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GAS GENERATION FROM LOW-LEVEL RADIOACTIVE WASTE: CONCERNS FOR DISPOSAL*

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ABSTRACT

The Advisory Committee on Nuclear Waste (ACNW) has urged the Nuclear Regulatory Commission (NRC) to reexamine the topic of hydrogen gas generation from low-level radioactive waste (LLW) in closed spaces to ensure that the slow buildup of hydrogen from water-bearing wastes in sealed containers does not become a problem for long-term safe disposal. Brookhaven National Laboratory (BNL) has prepared a report, summarized in this paper, for the NRC to respond to these concerns. The paper discusses the range of values for $G(H_2)$ reported for materials of relevance to LLW disposal; most of these values are in the range of 0.1 to 0.6. Most studies of radiolytic hydrogen generation indicate a leveling off of pressurization, probably because of chemical kinetics involving, in many cases, the radiolysis of water within the waste. Even if no leveling off occurs, realistic gas leakage rates (indicating poor closure by gaskets on drums and liners) will result in adequate relief of pressure for radiolytic gas generation from the majority of commercial sector LLW packages. Biodegradative gas generation, however, could pose a pressurization hazard even at realistic gas leakage rates. Recommendations include passive vents on LLW containers (as already specified for high integrity containers) and upper limits to the G values and/or the specific activity of the LLW.

INTRODUCTION

The ACNW in its review of the June 1990 draft of Revision 1 of the Nuclear Regulatory Commission (NRC) Technical Position on Waste Form raised a new issue which goes beyond the question of irradiation-induced damage in stabilized LLW, namely that of pressurization of waste containers as a result of the radiolytic generation of gases, particularly hydrogen gas. The ACNW noted that recent investigations of radiolytic gas generation at Argonne National Laboratory (ANL) indicated that for γ radiolysis of certain cement waste forms, there was no leveling off of the hydrogen gas pressure with increasing dose (1) as other investigators had reported at BNL and Savannah River Laboratory (SRL) (2,3). The ACNW, therefore, urged the NRC to reexamine the topic of hydrogen generation from LLW in closed spaces to ensure that the slow buildup of hydrogen from water-bearing wastes in sealed containers does not become a problem for long-term safe disposal.

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This paper summarizes the results of a report (4) prepared by BNL for the NRC in response to the concerns of the ACNW regarding gas generation from LLW in containers as an issue for disposal. The concern is the accumulation of quantities of gases sufficient to pose hazards due to combustibility, pressurization of the container, or both. The study approached the issue of gas generation in LLW by investigating the rate of gas generation within a container and the rate of gas leakage from the container. Since the rate of gas permeation from the container will depend on the concentration of the gas in the container, one may estimate the steady-state overpressures for any given gas generation conditions. Overpressure means the portion of the pressure within a container above the nominal external pressure of one atmosphere.

This paper will first consider the reported range of experimental values for radiolytic gas generation from materials of relevance to LLW disposal. It will also consider other sources of gas generation in LLW packages. The discussion then turns to leakage rates of gas from LLW containers. With information about the dependence of leakage rates on internal container pressures, one may estimate what rate of gas generation will result in a given overpressure. With these results, one may then determine if a given rate of gas generation within a container will result in overpressures of concern for flammability or container failure. Overpressures of concern are 4% and 40%. The lower flammability limit of H_2 gas in air is about 4%. The 40% figure is consistent with maximum sustained overpressures determined in actual 55-gallon (0.21-m^3) drums (5) and is thus indicative of excessive pressurization apart from flammability considerations.

RADIOLYTIC GAS GENERATION FROM LLW

Using the radiolytic gas generation rates calculated for extended storage of LLW (6) as a starting point, this report calculates the rate of hydrogen generation from cement-solidified LLW. The material parameter of interest is the G value, the quantity of any particular radiolytically generated species (e.g., the number of molecules of H_2 formed) per 100 eV of absorbed radiant energy. For H_2 generation by γ radiolysis from portland cement and related materials, the following values for $G(H_2)$ were reported:

by SRL (3)	0.03,
by BNL (2)	0.11 - 0.35,
by ANL (1)	0.14 - 0.22,
by Winfrith, UK (7)	0.13.

Note, however, that the waste-binder combinations used to solidify LLW at commercial power plants differ from those used in the studies of radiolytic gas generation discussed above. For example, many of the cements used to solidify Class B and Class C waste from commercial nuclear power reactors are formulated cements containing proprietary additives such as fly ash or other pozzolanic materials. (Although the ANL study used pozzolanic cemented waste formulations, these are not similar to LLW/pozzolanic-cement-binder formulations likely to be encountered in the NRC-regulated commercial sector.) Thus, the radiolytic yields of hydrogen from formulated cements containing pozzolanic constituents or other proprietary additives may be different from those obtained in the studies listed above.

In this context "different from" may mean either "greater than" or "less than." The relative radiolytic hydrogen yields from pozzolanic and non-pozzolanic cements remains an open question. The radiolytic products from cement are by some workers attributed to the radiolysis of the pore water in the cement. For example, according to Bibler and Orebaugh (3), the attainment of a steady-state pressure [of H_2] and its dose rate dependence are consistent with the free radical model for H_2 production from γ radiolysis of water. It appears, therefore, that the oxide components of the cement and plaster binder material matrix are not drastically altering the radiation chemistry of the water.

Based on the results of the irradiation of aqueous solutions, the radiolytic products from a cementitious waste form will depend greatly on the oxidizing or reducing capabilities of the solutes in the pore water of that waste form, especially those solutes originating from the waste or from any pozzolanic additives. In the absence of actual measurements of radiolytic hydrogen from pozzolanic binder materials and from representative LLW stabilized in such materials, it would be prudent to assume conservative (i.e., credibly large) values of radiolytic hydrogen yields for such materials in any preliminary analysis such as the one in the report.

From a recent compilation (8) of G values of interest in the context of radioactive waste, the G values for selected LLW and binder materials range up to 0.6 except for polyethylene with a G value of 2 and ion-exchange resins, for which $G(H_2)$ ranges from 0.1 to 3.1 (but most reported values range from 0.3 to 0.6). Anything beyond a preliminary analysis will require experimental data from laboratory or field systems. For cement-solidified ion-exchange resins, values of 0.19 to 0.24 are reported (9); for cement-solidified filter sludges consisting mainly of mixed "powdex" resins, $G(H_2)$ ranges from 0.11 to 0.17 (7).

Table I presents the radiolytic hydrogen generation rates for selected radionuclides for a range of $G(H_2)$ values. It is assumed that the radionuclides are distributed uniformly through unit density waste in a 55-gallon drum at their highest specific activities as listed in 10 CFR Section 61.55. For a 200-ft^3 (5.7-m^3) liner, assuming that the gas generation rate is directly proportional to the waste volume, one would have to multiply the tabulated gas generation rates by a factor of 27 to account for the increased waste volume. (For γ rays, the factor would be somewhat larger, since the larger the container, the smaller the surface-to-volume ratio and the larger the portion of the radiation which is absorbed within the waste.)

Certain features are common to most of the studies of gas generation due to γ radiolysis of portland cement, organic ion exchange resins, and resin-cement composites and, therefore, would be expected in similar studies.

a) There is usually an initial decrease in the total gas pressure due to radiolytic oxygen depletion. The pressure then rises as radiolytic hydrogen generation proceeds.

b) The value of $G(H_2)$ for γ irradiation usually ranges from 0.1 to 0.6.

c) Accompanying the production of radiolytic H_2 during the γ irradiation of ion exchange resins, there is often a concomitant production of CH_4 and/or CO_2. However, these latter gases generally constitute only a few percent of the total gas generation.

d) In several of the studies of γ radiolysis, a steady state H_2 pressure was attained at sufficiently high cumulative doses. (The ANL study is an apparent exception. The argument can always be made that the irradiation had not been carried out to a high enough cumulative dose. Based on chemical kinetic considerations, however, the dose rate determines the steady-state pressure of the radiolytically generated gas, but the void space into which the gas expands may be more significant than the total dose in determining when a steady state predominates.)

These features are also evident in the γ radiolysis studies of the SRL "concrete" and high-alumina cement formulations. For theoretical reasons (as well as from some limited empirical data) similar results would be expected for comparable β irradiation doses if the β rays (such as those from Sr-90 and Y-90) have linear energy transfer values similar to those of the γ rays of greatest interest (Co-60, Cs-137) (10).

OTHER SOURCES OF GAS GENERATION IN LLW

A related source of gas generation from LLW is chemical production of H_2 gas as a result of a corrosion process due to radiolytically generated acids (11). Such acid corrosion processes would not be expected in cement-solidified LLW because of the extreme alkalinity of the portland cement matrix but should be considered when evaluating other binder materials.

Another source of gas from LLW is biodegradation. Biodegradative gas generation rates are available for certain specified materials (12) and may be converted into equivalent generation rates per 55-gallon drum per hour:

Composite trash waste:	1.2×10^{-7} moles CO_2/g-day	=	2.4×10^{-2} ℓ/drum-h
Bitumen:	8.2×10^{-3} moles CO_2/drum-day	=	7.7×10^{-3} ℓ/drum-h
Trench leachate:	1.5×10^{-8} moles CH_4/g-day	=	2.9×10^{-3} ℓ/drum-h

Based on some preliminary laboratory results at BNL, biodegradation may be enhanced in organic polymers exposed to a radiation field, probably as a result of radiolytic breakdown of larger molecules into smaller ones more susceptible to microbial attack (13). Biodegradation is not expected to occur in the cement matrix of wastes stabilized by solidification in portland cement or similar materials, since the matrix would not be capable of supporting the growth of microorganisms. The alkalinity of the cement matrix also discourages microbial growth.

RATES OF GAS LEAKAGE FROM LLW CONTAINERS

The rate of gas leakage from 55-gallon drums has been calculated utilizing a diffusional model (14) and estimated from measurements of pressure drops in actual drums by workers at SRL (15). Based on this diffusional model of gas transport through the drum gasket, one may calculate the following leakage rates for H_2 gas:

$$5.6 \times 10^{-4}\ \ell/h \text{ at } 4\% \text{ overpressure}$$

$$5.6 \times 10^{-3}\ \ell/h \text{ at } 40\% \text{ overpressure}$$

These leakage rates are less than most of the gas generation rates in Table I, so that the steady-state overpressures will exceed the 4% flammability limit for most of the entries in that table. For Sr-90, the steady state pressure exceeds 40% overpressure for the tabulated G values of 0.1 and 0.6. Based on the limited data on biodegradative gas generation, the biodegradatively generated gases will have overpressures well over 40%. Average leak rates based on actual observations at SRL of the rate of gas leakage from 55-gallon drums, however, are estimated to be about 0.4 cc/min (= 2.4×10^{-2} ℓ/h) for drums with gas pressures of up to 1 psig (6.9 kPa gauge pressure, which equals about 7% overpressure). Leakage between the gasket and sealing surface has been reported to be the predominant mechanism of release.

Based on these actual leak rates, the only radionuclide in Table I to pose a potential flammability hazard for LLW in 55-gallon drums is Sr-90 near its Class C upper limit of specific activity, and then only for G values of about 0.6 or greater. For LLW in 200-ft^3 liners, however, (assuming that the gas generation rate is proportional to waste volume and that leakage characteristics are the same as those of 55-gallon drums) any of the first three radionuclides in Table I could pose a potential flammability hazard at the given specific activities for G values of about 0.1 or greater. Also, biodegradative gas generation, especially from composite trash waste, could pose a pressurization hazard even at realistic leak rates.

Even assuming steady-state pressures at increasing doses in accord with available data, this H_2 pressure could be as large as several psi and thus above the lower flammability limit **in the presence of oxygen**. The attainment of steady-state pressures of H_2, however, is associated in the experimental data with a concomitant consumption of O_2, so that flammable gas mixtures will exist only for relatively brief periods, if at all, unless breach of the container allows atmospheric O_2 to enter.

CONCLUSIONS AND RECOMMENDATIONS

It should be emphasized that accumulations of radiolytically generated gases in waste containers will result in flammable gas mixtures or pressurization of the waste container only under a combination of relatively extreme conditions, namely, radionuclide activities near the upper limit of Class C, relatively high G values (> 0.6 for 55-gallon drums; > 0.1 for 200-ft^3 liners) for the waste and binder media, and a tightly sealed container. The greatest source of uncertainty in assessing the accumulation of radiolytically generated gases is the magnitude of release of these gases from an intact container. Although the accumulation of radiolytically generated gas will be a concern only for a very small portion of the LLW produced by the NRC-regulated commercial sector, quantifying this portion of LLW is difficult because of the lack of information on gas release from intact containers. One may also consider overpressurization of LLW containers due to gas generated by biodegradation of organic waste and/or binder materials to be a cause for concern.

As a practical matter, gas generation from LLW and any associated flammability or pressurization hazards appear to be more of a potential hazard for storage, handling, and transport rather than for disposal. NRC has issued Information Notice 84-72 to address potential combustibility hazards arising during waste shipments from hydrogen gas generation. However, with engineered barrier systems constructed of concrete likely to replace shallow land burial at new disposal sites, there is the possibility that LLW received first in a disposal module may generate sufficient gas to become hazardous before the last LLW is emplaced and the disposal unit closed. This hazard is associated with the container itself, since the relatively high permeability of concrete compared to that of the drum gasket material renders both the accumulation of flammable mixtures and the buildup of pressure unlikely within a concrete disposal vault (12).

This paper concludes with the following recommendations:

1) The specification in the NRC Technical Position on Waste Form for passive vents on high integrity containers should be extended to other containers if there is a potential for gas generation from the LLW. provided that the waste generators, shippers, and handlers remain cognizant of the small potential for accumulation of flammable gases in storage and disposal areas.

2) The NRC should consider specifying an upper limit to the G value and/or to the specific activity of LLW to bound the radiolytic component of gases generated from LLW.

3) There is a need for better measurements of the radiolytic gas generation (and consumption) rates from various kinds of LLW, binder materials, and combinations thereof. In particular, the steady-state pressurization of radiolytically generated H_2 needs further investigation in order to determine the limiting parameters (e.g., cumulative dose, dose rate, gas expansion volume) for systems of interest. [Calculational methods also need some improvement. Calculational techniques presented by Flaherty et al. (16) are an important advance in this area.]

4) There is also a need for better measurements of the rates of gas release from the various types of containers intended for use in the disposal of LLW. Information is particularly needed about the dependence of the gas release rates on internal gas pressure, on chemical species of gas, and on the properties of the gasket and sealing surface.

5) The generation and the subsequent mobility through the waste and binder matrices of radiolytically generated acids should be considered when evaluating the performance after disposal of containers of waste solidified in binders other than cement. These acids can react with certain metallic container materials, e.g., mild steel, to produce H_2 as a result of chemical corrosion processes.

REFERENCES

1. M. A. LEWIS and D. W. WARREN, "Gas Generation from the Irradiation of Mortar," presented at the 91st Annual Meeting of the American Ceramic Society, Indianapolis, IN, 1989.

2. P. COLOMBO and R. M. NEILSON, JR., "Properties of Radioactive Wastes and Waste Containers" - First Topical Report, NUREG/CR-0619, August 1979.

3. N. E. BIBLER and E. G. OREBAUGH, "Radiolytic Gas Production from Tritiated Waste Forms - Gamma and Alpha Radiolysis Studies," DP-1459, July 1977.

4. B. SISKIND, Brookhaven National Laboratory, "Gas Generation from Low-Level Waste," WM-3175-16, August 1991.

5. N. MORCOS, R. DAYAL, and A. J. WEISS, "Properties of Radioactive Wastes and Waste Containers - Status Report October 1980 - September 1981," NUREG/CR-2617, April 1982.

6. B. SISKIND, D. R. DOUGHERTY, and D. R. MACKENZIE, "Extended Storage of Low-Level Radioactive Waste: Potential Problem Areas," NUREG/CR-4062, December 1985.

7. T. R. HOLLAND, "The Effect of Gamma Irradiation on the Stability of Cemented Winfrith Reactor (SGHWR) Sludge," AEEW-R 1924, January 1985.

8. C. R. PALMER, "Radwaste Radiolytic Gas Generation Literature Review," EPRI NP-5977, September 1988.

9. R. E. BARLETTA, K. J. SWYLER, S. F. CHAN, and R. E. DAVIS, "Solidification of Irradiated Epicor-II Waste Products," NUREG/CR-2969, May 1983.

10. A. CHARLESBY, Atomic Radiation and Polymers, Pergamon Press, Oxford, 1960.

11. K. J. SWYLER, C. J. DODGE, and R. DAYAL, " Assessment of Irradiation Effects in Radwaste Containing Organic Ion-Exchange Media," Topical Report, NUREG/CR-3812, May 1984.

12. D. R. MACKENZIE and B. S. BOWERMAN, "Gas Generation in Concrete Vaults Containing Buried LLW and the Need to Provide Vents for Relief of Pressure Buildup Due to Such Gas Generation," June 3, 1987, Memorandum to File reproduced as Appendix A to D. R. MacKenzie and M. G. Cowgill, Brookhaven National Laboratory, "Evaluation of Durability of Materials Used in Alternative Low-Level Waste Facilities," Technical Letter Report, WM-3951-7, October 1988.

13. B. S. BOWERMAN, J. H. CLINTON, and S. COWDERY, "Biodegradation of Ion-Exchange Media," NUREG/CR-5221, August 1988.

14. F. G. SMITH, III, "A Computer Model of Gas Generation and Transport Within TRU Waste Drums," DP-1754, June 1988.

15. J. P. RYAN, "Radiogenic Gas Accumulation in TRU Waste Storage Drums, " DP-1604, January 1982.

16. J. E. FLAHERTY, A. FUJITA, C. P. DELTETE, and G. J. QUINN, "A Calculational Technique to Predict Combustible Gas Generation in Sealed Radioactive Waste Containers," GEND 041, May 1986.

Table I. RADIOLYTIC H_2 GENERATION FROM LLW IN A 55-GALLON DRUM

Radionuclide	Specific Activity (Ci/m^3)	Rate of Gas Generation (ℓ/h-drum)			
		G = 0.03	G = 0.1	G = 0.3	G = 0.6
Co-60	700	2.1×10^{-4}	7.0×10^{-4}	2.1×10^{-3}	4.2×10^{-3}
Cs-137	4600	5.8×10^{-4}	1.9×10^{-3}	5.8×10^{-3}	1.2×10^{-2}
Sr-90	7000	2.4×10^{-3}	8.0×10^{-3}	2.4×10^{-2}	4.8×10^{-2}
α emitter	[100 nCi/g]	-	-	-	3.7×10^{-6}

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