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THE DEPENDENCE OF RADIOLYTIC H₂ GENERATION OF THE NITRATE CONCENTRATION IN HIGH-LEVEL SOLUTIONS (U)

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**THE DEPENDENCE OF RADIOLYTIC H₂ GENERATION ON THE NITRATE
CONCENTRATION IN HIGH-LEVEL WASTE SOLUTIONS (U)**

Summary

The rate at which hydrogen is produced from the radiolysis of high-activity waste solutions depends on the radiation dose rate to the solution and the concentration of nitrate ion in solution. At a constant dose rate, the hydrogen generation rate decreases as the nitrate ion concentration increases. Using previously measured rates of hydrogen production, an equation has been derived which calculates the hydrogen generation rate when the nitrate ion concentration is known. The hydrogen generation rate from this equation can be used to more accurately predict hydrogen production in waste tanks than is currently obtained assuming a fixed generation rate. The current fixed rate underestimates the hydrogen produced in dilute waste solutions.

Introduction

During the storage and handling of radioactive waste solutions, hydrogen is generated from the radiolysis of water. Flammable gas mixtures can form in the vapor space above the solutions if the space is not adequately ventilated. Whenever there is a planned or inadvertent ventilation shutdown on a high activity waste tank at the Savannah River Site, an estimate is made of the time required to reach a flammable gas mixture. Currently, these estimates are based on a yield of 6 ft³ of hydrogen per million BTU of decay heat¹ and the heat load in the tank.²

The generation rate for hydrogen production is dependent on the concentration of nitrate ion in the irradiated solution.³ As the nitrate ion concentration increases, the rate of hydrogen production decreases. The rate given in the preceding paragraph is that expected from a waste solution containing 1-2 molar nitrate

ion. This rate is adequate for most tanks containing concentrated waste. However, new processes which are to be run in the Tank Farm, such as Sludge Washing⁴ and In-Tank Precipitation,⁵ will generate waste solutions with high activities but low nitrate concentrations. Under these conditions, hydrogen accumulation rates in the vapor space in these tanks may exceed estimates made using the hydrogen generation rate given above.

Using previously published results on hydrogen generation by radiolysis, an equation has been derived which gives the rate as a function of the nitrate ion concentration.

Derivation of Equations

The rate of H₂ production is directly proportional to the radiolytic G-value (moles formed per 100 eV of energy sorbed). Table I lists the G-values for H₂ production, G(H₂), at different nitrate concentrations.^{3,6} The G-value is 0.45 molecules/100 eV in distilled water and decreases twenty-fold as the nitrate increases to 8 molar. These data are for both nitric acid solutions and neutral solutions of sodium nitrate. Even though the data are for acid and neutral solutions, the results are expected to be valid for caustic solutions such as the SRS waste. Draganic⁷ has shown that G(H₂) is independent of pH up to a pH of 13 and hydroxide ion is not expected to significantly effect G(H₂) at higher concentrations.

The equation for the hydrogen generation rate is given in Table II. The equation is applicable in the range 0.003 M nitrate to 8 molar nitrate. Below 0.003 molar, the G-value is the same as that for pure water (0.45 molecules/100 eV).⁶ A graph comparing the experimental data and the calculated G-values from the equation is shown in Figure 1.

The equation for the rate is given in two different sets of units: molecules of H₂ per 100 eV, and ft³ of H₂ per million BTU. As mentioned above, the radiochemical literature expresses chemical yields from radiolytic reactions as "G-values" in units of "molecules/100 eV". G-values are directly proportional to generation rates expressed as "ft³ per million BTU." The conversion is obtained as follows:

$$\begin{aligned}
 R\left(\frac{\text{ft}^3}{10^6 \text{ BTU}}\right) &= G\left(\frac{\text{molecules}}{100 \text{ eV}}\right) \times \frac{1 \text{ eV/sec}}{1.602 \times 10^{-19} \text{ watts}} \times \frac{1054 \text{ watt-sec}}{1 \text{ BTU}} \\
 &\quad \times \frac{24.46 \text{ L}}{6.022 \times 10^{23} \text{ molecules}} \times \frac{1 \text{ ft}^3}{28.32 \text{ L}} \\
 &= 94.37 \times G \frac{\text{molecules}}{100 \text{ eV}}
 \end{aligned}$$

The volume of one mole of hydrogen gas (24.46 L) assumes ideal behavior at 25°C.

The equation given in Table 1 is **not** the best fit to the data, but has been modified slightly to produce conservatively high estimates

of $G(H_2)$ over the data range. As can be seen in Fig.1 (solid line), the equation closely approximates Mahlman's experimental data points. The difference between the calculated G-value and the average of the experimental data is listed in Table I. The maximum difference approaches +40%, but the majority of the data is approximated to within +20%. Only at 5.0 molar nitrate is Mahlman's experimental measurement higher than that given by the equation and this is probably due to random error in the measurement.

Effect of Other Dissolved Salts

Nitrate is the major anion in soluble waste, but the waste also contains many other species, such as hydroxide, aluminate, sulfate, and nitrite. These other anions and the associated cations have a negligible effect on $G(H_2)$ compared to nitrate. This is because nitrate is the only species present that readily reacts with the molecular hydrogen precursors (H atoms or aqueous electrons) produced by the radiation.⁶ Bradley has irradiated a simulated waste solution containing the major species present in SRS waste.⁸ This solution (4 M $NaNO_3$, 2 M $NaNO_2$, 1 M $NaOH$, 0.6 M $NaAlO_2$, 0.5 M Na_2CO_3 , and 0.3 M Na_2SO_4)⁸ was irradiated at different dose rates and G-values for hydrogen were in the range 0.03 to 0.066 molecules/100 eV. The range is similar to Mahlman's data and is consistent with the values calculated from the equation.

Effect of Alpha Activity

The G-values used above are based on experiments using Co-60 gamma radiation to simulate the effects of a mixture of radionuclides in the waste. Although Co-60 is expected to adequately imitate gamma and beta emitters,⁸ it is not a good substitute for alpha emitters. Hydrogen G-values from alpha irradiation are up to three times higher than those from gamma.⁹ This effect is not important in estimating hydrogen generation in the soluble waste because the alpha emitters do not contribute significantly to overall radiation energy deposited in the waste. The actinides are highly insoluble in the alkaline waste and contribute less than 0.1% of the total decay energy.¹⁰ Most of the decay energy is from beta and gamma radiations from Cs-137 and Ba-137m.

In sludge wastes, the alpha contribution is higher and contributes approximately 10% of the total decay energy.¹⁰ Thus, the error in ignoring the alpha contribution is similar to the magnitude of the error between the equation and Mahlman's data.

Quality Assurance

The equations given in Table I were derived using Cricket Graph software (Version 1.2, Feb. 8, 1988, Cricket Software, Malvern, PA) on a Macintosh SE computer. The equations were then evaluated by hand and compared against the experimental data to obtain the errors listed in Table II. This information is recorded in Laboratory Notebook WSRC-NB-91-201, p 51-53, 64-65, 67-68.

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Table I. Data Used to Derive Equations

Nitrate (molar)	G(H ₂) (molecules/100 eV)		Equation	Avg % Difference
	Experimental			
	Data*			
	NaNO3	HNO3		
0.0012	0.42	0.43	0.47	+12
0.0032	0.39	0.41	0.45	+12
0.0079	0.39	0.37	0.42	+11
0.027	0.32		0.36	+12
0.031		0.34	0.36	+6
0.15	0.24	0.25	0.26	+8
0.31	0.19	0.19	0.21	+11
0.51	0.15	0.15	0.17	+13
0.70	0.12		0.14	+17
0.80		0.11	0.13	+18
1.0	0.096	0.091	0.118	+26
2.0	0.059	0.053	0.071	+27
3.0	0.045	0.042	0.049	+11
4.0	0.038	0.035	0.037	+3
5.0	0.035		0.031	-11
6.0	0.029	0.020	0.027	+12
7.0	0.025		0.025	0
8.0		0.018	0.025	+39

*Data taken from Reference 3. Where data is available for both acid and neutral solution, the average of the two has been used to calculate the % difference between the experimental data and the equation.

TABLE II. Equations for Hydrogen Generation Rates

Range of Nitrate (molar)	$G\left(\frac{\text{molecules H}_2}{100 \text{ eV}}\right)$	Equation*	$R\left(\frac{\text{ft}^3 \text{ H}_2}{10^6 \text{ BTU}}\right)$
0-0.003	0.45		42.
0.0003-8.0	$G = 0.536$ $- 0.651\{[\text{NO}_3^-]^{1/3}\}$ $+ 0.268\{[\text{NO}_3^-]^{2/3}\}$ $- 0.0352\{[\text{NO}_3^-]\}$	$G = 50.6$ $- 61.4\{[\text{NO}_3^-]^{1/3}\}$ $+ 25.3\{[\text{NO}_3^-]^{2/3}\}$ $- 3.32\{[\text{NO}_3^-]\}$	

*The units for $[\text{NO}_3^-]$ are "molar."

FIGURE 1. Experimental and Calculated G-Values

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