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## MEASUREMENT AND PREDICTION OF RADIOLYTIC HYDROGEN PRODUCTION IN DEFENSE WASTE PROCESSING SLURRIES AT SAVANNAH RIVER SITE

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### ABSTRACT

This paper presents results of measurements and predictions of radiolytic hydrogen production rates from two actual process slurries in the Defense Waste Processing Facility (DWPF) at Savannah River Site (SRS). Hydrogen is a flammable gas and its production in nuclear facilities can be a safety hazard if not mitigated. Measurements were made in the Shielded Cells of Savannah River National Laboratory (SRNL) using a sample of Sludge Batch 3 (SB3) currently being processed by the DWPF. Predictions were made using published values for rates of radiolytic reactions producing H<sub>2</sub> in aqueous solutions and the measured radionuclide and chemical compositions of the two slurries. The agreement between measured and predicted results for nine experiments ranged from complete agreement to 24% difference. This agreement indicates that if the composition of the slurry being processed is known, the rate of radiolytic hydrogen production can be reasonably estimated.

### INTRODUCTION

There is an aggressive program at SRS to remove and stabilize the radioactive high level waste (HLW) sludge slurries that are stored in the large underground tanks at SRS. Each tank can hold approximately 35 hundred cubic meters of HLW. Currently the DWPF is converting this waste into a durable borosilicate glass for permanent geologic disposal.

The wastes are stored as caustic sludge slurries. The main components in the insoluble solids in the caustic slurries are primarily hydrous oxides of Fe, Al, and other elements that were used in processing operations at SRS. Most of the radionuclides (actinides and U-235 fission products) are insoluble in caustic and are also in the sludge solids. The supernate of the slurries contain dissolved NaOH along with soluble nitrate, nitrite, and sulfate salts. The supernate also contains most of the fission product Cs-137 because it is soluble in caustic.

Hydrogen is continuously produced in the slurries by radiolysis of the water by the beta and alpha particles and the gamma rays from the radionuclides. In the caustic slurries the precursors of H<sub>2</sub> are aqueous electrons (e<sub>aq</sub><sup>-</sup>) and H atoms (H). [1] Based on data from many experimental studies, the chemical reactions that form H<sub>2</sub> are



with Reaction 1 being more important than Reaction 2 and Reaction 2 more important than Reaction 3. These studies are well summarized in Reference 1.

Hydrogen production in the HLW storage tanks and in the process tanks in the DWPF is a concern because of the possible formation of flammable mixtures in the vapor spaces of the tanks. A previous paper has discussed radiolytic H<sub>2</sub> production in the storage tanks and what is being done to prevent formation of flammable mixtures in those tanks. [2] This paper discusses radiolytic H<sub>2</sub> production in two DWPF process tanks. The DWPF tanks usually process ~30 cubic meters of slurry in these tanks.

To determine the rate of radiolytic H<sub>2</sub> production from process slurries in the DWPF, measurements of radiolytic H<sub>2</sub> production were made in the Shielded Cells of Savannah River National Laboratory (SRNL) using a sample of the slurry from Sludge Batch 3 (SB3) that is currently being processed by the DWPF. Measurements were made on two types of slurries that are processed in the DWPF. One was the caustic sludge slurry itself as it would be received by the DWPF for processing. The other was a slurry that resulted process steps in the DWPF. These steps include the addition of nitric and formic acids to the slurry. Nitric acid is added to destroy nitrites and carbonates in the slurry and to adjust the rheology of the slurry. Formic acid is added to reduce mercury so it can be steam stripped from the slurry. These steps occur in the Sludge Receipt and Adjustment Tank (SRAT) in the DWPF. To obtain a sample of SRAT slurry for measuring radiolytic H<sub>2</sub> production in Shielded Cells, the DWPF SRAT process was performed on a sample of SB3 slurry in the Shielded Cells. Measurements of radiolytic H<sub>2</sub> production for the both the sludge slurry and the SRAT slurry were then performed. The results were then compared to predictions based the radionuclides and chemical compositions of SB3 slurries coupled with published parameters for the radiation chemical reactions induced by alpha, beta and gamma radiations on water in the slurries. The predictions were in reasonable agreement with the results confirming that estimates of the radiolytic production of H<sub>2</sub> can be made if the composition of the slurry is known.

## **METHODOLOGY AND RESULTS FOR MEASUREMENTS OF RADIOLYTIC RATE OF HYDROGEN PRODUCTION IN SB3 SLUDGE AND SRAT SLURRIES**

### **General Description of Experimental Method**

Because of the intense radioactivity of the SB3 sample, all the radiolysis tests were performed remotely in the SRNL Shielded Cells. They were conducted at ambient the temperatures in the cells (nominally 15-23 °C).

For the experiments, an apparatus containing four vessels each equipped with an agitator, thermocouple, and a connection for a purge line was designed, fabricated and put into one of the Shielded Cells. For an experiment, each vessel could be attached to an air purge line that passed out of the back of the cell and flowed through a sampling system of a gas chromatograph (GC) that was in a radiological hood. The purge line then returned to the cell and vented in the cell. The vent gas was exhausted with the normal filtered air exhaust from the cell. (In this way the possibility of contaminated air from the vessels was prevented from exhausting into the back area of the cells.) The purge rate was usually 10 to 100 standard cubic centimeters per minute (sccm) from a calibrated mass flow control meter. At set intervals (usually 3 or 30 minutes) small samples of gas were automatically removed from the purge line by a pumping system in the GC. The sample was automatically injected into the GC and concentration of H<sub>2</sub>, in the purge air was measured.

Prior to putting a known amount of SB3 sludge or SRAT slurry into a vessel or performing an experiment after a slurry was already in a vessel, the slurry was agitated to remove as much of the

radiolytic H<sub>2</sub> as possible that had accumulated in the slurry before the experiment. When an experiment was initiated, the air that purged the vapor space of the vessel was started and passed through the pumping system of the GC. Radiolytic H<sub>2</sub> immediately started to accumulate in the slurry and diffuse into the vapor space of the vessel where it was swept through the sampling system of the GC, sampled and analyzed. The concentrations of the above gases were measured by the GC at the set sampling interval of the GC. In this manner the concentration of H<sub>2</sub> in the vapor space of a vessel was determined as a function of elapsed time after the initial agitation. At a known time in an experiment the slurry was agitated and the radiolytic H<sub>2</sub> that had accumulated in the slurry was released to the vapor space and also purged from the vessel and analyzed. After all of this H<sub>2</sub> had been removed from the slurry, the experiment was terminated. An experiment usually lasted from two to several days.

By knowing the concentrations of the H<sub>2</sub> in the purge air, the sampling frequency, and the flow rate of the purge gas, the rates of H<sub>2</sub> being purged from the vessel in terms of moles of H<sub>2</sub> per minute is given by Equation 1.

$$FR(H_2) = (H_2)_c \cdot (PR)_{air} \cdot \frac{1}{10^6} \cdot \frac{1 \text{ mol}}{22,400 \text{ cm}^3} \quad (\text{Eq. 1})$$

where  $FR(H_2)$  is flow rate of H<sub>2</sub> in moles per minute being purged from the vessel,  $(H_2)_c$  is the concentration of H<sub>2</sub> measured by the GC, and  $(PR)_{air}$  is the purge rate of the air in sccm. The constants convert from ppm H<sub>2</sub> to moles per minute. The constant of 22,400 cm<sup>3</sup>/mol is used because the mass flow control meter was calibrated to convert the mass of air flowing through the meter to a molar volume at 0 °C. Performing the experiment at ambient temperature did not affect the results because the change in temperature did not change the volumetric concentration of H<sub>2</sub> in the purge air being analyzed by the GC.

The total moles of H<sub>2</sub> purged from the vessel during a sampling interval was estimated by calculating the area of a trapezoid the base of which was the length of time of the sampling interval and the height equal to the average of the flow rate of H<sub>2</sub> at the beginning of that sampling interval and at the end of that sampling interval. The following equation applies for each interval.

$$(H_2)_i = \frac{1}{2} \cdot \left( [FR(H_2)]_i + [FR(H_2)]_{i-1} \right) \cdot t_i \cdot \frac{60 \text{ min}}{\text{h}} \quad (\text{Eq. 2})$$

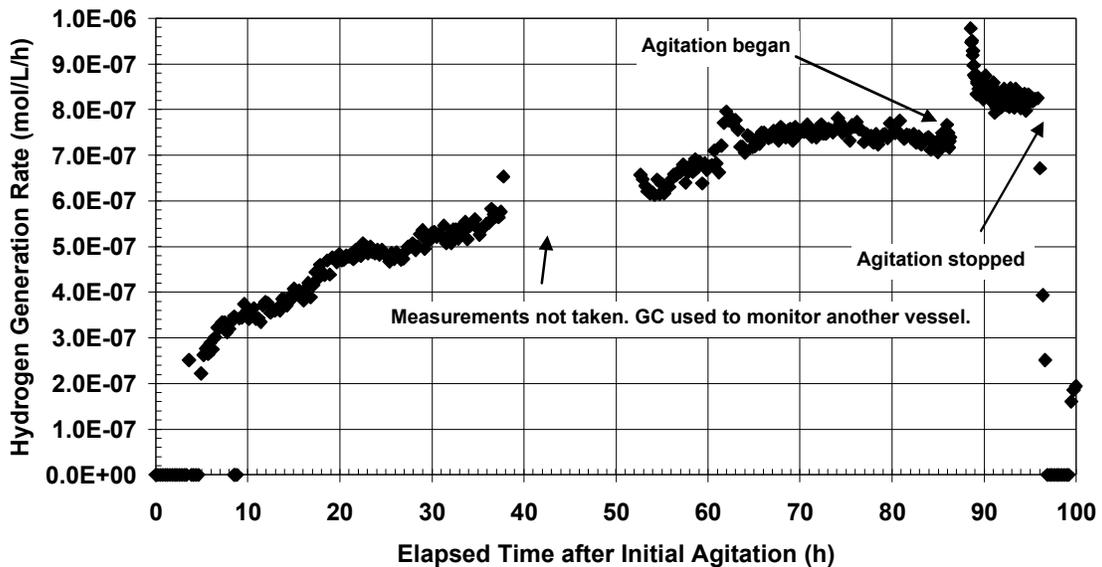
where  $(H_2)_i$  is the moles of H<sub>2</sub> purged from the vessel during sampling interval  $i$ ,  $[FR(H_2)]_i$  is flow rate of H<sub>2</sub> in moles per minute calculated from Equation 1 at the end of interval  $i$ ,  $[FR(H_2)]_{i-1}$  is the flow rate calculated at the end of the previous interval, and  $t_i$  is the time length of the interval in hours. Care was taken to adjust the sampling frequency so that the concentrations measured by the GC were representative of the continuous evolution of H<sub>2</sub> purged from the vessel. For example when the slurry was being agitated the sampling frequency was as short as possible (3 minutes) because H<sub>2</sub> was being released rapidly from the slurry due to the agitation. In this manner the total moles purged from the vapor space of a vessel during an experiment could be calculated by summing the amount released during agitation and the amount that diffused from the slurry while it was not agitated.

**Measurements and Results for the SB3 Sludge Slurry**

Experiments with the sludge slurry were performed by using a known amount of slurry from which the H<sub>2</sub> had been initially removed by agitation to set undisturbed in a vessel while the vessel was being purged. During this time the concentration of H<sub>2</sub> in the vapor space of the vessel was measured at set time intervals for the total time before the slurry was agitated. It was also measured in the vapor space during agitation of the vessel and a short time after agitation. A total of 13 tests were performed with samples of the sludge slurry using this method. The most reliable results were achieved from 7 long term tests where the concentration of the H<sub>2</sub> in the vapor space became constant prior to agitation of the slurry. Experimental details of these experiments are given in Table I. After the concentration of H<sub>2</sub> reached a steady state in the vapor space, the slurry was agitated and the amount of H<sub>2</sub> that had accumulated in the slurry was measured. Results for experiment DP-2 are shown in Figure 1.

Table I. Experimental Details of Long Term Purged Vessel Tests with Sludge Slurry

Experiment Designation	Volume of Slurry, liters	Time Between Initial and Final Agitations, hours	Height of Slurry in Vessel, cm	Purge Rate (sccm)
A-P5	0.24	163	7.8	10
A-P6	0.24	303	7.8	20
B-P1	0.24	400	7.8	10
C-P2	0.12	304	3.9	10
D-P1	0.12	67.1	3.9	10
D-P2	0.12	87.6	3.9	10
D-P4	0.12	327	3.9	10



**Fig. 1. Rate of radiolytic H<sub>2</sub> being purged from Vessel D before and during agitation in experiment DP2**

The results in Figure 1 will be discussed in some detail because the method is applicable to all the experiments discussed in this paper. In Figure 1, zero time on the X-axis is the time that the vessel was connected to the purge line to the GC and sampling of the gas was started. The vessel was continuously purged with air at 10 sccm and the GC was programmed to take a sample every 15 minutes. As can be seen in Figure 1, it took approximately 5 hours for the H<sub>2</sub> to increase to a sufficient concentration in the vapor space and in the purge gas so it could be detected by the GC (~1 ppm). The units of the Y axis are the measured rate of H<sub>2</sub> being purged from the vessel in terms of moles of H<sub>2</sub> per hour per liter of slurry. These rates were calculated from Equation 1 for each sampling time. The lack of measurements between 38 to 52 hours was due to the GC being used for measurements on another vessel in the Shielded Cells. During this time the rate of the purge air through the vessel remained constant at 10 sccm; however it vented directly to the cells and was not sampled by the GC. It can be seen from the data after 52 hours that the general trend of the measured H<sub>2</sub> purge rate continued to increase until it became essentially constant at 7.5E-07 moles per hour per liter of slurry. This rate is the average of 103 measurements taken by the GC at a frequency of one every 15 minutes. The percent relative standard deviation (%RSD) was 2.3 %. During this time the H<sub>2</sub> concentration in the purge air was at a steady state and the rate of H<sub>2</sub> diffusion from the slurry was equal to the rate of H<sub>2</sub> production in the slurry. At 85 hours agitation was initiated and the GC sampling frequency increased to every 3 minutes. The measured H<sub>2</sub> rate being purged from the vessel increased to a maximum of 3.6E-05 moles per hour per liter of slurry which is completely off scale in Figure 1 and corresponds to 157 ppm H<sub>2</sub> being measured by the GC. The rate then decreased over a period of ~2 hours and eventually reached a constant value of 8.3E-06 moles per hour per liter of slurry based on 104 GC measurements taken at a frequency of 1 sample every 3 minutes. After ~11 hours the agitator was stopped and the sampling frequency was decreased to 15 minutes. The H<sub>2</sub> concentration in the vapor phase immediately fell to zero because now all the radiolytic H<sub>2</sub> that was being produced was retained by the slurry. At ~100 hours the H<sub>2</sub> concentration in the vapor space was beginning to just reach the detection limit of the GC and the experiment was terminated.

In this test the radiolytic rate of H<sub>2</sub> production could be determined in three ways. The first two were from the steady state rates measured prior to and after agitation as described above. The third was by calculating the total moles of H<sub>2</sub> purged from the vessel and dividing this by the total time of the experiment. The total moles purged were 8.9E-06 and the total time of the experiment was 96.6 hours. The rate determined in this way was 7.7E-07 moles per hour per liter of slurry. The three rates are in fair agreement, however it can be speculated that the rate measured during agitation may be higher because of the sludge solids being more dispersed throughout the slurry. This could slightly increase the dose rate to the water in the slurry while decreasing the dose rate to the solids.

In the 6 other long term purge tests, the total H<sub>2</sub> that diffused from the slurry prior to agitation was not measured so the radiolytic rate from the total amount of H<sub>2</sub> produced could not be calculated. However the radiolytic rate was measured after a long purge time when the concentration of H<sub>2</sub> in the vapor space had reached a steady state. The rate of radiolytic H<sub>2</sub> was calculated from this steady state rate. The amount of H<sub>2</sub> that was released during agitation was measured in all the long term tests. These results appear in Table II. The heavy line in Table II separates results from the larger vessels that contained 0.24 liters of slurry from the results for smaller vessels that contained 0.12 liters of slurry.

Table II. Results for Long Term Purged Vessel Experiments with SB3 Sludge Slurry

Test	Time Between Initial and Final Agitations, hours	Measured H <sub>2</sub> Rate Just Prior to Final Agitation mol/h/liter	Measured H <sub>2</sub> in Sludge Slurry, mole	H <sub>2</sub> Concentration in Sludge Slurry, mole/liter
A-P5	163	5.8E-07	1.3E-05	5.4 E-05
A-P6	303	7.6E-07	1.3 E-05	5.3E-05
B-P1	400	6.8E-07	1.3 E-05	5.5E-05
C-P2	304	7.9E-07	3.8E-06	3.1E-05
D-P1	67.1	7.3E-07	2.0E-06	1.6E-05
D-P2	87.6	7.5E-07	2.5E-06	2.1E-05
D-P4	327	7.2E-07	2.2E-06	1.7E-05

Except for test A-P5, the measured radiolytic rates agree fairly well. The average radiolytic production rate is 7.4E-07 moles per hour per liter of slurry with a 5 % RSD. Also the measured concentration of radiolytic H<sub>2</sub> that is in each slurry at steady state is fairly constant for each of the two volumes of slurry. In the tests with 0.24 liters the average measured concentration is 5.4E-05 M, and for tests with 0.12 liters it is 2.1E-05 M. A higher steady state concentration occurs in the larger volume because the H<sub>2</sub> has a longer diffusion path to get out of the solution (7.8 cm compared to 3.9 cm). The lower steady state concentration of H<sub>2</sub> is in agreement with the result that it takes a shorter time to reach a steady state with the smaller volume.

### Measurements and Results for the SB3 SRAT Slurry

Two radiolysis tests were performed with the SB3 SRAT slurry. Both tests were conducted in the smaller vessels and followed the same procedure that was followed in test DP-2. Experimental details for the two experiments with the SRAT slurry (C-SRAT and D-SRAT) are given in Table III.

Table III. Experimental Details of Long Term Purged Vessel Tests with SRAT Slurry

Experiment and Vessel Designation	Volume of Slurry, liters	Time Between Initial and Final Agitations, hours	Duration of Agitation, hours	Height of Slurry in Vessel, cm.	Purge Rate, sccm
C-SRAT	0.12	87.2	8.2	3.9	10
D-SRAT	0.11	114	5.0	3.9	10

As with the experiments with the sludge slurry, the SRAT slurry was agitated immediately before putting samples into vessels C and D. The purge air to the vapor space of each vessel was then started. However, only the purge from experiment C-SRAT was passed through the sampling system of the GC where it was sampled and analyzed at a frequency of 1 hour during the long purge time. During this time vessel D was purged directly to the cell. The slurry in experiment C-SRAT was not agitated until the data indicated that the concentration of H<sub>2</sub> in the vapor space had reached a steady state. The measured rates for the C-SRAT experiment are shown in Figures 2 and 3. In these two figures the units on the Y-axis are in the same as those in Figure 1 for the sludge slurry. Just before turning on the agitator the sampling frequency was increased to every 3 minutes. During agitation the rate of H<sub>2</sub> being purged from the vessel was so high that plotting

all the data as in Figure 2 removed any detail from the rates measured prior to agitation. This detail is shown in Figure 3 where it can be seen that ~ 70 hours were necessary for the H<sub>2</sub> concentration to reach a steady state. Also it appears that the rate does not increase smoothly suggesting that there may be some sporadic behavior in the release of H<sub>2</sub> from the slurry. After agitation was initiated the data in Figure 4 indicate that it took only ~2 hours to purge the H<sub>2</sub> released from the slurry from the vapor space of the vessel. The rate of H<sub>2</sub> being purged during agitation then rapidly decreased and again reached a constant rate until the test was terminated.

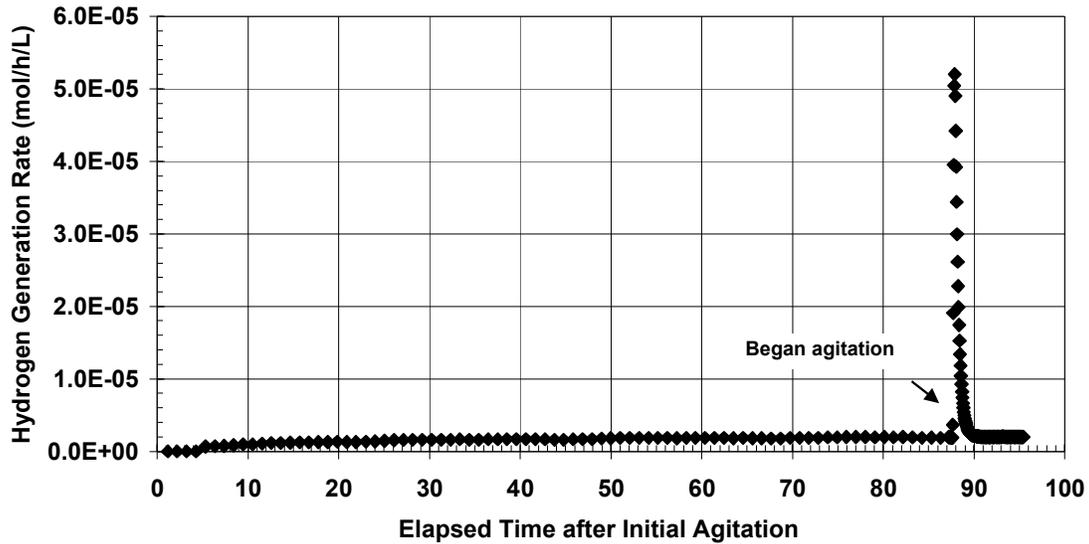


Fig.3. Rate of radiolytic H<sub>2</sub> production being purged from the SRAT slurry in experiment C-SRAT in vessel C before and during agitation

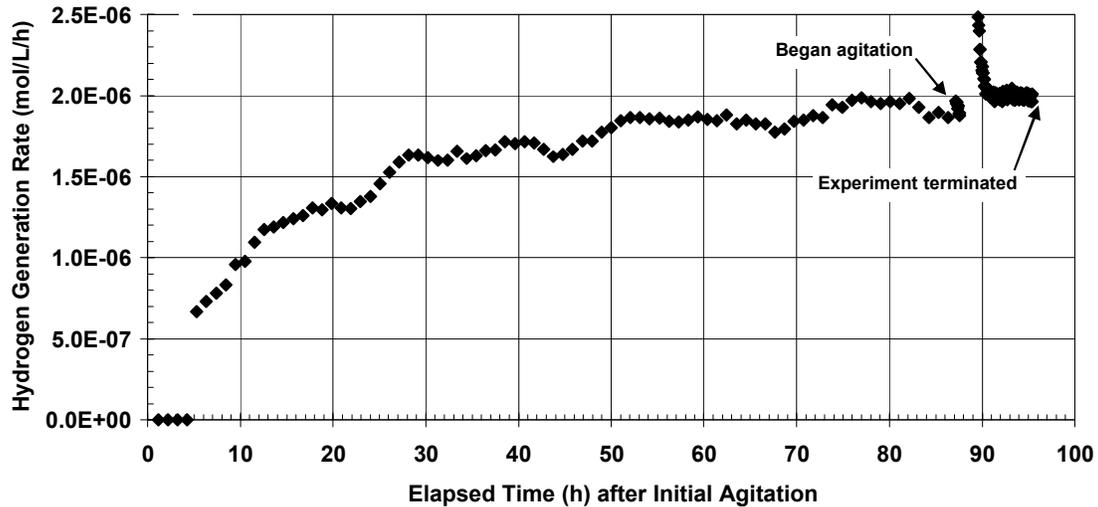


Fig 4. Detail of the rate of radiolytic H<sub>2</sub> being purged from the SRAT slurry in experiment C-SRAT in vessel C prior to agitation

After termination of experiment C-SRAT at ~95 hours the purge gas of vessel D was passed through the sampling system of the GC and H<sub>2</sub> concentrations were measured. Because vessel D had already been sitting for ~95 hours while measurements were being taken for experiment C-SRAT, the data from vessel D indicated that the rate of H<sub>2</sub> being purged in experiment D-SRAT had reached a steady state value. Consequently, measurements of this steady state rate were taken at 3 minute intervals for approximately only one hour before agitation was initiated. Before and during agitation the measured rates were similar to those for the test with vessel C and thus are not plotted in this paper.

For both tests, the radiolytic rates for H<sub>2</sub> production were calculated from the steady state rates measured prior to and after agitation. Average of the rates along with the %RSD based on 20 or more measurements of each are presented in Table IV. Also for both tests the total amounts of H<sub>2</sub> released from the slurry by agitation were also calculated using Equation 2. These are also shown in Table IV along with the calculated concentration of H<sub>2</sub> in the slurry during steady state.

Table IV. Results of Long Term Purge Tests with SRAT Product

Vessel and Test Designation	Average Radiolytic Rate During No Agitation (%RSD)	Average Radiolytic Rate During Agitation (%RSD)	Measured H <sub>2</sub> in Sludge Slurry, moles	H <sub>2</sub> Concentration in Slurry, moles/liter
C-SRAT	1.9E-06 (2.9)	2.0E-06 (1.0)	3.9E-06	3.3E-05
D-SRAT	2.1E-06 (1.2)	2.0E-06 (1.7)	3.1E-06	2.8E-05

For experiment C-SRAT where all the H<sub>2</sub> was measured, the radiolytic rate was also calculated from the total moles of H<sub>2</sub> measured divided by the total time of the test. For experiment C-SRAT a total of 2.2E-05 moles of H<sub>2</sub> were measured and the total time of the test was 95.4 hours giving a rate of 1.9E-06 moles of radiolytic H<sub>2</sub> produced per hour per liter of SRAT product in excellent agreement with the values in Table IV. Of this total H<sub>2</sub>, the amount that was retained in the slurry was 3.9E-06 moles (see Table IV) indicating that during the time the SRAT slurry was not agitated, 82% of the radiolytic H<sub>2</sub> that was produced diffused from the slurry. For both experiments, the steady state concentration of H<sub>2</sub> in the SRAT slurry was nominally 3.1E-05 M. This is somewhat higher than the concentration of 2.1E-05 M measured for the tests with the sludge slurry in the Vessel C and D (see Table IV). The higher steady state concentration for the SRAT slurry is probably due the fact that the radiolytic rate of H<sub>2</sub> production for the SRAT slurry was approximately a factor of 2.6 higher than that for the sludge slurry even though the concentrations of the radionuclides in the slurries were nearly equal as will be shown in the next section.

## METHODOLOGY AND RESULTS OF PREDICTIONS OF RADIOLYTIC RATE OF HYDROGEN PRODUCTION IN SB3 SLUDGE AND SRAT SLURRIES

### General Description of Methodology

The rate of radiolytic H<sub>2</sub> production in the SB3 Sludge and SRAT slurries depends on three factors.

- The total rate of beta, gamma and alpha radiation absorbed by the sludge or SRAT slurry. This rate is directly proportional to the concentrations of the radionuclides in the slurry and their decay energies. For the beta and gamma emitters, this rate also depends on the size of

the vessel. For these small vessels some of the beta and gamma radiation can escape the slurry and be absorbed in the glass of the vessel and its surroundings.

- The G values for H<sub>2</sub> (G(H<sub>2</sub>)) and for H atom (G(H)) production for beta, gamma and alpha radiation. The G value is defined as the number of H<sub>2</sub> molecules or H atoms produced per 100eV of energy absorbed.
- The nitrate, nitrite and formate concentrations in the liquid phase of the slurry. The nitrate and nitrite decrease the formation of H<sub>2</sub> by scavenging the radiolytic precursors of the H<sub>2</sub>. [3,4] Formate increases H<sub>2</sub> production by reacting with H atoms as shown in Reaction 4. [5]



### Calculation of the Rate of Radiation Absorbed by the SB3 Sludge and SRAT Slurries

The rate of total radiation absorbed for both slurries is calculated first. In the SB3 sample the concentrations of 51 radionuclides were measured, calculated from decay of their radioactive parents or estimated from the detection limits of the analytical method used to determine that specific radionuclide.[6] Of these 51, 14 contributed greater than 98% of the radiation energy that was absorbed by the slurry and produced H<sub>2</sub>. Concentrations of these in terms of watts per liter absorbed by the two slurries are given in Table V. The fraction of total watts is given in the final column of the table. The last two rows in Table V give the total alpha and total beta/gamma radiation rates absorbed by the slurries.

TableV. Radionuclides that Contribute >98% of the Radiolysis Energy to SB3 Sludge or SRAT Slurry and Total w/L Absorbed

Radionuclide	Decay Energy <sup>a</sup> , W/Ci	Principle Decay Mode	W/l of Sludge Slurry	W/l of SRAT Slurry	Fraction of Total Watts
Sr-90	1.2E-03	Beta	1.3E-03	1.3E-03	1.5E-01
Y-90c	5.5E-03	Beta	5.8E-03	6.0E-03	6.9E-01
Cs-137	1.0E-03	Beta	7.3E-05	7.5E-05	8.7E-03
Ba-137m	3.9E-03	Gamma	2.7E-05	2.8E-05	3.2E-03
Pm-147	3.7E-04	Beta	1.0E-04	1.0E-04	1.2E-02
Sm-151	7.4E-04	Beta	3.3E-05	3.4E-05	4.0E-03
Eu-154	9.1E-03	Beta	1.6E-05	1.6E-05	1.9E-03
Eu-155	7.6E-04	Beta	3.7E-07	3.8E-07	4.4E-05
Pu-238	3.3E-02	Alpha	1.9E-04	2.0E-04	2.3E-02
Pu-239	3.0E-02	Alpha	9.4E-05	9.7E-05	1.1E-02
Pu-240	3.1E-02	Alpha	3.4E-05	3.5E-05	4.0E-03
Am-241	3.3E-02	Alpha	1.4E-04	1.4E-04	1.7E-02
Am-243	3.2E-02	Alpha	1.1E-05	1.1E-05	1.3E-03
Cm-244	3.4E-02	Alpha	5.5E-04	5.6E-04	6.5E-02
Total Alpha	NA <sup>b</sup>	NA	1.0E-03	1.1E-03	1.3E-01
Total beta/gamma	NA	NA	7.3E-03	7.5E-03	8.7E-01

<sup>a</sup>Taken from Reference 7.

<sup>b</sup>NA = Not Applicable.

The results in the last column indicate that 84% of the energy is due to beta decay of Sr-90 and its daughter Y-90. Also only 13% of the energy is from alpha decaying radionuclides. In order to be conservative and to simplify the prediction, it was assumed that all the alpha energy was absorbed by the water and the amount absorbed by the solids in the slurry was negligible. The gamma energy from Ba-137m and the beta energy from the energetic beta decay of Y-90 were corrected to account the fraction of energy that was not absorbed by the slurry and interacted with the glass vessel or escaped the vessel. For the gamma energy, 90% was not absorbed by the slurry and for the beta, only 5% was not absorbed by the slurry. (For the large vessels in the DWPF where essentially all the radiation is absorbed by the slurry, the rate of absorbed energy would increase by only ~6% because the largest contributor to the radiolytic dose rate is energy from beta particles.) In these experiments in the small vessels the rate of radiation absorbed in by the SRAT slurry is slightly larger than that for the sludge slurry because the SRAT slurry had a slightly higher density than that for the sludge slurry. The measured values were 1.18 grams/liter and 1.15 grams/liter, respectively.

### Method for Prediction of Radiolytic Rate of H<sub>2</sub> Production for the SB3 Sludge and SRAT Slurries

The initial sludge slurry does not contain formic acid so Reaction 4 does not occur in this slurry. For the sludge slurry the following equation was used to calculate the radiolytic rate of H<sub>2</sub> production in the sludge slurry. Two equations are used because the G value for alpha radiation is different from the G values for beta and gamma radiation which are equal.

$$R_{H_2(Sludge)} = G_{H_2} \cdot \left( \sum_{i=1}^n C_i \right) \cdot k \quad (\text{Eq.3})$$

where,  $R_{H_2(Sludge)}$  is the rate of radiolytic H<sub>2</sub> production in moles of H<sub>2</sub> per hour per liter of sludge slurry,  $G_{H_2}$  is the radiolytic yield of H<sub>2</sub> in molecules of H<sub>2</sub> per 100 eV of energy absorbed, and  $C_i$  is the watts per liter of slurry for each radionuclide. The constant  $k$  is given by the following

$$k = \left( \frac{\text{eV}}{1.60 \times 10^{-19} \text{ watt} \cdot \text{sec}} \right) \cdot \left( \frac{3600 \text{ sec}}{\text{hr}} \right) \cdot \left( \frac{\text{mole}}{6.02 \times 10^{23} \text{ molecules}} \right) \quad (\text{Eq. 4})$$

$$k = 3.74 \times 10^{-2} \cdot \left( \frac{\text{eV} \cdot \text{mole}}{\text{watt} \cdot \text{hr} \cdot \text{molecule}} \right)$$

Radiation chemistry studies have shown that in pure water the value for  $G_{H_2}$  is equal to 0.45 molecules/100 eV for both gamma [Ref. 1, p 140] and U-235 fission product beta radiation [8]. For alpha radiation the value is 1.6 molecules per 100 eV of energy absorbed energy. [9] These G values are different because of the spatial distributions of the H<sub>2</sub> precursors are different for beta/gamma and for alpha radiation.

At SRS two empirical equations have been developed by the SRS Tank Farm based on published data that describe the effect of nitrate and nitrite to decrease the values for  $G(H_2)$ . Equation 5 is for beta/gamma radiolysis and Equation 6 is for alpha radiolysis.

$$G(H_2)_{bg} = 0.466 - 0.51 \cdot [NO_{eff}]^{1/3} + 0.14 \cdot [NO_{eff}]^{2/3} + 0.0055 \cdot [NO_{eff}] \quad (\text{Eq. 5})$$

$$G(H_2)_a = 1.3 - 0.79 \cdot [NO_{eff}]^{1/3} - 0.13 \cdot [NO_{eff}]^{2/3} + 0.11 \cdot [NO_{eff}] \quad (\text{Eq. 6})$$

The term  $NO_{eff}$  is given by Equation 7.

$$[NO_{eff}] = [NO_3^-] + 0.5 \cdot [NO_2^-] \quad (\text{Eq. 7})$$

This equation results because nitrite is nominally half as effective as nitrate in scavenging the precursors of hydrogen based on published rate constants. [10]

For prediction of the radiolytic rate of  $H_2$  production in the SRAT slurry an additional term has to be added to Equation 3 because of the reaction of H atoms with formate in the slurry to produce additional  $H_2$  as shown in Reaction 4. The equation then becomes

$$R_{H_2(SRAT)} = (G_{H_2} + G_H \cdot f_{formate}) \cdot \left( \sum_{i=1}^n C_i \right) \cdot k \quad (\text{Eq. 8})$$

where,  $R_{H_2(SRAT)}$  is now the rate of radiolytic  $H_2$  production in moles of  $H_2$  per hour per liter of SRAT slurry,  $G_H$  is the radiolytic yield of H atoms in atoms produced per 100 eV of energy absorbed, and  $f_{formate}$  is the fraction of H atoms that react with formate to produce  $H_2$  rather than reacting with nitrate or nitrite ions and not produce  $H_2$ . All the other terms in Equation 8 are the same as in Equation 3. Again two equations are necessary – one for beta/gamma radiation and one for alpha radiation.

In the radiolysis of water by beta/gamma radiation the yield of H atoms is 0.58 molecules per 100 eV. [Ref. 1, p140] The value for G(H) has not been measured for alpha radiation; however, it has been measured using 12 MeV  $He^{+2}$  ions which are identical to 12 MeV alpha particles. The measured value was 0.27 molecules/100 eV. [11] As a first approximation, this value can be used for the G value for radiolysis by alpha particles from U, Pu, Am, and Cm in the SRAT slurry since their alpha decay energies (5.2 to 5.5 MeV) [7] are somewhat close to that of the alpha particles used to measure G(H).

### Predicted Rate of Radiolytic of $H_2$ Production for the SB3 Sludge Slurry

The beta/gamma and alpha G values for the production of  $H_2$  were calculated based on the concentrations of  $NO_3^-$  and  $NO_2^-$  measured in the supernate of the SB3 sludge slurry by ion chromatography. The  $NO_3^-$  concentration was 0.201 M and the  $NO_2^-$  was 0.433 M. When these were substituted into Eq. 7 the value for  $NO_{eff}$  was 0.418 M. Based on Eq. 5 the G value for  $H_2$  from beta/gamma radiation was lowered to 0.17 molecules/100 eV. When this is substituted into Eq. 3 along with the value of k from Eq. 4 and the watts per liter of absorbed beta/gamma radiation from Table V, the predicted rate of radiolytic  $H_2$  production from the beta/gamma radiation is 4.6E-07 moles of  $H_2$  per hour per liter of the sludge slurry. For alpha radiation the G value is lowered to 0.68 molecules/100 eV and the predicted rate of radiolytic  $H_2$  production is

2.6E-07 moles per liter of the sludge slurry. The total predicted rate for the sludge slurry is then 7.2E-07 moles per hour per liter of the sludge slurry.

### **Predicted Rate of Radiolytic of H<sub>2</sub> Production for the SB3 SRAT Slurry**

For the SRAT slurry the predicted H<sub>2</sub> production rates were again calculated separately for both beta/gamma and alpha radiation. However, the values of  $G_H \cdot f_{formate}$  have to be included for both beta/gamma and alpha radiation.

For the first of the two G values in Equation 8, the effect of nitrate and nitrite in the supernate on  $G_{H_2}$  was calculated using Equations 5 and 6. In the supernate of the SRAT slurry the measured concentrations of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> ions were 0.512 M and 0.018 M, respectively, giving a value of 0.521 for  $NO_{eff}$ . When this is substituted into Eq. 5 the G value for beta/gamma radiation is lowered to 0.15 molecules/100 eV. When this is substituted into Eq. 8 along with the value for k from Eq. 4 and the watts per liter of absorbed beta/gamma radiation for the SRAT slurry from Table V, the predicted rate of radiolytic H<sub>2</sub> production based the first G value in Eq.8 is 4.2E-07 moles of H<sub>2</sub> per hour per liter of the sludge slurry for beta/gamma radiation. For alpha radiation the G value is lowered to 0.64 molecules per 100 eV using Eq. 6 and the predicted rate of radiolytic H<sub>2</sub> production is 2.6E-07 moles per hour per liter of the sludge slurry. The total predicted rate based on the first G value in Eq. 8 is then 6.8E-07 moles per hour per liter of the SRAT slurry. Note that this is very similar to the predicted rate for the sludge slurry.

The contribution of the radiolytic production of H<sub>2</sub> from Reaction 4 will now be estimated. Measurements by ion chromatography on the supernate of the SRAT slurry indicated that the concentration of formate in the supernate was 0.980 M. Based on the following discussion, it can be concluded that in the SRAT slurry ~94% of the H atoms produced by radiolysis react with the formate anions to produce H<sub>2</sub> rather than reacting with nitrate or nitrite ions and not producing H<sub>2</sub>.

Radiolytically produced H atoms can react with both formic acid and with formate anions. Rate constants have been measured for both reactions and the rate constant for the reaction with formic acid is ~ 450 times lower than the constant for the reaction with formate ions. [10] Also, the pH of the SRAT product measured by pH paper was ~6; therefore, based on the acid dissociation constant for formic acid (1.8E-04 M [12]), essentially all of the formic acid that was added in the SRAT process is dissociated into formate ions. The H<sup>+</sup> ions reacted with the caustic in the slurry.

Rate constants for the reaction of H atoms with formate, nitrate and nitrite anions have been measured and reported in the radiation chemistry literature. [10] The fractions of H atoms reacting with formate ions rather than nitrate or nitrite ions can be calculated using these rate constants and the concentrations of the respective anions in the supernate. These fractions are the ratio of the reactivity of H atoms to formate ions compared to their reactivity for the nitrate or nitrite ions in the slurry. The reactivity for each anion is the product of the concentration of the anion concentration times its rate constant for reacting with the H atom. Table VI presents measured rate constants for the reaction of H atoms with these anions, the concentrations of the anions in the supernate of the SRAT product and the calculated reactivities for the H atoms with these anions in the SRAT product. The last column of Table VI presents the fraction of H atoms reacting with nitrate or nitrite ions relative to formate. Only 0.3% of the H atoms formed by the radiolysis react with nitrate rather than formate and only 6% of the H atoms react with nitrite rather than formate in the two slurries. The results indicate that in the SRAT product slurry 94% of the radiolytic H atoms react with the formate anion to produce H<sub>2</sub>.

Table VI. Rate Constants and Reactivity of H Atoms for Formate, Nitrate, and Nitrite Anions in the SB3 SRAT Slurry

Anion	Rate Constant, <sup>a</sup> L/ mole·s	Concentration, moles/L	Reactivity, s <sup>-1</sup>	Fraction Reacting with Formate
CHO <sub>2</sub> <sup>-</sup>	2.1E08	0.980	2.1E08	0.94 <sup>b</sup>
NO <sub>3</sub> <sup>-</sup>	1.4E06	0.512	7.1E05	0.003 <sup>c</sup>
NO <sub>2</sub> <sup>-</sup>	7.1E08	0.018	1.3E07	0.06 <sup>c</sup>

<sup>a</sup>Taken from Reference 10.

<sup>b</sup>Calculated from  $1 - f_{\text{nitrate or nitrite}}$ .

<sup>c</sup>Calculated from ratio of reactivities of nitrate or nitrite to formate.

For beta/gamma radiolysis with a G value of 0.58 molecules/100 eV for H atoms and  $f_{\text{formate}}$  equal to 0.94, the calculated radiolytic rate of H<sub>2</sub> production for this term is 1.5E-06 moles H<sub>2</sub> per hour per liter of SRAT slurry. For alpha radiolysis and a G value of 0.27 molecules/100 eV for H atoms, the calculated rate for H<sub>2</sub> production is 1.0E-07 moles H<sub>2</sub> per hour per liter of SRAT slurry. The rate of H<sub>2</sub> production from the presence of formate is then 1.6E-06 moles of H<sub>2</sub> per hour per liter of SRAT slurry.

The total rate of radiolytic H<sub>2</sub> production in the SRAT slurry for both beta/gamma and alpha radiation after including the effect of formate is then predicted to be 2.3E-06 moles of H<sub>2</sub> per hour per liter (4.2E-07 M/h + 2.6E-07 M/h + 1.5E-06 M/h + 1.0E-07 M/h).

## COMPARISON OF PREDICTED AND MEASURED RADIOLYTIC H<sub>2</sub> PRODUCTION RATES

The predicted radiolytic rates for the sludge slurry and the SRAT slurry are compared to measured rates in Table VII shown on the next page. Table VII also presents the time the vessels were purged prior to the final agitation and the percent differences between the predicted and measured values.

Table VII. Comparison of Predicted and Measured Radiolytic Production Rates for Long Term Purge Tests of SB 3 Sludge and SRAT Slurries

Experiment Designation	Time Between Initial and Final Agitations, hours	Predicted H <sub>2</sub> Generation Rate, mol/L/h	Measured H <sub>2</sub> Rate Just Prior to Final Agitation mol/L/h	% Difference <sup>a</sup>
<b>Sludge Slurry</b>				
A-P5	163	7.2E-07	5.8E-07	24
A-P6	303	7.2E-07	7.6E-07	-5.3
B-P1	400	7.2E-07	6.8E-07	5.9
C-P2	304	7.2E-07	7.9E-07	-8.9
D-P1	67.1	7.2E-07	7.3E-07	-1.4
D-P2	87.6	7.2E-07	7.5E-07	-4.0
D-P4	327	7.2E-07	7.2E-07	0
<b>SRAT Slurry</b>				
C-SRAT	87.2	2.3E-06	1.9E-06 <sup>b</sup>	21
D-SRAT	114	2.3E-06	2.0E-06 <sup>b</sup>	15

<sup>a</sup>Percent difference =  $100 \times (\text{predicted rate} - \text{measured rate})/\text{measured rate}$

<sup>b</sup>Average of rate measured just prior to final agitation and the rate measured during agitation.

The results in the last column indicate that the agreement between the predicted and measured values for the 9 experiments varies somewhat. In some of the experiments the predictions are higher than the measured values (positive differences) and in some cases lower. However the agreement is not bad considering the complexity of the system (a suspension of solids in a slurry containing ~51 radionuclides) and all the data that went into developing the predictions. On this basis the agreement is sufficient to say that if the radioactive and chemical composition of a slurry is known, a reasonable estimation of the rate of radiolytic H<sub>2</sub> production can be made.

## REFERENCES

1. I. G. DRAGANIC; and Z. D. DRAGANIC, "The Radiation Chemistry of Water," p. 76, Academic Press: New York (1971).
2. D.T. HOBBS, et al., "Hydrogen Generation Rates in Savannah River Site High-Level Nuclear Waste", Waste Management '92 Symposium, Vol. 2, p 1063page, Tucson, AZ (1992).
3. H. A.. MAHLMAN, "The Effect of Nitrate on G(H<sub>2</sub>) in the Radiolysis of Water", *J. Phys. Chem.*, **64**, 936 (1961)
4. H. A.. SCHWARZ, and A. O. ALLEN, "The Radiation Chemistry of Nitrite Ion in Aqueous Solution", *J. Amer. Chem. Soc.*, **77**, 1324 (1955).
5. M. CHOURAQUI, , and J. SUTTON, "Origin of Hydrogen Atom Yield in Radiolysis of Aqueous Solutions", *Transactions of the Faraday Soc.*, **62**, 2111 (1966).

6. C. J. BANNOCHIE, and N. E. BIBLER, "Determination of Reportable Radionuclides for DWPF Sludge Batch 3 (Macrobatches 4)", Technical Report WSRC-TR-2005-00157, Rev 0, Savannah River Site: Aiken, SC (2005).
7. Integrated Data Base Report-1994, U. S. Spent Nuclear Fuel and Radioactive Waste Inventories, Projections, and Characteristics, Appendix B, "Characteristics of Important Radionuclides," DOE/RW-0006, Rev. 11, (1995).
8. M. C. SAUER, E. J. HART, K. F. FLYNN, and J. E. A. GINDLER, "Measurement of the Hydrogen in the Radiolysis of Water by Dissolved Fission Products", Technical Report ANL-76-46, Argonne National Laboratory: Argonne, IL (1976).
9. N. E. BIBLER, "Curium-244 Alpha Radiolysis of Nitric Acid. Oxygen Production from Direct Radiolysis of Nitrate Ions", *J. of Phys. Chem.* **78**, 211 (1974).
10. G. V. BUXTON, C. L. GREENSTOCK, W. P. HELMAN, A. B. ROSS, "Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals (OH/O<sup>-</sup>) in Aqueous Solution," *J. of Phys. and Chem. Ref. Data*, **17**, 513-886 (1988).
11. A. APPLEBY, and H. A. SCHWARZ, "Radical and Molecular Yields in Water Irradiated by Gamma Rays and Heavy Ions", *J. of Phys. Chem.*, **79**, 1937-1941 (1969).
12. Handbook of Chemistry and Physics; 77th Edition; D. R. Lide, Editor-in-Chief; CRC Press; New York, 1997; p 8-45 (1997).