

Increased Fissionable Material Loading of Vitrified Borosilicate Glass in Support of Efficient Disposition of Nuclear Materials at Savannah River - 15299

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ABSTRACT

The US DOE is vitrifying liquid HLW, converting it into a glass form suitable for long term storage and disposal. The waste includes fissionable isotopes and, as a consequence, may possess an inadvertent criticality hazard. The technical basis for determining when an inadvertent criticality hazard exists is unclear. ANS criticality safety standards do not provide relevant subcritical safety limits and little experimental data exist to support development of such a limit. As a result, the DOE has implemented a conservative limit of 897 grams of fissile nuclides per cubic meter of glass. However, this limit has the potential to impede efficient disposal of various fissionable materials at the Savannah River Site. Work is being conducted to establish an alternate fissionable material limit which would be less restrictive, but still ensure criticality safety.

A series of computer models are constructed and analyzed using a general purpose Monte Carlo N-Particle neutron transport code. First, a baseline model is established and analyzed. Next, numerous variations to the baseline model (i.e., perturbations) are analyzed with the code to understand the impact of the change. Based on the results, it is evident the atomic ratio of B-10 to equivalent Pu-239 would be an effective means to ensure subcriticality of HLW vitrified in a borosilicate glass matrix. The proposed limit, its technical basis, and all necessary application constraints are discussed. This proposed limit is expected to permit significantly higher quantities of fissile nuclides in the vitrified waste form. It will also account for several non-fissile, fissionable nuclides which are expected to add reactivity to the glass waste form. The proposed limit embodies large conservatisms intended to provide assurance of safety in spite of the significant uncertainties associated with its development. The single most important uncertainty arises from the inability to validate the calculations which form its technical basis. While they are done with the latest available nuclear data and well established analytical methods, they are, nonetheless, not validated as required for subcritical safety limits.

INTRODUCTION

The United States Department of Energy (DOE) is vitrifying liquid high level waste (HLW), converting it into a glass form suitable for long term storage and disposal. The waste includes fissionable isotopes and, as a consequence, raises the potential of an inadvertent criticality hazard. The technical basis for determining when an inadvertent criticality hazard exists is unclear. American Nuclear Society criticality safety standards do not provide relevant subcritical safety limits and little experimental data exist to support development of such a limit. As a consequence, the DOE has implemented a very conservative (and somewhat restrictive) limit of 897 grams of fissile nuclides per cubic meter of glass (i.e., 0.897 g/L). [1]

This work was conducted to establish a single parameter evaluation limit for any quantity of homogeneous vitrified borosilicate glass. The proposed evaluation limit is an atom ratio of B-10 to equivalent Plutonium-239. For ratios above the limit, the material is expected to be safely subcritical. Below the limit, additional technical basis would need to be developed to demonstrate criticality safety. This limit is expected to be far less restrictive than the current limit of 0.897 g/L of fissile nuclides.

SOLUTION METHODOLOGY

Overview

A series of computer models are constructed and analyzed using a general purpose Monte Carlo N-Particle code. The models represent an infinite glass matrix consisting of glass frit, fissionable isotope(s), and high level waste. First, a baseline model is analyzed and serves as a point of reference for subsequent variations. Next, numerous variations to the baseline model (i.e., perturbations) are analyzed with the code to understand the impact. In almost all cases, a void space is “reserved” for high level waste, but specific waste constituents are not included. Not explicitly modeling the waste constituents is done for two reasons; 1) their composition has the potential to vary greatly, and 2) their presence introduces additional parasitic neutron absorbers. Thus, their omission simplifies the study and is conservative from a criticality safety perspective. This is confirmed by a series of perturbations where the neutron scattering and absorption effects of including several common waste constituents, one at a time, are examined.

For the baseline model, as well as each perturbation, the following are examined: the neutron flux energy distribution within the glass matrix, the relative importance of the different neutron absorbers, and the neutron multiplication factor, k . As this study only considers infinite systems, only infinite multiplication factors, k_{∞} , are determined.

Following examination of all perturbations, a simplified glass matrix model is defined and analyzed for the purpose of establishing the proposed B-10 to Pu-239 equivalent evaluation limit. All necessary application constraints and Pu-239 equivalency rules are then distilled from the completed parametric studies.

Glass Matrix Models

The principle of conservation of volume is used to construct the glass matrix models (i.e., each compound is assumed to occupy some fraction of the available space based on the compound’s relative loading and its density). The following baseline model is analyzed and serves as the point of reference for all subsequent perturbations:

- 100% Pu-239 oxide (PuO_2) at 200 grams Pu-239 per liter of glass matrix;
- 30% volume void;
- glass frit with the composition given in Table I;
- a glass matrix temperature of 20.5°C.

TABLE I - Baseline glass frit composition

| Compound | Weight Percent |
|------------------------|----------------|
| Li_2O | 6.0 |
| B_2O_3 | 8.0 |
| Na_2O | 8.0 |
| SiO_2 | 78.0 |

Computer Code/Nuclear Data

MCNP5, Version 1.60, is used to analyze the glass matrix models. [2] Nuclear data is obtained from ENDF/B-VII.1. [3] This data was processed by NJOY99.368 and NJOY2010 to convert the data into the format needed by MCNP5. [4] All cross sections sets correspond to a temperature of 20.5°C, except those used in the temperature

perturbation. Information extracted from MCNP5 includes:

1. infinite neutron multiplication factor, k_{∞} ,
2. relative reaction rates among the various nuclides present in the matrix,
3. neutron flux energy spectrum, and
4. number of neutrons produced per fission.

Statistical errors resulting from the monte carlo solution method for the neutron multiplication factors are insignificant and are not included in the discussions that follow.

DISCUSSION

Baseline Model

The neutron flux energy spectrum in the baseline glass matrix consists of a single, wide hump with 99% of flux above 0.0003 MeV. Approximately 95% of the flux is distributed (relatively smoothly) between 5 MeV and 0.001 MeV. This spectrum differs from the neutron flux energy spectrum in plutonium metal which consists of a single hump with 99% of the neutron flux above 0.04 MeV. It also differs from the neutron flux energy spectrum in a well moderated homogenous plutonium metal – light water “solution”. Approximately half of the flux in the solution has energies below any meaningful flux in the glass matrix.

Approximately 38% of all neutron absorptions occur in Pu-239, with 71% of those absorptions resulting in fission. The remaining absorptions occur in non-fissionable nuclides, distributed as shown in Table II. The most significant neutron absorber is B-10. Even with its low relative abundance, its large cross section results in it being the dominant absorber. Li-6, also low in relative abundance, is the second most important absorber. The two isotopes combine to account for nearly 97% of neutron captures even though they represent only 1.3% of the non-fissionable nuclides present.

TABLE II – Relative neutron capture among non-fissionable nuclides for baseline glass matrix

| Nuclide | Relative Abundance (%) | Relative Captures (%) |
|----------------|-------------------------------|------------------------------|
| Li-6 | 0.5 | 16.2 |
| Li-7 | 6.7 | 0.0 |
| B-10 | 0.8 | 80.5 |
| B-11 | 3.3 | 0.0 |
| O-16 | 60.6 | 1.4 |
| Na-23 | 4.6 | 0.4 |
| Si-28 | 21.5 | 1.0 |
| Si-29 | 1.1 | 0.1 |
| Si-30 | 0.7 | 0.4 |

The infinite neutron multiplication factor, k_{∞} , for the baseline glass matrix is 0.78.

Perturbations

The following perturbations are examined to gain insight into how these changes affect the neutron flux energy distribution within the glass matrix, the relative importance of the different neutron absorbers, and the reactivity of the glass matrix.

Pu-239 Concentration

This perturbation involves varying the Pu-239 concentration in the glass matrix between 125 and 375 g/L, by 25 g/L increments.

Fissile Nuclide Isotopic Distribution

This perturbation involves examining the behavior of other fissile nuclides in the glass matrix. The three fissile nuclides considered are U-233, U-235, and Pu-241. Pu-239 is replaced by each of these, one at a time and at 25% increments. Total fissile nuclide mass concentration is maintained at 200 g/L for all variations.

Addition of Non-fissile, Fissionable Nuclides

This perturbation involves examining the effect of adding non-fissile, fissionable nuclides to the glass matrix. The following nuclides are considered: U-234, U-236, U-238, Np-237, Pu-238, Pu-240, Am-241, Am-243, Cm-244, and Cm-246. While U-236 and U-238 are not truly fissionable, they are considered within this study for completeness. A quantity of each nuclide is added to the void space of the matrix, maintaining all other properties of the baseline glass matrix. To examine trends, three separate quantities of each nuclide are considered.

Content in the Glass Frit

This perturbation examines the effect varying the frit recipe. Each of the following frit constituent oxides is varied, one at a time:

- B₂O₃ is varied between 0 and 16 weight percent, by 4 weight percent increments;
- Li₂O is varied between 0 and 12 weight percent, by 3 weight percent increments;
- Na₂O is varied between 0 and 16 weight percent, by 4 weight percent increments; and
- MgO is varied between 0 and 8 weight percent, by 2 weight percent increments.

In each case, the SiO₂ content is varied to compensate for the adjusted frit constituent. The total Pu-239 mass concentration is maintained at 200 g/L and the 30% void volume within the glass matrix is preserved.

Glass Temperature

This perturbation examines the effect varying glass matrix temperature. The glass matrix is examined at 627°C and 1,227°C. No adjustment is made for glass density changes as it is irrelevant in an infinite system. In fact, there are no “physical” changes from the baseline model. The only change is the temperature adjustment to the cross section data to account for Doppler broadening of absorption resonances.

Addition of Waste Constituents

This perturbation examines the effect introducing several common high level waste constituents. The constituents selected for evaluation are Al₂O₃, Fe₂O₃, and MnO. A quantity of each is added to the void space of the matrix, thereby maintaining all other properties of the baseline glass matrix. To examine trends, three separate quantities of each constituent were considered.

Addition of Light Water Moderation

This perturbation examines the effect of introducing moderation into the glass matrix. A quantity of light water is “homogenized” with the baseline glass matrix. In this approach, the quantities of the various glass matrix constituents remain constant with respect to each other. The only change is the addition of H₂O to the “homogenized mixture”. The quantity of water added is not limited to that permitted by the void space in the baseline glass matrix model. Instead, quantities are selected to span the full range of possible moderation (i.e., unmoderated to fully moderated) and could be envisioned as if the glass matrix was “dissolved” in an aqueous solution. This approach is taken to examine trends over the entire possible range of moderation.

Pu-240 and Pu-241 Inclusion

This perturbation is a variation of the single variable perturbation involving the substitution of other fissile nuclides for Pu-239. Specifically, Pu-239 is replaced by a combination of Pu-240 and Pu-241, at 25% increments. The substitute plutonium isotopic distributions considered are 25%/75%, 50%/50%, and 75%/25% Pu-240/Pu-241. Plutonium atom density in the glass matrix is maintained constant for all variations and at the same value as the baseline model.

Fissile Nuclide and Light Water Moderation

This perturbation is a variation of the single variable perturbation involving the introduction of light water moderation. Light water moderation is added as was done above. However, Pu-239 is replaced by either U-233, U-235, and Pu-241 (on an atom-by-atom basis) to study the effect moderation has on the glass matrix when it contains other fissile nuclides.

CONCLUSIONS

Proposed Evaluation Limit

Based on the results of the parametric studies, it is evident the atomic ratio of B-10 to equivalent Pu-239 would be an effective means to ensure subcriticality of HLW vitrified in a borosilicate glass matrix. Specifically, the following is proposed as a single parameter evaluation limit which will ensure adequate subcriticality of any quantity of homogeneous vitrified borosilicate waste:

B-10 to Pu-239 equivalent atom ratio ≥ 1.4 ,

Provided:

- glass frit composition is limited to silicon, boron, lithium, sodium, and magnesium oxides;
- only boron provided by the glass frit is used to satisfy the limit;
- Boron-10 content of the glass frit used to satisfy the limit cannot exceed that which is equal to 16 weight percent of the frit being B₂O₃, with 19.9% of the boron atoms being B-10; and
- Pu-240 content exceeds Pu-241 content.

Pu-239 equivalency is determined as follows:

- 1 atom of U-233 is treated as 1.5 atoms Pu-239;
- U-234, U-235, all plutonium isotopes, Cm-244 and Cm-246 are treated as Pu-239, atom-for-atom; and
- U-236, U-238, Np-237, Am-241, and Am-243 can be ignored.

Summary of Technical Bases

A glass matrix made of only PuO_2 , SiO_2 , and B_2O_3 was analyzed. Thus, the only significant parasitic neutron absorber is boron-10. The proposed evaluation limit corresponds to a calculated infinite neutron multiplication factor of less than 0.8.

As the B-10 content is increased, the neutron flux in the lower energy region is depressed, reducing the incremental negative reactivity worth of any additional B-10. Thus, the B-10 content must be constrained to protect the validity of the limit. The approach proposed is to only credit boron in the glass frit towards meeting the limit and limiting the amount of B-10 in the frit that can be credited. Glass frit could safely have a higher B-10 content, but the additional B-10 could not be used to permit additional Pu-239.

A constraint is placed on the make-up of the glass frit. The parametric studies showed introduction of these oxides, with the exception of Na_2O , reduces reactivity of the glass matrix. For Na_2O , the effect on reactivity is small and insignificant given the margins embodied in the proposed evaluation limit. While different amounts of these oxides do not adversely affect the basis of the proposed limit, it is not possible to assert a different oxide in the frit would not do so. Thus, inclusion of different frit constituents would require further evaluation.

The only constraint placed on the constituents of the high level waste applies to elements with an atomic number greater than or equal to 92. The addition of constituents with lower atomic numbers will reduce the reactivity of the glass matrix. For elements with an atomic number greater than or equal to 92, an equivalent Pu-239 model is proposed. The Pu-239 equivalency rules proposed conservatively account for the reactivity effects observed in the parametric studies described above.

Summary of Conservatism and Uncertainties

The proposed limit embodies large conservatism intended to provide assurance of safety in spite of significant uncertainties associated with its development. It does not provide margin to account for process upset conditions (e.g., non-homogeneity). Accordingly, if used, it would be the user's responsibility to evaluate their process to ensure any uncertainties in process conditions and credible abnormal upsets do not result in falling below the limit or jeopardizing its technical basis.

Conservatism

The 0.2 subcritical margin is large compared with margins normally provided by subcritical limits. Other conservatism embodied in the proposed limit include:

- ignores parasitic neutron absorption by any Li-6 which may be present;
- is based on a high concentration of B-10 (B-10 is a more effective parasitic neutron absorber at lower concentrations);
- ignores any parasitic neutron absorption by any non-fissionable HLW constituents;
- incorporates a conservative equivalency approach for fissionable HLW constituents; and
- is based on an infinite system.

Uncertainties

The single most significant uncertainty arises from the inability to validate the calculations which form the technical basis of the evaluation limit. While they are done with the latest available nuclear data and well established analytical methods, they are, nonetheless, not validated as required for subcritical safety limits. The evaluation limit also does not consider all possible fissionable isotopes. While many were examined, HLW streams could possess others.

Significance

The proposed evaluation limit would permit significantly higher quantities of fissile nuclides be included into the vitrified waste form, while concurrently accounting for any non-fissile, fissionable nuclides.

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