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Radwaste Radiolytic Gas Generation Literature Review

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Prepared by
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R E P O R T S U M M A R Y

SUBJECT	Low-level radioactive waste management	
TOPICS	Low-level radioactive wastes Radioactive waste disposal	Hydrogen production Literature reviews
AUDIENCE	Generation engineers and designers	

Radwaste Radiolytic Gas Generation Literature Review

This literature review provides information on the mechanisms and quantities of hydrogen gas generation in low-level radioactive waste transportation packages. Some waste forms generate much less hydrogen gas than originally thought, reducing concern about possible combustion within sealed packages.

BACKGROUND	Industry concern about requirements for testing to determine combustible gas generation in low-level radioactive waste (LLRW) transportation packages prompted NRC to revise certificates of compliance for radwaste transportation casks. The regulatory revision led to the subsequent issuing of NRC IE Information Notice 84-72. This notice describes NRC concern about the potential generation of combustible quantities of hydrogen, which might result in combustion and cask damage in the event of a transportation accident. The revised NRC regulations require testing and measurement to determine whether, in twice the expected shipment time, the package could generate hydrogen equaling or exceeding 5% of the volume of the transportation cask secondary container. NRC regulations permit calculational analysis to determine gas generation quantities. In lieu of testing or analysis, or if results show excess gas, oxygen in the secondary container—the drum, cask liner, or high-integrity container—may be diluted with an inert gas to less than 5% volume. Low specific activity packages shipped within 10 days of sealing or venting are exempted from this requirement.
OBJECTIVES	To examine and summarize the literature on radiation damage for information on the generation of combustible gases from LLRW.
APPROACH	Investigators reviewed chemical literature for information on chemical reactions in irradiated materials. The review identified the primary mechanisms for generation of hydrogen and other combustible gases and identified nonradiolytic chemical reactions leading to hydrogen production. They summarized their findings and compiled an annotated bibliography.
RESULTS	<ul style="list-style-type: none">• Water accounts for most LLRW radiolytic hydrogen generation.• Hydrogen reaction yields reported in the literature probably lead to conservatively high predictions of the amounts of hydrogen generated by

radiolysis in LLRW because of high radionuclide concentrations used in the studies. Concerns about combustion within a sealed package of LLRW are then unfounded.

- Of the LLRW solidification binders, vinyl ester styrene generates the least radiolytic hydrogen.
- Dried organic ion-exchange resins produce 10 times less radiolytic hydrogen than do fully swollen or dewatered resins.
- Cement solidification of waste does not appreciably reduce hydrogen yield, but it does fill the voids in dewatered resins.
- Chemical production of hydrogen in a corrosion process can overwhelm radiolytic production.
- Asphalted, cemented, and dewatered waste that is an appreciable fraction of the Class C limit and is stored for one to five years may require special considerations for hydrogen generation.

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PERSPECTIVE

Results of this literature review provide realistic estimates of hydrogen gas generation in LLRW transportation packages. This information may also significantly affect combustible gas testing requirements for LLRW transportation packages if the Department of Transportation incorporates International Atomic Energy Agency requirements.

PROJECT

RP2724-1

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Radwaste Radiolytic Gas Generation Literature Review

NP-5977
Research Project 2724-1

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ABSTRACT

This report presents the results of a literature review on radiolytic gas generation from Low-Level Radioactive Waste (LLRW) and includes an annotated bibliography of 37 references on the subject. The review shows that hydrogen is the only combustible radiolytic gas that is generated in sufficient quantities to be of concern. Water is consistently the major constituent of LLRW that produces radiolytic hydrogen. Examination of typical PWR and BWR waste streams indicates that most of the waste generated by utilities can be categorically excluded from concern with respect to hydrogen generation.

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SUMMARY

This report presents the results of a literature survey on radiolytic gas generation from the group of materials that constitutes low level radioactive waste (LLRW). This report includes an annotated bibliography of 37 references on the subject. It is intended that this report be used in conjunction with the development of calculational methods for the determination of the quantity of combustible gas generated by radiolysis of LLRW. This combustible gas determination is required of users of NRC approved transportation casks for Type B quantities of LLRW.

The basic process of radiation damage in the materials that constitute LLRW is the breaking of covalent chemical bonds by high energy gamma photons and beta particles. This results in the creation of highly reactive free radicals within the irradiated material. In organic materials, the hydrogen atom is produced. It then reacts with another nearby hydrogen atom to form molecular hydrogen gas. In water, another mechanism is available in addition to this. In water, free electrons can be produced that react with the water molecules to form hydrogen gas. Hydrogen can also be produced in a corrosion process in a sealed steel container of irradiated ion exchange resins.

A review of the available data shows that hydrogen is the only combustible radiolysis gas that is generated in sufficient quantities to be of concern. Data was obtained on hydrogen generation in the basic material constituents of LLRW, the binders used to solidify LLRW, organic and inorganic ion exchange resins and solidified LLRW. Water is the major source of radiolytic hydrogen gas and cement, organic ion exchange resins, and asphalt are all in the same order of magnitude as water. The radiolytic hydrogen yield, G-value, (molecules $H_2/100eV$ absorbed) for pure

water is reported as 0.45. For the radwaste solidification binders cement, asphalt and vinyl ester styrene G-values are reported as 0.11 to 0.35, 0.3 to 0.6, and 0.03, respectively. Organic ion exchange resins have G-values reported in the 0.1 to 0.6 range when fully swollen with water (dewatered). This yield is reduced by a factor of ten for dried resins.

Several conclusions can be reached from the data reviewed here. Water is consistently the major constituent of LLRW that produces radiolytic hydrogen. When water is removed from the waste form the hydrogen yield drops by a factor of ten. Another major material constituent of LLRW, styrene, is notably stable toward radiolytic gas generation, having hydrogen yields a factor of ten to one hundred less than other organic compounds.

When studying the radiolysis of cement and cement/waste mixtures, all researchers report a reduction in hydrogen yield at high container pressure. One researcher found this pressure to be consistently dose rate dependent, indicating a significant reduction in hydrogen yield at low dose rates. This is significant in that all of the work reviewed took place at high dose rates, many orders of magnitude greater than even high activity LLRW. It is probable that the hydrogen yields (G-values) reported in the literature for cement and other water containing waste forms are conservatively high for the purpose of combustible gas determination. Future research on hydrogen generation in LLRW should consider this dose rate dependence and be performed in part at dose rates approximating actual waste rather than the high dose rates used for accelerated studies.

Examination of typical PWR and BWR waste streams indicates that most of the waste generated by utilities can be categorically excluded from concern with

X Summary

respect to hydrogen generation. The waste that may be of concern is at most the upper portion of Class B and Class C waste that is stored on site for one to five years prior to shipment. This concern can be mitigated by removing water and non-aromatic hydrocarbons from the waste from.

To assess the combustible gas hazard by calculation, it is necessary that a reasonable and accurate method

for calculating absorbed dose be established. Many methods currently exist and computer codes using them have been written. These methods for calculating absorbed dose should be tested experimentally and evaluated carefully for their applicability to hydrogen generation. Possibly a standardized method could be chosen.

INTRODUCTION

During the past four decades, the study of the effects of ionizing radiation on all manner of materials has received great attention in the scientific community. A large part of this attention has been directed specifically at the materials which are used in the nuclear power industry. The purpose of this study was to examine the literature on radiation damage for information relating to the generation of hydrogen and other combustible gases from the broad group of materials which constitute low-level radioactive waste (LLRW).

IE Information Notice 84-72

This literature study was prompted by industry concerns over the testing requirements for determination of the generation of combustible gases in the packages used to transport LLRW. These concerns were incorporated into by regulatory requirements by the U.S. Nuclear Regulatory Commission (NRC) with the revision of the certificates of compliance for radwaste transport casks and the subsequent issuance of NRC IE Information Notice 84-72, entitled "Clarification of Conditions for Waste Shipments subject to Hydrogen Gas Generation."

IE Information Notice 84-72 describes the NRC concern that the potential exists for the generation of combustible quantities of hydrogen from LLRW. This could possibly result in combustion during a transportation accident causing damage to the transportation cask.

The NRC has defined the packaging requirements for the transportation of "Type B" quantities of radioactive waste in 10 CFR 71. This regulation states that packages used to transport moderately large quantities of radioactive material must be designed to withstand hypothetical accident conditions. The limits for the quantity of radioactivity which requires this special

packaging and the design requirements for the package are given in detail in 10CFR71. An exemption is given to wastes which contain low concentrations of radioactivity. These low specific activity (LSA) materials require packages designed only to meet the normal conditions of transport that are identical to those for Type A packages. However, both the Type B package and the LSA greater than Type A package must be NRC licensed. This licensing process is accomplished through the transport package (cask) certificate of compliance, and this certificate has been modified to incorporate the NRC's concern over hydrogen generation.

The waste forms identified as pertinent by the Information Notice are ion exchange resins, waste filter sludge, wet cartridge filters and radwaste solidified with binders. Dry compacted and uncompact waste and irradiated hardware are specifically excluded. The requirement for users of NRC approved packages is: for any package containing water and/or organic substances that could radiolytically generate combustible gases, it must be determined by tests and measurements of a representative package whether or not, for twice the expected shipment time, a quantity of hydrogen is generated which is equal 5% of the volume of the secondary container void (or equivalent limit for other inflammable gases). The secondary container is the drum or cask liner inside of the transportation cask. As of May 22, 1985 an alternative to testing and measurement was permitted by an NRC revision to the transportation cask certificate of compliance. The alternative is determination of gas quantities by analysis (calculation).

In lieu of the above test or analysis, or in case the results show excess gas, the secondary container (drum, cask liner or HIC) and cask cavity may be

2 Introduction

inerted by diluting to less than 5% oxygen by volume with an inert gas. An exemption is included for LSA materials, whereby packages shipped within ten days

of sealing or venting need not have the gas determination performed.

2

PRINCIPLES OF RADIATION DAMAGE

Nuclear radiation, such as alpha, beta, gamma, radiation, produces excited and ionized atoms and molecules as it passes through materials. These excited and ionized species can then undergo a variety of chemical reactions which manifest themselves as physical changes in the irradiated material. Some typical physical changes are embrittlement, volume change, and gassing in organic polymers; discoloration, dielectric constant change, embrittlement and gassing in inorganic crystals; and gassing, oxidation/reduction, and pH changes in water or aqueous systems.

Of particular interest in this survey are radiation induced changes which either directly or indirectly result in the production of combustible gases from the constituents of low-level radioactive waste (LLRW).

Quantitative data on the effects of ionizing radiation is often reported in terms of a "G-value." This value is defined as the number of molecules of a material which are consumed or produced for each 100 electron volts of energy *absorbed* (9, 25). It is a measure of the reaction yield.

The amount of energy absorbed by irradiated materials depends on the type of radiation (alpha, beta, or gamma), the absorption coefficient of the material and the system geometry. Energy is deposited over a very short distance when alpha and beta radiation passes through a material. For this reason, it can be assumed that all of the energy from alpha and beta radiation is deposited in the material.

The amount of energy deposited in a material as a result of gamma radiation depends on both the degree of interaction between the material and the gamma ray and the length of material through which the gamma ray must pass.

The degree of interaction is described numerically by the gamma ray mass absorption coefficient. This coefficient is a function of the electron density of the absorbing material and the energy of the gamma ray. *The Radiological Health Handbook* (6) graphs this coefficient for all of the elements. Fortunately, materials which have lower atomic numbers than iron (Fe) have electron densities which are very similar. This results in a group of elements which have similar absorption coefficient vs. energy curves. Most of the materials which compose LLRW fall into this group. For this reason, it can be assumed ($\pm 10\%$) that the mass absorption coefficient of irradiated LLRW materials is equivalent to that of the element carbon (C).

The other important factor in assessing the amount of gamma energy that is deposited in a material is the length of material through which the gamma ray passes. For LLRW, this is a complex matter, because many point sources of gamma rays are distributed relatively homogeneously throughout the material. The impact of each of these point sources on the entire waste form must be assessed. Many sophisticated computer codes exist to calculate this geometric effect over many different shapes. An example of a popular code is ISOSHIELD.

Hine and Brownell (21) have formulated a quantitative method to perform this assessment which is convenient for hand calculations. The pivotal parameter in their analysis is the calculation of an "average geometrical factor," which normalizes the dose of these spatially distributed sources over the geometry of the incorporating material. Hine and Brownell have tabulated average geometrical factors for cylinders up to 35 cm in radius and 100 cm in height.

This method for absorbed dose calculation was presented by Swyer, et. al. (32) in a calculation for

4 Principles of Radiation Damage

the dose absorbed by dewatered resins from the absorbed radionuclides as a function of time.

Colombo and Nielson (10) calculated the self dose for typical PWR and BWR wastes. Their calculation assumed uniform activity distributed through a waste form with a density of 2.0 g/cm³. This is representative of LLRW solidified with cement. The waste radionuclide compositions they used were taken from

WASH-1258 as being representative of a typical BWR and PWR. The results of their calculation are reproduced in Figures 2-1 and 2-2. Using a different spectrum of radionuclides would result in a different absorbed dose because the half life and decay energy are important parameters. It is therefore, necessary to perform this calculation on a case by case basis.

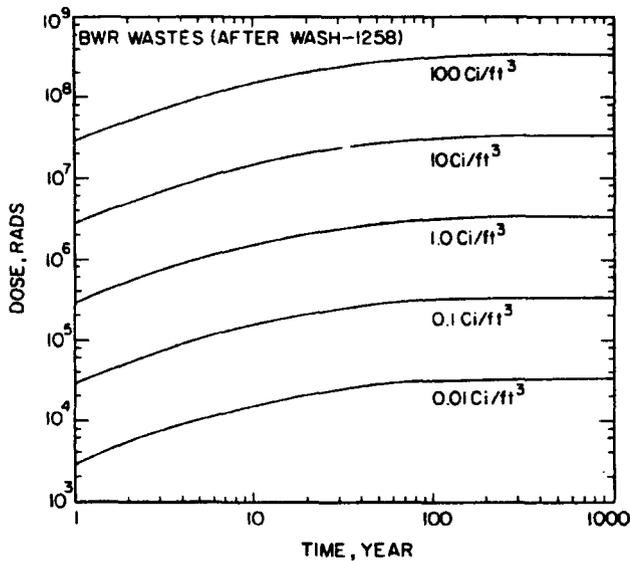


Figure 2-1. Cumulative radiation dose for BWR waste forms as a function of activity concentration. (10)

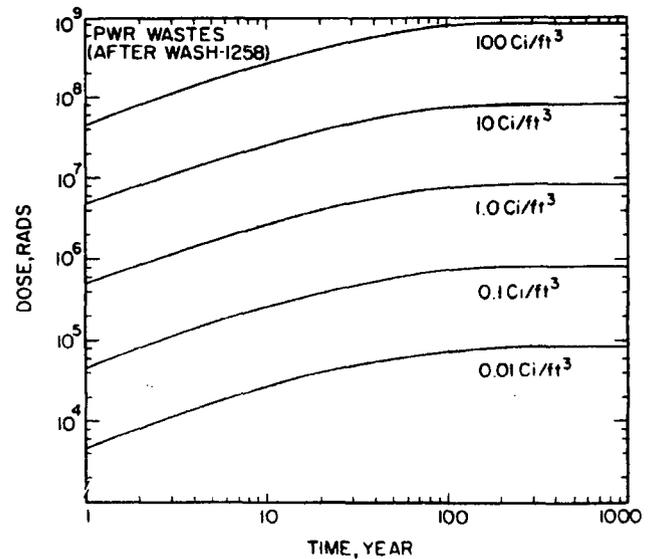


Figure 2-2. Cumulative radiation dose for PWR waste forms as a function of activity concentration. (10)

COMBUSTIBLE GAS PRODUCTION MECHANISMS

A great number of chemical reactions occur in irradiated materials and a large amount of information has been reported in the chemical literature concerning them. This survey identified the primary mechanisms by which hydrogen and other combustible gases are generated. Also, non-radiolytic chemical reactions which lead to hydrogen production were also identified.

Radiolysis of Hydrocarbons

The primary gaseous radiolysis product from the irradiation of organic liquids and polymers has been consistently found to be hydrogen. In organic materials which contain little oxygen, such as ion exchange resin, hydrogen accounts for over 90% of the total radiolysis gas formed. Unsaturated hydrocarbons such as the paraffins octane, butane, etc, generate the most hydrogen, having G-values from 2 to 6. Aromatic hydrocarbons such as benzene, styrene, etc. are the most stable, having hydrogen G-values from 0.04-0.4 (25).

When irradiating typical organic radwaste such as bead resins and vinyl ester styrene, carbon monoxide and dioxide are the next most abundant radiolysis gases produced, especially in systems open to the atmosphere. This is because of an efficient radiolytic reaction in which the carbon structure of the organic molecules is oxidized. In fact, in closed systems, oxygen present at the beginning of irradiation is quickly removed by this reaction (7). Swyler, et. al. (33) examined the kinetics of this reaction and found in a sealed dewatered bead resin system, oxygen is removed fast enough so that an explosive mixture of oxygen and radiolytic hydrogen does not exist.

Methane, ethane, etc. are also produced by hydrocarbon radiolysis; however, they usually account for less

than 1% of the total radiolysis gas produced by typical organic radwastes.

The mechanism by which hydrogen is formed in irradiated organic radwastes is by breaking the C-H bond and formation of a free radical hydrogen atom that reacts with a hydrogen atoms attached to a nearby carbon skeleton to form hydrogen gas. The remaining carbon frame-work then crosslinks, forms a double bond, or undergoes chain scission (degradation) to balance charge. Of the common commercial organic polymers, polystyrene was found by Bopp and Sisman (5) to be the most stable to this attack, having a hydrogen G-value of 0.008. This is important to radwaste in that polystyrene is the backbone of both organic ion exchange resins and VES, the Dow solidification agent.

Radiolysis of Water

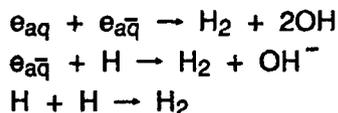
Water is the primary constituent of dewatered ion exchange resin (66%) and constitutes a fair proportion of hydrated cement (25-50%). The role of water in gas production over resins has been studied. Swyler (33) found the hydrogen yield to decrease by a factor of 10 when irradiating dry cation resin. Tulupov and Butaev (35) found the composition of the radiolysis gas over resins to change from 92% H₂ to less than 50% H₂ after drying the resins. They did not report total yields for this experiment but noted that the radiolysis of water was the primary source of gaseous hydrogen in bead resin. For these reasons the interaction of water and ionizing radiation is crucial to this survey.

As high energy radiation passes through water, it interacts with the water molecule in several ways. One type of interaction is for the radiation to increase the

vibrational or rotational energy of the water molecule. The resulting excited water molecule might then simply lose this energy to the liquid, resulting in an increase in liquid temperature. Or, if sufficient vibrational energy was given to the water molecule, it may break in H and OH fragments. These fragments are highly reactive and their fate can lie along many reaction pathways. However, a more likely interaction is for the high energy radiation to ionize the water molecule by dislodging an electron. The result of this energy transfer is an ionized water molecule, H_2O^+ , and a free electron. Because of the polar nature of water, the free electron can cause the dipole moments of the water molecules to line up in a pattern. This pattern generates an electro-magnetic field that will stabilize the free electron. An electron stabilized by non-randomly oriented water molecules such as this, is called a hydrated electron. Of course, this electron could simply recombine with the ionized water molecule, H_2O^+ , to form stable water. However, the hydration process occurs faster than the recombination process, resulting in a fair number of hydrated electrons which are free to interact with other water molecules, or molecules in solution, or materials in contact with the water. Free electrons can also be produced in cement or other solid radwaste.

The yield of these three highly reactive species, the H and OH fragments and the free hydrated electron, can be described in terms of G-values. Averaging several sources, these yields are: $G_{OH} = 2.7$, $G_H = 0.6$ and $G_e = 2.7$ (14). These reactive species can undergo many reactions after they are formed. Their reaction pathway will depend on the concentration of the molecules around them. There are three reactions which result in the formation of gaseous molecular hydrogen, H_2 .

These reactions are, in order of importance:



It is therefore understandable why many researchers have found that the existence of multivalent metal ions such as iron (Fe^{3+}) in irradiated hydrated materials has resulted in an appreciable decrease in gaseous hydrogen production. These metal ions are acting as electron scavengers and removing the

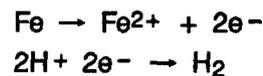
primary source of gaseous hydrogen, the hydrated electron. This effect has been noted in aqueous solutions (25), irradiated swollen resins (33) and cement solidified waste (4).

The other molecular product of the radiolysis of water is hydrogen peroxide, H_2O_2 . This molecule is formed by the reaction: $OH + OH \rightarrow H_2O_2$. The G-values for H_2 and H_2O_2 , the primary molecular radiolysis products of water, have been reported to be independent of solution pH. They are $G_{H_2} = 0.45$ and $G_{H_2O_2} = 0.7$ (14). These yields are, however, sensitive to, among other things, LET values, temperature, and concentration of electron scavengers.

A reaction also operates during the radiolysis of water that consumes gaseous hydrogen. This reaction is: $H_2 + OH \rightarrow H_2O + H$. However, this reaction proceeds at a rate that is 100 to 1000 times slower than the reactions which produce gaseous hydrogen. For this reason its effect on the gaseous hydrogen yield has been masked in most irradiation studies because they take place at extremely high dose rates, generally on the order of 10^4 to 10^7 rads per hour. However, three studies of the irradiation of cement have identified a reduced hydrogen yield at high pressures (4,10,2). This is the result of a backreaction that is pressure dependent and consumes hydrogen. The reaction at the root of this effect is probably the one described above.

Chemical Production of Hydrogen

It is a well known phenomenon for metals submerged in mineral acids to bubble, signalling the oxidation/reduction reaction which results in oxidation of the metal and the formation of gaseous hydrogen. Since many LLRW containers are constructed from carbon steel, the existence of acidic conditions and the contact of this acid with the metal container could result in the production of hydrogen gas. The hydrogen forming oxidation and reduction reactions are:



This is important because during the irradiation of hydrogen form cation ion exchange resins the primary radiolysis product has been identified by several investigators to be sulfuric and sulfurous acid (30,33,35). Furthermore, Swyler (34) has shown that

irradiating hydrogen form cation resins in the presence of mild steel coupons in a sealed system results in hydrogen gas formation at a rate which greatly exceeds that of radiolysis of the resins alone (34). This effect was greatly reduced by expending the cation resins with sodium prior to irradiation.

Gangwer and Pillay performed similar irradiations in vented systems and found accelerated corrosion of

the metal coupon (17). Since the system was vented, the primary reaction was most likely one involving oxygen consumption with no hydrogen gas formation. Nevertheless, the pH change and corrosive nature of irradiated ion exchange resins were well documented.

LLRW WASTE FORMS AND TYPES

Waste Types Affected

As stated earlier, IE Information Notice 84-72 applies to LLRW packages which contain water and/or organic substances (ion exchange resins, waste filter sludge, cartridge filters and radwaste solidified with binders) that could radiolytically generate combustible gases. In performing the literature review, information was gathered on both hydrogen generation from the waste types themselves, the binders used for solidification, and the composite waste form.

Ion Exchange Resins

Ion exchange resins used in radioactive service fall into two categories; organic and inorganic. Within the organic category, resins are further segregated by physical form into powdered or bead, and finally divided by chemical affinity into cation or anion form. However, all organic ion exchange resins can be described as a high polymer structure, such as polystyrene, onto which are placed ion exchange sites or functional groups, such as sulfonic acid.

Organic ion exchange resins which have been saturated with water can contain as much as 66% water by weight even though no water is visible. This water is adsorbed on the surface of the resin, absorbed within the resin's polymer structure, and chemically bound to the resins ion exchange sites.

Organic ion exchange resins that are commonly used in radioactive waste treatment are termed strong acid cation and strong base anion. These consist of a polystyrene-divinyl benzene copolymer backbone which has either sulfonic acid groups or a trimethyl amine groups attached to form the ion exchange sites. The polymer backbone, in chemical terminology, is largely aromatic in nature. Possible sources

of radiolytic hydrogen gas from organic resins are the water which is contained within the resin and the organic polymer backbone.

The other category of ion exchange resins used in radioactive service are the inorganic type. Zeolites and glass beads are members of this category. They are porous metal oxides and glasses whose pore size and surface characteristics are chosen to selectively remove radionuclides from liquid radwaste streams. The primary source for radiolytic hydrogen gas from inorganic ion exchangers is the water which adsorbs onto the exchanger particles or beads or is contained in the pores. This can be as much as 33% (wt).

Other Waste Types

The operation of large precoat filters at BWR's results in the generation of large amounts of filter sludge. This sludge consists of a mixture of the particle which were filtered out of a liquid stream and the precoat material which was placed on the filter to collect the particles. Precoat materials commonly used are diatomaceous earth, cellulose fibers, activated charcoal and powdered organic ion exchange resin. Other than the powdered organic ion exchange resin, the only source of radiolytic hydrogen gas from filter sludge is the water which remains in the waste after it is processed for disposal. Powdered resins behave as do the organic bead resins discussed previously.

In addition to the largely solid waste discussed above, Light Water Reactors (LWR) also produce concentrated liquid wastes. These wastes are aqueous solutions and slurries produced by evaporation and consist primarily of inorganic salts. Ultimate disposal of these wastes requires solidification with an appropriate binder such as cement or asphalt. The primary source of

radiolytic hydrogen gas from concentrated wastes is the water which is bound up in the solid matrix and any organic material used as the binder.

A waste stream which is primarily a characteristic of PWR's is spent cartridge filters. These filters are constructed from cloth, cellulose, metal and sometimes plastics. They are used to filter water that is relatively clean with respect to suspended particulates, but it can contain a high concentration of radionuclides. The primary source of radiolytic hydrogen from spent cartridge filters is any water remaining on the filter and the binder used to encapsulate the filter.

Waste Forms and Packages Affected

The waste types described above can be processed for disposal and packaged in a variety of ways. Processing the waste into a form acceptable for disposal is primarily governed by burial site requirements. Packaging is usually governed by transportation requirements. However, both processing and packaging requirements can be affected by either one. Only the most common processing and packaging combinations are described here. For the purpose of satisfying IE Notice 84-72 examination of the package characteristics is necessary on a case by case basis.

Dewatered Resin and Sludge

In addition to solidifying ion exchange resins and waste filter sludge, it is also an accepted practice to dewater this waste by either pumping or vacuuming essentially all of the free water out of the package. Depending on the concentration of radionuclides in the remaining sludge, the package commonly used for this process is either a 170-200 ft³ carbon steel cylinder called a cask liner or a similar sized high molecular weight polyethylene cylinder called a high integrity container (HIC). The sludge or resins which remains in the processed package may contain not more than a maximum of 1% by volume free water, plus all of the water that is absorbed, adsorbed and chemically bound to the resin or sludge.

Therefore, the available material inventory for the radiolytic generation of hydrogen gas is the remaining water in the package plus the organic material contained in the ion exchange resin. Hydrogen production

by chemical interaction with the container is a possibility for the carbon steel package, but because of the chemical inertness of polyethylene a reaction of this nature can be discounted for the polyethylene HIC.

Solidified Resin, Sludge, Concentrates and Filters

LLRW can also be bound together or encapsulated by a binder in a process called solidification. There are three binders which are used in nearly all LLRW solidification. These are Portland cement, vinyl ester styrene (Dow binder) and bitumen (asphalt). Solidification processes exist which utilize other plastic binders such as epoxy, polyethylene, and polyester.

Sources for hydrogen gas in a solidified waste form are the incorporated waste and the binder. The waste types and their source of hydrogen have been described above. Portland cement contains from 25% to 50% (wt) water. This water is primarily present as the water of hydration of the oxides which form the cementitious matrix, however some water is also trapped within the capillaries and interstices of the cement matrix.

VES can be used to solidify either wet wastes or dried wastes. With wet wastes, the waste and associated water, plus the VES are sources of hydrogen. VES is a largely aromatic polymer with some alkyl chains between the aromatic groups. Dried wastes such as the product from a dryer or incinerator when incorporated in VES will have as sources of hydrogen the VES and any residual organic matter as may result from the drying of ion exchange resins.

Asphalt is used as a binder in an evaporative solidification process which drives off nearly all water, leaving only the dried resin bead, sludge or inorganic salt and the asphalt binder. Sources of hydrogen here are any residual organic matter plus the asphalt binder. Asphalt can be purchased as distilled or air blown. Both forms contain primarily aromatic compounds along with long chain unsaturated hydrocarbons. Air blown is an oxidized form of asphalt. Both forms should behave similarly with respect to hydrogen gassing.

Spent cartridge filters may also be placed in HIC's for disposal; however, there is a relatively small amount of material available in this waste form for the generation of hydrogen.

5

SUMMARY AND REVIEW OF DATA

Data on the composition and yield of radiolysis gas was obtained for materials ranging from the individual constituents of LLRW to the binders used for solidification to actual waste forms. These data were not always taken under conditions that correspond completely to typical LLRW, however some general and specific conclusions can be reached from them as well as identifying some areas requiring further study.

Base Materials

Data was identified on the radiolytic gassing of the basic material constituents of LLRW which have a potential to generate combustible gases. The data are summarized in Table 5-1. Most of these data have been discussed in Section 2 and 3 of this report along with the development of the principles of radiation damage and hydrogen production mechanisms.

Of the materials that constitute LLRW, saturated and unsaturated hydrocarbons generate the most hydrogen, having hydrogen G-values in the 1-6 range. These organic materials do not account for very much of LLRW and are seldom present in waste forms that also contain sufficient radioactivity to generate hydrogen. Polyethylene is the most common of these materials in LLRW as it is used to fabricate High Integrity Containers (HIC) for the disposal of dewatered sludges and resins. Polyethylene has also been considered for use as a solidification binder.

A relatively narrow thickness (0.625 in) and small amount of polyethylene is exposed to radiation in a HIC, thus a small radiation dose will be absorbed and only a small amount of hydrogen could be transferred to the package interior. For these reasons, hydrogen gassing from a HIC should not be a transportation concern.

Contaminated oils also contain saturated and unsaturated hydrocarbons, however they rarely contain sufficient radioactivity to provide an absorbed dose large enough to produce any hydrogen of concern.

The next largest generator of hydrogen from the base material constituents of LLRW is water. Dragnic and Dragnic (14) have reported a G-value for pure water of 0.45. This value is independent of pH, however, it is dependent on the concentration of electron scavengers such as multivalent metals. Since water is found in most all LLRW waste forms, its effect on hydrogen generation is profound.

Finally, the class of materials found in LLRW that is most stable toward radiolytic hydrogen generation are the aromatic hydrocarbons. These materials are characterized by the presence of the benzene ring and have hydrogen G-values from 0.008 to 0.4. In LLRW they are found in the solidification binders asphalt and VES and in organic ion exchange resins. Polystyrene is among this class and is reported to be one of the most radiation stable polymers, having a hydrogen G-value of 0.008 to 0.04 (5,37). This is important, as polystyrene is the backbone of both VES and most organic ion exchange resins.

LLRW Solidification Binders

A fair number of studies have been performed on radiation effects in the group of materials which are used to solidify LLRW. The most frequently used of these solidification binders are cement, asphalt and VES. Hydrogen gassing data for these and other binders is summarized in Table 5-2.

Of the commonly used solidification binders, asphalt generates the most hydrogen. Radiolytic hydrogen

G-values for asphalt are reported to range from 0.3 to 0.6 (8,16,10,15). Colombo and Nielson (10) found the G-value to increase as the irradiation time increased, rising from an initial value of 0.07 to a value of 0.41 at the end of the irradiation period. This may be because hydrogen formed at the interior of the sample took some time to diffuse out to the monitor. Gases formed in asphalt tend to produce bubbles in the binder which have difficulty reaching the surface of the sample. Most other researchers heated the asphalt after irradiation to ensure that all hydrogen formed escaped from the sample. However, when the rate at which hydrogen will diffuse through asphalt is compared to the rate at which hydrogen is generated in a typical LLRW waste form, it becomes apparent that very little of the hydrogen formed will not escape from the binder (15). The hydrogen simply diffuses out of the binder faster than it is generated, making the phenomenon observed by Colombo and Nielson one that will probably not occur at the dose rates of typical LLRW. Colombo and Nielson's work took place at 4.6×10^6 R/hr, many orders of magnitude greater than will be seen for most LLRW.

There is no apparent difference in the hydrogen yield between air-blown and distilled asphalt. The difference in all of the reported values is within the experimental uncertainty.

The next largest producer of radiolytic hydrogen gas is hydraulic cement. Hydrogen gas G-values ranging from 0.11 to 0.35 have been reported (10). However, an interesting phenomenon has been observed in three independent studies on radiolytic gas generation from cement (2,4,10). Both the rate of gas evolution and hydrogen yield decreased in all cases as the pressure built up in the sealed container. This is evidence of a backreaction which consumes hydrogen that is pressure dependent. Bibler (4) also found that this phenomenon is dose rate dependent, with the backreaction having a greater effect at lower dose rates. For this reason, the G-values reported for cement will most likely be high when compared to LLRW, as the dose rates in these studies were several orders of magnitude greater than those in LLRW.

The commonly used binder that is most stable toward radiolytic gas production is VES. A hydrogen G-value of only 0.03 is reported for this binder (19). This low hydrogen yield is the result of the radiation stability

of the styrene functional group along with the complete lack of water in the binder.

Ion Exchange Resins

More work has been performed on the radiation behavior of ion exchange resins for any other single type of LLRW. This is because these resins have been used extensively on the extraction of radionuclides from high level wastes as well as in the decontamination of the damaged reactor at Three Mile Island. The data obtained for ion exchange resins is summarized in Table 5-3.

The inorganic zeolites have shown themselves to be uniquely stable toward radiation damage. The only hydrogen that is evolved from zeolites comes from the water that is adsorbed onto the beads. Pillay reports hydrogen G-values of 0.005 to 0.05 (30) for zeolites saturated with water. Capolupo reports higher G-values, ranging from 0.075 to 0.18 (7). Pillay observed a gradual increase in the hydrogen yield as the irradiation proceeded. This is probably because of hydrogen adsorption on the zeolite surface. Once the zeolite surface had become saturated with hydrogen, more could enter the gas phase and escape to the container. Capolupo reported the same trend.

Although they are apparently dry, organic ion exchange resins contain from $\frac{1}{2}$ to $\frac{2}{3}$ water as they are delivered from the manufacturer. This is essentially the same condition of the resin as when it is disposed of in its "dewatered" form.

The hydrogen gas G-value for fully swollen organic ion exchange resins is generally reported to be from 0.1 to 0.6 (4,28,33,27,2) with several special cases falling outside of this range.

Anion resin generates more hydrogen than cation resin (33). This is probably a result of radiolysis of the trimethyl amine functional group on the anion resin. No decrease in hydrogen yield has been observed at high container pressure in swollen ion exchange resins. This indicates that the hydrogen consuming reaction identified in cement either does not operate in ion exchange resins or operates at a slower rate. The latter is more likely as water is the primary hydrogen source in both cases. Dried resins have also been irradiated and their hydrogen gas G-value found

to be a factor of 10 less than swollen resins. Swyler, et. al. (33) found the G-value for resin dried to 7% water to be about 0.01. Capolupo (7) found it to be 0.067, and Mohorcic and Kramer (28) found it to be from 0.001 to 0.026. These values are near those reported for polystyrene alone, 0.008 to 0.0446 (5,37). It is, therefore, apparent that the water associated with ion exchange resins is the major contributor to hydrogen gassing and that with it removed by drying, a factor of 10 less hydrogen is generated.

This phenomenon was verified by the Russians, Tulupov and Butaev (35), however, the only effect they reported in numeric terms was the effect on gas composition. They went on to state in their analysis that the net hydrogen production was much less for the dried resin.

Solidified Waste Forms

Several studies have examined radiolytic gas formation from simulated solidified radioactive waste, and one reported on this phenomenon in actual solidified waste. The data reported in these studies is summarized in Table 5-4.

The data reported for asphalt indicate that incorporation of LLRW into this binder results in a waste form which generates less hydrogen than the binder alone. This is because the asphalt solidification process is evaporative, thereby removing almost all of the water present in the unsolidified LLRW. The remaining salt or dried resin beads account for 50% of the waste form and generate little or no hydrogen themselves. Solidified asphalt waste forms have hydrogen G-values reported in the 0.15 to 0.25 range (15,19). There is no discernable difference between air-blown and distilled asphalt with respect to hydrogen generation from simulated asphalt waste forms.

Barletta, et. al. (2) have studied a cement/ion exchange resin waste form for its radiolytic gas generation rate. The resin mixture was a proprietary formulation of organic and inorganic ion exchange resins that were used in the TMI-2 cleanup. Barletta, et. al. reported hydrogen G-values ranging from 0.19 to 0.24.

Bibler (4) studied cement waste forms containing oxides of iron, manganese, and nitrogen. Bibler does not report hydrogen yield in terms of a G-value for

cement because the gas production varied with time for gamma radiolysis. Bibler was able to identify a reaction which consumes hydrogen that is dependent upon both pressure and dose rate. As the pressure built up in the sealed containers, the rate of hydrogen production decreased until a steady state pressure developed, at which no further radiation dose would produce any increase in pressure indicating that the hydrogen production and consumption reactions had equilibrated. A G-value has no meaning in this condition. This steady state pressure was dose rate dependent, increasing with dose rate. Similar phenomena have been observed by Barletta, et. al. (2) and Colombo and Nielson (10). Bibler found the steady state pressure to be dependent on the incorporated metal oxide, indicating that the metal oxide was participating in a reaction that affects the hydrogen yield, possibly by electron scavenging.

It should be noted that Bibler could not develop a steady state pressure less than 200 psig for alpha radiolysis and for extremely high gamma dose rates. Therefore, the balance of reactions must be a function of both LET and dose rate. Bibler's work, as well as the work of Barletta, et. al. and Colombo and Nielson all took place at dose rates for exceeding that of most LLRW. This makes direct comparison difficult. However, it seems certain that the G-values reported for cement will be high, because the hydrogen consuming reaction identified by Bibler plays a larger role at the low dose rates typical of LLRW.

Effect of Irradiation Conditions

It has been shown that the chemical, physical and radiological conditions during irradiation all play a role in determining the composition and yield of the radiolysis gas produced.

Almost all experimenters report an initial drop in pressure when irradiating sealed containers. This is irrespective of the binder or waste type, organic or inorganic. This pressure drop has been shown (7, 33) to be the result of a radiolytic reaction that consumes oxygen. Conversely, when irradiating unsealed samples the yield of carbon dioxide and carbon monoxide increases, presumably as a result of the same reaction. However, in most cases hydrogen continues to be the dominant radiolysis gas produced and

certainly the dominant combustible gas produced. The oxygen consuming reaction will mitigate concerns over combustible mixtures forming within the secondary package (drum or liner). This reaction occurs many times faster than the hydrogen producing reactions, removing most of the oxygen before appreciable hydrogen can form. However, this reaction does nothing to remove oxygen from the transportation cask interior, thereby leaving open the possibility of a combustible mixture there should the secondary packages leak.

Through the work of Bibler (4) it has been shown that the dose rate can have a determining effect on the yield of hydrogen from irradiated cement waste forms, and possibly all wastes that contain water. By examining the three radiolytic reactions in water that result in hydrogen formation (see Section 3) it can be seen that all are second order in dose rate. That is, both reactive species are generated by radiation. This results in a squared dependence of hydrogen formation on dose rate. However, the reaction which con-

sumes hydrogen is only first order in dose rate. This results in a linear dependence of hydrogen consumption on dose rate. Furthermore, the hydrogen production reactions in water all operate 100 to 1000 times faster than the hydrogen consumption reaction (14).

The net hydrogen yield from water containing waste forms will depend on how these two sets of competing reactions balance out. Since the second order production reactions are more sensitive to dose rate than the first order consumption reactions, it is reasonable that the hydrogen yield will be lower at lower dose rates. This was verified by Bibler when he observed a lower steady state hydrogen pressure for lower dose rates. Increasing the hydrogen pressure increases the rate of the hydrogen consumption reaction. At lower dose rates, a significantly lower hydrogen pressure was required to establish steady state, indicating that the hydrogen production reactions had slowed significantly more than the hydrogen consumption reaction.

Table 5-1. Base Materials

Irradiated Material	G _{H2}	Dose Rate (R/hr)	Total Dose (rad)	Radiation Source	Remark	Ref.
Polystyrene	0.008			Test Reactor Neutron, Gamma	Sealed Samples	5
Polyethylene	2.0			Test Reactor Neutron, Gamma	Sealed Samples	5
Styrene/Butadiene Copolymer	0.01			Test Reactor Neutron, Gamma	Sealed Samples	5
Aromatic Liquids	0.05-0.1				11	
Pure Water	0.45				Unaffected by pH	14
Saturated Hydrocarbon (Paraffins)	2-6				25	
Unsaturated Hydrocarbons (Olefins)	1				25	
Aromatic Hydrocarbons	0.04-0.4				25	
Polystyrene	0.0262-0.0446			Co-60	37	

Table 5-2. Solidification Binders

Irradiated Material	G _{H2}	Dose Rate (R/hr)	Total Dose (rad)	Radiation Source	Remark	Ref.
Vinyl Ester Styrene (Dow Binder)	0.03				Mostly CO & CO ₂ , only 17% H ₂	19
Epoxy	0.10-0.23	6 × 10 ⁶	3 × 10 ⁹	Spent Fuel Gamma	Varied depending on resin/hardner combination	29
Cement	—	2.8 × 10 ⁷		Co-60	G _{H2} was time dependent, steady state pressure of 100 psig developed	4
Cement (Type II)	0.35-0.11	4.6 × 10 ⁶	10 ⁵ -10 ⁹	Co-60	33% H ₂ O; G _{H2} decreased with total dose as pressure built up in sealed container	10
Asphalt	0.3-0.6				Survey of four references, details not given	8
Asphalt-Distilled	0.41				16	
Asphalt-Air Blown	0.46				16	
Asphalt-Pioneer 221	0.07-0.41	4.6 × 10 ⁶	10 ⁵ -10 ⁹	Co-60	Increased with total dose (time)	10
Asphalt-Air Blown	0.43	10 ⁵	10 ⁹	Fuel Element Gamma	15	
Asphalt-Distilled	0.32	10 ⁵	10 ⁹	Fuel Element Gamma	15	

Table 5-3. Ion Exchange Resins

Irradiated Material	G _{H2}	Dose Rate (R/hr)	Total Dose (rad)	Radiation Source	Remark	Ref.
<i>Cation Resins</i>						
Dowex MSC-1	0.46	3.5×10^5	1.4×10^9	Co-60	Covered in 0.5 N HCl	24
Amberlite 252	0.53	3.5×10^5	1.4×10^9	Co-60	Covered in 0.5 N HCl	24
Duolite C-264	0.38	3.5×10^5	1.4×10^9	Co-60	Covered in 0.5 N HCl	24
Dowex 50W	0.10	1.25×10^6	5×10^8	Co-60	Air dried (66% H ₂ O)	22
Dowex HCR-S	0.05	5×10^6	2.5×10^9	Co-60	Fully swollen, dewatered, sodium form	27
Dowex 50	1.06	2.5×10^5	$5 \times 10^7 - 2 \times 10^8$	Co-60	H+ form, covered in water	28
Dowex 50	0.81	2.5×10^5	$5 \times 10^7 - 2 \times 10^8$	Co-60	Lithium form, covered in water	28
Zeo Karb 215	1.06	2.5×10^5	$5 \times 10^7 - 2 \times 10^8$	Co-60	H+ form, covered in water	28
Dowex 50	0.06	2.5×10^5	$5 \times 10^7 - 2 \times 10^8$	Co-60	H+ form, fully swollen	28
Dowex 50	0.07	2.5×10^5	$5 \times 10^7 - 2 \times 10^8$	Co-60	Lithium form, fully swollen	28
Zeo Karb 215	0.08	2.5×10^5	$5 \times 10^7 - 2 \times 10^8$	Co-60	H+ form, fully swollen	28
IRN-77	0.13	$4 \times 10^4 - 1.6 \times 10^6$	10^9	Co-60	H+ form, fully swollen	33
IRN-77	0.16	$4 \times 10^4 - 1.6 \times 10^6$	10^9	Co-60	Sodium form, fully swollen	33
<i>Anion Resins</i>						
Dowex 1	0.09	1.2×10^6	6×10^8	Co-60	Air dried (48% H ₂ O)	23
IRN-78	0.62	1.6×10^6	10^9	Co-60	Hydroxide form, fully swollen	33
IRN-78	0.34	1.6×10^6	10^9	Co-60	Chloride form, fully swollen	33
Dowex SBR-OH	0.38	5×10^6	7.9×10^8	Co-60	Borate form, fully swollen, dewatered	27
<i>Mixed Resin</i>						
IRN-150	0.3 - 0.5	$4 \times 10^4 - 1.6 \times 10^6$	10^9	Co-60	Varied with chemical from (degree of resin depletion)	33
D-Mix	0.19-0.24	4.5×10^6	9×10^8	Co-60	Proprietary formulation of TMI-2 cleanup resins, sodium borate form, fully swollen, dewatered	2
Dowex HGR-H Cation Resin	0.07	1.2×10^5	5×10^7	Co-60	Dried resin	7
IRN-77 Cation Resin	0.01		10^9	Co-60	Dried to 7% water content	33
Dowex 50 Cation Resin	0.03	2.5×10^5	$5 \times 10^7 - 2 \times 10^8$	Co-60	H+ form, dried resin	18
Dowex 50 Cation Resin	0.001	2.5×10^5	$5 \times 10^7 - 2 \times 10^8$	Co-60	Lithium form, dried resin	18
Zeo Karb 215 Cation Resin	0.05	2.5×10^5	$5 \times 10^7 - 2 \times 10^8$	Co-60	H+ form, dried resin	18
Ionsiv IE-95 Zeolite	0.05-0.005	3.9×10^5	1.4×10^8	Co-60	21-33% water content	30
Linde IE-95 Zeolite	0.75-0.18	1.2×10^5	5×10^7	Co-60	Saturated with water	7
Miscellaneous Resins	1-3.1				Work of the Russian Egorov, conditions not given, ca. 1965	18

Table 5-4. Solidified Waste

Irradiated Material	G _{H2}	Dose Rate (R/hr)	Total Dose (rad)	Radiation Source	Remark	Ref.
Cement/D-mix	0.19-0.24	4.5×10^6	9×10^8	Co-60	Proprietary resin formulation of TMI-2 cleanup resins solidified in a metasilicate modified cement	2
Cement/Fe ₂ O ₃	—	8.9×10^4		Co-60	30 psig steady state pressure developed	4
Cement/Fe ₂ O ₃	—	3.9×10^5		Co-60	50 psig steady state pressure developed	4
Cement/Fe ₂ O ₃	—	1.4×10^7		Co-60	100 psig steady state pressure developed	4
Cement/Fe ₂ O ₃	—	2.8×10^7		Co-60	120 psig steady state pressure developed	4
Cement/MnO ₂	—	8.9×10^4		Co-60	15 psig steady state pressure developed	4
Cement/MnO ₂	—	3.9×10^5		Co-60	25 psig steady state pressure developed	4
Cement/MnO ₂	—	1.4×10^7		Co-60	50 psig steady state pressure developed	4
Cement/MnO ₂	—	2.8×10^7		Co-60	65 psig steady state pressure developed	4
Cement/NO ₂ ⁻ , NO ₃ ⁻	—	8.9×10^4		Co-60	30 psig steady state pressure developed	4
Airblown Asphalt/ NaNO ₃	0.25	10 ⁶	10 ⁸	Fuel Element Gamma	50:50 mixture of asphalt and salt	15
Distilled Asphalt/ NaNO ₃	0.18-0.26	10 ⁶	10 ⁷ -10 ⁸	Fuel Element Gamma	50:50 mixture of asphalt and salt	15
Distilled Asphalt/ Mixed Resin	0.19-0.24 0.24	10 ⁶	10 ⁷ -10 ⁸	Fuel Element Gamma	50:50 mixture of asphalt and mixed resin in the lithium borate form	15
Asphalt/Resin	0.15		8×10^7		Resin expended with lithium borate, 10% residual water	16
Dow/Resin	0.57				2:1 resin to binder ratio	19

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CONCLUSION

Example Calculation

A good way to bring home some of the aspects of radiolytic hydrogen generation is to perform a sample calculation evaluating a common LLRW waste form. Such a calculation was performed and is included as the Appendix to this report. In this calculation the dose required to generate a combustible quantity of hydrogen in the void over a cement solidified drum of ion exchange resins was determined.

The first step of the analysis is to determine the volume in the package available for the gas to occupy. Burial site criteria require all packages to be at least 85% full. In addition to the free void, dewatered bead resins have approximately 35% void space between the beads. Because the particle size is smaller, dewatered sludges are only about 25% void. Therefore, the total void space into which hydrogen gas can expand is about 45% of the internal package volume for dewatered bead resin and 36% for dewatered sludges. Based on the 5% limit given in Information Notice 84-72, a maximum of 2.5% of the total internal package volume is available for hydrogen gas at room temperature and pressure dewatered bead resin. The corresponding volume is 1.8% for dewatered sludges. These limits apply to a package which is sealed and given no consideration for venting from the time of closure to the time of disposal. The volume available for hydrogen gas in a solidified waste form is limited to the unused space in the package above the waste. This is because the binder fills the voids that are present in dewatered resin and sludge. The free volume for hydrogen gas is dictated by the packaging process, but in all cases must be at most 15% (vol) of the internal package volume based on burial site criteria. Applying the 5% limit to this, a maximum

of 0.75% of the internal package volume is available for hydrogen gas at room temperature and pressure.

The next step is to determine the amount of hydrogen that will have to be formed to achieve a 5% concentration in this void. Finally, the energy and absorbed dose is determined that will generate this much hydrogen from the waste being considered. This energy depends on the hydrogen G-value of the material being studied. When evaluating data or making predictions of gas generation rates using a G-value, it is important to remember that this number is a ratio and its accuracy is dependent upon the accuracy of measuring both the reaction yield and the absorbed energy.

Now that the limiting absorbed dose is known which will generate a combustible quantity of hydrogen, this must be translated to an activity loading in the drum. This activity loading will be a characteristic of the waste stream, reactor type and hold up time before packaging. Using the results of Colombo and Nielson (10) for "typical" PWR and BWR wastes (Figures 2-1 and 2-2), an activity loading of about 1 Ci/ft³ will result in an absorbed dose on the order of 10⁶ rads after 5 years at either a PWR or BWR. This limiting activity loading increases by a factor of 3 to 5 if the drum is shipped prior to 1 year after being sealed. As a point of comparison, a 1 Ci/ft³ waste form having the same radionuclide composition as Colombo and Nielson's PWR waste would be classified as Class B according to the current Barnwell Waste Management Facility License. This waste would also be 35% of the Class C limit.

It would therefore appear that the primary impact of hydrogen generation on transportation will be from LLRW that is relatively highly loaded with radionuclides and also stored for a period of one to five years.

Waste stored less than one year will have to be near Class C to generate a combustible quantity of hydrogen prior to shipment.

Main Conclusions

The main conclusions of this investigation can be listed as:

- Water accounts for most of the radiolytic hydrogen generated by LLRW.
- Hydrogen G-Values reported in the literature for water containing species will probably result in conservatively high predictions of the amount of hydrogen generated by radiolysis in LLRW because these data were all taken at dose rates that are several orders of magnitude larger than exist in most LLRW. It has been shown that the hydrogen yield for cement will decrease at lower dose rates, and this may hold true for other water containing waste forms.
- Concerns over combustion within a sealed package of LLRW are unfounded. This is because an efficient radiolytic oxidation reaction removes oxygen from the atmosphere in a sealed package. The concern for combustion surfaces during a package failure situation, such as a transportation accident. This is the source of the requirement for limiting hydrogen or inerting the transportation cask interior. Another area of concern is extended storage of Class B and C waste in confined spaces where local concentrations of hydrogen can accumulate.
- Vinyl ester styrene generates the least radiolytic hydrogen of the LLRW solidification binders. This is because it contains no water and is a largely aromatic polymer. Asphalt and cement generate as much as a ten times more hydrogen.
- Dried organic ion exchange resins produce a factor of ten less radiolytic hydrogen than fully swollen (dewatered) resins.
- Cement solidification of waste does not appreciably reduce the hydrogen yield, but it does fill the voids in dewatered resin. This results in less void volume for the gas to fill, producing a combustible quantity of hydrogen at a lower absorbed dose. This effect can be significant because dewatered bead resin can contain as much as 35% void volume between the beads.
- Chemical production of hydrogen in a corrosion process can overwhelm radiolytic production. The importance of this reaction pathway is somewhat more elusive than that of hydrogen formation by direct irradiation of water or organics. Most LLRW transportation packages contain insufficient free water to support such a chemical reaction. However, rad-waste spent resin storage tanks do. It is possible that measurements may be taken in the field at the spent resin tank to verify the presence of hydrogen prior to packaging for disposal. For this reason, it is just as important to characterize the chemical nature of the spent resins as it is their radiological nature when performing field measurements of the hydrogen gas yields pursuant to IE-Notice 84-72. Furthermore, Swyler (33) identified that the irradiation of anion exchange resins results in a release from the resin bead of some of the bound water at absorbed doses on the order of 5×10^8 rads. Although, this radiation dose is quite large for typical LLRW, this release of water could provide enough acid contact with a metal surface to result in sufficient corrosion to produce hydrogen. Again, it is important to remember here that both the chemical and radiological conditions, as well as the nature of the package, must be considered jointly when examining a hydrogen production mechanism of this kind.
- Asphalted, cemented and dewatered waste that is an appreciable fraction of the Class C limit and is stored for one to five years may require special considerations for hydrogen generation.

Recommendations for Future Work

Several workers have identified a trend in cement solidified waste that the radiolytic hydrogen yield decreases with dose rate. This is not surprising in that dose rate dependence is common in the study of radiation effects in solids. There is also reason to believe that the reactions that operate in cement also operate in other water containing waste, such as dewatered ion exchange resins. Since all of the research to date has taken place in the 10^5 to 10^7 rad per hour range, and even Class C utility waste is

significantly below this, it would be beneficial to determine the hydrogen yield at dose rates which closer approximate LLRW. This will fill a large gap in the existing hydrogen generation data base.

Since measurements at low dose rates will produce hydrogen at correspondingly low rates, the accuracy of measuring the quantity of hydrogen produced will have to be carefully evaluated. Very sensitive analytical methods will be required to monitor this small quantity of hydrogen.

Since the calculation of the absorbed dose is so critical to the analytical determination of hydrogen generation,

methods for this calculation should be examined and a standardized calculation developed. Based on variations in the modelling technique, it is conceivable that 50-100% error can be made in the calculation of absorbed dose, leading to either gross underestimation or overestimation of the hydrogen produced between packaging and transportation. This is especially significant with the advent of the storage of large quantities of LLRW at reactor sites for periods of up to five years.

ANNOTATED BIBLIOGRAPHY

1. Ballantine, D.S., "The Significance to ASTM of Post-irradiation Effects in Irradiated Materials," *Materials in Nuclear Applications*, ASTM Special Technical Publication No. 276, 1960.

Identifies the basic radiolytic reactions which result in polymer degradation. Radiolytic ionization or excitation causes C-C or C-H bond rupture. This is followed by oxidation in the presence of oxygen, hydrogen gas formation, recombination, depolymerization or crosslinking. The reaction pathway depends on the size of the radical or ion and the viscosity or rigidity of the parent compound.

Evidence of the existence of trapped free radicals is cited. These trapped free radicals lead to post irradiation reactions. These radicals have been detected in polyethylene 3000 hours after irradiation at room temperature. The author stressed the importance of considering post irradiation reactions in the results of any materials testing.

2. Barletta, R. E., Swyler, K. J., Chan, S. F. and Davis, R. E., *Solidification of Irradiated Epicor-II Waste Products*, NUREG/CR-2969, BNL-NUREG-51590, May 1983.

Ion exchange resins similar to those used to decontaminate TMI-2 were irradiated in both dewatered and solidified form. These resins are a combination of organic and inorganic ion exchangers. The resins studied, termed "D-mix," were representative of those used in a deep bed prefilter. The resins were expended using sodium borate and irradiated with a cobalt-60 source at 4.5×10^6 rad/hr to a total dose of 9×10^8 rad. For dewatered D-mix, a hydrogen G-value of 0.19 to 0.24 is reported, with a total gas G-value of 0.25 to 0.33. Carbon dioxide was the other principal gas involved.

For cement solidified D-mix (composition: 350: 153: 514: 51, D-mix: water: Type I cement: sodium metasilicate, by weight) a total gas G-value of 0.19 to 0.24 is reported with hydrogen being the only significant gas produced (>98%). Specific gravity for the solidified D-mix was about 1.4, with 1.1 for D-mix alone.

3. Bibler, N. E., "Radiolytic Gas Production During Long-Term Storage of Nuclear Wastes," Savannah River Laboratory Technical Paper. No. DP-MS-76-51, 1976.

Presents the results of work which was later reported on in DP-1484. This work consisted of irradiating cement and simulated cement waste forms and monitoring the radiolysis gas. In addition to work discussed in DP-1484, gas generation results of irradiation of vermiculite containing absorbed organic liquids and cellulose (paper towels) containing alpha-emitting isotopes are presented.

4. Bibler, N. E., *Radiolytic Gas Generation From Concrete Containing Savannah River Plant Waste*, Savannah River Laboratory Report No. DP-1464, 1978.

Samples of cement and simulated cement waste forms containing Fe_2O_3 , MnO_2 , NO_3^- and NO_2^- were irradiated with both gamma and alpha radiation and radiolytic gas production was monitored. The effect of gamma dose rate was studied over the range of 8.9×10^4 to 2.8×10^7 rad per hour. Hydrogen was the only significant product for gamma radiolysis. A steady state hydrogen pressure was attained with gamma radiolysis that was dose rate dependent. This is evidence of a back reaction which consumes

hydrogen. No steady state pressure could be attained with alpha radiolysis.

5. Bopp, C. D. and Sisman, O., *Radiation Stability of Plastics and Elastomers*, ORNL-1373, July 23, 1953.

Plastics and elastomers were irradiated on the maximum flux region of the ORNL Graphite Reactor. To increase the gamma dose, some samples were rapped in cadmium during irradiation. Energy absorbed was calculated from the elemental composition of the materials by using calorimetrically determined values for the elements. Energy absorbed was highly dependent on hydrogen atom content, since a hydrogen atom has "high stopping power for fast neutrons."

0.2 to 0.5 gram samples were irradiated in sealed glass capsules. In the range of 1 to 50 ml (STP) of gas evolved, gas evolution was proportional to exposure (in nvt).

Total gas G-values are reported as:

Polystyrene	—	0.008
Polyethylene	—	2.0
Styrene/Butadiene Copolymer	—	.01

6. Bureau of Radiological Health and the Training Institute, Environmental Control Administration, *Radiological Health Handbook*, U.S. Government Print Office, Washington, D.C., 1970.

A general handbook containing data on the radioactive decay properties of the radioisotopes. Of particular interest are the energy and half-life data that is given for essentially all known radionuclides. Also given are mass absorption coefficients for many materials, along with other information pertaining to radiation dose calculations. These data are required for calculating the absorbed dose to a waste form from incorporated radionuclides.

7. Capolupo, W. P., Sheff, J. R., "Radiolytic Gas Generation and Oxygen Depletion in Ion Exchange Materials," *Scientific Basis for Nuclear Waste Management VI*, Materials Research Society Symposia Proceedings Vol. 15, 1983.

Both organic and inorganic ion exchangers were irradiated at 1.2×10^5 R/hr using a cobalt-60

source up to an absorbed dose of 5×10^7 rad. Particular emphasis was placed on the early stage of radiolysis. Rapid depletion of oxygen over the organic resin was observed, with 99.8% of the oxygen being consumed at 2.5×10^6 rad. No oxygen consumption was observed over the Zeolite. The Zeolite, Linde IE-95, was irradiated fully hydrated and yielded a total gas G-value of 0.075-0.18. The gas yield was low at low dose but increased at high dose, indicating some gas interaction with the Zeolite surface. The organic resin, Dowex HGR-H+, was irradiated both hydrated (50% water) and dried. Dried resin exhibited a total gas G-value of 0.067. No G-value was reported for wet resin as the pressure in the sealed container varied nonlinearly over the range of dose.

8. Carleson, G., *Radiation Stability of Solidified Ion-Exchange Resin* (In Swedish), Studsvik Technical Report NW-83/490, 1983.

A literature review of the period 1965-1982 is presented concerning the radiation stability of ion-exchange resins solidified with cement or bitumen. Sites 67 references from both the U.S. and world at large. Pays particular attention to radiolytic gas generation in binders. For cement, reports that in sealed systems, hydrogen production increases with dose to an equilibrium pressure of 5-20 bar, with the pressure being a function of dose rate. Reports total gas G-value for cement of 0.4 ± 0.2 . Reports hydrogen yields from bitumen of 7 ± 3 l/g Mrad, which translates to a G-value of 0.3-0.6. Reports decrease in gas generation with higher resin loading in bitumen waste forms.

9. Carswell, D.J., *Introduction to Nuclear Chemistry*, Elsevier Publishing Co., New York, N.Y., 1967.

A general textbook on Nuclear Chemistry. Provides a good description of the basic mechanisms of the chemical reactions occurring in irradiated materials. Also, defines G-value.

10. Colombo, P., Nielson, R.M., Jr., *Properties of Radioactive Wastes and Waste Containers — First Topical Report*, NUREG/CR-0619, BNL-NUREG-50957, August 1979.

A topical report on the results of research conducted by BNL on the properties of solidified radioactive wastes and their containers. Radiolytic gas formation from three radwaste binders during irradiation from a cobalt-60 source was studied. The binders that were studied were Portland Type II cement (33% WW H₂O), urea-formoldehyde, and Pioneer 221 asphalt. Also presented, is a calculation of absorbed dose as a function of specific activity and time for "typical" PWR and BWR wastes solidified in a waste form having a specific gravity of 2.0 g/cc.

11. Cosgrove, S.L., and Dueltgen, R.L., *The Effect of Nuclear Radiation on Lubricants and Hydraulic Fluids*, Radiation Effects Information Center (REIC) Report No. 19, Battelle Memorial Institute, May 31, 1961.

Gives quantitative data on radiation effects in all manner of organic fluids and polymers. For organic compounds similar to polystyrene, G-values for total gas production are given in the 0.05-0.1 range. Straight chain alkanes (paraffins) are reported as having the highest G-values for total gas production, being in the 4-6 range.

12. Collins, C.G., and Calkins, V.P., *Radiation Damage to Elastomers, Plastics and Organic Liquids*, General Electric Aircraft Nuclear Propulsion Department, APEX-261, Sept. 1956.

Presents a collection of data on radiation damage to organic materials, including physical properties, mechanical strength and gas generation. The Primary source for gas generation data is the work of O. Sisman and C.D. Bopp.

13. Dole, M., Keeling, C.D. and Rose, D.G., "The Pile Irradiation of Polyethylene," *J. Amer. Chem. Soc.*, 76, pp. 4304-4311 (1954).

Polyethylene in films and granules was irradiated in a heavy water reactor in vacuum and in air. Amount and composition of the radiolysis gases were determined. Exposure is reported in terms of hours and total dose is not reported, therefore, a G-value is not calculable. However, gas generation is plotted vs. time and is apparently linear for the three points shown.

The composition of the radiolysis gas in the evacuated container was 98.6% H₂, 0.2% CH₄ and the balance was higher degree saturated paraffins (C_nH_{2n} + 2).

14. Dragnic, I.G. and Dragnic, Z.D., *The Radiation Chemistry of Water*, Academic Press, New York, N.Y., 1971.

A thorough textbook on the radiation chemistry of water and aqueous systems. Gives the primary radiolysis products of water as H, OH, H₂O₂ and H₂. Reports that the hydrogen G-value of pure water is 0.45 regardless of pH. The primary radiolytic pathway for the production of molecular gaseous hydrogen is through the recombination reaction of two hydrated electrons. It has been documented that the presence of electron scavengers such as metal ions can greatly reduce the production rate of hydrogen gas in aqueous solutions.

15. Duschner, H., Schorr, W. and Starke, K., "Generation and Diffusion of Radiolysis Gases in Bituminized Radioactive Waste," *Radiochemica Acta*, 24, 133 (1977).

Simulated bituminized radioactive wastes were irradiated by a 10⁵ R/hr fuel element source to 10⁸ rads and the radiolysis gases studied. Both air blown and distilled bitumen binders were used. Wastes studied were sodium nitrate and mixed anion-cation organic ion exchange resin in the lithium borate form. Gas analysis was performed by mass spectrometry. Hydrogen accounted for about 95% of the radiolysis gas in all cases. Irradiations were performed in sealed containers with both air and argon atmospheres. Hydrogen diffusion experiments were also performed on asphalt discs, and the rate of permeation and absorption coefficient are reported. Hydrogen generation rates of 0.48 - 1.1 × 10⁻² cm³/MR per gram of simulated waste are reported. Results were linear with absorbed dose and dose rate effects were discounted based on work by others.

16. Eschrich, H., *Properties and Long-Term Behavior of Bitumen and Radioactive Waste-Bitumen Mixtures*, SKBK-KBS Technical Report 80-14, Oct. 1980.

Presents the results of a review of over 300 references on the properties of bitumen for rad-waste solidification. With respect to gas generation, hydrogen and methane are the primary radiolysis gases reported (75-95%). States that internal radiation sources yield approximately twice the hydrogen as external sources. Hydrogen generation in bituminized ion exchange resin is reported as 0.11 to 0.30 cc/g at 760 torr and 25°C when exposed to 8×10^7 rad. For pure asphalt, hydrogen G-values of 0.41 for distilled and 0.46 for air-blown are reported.

17. Gangwer, T.E., and Pillay, K. K. S., "Radiation-Induced Corrosion of Mild Steel In Contact with Ion-Exchange Materials," *Nuclear Technology* 58 (3), Sept. 1982.

Mild Steel coupons were irradiated while embedded in cation, anion and zeolite ion exchange materials. Steel weight loss from corrosion in the organic media was 13-32 mg loss per square centimeter after exposure to 2×10^9 rad from a ^{60}Co source. Weight losses of 5.2-27 mg/cm² were also observed after exposure to 4.4×10^8 rad from reactor fuel rads. Rust and pitting was visible on each of the metal coupons following exposure. It was not reported whether the irradiation took place in a sealed or open system.

18. Gangwer, T. E., Goldstein, M. and Pillay, K. K. S., *Radiation Effects on Ion Exchange Materials*, BNL-50781, Nov. 1977.

An extensive literature review and data compilation on the radiation damage of ion exchange resins. States that in the majority of the literature, experimenters have assumed that mass absorption coefficients for resin and water are approximately equal.

With respect to gas generation, the review is of the work of Kazanjian, et. al., and Mohorcic, et. al., as well as a 1965 review by the Russian, Egorov. Gaseous radiolysis products are dominated by H₂ with CO₂, CO, SO₂, CH₄, N₂, NO₂ and NO also being reported. Hydrogen G-values reported by Egorov are around 1.0 to 3.1, or an order of magnitude greater than those commonly reported in the U. S.

19. Haighton, A.P., *The Solidification of Ion Exchange Waste Part 6 — Characterization of a Vinyl Ester Binder*, NW/SS0/RR/75/80, Central Electric Generating Board, Manchester, United Kingdom, 1980.

Vinyl ester styrene (VES), also known as the Dow Binder, was irradiated both with and without simulated waste (containing water and ion exchange resins). For the pure binder, 0.41 cc/g-100 mR of total gas was evolved when irradiating to 1420 MRad. The gas composition was 35% H₂, 10% CO, 43% CO₂, 17% H₂ and CH₄. For the binder encapsulating water, 0.61 MRad. The gas composition was 40% H₂, 22% CO, 34.5% CO₂ and 3.5% CH₄. Finally, for the binder containing organic ion exchange resin in a 2:1 resin to binder ratio, 1.34 cc/g-100 mR total gas was evolved at 1030 MRad, with the gas being composed of 98% H₂.

20. Harrington, R., and Giberson, R., "Chemical and Physical Changes in Gamma-Irradiated Plastics," *Modern Plastics*, 36, p. 199 (Nov. 1958).

Films of plastic ranging from 3 to 20 mils were irradiated in a vacuum to 1×10^8 roentgens exposed dose. A 1.3×10^6 roentgen per hr. cobalt-60 source was used. Marlex polyethylene and polystyrene were among the plastics studied. Within the sensitivity of the instrumentation, no gassing was observed for the polystyrene at a total exposure dose of 1×10^8 roentgen. For the Marlex high density polyethylene the gas composition as 97.8% H₂, 0.10% CH₄, 1.1% C₂H_x with a mixture of light hydrocarbons comprising the balance. Total gas yield was not reported.

21. Hine, G.J., and Brownell, G.L., *Radioactive Dosimetry*, Academic Press, Inc. New York, N. Y., 1956.

A general textbook on radiation dosimetry. Describes a method for calculating the radiation dose absorbed by a cylinder of uniformly distributed gamma emitters. Relies on an "average geometrical factor," \bar{g} , to approximate the attenuation provided by a given shape of material.

22. Kazanjian, A.R. and Horrell, D.R., *Radiation Effects on Ion Exchange Resins, Part I: Gamma Irradiation of Dowex 50W*, Dow Chemical Rocky Flats Division Report No. RFP-2140, May 10, 1974.

Dowex 50W, a sulfonic acid cation exchange resin was irradiated to 5×10^9 rads using a 1.25×10^6 rad per hour cobalt-60 source. Gas yields were measured for hydrogen from air-dried resin (66% H₂O), resin in 0.1 N HCl, and 0.1 N HCl. Hydrogen G-values are reported as 0.10 for each.

23. Kazanjian, A.R., and Horrell, D.R., *Radiation Effects on Ion-Exchange Resins, Part II: Gamma Irradiation of Dowex 1*, Dow Chemical Rocky Flats Division Report No. RFP-2354, Feb. 27, 1975.

Dowex-1, a trimethylamine anion exchange resin, was irradiated to 6×10^9 rads using a 1.2×10^6 rad per hour cobalt-60 source. Gas yields were measured for nitrate form air dried resin (48% H₂O), resin in 7 N nitric acid, and 7 N nitric acid. The hydrogen G-value is reported as 0.09, 0.02 and 0.02, respectively. Carbon monoxide, and nitrous oxide are the only other gases reported for the dried resin. No methane is reported.

24. Kazanjian, A.R., and Stevens, J.R., *Radiation Effects on Dowex MSC-1, Amberlite 252, and Duolite C-264 Ion Exchange Resins*, Rockwell International Energy Systems Group Rocky Flats Plant Report No. RFP-3541, Sept. 12, 1983.

Three sulfonic cation exchange resins were irradiated to 1.38×10^9 rad using a 3.48×10^5 rad per hour cobalt-60 source. The samples were irradiated in sealed vials and were barely covered with 0.5 N hydrochloric acid. Hydrogen was the only combustible species detected, having a G-value of 0.46, 0.53 and 0.38 for the Dowex, Amberlite and Duolite resins, respectively.

25. Kircher, J.F., and Bowman, R.E., (ed.), *Effects of Radiation on Materials and Components*, Reinhold Publishing Corp., New York, NY, 1964.

A basic text on radiation damage which also contains a large amount of data. Gives the definition of "G-value" as "the number of product molecules formed or reactant molecules consumed per 100 ev of energy absorbed." For paraffins, hydrogen is always the major radiolysis product. Unsaturated aliphatics (eg. ethylene) react by chain mechanisms which lead to polymers and a low yield of gas, particularly

hydrogen. Aromatics (eg. benzene) are notably stable under irradiation because of the ability of the ring to absorb large amounts of energy without cleavage. Decomposition and gas formation rates in aromatics are an order of magnitude lower than for aliphatic compounds.

With respect to polymer radiolysis, says: "From the standpoint of change in physical properties and hydrogen evolution during irradiation, polystyrene is one of the most stable of all high polymers."

General hydrogen G-values are:

Saturated Hydrocarbons	2-6
Unsaturated Hydrocarbons	1
Aromatic Hydrocarbons	0.04-0.4

Radiation induced gas release from concrete is reported as 4-6 cc/g-day in pile reactor shields. Gas composition is 75% H₂ with some CO and CO₂.

26. MacKenzie, D. R., Lin, M., and Barletta, R. E., *Permissible Radionuclide Loading for Organic Ion Exchange Resins from Nuclear Power Plants*, NUREG/CR-2830, BNL-NUREG-51565, October 1983.

Reports on the results of a literature review and power plant survey on the radiation effects in ion exchange resins and the radionuclide loadings seen in the industry. Review of radiation effects considers gas generation. Primary references are the research of Mohorcic and Kramer, Kazanjian and Horrell, and McFarland, as well as the reviews of Gangwer, Goldstein and Pillay (BNL-50781), Swyler, Barletta and Davis (BNL-NUREG-28682), and Pillay (NUREG/CR-1863).

Proposes a permissible resin loading in terms of a delivered dose of 10^9 rad. A computer code is presented to calculate delivered dose based on Curie inventory, container size and length of decay. This code is developed using the method of Swyler, et al (BNL-NUREG-28682).

27. McFarland, R. C., *Analysis of Irradiated Ion Exchange Materials*, Final Research Report, Project A60-11. Published as Appendix C to Morcos, N. et. al, *Properties of Radioactive Wastes and*

Waste Containers, NUREG/CR-2617, BNL-NUREG-51515, April 1982.

Sodium form Dow HCR-5 cation and borate form Dow SBR-OH anion exchange resins were irradiated in sealed containers and gas pressure buildup and composition were monitored. A 5×10^6 rad per hour cobalt-60 source was used with absorbed dose totalling 7.9×10^8 rads for the anion resin and 2.5×10^9 rads for the cation resin. Resins were fully swollen and dewatered for the irradiation. For the anion resin, G-values were as follows: total gas = 0.68, hydrogen gas 0.38, methane = 0.04. For the cation resin, G-values were: total gas = 0.11, hydrogen gas = 0.05, and methane = 0.002.

28. Mohorcic, G, and Kramer, V., "Gases evolved by cobalt-60 Radiation Degradation of Strongly Acidic Ion Exchange Resins," *J. Polymer Science: Part C*, 16, pp 4185-4195 (1968).

Sealed sulfonic acid cation exchange resins were subjected to a 2.5×10^5 rad per hr cobalt-60 source to absorbed doses of 5 to 20×10^7 rads. Experimental conditions were hydrogen and lithium forms in excess water, swollen and dry states. Gas analysis showed linear dependence on absorbed dose over the range studied. Dowex-50, a polystyrene-divinylbenzene based resin, had hydrogen gas G-values of 0.026, 0.059 and 1.06 in dry, swollen and excess water conditions in hydrogen form. In lithium form, Dowex-50 had hydrogen gas G-values of 0.001, 0.069 and 0.812 in the same order of conditions. Zeo Karb 215, a phenol-formaldehyde based resin, had hydrogen G-values of 0.051, 0.075 and 1.06 under the same conditions combustible gases are reported, however, a large sulfur dioxide yield was reported for dry Dowex-50 ($G=0.87$). It should be noted that Mohorcic reported resin G-values in terms of dry resin only and these values have been converted to account for the additional weight of water in the swollen and excess water states.

29. Morgan, J.T., et al., *Gas Evolution from Epoxy Resins by High Energy Radiation*, Rutherford High Energy Lab Report No. RHEL/R-196, Aug. 1970.

Cast epoxy resins were exposed to gamma radiation from spent fuel in sealed tubes and the gas evolution rate and composition were monitored. The gas evolution rate was found to be constant up to 3×10^9 rad absorbed dose. Hydrogen G-values ranged from 0.10 to 0.23, depending on the epoxy resin/hardner combination and the resin curing temperature. Hydrogen accounted for 80-90% of the gas evolved in most cases except three, where carbon dioxide and monoxide prevailed. Trace quantities of the lower hydrocarbons, (methane, ethane, etc.) were also detected. The predominance of small molecules agrees with the "cage effect" in which large molecules are restricted from leaving the cage of the surrounding molecules and subsequently recombine, cross-link or cause chain scission. Small molecules can more readily diffuse away to react and form gases.

30. Pillay, K.K.S., *Radiation Effects on Ion Exchangers Used in Radioactive Waste Management*, Pennsylvania State University, NE/RWM-80-3, October 1980. Published as Appendix A of Morcos, N. and Weiss, A. J., *Properties of Radioactive Wastes and Waste Containers-Quarterly Progress Report July-Sept 1980*, NUREG-CR-1868, BNL-NUREG-51316, Jan 1981.

Report is an extension of Pillay's work on BNL-50781 (1977). The literature search done there is updated and augmented. Also, experiments are reported on the irradiation of sulfonic acid cation resins (Amberlite IR-120), amine anion resins (Amberlite IRA-400) and an inorganic Zeolite (IONSIV-IE-95). A pH change from 3.4 to 1.5 is reported for cation resin in both hydrogen and ammonium form after irradiating to 7×10^7 rads. The Zeolite (21-33% H_2O) was irradiated to 1.4×10^8 rads with gas evolution being monitored in a sealed, atmospheric container. From these data, a G-value for hydrogen of about 0.05 to 0.005 can be calculated. The low H_2 yield was hypothesized to be a result of a hydrogen adsorption on the Zeolite surface. Significant corrosion of up to 32.4 mg/cm² of mild steel coupons was also reported when irradiating them with the above ion exchangers.

31. Sun, K.H., "Effects of Atomic Radiation on High Polymers," *Modern Plastics*, 32, p.141 (Sept. 1954).

A review of the basics of radiation damage to polymers. The nature of radiation, units of dosimetry, principal chemical reactions and physical property changes are all discussed. With respect to gas formation it is stated that independent of the radiation type or polymer type, over 94% of the gas liberated is hydrogen, the rest being the light hydrocarbons (ie. methane, ethane, etc.). This is based on a review of the literature to date.

32. Swyler, K.J., Barletta, R.E. and Davis, R.E., *Review of Recent Studies of the Radiation Induced Behavior of Ion Exchange Media*, BNL-NUREG-28682, Nov. 1980.

Reviews the published work of R.C. McFarland and K.K.S. Pillay on radiation effects in ion exchangers. Also reviews their unpublished work performed at BNL which was later published as NUREG/CR-3383 and NUREG/CR-3812. Presents a method for calculating the dose absorbed by a cylindrical bed of organic ion exchange resin from absorbed radionuclides.

33. Swyler, K.J., Dodge, C.J., and Dayal, R. *Irradiation Effects on the Storage and Disposal of Radwaste Containing Organic Ion-Exchange Media*, NUREG/CR-3383, BNL-NUREG-51691, Oct. 1983.

This study consisted of irradiating cation, anion and mixed resins at dose rates from 10^4 to 10^6 Rad/hr until the absorbed dose totaled about 10^9 rad. Gaseous and aqueous radiolysis products were monitored both qualitatively and quantitatively. Two to six gram resin samples were irradiated in both sealed and open systems. Dried, saturated and submerged resins were studied.

The primary effect of radiolysis on the resin structure was observed to be the formation of sulfuric acid and sulfate salts resulting from radiolytic scission of the cation resins functional group. Anion resin exhibited a release of absorbed water at an absorbed dose of about 5×10^8 rad. This water amounted to 60% of the water absorbed in the resin. Measurements of the pH of this free water on mixed resin were in the 1 to 4 range, depending on the dose and degree of resin depletion.

Acidity was reduced by expending the cation resin as H^+ formed by radiolysis is exchanged with the cations on the undamaged resin.

Gas generation from both sealed and open systems was dominated by hydrogen, with carbon dioxide being second. Radiolysis of absorbed water was identified as the most likely source of hydrogen, as dried resin generated a factor of ten less hydrogen. In sealed systems, oxygen was rapidly depleted from the atmosphere by an efficient radiolytic oxidation reaction.

Hydrogen G-values of 0.13 and 0.16 are reported for cation resin in the hydrogen and sodium form, respectively. For anion resin, 0.62 and 0.34 are reported for hydroxide and chloride form, respectively.

The hydrogen gas G-value for mixed resins was measured at 0.3 to 0.5 depending on the degree of resin depletion. This is comparable to the value for pure water (0.45) and is relatively insensitive to dose rate over the range studied.

34. Swyler, K.J., Dodge, C.J., and Dayal, R., *Assessment of Irradiation Effects in Radwaste Containing Organic Ion Exchange Media*. NUREG/CR-3812, BNL-NUREG-51774, May 1984.

This study investigated the practical consequences of radiation on ion exchange resins and their impact on resin storage and disposal. The primary effect investigated was the corrosion of mild steel in irradiated resins. Radiolytic acid generation was found to be in competition with acid uptake in the corrosion process. Corrosion was found to be most extensive in H^+ form cation resins and decreased notably for depleted cation resins.

For H^+ form cation resins, hydrogen gas generation from the corrosion process far exceeded radiolytic hydrogen formation alone. For other resin forms, since corrosion was not extensive, no apparent effect could be determined.

Study also examined previously reported data from the TMI EPICOR resins. This data and BNL calculations show that a dose of 1.2×10^8 kg-rad being sufficient to remove 7 liters of oxygen from the atmosphere over liner PF-16. Estimated

hydrogen generation rates in liner PF-3 were 9.9 cm³/hr in which the pH was 2.6 to 4.9.

35. Tulupov, P.E., Butaev, A.M., and Greben, V.P., "Effect of Content of Divinylbenzene in KU-2 Cation-Exchange Resin on its Resistance to Irradiation to Water," *Russ. J. Phys. Chem*, 47 (4), 551 (1973).

Sulphonated polystyrene cation-exchange resins with varying divinylbenzene content were irradiated in swollen form with a small excess of water. The primary aqueous radiolysis product was identified as H₂SO₄ for the hydrogen form resins. Gaseous radiolysis products were not determined.

36. Tulupov, P.E., Butaev, A.M., "Role of Water in the Radiolysis of the Sulphonic Acid Groups in the KU-2 Cation Exchanger," *Russ J. Phys. Chem*, 54(12), 1765(1980).

The water content in a sulphonated cation ion exchange resin was varied from fully swollen to dried and the radiolysis products were determined. In the gas phase over dried resin,

hydrogen comprised 49.0% at 1.3×10⁷ rad and only 29% at 3.5×10⁸ rad, with carbon dioxide and monoxide accounting for most of the balance. Similar work by Russian scientists with cation resin in water is reported to have yielded 92.5% hydrogen in the gas phase. Total yield is not reported, however, it is stated that the primary source of hydrogen in swollen resins is through the radiolysis of the absorbed water.

37. Wall, L.A. and Brown, P.W., "Gamma-Irradiation of Polymethyl Methacrylate and Polystyrene," *J. Phys. Chem.* 61(2) p.129 (Feb. 21, 1957).

Disks of polystyrene were irradiated in evacuated sealed tubes and hydrogen gas yields were determined by mass spectroscopy. The source was cobalt-60. Deuterated polystyrene was studied for the effect of isotope substitution. Hydrogen G-values were found to range from 0.0262 to 0.0446, decreasing with deuterium content.

APPENDIX

Example Calculation of the dose required to generate 5% Hydrogen in a cemented drum of organic ion exchange resins.

Assumptions and Data:

Drum Internal Volume = 7.7 ft³
 Drum Fill Factor = 85%
 Density of Waste Form = 87.4 lb/ft³ ..(2)
 G_{H2} = 0.24(2)
 Ideal Gas Law: PV = nRT

$$\text{Volume Available for Hydrogen Gas} = (7.7 \text{ ft}^3) \times (0.15) \times (0.05) \\ = 5.8 \times 10^{-3} \text{ ft}^3$$

$$\text{Molecules of Hydrogen Gas} = N_{\text{H}_2} = \frac{PV}{RT} N_A$$

$$N_{\text{H}_2} = \frac{(1 \text{ atm}) \times (5.8 \times 10^{-3} \text{ ft}^3)}{(0.0029 \frac{\text{atm-ft}^3}{\text{mole-OK}} \times 2980 \text{ K})} \times 6.02 \times 10^{23} \frac{\text{molecules}}{\text{mole}}$$

$$N_{\text{H}_2} = 4.02 \times 10^{22} \text{ molecules H}_2$$

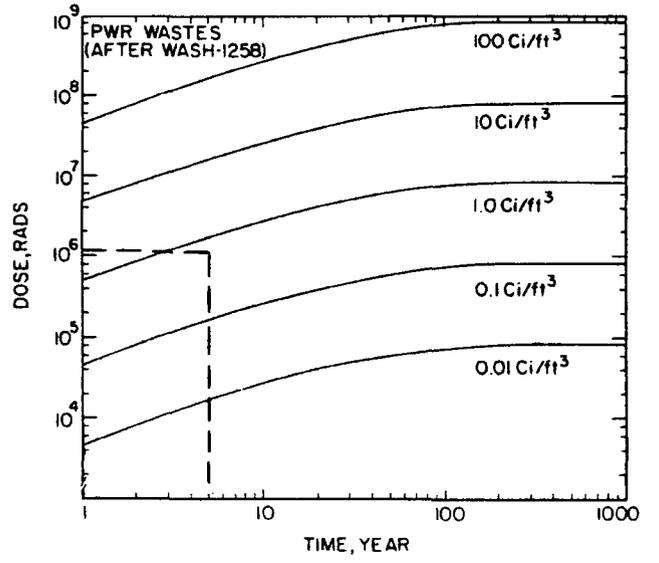
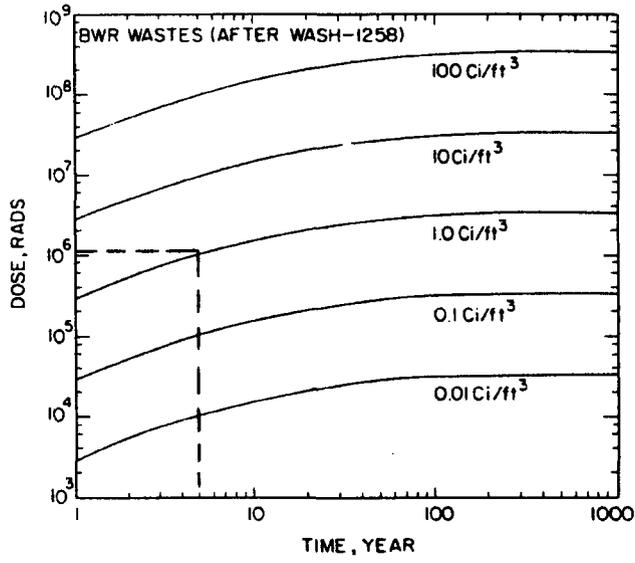
Absorbed Energy Required to form N_{H2} Molecules = E

$$E = \frac{N_{\text{H}_2}}{G_{\text{H}_2}} = \frac{4.02 \times 10^{22} \text{ molecules H}_2}{0.24 \frac{\text{molecules H}_2}{100 \text{ ev}}} = 1.68 \times 10^{25} \text{ eV}$$

Absorbed Dose Required to Deliver Energy E = D

$$D = (1.68 \times 10^{25} \text{ eV}) \times \frac{1 \text{ erg}}{6.241 \times 10^{11} \text{ eV}} \times \frac{1}{2.6 \times 10^5 \text{ g/drum}} \times \frac{1 \text{ rad}}{100 \text{ erg/g}}$$

$$D = 1.03 \times 10^6 \text{ rads}$$



Note: Figures taken from Colombo and Nielson (10)

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