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## **A Literature Review of Radiolytic Gas Generation as a Result of the Decomposition of Sodium Nitrate Wastes**

J. L. Kasten

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ORNL/TM-11632

Chemical Technology Division

**A LITERATURE REVIEW OF RADIOLYTIC GAS GENERATION AS A RESULT OF  
THE DECOMPOSITION OF SODIUM NITRATE WASTES**

J. L. Kasten

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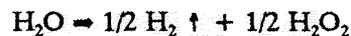
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## EXECUTIVE SUMMARY

Wastes containing radioactivity are capable of generating gases due to radiolytic decomposition of the waste constituents. Wastes destined for final disposal in repositories, such as the proposed Department of Energy (DOE) Waste Isolation Pilot Plant (WIPP), must comply with regulations—including restrictions on gas generation. The radioactive sodium nitrate wastes stored in the Melton Valley Storage Tanks (MVST) at Oak Ridge National Laboratory (ORNL) are an example of such wastes that may eventually be destined for disposal at the WIPP. A literature survey was conducted to determine the chemical reactions and the expected gas generation as a result of the radiolytic decomposition of such wastes.

There are many factors which affect radiolytic decomposition of wastes including the type of radiation and its penetration and absorption characteristics as well as waste properties such as pH, temperature, and chemical species present. The chemical reactions and associated gas generation for a sodium nitrate waste are determined by evaluating experimental studies pertaining to the radiolytic decomposition of water and sodium nitrates.

Basic chemical reactions which are capable of producing a gaseous product are identified from the literature study. The radiolytic decomposition of water is represented by the initial reactions



and



From these reactions, it appears that hydrogen is the gaseous product. The radiolytic decomposition of sodium nitrates is represented by the initial reaction



This reaction suggests that oxygen is the gaseous product generated by radiolytic decomposition of nitrates. The mechanisms of radiolytic decomposition are complex. Besides these initial reactions, back reactions and recombination reactions of the products of decomposition occur.

The gaseous products generated are measured by their G value, which is the expression for radiation chemical yields as molecules of gas formed per 100 eV of absorbed energy. The G values identified in this literature study were measured during experimental studies involving the radiolytic decomposition of water and sodium nitrate. These values can only indicate a range for expected products to be generated as the various types of sodium nitrate wastes have specific characteristics, such as radiation type, pH, temperature, chemical species present, etc., that will affect gas generation due to radiolytic decomposition. Experimental studies on a laboratory scale, as well as a full-scale demonstration, are recommended to determine G values by the actual measurement of the gas generation due to radiolytic decomposition of a specific sodium nitrate waste.

# A LITERATURE REVIEW OF RADIOLYTIC GAS GENERATION AS A RESULT OF THE DECOMPOSITION OF SODIUM NITRATE WASTES

J. L. Kasten

## ABSTRACT

The objective of this literature review is to determine expected chemical reactions and the gas generation associated with radiolytic decomposition of radioactive sodium nitrate wastes such as the wastes stored in the Melton Valley Storage Tanks (MVST) at Oak Ridge National Laboratory (ORNL). The literature survey summarizes expected chemical reactions and identifies the gases expected to be generated as a result of the radiolytic decomposition. The literature survey also identifies G values, which are the expression for radiation chemical yields as molecules of gas formed per 100 eV of absorbed energy, obtained from experimental studies of the radiolytic decomposition of water and sodium nitrate.

## 1. INTRODUCTION

The Department of Energy (DOE) Waste Isolation Pilot Plant (WIPP), located in southeastern New Mexico, is the proposed repository for the permanent disposal of transuranic (TRU) radioactive wastes. The WIPP requirements include compliance with the Environmental Protection Agency (EPA) standards for TRU waste disposal as presented in "Standards for the Management and Disposal of Spent Nuclear Fuel, High Level and Transuranic Radioactive Wastes" contained in the *Code of Federal Regulations* 40 CFR Part 191 (U.S. EPA, 1985). Although at this time EPA standards do not specify a gas generation limit, knowledge of gas generation rates from wastes destined for disposal at WIPP is necessary. A limit of 0.1 to 0.3 mol of gas generated per drum per year has been suggested by Al Lappin of Sandia National Laboratory as an acceptable gas generation rate for the proposed WIPP repository.<sup>1</sup>

The Department of Energy (DOE) has signed an agreement with the state of New Mexico that mandates shipment of TRU wastes in Nuclear Regulatory Commission (NRC) certified

packages. Thus, the NRC requirements on combustible mixtures of gases in shipping containers must be met by DOE in shipping TRU wastes to the WIPP. The requirements are given in the NRC's *Inspection Enforcement Information Notice No. 84-72: Clarification of Conditions for Waste Shipments Subject to Hydrogen Gas Generation* (September 1984). The gas generation in containers of wastes approved for transport may be demonstrated by actual measurement of the gas or by predictions from acceptable calculations.

The radioactive sodium nitrate wastes stored in the Melton Valley Storage Tanks (MVST) at Oak Ridge National Laboratory (ORNL) may eventually be disposed of at the WIPP. Thus, it is necessary to determine the type and amount of gases that may be produced as a result of the radiolytic decomposition of the wastes.

Sodium nitrate wastes containing radioactivity are capable of generating gases due to the radiolytic decomposition of compounds present in the wastes, including water and sodium nitrate. This mechanism for gas generation, called radiolysis, is the chemical dissociation of compounds due to energy from radiation. The nature of the radiolytic decomposition of these compounds is dependent on the waste characteristics (i.e., temperature, pH, chemical species, etc.) as well as the type of radiation. The expression for radiation chemical yields is the G value, which is the number of any species (ion, radical, molecules, etc.,) decomposed, formed, or reacted per 100 eV of absorbed energy. For example, G(X) refers to the number of molecules of product X formed upon irradiation per 100 eV of energy absorbed.

This report presents a literature review of expected chemical reactions and the associated G values recorded in studies pertaining to the radiolytic decomposition of water and sodium nitrates. These G values are necessary in order to perform calculations for gas generation rates as presented in the ORNL report, *Prediction of Hydrogen and Oxygen Generation Rates due to*

*Radiolysis in Solidified Melton Valley Storage Tank (MVST) Waste*, ORNL/TM-11717, by H. W. Godbee, T. C. Wright, and J. L. Kasten (in preparation).

## 2. BACKGROUND

A knowledge of the basic principles regarding energy from radiation will assist in the determination of gas generation due to radiolytic decomposition of waste. The following presents a brief summary of the properties associated with radioactive particles.

### 2.1 RADIATION ENERGY

Chemical decomposition is induced by the absorption of ionizing radiation produced by radioactive nuclei including alpha, beta, and gamma rays. An alpha ray is a stream of alpha particles; a beta ray is a stream of beta particles; and a gamma ray is a photon. Photons, whether emitted from the nucleus (gamma rays) or the shell (X rays) of an atom, have the same effect. Each particle (or photon) can ionize or excite a large number of molecules that are distributed along its path. The energy lost by a radioactive particle in passing through matter produces considerable numbers of ions and excited molecules in its track. The particles are not selective and may react with any molecule lying in their path. The rate of energy loss is generally expressed in terms of the linear energy transfer (LET), which is defined as the linear rate of loss of energy (locally absorbed) by an ionizing particle traversing a material medium.<sup>2</sup> The following charged particles are listed in order of increasing LET values: gamma rays, beta rays, and alpha rays.

The interaction of ionizing radiation can be described as:

1. primary interactions that involve electronic transitions of the molecules producing ions, excited species, radicals, etc. and, in certain circumstances, atom displacements; and

2. secondary interactions that usually involve the reactions of the ions, excited species, radicals, etc., to give the final products. In most cases, only the final (stable) products are actually observed and the nature of the intermediate or primary species, which are the precursors of the final products, is highly speculative.<sup>3</sup>

## 2.2 ALPHA RAYS

Alpha rays are heavy charged particles that are easily absorbed. Alpha particles are the nuclei of helium atoms, that is, helium atoms that have lost both electrons and, hence, have a double positive charge. On passing through matter, alpha particles lose energy principally by inelastic collisions with electrons lying in their path, which leads to excitation and ionization of the atoms and molecules to which these electrons belong. The great difference in mass between the alpha particle and the electron means that the alpha particle loses only a small fraction of its energy and is virtually undeflected by collision. As a consequence, alpha particles are slowed down gradually because of a large number of small energy losses and travel in a nearly straight path. Since each of the alpha particles from a radioactive element have the same energy, they will each have about the same range; the random nature of the collisions gives rise to small variations in the range of individual particles. The extent of the ionization caused by an alpha particle depends on the number of molecules it hits along its path and on the way in which it hits them.<sup>2</sup>

## 2.3 BETA RAYS

Beta particles are negatively charged electrons emitted by radioactive nuclei. In contrast to alpha particles, beta particles from a particular radioactive element are not all emitted with the same energy but with energies ranging from zero up to a maximum value that is characteristic of the element. Beta particles are much more penetrating than alpha particles. The beta particle has a much smaller mass and greater speed than the alpha particle. A beta particle may lose a large fraction of its energy in a single collision with an atomic electron. Beta particles are scattered much more easily by nuclei than are alpha particles, so their paths are usually not straight.<sup>24</sup>

## 2.4 GAMMA RAYS

Gamma radiation is electrically neutral. The gamma rays emitted by radioactive isotopes are either monoenergetic or have a small number of discrete energies. Unlike alpha and beta particles, which usually lose their energies gradually through a number of small energy transfers, gamma rays tend to lose the greater part of their energy through a single interaction.<sup>2</sup> The mechanism of the absorption of gamma rays by matter is different from that of charged particles such as alpha or beta particles. The difference is apparent in the much greater penetrating power of gamma rays, and the characteristic exponential absorption in matter. Gamma rays do not have a definite range as is found for charged particles.<sup>4</sup>

## 2.5 ENERGY PENETRATION CHARACTERISTICS

Positively charged short-range alpha radiation, negatively charged intermediate-range beta radiation, and electrically neutral penetrating gamma radiation are three types of radiation resulting from the decay of radioactive substances. Alpha emission is observed in all nuclides of atomic number greater than 83 that are stable to other modes of decay and in a few lighter nuclides, principally among the rare earth metals. The alpha particles interact very strongly with matter as they penetrate only a few centimeters of air and are stopped by paper-thin films of solid substances. The usual beta radiation can penetrate a millimeter or more of solid matter or about a meter of air, although some of the very low energy beta radiation is no more penetrating than alpha particles. Gamma rays are very penetrating.<sup>4,5</sup>

## 2.6 ENERGY ABSORPTION CHARACTERISTICS

The amount of energy absorbed by a waste as a result of the radioactive decay process is a function of curie loading, waste properties, and container geometry. It is reasonable to assume that the alpha and beta emission energies are absorbed in the waste. This is because of the relatively short travel length, or range, (as compared with gamma rays) required for alpha and beta

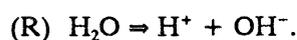
particles to give up their energy in the waste material, and the extremely low probability of such particles escaping the container. The gamma energy absorbed by the waste depends on the strength of the gamma emission, the amount of gamma ray energy absorbed by interaction (collision) with a waste particle, and the number of particles with which the gamma ray interacts. Because an interaction will either absorb or, more likely, attenuate an emission, the fraction of gamma energy absorbed depends on the number of interactions possible. Therefore, gamma energy absorption increases with increasing numbers of waste particles. For this reason, gamma absorption is a function of the contained waste density and geometry.<sup>6</sup>

### 3. RADIOLYTIC DECOMPOSITION OF SODIUM NITRATE WASTES

Chemical effects produced by ionizing radiations are known to depend on the energy and mass of the ionizing particles. Some radioactive materials have complex decay schemes. The decay spectra may include alpha energies, beta energies as well as gamma energies. Complete knowledge of the decay schemes are important for evaluation of the energy generated in the radioactive sources.<sup>5</sup> From the information presented in the literature,<sup>6</sup> the chemical species present in sodium nitrate wastes that are capable of producing gas by radiolytic decomposition include water (generating hydrogen) and nitrates (generating oxygen).

#### 3.1 RADIOLYTIC DECOMPOSITION OF WATER

The radiolysis of water has been studied more thoroughly than any other compound.<sup>7-17</sup> The two initial reactions include the initial formation of product molecules, which is known as the forward reaction (F), and the initial formation of radicals—the radical reaction (R),



Reaction F represents the molecular yield of hydrogen ( $H_2$ ) and hydrogen peroxide ( $H_2O_2$ ), and reaction R represents the radical yield of hydrogen and hydroxide ions ( $H^+$  and  $OH^-$ ).<sup>8,13</sup>

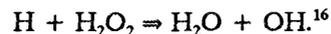
During the early work in radiation chemistry, it was found that pure water sealed in a tube and irradiated with X rays or gamma rays appeared to be quite stable, showing no decomposition. This apparent lack of decomposition of water is now understood to result from the reaction of free radicals,  $H^+$  and  $OH^-$ , with the molecular products,  $H_2$  and  $H_2O_2$ , which leads them to recombine to water. With alpha rays, the number of molecular decomposition products formed is too great to be converted back to water by the relatively small number of free radicals produced. Although oxygen gas is found among the water decomposition products, it seems to be formed not directly from the water but as a result of the action of the radicals on  $H_2O_2$ .<sup>4</sup>

The different yields for water decomposition by different kinds of irradiation may be due to the existence of recombination and back reactions of the products of the decomposition. The recombination of radicals refers to the union of  $H^+$  and  $OH^-$  radicals to yield water. The combination of radicals refers to reactions that do not yield water (e.g.,  $2OH \rightarrow H_2O_2$ ). Back reaction refers to any reaction that causes ultimate conversion of products to water (e.g.,  $OH + H_2 \Rightarrow H_2O + H$ ).<sup>15,16</sup>

In the absence of any solute, the free radicals formed by the decomposition of water will disappear by reaction with one another. For example, if an  $OH^-$  radical reacts with an  $H^+$  atom, water molecules result again; but if an  $H^+$  reacts with another  $H^+$  or an  $OH^-$  with another  $OH^-$ , the new molecules  $H_2$  and  $H_2O_2$  will be produced. These products, hydrogen and hydrogen peroxide, insofar as they stay dissolved in the water, will be able to react with the free radicals,  $H^+$  and  $OH^-$ , formed by the decomposition of further water molecules. The result will be destruction of the products and subsequent formation of water. The most probable equations are:



and



When pure water is irradiated, the products  $\text{H}_2$  and  $\text{H}_2\text{O}_2$  are expected to build up to a steady state concentration at which the rate of back reaction of these products to reform water is equal to the rate of their production from water.<sup>17</sup>

A basic observation in the irradiation of dilute aqueous solutions with light-particle radiation is that the major chemical change occurs in the dissolved material, while the water undergoes little or no decomposition.<sup>14</sup> Since water, as the major component, must have originally absorbed practically all the energy of the radiation, some way must exist for this energy to be funneled into the molecules of dissolved materials. In an early study by Hugo Fricke,<sup>14</sup> this phenomena was explained as the conversion of the water by the radiation to a form called "activated water" which was chemically reactive but stable enough to diffuse through the solution and react with solute molecules. The general opinion today is that this activated water consists of the molecular fragments or free radicals  $\text{H}^+$  and  $\text{OH}^-$  resulting from the break up of water molecules that react with dissolved materials present.<sup>14,16</sup>

Light-particle radiations yield predominately free radicals, whereas heavy-particle radiations yield principally hydrogen and hydrogen peroxide. Heavy-particle radiations lead to extensive decomposition of water while the effect on dissolved solutes is considerably less for a given energy input than with the light-particle types. These molecular decomposition products can also be found to exist with light-particle radiations, although their number is much smaller than the number of free radicals that are produced simultaneously.<sup>14,18</sup>

Although the independent formation of radical and molecular products is sufficient to explain the chemical reactions in irradiated solutions, the difference between the heavy- and light-particle radiations may result from the differing geometrical arrangements in which radicals are

produced. As radicals diffuse randomly, most of them will escape into the solution and react as free radicals with whatever solutes they may find; but a proportion will encounter one another before diffusing from the vicinity. If unlike radicals thus meet, they will recombine to form water, so that their existence will not be evident, but those that meet in like pairs will combine to form the molecules  $H_2$  and  $H_2O_2$ , which are the observed molecular products. The larger the number of radicals in a group, the greater the proportion which will combine instead of escaping into the solution. Hence, as the LET of the radiation increases, the proportion of the radicals produced that combine to the molecular products increases, while the proportion that diffuses into the solution and manifests itself as free radicals decreases.<sup>14</sup>

Larger yields of molecular products are obtained in the radiolysis with radiation of high LET (e.g., alpha particles). These concepts are shown in the comparison of alpha radiolysis with gamma or beta radiolysis. High molecular yields, such as hydrogen, are observed from the alpha radiolysis of pure water giving a  $G(H_2) = 1.2$  molecules/100 eV, while results from gamma radiolysis show a  $G(H_2) = 0.45$  molecules/100 eV. The lower yield from low LET radiation has been ascribed to radiation-induced recombination reactions.<sup>19</sup>

### 3.2 RADIOLYTIC DECOMPOSITION OF NITRATES

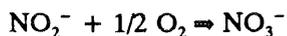
The ease of decomposition of various nitrate crystals is influenced by a number of factors related to the chemical nature and crystal structure of the material. The actual mechanism is probably very complex—possibly involving reactions of several ionic, free radical, and molecular intermediates (which might include  $NO_3$ ,  $NO_2$ , and  $O_2$ ).<sup>20</sup>

Large differences have been reported between the rates of radiation-induced decomposition of solid nitrates.<sup>19-22</sup> Although there have been a number of studies on the irradiation of inorganic nitrates, the decomposition mechanism is still open to question. The chemical effect of irradiation can, however, be summarized by a few general observations.

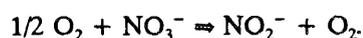
1. The net chemical reaction is



with a significant radiation induced back reaction



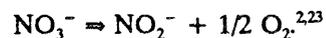
as well as the reaction



2. There is very little, if any, decomposition of the nitrite ion.<sup>19</sup> Thus, assuming the dissociation of the nitrate ions into  $\text{NO}_2^-$  and  $\text{O}^{2-}$ , the  $\text{O}^{2-}$  atom might: recombine with the  $\text{NO}_2^-$  ion produced simultaneously; react with an adjacent  $\text{NO}_3^-$  ion to form  $\text{NO}_2^-$  and  $\text{O}_2$ ; or diffuse through the lattice until it reacts with another O atom,  $\text{NO}_2^-$ , or  $\text{O}_2$ .<sup>20-21</sup>

Covalent bonds present in solids may be broken upon irradiation and bring about chemical changes. Nitrates decompose giving oxygen ( $\text{O}_2$ ) and nitrite ( $\text{NO}_2^-$ ), and it has been demonstrated that the final products are formed in the crystal.<sup>2</sup>

Conflicting results are found in the literature pertaining to the G value for oxygen generated as a result of the radiolytic decomposition of nitrates. Most studies have shown that if the irradiated nitrate is dissolved in water, both of the products can be measured and the ratio of nitrite to oxygen is found to be 2:1, as expected, for



Initial  $G(\text{NO}_2^-)$  values of solid nitrate salts are believed to be dependent on the cation of the salt and the radiolysis temperature. Oxygen production is generally colinear with  $\text{NO}_2^-$  production in the correct stoichiometric ratio.<sup>2,3</sup> The detectable amount of oxygen will decline with respect to  $\text{NO}_2^-$  when reaction of oxygen with metal atoms is favorable.<sup>19</sup>

One study, however, concluded that for irradiated nitrates, oxygen and nitrite were formed in equivalent amounts. Following radiation exposure, sodium nitrate salts evolved a gas that was shown to be mainly oxygen gas trapped in small pockets in the crystal during irradiation. When

irradiated crystals were heated below the melting point, the gas pockets grew and coalesced—this being accompanied by a decrease in crystal density.<sup>22</sup>

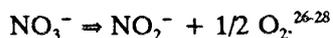
Large differences have been reported between the rates of radiation-induced decomposition of various solid nitrates. While there is general agreement that the primary process is unimolecular dissociation of an  $\text{NO}_3^-$  species producing  $\text{NO}_2^-$  and  $\text{O}_2$ , the varying sensitivities have been attributed to: (1) different polarizing power of the cations, (2) competition between  $\text{NO}_3^-$  ions and oxygen atoms for the oxygen fragments produced, and (3) differences in the closeness of packing of the crystal structures.<sup>24</sup>

The variation in decomposition yield for the potassium, sodium, and barium nitrates must be due to factors related to crystal structure, since the N-O bond strength does not vary appreciably between these compounds. For example, an O atom dissociating from a  $\text{NO}_3^-$  not only requires energy to break the N-O bond but probably needs additional energy to push aside other adjacent ions. Thus, from the densities of potassium nitrate ( $\text{KNO}_3$ ) and sodium nitrate ( $\text{NaNO}_3$ ) and the crystal radii of  $\text{K}^+$  and  $\text{Na}^+$  one finds about 20 percent more space available per nitrate ion in the  $\text{KNO}_3$  than in the  $\text{NaNO}_3$  crystal. The greater space available may partially account for the higher yield in the potassium salt.<sup>22</sup>

Although the concept of free space, which is related to the closeness of packing of the crystal structures, has been used to explain the difference in G values for the decomposition of various inorganic nitrates, there are discrepancies in the concept. Notably, cesium nitrate ( $\text{CsNO}_3$ ) has less free space than  $\text{KNO}_3$ , but the initial yield is appreciably higher.<sup>25</sup>

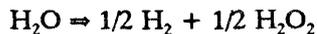
The observed chemical reactions in the radiolysis of aqueous  $\text{NaNO}_3$  solutions indicated that the oxygen came from two sources: (1) the joint participation of  $\text{H}_2\text{O}$  and  $\text{NO}_3^-$  and (2) from the  $\text{NO}_3^-$  alone. The origin of  $\text{O}_2$  formed in alkaline nitrate solutions was determined by irradiations of solutions made from  $^{18}\text{O}$ -enriched water. Experiments with  $^{18}\text{O}$  labelling were

performed at pH 13 to determine the origin of the O<sub>2</sub> produced by radiolysis. The results of these measurements indicate that most O<sub>2</sub> originates from water in dilute solutions, with an increasing fraction originating from nitrate at higher nitrate concentrations. The radiolysis of the nitrate ion in aqueous solutions is consistent with the reaction presented for the radiolysis of solid nitrates

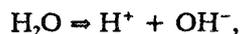


#### 4. RESULTS

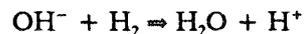
According to the literature, the gases generated as a result of the radiolytic decomposition of water and sodium nitrate will most likely be hydrogen (from water) and oxygen (from sodium nitrate). The basic initial chemical reactions due to the radiolytic decomposition of water include



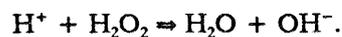
and



with the following probable back reactions:



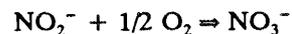
and



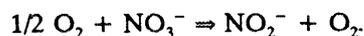
The reaction for the decomposition of nitrate is given by



with a significant radiation induced back reaction given by



as well as the combination reaction



From these equations, as well as other probable equations representing recombination and back reactions of the products of decompositions, it is apparent that the gases expected to be generated as a result of the radiolytic decomposition of sodium nitrate wastes include hydrogen and oxygen. The literature review gives insight to chemical reactions expected in the radiolytic decomposition of water (generating hydrogen) and nitrates (generating oxygen). Tables 1 and 2 present experimentally obtained G values given in the literature associated with the radiolytic decomposition of water and sodium nitrates, respectively.

## 5. SUMMARY

Basic principles that apply to the decomposition of water have been presented, although the actual mechanisms of radiolytic decomposition are complicated and not easily ascertained. Studies indicate that four main factors affect the decomposition of water:

1. The decomposition of water by radiation is dependent on the impurities present. The presence of other elements affects the combination of the free radicals and molecular products.
2. The amount of decomposition is a function of free volume above the water. The irradiation of water enclosed with a large free volume in a vacuum system resulted in large yields of hydrogen as opposed to small yields of hydrogen from the irradiation of water enclosed with a small free volume in a pressurized system.
3. A reduction in LET results in a shift in the equilibrium toward a greater recombination of products in the gas phase. Conversely, the yield of molecular products increases relative to the free radical yield at higher LET. Values for the radical and molecular products from water in alpha radiolysis differ by factors ranging from 3 to 5 from those in gamma radiolysis.

Table 1. G values for the generation of hydrogen, G(H<sub>2</sub>), due to the radiolytic decomposition of water<sup>a</sup>

Source	Original author	Molecules of H <sub>2</sub> generated per 100 eV of radiation energy absorbed		
		Alpha	Beta	Gamma
H. A. Dewhurst, A. H. Samuel, J. L. Magee, <i>Radiat. Res.</i> 1, 62 (1954)	W. Duene, O. Scheuer, <i>Le Radium</i> 10, 33 (1913)	4.6		
H. A. Dewhurst, A. H. Samuel, J. L. Magee, <i>Radiat. Res.</i> 1, 62 (1954)	C. Nurnberger, <i>J. Phys. Chem.</i> 38, 47 (1934)	4.4		
H. A. Dewhurst, A. H. Samuel, J. L. Magee, <i>Radiat. Res.</i> 1, 62 (1954)	M. Lefort, <i>Chim. Phys.</i> 48, 339 (1951)	3.6		
H. A. Dewhurst, A. H. Samuel, J. L. Magee, <i>Radiat. Res.</i> 1, 62 (1954)	E. J. Hart, <i>J. Phys. Chem.</i> 56, 594 (1952)		1.0	
A. O. Allen, <i>Radiat. Res.</i> 1, 85 (1954)	Same as source	1.8		0.6
N. F. Barr, A. O. Allen, <i>J. Phys. Chem.</i> 63, 928 (1959)	Same as source			0.45
P. V. Phung, Milton Burton, <i>Radiat. Res.</i> 7, 199 (1957)	Same as source			0.41 ± 0.01
P. V. Phung, Milton Burton, <i>Radiat. Res.</i> 7, 199 (1957)	A. O. Allen, <i>Int. Conf. Peaceful Uses of Atomic Energy</i> 7, 514 (1956)			0.45
P. V. Phung, Milton Burton, <i>Radiat. Res.</i> 7, 199 (1957)	J. A. Ghormley, C. J. Hochandel, <i>J. Am. Chem. Soc.</i> 76, 3351 (1954)			0.41
J. W. T. Spinks, R. J. Woods, <i>Introduction to Radiation Chemistry</i> (1964)	C. J. Hochandel, S. C. Lind, <i>Ann. Rev. Phys. Chem.</i> 7, 83 (1956)			0.40 <sup>b</sup>
J. W. T. Spinks, R. J. Woods, <i>Introduction to Radiation Chemistry</i> (1964)	M. Lefort, X. Tarrago, <i>J. Phys. Chem.</i> 63, 833 (1959)	1.57 <sup>b</sup>		

Table 1 (continued)

Source	Original author	Molecules of H <sub>2</sub> generated per 100 eV of radiation energy absorbed		
		Alpha	Beta	Gamma
J. W. T. Spinks, R. J. Woods, <i>Introduction to Radiation Chemistry</i> (1964)	E. Collinson, F. S. Dainton, J. Kroh, <i>Nature</i> <b>187</b> , 475 (1960)		0.60 <sup>c</sup>	
J. W. T. Spinks, R. J. Woods, <i>Introduction to Radiation Chemistry</i> (1964)	J. Ralani, G. Stein, <i>J. Chem. Phys.</i> <b>37</b> , 1865 (1962)			0.50 <sup>d</sup>
J. W. T. Spinks, R. J. Woods, <i>Introduction to Radiation Chemistry</i> (1964)	J. H. Baxendale, G. K. Thomas, T. Woodward, reported by M. S. Matheson, <i>Ann. Rev. Phys. Chem.</i> <b>13</b> , 77 (1962)			0.55, <sup>c</sup> 0.60, <sup>f</sup> 0.70 <sup>g</sup>
J. W. T. Spinks, R. J. Woods, <i>Introduction to Radiation Chemistry</i> (1964)	A. O. Allen, H. A. Schwarz, <i>Proc. 2nd Intern. Conf. Peaceful Uses Atomic Energy</i> , UN, Geneva, <b>29</b> , 30 (1958)			0.42
F. S. Dainton, W. S. Watt, <i>Nature</i> <b>195</b> , 1294 (1962)	Same as source			0.45
A. O. Allen, <i>J. Phys. &amp; Colloid Chem.</i> , <b>52</b> , 479 (1948)	Same as source	2.0		
P. Offermann, <i>Scientific Basis for Nuclear Waste Management XII</i> , <b>127</b> , 461 (1989)	Same as source	1.3	0.45, 0.425 <sup>h</sup>	0.45, 0.425 <sup>h</sup>
E. J. Hart, <i>Radiat. Res.</i> <b>1</b> , 53 (1954)	Same as source	1.57	0.51	0.44

<sup>a</sup>The G(H<sub>2</sub>) value is determined from water with a pH of 7 unless otherwise noted.

<sup>b</sup>The water has a pH of 0.5.

<sup>c</sup>The water has a pH of 1.

<sup>d</sup>The water has a pH of 2-4.

<sup>e</sup>The water has a pH of 5.

<sup>f</sup>The water has a pH of 8.

<sup>g</sup>The water has a pH of 13.

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Table 2. G values for the generation of oxygen, G(O<sub>2</sub>), due to the radiolytic decomposition of sodium nitrate

Source (original author)	System	Molecules of O <sub>2</sub> generated per 100 eV of radiation energy absorbed	
		Alpha	Gamma
C. J. Hochandel, T. W. Davis, <i>J. Chem. Phys.</i> 27, 333 (1957)	Solid sodium nitrate crystals		0.12 ± 0.02 <sup>a</sup>
C. J. Hochandel, <i>Radiat. Res.</i> 16, 286 (1962)	Solid sodium nitrate crystals	0.65 <sup>a,b</sup> 0.55 <sup>a,d</sup>	0.135 <sup>a,c</sup> 0.5 <sup>a,e</sup>
G. Hennig, R. Lees, M. S. Matheson, <i>J. Chem. Phys.</i> 21, 664 (1953)	Solid sodium nitrate crystals		0.3 <sup>f</sup>
H. A. Mahlman, <i>J. Phys. Chem.</i> 67, 1466 (1963)	Aqueous sodium nitrate solutions		
	1.0 M NaNO <sub>3</sub>		0.09, <sup>g</sup> 0.20 <sup>h</sup>
	2.0 M NaNO <sub>3</sub>		0.18, <sup>g</sup> 0.31 <sup>h</sup>
	3.0 M NaNO <sub>3</sub>		0.25, <sup>g</sup> 0.42 <sup>h</sup>
	4.0 M NaNO <sub>3</sub>		0.30, <sup>g</sup> 0.50 <sup>h</sup>
	5.0 M NaNO <sub>3</sub>		0.36, <sup>g</sup> 0.56 <sup>h</sup>
	6.0 M NaNO <sub>3</sub>		0.43, <sup>g</sup> 0.63 <sup>h</sup>
M. L. Hyder, <i>J. Phys. Chem.</i> 69, 1858 (1965)	Aqueous sodium nitrate solutions		
	0.12 M NaNO <sub>3</sub>		0.06, <sup>g</sup> 2.0 <sup>h</sup>
	0.50 M NaNO <sub>3</sub>		0.21, <sup>g</sup> 2.35 <sup>h</sup>
	1.0 M NaNO <sub>3</sub>		0.38, <sup>g</sup> 2.40 <sup>h</sup>
	2.5 M NaNO <sub>3</sub>		0.70, <sup>g</sup> 2.35 <sup>h</sup>
	4.0 M NaNO <sub>3</sub>		0.90, <sup>g</sup> 2.30 <sup>h</sup>

<sup>a</sup>The G(NO<sub>2</sub>) value is given in the source; the G(O<sub>2</sub>) value is determined from the reaction NO<sub>3</sub><sup>-</sup> → NO<sub>2</sub><sup>-</sup> + 1/2 O<sub>2</sub> where the ratio of nitrite to oxygen is 2:1.

<sup>b</sup>Temperature of 25°C.

<sup>c</sup>Temperature of 30°C.

<sup>d</sup>Temperature of 120°C.

<sup>e</sup>Temperature of 150°C.

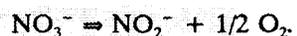
<sup>f</sup>The oxygen gas was measured in the sodium nitrate crystals.

<sup>g</sup>The value for G(O<sub>2</sub>) is believed to be due to the radiolytic decomposition of the nitrate ions.

<sup>h</sup>The value for G(O<sub>2</sub>) is believed to be due to the radiolytic decomposition of the combination of the water and the nitrate ions.

4. Water decomposition is a function of pH. It has been observed that the radical yields ( $H^+$  and  $OH^-$ ) from the decomposition of water due to ionizing radiations on aqueous solutions are markedly influenced by changes in pH. For the molecular yield of  $H_2$ ; however, the  $G(H_2)$  value remains constant despite changes in the pH.<sup>14,18-19,29-31</sup>

Most experimental evidence for the radiolysis of solid nitrates as well as aqueous nitrate solutions indicates that the G value,  $G(NO_2^-)$ , for the nitrate ion is equal to twice that for  $G(O_2)$  substantiating the stoichiometry indicated by the reaction



It has been concluded that  $O_2$  is produced by a direct effect on the radiolysis of  $NO_3^-$  in alpha radiolysis as in gamma radiolysis for solid nitrates only.<sup>29</sup>

Although the radiolysis of solid nitrates is complex, possible mechanisms of decomposition of nitrate crystals have been observed.

1. The nitrite and oxygen are produced in the solid and most of the oxygen is retained by the crystals at room temperature. Sodium nitrate must be heated to near melting in order to release all its oxygen. Both the initial yields and the steady-state concentrations increase with increased temperature for decomposition by gamma rays. A 50% increase in the G values resulting from the decomposition of  $NaNO_3$  was observed when the temperature was increased from 25 to 60°C.<sup>32</sup> The influences of increased temperature may be due to the loosening of the lattice structure or supplying activation energy for various processes. For irradiation by alpha particles, however, the yield of  $NaNO_3$  actually decreased slightly with increased temperature.

2. Yields generally decrease with increased dose of radioactivity, suggesting an approach to steady state; however, the decrease in yield may merely result from loss of energy to product molecules.

3. There is an effect of LET both on the initial yield and also apparently on steady states. The initial yield for  $\text{NaNO}_3$  has been observed to be about five times as great for alpha irradiation as for gamma irradiation at room temperature.<sup>20</sup>

## 6. RECOMMENDATIONS

Radiological, physical, and chemical conditions each play a role in radiolytic gas generation from wastes. The characterization of the waste composition must be complete to determine defensible gas generation rates. The radionuclides plus the daughters, if present, must be considered, and knowledge to ascertain the stage of decay of the waste is necessary. Unless it can be conclusively proven that the daughters of a radionuclide are not present (either by analyses or knowledge of the complete history of the waste) the daughters should be included so that gas generation results are conservative (i.e., the gas generation is at a maximum). The capabilities of the wastes to absorb radiation energy influences the decomposition of the waste constituents. Chemical reactions such as recombination and back reactions affect the amount of gas generated due to radiolytic decomposition.

The G values associated with radiolytic decomposition indicating molecules of gas generated by waste constituents per 100 eV absorbed by the waste constituents is complex. The G values obtained from literature can only indicate a range for expected G values due to radiolytic decomposition of a sodium nitrate waste since there are many waste-specific factors that influence gas generation rates. Experimental studies are recommended where the G values are obtained by the actual measurement of the gas generation.

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