GAS GENERATION FROM CH-TRU WASTES: TRANSPORT PACKAGING DESIGN IMPLICATIONS OF REGULATORY REQUIREMENTS

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ABSTRACT

Radioactive waste generates gas by several mechanisms, which can result in hydrogen and pressure buildup in a sealed packaging. This gas generation has become a major design issue for a packaging to transport plutonium contaminated wastes. Data for existing transuranic waste at Department of Energy sites are reviewed, and recommendations are made for further research. Catalytic recombiners are recommended for prevention of flammable gas buildup due to hydrogen or methane generation. Waste containers that generate large quantities of gas may need to be mixed with those that generate little gas in order to be shipped. A simple calculational method to aid this load management is described.

INTRODUCTION

Gases may be generated and consumed in organic or wet radioactive waste materials by a number of mechanisms. Radiolysis is the absorption of ionizing radiation energy in the waste material, resulting in the breaking of molecular bonds, e.g., the breakdown of water into hydrogen and oxygen. Elevated temperatures can also cause molecular breakdown (thermolysis) as well as vaporization and oxidation. Biological organisms can consume cellulosic waste materials such as paper, cloth or wood, releasing carbon dioxide, methane, or other gases, depending on the environment and the organism. Corrosion of iron will release hydrogen from water.

Transuranic waste currently stored a various national laboratories and weapons production facilities is scheduled to be transported to the Waste Isolation Pilot Plant (WIPP) beginning in 1988. Gas generation has been studied to determine its importance for long term storage at WIPP, and studies have been performed (1) to determine the rate at which these various mechanisms generate gases. Strategies to limit the buildup of hydrogen in storage, such as filtered venting of containers, have been developed and hydrogen transport through plastic bagging (2) has been analyzed. Nevertheless, gas generation has not up to now been perceived as a significant aspect of the design of a transport packaging for these wastes. In part, this was due to the experience of the waste generators: after all, serious overpressure had not been found in stored drums, and wastes had been shipped for years without addressing these concerns. The design problem arises, however, not from the conditions experienced in practice, but from the extreme conditions required when designing a packaging without exception to the governing regulations.

The first legal weight truck transport packaging designed specifically for contact handled* transuranic wastes, the TRUPACT-I, consisted of a rectangular single containment with filtered vents. Because of the venting, the designers were able to demonstrate, using very conservative gas generation data, that neither unacceptable pressure nor flammable gas buildup occurred. Also because of the venting, among other things, it was questionable whether the DOE would license the TRUPACT-I. When Transnuclear began work on a second generation design, TRUPACT-II, which included double containment and eliminated venting, the problem of gas generation became a major consideration.

THE EFFECT OF THE REGULATIONS

Two aspects of the gas generation problem are governed by separate regulations. Flammable gas buildup is governed by NRC IE Notice 84-72 (2), which requires shippers to demonstrate that a mixture of gas which includes both oxygen and hydrogen in excess of 4% will not be formed in the package, nor in the individual waste containers, within twice the expected period from closure through shipment and reopening of a package. Pressure buildup is governed by the definition of maximum normal operating pressure (MNOP) in 10CFR71 (3): the pressure at the end of one year, without venting, under ambient conditions of constant 38°C still air and a 12-hours-on, 12-hours-off cycle of solar load. The MNOP must be considered in combination with other regulatory tests, including reduction of the external atmospheric pressure to 24.1 kPa (3.5 psi) abs. The packaging must also be tested to 1.5 times the MNOP.

For transport of plutonium in excess of 20 curies, 10CFR71 also requires a separate inner container which

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* Less than 0.556 micro sv/s (200 mrem/hr) at the container surface.

meets the same leakage criteria as the outer Type B packaging.

In analyses performed for the Department of Energy when the idea of a non-vented TRUPACT was first considered (4,5), it was determined that a flammable gas mixture would be generated before the design pressure of the TRUPACT-I, 34.5 kPa (5 psi) gage, was exceeded. On this basis it was believed that attention needed to be focused on preventing the flammable gas buildup and that pressure buildup would not be a major design consideration. These analyses did not take into account the one year period nor the ambient thermal conditions outlined above. Transnuclear's calculations of the MNOP based on regulatory requirements found that, using the 375 TBq (10140 Ci) payload of the TRUPACT-I, and varying such parameters as the void volume in the waste and the radiolysis constant, the pressure could range from 0.365 to 1.38 MPa (3.6 to 13.6 atm) gage.

DESIGN OPTIONS

Various solutions to the problems of gas generation had previously been developed in connection with the transport of waste from the Three Mile Island cleanup (6). The TRUPACT problem was unique, however, in the inherently low pressure capacity of a rectangular packaging, the lightweight design, possible because of negligible shielding requirements, and the widely varying nature of the waste materials. The options investigated in the course of the TRUPACT-II design included reducing the design radioactivity capacity, increasing the design pressure, and using recombiners or getters to remove generated gases.

Reduction of the design radioactivity results in a reduction of both radiolytically generated gas and internal temperature. Discussions with the waste generating sites indicated that a design capacity of 74 alpha TBq (2000 Ci) was the minimum acceptable. Although 74 alpha TBq at 0.88 pJ (5.5 MeV)/alpha is equivalent only to about 100 watts, analysis indicated that under the regulatory thermal environment, the cavity wall of the TRUPACT-II would reach an equilibrium temperature of 60-70°C after about 2 weeks, principally because the TRUPACT-II was surrounded by a thick layer of shock-absorbing foam which also acted as an insulator.

Within the legal truck weight and size limits, the introduction of double containment had already created a formidable problem of maintaining the TRUPACT-I capacity of thirty six 210 liter drums and 6985 kg. This problem was compounded by the need to increase the design pressure. To achieve this increase while minimizing the reduction of capacity, the containment walls were redesigned using honeycomb panels. The final design achieved a capacity of 36 drums and 5895 kg with an MNOP of 89.6 kPa (13 psi) gage.

RECOMBINERS AND GETTERS

Catalyst beds using platinum or palladium on ceramic pellets have been used to recombine hydrogen with oxygen both in transport packages and in vented storage drums (6). These applications had demonstrated the effectiveness of the recombiners in preventing the creation of a flammable gas mixture, but prior to TRUPACT-II they had not been used specifically for pressure reduction.

The most obvious limitation on the effectiveness of recombiners is the availability of oxygen. Although radiolysis of water generates stochiometric quantities of hydrogen and oxygen, the radiolysis of organic materials generates free radicals which can scavenge oxygen. Thermal and biological effects can also scavenge oxygen. The concern about the buildup of hydrogen after oxygen depletion has been clearly addressed by the NRC: hydrogen without oxygen does not constitute a flammable mixture and is acceptable under IE Notice 84-72. However, it does present an operational concern, and may require measurement of hydrogen concentration when the containments are vented prior to opening.

To credit recombination for pressure reduction, the scavenging of oxygen by the waste must be accounted for and quantified. The leakage characteristics of the waste containers and the oxygen available in the containers are additional variables to be considered.

Carbon monoxide and water vapor can reduce the effectiveness of the recombiners. Sampling of waste drums has not revealed significant quantities of carbon monoxide, and at slow rates of carbon monoxide generation, the recombiners will catalyze the formation of carbon dioxide from the monoxide. In addition, Atomic Energy of Canada has developed recombiners whose effectiveness is not reduced by carbon monoxide or water vapor.

A concern has been raised that if all the oxygen is scavenged or recombined, and hydrogen continues to be generated, pyrophoric platinum and palladium hydrides will form on the recombiners (7). There are several reasons why it is not in principal a serious problem. Platinum hydride is very unstable, and will not be formed. Palladium hydride will form and is stable at a minimum hydrogen partial pressure, which increases with temperature. However, palladium hydride is not pyrophoric in the sense that although when exposed to air it will decompose and at the same time catalyze the formation of water from the evolving hydrogen, it will not spontaneously burn in bulk as some metal hydrides do.

For pressure control, getters which would scavenge carbon dioxide and hydrogen in the absence of oxygen were investigated. The only carbon dioxide getter found was caustic soda, which is not desirable for use in a transport packaging. Organic hydrogen getters have been developed

(7), but they can absorb only a limited amount of hydrogen. Because of concern about how often they would need to be replaced, and because initial estimates of the amount required to absorb hydrogen for one year were high, recombiners were not used in the TRUPACT-II design. Getter technology continues to develop, however, and bears watching.

The final TRUPACT-II design incorporated about 2 kg of recombiners in the cavity to achieve three goals:

A) To reduce pressure;

B) To prevent the buildup of a flammable gas mixture in the TRUPACT-II cavity; and

C) To provide a gradient in hydrogen and oxygen concentration between the TRUPACT-II cavity and those waste containers with filtered venting, to prevent the buildup of a flammable gas mixture within the containers themselves.

LOAD MANAGEMENT

Simultaneously with Transnuclear's design efforts, the DOE commissioned a review of existing gas generation data for transuranic waste to determine gas generation rates which could serve as an envelope for all such wastes. The resulting report (8) recommended the values shown in Table I. Using these values resulted in an MNOP in excess of the TRUPACT-II design pressure, as shown in Table II.

As it turns out, the gas generation envelope is controlled by combustible wastes, especially cellulosics. Non-organic wastes, even those containing water, have far lower rates of radiolysis, and are not subject to thermal or biological breakdown. It was clear, therefore, that some method of load management would be necessary in order to mix low and high gas generating waste containers in a given shipment so that the design MNOP for the TRUPACT-II would not be exceeded.

To facilitate the load management, Transnuclear developed a simple calculation of MNOP, to be used by shippers for qualification of each shipment. Incorporating the results of thermal analysis in a formula for waste temperature versus alpha curie content, the calculation determines the following: waste gas generation for one year from radiolysis, thermal, and biological effects; gas depletion by recombination and oxygen scavenging; pressure based on the ideal gas law; and the partial pressure of saturated water vapor. The recombiners and waste are assumed to have equal access to available oxygen, i.e., no barrier is assumed between the wastes and the TRUPACT-II cavity. Calculations performed independently using an explicit model for diffusion across drum vents verified that this simplification did not significantly affect the final pressure. The required input includes the alpha radioactivity of the

TABLE I

Envelope Gas Generation Data For Transuranic Waste

Radiolytic: G(Carbon Dioxide) = 1.0
G(Hydrogen) = 1.9
G(Oxygen) = -1.0

Thermal: Carbon Dioxide
60°C : 2.6 moles/drum/year
70°C : 5.2 moles/drum/year
100°C : 44 moles/drum/year

Biological: Carbon Dioxide; below 70°C only
aerobic: 4.2 moles/drum/year
anaerobic: 7.3 moles/drum/year

Corrosion: negligible

Average void volume in waste containers: 50%

Water available in waste: Sufficient to saturate volume of TRUPACT-II at normal and accident temperatures.

Notes:

1. The radiolytic gas generation factor "G" is in units of molecules of gas generated per 100 eV of energy absorbed in the waste. For transuranic waste, alpha energy is between 5 and 5.5 MeV, all of which is absorbed in the waste.
2. Thermal and biological activity are presumed proportional to the mass of waste. The rates given are for a drum containing 51.4 kg of waste.

TABLE II

Components of Pressure in Trupact-II Using Envelope Data

Contributor	Pressure	
	kPa	(psi)
Ideal gas heating	13.9	(2.01)
Water vapor (saturated)	19.9	(2.89)
Radiolysis	79.3	(11.50)
Thermal	25.9	(3.75)
Biological	42.2	(6.12)
Total	181.2	(26.27)
Recombination	-43.0	(-6.23)
Oxygen Scavenging	-10.4	(-1.51)
Net	127.8	(18.5)

Basis: 36 waste drums, 74 alpha TBq (2000 Ci), 20°C at loading, 60°C equilibrium waste and gas temperature

Note: Only 2/3 of the oxygen in the drums was assumed available for scavenging by the waste. The remainder, and the oxygen in the TRUPACT-II cavity, was assumed available for recombination. This assumption is not necessarily conservative.

wastes, the mass of wastes, the waste volume, and the waste material category. These data, except for waste volume, are already required by WIPP. Waste volume could be estimated from weight and density, or from radiographic viewing of the waste.

To test the load management idea, Transnuclear assumed that organic wastes could be characterized by the envelope gas generation data. Non-organic wastes which include water (sludges, concretes), and dry non-organics (glass, ceramic, metal), which usually include some plastic bagging, were assumed to generate hydrogen by radiolysis at about 0.6 molecules per 100 eV (G(hydrogen) = 0.6). The calculated pressures shown in Table III indicate that it would be feasible to mix cellulosic wastes with other wastes and remain below the TRUPACT-II design pressure with a reasonably high alpha radioactivity capacity.

IMPROVED GAS GENERATION DATA

In order to implement the load management program, it was necessary to develop a minimum number of waste categories, and corresponding gas generation data, to encompass all wastes. To facilitate the DOE's development of these data, Transnuclear recommended further research to resolve a number of questions that had been raised in the course of reviewing the existing literature.

TABLE III

Load Management Pressure Calculation For Trupact-II

TRUPACT-II Load	Pressure	
	kPa	(psi)
36 drums organic waste, 2100 kg @ 700 kg/m^3, 0.93 TBq (25 Ci)	896	(13)
36 drums non-organic waste, 5000 kg @ 2000 kg/m^3, 155 TBq (4200 Ci)	896	(13)
12 drums organic, 500 kg, 18.5 TBq (500 Ci) 24 drums non-organic, 5000 kg, 55.5 TBq (1500 Ci)	758	(11)

Probably the most significant question which relates to all three gas generation mechanisms is the relation of oxygen consumption to carbon dioxide and monoxide formation. Reported rates of radiolytic formation of carbon oxides are close to the reported rates of oxygen depletion for combustible wastes, and field sampling (9) often finds drums with significant carbon dioxide to be highly depleted in oxygen. Similarly, bacterial activity and oxidation would be expected to couple oxygen consumption with formation of carbon oxides. The implication is that much of the generation of carbon oxides does not contribute to a net pressure increase, and to assume so may be unnecessarily conservative. In addition, a quantification of oxygen consumption is necessary if recombiners are to be given credit for pressure reduction.

Molecke reports a temperature dependence of radiolysis. It needs to be determined if this is true, or whether it is merely a superposition of thermal and radiolytic effects. In principle, radiolysis and thermolysis could enhance each other, and the two processes may be inseparable. It may be possible to take credit for the integrated dose dependence of radiolysis due to depletion of the matrix surrounding the radiation sources; some data indicate that radiolysis is reduced significantly in only a period of months for drums containing as little as one curie.

Molecke concludes that biological breakdown offers the greatest potential for gas generation. Waste generators have insisted that in real wastes, as opposed to simulated wastes in laboratory conditions, biological activity is negligible; the source of carbon dioxide in field-examined waste is, however, a subject of dispute (9). It also seems anomalous that the data reported by Molecke attribute higher rates of carbon dioxide formation to anaerobic than to aerobic bacteria, without the expected methane formation.

The data on thermal breakdown are sparse and conflicting. For example, the product of polyethylene breakdown is reported as 93% oxygen. The relative importance and time dependence of vaporization, oxidation, and thermolysis need to be investigated at temperatures up to 200°C in order to include regulatory thermal accident conditions.

Because the thermal and bacterial rates are so uncertain, because of the large impact they have on the ability to transport combustible wastes, and because they are easily investigated experimentally (relative to radiolysis), Transnuclear recommended further experimental work in these two areas.

EPILOGUE

In May of 1987, DOE decided that it would seek an NRC license for its contact handled transuranic waste transport packaging, and based on this decision it abandoned the rectangular design in favor of a cylindrical one. Subsequently, the NRC indicated that it was willing to accept a time period shorter than one year for the calculation of MNOP.

Together, these changes substantially expand the proportion of existing waste which can be transported under an envelope of gas generation values, without load management, as initially attempted with the rectangular TRUPACT-II. High radioactivity combustible waste remains the one item difficult to ship using the current data. One might reasonably argue that it is unnecessary to design to seriously flawed thermal and bacterial data until further research is done, since significant pressure buildup has not been seen in shipping commercial combustible radwastes.

CONCLUSION

Under current regulations, pressure buildup due to the generation of gases by radioactive waste is a significant consideration for the design of Type B waste transport packagings, especially those that do not require a heavy structure for shielding purposes.

The use of catalytic recombiners is an economical, passive, and reliable method to prevent the buildup of flammable gas mixtures due to the production of hydrogen or methane. Oxygen consumption by the waste must be accounted for if credit is to be taken for pressure reduction due to recombination. Thermal and biological gas generation data for cellulosic and other organic wastes are sparse and questionable, and need to be further investigated. If further research verifies that certain categories of waste, especially organic waste with high alpha radioactivity, generate gas in far greater quantities than other categories, load management will be necessary to ship these wastes. The calculational method developed by Transnuclear provides a simple method to do this.

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