DOE PCP Guidance for
Inerting Containment Vessels of Type B or Type AF
Radioactive Material Transportation Packages,
Revision 0

September 23, 2021

Prepared by

Lawrence Livermore National Laboratory
SARP Review Team Members:
B. Anderson and S. Sitaraman

This work was performed under the auspices of the U.S. Department of Energy by
Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344
DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.
DOE Guidance for Inerting Containment Vessels of Type B or Type AF Radioactive Material Transportation Packages

1. Introduction

This document presents the motivation and best practices used to inert the containment vessels of Type B or Type AF radioactive material transportation packages when the contents are pyrophoric and/or can generate flammable gasses through thermolysis or radiolysis.

The general requirement of 10 CFR 71.43(d)[1] for all packages that, A package must be made of materials and construction that assure that there will be no significant chemical, galvanic, or other reaction among the packaging components, among package contents, or between the packaging components and the package contents, including possible reaction resulting from inleakage of water, to the maximum credible extent. Account must be taken of the behavior of materials under irradiation, allows that the containment vessel may be inerted to prevent reaction of pyrophoric materials and to prevent flammable gas mixtures from accumulating during transportation. Alternatively, package closure time may be limited to ensure that accumulated flammable gases do not reach combustible levels.

Inerting of a Type B or Type AF radioactive material transportation package containment vessel (CV) is necessary when there is a concern with flammability of the contents and/or the gases that are generated. This document contains guidance on inerting a CV when the contents are pyrophoric and/or when the contents and packaging material in the CV can generate flammable gas mixtures due to thermal decomposition and/or radiolysis. This guidance for inerting the CV also applies to any confined volume within the CV.

A substance is pyrophoric if it ignites spontaneously in air at or below 54 °C (129 °F) (for gases) or within 5 minutes after coming into contact with air (for liquids and solids).[2] Pyrophoric materials are often water-reactive as well and will ignite when they contact water or humid air. Contents such as uranium[3] or plutonium[4] turnings or shavings, or other finely divided metals or metal compounds can be pyrophoric. Pyrophoric plutonium has been defined as plutonium metal that will ignite spontaneously in air at a temperature of 150 C or below in the absence of external heat, shock, or friction.[4, 5] Many plutonium compounds are pyrophoric, for example: hydrides, carbides, oxycarbides, nitrides, and some oxides (i.e.,Pu₂O₃).[5]

Various decomposition-type reactions among the contents and the packaging materials within the CV can generate flammable gases. Thermal decomposition (i.e., thermolysis) of organic materials can release flammable gases even at temperatures consistent with Normal Conditions of Transport. Also, radiolytic decomposition (i.e., radiolysis), where ionizing radiation decomposes water and organic materials by breaking chemical bonds, can generate significant amounts of flammable gases.
2. Pyrophoric Materials

In general, pyrophoric materials include several types of chemical compounds and forms, including: organo-metallic reagents, alkali earth elements, metal hydrides, alkyl metal hydrides, metal carbynls, silicon halides, some gasses, and metal fines. The pyrophoric materials of interest for shipment in radioactive material transportation packages are typically finely-divided radioactive metals and metal compounds (e.g., powders, fines, turnings). Additionally, radioactive pyrophoric materials associated with moisture and/or organic materials can generate hydrogen and other flammable gases via radiolysis.

Pyrophoric materials react with the oxygen in air, and/or with moisture in air. Typical reactions that occur are oxidation and hydrolysis, and the heat generated by the reactions may ignite the element or compound. In some cases, these reactions, liberate flammable gases which can result in deflagration or detonation. In addition, pyrophoric radioactive materials can cause radiolysis of moisture and organic materials.[6]

Uranium in a pyrophoric form generally includes finely divided metallic saw turnings and chips, sawdust, and abrasive saw sludge. Moisture in the form of water or machining coolants may be present on the finely divided material, contributing to its reactivity due to the radiolytic decomposition of the water reacting with the base metal to create hydrogen gas. Hydrogen gas generation and reactivity will vary with the particle size or specific surface area (surface area to mass) of the fines, free moisture content, and age of the material.


Pyrophoric Class 7 (radioactive) materials, as referenced in the § 172.101 table of this subchapter, in quantities not exceeding A2 per package must be transported in DOT Specification 7A packagings constructed of materials that will not react with, nor be decomposed by, the contents. Contents of the package must be -

(a) In solid form and must not be fissile unless excepted by § 173.453;

(b) Contained in sealed and corrosion resistant receptacles with positive closures (friction or slip-fit covers or stoppers are not authorized);

(c) Free of water and contaminants that would increase the reactivity of the material; and

(d) Inerted to prevent self-ignition during transport by either -

(1) Mixing with large volumes of inerting materials, such as graphite, dry sand, or other suitable inerting material, or blended into a matrix of hardened concrete; or

(2) Filling the innermost receptacle with an appropriate inert gas or liquid.
(e) Pyrophoric Class 7 (radioactive) materials transported by aircraft must be packaged in Type B packages.

Although § 173.418 generally applies to Type A packages, and to Type B packages transported by aircraft, the guidance for inerting in §173.418(d)(2) when the contents are pyrophoric is applicable to all transportation modes of Type B and Type AF packages to mitigate potential risks due to pyrophoricity.

Content control(s) to prevent pyrophoricity are typically limits on specific surface area and amount of moisture. The specific surface area controls may limit or omit many filings, turnings, and foils.

NRC Information Notice 80-25, Transportation of Pyrophoric Uranium,\(^8\) summarizes the risks that can occur when pyrophoric radioactive material is combined with moisture:

Uranium in a pyrophoric form…generally include finely divided metallic saw turnings and chips, sawdust, and abrasive saw sludge. Moisture in the form of water or machining coolants is usually present on the finely divided material, contributing to its reactivity due to the radiolytic decomposition of the water reacting with the base metal to create hydrogen gas. Hydrogen gas generation and reactivity will vary with the particle size (surface area to volume ratio) of the fines, free moisture content, and age of the material.

3. Flammable Gases

Since the contents and its packaging must satisfy 10 CFR 71.43(d) that, A package must be made of materials and construction that assure that there will be no significant chemical, galvanic, or other reaction among the packaging components, among package contents, or between the packaging components and the package contents..., it follows that a package CV cannot be sealed with a flammable or explosive mixture of gases present.

Gas generation, including flammable gas generation, can occur due to radiolysis and/or thermal degradation. Gas generation due to chemical reaction, including corrosion, is typically avoided through appropriate package (i.e., content and packaging) design. Radiolysis or thermal degradation can occur after the CV is sealed producing potentially flammable gas mixtures. Radiolysis occurs when ionizing radiation (i.e., alpha particles, beta particles, or gamma rays) impinge on water or organic material, resulting in hydrogen and other potentially flammable small molecules. Gas release, including flammable gas release, due to non-combustion thermal degradation of organic materials involves the chemical breakdown of materials into airborne particulates, gases, and/or vapors when heat is applied.\[^{[9, 10, 11]}\]

Even when the contents are pretreated (i.e., calcined) to remove most of the water and organic material, and minimal plastic bagging is used for contamination control, sufficient water and/or organic materials can often remain to generate a radiolytically-produced flammable gas mixture in the CV during transportation. For these cases when content pretreatment measures and limiting organic materials cannot prevent the accumulation of a potentially flammable gas
mixture in the CV, the fill gases should be inerted prior to sealing the CV to preclude the formation of a flammable or detonatable gas mixture during transportation.

Guidance in Section 3.4.5.2, *Maximum Normal Operating Pressure*, of NUREG-2216,[12] *Standard Review Plan for Transportation Packages for Spent Fuel and Radioactive Material*, stipulates that combustible gas concentrations should not exceed 5% (by volume), or lower if warranted by the type of flammable gas, in any confined region of the package under Normal Conditions of Transport or Hypothetical Accident Conditions.

Combustible gases in radioactive material transportation packages are further restricted in the NRC Information Notice 84-72, *Clarification of Condition for Waste Shipments Subject to Hydrogen gas Generation*,[13] where flammable gas concentrations are limited to 5% by volume in any confined region of a package over a period that is twice the shipping period. Although the NRC Information Notice 84-72 addresses waste shipments, the combustible gas limit has generally been applied to Type AF, Type B, and Type BF packages regardless of the content. Since the Maximum Normal Operating Pressure (MNOP) is determined for a period of 1-year for Type AF and Type B packages, and the periodic leakage test is required within one-year of shipment, the shipping period is typically taken as one-year and therefore, according to NRC Information Notice 84-72, the flammable gas limit is usually taken as no more than 5% combustible gases over a period of two-years.

The applicant should calculate the time it takes to reach 5% by volume combustible gas in any confined volume for each of the approved contents [or by another method of demonstration acceptable to the DOE Package Certification Program (PCP)]. If the total combustible gas inventory within any confined volume exceeds 5% by volume in less than two-years, it is recommended that the CV be inerted upon sealing to ensure that oxygen inventory does not exceed 5%, and/or a limit added as a condition in the DOE Certificate of Compliance to restrict the time the CV is sealed to one-half the time it takes to reach 5% total combustible gas.

The evaluation of flammable gases in the CV should include all possible sources of gas generation, including thermal decomposition, corrosion and other reactions, and radiolysis. The evaluation of flammable gases in the CV cannot include credit for getters, catalysts, or other recombination devices.[13] However, credit may be taken for diffusion and/or leakage of the flammable gas out of the CV to evaluate the combustible gas release rate versus the combustible gas generation rate. Also, the evaluation of flammable gases in the CV (and within all volumes within the CV) must be calculated using worst-case assumptions, the ‘convenience containers’ within the CV must be assumed to leak (even if they have been leak tested), unless other conditions are a worst-case.

Additional guidance on issues concerning combustible-gas generation in Type B package containment vessels can be found in NUREG/CR-6673, *Hydrogen Generation in TRU Waste Transportation Packages*,[14] and NUREG/CR-6487, *Containment Analysis for Type B Packages Used to Transport Various Contents*.[15]
3.1 Operational Concerns
For package containment vessels that have significant flammable gas generation and are inerted for purposes of transportation safety, there may be personnel safety concerns associated with opening the CV. After a content with a high flammable gas generation potential is inerted and sealed in a CV for a period of time, the gases inside the CV may be predominantly flammable gas with a relatively small percentage of inerting gas. If such a CV were to be opened in still air, some of the gases from the CV would mix with some of the surrounding air and there would most likely be a gas region above the CV opening containing a cloud of flammable or detonable gas. For packages with high flammable gas generating potential, it is recommended that a warning be noted in the Operations section of the SARP.

4. Preventing/Limiting Pyrophoricity and Flammability Risks

4.1 Eliminating Hazards
Elimination of the flammability hazards associated with transporting pyrophoric radioactive materials is achieved by rendering the material relatively non-reactive and non-pyrophoric. Example methods of ‘stabilization’ of pyrophoric materials are given in NRC Information Notice 80-25,[8] including incineration to a non-pyrophoric oxide or mixing and solidifying in a large matrix of concrete. Elimination of the hazards associated with radiolysis involves elimination of moisture and organic materials from the CV or shielding these materials from ionizing radiation. When it is not possible to eliminate the flammability risks associated with pyrophoric materials and/or radiolysis in the CV, engineered controls and/or administrative controls need to be employed to mitigate the associated flammability risks. See the DOE Standard, Stabilization, Packaging, and Storage of Plutonium-Bearing Materials,[16] for a complete discussion of methods used to stabilize plutonium.

4.2 Controls
4.2.1 Limiting Contents
The primary content control to prevent pyrophoricity is a limit on the specific surface area of the material. For example, pieces of plutonium characterized as having a minimum thickness greater than 1.0 mm (0.04 in) and a specific surface area less than 1 cm$^2$/g (71 in$^2$/lb) requires temperatures in excess of 400°C (752°F) to ignite.[5,17] These specific surface area limits can severely restrict or omit many metal powders, filings, turnings, and foils.

Limits on the isotopic content mass can be useful to mitigate the risks of flammability due to radiolysis. Under the guidance in NRC Information Notice 84-72, if the content is limited so that the time to reach a flammable mixture in air is greater than two-years, the flammability risk for packages approved under 10 CFR 71 would be mitigated. For pyrophoric contents, limits on the content mass would limit but not eliminate pyrophoricity risks. For contents where radiolytic hydrogen (and other flammable gases) generation is a concern, limits on water/organics and/or limits on the mass of radioisotopes, may limit the hydrogen accumulation to no more than 5% within two years after sealing of the containment vessel. Normally, limits on content mass might be considered an administrative control, however, in the context of a SARP with an approved content mass limit, the control may be considered as an engineered control since it is based on engineering analysis of the package structural, thermal, shielding, criticality, and containment attributes.
4.2.2 Convenience Cans and Engineered Shielded Containers
A convenience container, such as a ‘food-pack’ type can, is often used in the CV for handling and contamination control, and can be useful for limiting gas generation. The term “food-pack” can includes metal cans with crimped-seal closures, “slip-lid” closures, or site-specific “convenience containers.” Crimp-sealed food-pack cans are typically fabricated in accordance with Federal Specification PPP-C-96E, or equivalent, and meet the size specification as defined by the Can Manufacturers Institute (CMI) Voluntary Can and End Dimension Reference Manual.[18] Convenience containers are typically application-specific designs that incorporate screw thread, crimp sealed, or welded closures, and are typically made from tin-plated mild steel or stainless steel. A method for mitigating the accumulation of flammable gases due to radiolysis in a CV may be to place the radioisotopes in a convenience can and/or an engineered shielded container that effectively prevents the ionizing radiation from reaching the moisture and/or organic materials in the remainder of the CV and thereby prevents radiolysis and the potential for the development of flammable gas mixtures.

A common practice within DOE when shipping radionuclides that are primarily alpha-emitters, is to have a can-bag-can arrangement around the radionuclides within the CV, where an inner stainless or tin plated can provides a barrier between the radioactive material and the plastic contamination control bag, and the outer can will allow a means of lifting the contents and placing them in the package containment without having to lift by a bag.

Convenience containers, including 3013 containers, hex cans, and food-pack can, are not credited with retaining gas while in the CV. When analyzing gas constituents within the CV, the convenience containers should be assumed to leak where the gas fill in the CV is mixed with the gas fill of the convenience containers (unless other conditions are a worst-case).

4.2.3 Inerting a Containment Vessel
Inerting the containment vessel may become necessary when content limitations, the use of an engineered shielded container, and/or other engineered controls are not effective at limiting pyrophoric and/or flammability risks.

When inerting is necessary, all the containers within the CV will need to be inerted. However, it is often the case that the inner content containers, such as food-pack cans, Hex cans, 3013 containers, and even plastic bags, are inerted with a different inert gas than that used in the CV due operational or other considerations. The inert gas used can even depend on the decay heat of the contents due to heat transfer considerations.

If inerting is proposed, at a minimum:

- Demonstrate the inerting process will prevent the development of flammable gas mixtures in any confined area of the package throughout the entire shipment period
- Provide a detailed evaluation or analysis to demonstrate that there are no flammable gas mixtures (considering the worst case concentration of hydrogen or any other flammable gas, and oxygen) during shipment
• Provide a detailed configuration of all passages and explain how the inerting gas is introduced effectively (e.g., injection path, port orientation) to the innermost packaging or other confined areas within the containment system of the package

• Demonstrate that the inerting gas either effectively occupies the containment vessel (CV) or is in uniform concentration throughout the CV

• Discuss how the concentrations of combustible gases are quantitatively analyzed, and

• Provide detailed information on the different steps of the inerting process in the Package Operations section of the SARP

• Provide detailed information on the inerting of the content convenience containers (plastic bags, food-pack cans, Hex cans, 3013 containers, etc.)

The development and maintenance of an inert atmosphere in the CV is a safety-critical measure. Unless the package CV and all containers inside the CV are closed within a well-controlled inert atmosphere, a process to deliver the inert atmosphere into the package containment must be developed. This procedure for inerting the package should be a qualified procedure where proof testing has been performed on the adequacy of the procedure by taking quantitative gas measurements at important containment vessel locations to ensure that the desired level of gas inerting is achieved. Also, it must be demonstrated that the inerting gases remain in the CV at sufficient levels for the duration of the shipment. The initial qualification of the inerting procedure is performed by the package SARP developers but may also need to be performed by package users if their inerting equipment differs from that used in the initial procedure qualification.

Consideration should be given to the reliability of the control systems employed for the inerting process. In developing the inerting process for the Model 9978 package, a Proof of Principle Testing for Inerting a 9978 Containment Vessel, was performed.\[19\] From their experience performing these tests, the authors state that “The Proof of Principle Testing also demonstrated that simply following a set of procedural steps would not ensure the inerting will be acceptable (e.g., small leak in the glove bag may result in an unacceptable inerting).” The testing approach used an oxygen meter to ensure that the necessary inerting was achieved.

4.2.4 Transportation Time Controls
When content controls do not limit the flammable gases in the CV to less than 5 volume percent for a CV sealing time of two-years (i.e., twice the MNOP time of one-year), and inerting of the CV is not practical, then the shipping time (i.e., the time the CV is sealed) should be limited to the time it takes for the flammable gases to reach 2.5%. This administrative control on shipping time may require conveyance location monitoring.

4.2.5 Examples of Controls on DOE Packages to Address Flammability Risks
Below are some examples of controls placed on DOE-certified packages, such as inerting requirements (i.e., limits on oxygen content), limits on shipping time, limits on moisture and hydrogenous materials, limits on content mass, limits on specific surface area, and limits on content decay heat, all to address potential flammability and detonation risks.
4.2.5.1 Model 9975 Package
For certain oxide contents, the PCV (or PCV and SCV) is backfilled with an inert gas prior to closing. For Content Envelopes C.4 or C.11 (Pu/U oxides), the PCV shall be inerted with nitrogen (depending on content density) so that at the time of closure the oxygen content is all void spaces is no greater than 5% by volume [See Addendum, 5(e)(4)]. For Content Envelope C1, C3, C5, C6 or C10, each (un clad) metal piece shall have a minimum thickness of 1.0 mm (0.04 inches) and a specific surface area less than 100 mm²/g (71 in²/lb.) per DOE-STD-3013-2004. For Content Envelope C.8 (Np oxide), all containers (food-pack cans, PCV, and SCV) shall be inerted with argon, such that oxygen content in all void spaces is no greater than 3% by volume at closure, and there is a limit on hydrogenous material.[20]

4.2.5.2 Model 9516 Package
The CV is filled with a combination of argon and helium gas at 1 atm at the time the closure weld is accomplished, and its content (Pu-238 oxide) contains no moisture or other hydrogenous material, and therefore there is no hydrogen generation and buildup concerns. The containers inside the CV are welded enclosures filled with an inert gas consisting of argon and/or helium.

4.2.5.3 Model 9978 Package
For Content Envelope C1 (238-Pu Heat Sources), either in foodpack cans or an engineered container (within the CV), the plastic mass is limited to 100 grams. For Content Envelope C2 (Plutonium and Uranium Metal), the content must be stabilized according to DOE-STD-3031,[16] and when in foodpack cans the limit on plastic is 100 grams.[21]

4.2.5.4 Model 9979 Package
Package hydrogen generation and accumulation concerns are addressed by limiting the shipment time, 30-gallon drum purging using nitrogen to reset the shipment time, or a hydrogen gas concentration sampling and measurement method.[22]

4.2.5.5 Model 9204 (i.e., 10-160) Package
Condition (d)(3): Flammable gas (hydrogen) concentration is limited to less than 5% in volume. For contents other than TRU waste, inverting is not allowed to limit the concentration of flammable gases. For TRU waste, compliance with the 5% hydrogen concentration limit is determined by the methods discussed in Appendix 4.10.2 of the SAR as supplemented. For contents with a radioactivity concentration not exceeding that for Low Specific Activity material, the hydrogen concentration can be assumed to be less than 5% provided the package is shipped within 10 days of preparation, or within 10 days after venting of the drums or other secondary containers.[23]

4.2.5.6 Model 9315 (i.e., ES-3100) Package
Although there is no requirement for the model ES-3100 CV to be inerted, there are contents that are required to be in inerted convenience containers. Analysis conducted in Appendix 3.5.4 of the SARP evaluates the different packaging arrangements for the generation of hydrogen gas due to the radiolysis of water vapor, free water, interstitial water, polyurethane bags, and polyurethane or Teflon bottles. By limiting the mass and the material composition
as shown in Appendix 3.5.4, the combustible gas concentration limit stated in NUREG-2216 is found not exceeded. However, for metal uranium, particles and small shapes which do not pass the size restriction tests, and powders, foils, turnings, and wires, are not permitted unless they are in a sealed, inerted convenience container. Enriched uranium oxide in the form of UO$_2$-Mg is packed inside glass bottles, which are placed inside sealed, inerted metal convenience cans.$^{[24]}$ Pyrophoric materials in the ES-3100 have limited seal time during shipment. Whereby once the CV is sealed, the package must be delivered and opened by the “seal time” in the SARP.
References


