# HYDROGEN GENERATION IN TRANSURANIC WASTE

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## ABSTRACT

During the past two years, we have performed several studies to evaluate various aspects of the problem of hydrogen generation in transuranic (TRU) waste. These studies were both theoretical and experimental in nature, and considered such problems as the pressurization of containers, the potential for the generation of flammable gas concentrations, and the relative effectiveness of various types of vents intended to prevent buildup of flammable gas concentrations in TRU waste containers. This paper summarizes the results of these studies.

## BACKGROUND

As a result of concern over the generation of hydrogen in TRU waste containers, a strategy of venting containers having a significant potential for buildup of flammable concentrations has been developed. In conjunction with this effort, several modeling, experimental, and field sampling projects have been conducted.

## THEORETICAL STUDIES

An initial study by Smith et al.,[1] approached the problem of hydrogen buildup and decay from a theoretical perspective. In this study, a general model of TRU waste hydrogen production and removal was developed to provide a basis for evaluating the performance of the various hydrogen removal mechanisms.

The general model consists of differential equations describing the principal phenomena. Since the general system of equations is too complex to be solved analytically, a numerical approach was developed. To evaluate a broad spectrum of potential problems, this approach was applied using a microcomputer compatible FORTRAN program.

To verify the general model, analytical solutions were obtained for certain special cases and compared with the numerical model solutions. Comparative evaluation indicated that the numerical solutions were in very close agreement with the results obtained from the analytical calculations, provided the selected time steps were appropriately small.

A general multi-region TRU waste container was assumed in the model allowing the inclusion of up to nine separate regions. Hydrogen and other gases were assumed to be produced in the waste bearing regions, which may be any or all of the regions included in the container model. These gases are assumed to migrate quickly to the accessible active volume ($V_i$) of the appropriate region. For the purposes of model development, the migration time within a given region is assumed to be instantaneous.

The rate of hydrogen production $[h_i(t)]$ is dependent on the radioactivity level. Thus, hydrogen is generated at a rate given by:

$$h_i(t) = h_{i,o} e^{-\lambda_i t} \qquad (1)$$

where $h_{i,o}$ is the production rate at time t = 0 and $\lambda_i$ is the decay constant for gas generation that includes radioactive decay as well as other appropriate decay parameters. An analogous equation holds for the generation of non-flammable gases such as $CO_2$. Both equations are included in the general model.

Once dispersed in the active volume of a waste container region, the released gases are assumed to be uniformly incorporated into the existing hydrogen-air mixture. The hydrogen concentration within a given container region $[C_i(t)]$ is the ratio of the number of hydrogen molecules $[n_i(t)]$ to the total number of gas molecules $[N_i(t)]$ in that region.

If a given region is vented, i.e., there exists a path to equilibrate pressure across region boundaries, then the production of gas within a region will create a driving force to move gas molecules from region to region. In the absence of any other effects, the addition of a hydrogen to the $i^{th}$ container region will increase $n_i(t)$ and $N_i(t)$ by one. In contrast, the addition of a molecule of gas other than hydrogen will increase only $N_i(t)$. In order to maintain a constant gas inventory $[N_i(t)]$ (true for vented regions), one gas molecule must be released from the active volume ($V_i$) for each gas molecule generated. The probability that the released molecule will be hydrogen is given by the relative concentration $[C_i(t)]$.

There are a number of potential loss mechanisms for gas. For example, a given waste container region may contain a hydrogen absorbent material within its active volume. The rate of hydrogen removal has been modelled as an $\ell^{th}$ order concentration process with an $m^{th}$ order dependence upon the remaining number of absorption sites. Thus, the absorption rate $[r_i(t)]$ can be described by

$$r_i(t) = k_{r,i} \left\{C_i(t)\right\}^{\ell} \left\{1 - \frac{1}{N_{site}} \int_0^t r_i(t')dt'\right\}^m \quad (2)$$

where $k_{r,i}$ is the absorption rate proportionality constant and $N_{site}$ is the initial total number of absorption sites.

Hydrogen readily diffuses through many materials, including some container region walls. The diffusion rate is generally proportional to the difference in concentration across the wall. Thus, the diffusion rate $[d_i(t)]$ may be expressed as:

$$d_i(t) = D_i[c_i(t) - c_{i+1}(t)] \quad (3)$$

where $D_i$ is the diffusion constant of the $i^{th}$ container region wall material or vent. For diffusion through the outermost canister, the hydrogen concentration of the surrounding environment is taken as zero.

Hydrogen may also be released due to changes in ambient pressure or temperature. Hydrogen or other gases may be "inhaled" if ambient pressure rises or temperature falls. This flow of gas into or out of a container in response to changes in the environmental conditions can be referred to as "breathing." The breathing flow rate from the $i^{th}$ container region is represented by $q_i(t)$. The flowrate is positive in the outward direction and negative in the inward direction. Note that for an unvented container, $q_i(t)$ is always zero since there is no breathing flow path. Releasing gas in an unvented container will raise the internal pressure, although a drop in environmental temperature could also cause the container pressure to fall. Environmental temperature and pressure changes can be modelled as sine waves with user-controlled parameters to reflect changing ambient conditions. The effects of these changes are calculated from the ideal gas law. The model also includes the effects of forced flow ventilation on gas concentration within the containers.

The net hydrogen production rate for each region can be expressed as a differential equation obtained by summing the terms described above. This system of coupled differential equations describes the n-region model and may be used to calculate the hydrogen inventory $[n_i(t)]$, total gas inventory $[N_i(t)]$ and hydrogen concentration $[c_i(t)]$ for each region as a function of time. Since the complexity of the system of equations generally precludes an exact mathematical solution, the FORTRAN program implements an iterative numerical solution to the problem.

## EXPERIMENTAL ANALYSES

A concurrent experimental program has also been conducted primarily to evaluate various approaches to reduce the potential for buildup of flammable concentration of hydrogen (4% by volume). For this purpose, various methods for venting containers with a potential for significant gas generation have been evaluated using simulated TRU containers. Three venting methods have been considered: the breathable gasket, the vent clip, and the filter. Smith et al.,[2] tested these three vent types to determine their effectiveness in permitting the dissipation of hydrogen gas from TRU waste containers with the intent of maintaining hydrogen concentration below the lower flammable limit. Other objectives of the study were: to identify the importance of various mechanisms for hydrogen dissipation; to provide data for the validation of the theoretical assessment techniques; and to develop cost-efficient procedures for testing the performance of hydrogen venting mechanisms.

The breathable gasket is a semi-permeable gasket used to seal the lids of 55-gallon TRU waste drums. This "breathable" gasket forms a semi-permeable seal, allowing a path for hydrogen and other gases to escape from the container while keeping particulates in containment. There are at least two general types of breathable gaskets available: a spongy, rope-like polymer ring which is placed in the lid of the drum before sealing, and a "flowed-in" gasket composed of styrene-butadiene, which is actually formed in the lid and becomes an integral part of it.

Another venting approach uses a simple device known as a vent clip. The vent clip is a piece of metal slipped over the rim of the drum and used in conjunction with a standard drum gasket. The vent clip prevents complete contact of the metal of the drum and the gasket in a small region, and so provides a flow path around the seal.

The third venting approach involves the use of a carbon-composite or other high-efficiency particulate filter. The filter is fitted into a threaded hole in the drum lid. Gases escape through the filter, while particulate integrity is maintained. Filters in use differ primarily in design dimensions and the filter material.

The experimental apparatus consists primarily of two modified 55-gallon drums; one placed in a temperature controlled environment (i.e., an air conditioned room), the other in an "uncontrolled" environment where the temperature was allowed to follow normal fluctuations.

The hydrogen concentrations were monitored using commercially available gas sensors that utilize a platinum electrode (which catalyzes the oxidation of hydrogen). Various tests were performed to calibrate the sensor's performance during the experiment.

In the experimental tests, the drum atmospheres were initially set at or near the lower flammable limit of 4% hydrogen. The hydrogen concentration was then monitored over a period of 5-9 days to observe its decay as a function of time. The decay constant under these conditions is considered to be dependent upon the ability of the specific vent mechanism to provide a dissipation path for the hydrogen. Figure 1 presents a best fit plot of the data for the 3 vent mechanisms as measured in the temperature-controlled

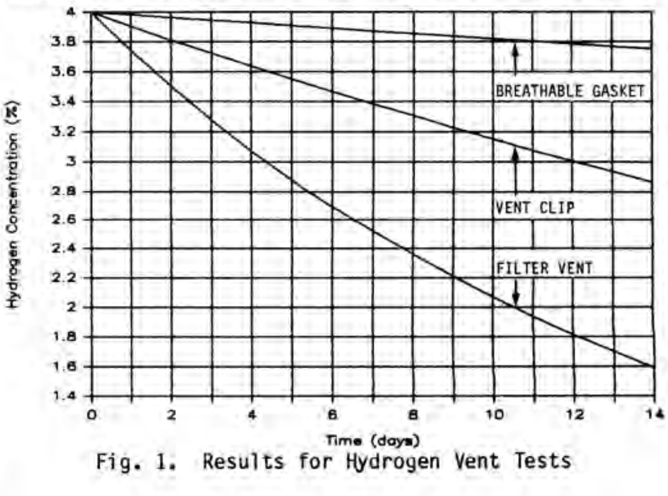


Fig. 1. Results for Hydrogen Vent Tests

experiment. Results for the uncontrolled environment indicated little difference between the vent clip and the breathable gasket, while the filter vent provided a significantly higher rate of dissipation.

## RESULTS AND DISCUSSION

The studies summarized in this paper represent the development and application of theoretical as well as experimental tools for evaluating the problem of hydrogen venting from TRU waste containers. Test information to date indicates significant differences in the ability of different venting mechanisms to dissipate hydrogen buildup. While all of the approaches tested are effective in relieving pressure buildup due to gas generation, the carbon composite filter was found to be more effective in allowing for hydrogen venting from the container.

Cost effectiveness, however, requires that additional factors be taken into consideration. The carbon composite filter is somewhat more expensive than the breathable gasket or vent clip. Given the relative effectiveness of each, a reasonable approach would be to use the vent clip or gasket for those containers where the possibility for hydrogen buildup is minimal, reserving the filter for those cases where there could be a higher potential for generating flammable gas concentrations.

Previous studies indicate that most TRU waste packages do not generate flammable gas concentrations, even after several years of storage. For example, Clements[3] examined 210 drums of stored TRU waste at the Idaho National Engineering Laboratory (INEL). These drums had been stored for periods ranging from six months to twelve years and contained various waste form matrices including: cellulosics, metals, plastics, glass, sludges, and resins. Of these drums, only 37% contained detectable levels of hydrogen, 14% contained hydrogen concentrations greater than 4%, and only 5% of the drums contained sufficient levels of hydrogen and oxygen to constitute a flammable mixture. Accordingly, it should be noted that the necessity to provide the most effective methods for hydrogen dissipation (e.g., the composite filter) may be limited to a relatively small fraction of the total inventory of TRU waste containers.

On the other hand, because of the presence of organics in many TRU waste forms and because of the corresponding potential for generation of hydrogen at levels that are uncertain (i.e., gas generation values for a given waste form are generally highly variable), the use of breathable gaskets and/or vent clips in TRU waste containers with low or marginal hydrogen generation potential can provide an acceptable margin of safety.

In comparing hydrogen generation evaluations to date, Nielsen[4] reviewed data from Smith et al.,[2] Clements[3] and Kazanjian et al.,[5] on the performance of vent mechanisms for TRU containers. Some of these data are summarized in Table I. The SAIC data indicate the drum inventories, given a gas generation (G) value for hydrogen of 1.0 molecule per 100 ev of absorbed radiation, that would result in the generation of an equilibrium level of 4% hydrogen by volume. These values correspond to the results of the measurements in an uncontrolled environment in contrast to those of Fig. 1. The RFP and LANL data indicate measured G values for gas generation, curie contents and hydrogen concentrations for the samples evaluated. For the RFP data, a calculated G value for hydrogen is also given. These data indicate that the SAIC experimental results are consistent with the observed data for the field evaluations, taking into account the combination of G values and inventory in comparison with measured hydrogen buildup. However, it is also noted that a high degree of variability exists in the field data.

Continuing gas generation study efforts include the refinement of the theoretical models into forms that are tailored to the desired applications, and additional experimental evaluations of venting approaches and mechanisms. These experimental efforts are intended to resolve the issues of experimental variability of results as well as to evaluate alternative vent mechanisms including multiple vents, different gasket and filter media, and the impact of getters and interior sealed containers.

One final point should be made. The data on which the comparisons between the various vent types have been made are relatively limited and involved variable experimental results indicating the possible existence of phenomena that may not be completely understood. Accordingly, the conclusions of this study are considered to be tentative in nature, subject to the results of further analysis and experimentation.

TABLE I

Vent Performance for TRU Containers

| VENT | SAIC[2] Experimental G = 1 | RFP[3] | | | | LANL[4] | | |
|---|---|---|---|---|---|---|---|---|
| | | GT | GCH | Ci | $H_2$ Vol% | GT | Ci | $H_2$ Vol% |
| Breathable Gasket | 8 Ci | 0.6-2 | 0.39 | 2 | 0.7 | | | |
| | | 1.0 | 0.16 | 6.5 | 0.6 | | | |
| Vent Clip | 8 Ci | 1.0 | 0.19 | 13.9 | 1.2 | | | |
| | | 0.6-2 | 0.79 | 1.7 | 0.3 | | | |
| Filter | 48 Ci | 1.0 | 0.3 | 4.6 | 0.25 | 0.6-2 | 218 | 6 |
| | | 1.0 | 0.28 | 3.5 | 0.25 | " | 31 | 1.2 |
| | | --- | 15.1 | 0.3 | 1.3 | " | 166 | 5.2 |
| | | --- | 22.5 | 0.2 | 0.4 | " | 22 | 0.5 |
| | | 0.6-2 | 2.1 | 1.0 | 0.25 | " | 69 | 2.8 |
| | | " | 1.4 | 1.8 | 0.6 | " | 32 | 0.6 |
| | | " | 0.74 | 0.9 | 0.1 | " | 16 | 0.5 |
| | | " | 0.52 | 1.6 | 0.15 | " | 42 | 0.1 |
| | | 0.3-2 | 1.1 | 1.7 | 0.25 | | | |
| | | " | 0.7 | 2.1 | 0.7 | | | |
| | | 0.37 | 0.3 | 0.1 | 0.05 | | | |
| | | " | 0.95 | 11.0 | 1.4 | | | |

GT = G-value (total)

GCH = G-value (calculated, hydrogen)

Ci = Alpha curies

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