Alternative Repository Criticality-Control Strategies for Fissile Uranium Wastes

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ABSTRACT

Methods to prevent long-term, disposal-site nuclear criticality from fissile uranium isotopes in wastes were investigated. Long-term refers to the time period after waste package (WP) failure and the subsequent loss of geometry and chemistry control within the WP. The preferred method of control was found to be the addition of sufficient depleted uranium to each WP so that the uranium enrichment is reduced to <1 wt % \( ^{235}\text{U} \) and <0.66 wt % \( ^{233}\text{U} \) in \( ^{238}\text{U} \).

1. INTRODUCTION

Several types of fissile uranium wastes containing \( ^{233}\text{U} \) or \( ^{235}\text{U} \) require disposal. The wastes vary (1) from contaminated trash; (2) to excess fissile \( ^{233}\text{U} \) and \( ^{235}\text{U} \) which, because of the specific isotopic compositions, may not be suitable for recycle into power reactors; (3) to high-enriched-uranium (HEU) spent nuclear fuel (SNF). A series of studies were conducted to evaluate alternative, long-term, disposal-facility, criticality-control strategies.

2. NEED FOR CONTROL OF NUCLEAR CRITICALITY IN A DISPOSAL SITE

Nuclear reactors naturally occurring in the geological past indicate that such events generate added radioactivity and heat for hundreds of thousands of years. This experience suggests that nuclear criticality can occur under certain conditions in waste disposal sites. Nuclear criticality is to be avoided in a disposal site because it can degrade the performance of the disposal site in protecting the public from the radionuclides. Additional fission products increase the hazards of the wastes. The heat causes higher temperatures that, in turn, (1) accelerate chemical reactions, which then accelerate the degradation of WPs and other man-made barriers to radionuclide release; (2) cause water movement that may transport radioactivity to the open environment; and (3) create uncertainties in disposal facility performance. If the fissionable materials are transported beyond the facility boundaries, nuclear criticality may occur beyond the specific geology chosen to contain the radionuclides.

3. FISSILE URANIUM ISOTOPES ARE THE DOMINANT CRITICALITY CONCERN

Two factors determine whether a fissile isotope may cause nuclear criticality in a disposal site: radioactive decay half-life and geochemistry.

Radioactive Decay Half-Life

Except in the most unlikely and improbable events, only long-lived fissile materials can cause nuclear criticality in a disposal site. For operational safety, fissile-containing wastes are packaged to avoid the potential for short-term nuclear criticality events. Some disposal sites, such as high-level waste and SNF repositories, require WPs that are long-lived and slow to deteriorate. Geological processes that can dissolve and reprecipitate fissile materials into a critical mass (CM) require significant time. Short-lived fissile isotopes decay before they can cause nuclear criticality.

The primary isotopes of concern \( ^{233}\text{U} \left( T_{1/2} = 160,000 \text{ years} \right) , ^{235}\text{U} \left( T_{1/2} = 700,000,000 \text{ years} \right) , ^{237}\text{Np} \left( T_{1/2} = 2,000,000 \text{ years} \right) \) and \( ^{239}\text{Pu} \left( T_{1/2} = 24,000 \text{ years} \right) \) are derived by examination of the half-lives and decay schemes for all fissionable isotopes with half-lives in excess of 1 year, as shown in Fig. 1. The figure also shows the subcritical-mass limits (SCMLs). The CM for a specific isotope is just above the SCML. The fissile uranium isotopes are the primary criticality concerns because of (1) their long half-lives and (2) the decay of other fissile isotopes (including \( ^{239}\text{Pu} \)) into fissile uranium isotopes.

Geochemistry

For criticality to occur, natural geochemical processes must provide a mechanism to concentrate fissile materials into a CM. Geochemical processes concentrate uranium, but not plutonium and neptunium. Plutonium is immobile in most environments. However, neptunium is a major concern in repository design because of its tendency to migrate in groundwater. The same chemical behavior that allows its transport in groundwater also makes the concentration of neptunium into a CM unlikely.
Fig. 1 Decay pathways, half-lives, and subcritical mass limits of fissionable isotopes.
Uranium (of any isotopic makeup) in any disposal site will ultimately dissolve into the groundwater, be transported, and reprecipitate. The same processes that have created uranium ore bodies over the last several billion years still operate on uranium within and beyond a disposal site.

The planet exists under chemically reducing conditions and initially had a chemically reducing atmosphere. With the evolution of life and photosynthesis about two-billion years ago, the atmosphere was converted from a reducing atmosphere to an oxidizing atmosphere. On land, the oxidizing conditions extend from the atmosphere to below the earth’s surface for distances measured from <1 cm (coal deposits, swamps, etc.) to >1000 m. The ocean condition is oxidizing, but sludges on the bottom are, for the most part, under chemically reducing conditions because of the decomposition of organic material.

The solubility of uranium compounds is strongly dependent upon the oxidation conditions of the environment. Under geochemical reducing conditions, uranium is in the +4 valence state, is highly insoluble in water (<1 pph), and is often found as uranium dioxide (UO₂). Under chemically oxidizing conditions, uranium is in the +6 valence state, is 2 to 4 orders of magnitude more soluble than under reducing conditions, and is almost always found as a uranyl (UO₂²⁺) ion. Oxygen dissolved in water will oxidize uranium from the +4 to the +6 valence state. Because of these chemical characteristics, many uranium ore deposits are formed by (1) oxidation of uranium from the +4 to the +6 valence state by oxidizing groundwater (from rain), (2) subsequent dissolution in groundwater, (3) transport in groundwater, and (4) reprecipitation when the groundwater flows through a chemically reducing environment, which reduces uranium from the +6 back to the +4 valence state (Fig. 2). Chemically reducing environments are primarily, but not exclusively, created by organic materials and iron in the +2 valence state and the metal state.

This relatively unusual redox chemistry implies that, unlike most other types of ore deposits, many uranium ore deposits migrate over time. Flowing oxidizing groundwater will also oxidize other reducing agents within the rock. Uranium precipitated by chemical reduction will then be reoxidized, dissolved, transported, and reprecipitated. The uranium remains at the boundary where chemically oxidizing and reducing rock conditions and moves as oxidizing groundwater alters the location of this chemical interface. Such uranium ore deposits are known as "roll-front" deposits, and some of these roll-front deposits have moved many kilometers over long-time periods.

These mechanisms have extracted uranium from rock at concentrations of a few parts per million and created ore bodies with uranium concentrations of several tens of percent by weight. The concentration process separates uranium from most other elements, including boron, cadmium, and rare earths. The only elements consistently found with natural uranium ore bodies are silicon, oxygen, and hydrogen in the chemical forms of silica, silicates, and water. Several other mechanisms also concentrate uranium over long time periods.

4. THREE FATES OF FISSILE URANIUM IN A DISPOSAL SITE

Disposal site uranium has the same geochemistry as natural uranium and behaves similarly in the natural environment. For fissile uranium in a disposal facility, there are three possible fates:

- **Fission.** The earth's geochemistry can concentrate uranium. Most shallow-land disposal facilities and some proposed repositories (e.g., Yucca Mountain (YM)) have geochemically oxidizing conditions. Many other sites will ultimately have oxidizing conditions caused by flow of oxidizing groundwater. Many WP systems contain iron-based alloys or carbon-containing compounds that provide man-made reducing agents within the disposal facility. The same geological processes will occur within the WP, the facility, and beyond the boundaries of the facility with (1) cycles of uranium oxidation, dissolution, transport, and precipitation and (2) continuously changing concentrations and geometries of uranium deposits. This can lead to conditions that allow nuclear criticality and fissioning of uranium, as has occurred in natural uranium ores deposits in the past.

- **Isotopic dilution with natural uranium.** In time, dissolved uranium in groundwater with fissionable concentrations different from those of natural uranium will isotopically exchange with natural uranium in the rock and be isotopically diluted to ~0.7 wt % ²³⁵U and trace quantities of ²³³U if the fissile uranium contains ²³³U. This process eliminates the potential for nuclear criticality.

- **Radioactive decay.** Fissile uranium isotopes decay to nonfissile isotopes. Radioactive decay eliminates the potential for nuclear criticality.

The half-life of ²³⁵U is 700-million years. However, geochemical processes that result in mountain building and destruction by erosion are an order of magnitude faster than this; thus, enriched uranium is preferentially destroyed by fission or isotopic dilution before significant radioactive decay occurs. Determining whether nuclear criticality occurs depends upon (1) the total fissionable material inventory at the disposal site, (2) the fissile concentration of the uranium, (3) the climate of the disposal site and its variation with time, (4) the design of the waste facility, (5) the local geology, and (6) the geochemical evolution of the disposal facility and local geology (uplift, erosion, etc.) over time.
Formation of uranium ore deposits from uranium in rock

Rain

Dissolve uranium in oxidizing groundwater

(\(U^{+4} \rightarrow U^{+8}\))

Roll front uranium deposit

(\(U^{+6} \rightarrow U^{+4}\))

Reducing groundwater

(often uranium)

Reducing geology

(little uranium)

Oxidizing groundwater

Formation of uranium ore deposits from waste containing uranium

Rain

Oxidizing groundwater

Dissolved uranium in groundwater

(U+4)

Uranium deposit

(\(U^{+6} \rightarrow U^{+4}\))

Reducing groundwater

(little uranium)

Degraded waste package with uranium

Iron (waste package, rock bolts, etc.) and organics

Fig. 2. Natural and man-made formation of uranium ore deposits.

5. CRITICALITY CONTROL STRATEGIES

There are alternative criticality control strategies.

- **Predict future evolution of the disposal site.** Current efforts are underway to model the long-term behavior of disposal sites. These efforts include the study of the migration of fissile uranium to determine the probability and consequences of nuclear criticality associated with a disposal site. If the estimated risk from nuclear criticality is judged to be unacceptable, the repository design can be changed so that the risks are acceptable.

- **Add Depleted Uranium (DU).** DU can be added to the fissile uranium in the waste until nuclear criticality is not credible. Having the same chemistry as fissionable uranium, DU is the only neutron absorber that cannot separate from fissionable uranium isotopes via operating geochemical processes over geological time.

The choice of strategy depends upon the requirements. For fissile uranium criticality control, isotopic dilution with \(^{238}\text{U}\) is a preferred technical strategy based on several considerations.

- **Cost.** Criticality considerations can limit the quantity of fissile uranium in a waste stream sent to a disposal site. For 1 kg of HEU, the minimum waste volume is 0.01 m\(^3\) (10 g U/cm\(^3\)) if criticality control is by isotopic dilution with DU to 1 wt % \(^{235}\text{U}\) in \(^{238}\text{U}\) vs 1 m\(^3\) if criticality control is by concentration limits using the Waste Isolation Pilot Plant (WIPP) criticality control strategy. WIPP controls nuclear criticality by concentration limits on fissile materials in the wastes. The corresponding numbers for \(^{233}\text{U}\) are 0.02 m\(^3\) and 1 m\(^3\). The addition of DU to fissile uranium waste streams may result in the counter-intuitive result of minimizing waste volumes. This result is a consequence of changing the approach to criticality control from a concentration control mechanism to isotopic dilution.
The U.S. Nuclear Regulatory Commission (NRC) analyzed use of geometry control to prevent nuclear criticality from HEU in shallow-land disposal sites. That analysis also indicated serious restrictions on the areal density of fissile uranium in a burial ground when criticality control is based on geometry rather than isotopic dilution.

- **Precedent.** An analysis for disposition of surplus HEU that is declared as waste (because the mix of uranium isotopes make it uneconomic for use in power reactors) concluded that the uranium enrichment should be reduced (potentially to as low as 0.9 wt % $^{235}$U in $^{238}$U) for long-term criticality control.

- **Licensing and acceptance within the technical community.** The Nuclear Waste Technical Review Board—the Congressionally-mandated independent technical review board for the YM project that makes recommendations to Congress and the U.S. Secretary of Energy—analyzed long-term repository criticality issues associated with the proposed YM repository and stated: “Although external (to the WP) criticality may be unlikely, it can not be dismissed without thorough analysis. The Board understands that DOE intends to use probabilistic risk analysis methodology to address external criticality. While such an approach is appealing, it may turn out to be costly and time-consuming to the point of impracticality in a repository context because of the very large number of events and geometric configurations possible in a repository. . . .” The board subsequently recommended the consideration of the use of DU for control of nuclear criticality in such facilities. This board recommendation reflects the perspective of much of the scientific community that we do not currently have the ability to predict migration of uranium and, thus, the potential for nuclear criticality for high-assay fissile uranium waste streams.

6. **REQUIRED ISOTOPIC DILUTION OF FISSILE URANIUM**

If isotopic dilution (addition of $^{238}$U) is to be used to minimize the potential for nuclear criticality, the technical question is: How much DU is required? There are both direct and indirect geological data on nuclear criticality in the natural environment that can provide this information:

- **History.** The historical geological record shows that nuclear criticality has occurred in natural uranium ore bodies. For example, 16 natural nuclear reactors have been identified at Oklo, Gabon, Africa. The nuclear chain reactions began when the $^{235}$U enrichment of natural uranium was about 3.6 wt %. After operation and the ensuing generation of heat and fission products, $^{235}$U enrichments of the uranium were as low as 1.3 wt %—equivalent to 0.74 wt % $^{233}$U in DU with a $^{235}$U content of 0.2 wt %. Today, natural uranium deposits have a $^{235}$U enrichment level of 0.71 wt % because of the long-term decay of $^{235}$U. Nuclear criticality can no longer occur in natural uranium ore bodies under geological conditions because of these low enrichment levels.

- **Geochemical modeling of uranium ore deposits.** The Commissariat a L'Energie Atomeique (French Atomic Energy Commission) has studied the conditions during which natural nuclear reactors (ore deposits) form during the concentrating of uranium from rock. The analysis indicates that nuclear criticality may occur at enrichments as low as 1.28 wt % $^{235}$U in $^{238}$U and that criticality becomes reasonably probable in some geological environments as enrichments approach 1.64 wt % $^{235}$U in $^{238}$U. Others have estimated that criticality may occur in natural environments with enrichments approaching only 1 wt % $^{235}$U in $^{238}$U.

- **Geochemical modeling of low-level radioactive disposal sites.** The NRC has modeled shallow-land disposal sites to determine the potential for nuclear criticality from enriched uranium. The analysis indicates a significant potential for nuclear criticality because of geochemical concentration processes unless the fissile content in the waste is severely restricted or the fissile uranium is isotopically diluted with DU.

There is a large industrial experience in criticality control. Waste process equipment, waste tanks, low-level waste disposal sites, and other waste management facilities contain wastes with small quantities of enriched uranium. In many facilities, it is not practicable to control the system geometry, the chemistry, or the presence of neutron absorbers. Based on analysis and experiments, many sites require isotopic dilution of $^{235}$U with $^{238}$U to ensure that nuclear criticality does not occur. For example, Oak Ridge National Laboratory requires that any uranium sent to the liquid process waste system contain at least 100 parts $^{238}$U per part $^{235}$U.

The previous data suggest that a reasonable strategy to prevent nuclear criticality in disposal facilities is to require sufficient DU fill in each WP such that the ratio of $^{235}$U to $^{238}$U is $<1$ wt % $^{235}$U equivalent. The 1 wt % is also the homogeneous criticality limit for $^{235}$U in an optimized system containing water and silicon oxide. Such a limit can be extended to any other fissionable uranium isotope by determining the corresponding homogeneous criticality limit for that specific isotope in a system containing the isotope, water, and silicon oxide. This has been done for $^{233}$U with the result that 1 wt % $^{235}$U in $^{238}$U is equivalent to 0.66 wt % $^{233}$U in $^{238}$U or 0.53 wt % $^{235}$U in DU with a $^{235}$U content of 0.2 wt %.
A large excess of DU exists worldwide that far exceeds the potential needs for criticality control. Currently, no substantial use exists for this material. In the United States, about 400,000 t of DU is in storage. The U.S. Department of Energy (DOE) is currently looking for potential uses for this material.

7. THREE APPROACHES TO USE OF DU

There is a growing knowledge base on methods of adding DU to wastes to address criticality concerns. Three examples are described in the following.

HEU

DOE has decided to dispose of excess HEU. Where economically justified, the HEU will be converted to low-enriched uranium (LEU) to be used as fuel in nuclear power reactors. HEU is converted to LEU by addition of LEU, natural uranium, or DU. For HEU not suitable for conversion to power reactor fuel (because of other uranium isotopes), the HEU is to be isotopically blended with DU and disposed of as waste. The final enrichment level is to be below 1 wt % to minimize the potential for nuclear criticality in disposal facilities.

Light-Water Reactor (LWR) SNF

An advanced WP concept is being developed to improve geological repository disposal of LWR SNF by (1) reducing the potential of radionuclides leaving the WP over long time periods and (2) minimizing the potential for long-term nuclear criticality in a geological repository. The WP is filled with SNF, then depleted UO₂ in particulate form is poured into the WP to fill all the void spaces including SNF coolant channels.

The use of DU reduces the potential for nuclear criticality. A SNF WP has many CMs of fissile material and thus the potential for criticality by both selective leaching of conventional neutron absorbers (boron) from the WP and by long-term dissolution, migration, and precipitation of uranium. Because DU dioxide has essentially the same chemical behavior as LWR SNF UO₂, the DU will also be dissolved, mixed, and transported along with the SNF uranium and thus prevent nuclear criticality. Analysis and experiments indicate that the 239Pu will decay to 235U before significant dissolution of the DU occurs. DU is the only material with the same geochemical characteristics as SNF uranium and thus will not separate from SNF uranium over time.

For this application, existing data indicate that perfect isotopic mixing in the waste is not required for long-term criticality control. The requirement is that the 233U and DU mix from multiple WPs as the WPs degrade and uranium is dissolved, transported, and precipitated. Uranium in a WP, over time, will be found in multiple chemical forms. The uranium dissolution process is a multistep process. Fortuitously, laboratory experiments indicate that the dissolution rate-limiting step is the same for different uranium compounds. Because of this characteristic of uranium dissolution, perfect mixing of 233U with DU and converting all uranium to the same chemical form within a single WP is not required for long-term criticality control.

For wastes that are being packaged for disposal, the following approach may be used: Determine from records or measurements the quantity of 233U in the waste and then add DU in oxide form to the WP or in an appropriate form to the waste process as the 233U-containing wastes are added. For packaging of dry waste, DU may be added as prepackaged uranium oxides in paper, cloth, or plastic bags with an appropriate number of bags added to each waste drum to address long-term criticality issues. DU oxides are preferred because they are relatively chemically stable. The use of prepackaged DU oxides avoids potential handling difficulties (e.g., dusting). If the activity is packaging the wastes in drums, the only performance requirements on the bags are that they do not fail during handling operations and that they degrade and fail more rapidly than uranium dissolves in groundwater. Most plastic, paper, and cloth materials meet these requirements.

8. CONCLUSIONS

Fissile uranium isotopes are the primary potential cause of long-term (after WP failure) criticality in a disposal site. The addition of DU to WPs can minimize the potential for nuclear criticality and provides the easiest method to demonstrate criticality control. Excess DU is available.
REFERENCES


