Sandia National Laboratories

Operated for the United States Department of Energy
by National Technology and Engineering Solutions
of Sandia, LLC.

Carlsbad, NM 88220

*date:* February 12, 2019

*to:* Records Center

*from:* Brad Day

*reviewed by:* Daniel Clayton, Jay Jang

*subject:* Reassessment of Need and Parameter Justification for Modeling Gas Generation due to Radiolysis of Brine and Cellulose/Plastic/Rubber in WIPP for CRA-2019

## Executive Summary

Gas generation due to radiolysis of brine from radionuclides in solution and in wetted-solid form is to be "screened-in" for CRA-2019. Due to the potential for radiolytic brine gas generation to be a significant gas generation source and to impact repository pressure and brine saturation conditions, it is to be modeled within BRAGFLO utilizing the parameters justified herein. Gas generation due to radiolysis of cellulose, plastics, and rubber (CPR) is to be "screened-out" for the Compliance Recertification Application 2019 (CRA-2019) as not having a significant impact on the performance of the repository due to matrix depletion.

## Introduction

For each Performance Assessment (PA) calculation since the 1996 Compliance Certification Application, gas generation due to radiolysis of both brine and cellulose has been eliminated (or screened-out) as part of the "features, events, or processes" (FEPs) analysis of the performance of the WIPP repository. Although radiolysis was acknowledged as a legitimate chemical process that could generate gas, gas generation from radiolysis was screened based on low consequence to the performance of the disposal system because the estimated quantities of radiolytic gas generation were considered small in comparison to gas generation from iron corrosion and microbial degradation (Molecke 1979).

One issue with the previous estimate of gas generation due to brine radiolysis is that only the disintegration energy from alpha-emitting radionuclides in solution was considered; the effect of brine radiolysis from wetted-solid radionuclides was ignored. Due to the particle size distribution of alpha-emitting radionuclides in the WIPP inventory, some portion of the disintegration energy from the solid particles could be released (i.e., not be self-absorbed) and thus is available to radiolytically decompose brine in contact with the solid. This represents a potential non-conservatism that should be considered.

Microbial degradation and iron corrosion gas generation rates have been subject to revision over time and the rates have generally been reduced such that a revised comparative evaluation is needed along with the need to consider the impact of other hydrogen-bearing compounds in the waste inventory that could be subject to radiolytic decay. The matrix depletion characteristics of CPR in the waste matrix subject to radiolytic decomposition (see Cellulose/Plastic/Rubber section below) should be considered in assessing the relative importance of CPR radiolysis to other gas generation sources.

Due to the interplay between gas generation, pore-pressure, and brine saturation in the waste areas of the repository, an assessment of the relative importance of gas generation sources on repository performance is not readily ascertained. Furthermore, the cumulative gas generation from each source depends on the transient repository inventory and brine saturation conditions (i.e., biodegradation = $f$(CPR mass, brine saturation), corrosion = $f$(Fe mass, brine saturation), and radiolysis = $f$(CPR mass, brine saturation,

radionuclide mobilization potential, and alpha-emitting radionuclide activity)). In some cases, a screening method for insignificant gas contributors may be applied. An assessment of the relative importance of each gas generation source can be more readily established by modeling the repository to determine the brine and gas flows with all relevant, participating gas generation sources.

## Brine Radiolysis

Ionizing radiation affects the chemistry of aqueous solutions through generation of free radical, ionic, and molecular products. The principal radiolytic products in pure water or dilute aqueous solutions are listed in Table 1 (Gray 1984). Their production rates are known as G-values which are defined as the number of a given species produced per 100 eV of absorbed energy. G-values depend on the type and energy of radiation; typical values for gamma radiation from a cobalt-60 source and for approximately 5 MeV alpha radiation are also given in Table 1.

**Table 1 – Primary Products in Irradiated Water (Gray 1984)**

| | G-Values (molecules per 100 eV) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $H_2$ | H | $e^-_{aq}$ | $H_2O_2$ | OH | $HO_2$ | $H^+$ |
| Gamma | 0.43 | 0.61 | 2.7 | 0.61 | 2.86 | 0.03 | 2.7 |
| Alpha | 1.4 | 0.30 | 0.30 | 1.3 | 0.50 | 0.10 | 0.30 |

Equilibrium concentrations of these primary products in pure water are very small because a host of reactions have the net effect of regenerating the water. However, the only species that reacts with the $H_2$ molecule is the OH radical. Thus, if some scavenger species that compete with $H_2$ for the OH radical are present in the water (e.g., $Cl^-$ or $Br^-$), the concentration of $H_2$ in the water will increase as will the resulting pressure of $H_2$ in the gas phase. Oxygen gas is also generated by irradiation of salt brines via secondary reactions among the principal radiolytic products and species present in the brine.

The $G(H_2)$ for water strongly depends on linear energy transfer (LET), increasing by a factor of 3-4 from gamma radiolysis to alpha radiolysis. LET is the rate of energy loss by an ionizing particle traveling through a material, where $E$ is energy (MeV) and $x$ is the distance traveled (μm) as follows:

$$LET = -\frac{dE}{dx} \quad \left(\frac{\text{MeV}}{\mu\text{m}}\right) \tag{1}$$

The lower $G(H_2)$ for gamma radiation along with the relatively low gamma radiation field predominant in WIPP (e.g., contact-handled container dose rates less than 200 mrem/hr) support consideration of only the alpha radiation in radiolytic gas generation evaluations affecting PA.

Reed et al. (Reed et al. 1993) conducted WIPP-relevant radiolytic gas generation experiments lasting between 155 and 182 days. These experiments involved both synthetic Salado and Castile formation brines (ERDA-6 and Brine A) as well as real brines (DH-36 and G8-B) sampled from the Salado in the repository workings. The brines were spiked with $^{239}Pu(VI)$ at concentrations between $6.9 \times 10^{-9}$ and $3.4 \times 10^{-4}$ molal. During these relatively short-term experiments, hydrogen gas was observed as the product of radiolysis. Oxygen gas was not observed; this was attributed to the formation of intermediate oxygen-bearing species that could, given sufficient exposure to alpha-emissions, produce oxygen. However, the secondary production of oxygen in WIPP is not considered a viable long-term contributor to gas production due to its reaction with the significant quantity of metals present in the WIPP waste inventory. This assertion supports consideration of only the production of hydrogen gas in radiolytic gas generation evaluations affecting PA (i.e., one mole of gas produced for each net mole of water consumed). The WIPP-relevant $G(H_2)$ values experimentally determined by Reed et al. are summarized in Table 2.

**Table 2 – "Best Value" $H_2$ Yields in WIPP Brines (Reed 1993)**

| WIPP Brine | G-Values (molecules per 100 eV) |
|---|---|
| Brine A | 1.4 ± 0.1 |
| ERDA-6 | 0.9 ± 0.2 |
| DH-36 | 1.3 ± 0.1 |
| G8-B (GSEEP) | 1.3 ± 0.1 |

The $G(H_2)$ values shown in Table 2 were experimentally determined with $^{239}Pu$ in solution such that effectively all the alpha disintegration energy associated with the Pu contributed to the dissociation of water and $H_2$ production. In WIPP, the inventory of alpha-emitting radionuclides is sufficiently large, and the solubility coefficients and brine volumes are sufficiently small, such that only a small fraction of the total alpha-emitting inventory can be dissolved. Although not dissolved, the remaining solid alpha-emitting radionuclide inventory in close-proximity to brine can also contribute to radiolytic gas generation. Only a portion of the disintegration energy associated with wetted-solid alpha-emitting radionuclides in the inventory will contribute to radiolytic $H_2$ generation due to several factors.

The BRAGG curve provided in Figure 1 gives LET for $PuO_2$ as a function of alpha particle energy (DOE 2012). The fraction of alpha disintegration energy escaping from a spherical particle of $PuO_2$ of various diameters has been determined as shown in Figure 2 (DOE 2012). Particles with diameters greater than 20 μm release less than half of their disintegration energy while larger (>100 μm) particles release less than 10%. In addition to this particle-size dependence, the proximity of the radionuclide particle to brine and other attenuating substrates can also affect the quantity of released disintegration energy that contributes to radiolytic gas generation. For example, small non-spherical particles (< 5 μm) that have negligible self-attenuation, but are adhered/embedded to attenuating substrates on one side and in close-proximity to brine on the other, can contribute no more than 50% of the disintegration energy that exits the particle simply due to geometric considerations.

A detailed understanding of the overall distribution of alpha-emitting radionuclide particle size in the WIPP waste inventory is largely unknown. However, the majority of WIPP alpha-emitting inventory disintegration energy is attributed to $^{239}Pu$ from plutonium processes utilized throughout the DOE complex. Nalesky et al. (2012) evaluated $PuO_2$ particle size distributions in representative samples generated by various processes at Rocky Flats, Hanford, and Los Alamos. Results from of the Materials Identification and Surveillance (MIS) Program at LANL confirms the wide range of plutonium particle sizes produced by aqueous processing, metal oxidation, mixed actinide operations, molten salt operations, and other miscellaneous processes. The mean particle size over all processes and samples ranged from 3.60 to 79.6 μm and averaged 20.5 μm. Based on the energy release results provided in Figure 2, the average $PuO_2$ particle size would release 45% of its disintegration energy with the remainder being self-attenuated within the particle itself.

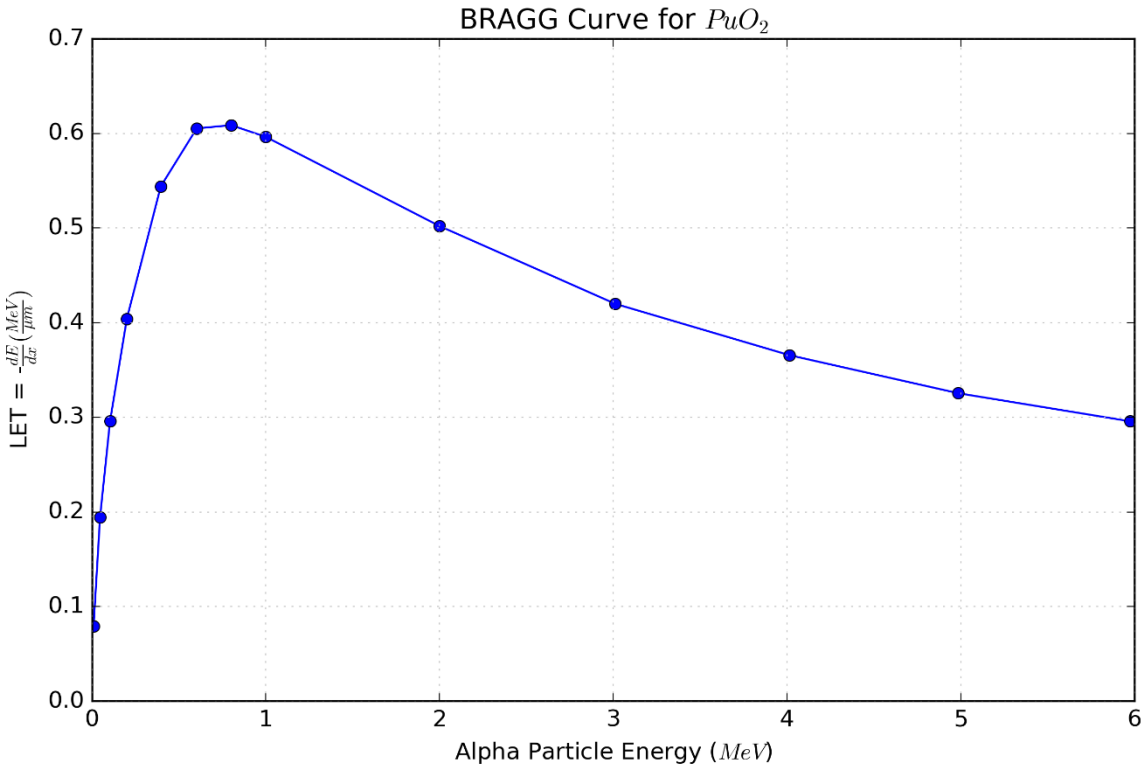



**Figure 1 – Estimated BRAGG Curve for $PuO_2$**

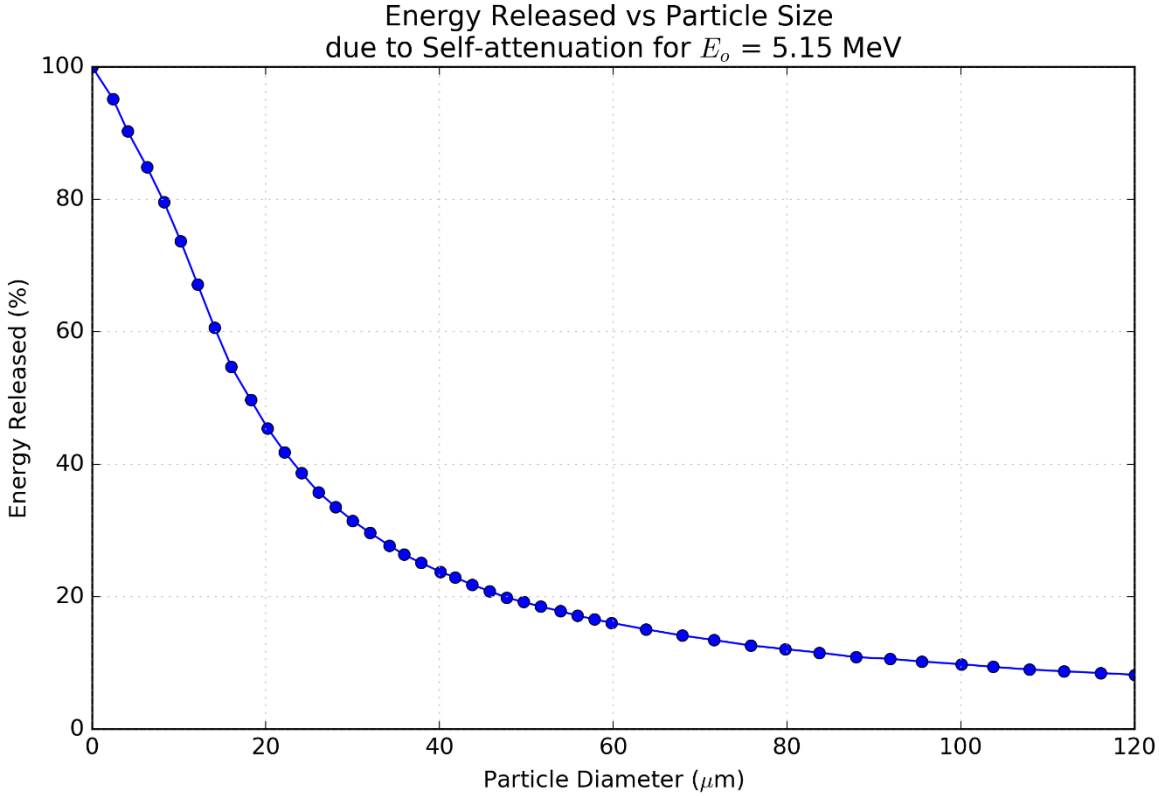



**Figure 2 – Fractional Energy vs Particle Diameter for $PuO_2$**

Consideration of the above leads to the following implementation that quantifies the rate of hydrogen gas generation due to radiolytic decomposition of brine in WIPP from radionuclides in solution and a fractional contribution from the wetted solid form of the radionuclides.

*Brine Radiolysis Implementation*

The total quantity of each radionuclide resulting from radionuclide decay, $M(t)$ [mol], is a function of the radionuclide radioactive decay constant, $\lambda$ [1/s], the initial inventory equally distributed in the waste material, $M_o$ [mol], and the elapsed time, $t$ [s], for which the amount of decay is determined, where the radionuclide decay constant, $\lambda$, is a function of the radionuclide half-life, $T_{1/2}$ [s], as follows:

$$\lambda = \left( \frac{\ln(2)}{T_{1/2}} \right) \tag{2}$$

$$M(t) = M_o \times e^{-\lambda t} \tag{3}$$

A closed-form analytical solution of the Bateman (1910) equations is implemented to determine the decay and ingrowth for radionuclides and their associated daughters.

The total radiolytic $H_2$ generation rate (and brine consumption rate) is due to contributions from one or more decaying radionuclides in the waste volume. The amount of each radionuclide contributing to radiolysis is from the amount of each radionuclide in solution and the remaining amount of each radionuclide in solid form that is wetted by brine. The radionuclide mobilization potential, $S_{sol}$ [mol/m$^3$], is defined on an elemental basis such that the calculation of the quantity of dissolved and sorbed (onto suspended colloids) radionuclides, $M(t)_{sol}$ [mol] is a function of the brine volume, i.e., waste volume, $V_{waste}$ [m$^3$], the porosity of the waste, $\phi$, and the brine saturation of the waste, $S_w$.

$$M(t)_{sol,i} = V_{waste} \times \phi \times S_w \times S_{sol,i} \times mf_i \tag{4}$$

The mole fraction of that radionuclide with respect to other radionuclides of the same element, $mf$, is:

$$mf_i = \frac{M(t)_i}{\sum_{j=1}^{n} M(t)_j}, \tag{5}$$

where

$i$ = index of radionuclides in the inventory

$j$ = index of radionuclides of an element in the inventory

$n$ = total number of radionuclides of an element in the inventory

In cases where the quantity of radionuclides in solution that are determined in equation (3) is limited by the quantity of radionuclides in the total inventory, the quantity of radionuclides in solution is set equal to the quantity of radionuclides in the total inventory.

The quantity of wetted solid radionuclides, $M(t)_{wet}$ [mol], is the difference between the total inventory and the inventory in solution multiplied by the brine saturation as follows:

$$M(t)_{wet,i} = \left( M(t)_i - M(t)_{sol,i} \right) \times S_w \tag{6}$$

The hydrogen generation rate, $R_{H2}$ [mol/sec], due to brine radiolysis from radionuclides in solution and due to a fractional contribution from the wetted solid form of the radionuclides is defined as follows:

$$R_{H_2,i} = \left( M(t)_{sol,i} + M(t)_{wet,i} \times P_{dep} \right) \left( \lambda_i \times E_{dis,i} \times G(H_2)_{avg} \right) \quad (7)$$

where

$P_{dep}$ = energy deposition probability for wetted solids (GDEPFAC)

$E_{dis,i}$ = disintegration energy of radionuclide [eV], *i* (DECAYNRG)
*(note that the disintegration energy is specified in units of MeV and BRAGFLO converts from MeV to eV internally)*

$G(H_2)_{avg}$ = average "G" value for $H_2$ [molecule/eV] (GH2AVG)

When radiolysis dissociates water into $H_2$, and ultimately through secondary reactions to $O_2$, the $O_2$ can be treated (through a stoichiometric coefficient) as an additional contributor by assuming that the $O_2$ is inert (SRADO2 = 0.5) or ignored (SRADO2 = 0.0) by assuming that the $O_2$ instantaneously reacts with other materials.

*Brine Radiolysis Parameters*

Radionuclide properties such as half-life and atomic weight are reference constants that have previously been established as PA analysis parameters. Methodologies for establishment of inventory-specific PA parameters such as inventory activity and element solubility and mobilization potential have been previously established. Updated parameters will be calculated and implemented in support of the CRA-2019 PA. Implementation of gas generation due to radiolysis of brine in BRAGFLO necessitates the creation of new PA parameters that are defined via the rationale summarized in Table 3.

## Table 3 – New PA Parameters for Brine Radiolysis

| Parameter (MATERIAL:PROPERTY) | Description | Distribution Type:Value (Units) | Justification Summary |
|---|---|---|---|
| GLOBAL:GH2AVG | Average G-value for $H_2$ | Constant: 0.014 (molecule/eV) | Based on the selection of the largest nominal value associated with WIPP-relevant brine radiolysis experiments (Reed et al. 1993) |
| *RADIONUCLIDE*:DECAYNRG | Radionuclide disintegration energy | Constant: Various (MeV) | Conservative adoption of the Total Emitted Energy from Annex A. Radionuclides of the ICRP-07 Collection (ICRP 2008)<br>Note: *RADIONUCLIDE* represents a list of radionuclide material names (e.g. AM241, PU238, PU239, PU240, PU242). |
| GLOBAL:GDEPFAC | Energy deposition probability for wetted solid radionuclides | Uniform: 0 to 0.5 (dimensionless) | Selection of a uniform sample distribution from 0 to 0.5 accounts for the uncertainty in the actual probability for wetted solid radionuclides to contribute to radiolytic gas generation. Through use of this distribution of sampled values, the upper bound of 50% energy deposition accommodates the minimum energy self-attenuation that would be expected over the entire inventory based primarily on a particle size distribution average that is derived from the particle size distribution average of multiple representative plutonium processes utilized in the DOE complex (Narlesky et al. 2012). The upper bound of 50% energy deposition also accommodates the potential for a repository waste inventory particle size average being less than the DOE process average due to other sources of energy attenuation discussed below. A lower bound of 0% accommodates the extreme of full energy attenuation resulting from a combination of conditions such as the particle size based self-attenuation combined with additional attenuation due to adherence to and coating by non-hydrogenous materials. Additionally, a lower bound of 0% guards against over-estimation of the energy contribution to radiolysis associated with the wetted solid radionuclides. A lower bound on the distribution greater than 0% may increase radiolytic gas generation, but in a full PA context would also increase brine consumption, lower brine saturations, and potentially under predict direct brine releases that require a minimum quantity of brine to occur. In general, a uniform distribution of sampled values is appropriate because there is no additional information that would support a skewed (e.g., log uniform) distribution. |
| GLOBAL:SRADO2 | Stoichiometric coefficient for $O_2$ from radiolysis | Constant: 0 (mol $O_2$/mol $H_2$) | Based on the assertion that any $O_2$ generated by secondary radiolytic reactions will quickly react with metals in the waste and not contribute to long-term gas generation within the repository. |

## Cellulose/Plastic/Rubber Radiolysis

The basis for screening radiolytic gas generation of cellulose is reevaluated to consider the radiolytic gas generation from the waste constituents cellulose, plastic, and rubber. Microbial degradation and radiolytic decomposition processes can each contribute to depletion of the single solid hydrogenous waste matrix material source term. Currently, with only microbial degradation processes modeled, not every realization in PA results in complete degradation of CPR due to microbes. Therefore, additional gas generation from radiolysis of CPR could potentially be achieved for some realizations if sufficient radiolysis of CPR were to occur over time.

The short range of alpha-particles contributes to an attribute of radiolytic decomposition in a solid waste matrix that is typically not considered. Radiolytic hydrogen gas generation rates reach a plateau and then monotonically decrease over time in direct proportion to cumulative dose deposited from alpha sources. This effect known as "matrix depletion" occurs in the solid waste matrix because the radiolytic sources are generally spatially fixed with respect to the surrounding hydrogen-bearing material. Over time, as surrounding hydrogen bonds are broken, less hydrogen-bearing material is exposed to each short-range alpha-emitting source in the waste matrix and the probability of breaking additional bonds decreases. This decline in hydrogen generation rate is not significantly dependent upon the radioactive lifetime of the source. The matrix depletion effect is more a measure of the homogeneity of mixing the radioactive source material within the hydrogenous solid matrix than of the specific radioactivity of the source (INEEL 1990).

In the case of transuranic (TRU) waste destined for disposal in WIPP, the dominant source of radiation is plutonium. Because there is relatively little physical movement capable of exposing ionizing particles within in the WIPP solid waste matrix to new hydrogen atoms, radiolytic decomposition of the solid waste matrix will ultimately cease due to matrix depletion. It is acknowledged that some differential movement is possible through the creep-closure processes that will consolidate waste within the repository, but experiments evaluating the effects of vibration and settling of contents within transuranic waste containers have concluded that there was no appreciable change in depleted radiolytic gas generation rates due to transportation-driven consolidation processes (Zerwekh 1993).

Considering the 10,000 yr regulatory lifetime of the WIPP repository, it is appropriate to conclude that depletion of the solid CPR waste matrix ensures that radiolytic gas generation from CPR is insignificant in comparison to that already considered due to other gas generation sources. This conclusion is based on extrapolation of G(gas) values for cellulose and cellulose, plastic, and rubber TRU waste mixtures that were experimentally-determined for elapsed times up to 4.9 yr (Zerwekh 1979). Utilizing the curve-fit equations provided in Figure 20 – Figure 28 of Zerwekh, the average G(gas) value for all waste matrices at 100 yr is less than 1% of the initial average G(gas) value as summarized/reproduced in Table 4 and Figure 3.

Therefore, the potential for radiolytic gas generation from CPR for 99% of the repository regulatory timeframe would be associated with a $G(H_2)$ value that is less than 1% of the initial $G(H_2)$ value. When this data is considered along with the fact that other degradation sources will be competing for the solid CPR waste matrix (i.e., microbial degradation) and the age of many legacy TRU waste payload containers at the time of WIPP closure will already be a considerable fraction of the 100 yr used as the depletion benchmark, radiolytic gas generation of CPR is concluded to be an insignificant contributor to total gas generation within WIPP. As such, radiolysis of CPR is to be "screened-out" for CRA-2019 as not having a significant impact on the performance of the repository.

**Table 4 – Matrix Depletion for CPR**

| Elapsed Time | | Test Cylinder and Contents | | | | | G(gas) | $G(gas)/G_o(gas)$ |
|---|---|---|---|---|---|---|---|---|
| Years | Days | Cyl 22 - cellulosics | Cyl 1 - cellulosics | Cyl 26 - cellulosics | Cyl 24 - cellulosics, plastics, rubbers | Cyl 27 - cellulosics | Average (molecule/100 eV) | Percent |
| 0.001 | 0.365 | 1.47E+00 | 1.60E+00 | 6.89E-01 | 1.41E+00 | 1.05E+00 | 1.24E+00 | 100% |
| 1 | 365 | 1.10E+00 | 1.12E+00 | 4.78E-01 | 9.46E-01 | 7.19E-01 | 8.73E-01 | 70% |
| 5 | 1825 | 3.48E-01 | 2.68E-01 | 2.15E-01 | 1.90E-01 | 3.18E-01 | 2.68E-01 | 22% |
| 10 | 3650 | 8.24E-02 | 4.48E-02 | 1.27E-01 | 2.55E-02 | 1.88E-01 | 9.34E-02 | 7.5% |
| 100 | 36500 | 4.42E-13 | 4.67E-16 | 1.52E-02 | 5.17E-18 | 2.23E-02 | 7.51E-03 | 0.6% |
| 1000 | 365000 | 8.70E-126 | 7.20E-156 | 1.55E-03 | 6.04E-175 | 2.28E-03 | 7.66E-04 | 0.1% |

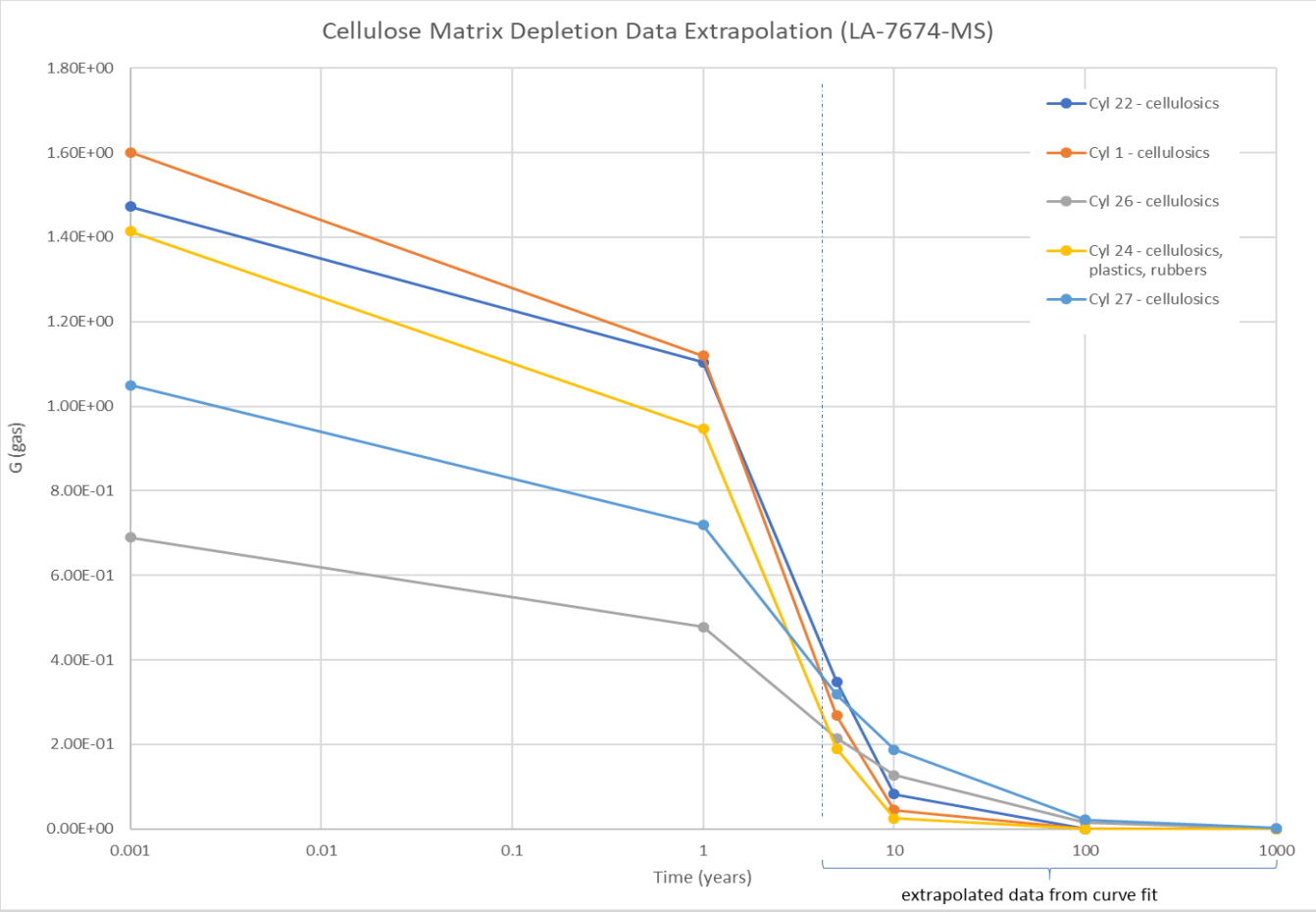



**Figure 3 – Matrix Depletion for CPR**

## References

Bateman, H. 1910. *The solution of a system of differential equations occurring in the theory of radioactive transformations.* In Proc. Cambridge Philos. Soc (Vol. 15, No. pt V, pp. 423–427).

Gray, W. J. and S. A. Simonson. 1984. *Gamma and Alpha Radiolysis of Salt Brines*, PNL-SA-12746, 1984 Fall Meeting of the Materials Research Society in Boston, Mass., November 1984.

ICRP, 2008. *Nuclear Decay Data for Dosimetric Calculations*. ICRP Publication 107. Ann. ICRP 38

Idaho National Engineering and Environmental Laboratory, 1990, "*TRUPACT-II Matrix Depletion Program Final Report*," INEL/EXT-98-00987, Rev. 1, prepared for the U.S. Department of Energy, Idaho Operations Office, Idaho Falls, Idaho.

Molecke, M.A. 1979. *Gas Generation from Transuranic Waste Degradation*. SAND79-0911C. ERMS 228093. Albuquerque, NM: Sandia National Laboratories.

Narlesky, J. E., M. A. Stroud, P. H. Smith, D. M. Wayne, R. E. Mason, L.A Worl, 2012. *Characterization of Representative Materials in Support of Safe, Long Term Storage of Surplus Plutonium in DOE-STD-3013 Containers*, LA-UR-12-23790, Los Alamos National Laboratory, Los Alamos, NM.

Reed, D.T., S. Okajima, L.H. Brush, and M.A. Molecke. 1993. *Radiolytically-Induced Gas Production in Plutonium-Spiked WIPP Brine, Scientific Basis for Nuclear Waste Management XVI, Materials Research Society Symposium Proceedings, Boston, MA, November 30 – December 4, 1992.* C.G. Interrante and R.T. Pabalan, eds. SAND92-7283C. ERMS 228637. Materials Research Society, Pittsburgh, PA. Vol. 294, pp. 431–438.

U.S. DOE. 2012. *CH-TRU Payload Appendices*, Rev. 3, December 2012. Carlsbad, NM.

Zerwekh, A. 1979. "*Gas Generation from Radiolytic Attack of TRU-Contaminated Hydrogenous Waste,"* LA-7674-MS, Los Alamos National Laboratory, Los Alamos, NM.

Zerwekh, A., J. Warren, and S. Kosiewicz, 1993. "*The Effect of Vibration on Alpha Radiolysis of Transuranic (TRU) Waste*," Proceedings of Symposium on Waste Management, Tucson, AZ.