GAS GENERATION PHENOMENA IN RADIOACTIVE WASTE TRANSPORTATION PACKAGING

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SUMMARY

The interaction of radiation from radioactive materials with the waste matrix can lead to the deterioration of the waste form resulting in the possible formation of gaseous species. Depending on the type and characteristics of the radiation source, the generation of hydrogen may predominate. Since the interaction of alpha particles with the waste form results in significant energy transfer, other gases such as carbon oxides, methane, nitrogen oxides, oxygen, water, and helium are possible. The type of gases produced from the waste forms is determined by the mechanisms involved in the waste degradation. For transuranic wastes, the identified degradation mechanisms are reported to be caused by radiolysis, thermal decomposition or dewatering, chemical corrosion, and bacterial action. While all these mechanisms may be responsible for the buildup of gases during the storage of wastes, radiolysis and thermal decomposition appear to be the main contributors during waste transport operations.

In this paper, we provide a review of applicable gas generation data resulting from the degradation of various waste forms under conditions typical for transport. The effects of radiolytic and thermal degradation mechanisms will be discussed in the context of transportation safety.

INTRODUCTION

The interaction of radiation with hydrogenous material, i.e., organic compounds containing hydrogen, results in the evolution or generation of gases under certain conditions. This phenomenon is caused by the ability of ionizing radiation to break molecular bonds in the irradiated materials producing free radical species. The recombination of these radicals produces gases in many cases. If the irradiated materials have a large number of hydrogen bonds, as do most polymeric materials, cellulosics, and water, the major gas produced is hydrogen (Molecke 1979).

This molecular fragmentation process in materials is referred to as radiolysis and as such is a widely recognized phenomenon of radiation chemistry. In the United States, work in support of transuranic (TRU) waste transportation to the Waste Isolation Pilot Plant (WIPP) in Carlsbad, NM has resulted in considerable information about this process (see, for example, Brush et al, 1992). However, much of the information available from WIPP-related activity concentrates more on conditions that were to be expected for storage, especially deep geological disposition. Under these conditions, the mechanisms responsible for the formation of gases in wastes have been reported to be due to radiolysis, thermal, chemical corrosion, and bacterial degradation (Molecke 1979). Since the timescale for these mechanisms to be operative in repository environments is much longer than during typical transportation activities, the emphasis in this paper was to identify and determine whether radiolytic and thermal mechanisms are the primary contributors to the production of gases in transportation packagings.

In addition to the large body of information available for TRU waste intended for disposal at WIPP, studies of radioactive waste produced from the operation of commercial nuclear power plants have been another source of useful literature (Palmer 1988). The character of this waste is somewhat different from defense wastes since it consists of ion exchange resins, binders, sludges, and wet filters. Because of the large radionuclide loading in these materials, radiolysis is the major operative material degradation mechanisms. More recently, the Flammable Gas Safety Program at Pacific Northwest National Laboratory (Bryan et al. 1996) also has resulted in the publication of numerous reports dealing with the mitigation of potential safety hazards associated with the waste tanks at the U.S. DOE Hanford Site in Washington State. While this literature might at first glance seem unrelated to transportation activities, the information is very useful because radiolysis, coupled with thermal conditions in the tanks is the primary mechanism for the generation of gases in these tanks.

Similar to the information available from WIPP activities, a sizable information source were European nuclear energy research organization who had geologic waste disposal programs in their countries. Most notable among these were the German and French. Much of the literature involved waste forms encapsulated in cement, bitumen and polymers (Moeckel and Koester 1982).

APPROACH

An extensive computerized literature search was undertaken through the Technical Library at Sandia National Laboratories (SNL). The search was confined to the published literature from 1967 to the present. Additionally, since SNL has had programs (Brush et al. 1992) that specifically investigated gas generation issues for the WIPP, an internal database was searched to identify other literature. Finally, the meeting minutes of specific working groups (Connolly et al. 1996) engaged in continuing studies of gas generation in the transportation area were acquired and reviewed.

DISCUSSION

The formation of flammable gases in transport containers is a major safety concern during transport operations to the WIPP. For TRU wastes contained in 55-gal carbon-steel drums and being transported in the TRUPACT-II shipping package, the amount of decay energy deposited on the TRU waste material and surrounding packaging must be assured such that the concentration of hydrogen produced will be less than the explosive limit of 5 volume percent in the innermost confinement layer at the end of the maximum 60-day shipping period. Thus, the generation of potentially flammable concentrations of hydrogen gas will be controlled by limiting the decay heat for a specific payload. TRUPACT-II Content Codes (TRUCON 1989) set limits on the maximum allowable decay heat or wattage for a given waste type and payload container identified by the content code. In addition, TRUPACT-II Authorized Methods for Payload Control (TRAMPAC; TRUPACT-II SAR 1989) specifies that potentially flammable organic compounds will be limited to 500 ppm in the headspace of the payload container. Compliance with TRAMPAC is intended to minimize the risk of explosion from volatile, flammable organic compounds during transportation.

I have previously mentioned that the identified gas production mechanisms in TRU wastes are radiolysis, thermal decomposition, chemical corrosion, and bacterial action. The primary gases produced from these mechanisms are hydrogen, carbon oxides (carbon monoxide and carbon dioxide), methane, oxygen, nitrogen oxides, and helium. The predominant source of hydrogen generation in the TRUPACT-II Package is radiolysis of the hydrogenous materials in the payload. The amount of hydrogen or the gas generation rate that can be generated from each material is proportional to its G-value. The G-value is calculated by the expression given below and is defined as the number of molecules of gas produced (or consumed) per 100 eV of energy absorbed from the respective radiation type.

$$G = (\text{moles gas produced})\ (6.02 \times 10^{23}\ \text{molecules/mole})/\ (\text{eV}/100)$$

Cellulose, polyvinylchloride, polyethylene, plexiglas, and oil have relatively large G-values between 0.3 and 11. Since hydrogen generation is a direct consequence of radiolysis, the need to control the radiolytic gas generation rate imposes an upper bound on the quantity of radionuclides which can be transported per drum. The magnitude of this upper bound depends on a number of TRU waste parameters. These are:

- Waste configuration
- Release rates of hydrogen from each of the confinement layers
- Hydrogen generation rates quantified by G-values
- Operating temperature for the TRUPACT-II Package payload
- Available TRUPACT-II Package inner containment vessel void volume
- Duration of the shipping period.

As is evident from the previous listing, the temperature of the payload is one of six parameters in determining the magnitude of the gas generation rate. The decay heat generated by the radionuclides in the waste is a primary contributor to the temperature of the payload. Steady state thermal calculations for the TRUPACT-II Packaging established a maximum normal transport temperature of 154°F or 68°C. Since the calculations included solar thermal loads, a temperature of 70°C has been used by several experimentalists (Kosiewicz et al. 1980) to measure the possible synergistic effects of temperature and alpha radiolysis on gas generation rates in cellulosics and plastics. An experimentally observed (Connolly et al, 1996) decrease in gas generation with time has been ascribed to a matrix depletion phenomenon, i.e., alteration of the waste material (by evaporation, reaction or decomposition) into a material of lower gas generation potential.

While gas generation in TRU wastes during transportation may be dominated by radiolytic and thermal mechanisms, purely thermal processes such as the thermal degradation of the waste matrix can be a significant source of gases. Studies revealed that with the exception of cellulosics (paper), which decomposes at 70°C, most organic materials decompose at temperatures above 150°C (Kosiewicz 1980a). The gases evolved during thermal decomposition in air are primarily carbon dioxide and hydrogen. Water may also be produced especially where decomposition occurs above 100°C. From a transportation perspective, the impact of thermal dewatering may be in the corrosion of the primary waste containment container. However, the amount of corrosion of the steel containers over a typical shipping operation will be negligible. The greater concern from a transportation perspective, is the radiolysis of the water vapor within the container during transport. The formation of gaseous hydrogen and oxygen under certain conditions are certainly possible from alpha radiolysis of water vapor.

In the previous discussions, all the emphasis was on normal transport conditions. Let me now turn attention to hypothetical transportation accident conditions. These conditions involve exposure of a Type B transport package to environments that might be encountered during transportation accidents such as drops, puncture, fire, and water submersion. The thermal test performed at SNL for certification on two prototype TRUPACT-II Packages revealed that the average drum wall temperatures ranged from 132 (55) to 153°F (67°C) for the two packages (TRUPACT-II SAR). Since these temperatures were similar to those found for the normal transport conditions, the gas generation rates resulting from thermal decomposition reactions in the TRUPACT-II Shipping Package under accident conditions are similar to those encountered under normal transport conditions.

Since all previous discussions have dealt with TRU waste, where thermal effects on the wastes may or may not play a major role in the generation of gases, I now turn my attention to the Hanford Tank wastes. For these high-volume and high activity semi-liquid waste forms, numerous studies (Bryan et al. 1996) have been performed to determine how radiological and thermal processes have contributed to gas generation. For tests conducted at an approximate tank temperature (65°C), hydrogen was the predominant product, whereas at 100°C, hydrogen, nitrous oxide, and nitrogen were produced approximately equally. Under thermal/radiolytic conditions larger gas generation rates for hydrogen were believed to be due to both abstraction of an organic hydrogen by a hydrogen radical and by the direct radiolysis of water. In addition to the formation of hydrogen, the thermal decomposition of organic materials in the presence of sodium nitrate (a strong oxidizer) is a major safety concern. Particular hazards in this area are uncontrolled exothermic oxidation reactions of organic compounds by nitrate and nitrite species. However, the picture which has recently emerged (Camaioni et al. 1996) as a result of their Waste Aging Studies is that concurrent with the production of the above mentioned gases is the disappearance of energetic organic compounds and appearance of less energetic oxidized products. These results suggest that the hazards of uncontrolled oxidation reactions may not be as severe as originally thought.

Analysis

From previous discussion, a generalized statement for the generation of gases by radiolytic and/or thermal means can be made. The magnitude of the G-value of the materials and the heat load of the transportation package will determine the gas generation rates of the contents when radiolytic mechanisms are operative. The rate of gas generation (n) in moles per second from a material is given by:

$$n = W \times \Sigma_i (F_i \times G_i) \times C$$

where W is the total decay heat in watts, F is the fraction of energy emitted that is the radiation type i and is absorbed by the material, G is the number of molecules of gas produced per 100 eV of energy absorbed from radiation i, and C is the conversion constant [$\sim 1 \times 10^{-7}$ (g-mole)(100 eV)/molecule)(W-s)].

For gas generation from thermal mechanisms, i.e., by thermolysis, the physical and chemical character of the material together with the magnitude of the temperature prevailing within the packaging will determine the rate of gas production (Kosiewicz 1980a). Since Type B packaging must by necessity be designed to withstand hypothetical accident conditions, the double containment features of the packaging, the thermal insulation and the large thermal mass are incorporated into packaging design result in an attenuation of temperature increases when temperatures increase inside and outside the package. Because Type A packaging by definition is used to transport smaller quantities of radioactive materials, the insulation and packaging mass is correspondingly reduced. Specifically according to U.S. Transport Regulations (49 CFR 173), the temperature of the external surfaces of the loaded package will not, assuming still air in the shade at an ambient temperature of 38°C (100°F), exceeding either: (1) 50°C (122°F) in other than exclusive use shipments; or (2) 82°C (180°F) in an exclusive shipment. Since I have concentrated on radiolytic and thermal means of generating gases in transport packaging, decreasing quantities of radionuclides will result in lower gas generation due to radiolysis and possibly raise gas generation due to thermolysis under the appropriate conditions. These conditions are dependent on variables such as the physical and chemical character of the contents and the temperature of the package.

Temperature plays an important part in the rate at which reactions occur, i.e., determines the kinetics of the chemical reaction. Chemical reaction rates, in general, whether they be due to radiolysis or thermolysis, are therefore temperature dependent. The rate (k) of a chemical reaction can be expressed by: $k = A\exp(-B/T)$ where T is the absolute temperature, and A and B are constants. The equation can be written in the form of k =

Aexp(-E_a/RT), generally known as the Arrhenius law. E_a is the activation energy and will have different values for different chemical reactions. The activation energy (E_a) for G-values for gas generation from most materials appears to be less than or equal to 3 kcal/g-mole, giving a weak temperature dependence compared to many other chemical reactions. For most polymers, the radiolytic gas generation rates at 70°C (343°K) was calculated to be no more than approximately 2 times the gas generation rate at room temperature 25°C (298°K). Such an increase in gas generation rates has been experimentally observed for the thermal degradation of TRU-waste between 20 and 70°C.

For a chemical reaction involving only thermal degradation of the material, the thermal gas generation rates were dependent on the waste material. Rates of 0.05 - 0.08 x 10^{-6} moles/day-gram waste were observed at 70°C (Kosiwiecz et al. 1980b). In TRU-waste experiments conducted at 100°C, a more than two-fold increase in gas generation rates was found for the purely thermal reactions at this temperature and for similar exposure times. What is evident from the collected literature is that insufficient experimental data is presently available to verify that thermal mechanisms might indeed be responsible for the larger gas generation than from radiolysis when temperatures in excess of 100°C are encountered within different waste materials during transportation operations.

In the previous discussion of gas generation rates for TRU wastes, the interaction of radiation and heat with the waste matrix were essentially solid-state reactions. I now address reactions occurring in solution and heterogeneous solutions, i.e., solutions with suspended solids. With regard to studies involving radiolytic and thermal reactions of simulant tank waste, work performed at Pacific Northwest Laboratory (Bryan and Pederson, 1995) provides some useful insight. While TRU waste is a complex mixture of many materials, radionuclides, and hazardous chemicals, the Hanford Tank waste is an equally complex mixture of radionuclides and chemical species. A simple generic description of these wastes is that it consists of a mostly inorganic components and fewer organic components. The underground storage tanks at the Hanford Site are of two general varieties: (1) a single-shell tank (SST) design containing the older (pre-1980) wastes, and (2) a double-shell tank (DST) design containing the newer liquid wastes as well as some of the liquid from the SSTs. By far the greatest technical effort has been expended to understand the chemical mechanisms leading to flammable gas formation in a periodically "burping" DST, Tank 241-SY-101. Gas generation from a homogeneous simulant and a heterogeneous simulant, both of which contain only the major inorganic components of the actual waste and complexing agent, were compared under thermal conditions (90°C). Thermal gas generation rates from the homogeneous simulant were more than ten times smaller than those obtained for the heterogeneous simulant. The main gases produced under these purely thermal conditions for heterogeneous simulants in decreasing order were nitrous oxide, nitrogen, and hydrogen. Thermal gas generation rates for hydrogen was ~ 3 x 10^{-8} moles/g-day. Results suggest that liquid wastes show a greater temperature dependence of the gas generation rate than do solid wastes. Under combined radiolytic (600,000 R/hr) and thermal conditions, the quantity of gases produced from the heterogeneous simulant waste was greater than under purely thermal conditions. The main gases produced in decreasing order were nitrous oxide, hydrogen, and nitrogen. Hydrogen gas generation rates under these combined conditions were ~ 1 x 10^{-6} moles/g-day.

Since the above analyzed data was for a simulant tank waste, it is worthwhile to mention a more recent study (Bryan et al. 1996) in which real waste samples from Tank 241-SY-103 were used to measure gas generation rates under thermal conditions. In these studies, liquid tank-core samples were heated from 60 to 120°C and the evolved gases were measured. An increase in the gas generation rates for these gases were observed at 90°C. At this temperature, the gas generation rate for hydrogen was found to be ~ 6 x 10^{-8} moles/g-day. The activation energy for total gas formation was found to be 22 ± 1 kcal/mole. The calculated activation energies permit an assessment of the contribution of the radiolytic gas generation and compared with the measured thermal gas generation rates. It was determined that the radiolytic component for hydrogen generation was insignificant for those temperatures higher than 60°C.

In Table 1, an attempt was made to present data from purely thermal gas generation rate with combined radiolytic/thermal gas generation rate. The temperature at which the data was obtained ranged from a low of 70°C to a high of 100°C. While other data for some of these reactions is available outside this temperature range, these temperatures were selected to afford relative comparison. It should also be mentioned that for TRU waste very low gas generation rates were observed for both thermal and radiolytic reactions. The data in Table 1 shows that, with the exception of a TRU waste simulant held at 100°C, higher gas generation rates were observed for a combination of radiolytic and thermal reactions. These results suggest that purely thermal reactions generate smaller quantities of gases in a transport package than radiolytic reactions provided that the temperature of the packaging is kept below 100°C. From the data, it is also evident that both reactions contribute gases at similar rates, i.e, both rates are of the same order of magnitude. Thus for transportation conditions, gas generation from radiolytic and thermal reactions must be considered in order to assess the safety provided by the packaging.

Table 1. Gas Generation Rates (mole/g/day) for Thermal and Combined Radiolytic/Thermal Reactions for Different Wastes Forms at Various Temperatures.

Waste Type	Thermal Reactions	Radiolytic & Thermal
Cellulosic TRU (70°C)[+]	0.05 - 0.08 x 10^{-6}	0.3 - 0.5 x 10^{-6}
Simulant TRU (100°C)[++]	2.8 x 10^{-6}	1.4 x 10^{-6}
Heterogeneous Hanford Waste (90°C)[*]	1 x 10^{-6}	6 x 10^{-5}
Homogeneous HW Simulant (90°C)[*]	2 x 10^{-5}	5 x 10^{-5}
Homogeneous HW (90°C)[**]	2 x 10^{-7}	Unavailable

+ Kosiewicz, 1979, ++ Kosiewicz et al. 1980b, * Bryan and Pederson 1994, ** Bryan et al. 1996

CONCLUSIONS AND RECOMMENDATIONS

This paper synthesizes the results of gas generation determinations from 1967 to the present as reflected in the literature. An analysis of the data identified two primary sources for the generation of gases by thermal and radiolytic reactions. These sources included TRU wastes and high-level tank wastes located at the Hanford Site. A possibility additional source of thermal gas generation potential was suggested in chemical commodity packaging. For these sources, gas generation plays a small but still significant role at temperatures above 50°C (122°F). When temperatures above 100°C (212°F) are encountered, thermal reactions start to become a major contributor to the generated gases.

From the paucity of available experimental data in the literature for gas generation in radioactive wastes containing hazardous constituents, i.e., mixed wastes, at temperatures in excess of 100°C, additional studies are required to completely address the issue of thermal and radiolytic gas generation rates in mixed wastes. Especially useful would be the identity and quantities of gases being evolved during the thermolysis of the waste matrix at higher temperatures. The types of known gases generated by thermal and radiolytic reactions include flammable gases such as hydrogen and methane as well as non-flammable gases like carbon oxides and nitrogen oxides. To prevent pressure-buildup in transport packaging from these gases, packaging should include appropriate designed vessels that can accommodate the expected pressure increase over the operational temperature range of the packaging. Where possible pressure-relief devices such as filters should be included. Since the temperature of the packaging plays an important role, design features such as improved thermal insulation for the packing are also highly desirable.

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