# HYDROGEN GENERATION RATES IN SAVANNAH RIVER SITE HIGH-LEVEL NUCLEAR WASTE

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## ABSTRACT

High-level nuclear waste (HLW) is stored at the Savannah River Site (SRS) as alkaline, high-nitrate slurries in underground carbon steel tanks. Hydrogen is continuously generated in the waste tanks as a result of the radiolysis of water. Hydrogen generation rates have recently been measured in several waste tanks containing different types of waste. The measured rates ranged from 1.1 to 6.7 cubic feet per million Btu of decay heat. The measured rates are consistent with laboratory data which show that the hydrogen generation rate depends on the nitrate concentration and the decay heat content of the waste. Sampling at different locations indicated that the hydrogen is uniformly distributed radially within the tank.

## INTRODUCTION

HLW from chemical separations processes at the SRS is stored in underground carbon steel tanks. The waste contains radioactive byproducts and nonradioactive reactor tubing cladding materials and processing chemicals. The nitric acid processing solutions are neutralized with sodium hydroxide before storage in the tanks to prevent corrosion of the carbon steel. Approximately 90% of the waste consists of water-soluble salts such as sodium nitrate and sodium aluminate. The remaining 10% is an insoluble fraction or sludge consisting of transition metal, aluminum, and transuranic hydroxides and oxides formed upon neutralization of the acid processing solutions.

Hydrogen is continuously generated in the waste tanks as a result of the radiolytic decomposition of water. To prevent the accumulation of flammable mixtures of hydrogen, each tank is continuously purged with air. Air sweep rates are set such that the hydrogen concentration is well below the lower flammability limit (LFL) for hydrogen/air mixtures.

Whenever there is a planned or inadvertent shutdown of a ventilation system, an estimate is made of the time required to reach a flammable gas mixture. Currently, these estimates are based on a yield of 6.0 cubic feet of hydrogen per million Btu of decay heat (1). To confirm that the control limits are conservative, the hydrogen generation rates were determined for several tanks containing a variety of wastes that have different decay heats.

## DISCUSSION

### Waste Tank Designs

At present, SRS has 51 waste tanks for the processing and storage of high-level nuclear waste. All of the tanks are constructed of carbon steel and reinforced concrete. Three designs (types I, II, and III) have double steel walls and forced water cooling systems and are used primarily for high-heat waste. The fourth design (type IV) has a single steel wall and no forced cooling, and has been used primarily for low-heat waste. The type III design is the newest design and is most actively used for the receipt of fresh waste from chemical processing operations. The number of tanks, the capacity, and the construction time period for tanks of each design are given in Table I. A diagram of a type III waste tank is presented in Fig. 1.

The ventilation system is similar for all of the tank designs. Air enters the tank through a HEPA filter on one side, passes to the other side of the tank where it exits through a demister, a condenser, a heater, and a HEPA filter; it is then discharged to the atmosphere through an exhaust blower. A slight negative pressure is maintained inside the waste tank to control the spread of radioactive contamination.

All of the type III and some of the type I, II, and IV tanks have permanently installed instruments, which continuously monitor the vapor space for flammable vapor mixtures. All other tanks are monitored on a weekly basis using portable instruments. In the event of a planned or inadvertent shutdown of the ventilation system, the monitoring frequency is increased.

### Generation of Hydrogen

Hydrogen is generated in high-level nuclear waste as a result of the radiolysis of water. Laboratory studies have shown that the rate of hydrogen generation depends on the radiation dose rate to the solution and the concentration of nitrate ion in solution. At constant dose rates, the hydrogen generation rate decreases as the nitrate ion concentration increases. Figure 2 shows a plot of the hydrogen generation rate as a function of the nitrate concentration assuming a gas temperature of 25°C (2).

### Tank Vapor Space Measurements

With the ventilation system operating, vapor space samples were collected at the hydrogen monitoring station and at the purge air exhaust stack (see Fig. 1). The hydrogen concentration was determined by gas chromatography. For all of the samples, the hydrogen concentration was below 100 ppm, which is well below the LFL of 4% for hydrogen/air mixtures (Table II).

Hydrogen generation rates were calculated based on the measured hydrogen concentration, the estimated radioactive decay heat content in the tank, and the purge air flow recorded at the time of sampling. For tanks containing concentrated waste, the rates ranged from 1.1 to 6.7 $ft^3$/million Btu of radioactive decay heat. For tanks containing dilute waste (lower nitrate concentrations), the decay heat loads were very low (< 10,000 Btu/hr), and the concentrations of hydrogen were below the lower quantifiable limit of 5 ppm. As a result,

**TABLE I**

SRS Waste Tank Designs

| Type | No. of Tanks | Capacity (gal) | Cooling | Constructed |
|---|---|---|---|---|
| I | 12 | 750,000 | yes | 1951-1953 |
| II | 4 | 1,030,000 | yes | 1955-1956 |
| III | 27 | 1,300,000 | yes | 1967-1981 |
| IV | 8 | 1,300,000 | no | 1958-1961 |

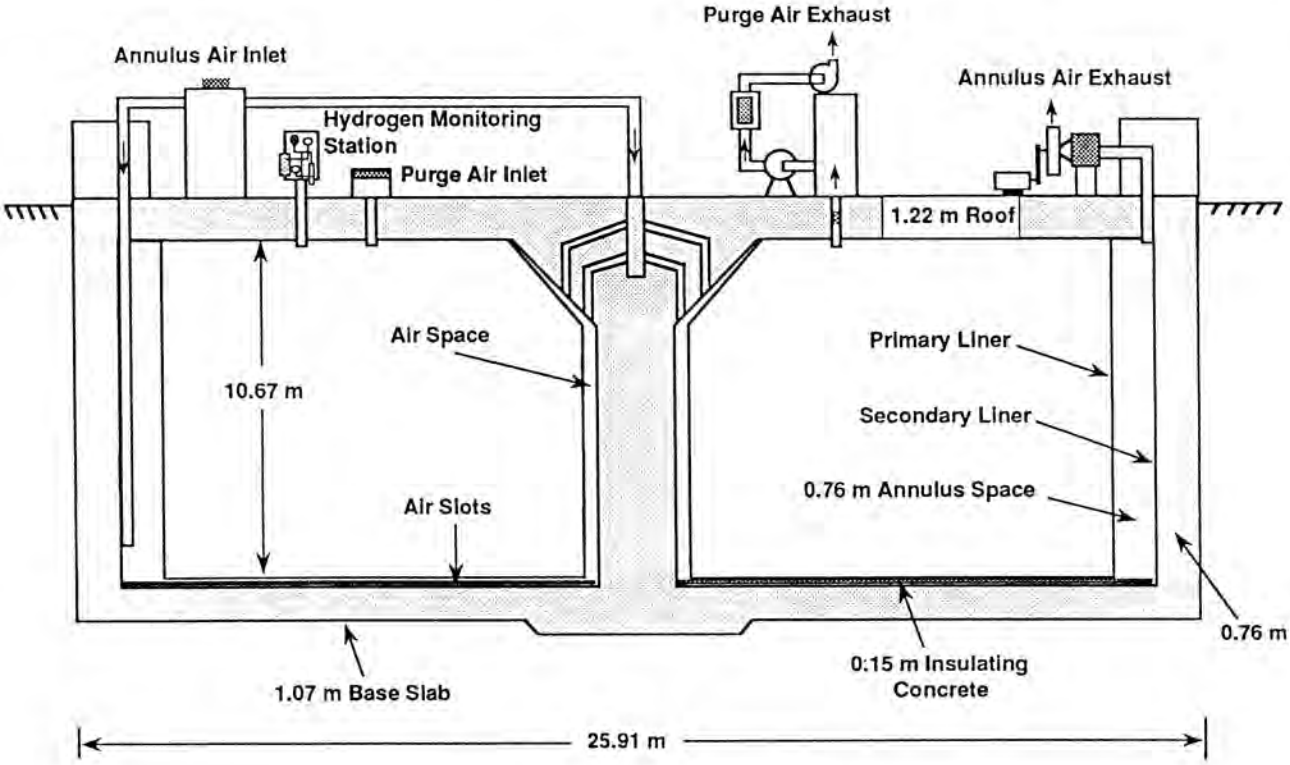


Fig. 1. Diagram of type III waste tank.

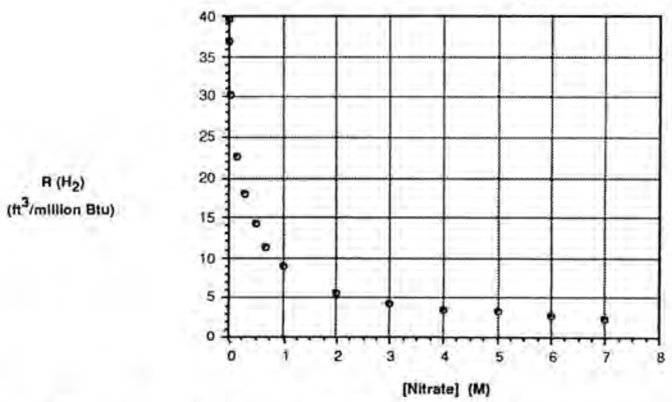


Fig. 2. Hydrogen generation rate as a function of the nitrate concentration.

the hydrogen generation rates could not be determined in these tanks.

The hydrogen generation rate was also determined in Tank 35 by monitoring the increase in the hydrogen concentration with the ventilation system shut off. Samples were taken every three hours over a 24-hour period from two different locations approximately 45 feet apart. The concentration of hydrogen increased linearly during this time period as shown in Fig. 3. From linear regression analysis of the data, the rate of change in the hydrogen concentration was determined to be 44 ppm/hr at each sampling location. Based on this rate and the vapor space volume and decay heat content in Tank 35, the hydrogen generation rate was determined to be 1.3 $ft^3$/million Btu. This rate is lower than that previously determined by the single sampling method with the ventilation system operating.

Several tanks were sampled at two different locations to confirm that a representative sample is obtained at the hydrogen monitoring station. For all of the tanks sampled, including Tank 35 when the ventilation system was shut off, there were no differences in the hydrogen concentrations between the duplicate samples. This result indicates that hydrogen is uniformly distributed radially in the vapor space of the tank, and that a representative sample is obtained at the hydrogen monitoring station.

**TABLE II**

Hydrogen Concentrations and Generation Rates in SRS Waste Tanks

| Tank | Tank Contents or Usage | [Nitrate] (mole/L) | Decay Heat (Btu/hr) | $[H_2]$ (ppm) | R(H2) ($ft^3/10^6$ Btu) |
|---|---|---|---|---|---|
| 31 | Salt Storage | 2.72 | 205,400 | bql[a] | - |
| 32 | Sludge Storage | 2.88 | 485,100 | 40 | 1.1 ± 0.6 |
| 35 | Waste Receipt | 3.07 | 550,400 | 78 | 3.8 ± 1.9 |
| 38 | Salt Storage | 1.88 | 5,193 | bql | - |
| 39 | Waste Receipt | 3.27 | 476,400 | 60 | 3.4 ± 1.7 |
| 40 | Sludge Processing | 0.89 | 1,404 | bql | - |
| 42 | Sludge Processing | 1.04 | 101,900 | 43 | 6.7 ± 3.4 |
| 43 | Waste Receipt | 0.99 | 3,898 | bql | - |
| 48 | ITP Processing | 0.030 | 1,345 | bql | - |
| 51 | Sludge Processing | 0.80 | 3,251 | bql | - |

[a]bql = below quantifiable lower limit of ≤5 ppm.

Tank 42 contains sludge waste which has been partially washed in preparation for feed to the Defense Waste Processing Facility (DWPF) for vitrification. As a result of washing, the nitrate concentration has been reduced to 1.04M. Because of the lower nitrate concentration, the hydrogen generation rate is about 2-5 times higher than that determined for concentrated waste having higher nitrate concentrations. Based on literature G values, the hydrogen generation rate at the lower nitrate concentration should be about 2.5 times that of the wastes having the higher nitrate concentrations (2). The hydrogen generation rate of 6.7 $ft^3$ $H_2$/million Btu is also slightly above the fixed rate of 6.0, which is currently used to calculate the time to reach the LFL in the event the ventilation system is shut down.

During storage, the nitrate concentration of the concentrated HLW is typically >2.5M and does not change significantly. However, waste removal and feed preparation operations which will prepare the HLW for permanent disposal can significantly change the nitrate concentration. Using the fixed rate of 6.0 $ft^3$ $H_2$/million Btu, the hydrogen generation rate is underestimated in waste solutions having a nitrate concentration of <2.3M. Therefore, it has been recommended that the hydrogen generation rate which is used for calculating the time to reach the LFL be determined using the following equation, when the nitrate concentration is known (3):

$$R\ (ft^3 H_2/10^6\ Btu) = 50.6 - 61.4*[NO_3^-]^{1/3} + 25.3*[NO_3^-]^{2/3} - 3.32*[NO_3^-] \quad \text{(Eq. 1)}$$

where $[NO_3^-]$ is the nitrate concentration in moles/L.

The hydrogen generation rates determined from the sampling program are all below those calculated based on laboratory G values as shown in Fig. 2. This result indicates that using the hydrogen generation rate derived from Eq. 1 is conservative for SRS wastes. The lower generation rate is expected since using the decay heat content as the dose rate overestimates the dose rate received by the waste solution. A significant fraction of the decay energy is lost as heat to the cooling coils and tank walls and bottom.

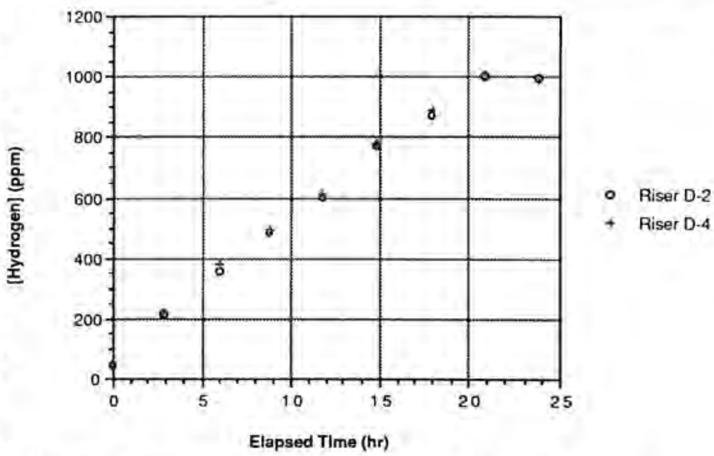


Fig. 3. Hydrogen concentration in tank 35 vapor space samples.

In a different experiment, a more concentrated sample of the evolved gas was obtained by drawing supernate from a HLW tank into a partially evacuated pipe, allowing the apparatus to remain undisturbed for a period of time, and then sampling the vapor space of the pipe. Gas chromatographic analysis revealed that the major gases were 7.5% hydrogen, 56.4% oxygen, and 36.8% nitrogen. The nitrogen resulted from the air originally in the pipe. Correcting for the $O_2/N_2$ ratio in air, the evolved gas composition was calculated to be 86% $O_2$ and 14% $H_2$, which is a $O_2/H_2$ ratio of 6.1. This ratio is consistent with the high nitrate concentrations of the SRS high-level waste solutions and literature results. For example, the evolved $O_2/H_2$ ratio for a 2.0M sodium nitrate solution is 5.2 (2).

## CONCLUSIONS

Hydrogen is continuously generated in SRS waste tanks as a result of the radiolysis of water. Hydrogen generation rates have recently been measured in several waste tanks containing different types of waste. The measured rates are consistent with laboratory data which show that the hydrogen generation rate depends on the nitrate concentration and the decay heat content of the waste. Sampling at different locations indicates that the hydrogen is uniformly distributed radially within the tank and that representative vapor space samples are obtained at the hydrogen monitoring stations.

## REFERENCES


1. Safety Analysis - 200-Area, Liquid Radioactive Waste Handling Facilities, DPSTSA-200-10, SUP 18, Westinghouse Savannah River Company, Savannah River Site, Aiken, SC 29808 (August 1988).
2. H. A. MAHLMAN, J. Phys. Chem., 64, 936 (1961).
3. D. D. WALKER and N. E. BIBLER, "The Dependence of Radiolytic H2 Generation on the Nitrate Concentration in High-Level Waste Solutions", WSRC-RP-91-1171, Westinghouse Savannah River Company, Savannah River Site, Aiken, SC 29808 (November 19, 1991).