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**RADIOLYTIC HYDROGEN PRODUCTION FROM PROCESS
VESSELS IN HB LINE - PRODUCTION RATES COMPARED
TO EVOLUTION RATES AND DISCUSSION OF LASL
REVIEWS (U)**

by N. E. Bibler

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NOVEMBER 12, 1992

TO: R. MAHER
FROM: N. E. BIBLER

NEB

**RADIOLYTIC HYDROGEN PRODUCTION FROM PROCESS VESSELS IN HB LINE -
PRODUCTION RATES COMPARED TO EVOLUTION RATES AND DISCUSSION OF
LASL REVIEWS**

INTRODUCTION AND SUMMARY

Hydrogen production from radiolysis of aqueous solutions can create a safety hazard since hydrogen is flammable. At times this production can be significant, especially in HB line where nitric acid solutions containing high concentrations of Pu-238, an intense alpha emitter, are processed. The hydrogen production rates from these solutions are necessary for safety analyses of these process systems. In 1974 I measured hydrogen production rates from alpha radiolysis of nitric acid solutions using Cm-244 as the source of the alpha particles (1). Recently there has been some discussion concerning whether my rates are applicable for the safety analyses or whether results from tests with Pu-239 (2,3) should be used. The tests with Pu-239 measured the rates of gas evolution from nitric acid solutions and my tests measured maximum hydrogen production rates. To gain further information on this subject, scientists at Los Alamos Scientific Laboratory (LASL) were asked to compare my results to the results with Pu-239. This memorandum compares my measured production rates with the measured evolved hydrogen rates. The results of the reviews by two scientists at LASL are also presented and discussed. Based on analysis of produced versus evolved hydrogen rates, I recommend that the production rates that I measured be used in safety analyses. The reviewers at LASL are in complete agreement with this recommendation.

HYDROGEN PRODUCTION RATES COMPARED TO EVOLUTION RATES

Figures 1 and 2 show the results of all the experiments measuring hydrogen rates from alpha radiolysis of nitric acid solutions. A literature search performed this week indicated no work had been done in this field since mine in 1974(1). The rates in Figures 1 and 2 are presented as molecules of hydrogen measured per 100eV of alpha energy absorbed by the solution. This quantity is called the G-value for hydrogen, G(H₂). With this value and knowing the concentration of alpha emitters in solution, the rate of hydrogen formation can be calculated. Figure 1 shows measured G-values for tests where efforts were taken to ensure that all of the hydrogen gas that was produced was removed from the nitric acid solution and measured. Reference 1 used Cm-244 (an intense alpha emitter with t_{1/2} = 17.9 years) as the source of the alpha particles. The solution was agitated to ensure that all the gas was removed from solution. The volume of gas produced as a function of time or alpha dose was measured. The composition of the gas was also measured. Figure 1 also shows the results of studies where Po-210 (t_{1/2} = 0.38 years) was used as the source of the alpha particles (4). In these tests, the solutions were pumped on after various times to ensure that all the gas was removed from the solutions. The amount of gas obtained was measured and its composition determined. Note in Figure 1 that the results with Cm-244 and Po-210 are in excellent agreement. The data in Figure 1 indicate that G(H₂) decreases as the nitrate concentration increases. This is due to the fact that nitrate ions can successfully compete for H atoms formed by the radiation. These H atoms are the precursors of the hydrogen (5). The appropriate chemical reactions are:

Figure 2 compares the data from Figure 1 with data from tests where only the gas evolved from solution was measured. These data are presented on a logarithmic rather than a linear scale to more clearly illustrate the differences in the data at large nitrate concentrations. In tests where only the evolved gas was measured (References 2 and 3), the solutions were not agitated or pumped on. They were simply stored at ambient temperature for a period of time and the pressure above the solution measured as a function of alpha dose. The results of two non agitated tests with Cm-244 (1) are also presented in Figure 2. In these two tests the volume of gas evolving from a non agitated solution was measured. Note in Figure 2 that the values for G(H₂) are lower in all cases where the hydrogen rates were measured based on gas removed from solution. In the tests where all the gas that was produced was measured, these rates are the maximum hydrogen production rates. The rates at which hydrogen is released from the solution are dependent on various factors such as the agitation of the

solution, the solubility of hydrogen in the solution, and even the shape of the vessel. With regard to agitation, consider the amount of gas released from a bottle of coca cola that has been shaken compared to one that has not been shaken. Concerning the shape of the vessel, consider gas escaping from a solution stored in a wide tank to one stored in a pipe where the liquid-gas interface is less. When these factors are considered, it is apparent that it is difficult to reliably predict how fast a radiolytically produced gas escapes from a solution without performing tests on the solution in the actual tank in which it will be stored. Consequently, when performing a safety analysis it is best to use the maximum rate of hydrogen production. This is known only when all the hydrogen produced is measured. As indicated in the next section, the reviewers at LASL agree with this.

LASL REVIEWS OF RADIOLYTIC PRODUCTION OF HYDROGEN

At the request of Mr. Victor Stello, Jr., Principal Deputy Assistant Secretary for Facilities of the U. S. Department of Energy, the papers reporting my work with Cm-244 (1) and Sheppard's work with Pu-239 (2) were sent to Dr. D. R. Harbur at LASL for review. Mr. Stello wanted LASL to review the works and offer an opinion concerning which rates of hydrogen production should be used for safety calculations at SRS - mine or Sheppard's. At LASL the works were reviewed by Dr. S. F. Marsh and Dr. K. K. S. Pillay. A copy of each of these reviews is attached. I've also attached a copy of a letter that Dr. Harbur sent to Mr. Stello summarizing the reviews. All three scientists at LASL recommend that my values for the rates of hydrogen production be used for safety analyses and not the values measured by Sheppard. The rates of hydrogen production that I measured are the maximum rates at which hydrogen can be released from solution. Even though the reviewers agree that my values should be used, I have one major problem with their reviews. I think both reviewers place too much emphasis on the role of Pu in influencing the chemistry that is occurring during radiolysis. In my study I did two experiments with 0.21M Pu present as well as the Cm-244 (1). These tests were at 5.6 and 10M nitric acid. The results agreed well with results in absence of Pu suggesting that Pu was not affecting the rate of hydrogen production. Further, it appears that Marsh has misinterpreted my results when he states that my results agree with Sheppard's (and Kazanjian's) when Pu is present. For example, at 10M acid I found that $G(H_2)$ is 0.1, while the other workers found values approximately 4X less. To me a factor of four indicates disagreement. However, this disagreement does not affect the conclusion that my G-values should be used for safety analysis calculations.

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1. N. E. Bibler, "Curium-244 Alpha Radiolysis of Nitric Acid, Oxygen Production from Direct Radiolysis of Nitrate Ions," J. Phys. Chem 78(3) pp. 211-214 (1974).
2. J. C. Sheppard, "Alpha Radiolysis of Plutonium (IV)-Nitric Acid Solutions," Pacific Northwest Laboratory Report BNWL-751 (May 1968).
3. Y. I. Savel'ev, A. V. Ershova, and M. V. Vladimirova, "Alpha-Radiolysis of Aqueous Solutions of Nitric Acid," Radiokhim, 9(2) pp. 225-230 (1966).
4. A. R. Kazanjian and D. R. Horrell, "Radiolytically Generated Gases in Plutonium-Nitric Acid Solutions," Radiat. Effects 13, pp. 277-280 (1972).
5. I. G. Dranganic and Z. D. Dranganic, The Radiation Chemistry of Water, p. 76, Academic Press, NY (1971).

Figure 1. Hydrogen production rate from alpha radiolysis of nitric acid solutions. Cm-244 was used as the alpha source in Reference 1. Po-210 was used in Reference 4.

Figure 2. Measured hydrogen rates from alpha radiolysis of nitric acid solutions. The open symbols and solid line define data from tests where all the gas that was produced was measured. The solid symbols and dashed lines are for tests where only the evolved gas was measured.

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DATE: November 4, 1992
IN REPLY REFER TO: NMT-DO: (U) 92-721
MAIL STOP: E500
TELEPHONE: (505) 667-2556
FAX: (505) 667-7966

Victor Stello, Jr.
Principal Deputy Assistant
Secretary for Facilities
U.S. Department of Energy
FORS/DP-6/4A-043
1000 Independence Ave., S.W.
Washington, DC 20585

Dear Mr. Stello: *Via*

**SUBJECT: HYDROGEN GAS BUILDUP IN SAVANNAH RIVER PROCESS
VESSELS**

In reviewing the documents from Savannah River sent to us yesterday, we agree with their calculations concerning hydrogen gas generation in the October 12, 1992, memo. This memo uses the $G(H_2)$ from Sheppard's work. While I believe there are several valid reasons for explaining why Bibler's $G(H_2)$ values are higher (some of which are articulated in the attached review by Fred Marsh), I would tend to agree that the higher values should be used for safety analysis calculations. With enough supporting evidence, it might be possible to argue that hydrogen generation and ultimate hydrogen gas buildup in the vapor phase are very different for a particular vessel, but that evidence does not yet exist. Further, it would appear that the difference between hydrogen generation and ultimate hydrogen gas buildup would be dependent upon multiple variables.

There are several methods such as purging or catalysis that could mitigate the risk posed by this potential hazard and I believe that they need to be considered.

Sincerely,

Delbert R. Harbur
Division Leader
Nuclear Materials Technology

DRH:srw

Attach. & Dist. on page 2.

NMT-DO:(U)92-721
Harbur to Stallo

November 4, 1992
page 2

Attach.: 1) Memo dated 11/4/92, Marsh to Harbur, same subj.
2) FAX dated 11/4/92, Pillay to Harbur

xc: CRM-4, MS A150
E. M. Wewerka, ADCM, MS A102
D. R. Harbur, NMT-DO, MS E500
NMT-DO file

bcc: N. Bibler, WH-SRC (FAX #803-725-4704)

November 4, 1992

To: D. R. Harbur, NMT Division Leader, MS E500

From: S. F. Marsh, NMT-2, MS E501

Subject: Hydrogen Gas Buildup in Savannah River Process Vessels

I have reviewed the documents FAXed to you by Chuck Mason and have also attempted to quickly review other published material that might be pertinent.

$G(H_2)$ values are highest in pure water and decrease with increasing nitric acid concentration. This effect is attributed to the reaction of nitrate ion with atomic hydrogen radicals before they can form molecular hydrogen.¹ Iron is known to have a similar effect. It would not surprise me if plutonium, which can have significant amounts of (III), (IV), and (VI) oxidation states simultaneously existing in acid solution, could also affect $G(H_2)$. Although Kazanjian² studied the effect of two high concentrations of plutonium (50 and 100 g/L), I find no investigation of the effect of much lower levels of a high-specific-activity isotope, such as ^{238}Pu . The possibility of chemical reactions that involve plutonium should be considered. The $G(H_2)$ values of Bibler,³ Sheppard,⁴ and Kazanjian², all of whom had appreciable plutonium in solution, are in reasonable agreement (with the exception of Bibler's value for static 10.1 M acid). However, Savel'ev,⁵ who used a ^{210}Po alpha source in plutonium-free solutions, reports somewhat higher $G(H_2)$ values.

Some literature values for $G(H_2)$ from alpha radiolysis are:

<u>Nitric Acid Molarity</u>	<u>Pu g/L</u>	<u>$G(H_2)$</u>	<u>Reference</u>
5.6 (agitated)	50	0.13	Bibler
5.6 (static)	50	0.08	Bibler
10.1 (agitated)	50	0.10	Bibler
10.1 (static)	50	0.07	Bibler
1.0	58	0.28	Sheppard
2.4	117	0.13	Sheppard
4.2	112	0.039	Sheppard
6.6	113	0.057	Sheppard
8.0	112	0.024	Sheppard
0.1	?	0.5	Bakh
1.0	?	0.18	Bakh
5.0	?	0.05	Bakh
1	50	0.20	Kazanjian
1	100	0.19	Kazanjian
5	50	0.056	Kazanjian
5	100	0.050	Kazanjian
10	50	0.018	Kazanjian
10	100	0.027	Kazanjian

0.01	(none) ^{210}Po	1.203	Savel'ev
0.05	(none) ^{210}Po	0.926	Savel'ev
0.1	(none) ^{210}Po	0.916	Savel'ev
0.5	(none) ^{210}Po	0.648	Savel'ev
1.0	(none) ^{210}Po	0.448	Savel'ev
2.0	(none) ^{210}Po	0.347	Savel'ev
4.0	(none) ^{210}Po	0.160	Savel'ev
6.0	(none) ^{210}Po	0.086	Savel'ev

Comments

1. Observed differences in $G(\text{H}_2)$ values might reflect a contribution from the multiple oxidation states (and disproportionation) of plutonium. The higher $G(\text{H}_2)$ values of Savel'ev, who used polonium as the alpha source in the absence of plutonium, supports this possibility.

2. Bibler reported higher $G(\text{H}_2)$ values when the solutions were agitated. Agitation would be expected to sweep out the molecular hydrogen gas before it could react with solution components, and also give less opportunity for intermediate radiolytic species to recombine. Bibler's findings suggest that agitation should be avoided during processing, if possible.

3. Plutonium is known to disproportionate more readily at lower concentrations of nitric acid. Radiolytic hydrogen peroxide then reoxidizes Pu(III) to (IV) , which again disproportionates to Pu(III) and (VI) . Perhaps this also plays a role in side-reactions that decrease the formation of molecular hydrogen.

4. Sheppard demonstrated that a palladium catalyst is very effective in preventing the buildup of radiolytic gases, and even causes already existing gas pressure to decrease when palladium is added. An appropriate quantity of this catalyst could be available to expose to the vapor phase if hydrogen increases above a specified limit. Sheppard found that the palladium catalyst kept gas pressure down for nearly a month, which provides a long time to take corrective action. This seems like an obvious way to address safety concerns, which should be the main issue.

References

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2. A. R. Kazanjian and D. R. Horrell, "Radiolytically Generated Gases in Plutonium-Nitric Acid Solutions," *Radiat. Effects* 13, pp. 277-280 (1972).
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Los Alamos National LaboratorySafeguards Systems Group
N-4, Mail Stop: E-541 / 7-7777**FAX COVER SHEET****To: Dr. Delbert R. Harbur**
NMT/DO**FAX No. 7-7966**

Verify:

From: Dr. K. K. S. Pillay
N-4, Mail Stop: E-541
Los Alamos National Laboratory
Los Alamos, NM 87545 (USA).

Fax# (505)667-7626

Verify (505)667-5428

Message:**November 4, 1992**

Dear Del Harbur:

Yesterday evening Gordon Jarvinen of NMT-2 brought me a copy of the FAX message you received from Chuck Mason of Savannah River Field Office. Although Gordon was not clear as to what was expected of us, I read the package carefully and recognized the differences in the results of the two studies by Bibler & Shepperd. Also, I looked at some of the other literature on the subject and they all have somewhat different G-values for hydrogen evolution from nitrate media. I am not surprised at the difference considering the differences in experimental conditions and the scavenging actions of other ionic species in the media. If the questions asked of you is to recommend actions to improve safety, my thoughts are as follows.

1. SRP should use Ned Bibler's conservative numbers on G-values for designing systems and in evaluating pressure spikes.
2. It would be prudent to install Pd-based catalysts to remove hydrogen accumulated in tanks routinely, especially when the purge system fail.

I talked with Fred Marsh this morning and we seem to generally agree on this.

Incidentally, there was a similar request from DOE/DP-62 to N-6 Group who consulted me on the subject. They also seem to agree with my suggestions as a reasonable answer to the concerns raised.

If I can be further assistance, please let me hear from you.

Regards.
SAM Pillay

P. S.: I am looking forward to joining NMT/Dn. soon. Rita Berry is trying find some office space for me.

**DATE
FILMED**

8 / 16 / 93

END