/gamma and alpha and for NO_3^- and NO_2^- concentrations in the SRS HLW tanks we have calculated the hydrogen generation rates in cubic feet per hour using the two different models. In the comparisons, we found that the results for the two models are similar but in some cases they may differ by up to 30%.

1.1 The SRS Model for Predicting $G(H_2)$

In the literature of radiation chemistry there is data that indicates that the precursor for H_2 is the hydrated electron.[1] This is an electron that has been displaced from a water molecule as a result of the radiation. This electron can then be trapped in a quasi stable form and become what is called a hydrated electron. It is the combination of two hydrated electrons that forms the H_2.[1] As mentioned before, in HLW tanks the best scavengers for the hydrated electron are NO_3^- and NO_2^-ions. SRS personnel have developed equations that predict values of $G(H_2)$ as a function of the NO_3^- and NO_2^-concentrations. These equations were developed from data from an extensive amount of laboratory studies. For beta gamma radiation, the equation was developed from $G(H_2)$ values measured by gamma radiolysis experiments on nitrate, nitrite and mixed nitrate/nitrite aqueous solutions.[6-8] For alpha radiation, the equation was developed based on $G(H_2)$ values measured in alpha radiolysis experiments on acid nitrate solutions using dissolved Cm-244[9] or Po-210[10]. In both equations the scavenger capacity of the nitrate and nitrite ions for the precursors of the H_2 is combined into an 'effective nitrate concentration', or NO_{eff}, concentration.[2] This effective concentration is the sum of the nitrate concentration plus one half the nitrite concentration. The factor of 0.5 results from the measured rate coefficients of nitrate and nitrite with the hydrated electron, the precursor of H_2 in the SRS model. For nitrite the coefficient is $4.1E9M^{-1}sec^{-1}$and for nitrate it is $9.7E9M^{-1}sec^{-1}$.[11] Thus nitrite ions are only ~0.5 as effective as nitrate ions. Appendix B contains the predictive equations developed for both beta/gamma and for alpha radiation. In the application of the SRS model to the SRS HLW tanks, the results of these equations are increased by 10% for conservatism. These G value predictions are the current basis for hydrogen generation rate calculations used for HLW tanks at SRS.[12]

1.2 The Hanford Model for Predicting $G(H_2)$

Researchers at the University of Notre Dame have published evidence for a second mechanism for radiolytic hydrogen production that involves the precursor of the hydrated electron.[3,13] As a result, Hanford personnel have incorporated into their model for H_2 production these competing mechanistic pathways for radiolytic hydrogen production involving the two different hydrogen precursors (the precursor of the hydrated electron and the hydrated electron itself).[4,5] Appendix B contains the recently developed equations by the Hanford personnel for both beta/gamma and for alpha radiation. The equation for beta/gamma radiation was developed from gamma radiolysis data generated at Notre Dame on solutions containing nitrate and nitrite ions as well as other ions as scavengers for both types of H_2 precursors.[13] Hanford personnel did not use any of the beta/gamma data that formed the basis of the SRS model. The equation for alpha radiation was developed using data from Notre Dame on the 5 MeV helium ion radiolysis of solutions containing H_2O_2, $Cr_2O_7^{2-}$, and SeO_4^{2-} ions as scavengers for the precursors of hydrated electron.[3] An accelerator was used to generate the 5 MeV helium ions. Radiolysis by 5 MeV helium ions correctly simulates the alpha radiolysis by alpha emitters dissolved in the waste. Results of the experiments with the helium ions were then used to develop the equation for the effect of NO_3^- and NO_2^-scavengers on $G(H_2)$ for alpha radiation. Currently there is no data for 5 MeV helium ion radiolysis of nitrate and nitrite solutions. The Hanford personnel did not use the results for alpha radiolysis of nitrate solutions containing dissolved Cm-244 [9] or Po-210 [10] when developing their equation. Both the beta/gamma and the alpha equations in the Hanford model include terms that incorporate the reaction rate coefficients of nitrate and nitrite with the precursor of the hydrated electron as well as the reaction rate coefficients for hydrated electron itself. The estimated rate coefficients for nitrate and nitrite with the precursor to the hydrated electron are 2.2E13$M^{-1}sec^{-1}$ and 0.57E13$M^{-1}sec^{-1}$, respectively.[13]

2.0 RESULTS AND DISCUSSION

2.1 Comparison of $G(H_2)$ Values Predicted by the Two Models At Various NO_2^- and NO_3^- Concentrations

In order to compare the predictions of the two models for hydrogen generation, we obtained from SRS personnel recent data for nitrite and nitrate concentrations in SRS HLW tanks.[14] These nitrate and nitrite data were then used in the equations to predict hydrogen generation using both the SRS model based on the hydrated electron, and the Hanford model involving both the precursor of the hydrated electron and the hydrated electron reactions. Results are presented in Table 2-1 for beta/gamma radiation and Table 2-2 for alpha radiation. The results in Table 2-1 and Table 2-2 are for the hypothetical situations in which all the individual tank decay heats are assumed to be either totally from beta/gamma (Table 2-1) or totally from alpha (Table 2-2).

Columns two and three of Table 2-1 and Table 2-2 show the nitrite and nitrate concentrations in the 47 active SRS HLW tanks. In column four of each table are the calculated values for NO_{eff} for the SRS model. The largest value is found in Tank 14 where $NO_3^- + .5NO_2^- = 5.15$. The lowest level is in Tank 23 where $NO_3^- + .5NO_2^- = 0.14$. The predicted G values for hydrogen production were then calculated for both models. The equations used for each model are shown in Appendix B. For the SRS model, Equation 1 was used for beta gamma radiation and Equation 4 for alpha radiation. The calculated G values were then increased by 10% as prescribed in the SRS model. These values are presented in column five of each table.

For the Hanford model, Equation 7 shown in Appendix II was used to predict $G(H_2)$ for beta gamma radiation and Equation 9 for alpha radiation. Results for the Hanford model are presented in column six of each table. The last column of each table shows the percentage change going from the SRS to the Hanford prediction.

One can see by comparing columns five and six of Table 2-1 for beta/gamma radiations that in most cases the Hanford model gives more conservative (higher) predicted G-values for H_2 production. The range for the percentage increase is 2-18%. It should be noted that while the Hanford model does predict on the average higher G-values, there are several combinations of nitrite and nitrate concentrations that give essentially the same predicted values to within ±10%. These are the nitrite and nitrate concentrations in 21 of the tanks (Tanks 5, 10, 11, 15-25, 29, 33-35, 39-41, 43, 44, 47, 48 and 50.

For alpha radiation the Hanford model predicts lower G-values (36 % on average) than the SRS model. Thus, the SRS model for predicting hydrogen G-values from alpha radiolysis is always more conservative (predicts higher G-values) than Hanford model.

Table 2-1 Comparison of G(H_2) Values for Beta/Gamma Radiation Predicted by the Two Models Using NO_2^- and NO_3^- Concentrations in SRS HLW Tanks

Tank	NO_2^- Conc. (M)	NO_3^- Conc. (M)	NO_{eff}	Predicted G(H_2) SRS Model	Predicted G(H_2) Hanford Model	% Change, SRS to Hanford
1	2.75	2.00	3.38	0.039	0.045	15
2	3.04	2.25	3.77	0.036	0.041	14
3	2.26	1.71	2.84	0.045	0.052	16
4	1.57	2.01	2.80	0.045	0.050	11
5	0.68	2.32	2.66	0.048	0.049	2
6	0.61	0.15	0.46	0.173	0.196	13
7	1.97	1.47	2.45	0.052	0.059	13
8	0.74	0.19	0.56	0.157	0.178	13
9	3.20	1.90	3.50	0.038	0.045	18
10	0.36	3.82	4.00	0.035	0.033	-6
11	**3.24**	3.36	4.98	0.034	0.031	-9
12	1.70	1.45	2.30	0.055	0.061	11
13	2.23	1.84	2.96	0.043	0.050	16
14	2.90	3.70	**5.15**	0.035	0.029	-17
15	0.10	1.10	1.15	0.101	0.092	-9
19	0.99	1.01	1.50	0.082	0.084	2
21	0.24	0.06	0.18	0.243	0.266	9
22	0.23	0.08	0.19	0.240	0.260	8
23	0.20	**0.04**	**0.14**	0.262	0.285	9
24	0.28	0.07	0.21	0.235	0.259	10
25	1.16	1.36	1.95	0.064	0.068	6
26	1.73	1.58	2.45	0.052	0.058	12
27	1.68	1.21	2.05	0.061	0.069	13
28	2.26	2.17	3.30	0.039	0.045	15
29	1.40	1.28	1.98	0.063	0.069	10
30	1.97	1.19	2.17	0.058	0.067	16
31	2.44	1.87	3.09	0.042	0.049	17
32	2.88	2.06	3.50	0.038	0.044	16
33	1.16	1.35	1.93	0.065	0.069	6
34	1.18	2.27	2.86	0.044	0.047	7
35	1.13	2.66	3.23	0.040	0.042	5
36	1.89	1.57	2.52	0.050	0.057	14
37	2.11	1.60	2.65	0.048	0.055	15
38	2.09	2.40	3.44	0.038	0.042	11
39	1.11	1.89	2.45	0.052	0.055	6
40	0.49	0.18	0.42	0.180	0.198	10
41	0.57	**4.08**	4.37	0.034	0.030	-12
42	2.55	2.04	3.32	0.039	0.045	15
43	1.55	1.72	2.49	0.051	0.056	10
44	1.34	1.10	1.77	0.071	0.076	7
45	1.86	1.40	2.33	0.054	0.062	15
46	2.21	1.82	2.93	0.044	0.050	14
47	0.54	3.24	3.51	0.038	0.037	-3
48	0.59	0.25	0.55	0.159	0.173	9
49	2.90	2.27	3.72	0.036	0.041	14
50	**0.01**	1.87	1.88	0.067	0.062	-7
51	0.72	0.24	0.60	0.152	0.170	12

Notes:	Tank 23 contains lowest Nitrate
	Tank 41 contains highest Nitrate
	Tank 50 contains lowest Nitrite
	Tank 11 contains highest Nitrite
	Tank 23 contains lowest total (Nitrate + Nitrite)
	Tank 14 contains highest total (Nitrate + Nitrite)

Table 2-2 Comparison of $G(H_2)$ Values for Alpha Radiation Predicted by the Two Models Using NO_2^- and NO_3^- Concentrations in SRS HLW Tanks

Tank	NO_2^- Conc. (M)	NO_3^- Conc. (M)	NO_{eff}	Predicted $G(H_2)$ SRS Model	Predicted $G(H_2)$ Hanford Model	% Change, SRS to Hanford
1	2.75	2.00	3.38	0.221	0.139	-37
2	3.04	2.25	3.77	0.196	0.126	-36
3	2.26	1.71	2.84	0.262	0.160	-39
4	1.57	2.01	2.80	0.266	0.153	-42
5	0.68	2.32	2.66	0.279	0.149	-47
6	0.61	0.15	0.46	0.727	0.597	-18
7	1.97	1.47	2.45	0.300	0.182	-39
8	0.74	0.19	0.56	0.682	0.545	-20
9	3.20	1.90	3.50	0.213	0.138	-35
10	0.36	3.82	4.00	0.184	0.100	-46
11	**3.24**	3.36	4.98	0.144	0.094	-35
12	1.70	1.45	2.30	0.317	0.188	-41
13	2.23	1.84	2.96	0.252	0.153	-39
14	2.90	3.70	**5.15**	0.139	0.089	-36
15	0.10	1.10	1.15	0.503	0.282	-44
19	0.99	1.01	1.50	0.431	0.259	-40
21	0.24	0.06	0.18	0.909	0.807	-11
22	0.23	0.08	0.19	0.900	0.789	-12
23	0.20	**0.04**	**0.14**	0.953	0.860	-10
24	0.28	0.07	0.21	0.889	0.786	-12
25	1.16	1.36	1.95	0.361	0.209	-42
26	1.73	1.58	2.45	0.301	0.178	-41
27	1.68	1.21	2.05	0.347	0.211	-39
28	2.26	2.17	3.30	0.226	0.137	-39
29	1.40	1.28	1.98	0.356	0.211	-41
30	1.97	1.19	2.17	0.332	0.206	-38
31	2.44	1.87	3.09	0.242	0.149	-38
32	2.88	2.06	3.50	0.213	0.135	-37
33	1.16	1.35	1.93	0.363	0.210	-42
34	1.18	2.27	2.86	0.261	0.145	-44
35	1.13	2.66	3.23	0.231	0.129	-44
36	1.89	1.57	2.52	0.293	0.175	-40
37	2.11	1.60	2.65	0.280	0.170	-39
38	2.09	2.40	3.44	0.216	0.129	-40
39	1.11	1.89	2.45	0.301	0.167	-45
40	0.49	0.18	0.42	0.747	0.605	-19
41	0.57	**4.08**	4.37	0.167	0.093	-44
42	2.55	2.04	3.32	0.225	0.139	-38
43	1.55	1.72	2.49	0.296	0.171	-42
44	1.34	1.10	1.77	0.387	0.234	-40
45	1.86	1.40	2.33	0.314	0.189	-40
46	2.21	1.82	2.93	0.255	0.155	-39
47	0.54	3.24	3.51	0.212	0.114	-46
48	0.59	0.25	0.55	0.687	0.529	-23
49	2.90	2.27	3.72	0.199	0.126	-37
50	**0.01**	1.87	1.88	0.371	0.190	-49
51	0.72	0.24	0.60	0.667	0.519	-22

Notes:	Tank 23 contains lowest Nitrate
	Tank 41 contains highest Nitrate
	Tank 50 contains lowest Nitrite
	Tank 11 contains highest Nitrite
	Tank 23 contains lowest total (Nitrate + Nitrite)
	Tank 14 contains highest total (Nitrate + Nitrite)

2.2 Predictions for $G(H_2)$ Compared to Experimentally Measured Values for $G(H_2)$ from Laboratory Studies

In this section, the predicted G values from Table 2-1 for beta/gamma radiation and Table 2-2 for alpha radiation are compared graphically to measured G values from laboratory studies investigating the radiolysis of nitrate and/or nitrite solutions. For the SRS model the predicted and measured G values are plotted against the cube root of NO_{eff}.[2] For the Hanford model the predicted and measured G values are plotted against the scavenging capacity in the nitrate and/or nitrite solutions.[4,5] Figures are presented for both models for both beta/gamma (See Section 2.2.1) and alpha (See Section 2.2.2) radiation.

2.2.1 Results for Beta/Gamma Radiation

Results for beta/gamma radiation are shown in Figure 2-1 and Figure 2-2. The plots incorporate experimental data (solid diamonds) from previous gamma radiolysis studies used to develop the SRS model [6-8], and the recent gamma radiolysis data from Laverne and coworkers [13] for nitrate and nitrite solutions used to develop the Hanford model. Figure 2-1 shows the measured and the predicted hydrogen G-values plotted vs. the cube root of NO_{eff} for beta and gamma radiation. This method of plotting is used in the SRS model because more of the data is a linear function of $(NO_{eff})^{1/3}$ than if plotted against NO_{eff} itself. This makes the data easier to model. Predicted values from both the SRS model (solid squares) and the Hanford model (solid triangles) are plotted for all of the 47 SRS HLW tank nitrite/nitrate combinations previously shown in Table 2-1. Figure 2-1 shows that there is fair agreement between G values predicted by the two different models, and both models predict hydrogen G-values close to the experimental values. However, the Hanford model of predicting hydrogen G-values shows slightly higher (more conservative) values for $G(H_2)$ at $(NO_{eff})^{1/3}$ values in the range of 0.4 to 0.8.

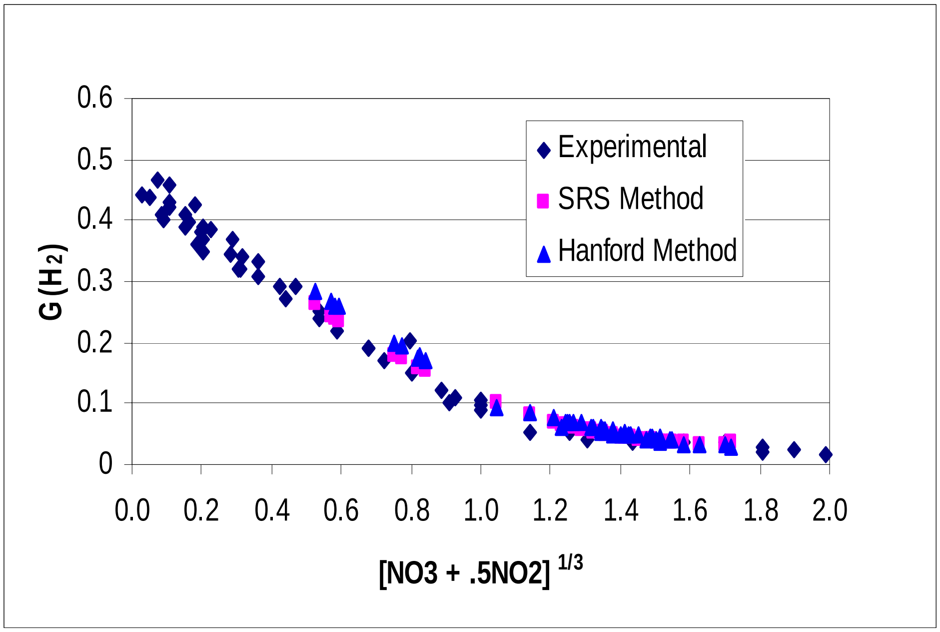

Figure 2-1 Measured and Predicted Values for $G(H_2)$ for Beta/Gamma Radiolysis Plotted vs. Cube Root of NO_{eff}. Note: Solid diamonds are the measured G values from laboratory studies. Solid squares are the G values predicted by the SRS model for SRS HLW tanks and sold triangles are G values predicted by the Hanford model for SRS HLW tanks.

Figure 2-2 shows the beta/gamma data and the predictions of both models plotted using the scavenging capacity as the X-axis. This method of plotting is used in the Hanford model.[4,5] The scavenging capacity is defined as the sum of the products of the various rate coefficients (in units of $M^{-1}sec^{-1}$) times their respective nitrate or nitrite scavenger concentrations (in units of M). Such plots of hydrogen G-values vs. summed scavenging capacity (sec^{-1}) have been used extensively in the Notre Dame studies.[3,13] Again, there is reasonable agreement between the predictions of both models and the experimentally determined values from radiolysis of nitrate and/or nitrite solutions.

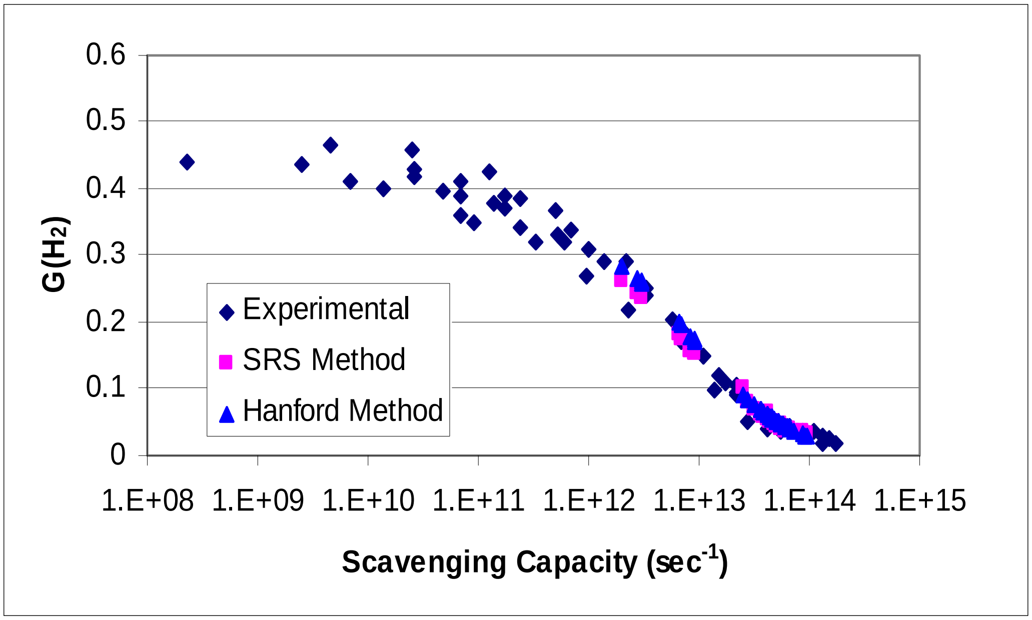

Figure 2-2 Measured and Predicted Values for $G(H_2)$ for Beta/Gamma Radiolysis Plotted vs. Summed Scavenging Capacity. Note: Solid diamonds are the measured G values from laboratory studies. Solid squares are the G values predicted by the SRS model for SRS HLW tanks and solids triangles are G values predicted by the Hanford model for SRS HLW tanks.

2.2.2 Results for Alpha Radiation

The predicted values for $G(H_2)$ for the nitrate/nitrite concentrations from Table 2-2 for alpha radiolysis are compared to experimental values in Figure 2-3 and in Figure 2-4. Figure 2-3 shows the experimental data and the predictions plotted vs. the $(NO_{eff})^{1/3}$ as used in the SRS model. The experimental data in Figure 2-3 shown as solid circles are from alpha radiolysis studies of nitrate solutions using dissolved Cm-244[9] and dissolved Po-210 [10]. The predicted G-values shown in Figure 2-3 as solid triangles using the model proposed by Hanford are consistently lower than the experimental values. The predictions from the SRS model (solid squares) agree reasonably well with the data. Clearly the G values predicted from the SRS model are more conservative than the G values predicted from the Hanford model. During the course of this study, we found in the Russian radiation chemistry literature the results of a study of the radiolysis of nitrite solutions containing dissolved Po-210.[15] This paper also presented more data on the alpha radiolysis of nitrate solutions. These data are also presented in Figure 2-3. The solid diamonds are the nitrite data and the modified x's are the nitrate results. Note that with the exception of one data point at $(NO_{eff})^{1/3}$ of ~1.15, the nitrate results (modified x's) agree well with the experimental data (solid circles) used to develop the SRS model. At $(NO_{eff})^{1/3}$ values greater than 0.4 the nitrite results (solid diamonds) are lower than the experimental data (solid circles) used to develop the SRS model.

The same data and predictions are again plotted in Figure 2-4 using the summed scavenging capacity (both nitrate and nitrite with both hydrated and dry electron) as the X-axis. The experimental results from Notre Dame using 5 MeV helium ions to irradiate aqueous solutions of

SeO_4^{2-}, $Cr_2O_7^{2-}$ and H_2O_2 are also plotted.[3] The Hanford model was developed using this latter data set thus, the Hanford predictions fit this data set better than the alpha radiolysis of nitrate solutions. As mentioned before there have been no studies of the radiolysis of nitrate or nitrite solutions with 5 MeV helium ions. Again most of the results for alpha radiolysis of nitrite solutions with dissolved Po-210 are lower than the nitrate experimental data (solid circles) and the predictions (either the solid squares or the solid triangles). Note that the predictions from the SRS model (solid squares) are still more conservative than the Hanford predictions (solid triangles).

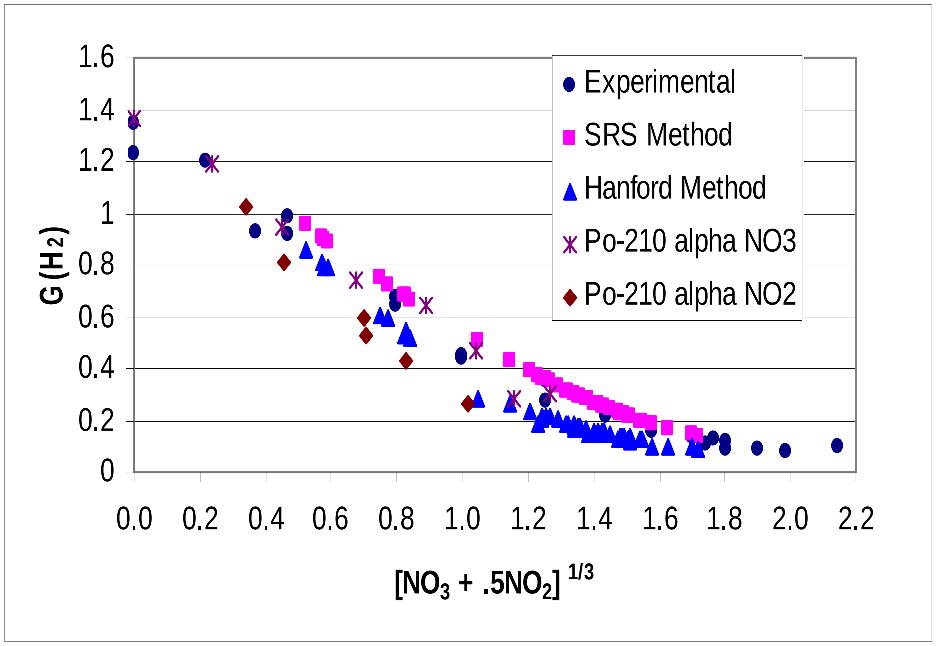

Figure 2-3 Measured and Predicted Values for $G(H_2)$ for Alpha Radiolysis Plotted vs. Cube Root of NO_{eff}. Note: Solids circles are the measured G values in laboratory tests with dissolved alpha emitters [9,10] Solid diamonds and modified x's are the newly found data for nitrite and nitrates [15], solid squares are the G values predicted by the SRS model for SRS HLW tanks and solid triangles are G values predicted by the Hanford model for SRS HLW tanks.

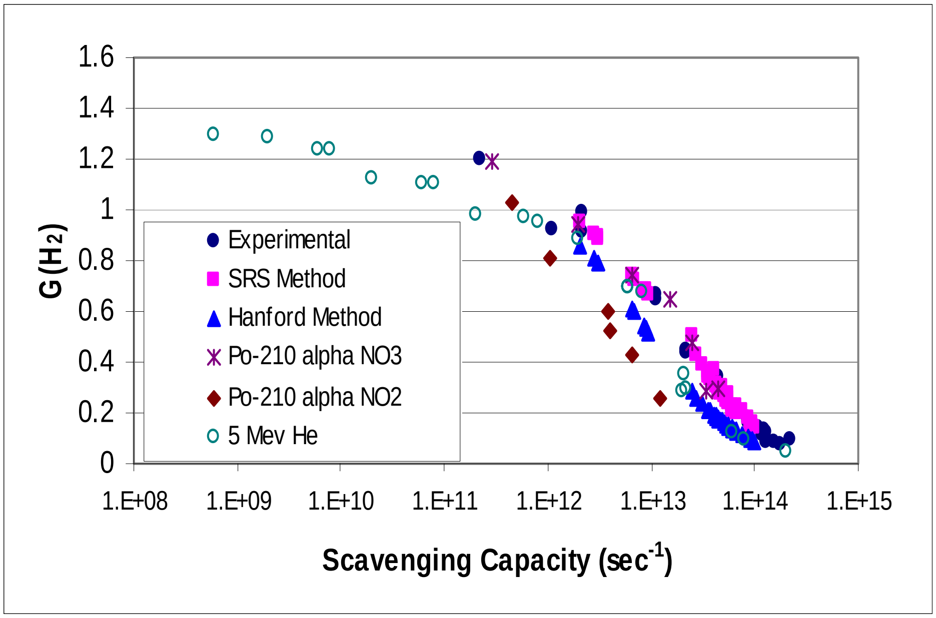

Figure 2-4 Measured and Predicted Values for $G(H_2)$ for Alpha Radiolysis Plotted vs. Summed Scavenging Capacity. Solid circles are the measured G values in laboratory tests with dissolved alpha emitters. [9,10] Solid diamonds and modified x's are the newly found data for nitrite and nitrate solutions [15], solid squares are the G values predicted by the SRS model for SRS HLW tanks and solid triangles are G values predicted by the Hanford model for SRS HLW tanks. The open circles are the G values from the helium ion radiolysis studies on aqueous SeO_4^{2-}, $Cr_2O_7^{2-}$ and H_2O_2 solutions at Notre Dame. [2]

2.3 Predictions for $G(H_2)$ Compared to Experimentally Measured Values for $G(H_2)$ for Four SRS HLW Tanks

Values for $G(H_2)$ were measured in 1991 by Hobbs, et al. for four SRS HLW tanks.[16] In this section we compare these measurements with predicted values for $G(H_2)$ using both the SRS and Hanford models. Table 2-3 shows pertinent data and results for the four HLW tanks. The hydrogen was measured by collecting vapor space samples at the hydrogen monitoring station at the purge air exhaust stack of each of the four HLW tanks with the ventilation system operating. Column six gives the measured H_2 concentrations in ppm in the ventilation air. The total decay heat for each tank was estimated by SRS HLW personnel from the various radionuclides present at the time of sampling (see column five of Table 2-3). This decay heat was only beta gamma heat because alpha data was not available. Using the measured hydrogen concentrations in the ventilation air and the ventilation flow rate at the time of sampling, hydrogen generation rates were calculated in terms of $R(H_2)$ values, or cubic feet of H_2 (at STP) per 10^6 Btu of decay heat. These $R(H_2)$ values (in units of $ft^3/10^6$ Btu) were converted to $G(H_2)$ values (in units of # molecules/100 eV) using the following relationship:

$$G(H_2)\ (\#\ \text{molecules}/100\ \text{eV}) = R(H_2)\ (ft^3/10^6\ \text{Btu})\ \ /\ 94.37\ (ft^3/10^6\ \text{Btu})$$

The nitrate and nitrite concentrations of these tanks at the time of sampling are presented in columns four and five in Table 2-3. Using these concentrations, values for $G(H_2)$ were predicted using the SRS and Hanford models. These results are shown in the final two columns of Table 2-3. Note that for two of the tanks (Tanks 35 and 39) both models predict results that are within ± 10% agreement with the measurements. For the other two tanks (Tanks 32H and 42H) the predictions are conservative in that they predict higher G values than those measured for the tanks. Similar data involving measured hydrogen generation rates that are lower than predicted rates have recently been reported by Hester for SRS HLW Tanks 32H, 33F, 35H, 36H and 38H.[17]

Table 2-3 Comparison of Measured $G(H_2)$ Values in Four SRS HLW Tanks in 1991 by Hobbs et.al [16] with Predicted Values Based on SRS and Hanford Models

Tank	Tank Contents or Usage*	$[NO_3]$* (mol/L)	$[NO_2]$* (mol/L)	Decay Heat* (Btu/hr)	H_2, ppm	$R(H_2)$ ($ft^3/10^6$ Btu)	$G(H_2)$	$G(H_2)$ SRS Model	$G(H_2)$ Hanford Model
32	Sludge Storage	2.88	0.80	485,100	40	1.1±0.6	0.01	0.039	0.040
35	Waste Receipt	3.07	1.52	550,400	78	3.8±1.9	0.04	0.036	0.036
39	Waste Receipt	3.27	0.76	476,400	60	3.4±1.7	0.04	0.037	0.036
42	Sludge Processing	0.16**	0.60	101,900	43	6.7±3.4	0.07	0.17	0.19

* Tank designations, nitrate and nitrite concentrations and estimated decay heats as of late 1991.

** Upon recent review of the 1991 tank farm chemistry data in preparation for this report, this nitrate concentration has been revised (lowered) to accurately reflect the correct value compared to a higher (inaccurate) value of 1.04 presented in the original data set [16].

Figure 2-5 and Figure 2-6 show the beta /gamma plots of experimental laboratory data, the measured values from the HLW Tanks 32, 35, 39 and 42, and the predicted hydrogen G-values for the specific 1991 nitrate and nitrite concentrations in the tanks. Except for Tanks 42 ($(NO_{eff})^{1/3}$ value of 0.77) and 32 ($(NO_{eff})^{1/3}$ value of 1.48), the results are in agreement.

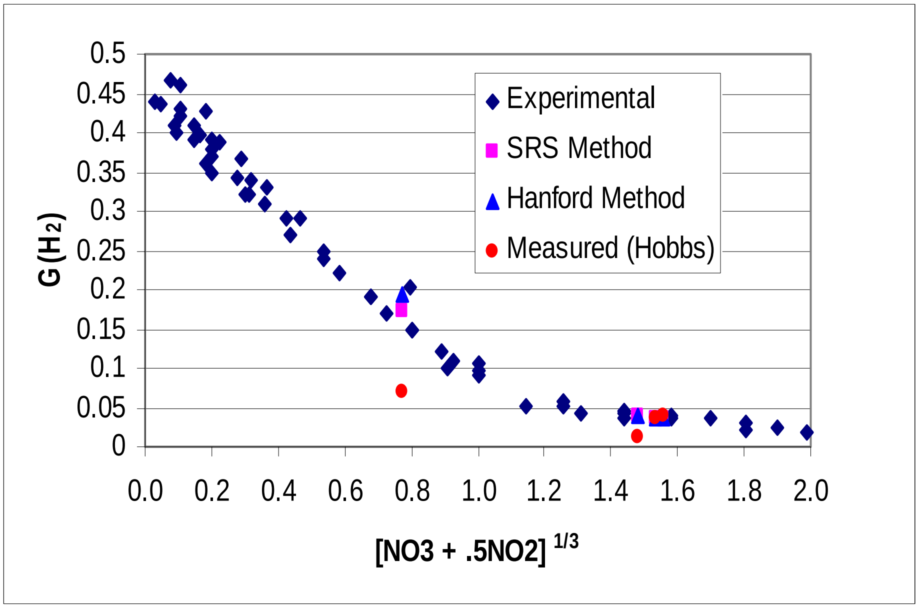

Figure 2-5 Predicted Values for $G(H_2)$ for Beta/Gamma Radiolysis and Measured $G(H_2)$ Values from SRS HLW Tanks 32,35,39 and 42 from 1991 Plotted vs. Cube Root of NO_{eff}

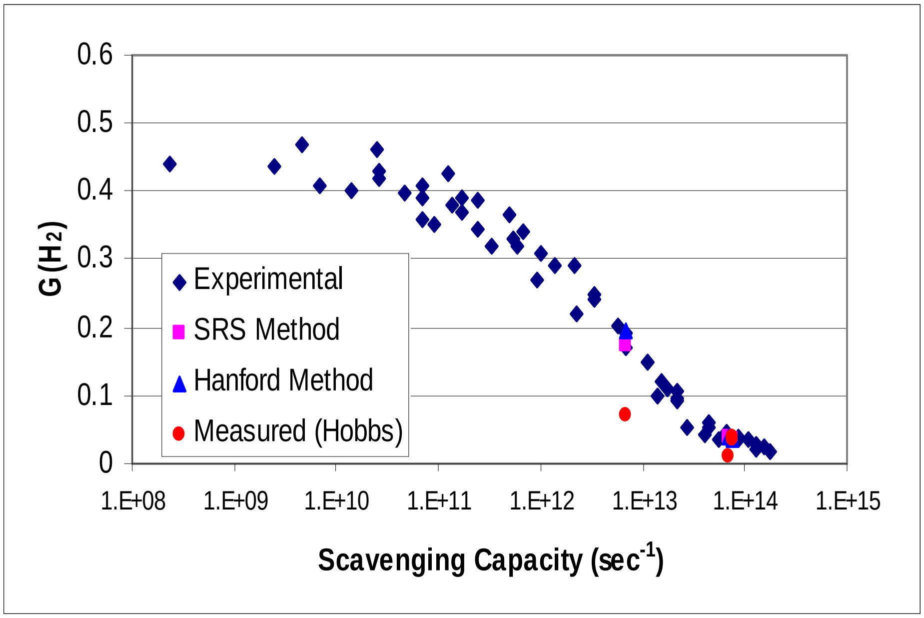

Figure 2-6 Predicted Values for $G(H_2)$ for Beta/Gamma Radiolysis and Measured $G(H_2)$ Values from SRS HLW Tanks 32, 35, 39 and 42 from 1991 Plotted vs. Summed Scavenging Capacity

2.4 Calculation of the H_2 Generation Rates for the Active SRS HLW Tanks as of June, 2004

Radioactive decay heat in the SRS HLW tanks is estimated for both beta/gamma and alpha components based on the radionuclides put into each tank.[12] Three different phases are considered in each tank, a sludge phase, a saturated salt phase, and the liquid supernate fraction. Table 2-4 presents the decay heat projections made in June 2004, for 49 of the SRS HLW tanks.[18] Tanks 16 and 20 have been emptied, thus no data exists for these. As shown in Table 2-4, the higher fraction of decay heat in most of the tanks is associated with the beta/gamma emitting radionuclides in the waste. These fractions are in the final two columns in Table 2-4. The beta/gamma emitting radionuclides in the waste are primarily fission products of U-235 and the alpha emitting radionuclides are actinides.

Table 2-4 Estimated Decay Heats (Btu/hr) in SRS HLW Tanks as of June, 2004

Tank	Sludge Beta-Gamma Heat	Sludge Alpha Heat	Sludge Total Heat	Salt Insolubles Beta-Gamma Heat	Salt Insolubles Alpha Heat	Salt Insolubles Total Heat	Supernate Beta-Gamma Heat	Supernate Alpha Heat	Supernate Total Heat	Overall Beta-Gamma Heat	Overall Alpha Heat	Overall Total Heat	% of Total Heat from Beta-Gamma	% of Total Heat from Alpha
1	1.4E+04	3.2E+02	1.4E+04	4.0E+03	2.5E+02	4.3E+03	3.8E+04	3.0E+00	3.8E+04	5.6E+04	5.7E+02	5.6E+04	99	1
2	1.7E+03	5.2E+01	1.8E+03	4.5E+03	2.8E+02	4.8E+03	1.3E+04	2.8E+00	1.3E+04	1.9E+04	3.3E+02	2.0E+04	98	2
3	1.6E+03	5.1E+01	1.6E+03	4.5E+03	2.8E+02	4.8E+03	1.3E+04	2.8E+00	1.3E+04	1.9E+04	3.3E+02	2.0E+04	98	2
4	9.1E+04	3.3E+03	9.5E+04	2.8E+02	1.8E+01	3.0E+02	5.4E+04	1.0E+01	5.4E+04	1.5E+05	3.4E+03	1.5E+05	98	2
5	6.5E+04	1.4E+03	6.7E+04	0	0	0	1.2E+03	1.1E+00	1.2E+03	6.7E+04	1.4E+03	6.8E+04	98	2
6	7.6E+04	1.3E+03	7.7E+04	0	0	0	1.6E+02	6.8E+00	1.6E+02	7.6E+04	1.3E+03	7.7E+04	98	2
7	2.9E+03	3.6E+02	3.3E+03	0	0	0	3.6E+02	2.7E+00	3.7E+02	3.3E+03	3.6E+02	3.6E+03	90	10
8	2.8E+03	1.8E+02	3.0E+03	0	0	0	5.5E+02	2.4E+00	5.5E+02	3.3E+03	1.9E+02	3.5E+03	95	5
9	1.9E+03	4.2E+01	1.9E+03	4.5E+03	2.8E+02	4.7E+03	1.3E+04	3.0E+00	1.3E+04	2.0E+04	3.2E+02	2.0E+04	98	2
10	2.0E+02	6.7E+00	2.1E+02	1.8E+03	1.1E+02	1.9E+03	9.0E+02	1.1E+00	9.0E+02	2.9E+03	1.2E+02	3.0E+03	96	4
11	1.3E+05	1.9E+04	1.4E+05	0	0	0	4.5E+03	5.7E+00	4.5E+03	1.3E+05	1.9E+04	1.5E+05	87	13
12	1.9E+05	1.8E+04	2.1E+05	5.0E+02	3.1E+01	5.3E+02	0	0	0	1.9E+05	1.8E+04	2.1E+05	91	9
13	1.8E+05	8.7E+03	1.9E+05	0	0	0	1.8E+05	1.8E+01	1.8E+05	3.5E+05	8.7E+03	3.6E+05	98	2
14	4.5E+03	1.1E+02	4.6E+03	1.1E+03	6.7E+01	1.2E+03	1.6E+04	1.5E+00	1.6E+04	2.1E+04	1.8E+02	2.2E+04	99	1
15	1.7E+05	8.2E+03	1.8E+05	0	0	0	0	0	0	1.7E+05	8.2E+03	1.8E+05	95	5
16	0	0	0	0	0	0	0	0	0	0	0	0	-	-
17	1.8E+01	1.8E+01	3.6E+01	0	0	0	0	0	0	1.8E+01	1.8E+01	3.6E+01	50	50
18	2.1E+02	3.9E+01	2.5E+02	0	0	0	2.0E+00	1.6E-01	2.2E+00	2.1E+02	4.0E+01	2.5E+02	84	16
19	4.1E+00	4.5E+00	8.5E+00	1.1E+02	6.8E+00	1.2E+02	3.8E+00	3.1E-01	4.1E+00	1.2E+02	1.2E+01	1.3E+02	91	9
20	0	0	0	0	0	0	0	0	0	0	0	0	-	-
21	1.3E+03	1.1E+02	1.4E+03	0	0	0	5.1E+01	1.7E+01	6.8E+01	1.3E+03	1.3E+02	1.4E+03	91	9
22	2.6E+03	1.9E+02	2.8E+03	0	0	0	7.6E+01	2.5E+01	1.0E+02	2.7E+03	2.1E+02	2.9E+03	93	7
23	6.4E+00	0.0E+00	6.4E+00	0	0	0	3.9E+00	0	3.9E+00	1.0E+01	0	1.0E+01	100	0
24	0	0	0	0	0	0	3.8E+01	0	3.8E+01	3.8E+01	0	3.8E+01	100	0
25	0	0	0	9.2E+03	5.7E+02	9.8E+03	2.2E+04	3.3E+02	2.2E+04	3.1E+04	9.0E+02	3.2E+04	97	3

Table 2-4 (continued) Estimated Decay Heats (Btu/hr) in SRS HLW Tanks as of June, 2004

Tank	Sludge Beta-Gamma Heat	Sludge Alpha Heat	Sludge Total Heat	Salt Insolubles Beta-Gamma Heat	Salt Insolubles Alpha Heat	Salt Insolubles Total Heat	Supernate Beta-Gamma Heat	Supernate Alpha Heat	Supernate Total Heat	Overall Beta-Gamma Heat	Overall Alpha Heat	Overall Total Heat	% of Total from Beta-Gamma	% of Total from Alpha
26	4.7E+03	2.2E+03	6.9E+03	0	0	0	7.5E+04	9.1E+02	7.6E+04	8.0E+04	3.1E+03	8.3E+04	96	4
27	0	0	0	3.9E+03	2.4E+02	4.2E+03	7.3E+04	6.9E+02	7.4E+04	7.7E+04	9.3E+02	7.8E+04	99	1
28	0	0	0	8.6E+03	5.4E+02	9.2E+03	2.7E+04	3.3E+02	2.8E+04	3.6E+04	8.6E+02	3.7E+04	98	2
29	0	0	0	8.6E+03	5.3E+02	9.1E+03	6.5E+03	1.0E+01	6.5E+03	1.5E+04	5.4E+02	1.6E+04	97	3
30	9.7E+02	4.2E+02	1.4E+03	2.1E+03	1.3E+02	2.2E+03	2.1E+05	2.3E+01	2.1E+05	2.2E+05	5.7E+02	2.2E+05	100	0
31	0	0	0	9.6E+03	6.0E+02	1.0E+04	6.1E+04	8.6E+00	6.1E+04	7.1E+04	6.1E+02	7.2E+04	99	1
32	2.4E+05	4.9E+04	2.9E+05	0	0	0	1.4E+05	7.4E+02	1.4E+05	3.8E+05	4.9E+04	4.3E+05	89	11
33	1.3E+05	3.2E+03	1.3E+05	2.5E+03	1.5E+02	2.6E+03	3.5E+04	5.9E+02	3.6E+04	1.7E+05	3.9E+03	1.7E+05	98	2
34	1.9E+05	1.7E+04	2.1E+05	1.6E+03	9.9E+01	1.7E+03	6.4E+04	8.7E+02	6.5E+04	2.6E+05	1.8E+04	2.8E+05	93	7
35	2.2E+05	4.9E+04	2.7E+05	0	0	0	5.3E+04	8.6E+02	5.4E+04	2.7E+05	5.0E+04	3.2E+05	85	15
36	2.4E+02	7.5E+01	3.1E+02	8.7E+03	5.4E+02	9.2E+03	1.4E+05	1.1E+01	1.4E+05	1.5E+05	6.3E+02	1.5E+05	100	0
37	0	0	0	5.8E+03	3.6E+02	6.1E+03	1.6E+05	1.7E+01	1.6E+05	1.7E+05	3.8E+02	1.7E+05	100	0
38	0	0	0	7.2E+03	4.5E+02	7.7E+03	5.7E+03	3.8E+02	6.0E+03	1.3E+04	8.3E+02	1.4E+04	94	6
39	2.1E+05	1.1E+05	3.2E+05	0	0	0	2.8E+04	7.7E+02	2.8E+04	2.4E+05	1.1E+05	3.5E+05	69	31
40	8.8E+04	1.9E+04	1.1E+05	0	0	0	7.1E+02	4.9E+02	1.2E+03	8.9E+04	1.9E+04	1.1E+05	82	18
41	3.1E+02	2.4E+01	3.4E+02	1.0E+04	6.4E+02	1.1E+04	3.8E+03	2.1E+02	4.0E+03	1.4E+04	8.7E+02	1.5E+04	94	6
42	7.3E+03	4.5E+02	7.7E+03	0	0	0	1.6E+05	8.6E+02	1.6E+05	1.6E+05	1.3E+03	1.6E+05	99	1
43	2.3E+04	1.3E+04	3.6E+04	0	0	0	8.2E+03	9.3E+02	9.1E+03	3.1E+04	1.4E+04	4.5E+04	68	32
44	0	0	0	8.4E+03	5.2E+02	8.9E+03	3.9E+04	3.9E+02	4.0E+04	4.8E+04	9.2E+02	4.9E+04	98	2
45	0	0	0	9.3E+03	5.8E+02	9.8E+03	3.1E+04	3.3E+02	3.1E+04	4.0E+04	9.0E+02	4.1E+04	98	2
46	0	0	0	7.2E+03	4.5E+02	7.7E+03	6.4E+04	4.5E+02	6.5E+04	7.1E+04	9.0E+02	7.2E+04	99	1
47	3.3E+03	2.1E+03	5.4E+03	9.1E+03	5.6E+02	9.6E+03	8.2E+03	3.1E+02	8.5E+03	2.0E+04	3.0E+03	2.3E+04	87	13
48	0	0	0	0	0	0	1.9E+02	0	1.9E+02	1.9E+02	0	1.9E+02	100	0
49	0	0	0	2.6E+02	1.6E+01	2.7E+02	1.5E+04	0	1.5E+04	1.6E+04	1.6E+01	1.6E+04	100	0
50	0	0	0	0	0	0	7.7E-02	0	7.7E-02	7.7E-02	0	7.7E-02	100	0
51	1.8E+04	6.7E+03	2.5E+04	0	0	0	1.9E+02	1.0E+02	2.9E+02	1.9E+04	6.8E+03	2.5E+04	73	27

The overall total decay heats in Table 2-4 for each tank for both beta/gamma and alpha radiation were used in calculating the total rate of H_2 generation for each tank predicted by the SRS and Hanford models. Pertinent data and results are given in Table 2-5. Concentrations of nitrite and nitrate in the tanks are given in columns two and three of the table. These concentrations were used in both models to predict G values for beta/gamma radiation and for alpha radiation. These G values were then converted to R values (ft^3 H_2 per 10^6 Btu) using the equation given in Section 2.3. The R values predicted from the SRS model for beta/gamma radiation and for alpha radiation are shown in columns six and seven, respectively. R values predicted by the Hanford model are given in columns nine and ten. These R values were then multiplied by the overall beta/gamma and alpha heats for each tank to give H_2 generation rates (ft^3/hr) for each type of radiation. For each tank the sum of each of these rates is then the total H_2 generation rate. The total rate predicted by the SRS model for each tank is presented in column eight of the table. The rates predicted from the Hanford model are presented in column eleven. Column twelve of Table 2-5 shows the percentage change in going from the SRS prediction to the Hanford prediction. The last column of Table 2-5 shows whether the Hanford prediction is more, less than, or equal to within ±10% of the SRS prediction. Note that in 25 of the 47 tanks the predictions are within ±10% of each other. The Hanford prediction is more conservative for 13 tanks (maximum of 19% more) and the SRS prediction is more conservative for 9 tanks (maximum of 30% more). The tanks where the SRS model is more conservative are the tanks with the largest alpha heat load compared to the beta/gamma.

Table 2-5 Comparison of Predicted H_2 Generation Rates (ft^3/hr) in SRS Tanks Based on the SRS and Hanford Models

Tank	NO_2^- Conc. (M)	NO_3^- Conc, (M)	Overall Beta-Gamma Heat (10^6Btu/hr)	Overall Alpha Heat (10^6Btu/hr)	SRS Model Beta/Gamma R-value ($ft^3/10^6Btu$)	SRS Model Alpha R-value ($ft^3/10^6Btu$)	SRS Model Total (ft^3/hr)	Hanford Model Beta/Gamma R-value ($ft^3/10^6Btu$)	Hanford Model Alpha R-value ($ft^3/10^6Btu$)	Hanford Model Total (ft^3/hr)	Percentage Change, SRS to Hanford	Hanford* Model MORE or LESS Conservative
1	2.75	2.00	5.6E-02	5.7E-04	3.6	20.9	2.1E-01	4.3	13.1	2.5E-01	19	More
2	3.04	2.25	1.9E-02	3.3E-04	3.4	18.5	7.2E-02	3.9	11.9	7.9E-02	10	NA
3	2.26	1.71	1.9E-02	3.3E-04	4.2	24.8	9.0E-02	4.9	15.1	1.0E-01	11	More
4	1.57	2.01	1.5E-01	3.4E-03	4.3	25.1	7.1E-01	4.7	14.5	7.4E-01	4	NA
5	0.68	2.32	6.7E-02	1.4E-03	4.5	26.3	3.4E-01	4.6	14.1	3.3E-01	-3	NA
6	0.61	0.15	7.6E-02	1.3E-03	16.3	68.6	1.3E+00	18.4	56.4	1.5E+00	15	More
7	1.97	1.47	3.3E-03	3.6E-04	4.9	28.3	2.6E-02	5.6	17.2	2.4E-02	-8	NA
8	0.74	0.19	3.3E-03	1.9E-04	14.9	64.3	6.2E-02	16.8	51.4	6.6E-02	6	NA
9	3.20	1.90	2.0E-02	3.2E-04	3.5	20.1	7.7E-02	4.2	13.0	8.8E-02	14	More
10	0.36	3.82	2.9E-03	1.2E-04	3.3	17.4	1.1E-02	3.1	9.5	1.0E-02	-9	NA
11	3.24	3.36	1.3E-01	1.9E-02	3.2	13.6	6.7E-01	2.9	8.9	5.4E-01	-19	Less
12	1.70	1.45	1.9E-01	1.8E-02	5.2	29.9	1.5E+00	5.8	17.8	1.4E+00	-7	NA
13	2.23	1.84	3.5E-01	8.7E-03	4.1	23.8	1.6E+00	4.7	14.4	1.8E+00	13	More
14	2.90	3.70	2.1E-02	1.8E-04	3.3	13.1	7.2E-02	2.7	8.4	6.0E-02	-17	Less
15	0.10	1.10	1.7E-01	8.2E-03	9.5	47.4	2.0E+00	8.7	26.6	1.7E+00	-15	Less
19	0.99	1.01	1.2E-04	1.2E-05	7.7	40.7	1.4E-03	8.0	24.4	1.2E-03	-14	Less
21	0.24	0.06	1.3E-03	1.3E-04	23.0	85.7	4.1E-02	25.1	76.1	4.2E-02	2	NA
22	0.23	0.08	2.7E-03	2.1E-04	22.6	84.9	8.0E-02	24.6	74.5	8.3E-02	4	NA
23	0.20	0.04	1.0E-05	0	24.7	89.9	2.6E-04	26.9	81.1	2.8E-04	8	NA
24	0.28	0.07	3.8E-05	0	22.2	83.9	8.4E-04	24.5	74.2	9.3E-04	11	More
25	1.16	1.36	3.1E-02	9.0E-04	6.1	34.1	2.2E-01	6.4	19.7	2.2E-01	0	NA
26	1.73	1.58	8.0E-02	3.1E-03	4.9	28.4	4.8E-01	5.5	16.8	4.9E-01	2	NA
27	1.68	1.21	7.7E-02	9.3E-04	5.8	32.8	4.8E-01	6.5	19.9	5.2E-01	8	NA

* Hanford values MORE conservative give > 10% change, LESS conservative give > (-)10% change, NA values within +/- 10%

Table 2-5 (continued) Comparison of Predicted H_2 Generation Rates (ft^3/hr) in SRS Tanks Based on the SRS and Hanford Models

Tank	NO_2^- Conc. (M)	NO_3^- Conc, (M)	Overall Beta-Gamma Heat (10^6Btu/hr)	Overall Alpha Heat (10^6Btu/hr)	SRS Model Beta/Gamma R-value ($ft^3/10^6$Btu)	SRS Model Alpha R-value ($ft^3/10^6$Btu)	SRS Model Total (ft^3/hr)	Hanford Model Beta/Gamma R-value ($ft^3/10^6$Btu)	Hanford Model Alpha R-value ($ft^3/10^6$Btu)	Hanford Model Total (ft^3/hr)	Percentage Change, SRS to Hanford	Hanford* Model MORE or LESS Conservative
28	2.26	2.17	3.6E-02	8.6E-04	3.7	21.3	1.5E-01	4.2	12.9	1.6E-01	7	NA
29	1.40	1.28	1.5E-02	5.4E-04	6.0	33.6	1.1E-01	6.5	19.9	1.1E-01	0	NA
30	1.97	1.19	2.2E-01	5.7E-04	5.5	31.4	1.2E+00	6.3	19.4	1.4E+00	17	More
31	2.44	1.87	7.1E-02	6.1E-04	3.9	22.8	2.9E-01	4.6	14.0	3.3E-01	14	More
32	2.88	2.06	3.8E-01	4.9E-02	3.5	20.1	2.3E+00	4.1	12.7	2.2E+00	-4	NA
33	1.16	1.35	1.7E-01	3.9E-03	6.1	34.3	1.2E+00	6.5	19.8	1.2E+00	0	NA
34	1.18	2.27	2.6E-01	1.8E-02	4.2	24.6	1.5E+00	4.5	13.7	1.4E+00	-7	NA
35	1.13	2.66	2.7E-01	5.0E-02	3.8	21.8	2.1E+00	4.0	12.2	1.7E+00	-19	Less
36	1.89	1.57	1.5E-01	6.3E-04	4.7	27.6	7.2E-01	5.4	16.5	8.1E-01	13	More
37	2.11	1.60	1.7E-01	3.8E-04	4.5	26.4	7.6E-01	5.2	16.0	8.8E-01	16	More
38	2.09	2.40	1.3E-02	8.3E-04	3.6	20.4	6.3E-02	4.0	12.2	6.1E-02	-3	NA
39	1.11	1.89	2.4E-01	1.1E-01	4.9	28.4	4.3E+00	5.2	15.8	3.0E+00	-30	Less
40	0.49	0.18	8.9E-02	1.9E-02	17.0	70.4	2.9E+00	18.7	57.1	2.8E+00	-3	NA
41	0.57	4.08	1.4E-02	8.7E-04	3.2	15.7	6.0E-02	2.9	8.8	4.9E-02	-18	Less
42	2.55	2.04	1.6E-01	1.3E-03	3.7	21.2	6.3E-01	4.3	13.1	7.2E-01	14	More
43	1.55	1.72	3.1E-02	1.4E-02	4.8	27.9	5.5E-01	5.3	16.2	3.9E-01	-29	Less
44	1.34	1.10	4.8E-02	9.2E-04	6.7	36.5	3.5E-01	7.2	22.0	3.6E-01	3	NA
45	1.86	1.40	4.0E-02	9.0E-04	5.1	29.6	2.3E-01	5.8	17.9	2.5E-01	9	NA
46	2.21	1.82	7.1E-02	9.0E-04	4.1	24.1	3.2E-01	4.8	14.6	3.5E-01	9	NA
47	0.54	3.24	2.0E-02	3.0E-03	3.5	20.0	1.3E-01	3.5	10.8	1.0E-01	-23	Less
48	0.59	0.25	1.9E-04	0	15.0	64.9	2.8E-03	16.3	50.0	3.1E-03	11	More
49	2.90	2.27	1.6E-02	1.6E-05	3.4	18.8	5.4E-02	3.9	11.9	6.1E-02	13	More
50	0.01	1.87	7.7E-08	0	6.3	35.0	4.8E-07	5.8	17.9	4.5E-07	-6	NA
51	0.72	0.24	1.9E-02	6.8E-03	14.4	63.0	7.0E-01	16.0	48.9	6.3E-01	-10	NA

* Hanford values MORE conservative give > 10% change, LESS conservative give > (-)10% change, NA values within +/- 10%

3.0 CONCLUSIONS

Results of calculations presented in this report support the following conlusions.

For beta gamma radiation, the following results were found when the two correlations were used to predict G values for H_2 for the 47 HLW Tanks in service at SRS (assuming hypothetically that 100% of the radiation is from beta/gamma radiation).

- For 7 of the 47 tanks the new mechanism (Hanford model) predicted G values that were lower by 3 to 17% than the rates predicted by the current mechanism (SRS correlation).

- For the remaining 40 tanks, the new mechanism (Hanford model) predicted G values that were 2 to 18% higher than those predicted by the current mechanism (SRS model). For 17 tanks the results were higher by only 11% or less. For the remaining 23 tanks, the results were up to 20% higher, or more conservative.

For alpha radiation, the following result was found when the two models were used to predict G-values for H_2 for the 47 HLW Tanks in service at SRS (assuming hypothetically that 100% of the radiation is from alpha radiation).

- For all 47 tanks, the current mechanism (SRS model) predicted G values that were 10 to 49% higher than the rates predicted by the new mechanism (Hanford correlation). Thus, in all cases examined, the current mechanism is more conservative than the new mechanism.

For four SRS tanks, we compared measured G values to those predicted by the two different correlations, assuming all radiation is from beta/gamma. For two of the tanks the measured G values for H_2 production were 3 to 4X lower than those predicted by either mechanism indicating that in these two cases predictions by either correlation were conservative. Measured G-values for the other two tanks were in good agreement with both correlations.

The predictions of the models for total H_2 generation rates from the 47 active SRS waste were, for the most part, similar. For example, the predictions for both models for 25 tanks agreed within ±10% of each other. For the remaining 22 tanks, the SRS prediction was more conservative for 9 tanks (maximum 29% higher) and the Hanford prediction was more conservative for 13 tanks (maximum 19% higher).

4.0 SUGGESTIONS FOR FUTURE WORK

In this section we briefly discuss work that would place the SRS model on a firmer basis. Both the SRS model is primarily based on tests with clear solutions rather than slurries. The slurries that have been irradiated to furnish data for the model are primarily cesium tetraphenylborate slurries and not sludge slurries.[8] Also, a very limited amount of work has been done with salt slurries.[8] Further, nearly all the solutions irradiated from which data was used to formulate the SRS model were acid or neutral aqueous solutions. For the Hanford model the solutions were all neutral solutions containing no solids. A summary of the suggested work is given below.

- Using the Co-60 gamma ray sources at SRNL we suggest an investigation of the radiolysis of caustics slurries that more closely simulate the SRS HLW slurries. Such work would give more realistic measurements applicable to H_2 production from the beta gamma radiation in the HLW tanks. Tests could also be designed to determine the amount of H_2 that is retained in a waste tank by the sludge or salt slurries during the quiescent time (Q-time) of the slurry. This could lead to a better estimation of the necessary Q-times. It has to be said however that these gamma radiolysis tests may not be definitive in determining whether the SRS or the Hanford model is more mechanistically correct. But, the results of such tests would certainly be more applicable to the HLW tanks at SRS than tests with clear neutral solutions.

- As mentioned before, the SRS model for predicting $G(H_2)$ for alpha radiolysis is based on the radiolysis of nitrate solutions. These experiments used either Cm-244[9] or Po-210[10] as the source of the alpha particles and the experiments were performed in acid solutions where these isotopes are soluble. The newly found results for alpha radiolysis of nitrite solutions using dissolved Po-210 were also presumably done in acid solutions although it is not specifically stated in their paper what the pH of their solutions were.[15] The HLW solutions at SRS and at Hanford are caustic. The efficiency of nitrate and nitrite to scavenge the precursors of H_2 may be different in caustic solutions compared to acid solutions. It is now possible using 5MeV accelerated helium ions to obtain alpha radiolysis data for caustic solutions that more closely simulate the HLW solutions. An accelerator at the University of Notre Dame could be used for these irradiations. Both nitrate and nitrate solutions as well as combinations of them could be irradiated and $G(H_2)$ measured. Such data could be used to further refine the SRS model. It would also be applicable to the Hanford model where <u>neither</u> nitrate or nitrite data were used to develop the model. We suggest that the possibility of this collaborative study between SRNL and Notre Dame be explored.

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APPENDIX A.

TEXT OF THE DNFSB MEMORANDUM SENT TO SRS PERSONNEL

TEXT OF THE DNFSB MEMORANDUM SENT TO SRS PERSONNEL

(Draft – May 13, 2004)

Questions on Hydrogen Generation in SRS HLW Tanks

1. For hydrogen generation due to radiolysis of water containing scavengers such as nitrate and nitrite, SRS uses the relationship for molecular hydrogen yields as a function of the cube root of the scavenger concentration. Additionally the scavenger concentration is modified using "effective nitrate" defined as the sum of nitrate and one half the nitrite concentrations. This is based on past data that nitrate and nitrite scavenging rates for the aqueous electron, the precursor to molecular hydrogen, are in the ratio of 2:1. However, researchers at Notre Dame recently discovered a new mechanism for radiolysis of water that indicated two precursors for molecular hydrogen, the unhydrated electron as well as the aqueous electron. The scavenging rates of nitrate and nitrite for the unhydrated electron are different than the aqueous electron; their scavenging rates are in the ratio of approximately 4:1. This would imply that scavenging of the unhydrated electron precursor would use an effective nitrate defined as the sum of the nitrate and one-fourth the nitrite concentration. The "weighted effective nitrate" should be proportional product of the lifetimes of each of the precursor species and its scavenging rate constant.

Will the new radiolysis mechanism be incorporated into the SRS Hydrogen Generation Model?

If the new radiolysis mechanism is used, would the resultant Hydrogen Generation Model be more or less conservative than the one presently being used?

2. The Hydrogen Generation Model due to alpha is based on data that has no nitrite in the analysis (see WSRC-TR-98-00303, Rev 0). There appears to be enough literature data for the scavenging effects of nitrite to be incorporated into the fitted equation for alpha generation of molecular hydrogen. Also, recent information indicates that the defined effective nitrate is not true for at least one of the precursors of hydrogen (see 1 above).

Will additional nitrite data be added to the analysis for generating a fitted equation for the alpha Hydrogen Generation Model?

If real nitrite data is used, is the fitted equation more or less conservative than the one now presently being used?

If the new radiolysis mechanism is also incorporated into the alpha Hydrogen Generation Model, is it more or less conservative than the one now presently being used?

3. How are possible Buoyant Displaced Gas Release Events (BDGREs) mitigated at SRS?

4. Are there any indications of gas retention in the sludges in HLW at SRS? If there are, what controls are in place to mitigate the effects of gas releases or a BDGRE?

APPENDIX B

EQUATIONS USED IN THE SRS AND HANFORD MODELS TO PREDICT VALUES FOR G(H_2) AT VARIOUS NITRATE AND NITRITE CONCENTRATIONS

EQUATIONS USED IN THE SRS AND HANFORD MODELS TO PREDICT VALUES FOR G(H_2) AT VARIOUS NITRATE AND NITRITE CONCENTRATIONS

Equations Used in in the SRS Model to Predict H_2 Generation Rates in SRS HLW Tanks

The following equations are currently used to predict hydrogen generation rates in SRS HLW tanks.[2] Hydrogen G-values from beta/gamma radiation are given as:

$$G(H_2)_{\beta/\gamma} = 0.466-0.51\cdot[NO_{eff}]^{1/3}+0.14\ [NO_{eff}]^{2/3}+0.0055\ [NO_{eff}] \qquad (1)$$

With $$[NO_{eff}] = [NO_3] + 0.5\ [NO_2]. \qquad (2)$$

The calculated value for G(H_2) is then increased by 10% to bound the experimental data and be conservative. The hydrogen generation rate in terms of R-values, or ft^3 H_2/ 10^6 Btu (including the 10% increase) is given by the following equation.

$$R_{\beta/\gamma} = 48.36 – 52.78 * [NO_{eff}]^{1/3} + 14.1 * [NO_{eff}]^{2/3} + 0.572 * [NO_{eff}] \qquad (3)$$

Similar correlations are used for hydrogen generation prediction involving alpha radiolysis.[2] These are as follows:

$$G_\alpha = 1.3 - .79 * [NO_{eff}]^{1/3} - 0.13 * [NO_{eff}]^{2/3} + 0.11 * [NO_{eff}] \qquad (4)$$

This correlation is also increased by 10% to bound experimental data to give the hydrogen generation in terms of R-values for alpha radiation, as:

$$R_\alpha = 134.7 – 82.3 * [NO_{eff}]^{1/3} – 13.6 * [NO_{eff}]^{2/3} + 11.8 * [NO_{eff}] \qquad (5)$$

Equations Used in in the Hanford Model to Predict H_2 Generation Rates

The following equations correlate hydrogen G-values with the rate coefficients and scavenger concentrations for both the dry electron and the hydrated electron.[4] The G-value predicted for hydrogen from beta/gamma radiolysis is given as:

$$G(H_2)_{\beta/\gamma} = G_0(H_2)_{\beta/\gamma} * [\tau^{-1} / (\tau^{-1} + k[S])] +$$

$$(G(H_2)_{,[S]=0})_{\beta/\gamma} – G_0(H_2)_{\beta/\gamma}) * [\tau_2^{-1} / (\tau_2^{-1} + k_2[S])] \qquad (6)$$

with, $G_0(H_2)_{\beta/\gamma} = 0.34$
$G(H_2)_{,[S]=0})_{\beta/\gamma} = 0.45$

τ = 110 femtoseconds (fs) = lifetime of precursor to hydrated electron
τ_2 = 12.3 nanoseconds (ns), fitted parameter

and the rate coefficients (k) values at zero ionic strength from Reference 13 given as:

k for (NO_3 + precursor to solvated electron) = 2.19E13$M^{-1}sec^{-1}$
k for (NO_2 + precursor to solvated electron) = 0.57E13M^{-1} sec^{-1}
k_2 for ($NO_3 + e_{aq}^-$) = 9.7E9M^{-1} sec^{-1}
k_2 for ($NO_2 + e_{aq}^-$) = 4.1E9M^{-1}s sec^{-1}

Substituting in the fitted parameters for nitrate and nitrite and the known rate coefficients into the equation above, the following equation expresses the G-value for beta/gamma radiolysis of solutions containing nitrate and nitrite:

$$G(H_2)_{\beta/\gamma} = 0.34 * [\ 1 / \{1 + 2.42[NO_3^-] + 0.627[NO_2^-]\}] +$$

$$0.11 * [1 / \{1 + 119.3[NO_3^-] + 50.4[NO_2^-]\}] \qquad (7)$$

Note that equation 7 differs slightly in the last term for the coefficient for nitrite (50.4) vs. the coefficient (43) used in reference 4. This is due to the slight difference in the rate coefficient value used for the reaction of nitrite with the hydrated electron. Equation 7 above uses the rate coefficient from reference 4 (4. 1E9M^{-1}s sec^{-1}) vs. a slightly lower value shown in reference 4 and 5 of 3.5E9M^{-1}s sec^{-1}

Similar correlations are used for hydrogen generation prediction involving alpha radiolysis.[5] These are as follows:

$$G(H_2)_\alpha = G_0(H_2)_\alpha * [\tau^{-1} / (\tau^{-1} + k[S])] +$$

$$(G(H_2)_{,[S]=0})_\alpha - G_0(H_2)_\alpha) * [\tau_2^{-1} / (\tau_2^{-1} + k_2[S])] \qquad (8)$$

with, $G_0(H_2)_\alpha = 1.05$
$G(H_2)_{,[S]=0})_\alpha = 1.4$

τ = 110 femtoseconds (fs) = lifetime of precursor to hydrated electron
τ_2 = 400 nanoseconds (ns), fitted parameter

and rate coefficients (k) values at zero ionic strength are the same as those given above since the rate coefficient is independent of the type of radiation the formed the reactant.

Substituting the fitted parameters for nitrate and nitrite and the known rate coefficients into the equation above, the following equation expresses the G-value for alpha radiolysis of solutions containing nitrate and nitrite:

$$G(H_2)_\alpha = 1.05 * [\ 1 / \{1 + 2.42[NO_3^-] + 0.627[NO_2^-]\}] +$$

$$0.35 * [1 / \{1 + 3880[NO_3^-] + 1640[NO_2^-]\}] \qquad (9)$$

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