VALIDATION AND UTILITY APPLICATION OF

LOW-LEVEL WASTE GAS GENERATION

PREDICTION METHODOLOGY

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ABSTRACT

In September 1984, the U.S. Nuclear Regulatory Commission (NRC) issued I&E Notice #84-72 dealing with the generation of hydrogen (H_2) and other combustible gases in radioactive waste containers. As an alternative to the tests and/or measurements required by the Notice, a calculational procedure was developed to predict the concentration of H_2 present inside a waste container after a specified storage duration. To "benchmark" the theoretical predictions against actual gas measurements from representative waste packages, liners containing dewatered resin waste that originated during cleanup operations at TMI-2 were used for comparison. On average, the predicted H_2 gas concentrations using the calculational model were within 20% of the H_2 concentrations measured when the liners were vented prior to shipment. The calculational methodology determines the total dose absorbed by the waste as a function of curie loading, waste density, and container geometry, and then calculates H_2 generation as a function of absorbed dose and a predetermined gas generation constant. The entire calculational procedure has been implemented on a desk top computer "electronic spreadsheet," designed to be a simple, easy-to-implement tool to calculate H_2 generation in waste containers with minimal input by the user.

INTRODUCTION

The production of combustible gases (primarily hydrogen) in sealed radioactive waste containers has been identified as a potential safety concern relative to handling, shipping, and storage of radioactive waste. Combustible gases may be produced through the degradation of both dewatered and solidified ion exchange media and/or through the radiolysis of residual water held within the interstitial spaces of dewatered or solidified resin media, concentrates, cartridge filters, etc.

Current requirements established by the U.S. Nuclear Regulatory Commission (NRC) dictate that containers having the potential to radiolytically generate combustible gases must meet certain criteria. Specifically, the following must be observed during a period twice the expected shipping time:

1. Hydrogen gas concentration must be limited to no more than 5% by volume of the secondary container gas void, <u>or</u>

2. The secondary container and cask cavity must be inerted to ensure that oxygen is limited to 5% by volume in those portions of the waste package that could have greater than 5% hydrogen gas.

The above criteria do not apply if the contents can be classified as low specific activity (LSA) waste <u>and</u> if the canister is shipped within 10 days of <u>sealing</u> or venting.

In September 1984, the NRC issued I&E Notice #84-72 dealing with the generation of hydrogen (H_2) and other combustible gases in radioactive waste packages. The I&E Notice required waste generators to demonstrate through tests or measurements that a combustible gas mixture would not exist in specifically defined waste packages during shipment. A calculational method for determining gas concentrations in waste packages was not included in the acceptable alternatives for ensuring compliance with the Notice.

In response to the generic nuclear utility implications of this I&E Notice, an investigation into calculational methods to predict the radiolytic generation of combustible gases was initiated by the U.S. Department of Energy (DOE) and its prime contractor, EG&G, together with the Electric Power Research Institute (EPRI) TMI-2 Technology Transfer Office. This work was conducted at the request of the Edison Electric Institute's Utility Nuclear Waste Management Group (UNWMG), and has resulted in an analytical method, which was presented to the NRC in early April 1985, as an alternative to measurements or tests to demonstrate compliance with the I&E Notice. Based upon the presentation, the NRC agreed to revise shipping cask Certificates of Compliance to recognize the acceptability of a calculational method to confirm the absence of combustible gas mixtures in low-level waste packages.

Formal documentation of the methodology developed by DOE/EG&G and EPRI has been assembled into a report which will be published in early 1986 as GEND-041[1]. In addition, a calculational procedure, in the form of a microcomputer-based electronic spreadsheet, based on the reference 1 methodology was developed by EPRI as an easy-to-implement tool for estimating the generation of combustible gases in waste packages. The spreadsheet can be used as is, or can be easily modified for use with a plant's specific waste, container, and measurement characteristics. The spreadsheet was initially written for use on an Apple

Lisa™ business computer, however, the program has been modified for use on other desk top computers such as the IBM-PC™, Compaq™, etc.. This program will be published by EPRI as a formal report in early 1986 [2].

CALCULATIONAL METHODOLOGY

As described in GEND-041[1], the quantity of combustible gas generated in a specific waste container is a function of the amount of energy absorbed by the waste form during the radioactive decay process. The amount of energy absorbed by the waste form (absorbed dose) is a function of curie loading, waste properties, and container geometry.

The calculational methodology reported herein uses each isotope's individual decay characteristics, along with the volume and density of the waste material, to calculate the total energy deposited in the waste during decay of the isotope. Low energy x-ray and beta energies are assumed to sustain 100% absorption in the waste form. The gamma energy absorbed by the waste, however, is dependent on the strength of the gamma ray emitted, the amount of energy absorbed by a waste particle during a collision, and the number of particles with which the gamma ray interacts.

To calculate the fractional gamma energy absorption, a polynomial equation was used, and is derived from statistical analysis of four hypothetical containers with varying geometry, gamma energy, and waste density. The equation conservatively assumes gamma absorption for energies below 0.4 MeV by assuming a linear relationship from the calculated absorption at 0.4 MeV to 100% absorption at 0.0 MeV.

The total integrated energy absorbed by the waste media is then calculated, for the time period the container has been sealed, as a function of each individual isotope, and summed for the entire container. The total volume of hydrogen gas generated is calculated using the total absorbed dose and a gas generation constant (G-value) for the specific waste material. The G-value is an experimentally measured value which quantifies the number of gas molecules produced per unit of absorbed energy for a specific waste form. The concentration of hydrogen is then calculated based on the total volume of H_2 and the free (void) volume inside the waste container.

COMPUTER PROGRAM DESCRIPTION

The program, developed by EPRI, can either calculate the concentration of combustible gas after a certain specified storage period, or can estimate the allowable storage time before the generated gas reaches a preselected limit. Actual waste parameters, including deposited curies, are used to calculate a total integrated dose to the waste material. The total dose is then used to determine the buildup of gases based upon gas constants available for use by the nuclear industry [3]. The program can be used to calculate H_2 generation in various waste forms including dewatered and/or solidified bead resin, powdered resin, concentrates, filter media, cartridge filter elements, etc.

The combustible gas generation program comprises several sections in which data are either entered by the user, calculated via the program, or stored as "built-in" data to minimize the need for input preparation by the user. The user enters the data necessary to calculate combustible gas generation in a given waste container into 4 sections of the program.

Container General Information

This section of the program is used to enter information pertaining to the type(s) of waste in the container, container type, data for decay correction, allowable H_2 concentrations, and storage duration. The container type can be one of four different classes of typical utility waste packages for which detailed gamma energy absorption calculations have been performed.

Package Information

This section of the program is used to enter data pertaining to the internal volume of the storage container, waste weight, and the volume of waste stored in the container. These values are, in turn, used to calculate the void fraction in the waste and the resultant concentration of hydrogen within the void space inside the container.

Gas Generation Constant

This section of the program is used to enter (or calculate) the waste's gas generation constant or G-value. As discussed in Reference 1 , the quantity of gas produced inside a container is a function of the amount of energy absorbed by the waste. The G-value is the relationship between gas production and energy absorption, defined as the number of radicals or molecules formed or decomposed per 100 eV absorbed. Hydrogen gas generation constants ($G\text{-}H_2$) have been determined for various waste forms through experimental analysis, and are available through several sources, particularly references 1 and 3.

Radionuclides Data

This is the final section of the program into which data must be entered by the user, and is used to enter the activities of each of the radionuclides present in the waste container. Provisions exist to enter up to 46 radionuclides commonly found in the nuclear industry's waste streams, including those radionuclides used for waste classification in 10CFR61.

The major parent-daughter radionuclide chains commonly found in waste streams are also considered in the program. For parent-daughter chains, only the activities of the parent are entered by the user into the program. Daughter products, whose energies are calculated as a percentage of the parent radioisotope, are assumed to be in equilibrium with the parent and are therefore decayed based upon the same half-life as the parent. Although this represents a simplified approach, the procedure is considered sufficiently valid for this application.

Uranium and Transuranic (TRU) radionuclides have not been included in the calculational methodology because, at the commercial burial limit of 100 nanocuries per gram for these radionuclides, the contribution from these alpha emitters is not significant enough to warrant calculation.

BUILT-IN DATA

A built-in library of appropriate data for each of the 46 radioisotopes is included in the program. Provided are: decay constants, average Beta energies, average low-energy x-ray energies, gamma energies, and associated gamma decay intensities. Absorption coefficients for 4 representative container sizes are also provided to permit the program to approximate the gamma energy absorption in the container as a function of energy and waste density.

H_2 CALCULATION SUMMARY

The calculational method contained in this program is used to obtain the following results:

1. The total calculated dose (in rads) from the radionuclides present in the waste.
2. The calculated volume (in cubic centimeters) of H_2 in the waste container either after the calculated storage duration or at the time the allowable H_2 concentration is reached.
3. The calculated H_2 concentration (in percent) in the waste container either after the calculated storage duration or at the time the allowable H_2 concentration is reached, depending upon user supplied data.
4. The calculated average rate at which H_2 is generated inside the waste container (in cubic centimeters per hour) during the storage period.

VALIDATION

An important element in the overall program to justify use of a calculational technique to predict radiolytic gas generation, was the need to "benchmark" theoretical predictions against actual gas measurements in representative waste packages. Although there has been considerable research into this area (nearly all published by the NRC), most of the published work in the U.S. has been directed toward laboratory-scale investigations to determine the constants for gas generation as a function of deposited energy (e.g., the G-value), or to assess the effects of organic resin degradation under high integrated radiation doses. There has been little study, however, of actual size and similarly configured waste packages representative of nuclear utility wastes.

The exception to this was the considerable experience gained at Three Mile Island Unit 2 (TMI-2) during shipment of the EPICOR II ion exchange resin prefilters and Submerged Demineralizer System (SDS) inorganic zeolite liners. The dewatered resin wastes from both of these systems originated during cleanup operations since the 1979 accident at TMI-2. The H_2 generation characteristics for each of these waste forms had been evaluated previously to support waste shipments from TMI between 1982 and 1984, and it was felt that the EPICOR II prefilters might offer sound operational data on H_2 generation rates for use by EG&G in validating the technique.

Consequently, it was determined that an in-depth evaluation of actual gas measurement data from TMI-2 dewatered resin waste, particularly the EPICOR II prefilters, would be undertaken by EPRI's Technology Transfer Office in conjunction with GPU Nuclear. The evaluation program was intended to summarize the available measurements of H_2 gas in EPICOR II prefilters for use to "benchmark" the DOE/EG&G calculational model, and to validate the computer program developed by EPRI to predict the generation of gases in representative waste containers.

Based upon results of a preliminary investigation, which concluded that only 28 of the original 50 prefilters were relatively leak-tight (and therefore contained most of the H_2 gas generated during the nearly 3 years of storage at TMI-2), only these 28 liners were subjected to the detailed theoretical predictions conducted for this program.

Detailed EPICOR II prefilter container and resin waste characteristics (including residual moisture content, free volume, specific activity, isotopic distribution, etc.) necessary for use with the DOE/EG&G theoretical model were entered in the program specifically developed by EPRI for this purpose. On average, the predicted H_2 gas concentrations using the GEND-041 model were within 20% of the H_2 concentration measured when the liner was vented prior to shipment.

This degree of accuracy in comparing actual wastes, resulted in the conclusion that the GEND-041 methodology, coupled with the EPRI-developed computer program, is sufficiently valid for general use in predicting combustible gas generation in utility waste containers.

APPLICATION

There are several applications for this calculational program, all of which should be of direct value to a utility radwaste manager. Since the NRC now permits the use of calculational techniques to comply with I&E Notice 84-72, an operator can use the EPRI program to demonstrate compliance with shipping cask Certificates of Compliance regarding combustible gas concentrations. In addition, the program can be used to estimate the duration a waste container can be stored before accumulated combustible gas production reaches concentrations of concern. Since the program must calculate absorbed dose in order to determine gas production, an estimate of the total integrated dose received by a waste material is also available through the use of this program.

CONCLUSIONS

From the work performed to support preparation of this paper, several important conclusions have emerged. First, the production of combustible gases from the radiolysis of residual moisture in low-level waste containers does exist, and is a linear function of absorbed dose in the waste. Second, the theoretical methodology developed by DOE/EG&G, and reported in GEND-041, can be used to accurately calculate the hydrogen gas concentration in a variety of waste forms and containers representative of those in use by the nuclear utility industry. And third, the computer program developed by EPRI, and validated against gas measurements from actual waste packages, has been demonstrated to be a useful tool for utility waste managers in addressing gas generation concerns in the waste containers during either shipping or storage periods.

REFERENCES

1. J.E. Flaherty, A. Fujita, C.P. Deltete, and G.J. Quinn, "A Calculational Technique to Predict Combustible Gas Generation in Sealed Waste Containers," GEND-041, EG&G Idaho, 1986.

2. C.P. Deltete, "Methodology for Determining the Combustible Gas Concentration in Radwaste Containers," Draft Report, EPRI Contract 2558-6-2, 1986.

3. "Radwaste Radiolytic Gas Generation Literature Survey" - Draft Report, EPRI Contract No. RP-2724-1, Sargent & Lundy, September 1985.