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Weapons-Grade Plutonium Disposition: An Alternate Immobilization Strategy

by

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Abstract

A strategy for the disposition of US and Russian surplus Pu is proposed. The US would, in cooperation with Russia, immobilize its Pu with sufficient rare earth neutron poisons to comply with expected regulatory limits for subcriticality in a geologic repository. If proven feasible, remote tracking capability would be added as an integral part of the matrix as a deterrent for unauthorized diversion. Russia would retain the right to retrieve the Pu for direct use in civilian nuclear fuel. Alternatively the US could compensate Russia for the fuel value of its dispositioned Pu. A market based method for pricing Pu using derivative theory is proposed. Plutonium is valued as a European call option on the equivalent amount of uranium fuel. With the assumed parameters the maximum value of holding 50 tonnes of WGPu (with no storage costs) was found to be $524 M.

The environmental durability of a Pu loaded borosilicate glass was investigated. Leach tests in deionized water at 90 °C demonstrated that the durability of the reference glass, which contained simulated fission products, was not affected by the addition of an analog for Pu in glass (Th) and several rare earth elements (Eu, Gd, Sm) each at 2 wt% (oxide). After one year of testing, leachate concentrations for the added elements remained at or below instrumental (ICP-AES) detection limits. A coupled glass dissolution and criticality model was developed to assess the potential for a repository criticality event. Bounding calculations indicated that the reference waste glass could reach a critical state due to glass reaction with groundwater, and subsequent boron removal, at weapons-grade PuO_2 loadings greater than 0.45 wt%. The addition of relatively small quantities of rare earth elements was shown to increase the predicted time to criticality to millions of years, however indefinite subcriticality could not be assured under the assumed conditions.

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1.0 Introduction

Historic achievements in arms control were the catalyst for an international debate on surplus weapons-grade plutonium disposition. For the first time, superpowers are developing strategies for eliminating a portion of their nuclear stockpiles. While the reductions are welcomed, managing the fissile materials from retired warheads is a complex technical and political challenge. To be implemented, any proposal must satisfy constraints imposed in both areas

The nuclear arms race is estimated to have produced more than 200 metric tonnes (MT) of weapons-grade plutonium (WGPu).[1] Surplus and scrap WGPu represents a proliferation hazard and to some a fuel source of the future. No longer needed for mutually assured destruction, the question becomes "how should surplus plutonium be managed?" Each country will assess the question from decidedly different perspectives.

Russia is facing uncertain times as a newly democratic nation. It has a transition economy struggling to provide basic goods and services, and compensation for its people. This instability provides adequate reason for avoiding non-essential expenditures and focusing on near-term revenues when possible.

To some degree the management of surplus special nuclear material has reflected this larger reality. Russia has welcomed the opportunity to blend and sell its highly-enriched uranium (HEU) as low-enriched uranium fuel. However, an acceptable market for WGPu does not exist. Absent of a financial incentive to act, Russia continues to store its plutonium as part of its long-term energy policy.

The United States is Russia's opposite in these areas. It has relatively stable economic markets with no official energy policy. In the US, plutonium is presently viewed as an uneconomical energy resource. The official government policy is to not encourage the use of a Pu fuel cycle due to the associated proliferation risks.

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[1] Data taken from Albright (1993: 34 and 37). US 97 MT and Russia 115 MT.

While steps are underway to blend its HEU, the US also views surplus WGPu as a "clear and present danger." The US is vigorously pursuing alternatives to process its Pu to meet the Spent Fuel Standard.[2] While Russia has expressed little interest in US plutonium activities, a major objective of the US plan is to spur Russian action. The storage of Pu in Russia during a period of economic and political volatility is a source of concern for the US. Clearly each country has different objectives and priorities related to surplus plutonium.

In the present work, a strategy for WGPu disposition has been developed by the author that is sensitive to technical realities, national objectives and future uncertainties. The option of immobilizing surplus Pu without fission products was deemed attractive as it provides a relatively quick and inexpensive way to move the material to a verifiable, safe and disposable form.

While adding a radiation barrier may provide some security benefits there are risks. Requiring Pu to be treated as either a fuel or a waste is likely to cause disposition delays. Russia will not dispose of its potential fuel source and the US is reluctant to finance Pu fuel cycle investments in Russia. In contrast, processing Pu into large, environmentally durable, matrices without fission products could be supported by both nations. Such a form would be easily verified and safeguarded, providing virtually all the nonproliferation benefits attainable by material processing. Adding remote tracking capability as an inherent part of the matrix would provide security approaching that of the Spent Fuel Standard, if not exceeding it.

A complementary strategy was also devised to compensate Russia for any WGPu she would transfer to the US for dispositioning. A market based valuation of Pu was performed using derivative theory. The reasoning and methodology used to develop both strategies are outlined in the remaining chapters.

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[2] The Spent Fuel Standard seeks to make excess Pu from weapons as inaccessible and unattractive for weapons use as the much larger quantity of plutonium that exists in spent fuel.

Chapter 2 provides a description of WGPu issues and national initiatives. In Chapter 3 the system analysis used in strategy formulation is discussed and a proposal for WGPu disposition is presented. Disposition objectives were identified and various processing steps evaluated to determine their effect on postulated proliferators. Chapter 4 contains a technical evaluation of WGPu vitrification. The environmental durability of a glass matrix was experimentally tested. A coupled dissolution and criticality model was used to assess the potential for criticality in a geologic repository. Chapter 5 proposes a financial strategy for pricing Pu so that the US could purchase Russian WGPu or allow vitrification to proceed in Russia. Chapter 6 contains a summary of the work performed and presents the conclusions. The appendices contain detailed data, calculations and analyses as referred to in the body of the thesis.

2.0 Background for Surplus Pu Management

2.1 Arms Control Agreements

Weapons-grade plutonium (WGPu) will be retired from military use in Russia and the US as a result of a series of arms control treaties. The Intermediate-Range Nuclear Forces Treaty (INF) was signed December 8, 1987 by President Reagan and General Secretary Gorbachev. The Treaty called for the dismantling and destruction of the delivery systems for all intermediate and shorter range missile systems in the US and the (then) Soviet Union. The treaty was ratified on June 1, 1988 and by May 1991 the US had eliminated all of its delivery systems covered under the treaty.[3]

The Strategic Arms Reduction Treaty (known as START I) was signed by President Bush and General Secretary Gorbachev on July 31, 1991. The intent of this treaty was to reduce stockpiles of strategic weapons to equal aggregate levels. The initial goal was to limit the number of strategic warheads to no more than 9,000 in each country. Follow-on agreements (Memoranda of Understanding) have placed the limits at 8111 warheads for the US and 7984 warheads for Russia.[4] The Treaty entered into force on December 5, 1994 and is scheduled for completion in 15 years.[5]

On January 3, 1993, and before START I was ratified, Presidents Bush and Yeltsin signed a treaty to pursue further strategic arms reductions. Under the so-called START II Treaty, the number of strategic warheads would be reduced to 3,000 for Russia and 3,500 for the US by the year 2003. This agreement effectively encompasses START I by requiring lower warhead levels to be achieved by an earlier deadline.

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[3] The INF Treaty does not require the actual dismantlement of nuclear warheads.

[4] US Arms Control and Disarmament Agency, Office of Public Affairs, April 1, 1997. Information related to the START treaties can be obtained through the US ACDA web site: http://www.acda.gov.

[5] After the dissolution of the Soviet Union on Dec. 25, 1991 a separate agreement called the Lisbon Protocol was signed that made the new republics Belarus, Kazakhstan, Russia and Ukraine Parties to START I.

The two Presidents further agreed that, once the START II Treaty is ratified, the US and Russia will deactivate all delivery systems covered by START II by removing their nuclear warheads or taking other necessary steps to remove them from combat status. They also expressed a desire for additional strategic arms reductions in the future.

Execution of the START agreements will reduce the number of deployed, strategic warheads for each country by more than 70%.[6] Adding warheads from tactical weapons scheduled for dismantling, the US could have as many as 15,000 retired warheads to disposition.[7] The total number of strategic and tactical warheads for Russia is unknown but is expected to be greater than that of the US. Using official CIA estimates for the number of Russian tactical weapons, the total number of Russian warheads for retirement is between 14,000 and 22,000.[8]

These arms control agreements contain detailed verification and monitoring protocols to eliminate nuclear equipped missiles, aircraft and launchers. However, provisions for the elimination of the fissile materials to be removed from dismantled warheads were not included.

2.2 Inventories of Separated Pu in Russia and US

The total US inventory of all grades of Pu (both in the Department of Energy and Department of Defense) is 99.5 MT (OFMD 1996b: Ch.1 p.2). This includes 85 MT of WGPu (<7% Pu-240), 13.2 MT fuel grade (7-19% Pu-240), and 1.3 MT of RGPu (>19% Pu-

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6. It is estimated that the US had 12,646 deployed strategic warheads and Russia had 11,012 in 1990 (Mendelsohn 1992).
7. Of the estimated 8,000 US warheads from tactical weapons, 1,600 are likely to be retained (NAS 1994: 40).
8. Some estimates of the initial Soviet stockpile are much higher and could mean that 30,000 Russian warheads or more could ultimately be retired (NAS 1994: 41).

240).[9] The Russian inventory has been estimated at a total of 140 MT of Pu but Russia has not made public the true value.

With an assumed mass of 4 kg WGPu per warhead the US would have 60 MT and Russia 56 to 88 MT of Pu to disposition as a result of the arms control treaties described in Section 2.1. The Pu inventories of each country are categorized in Table 1.

TABLE 1. Estimated Plutonium Inventories (metric tonnes)

	US[1]	**Russia**
Deployed (START II Levels)	14	12
Retired (post-START II)	60	56-88[2]
Other Military Use	25.5	15-47[3]
Separated Civilian	~0	25[4]
Total	99.5	140

1. US figures taken from declassified DOE data.
2. CIA estimates (NAS 1994: 41)
3. Based on an estimated total production of 115 MT of WGPu (Albright 1993: 37).
4. (Albright 1993: 109).

The 25.5 MT figure in Table 1, for US Pu other than that deployed in or retired from warheads, includes 7 MT of Pu in the form of scrap and residues (Dalton 1995). However, this relatively small amount of Pu is contained in over 200 MT of solid residues and 400 MT of solutions. The amount of Pu in scrap form in Russia is unknown and may be very small. The Russians have stated that they reprocessed their scrap material to retrieve any Pu.[10]

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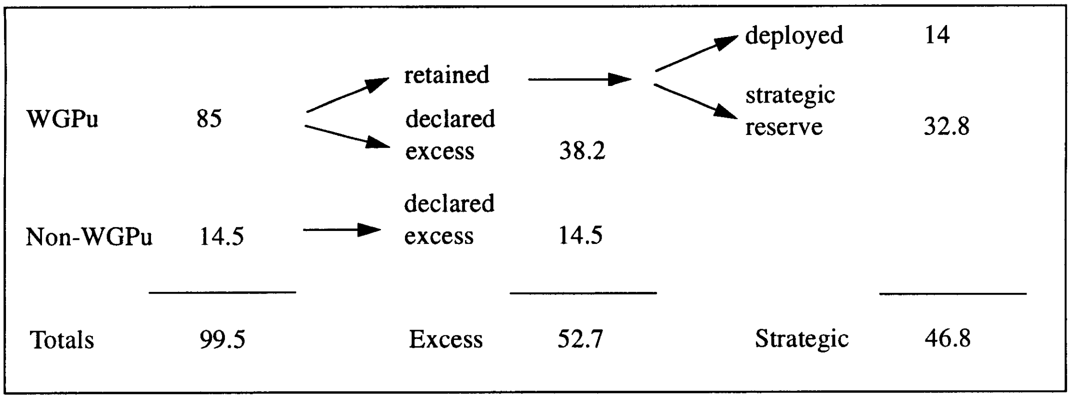
[9] The isotopic concentration of Pu-240 in Pu determines its classification as the spontaneous fission of this isotope increases the potential for predetonation in an explosive device. The effect of Pu isotopics on weapons design is discussed in Section 2.9.

[10] Communication with Matthew Bunn, former Plutonium Study Director, National Academy of Sciences. April 17, 1997.

On March 1, 1995 President Clinton declared 38.2 MT of WGPu Surplus to national security needs.[11] The DOE has also designated all of its non-WGPu as excess to national security needs (GAO 1997: 6). Figure 1 describes the how Pu in the US stockpile will be designated after START II is implemented.

FIGURE 1. Post START II Pu Stockpile Configuration (quantities in MT)



On the basis of present arms control agreements and official declarations a total of 52.7 MT will be dispositioned in some manner. If no further arms reductions are pursued, 14 MT will remain deployed and a strategic reserve of 32.8 MT of WGPu will be maintained. The following section describes how the present US disposition framework developed.

2.3 US Disposition Framework

In a speech before the United Nations on September 27, 1993 President Clinton announced a series of initiatives designed to reduce the risk of nuclear weapons proliferation. The President stated that the US would "seek to eliminate where possible accumulation of stockpiles of highly enriched uranium or plutonium and to ensure that where these materials already exist they are subject to the highest standards of safety, security, and international accountability" (Clinton 1993).[12] He also called for "a comprehensive

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[11] Bill Clinton, Address to the Nixon for Peace and Freedom Policy Conference and the Department of Energy, March 1, 1995.

[12] White House Press Release, Office of the Press Secretary, September 27, 1993.

review of long-term options for plutonium disposition, taking into account technical, nonproliferation, environmental, budgetary and economic conditions." President Clinton invited Russia and other nations with relevant interests and experience to participate in the study. This set of initiatives was termed the U.S. Nonproliferation and Export Control Policy.

In a related press release the President reaffirmed US Pu fuel cycle policy. The policy reads: "The United States does not encourage the civil use of plutonium and, accordingly, does not itself engage in plutonium reprocessing for either nuclear power or nuclear explosive purposes."[13] However, it was also noted that the policy does not prevent the US from maintaining existing commitments involving the civilian Pu programs of Western Europe and Japan.

In January of 1994 President Clinton and President Yeltsin issued a joint statement on nonproliferation of weapons of mass destruction and means of their delivery. The presidents stated that the proliferation of such systems represents "an acute threat to international security in the period following the end of the Cold War."[14] They also established a joint working group to investigate ways of ensuring the transparency and irreversibility of arms reduction.

As a result of these policies the following US nonproliferation objectives were adopted (OFMD 1996a: S-1):

1. secure nuclear materials in the former Soviet Union;
2. ensure safe, secure, long-term storage and disposition of surplus fissile materials;
3. establish transparent and irreversible nuclear reductions;
4. strengthen the nuclear nonproliferation regime; and
5. control nuclear exports.

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[13] ibid.

[14] Office of Fissile Materials Disposition, US Department of Energy, "Strategic Plan," September, 1995.

To coordinate the DOE's disposition efforts, the Office of Fissile Materials Disposition was formed. The Office was given responsibility for "all activities of the Department relating to the management, storage and disposition of fissile materials from weapons and weapons systems that are excess to the national security needs of the United States."[15]

A major portion of OFMD's responsibility was to analyze disposition options and prepare a Programmatic Environmental Impact Statement (PEIS). The PEIS attempts to identify any significant environmental impacts from long-term storage or disposition of WGPu as required by the National Environmental Policy Act (NEPA). The results of this assessment were to be combined with nonproliferation and technical assessments to aid the Secretary of Energy's Record of Decision (ROD). The ROD determines a course of action for the Department. Following a decision, a detailed Environmental Impact Assessment is required for activities to be undertaken pursuant to the ROD. The PEIS has been completed and a ROD issued. Both documents are discussed later in this chapter.

2.4 National Academy of Sciences Report on Pu Disposition

At the request of the National Security Advisor in President Bush's administration, the National Academy of Sciences' Committee on International Security and Arms Control (CISAC) was asked to perform a study of the management and disposition options for plutonium. The CISAC committee is comprised of a variety of distinguished scientists, engineers, and policy experts. Their report entitled "Management and Disposition of Excess Weapons Plutonium" was published in 1994.

The NAS Report included several recommendations related to fissile material management. It encouraged a reciprocal and transparent regime for monitoring warhead dismantlement in Russia and the US, and a halt in the production of fissile materials for weapons. The Committee recommended the application and improvement of safeguards for fissile materials both from weapons and other sources.

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[15] The National Defense Authorization Act for Fiscal Year 1995 (P.L. 103-335)

Regarding disposition of excess Pu, the Committee identified several objectives (NAS 1994: 2):

1. minimize the time during which the plutonium is stored in forms readily usable for nuclear weapons
2. preserve material safeguards and security during the disposition process, seeking to maintain the same high standards of security and accounting applied to stored nuclear weapons
3. result in a form which the plutonium would be as difficult to recover for weapons use as the larger and growing quantity of plutonium in commercial spent fuel; and
4. meet high standards of protection for public and worker health and for the environment.

Of particular interest to the development of Pu disposition alternatives is the third NAS objective listed above. This recommendation was formalized into the Spent Fuel Standard (SFS). The Committee determined that all surplus Pu should be processed so that it meets this standard.

The NAS report stated that disposition options that did not meet this standard would represent "a unique safeguards problem indefinitely" (NAS 1994: 12). It was also noted that going beyond the standard would not be justified unless the same treatment was performed on the much larger stocks of Pu presently found in spent fuel. As this seemed unlikely, due to the enormous cost and complexities, the SFS was adopted.

The Standard was subsequently revised by the DOE. The more precise disposition goal was restated as: "to make the plutonium as unattractive and inaccessible for retrieval and weapons use as the residual plutonium in the spent fuel from commercial reactors" (OFMD 1996c: ES-1). The word *unattractive* was added ostensibly to avoid debate regarding the inaccessibility of various Pu matrices. The modification is widely interpreted as requiring a radiation barrier.[16] However, no specific measurable parameters were, nor have been, established to determine compliance with the Standard.

The Standard has become the basis for the administration's disposition activities. The Standard was used by the OFMD in its screening of options for inclusion in its disposition PEIS as described in Section 2.7. Indeed it has received international attention. At the Nuclear Safety and Security Summit in April of 1996, the Leaders of the P-8 countries expressed support for the Standard. It has had a major impact in defining and bounding the national and international debate on surplus Pu management.

The NAS report identified several preferred options for meeting the SFS. The primary two were burning the Pu in existing or modified reactors and vitrification with high-level waste. The option of disposing of Pu in deep boreholes was mentioned as potentially having comparable benefits but had not been studied as extensively. As the borehole option was ultimately not chosen as part of the preferred US disposition strategy it is not discussed further in this document.

Reactor Burning

Surplus WGPu can be fabricated into mixed-oxide fuel (MOX) and used to produce energy in a reactor. The exposure to a thermal neutron flux would reduce the isotopic concentration of fissile isotopes in the Pu. A portion of the Pu would also be eliminated. Complete elimination of Pu in present light-water reactors (LWRs) is not possible in a once-through cycle unless non-fertile fuels are utilized. If U-238 is present in the fuel additional Pu will be bred as the fuel is burned. By definition the Pu matrix produced by this form would meet the SFS.

The prospect of using current LWRs as well as new reactors in the US, Russia and Canada was evaluated. While the US has no industrial MOX fabrication capability, Pu fuel has

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[16] Actually a radiation barrier would not be required for the direct disposal in deep boreholes or space disposal options.

been fabricated and burned in LWRs for a number of years in Europe. The Committee did not identify any technical difficulties associated with this option.

If new reactors were to be built the Committee recommended proven designs rather than advanced (e.g. liquid metal, high temperature gas cooled, etc...). They predicted that costs and delays in the licensing of advanced reactors would make them inferior to other options.

Vitrification

In this disposition alternative, WGPu would be mixed with radioactive high-level waste (HLW) and immobilized via vitrification (turning into glass). Aqueous HLW produced during the chemical processing required to retrieve Pu from irradiated fuel would be used.

The process involves mixing preprocessed HLW with glass forming elements and heating to the requisite temperature. The melt is then poured into stainless steel canisters, decontaminated, sealed and allowed to cool. The Academy considered that the presence of radioactive elements and other chemical constituents in a multi-tonne glass 'log' would approximate the diversion barrier of spent fuel. Therefore the Academy affirmed that vitrification with HLW would meet the SFS.

The US currently has an operating HLW vitrification facility in Aiken, South Carolina. The Defense Waste Processing Facility (DWPF) is scheduled to operate until 2021 and will vitrify the roughly 430 MCi of radioactive waste at the site.[17]

The NAS found this approach to be technically feasible but noted further research was needed. In particular the Report noted the potential problem of repository criticality in Pu loaded glass logs. Over extended periods of exposure to groundwater, sufficient neutron absorbers could migrate from the near-field to induce criticality. Plutonium has a half-life of 24,000 yrs and decays to fissile U-235. Uranium can be relatively insoluble as well. Criticality is a concern as fresh fission products would be given an aqueous transport path-

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17. US Department of Environmental Management (1995: Table 2.2).

way, potentially to the biosphere. Such concerns during processing or in a repository could force a reduction in Pu loading.

In characterizing the security risks from surplus Pu, the NAS report identified the risk of theft of nuclear weapons in Russia as "serious" (NAS 1994: 45). The Soviet system of security relied heavily on command and control to protect its weapons and sensitive nuclear material. The Committee noted that while weapons seemed to remain under firm control in Russia, other fissile material in Russia was at risk.

At the time the NAS report was written, dozens of unconfirmed thefts had been reported. The Minister of Atomic Energy, Viktor Mikhailov confirmed one theft of HEU and noted that "many people in Russia live on the edge of poverty and there is a great temptation to steal in these plants."[18] The following section further describes the security of fissile materials stored in Russia and several proposals to mitigate nonproliferation concerns.

2.5 Security in Russia

Concern over the control of sensitive nuclear material in the former Soviet Union prompted US legislative action. In order to combat the immediate risk of theft Congress passed The Soviet Nuclear Threat Reduction Act of 1991, also known as the Nunn-Lugar Act. The primary purpose of Nunn-Lugar was to support the safe secure storage, transportation and dismantlement of nuclear weapons in the New Independent States (NIS). This legislation provided the funding authority for several US nonproliferation initiatives.

The act provided funding for the Cooperative Threat Reduction Program for a variety of activities in the NIS. The Program provided equipment and services to aid the dismantling and actual destruction of weapons delivery systems and secure nuclear material. Assistance was also given to support the return of warheads to Russia as required under the Lisbon Protocol.

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[18] Reported in NAS (1994: 46) from an interview conducted by Elizabeth Martin, "A Conversation with Viktor Mikhailov," NUKEM Market Report, October, 1993.

In order to promote demilitarization, the CRT promoted defense conversion industrial partnerships. This effort provided US funds to support joint ventures between US companies and NIS weapons scientists. This was designed to reduce the incentive for weapon designers to sell their skills abroad.

In the area of Material Protection, Control and Accounting (MPC&A,) the Nunn-Lugar Program was less successful. A series of failed negotiations prevented any meaningful improvements in this area until June of 1995. At that time an agreement was reached to improve MPC&A at five sites in Russia. The sluggish start was blamed in part on US requirements to "buy American" whenever possible (Allison 1996: 83). Failure to purchase Russian goods and services did not foster cooperation.

Efforts to build a storage facility for the fissile components of dismantled Russian warheads have generated similar results. Funded by the Nunn-Lugar Program in 1992, disagreements of inspection rights and details related to the specific materials to be stored in the facility have produced many delays. The facility will store only intact weapon components. While construction commenced in 1994, the facility is not scheduled to open until 1998 at the earliest.

In contrast a US-funded collaboration between weapons laboratories in each country was somewhat more effective. This smaller initiative did not have to meet the procurement requirements of the Nunn-Lugar Program and was free to spend US money in Russia. Within a year, new fences, portal monitors, alarms and other security devices were installed at the Kurchatov Institute which contained more than 150 lbs of HEU. Similar success were obtained at sites containing other sensitive material. However, it has been noted that US MPC&A programs have not targeted the largest Russian facilities where much greater quantities of fissile material exist (Allison 1996: 101).

Unfortunately the improvements in MPC&A did not stop reports of unauthorized diversion in Russia. During Senate testimony in 1996, John Deutch, then Director of the Central Intelligence Agency, described four confirmed thefts of weapons-usable material. This included thefts of 6 grams of Pu, a single gram of HEU, and approximately 500 grams of a Pu/U mixture (Deutch 1996: 9). The most significant was a case involving three kg of HEU in December of 1994.

Dr. Deutch also stated that while theft from non-Ministry of Defense sites was more likely, insider theft at a weapons facility was still a concern. Citing a Russian source, Deutch said that warhead accounting procedures were so bad that an officer with access "could remove a warhead, replace it with a readily available training dummy, and authorities might not discover the switch for as long as six months."

Several proposals have been made to address security concerns in Russia. Thomas Neff of MIT proposed a direct purchase of Russian HEU. The US, through its legislated executor the US Enrichment Corporation (USEC), approved the purchase of 500 MT HEU over 20 years. The uranium, blended to LEU, had an estimated value of $12 B.

Due to its structure, the execution of the HEU agreement has been problematic. USEC is not required to purchase any uranium from Russia. Indeed if a price cannot be negotiated that is favorable to USEC it has been demonstrated that a purchase will not be executed. If executed as proposed the purchase would be a major arms control success. This plan is described in more detail in Chapter 6.

Removal of Pu from Russia via a direct purchase has also been proposed. Brian Chow of the RAND Corporation suggested a price based on the value of equivalent uranium fuel in LWRs. The author presents another approach to valuing Pu in Section 5.0.

The NAS study considered a US purchase of Russian Pu but did not recommend it as a primary objective. The Committee determined that if it were only limited to excess Pu, significant amounts of Pu remaining in Russia would still represent a threat (NAS 1994: 129). It also noted that the purchase could not be justified based on economics as a legitimate market does not exist for Pu.

If incentives were to be pursued the Academy stated that they should be carefully negotiated such that additional reprocessing was not encouraged. Despite advising flexibility on financial incentives for Russia, the NAS criticized the option to burn Pu in Canadian reactors due to the likelihood of having to "pay Russia for the Pu as well."

The reluctance to transfer funds to Russia seems prevalent in US disposition policy. The HEU deal provides Russia with a market price for her HEU, but the US government is not contracted to provide funds for the material. The effectiveness of the Nunn-Lugar program was reduced due to spending restrictions in Russia. Indeed others have noted that many US legislators view security projects in Russia as unpopular foreign aid (Allison 1996: 136).

2.6 Russian Disposition Strategy

Russia has recognized the importance of WGPu disposition and has expressed interest in progressing with the US. Indeed the US will not process its Pu until equivalent action has been taken on Russian Pu (MacDonald 1996). However, it has been repeatedly stated that the technology used will not necessarily be the same.

From the beginning of Pu disposition discussions, Russia has made clear its intention to use Pu in a MOX fuel cycle. This represents a continuation of Soviet plans to develop a closed nuclear fuel cycle utilizing fast reactors. Russia presently has two experimental fast reactors, a BN-600 in Russia and a BN-350 in Kazakhstan that have operated primarily on HEU (NAS 1994: 242). It also has several small scale Pu fuel fabrication facilities and is constructing a large MOX facility at Chelyabinsk. Construction is 50% complete but has been halted for several years due to lack of funds.

Minatom wishes to use surplus WGPu in commercial-scale 800 MW fast reactors (BN-800 reactors) initially operating in a once-through cycle.[19] It has plans to construct 3-4 of these reactors when funding can be attained. Russia could burn Pu in the VVER-1000 (LWR) reactors that it possesses or sell MOX fuel abroad. However, pending the completion of its MOX fabrication facility, Russia's current plan is to store its separated Pu.

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[19] Working Group on Plutonium Disposition, "Interim Report to the President's Advisor on Science and Technology," December 12, 1994.

To aid the Russian disposition effort the US could fund the completion of Russian MOX fabrication facilities and/or fast reactors. Alternatively, proposals have been made to fabricate Russian Pu into MOX in European plants, presumably with US financing (von Hippel 1994). However, on the surface these approaches would appear to be in direct conflict with US Pu fuel cycle policies.

Immobilizing Russian Pu with HLW would have a higher probability of US financial support. It has been reported that 250,000 m^3 of liquid radioactive waste with 570 MCi exists in tanks in Russia (Kushnikov 1995: 25). Another 400 million m^3 with 700 MCi is stored in open ponds and pools. For comparison, the Savannah River Site currently possesses 432.5 MCi of HLW and Hanford 324.4 MCi.[20] However Russia has flatly rejected any proposal that would not extract the fuel value of the Pu.

Even if Russia could afford to build the required infrastructure today, it may not not burn its WGPu first. It has been proposed that WGPu burning would not proceed until RGPu has been depleted (Kushnikov 1995: 29). This is likely due to the buildup of Am-241 which is a radiological hazard due to its 60 keV gamma.

2.7 Programmatic Environmental Impact Statement

As mentioned in Section 2.3, the Office of Fissile Material Disposition was tasked with producing a Programmatic Environmental Impact Statement (PEIS) for Pu disposition. For the immobilization option a screening process was necessary to identify options for full evaluation in the PEIS.

The PEIS screening process had a major impact on the US disposition program. The results of the screening not only identified potentially environmentally acceptable options but define which alternatives were to be studied at all.

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[20] Data taken from US Department of Environemental Management (EM 1994)

The screening process began by gathering information from a variety of resources. The NAS report, various technical summaries and expert briefings were used to identify alternatives for consideration. This produced thirty-seven distinct options for Pu disposition (OFMD 1995: Ch.1 p.5). These options were organized into categories: continued storage, direct disposal, immobilization with radionuclides, and reactor/accelerator consumption.

An initial screening was performed to eliminate 'unreasonable' alternatives. Eliminated options were deemed to have a fatal flaw relative to disposition criteria. The criteria were selected to reflect the policy objectives of the US Nonproliferation And Export Control Policy of September 1993 (see Section 2.3) and the analytical framework set forth by the NAS Report. The adopted criteria were (OFMD 1995):

1. Resistance to Theft or Diversion in Processing and Storage
2. Resistance to Retrieval, Extraction and Reuse
3. Technical Viability
4. Environmental Health and Safety (EH&S)
5. Cost Effectiveness
6. Timeliness
7. Cooperation With Russia and Other Countries
8. Public and Institutional Acceptance
9. Additional Benefits

If an alternative could not meet one or more of these criteria it was immediately dropped from consideration. Several of the criteria warrant further explanation. The Resistance to Theft criterion required adherence to the Spent Fuel Standard at disposition. To be excluded on the basis of Resistance to Retrieval was taken to mean the form offered no nonproliferation benefits over long term storage in pit form. Assurance of detection was a factor used in the Retrieval criterion. The Technical Viability criteria required that an option could be demonstrated in time for the option to be considered in the decision process itself.

Cooperation With Russia was taken to mean an appropriate international standards for disposition of nuclear materials was produced. A description of factors affecting this criterion included language concerning leverage for negotiating with Russia and other countries. The measure for assessing the capability of a disposition option to provide such leverage was not identified.

Of the 37 options, 13 could not meet all of the criteria listed above and were eliminated. The remaining were given rough scores of high, medium and low by a panel of technical advisors chosen by OFMD. Alternatives were given scores based on their ability to achieve each criteria but the criteria themselves were not weighted. Instead, alternatives that were rated low for a "significant" number of criteria and/or were dominated by a similar alternative were eliminated. This removed another 12 alternative from consideration.

This left 11 options for further evaluation in the PEIS. These included reactor burning options in the US, Europe and Canada, emplacement in deep boreholes, and various immobilization options. As the focus of the work presented in this document relates to the immobilization options, only these alternatives will be elaborated upon. The PEIS and related documents can be surveyed for information regarding the reactor and borehole options.

The selected immobilization options resulted in several different Pu storage forms. Each involved mixing Pu with radionuclides and ultimately disposing of the material in a geologic repository. The material forms considered included glass, ceramic, or metal castings. These options were then analyzed in the PEIS.

The vitrification option actually consisted of several variants. The 'vitrification -greenfield' option would vitrify Pu at an entirely new facility. The 'vitrification - adjunct melter' option would use a new melter at the DWPF for dispositioning. These two variants would use separated Cs-137 from either the Savannah River Site or the Hanford Site. The 'vitrification - can-in-can' variant would vitrify the Pu in small canisters without additional radionuclides prior to insertion in a DWPF canister. High-level waste glass would then be poured into the canister, encasing the smaller cans.

The option of using the current DWPF melter for commingling Pu directly with HLW was eliminated. Criticality regulations require double contingency, "two unlikely, independent and concurrent changes in the process conditions before a criticality event is possible" (Gray 1995: 8). The order gives preference to passive geometry controls whenever possible. Because the Pu loading in HLW is extremely low the present DWPF melter and feed lines were not designed to be criticality safe. Therefore the Facility would have to be modified for Pu disposition.

As the Facility is currently 'hot,' this would increase worker exposure and delay the DWPF mission. The adjunct melter seemed a reasonable alternative therefore this option was not developed further. As noted in the Technical Summary Report (discussed in the following section) all immobilization alternatives will be two stage approaches - initial immobilization and then the addition of a radiation barrier - due to criticality concerns.

The ceramic variants are similar to those of the vitrification option except a ceramic host form will be the Pu host matrix. The metal castings option refers to an electrochemical process under development for treating DOE spent fuel. In this process Pu is converted to chloride form, dissolved in a molten-salt solution, sorbed on zeolites and then immobilized in a glass-bonded zeolite waste form (LLNL 1996a).

The PEIS compiled a variety of data related to the expected environmental impact of the selected alternatives. Issues assessed ranged from land resources to socioeconomic effects. The environmentally preferred alternative was the "No Disposition" alternative as Pu would remain in storage and no new federal actions would be required. However, this alternative was not selected by the Secretary of Energy in her ROD. A discussion of the environmental impacts of the elected alternative, a so-called hybrid option that includes reactor burning and immobilization in glass or a ceramic, is discussed in Section 2.10 along with the ROD.

2.8 Technical Assessment

The Technical Summary Report For Weapons-Usable Plutonium Disposition contains information related to the technical viability, cost and schedule of the PEIS alternatives. This section describes the key findings in each of these areas.

Technical Viability

The recovery of Pu from pits is a necessary step for all alternatives. For Pu-bearing materials and other mixed forms processing will be required for use in the reactor alternatives. For many alternatives this head-end processing composes the majority of technical effort and costs associated with dispositioning.

For extracting Pu from pits a dry separation process termed the Advanced Recovery and Integrated Extraction System (ARIES) has been developed. In the ARIES process, the Pu pit is sliced into two hemispheres and Pu is purified through a hydride/dehydride step. Either plutonium oxide or metal can be formed in the process.

Each of the immobilization forms are expected to be acceptable for geologic disposal according to the DOE's Office of Civilian Radioactive Waste Management (OFMD 1996c: Ch.3 p.9). However the Summary Report stated that all matrices will require additional R&D for waste form qualification purposes. Little data exists on the environmental durability of the glass-bonded zeolite. It was noted that a ceramic form could have beneficial long term performance over borosilicate glass. Processing issues remain for each of the immobilization options.

For the options that use Pu vitrified in glass several different formulations are under investigations. A lanthanum borosilicate glass, termed a Loffler glass, is being investigated for the vitrification can-in-can variant. This glass is expected to have high durability and can accept large loadings of neutron poisons. An alkali-tin-silicate or ATS glass may be used for the adjunct melter variant. This glass would possess a low melting temperature to prevent the volatilization of Cs. These glasses are discussed in greater detail in Section 4.2.4.

As noted previously long term criticality is a concern, for the reactor waste forms as well as the immobilization alternatives. The Summary Report noted that criticality assessments have been made but only for completely intact waste forms (OFMD 1996c: Ch.3 p.5). The prospect of a criticality event occurring during the dissolution of a borosilicate glass is evaluated in Section 4.9.

The reactor alternatives utilizing existing LWRs were noted as possessing fewer technical uncertainties. The Report said these reactors could be easily modified to support Pu burning. There is also an experimental database for MOX burning in LWRs in Europe. However, technical risks would be higher for options using CANDU reactors, unfinished or new reactors.

A caveat was added that the reactor options may require additional aqueous processing after Pu removal from pits in order to remove gallium (OFMD 1996c: Ch.3 p.6). Gallium was used to alloy WGPu in a thermally stable phase. Aqueous processing (after a dry ARIES type process) may be required as Ga is a reactive metal and could have an impact on fuel fabrication and performance. In addition adequate particle size for MOX fabrication has not been proven for dry processing.

Cost & Schedule

Large cost uncertainties exist for both the reactor and immobilization options. Regulatory oversight was noted as an important and common factor for both. Reactor cost are dependent on business agreements for burning with individual utilities. Immobilization costs are dependent on waste form qualification expenses. It was estimated that immobilization could begin in 7 years and reactor alternatives 10 years. Both require roughly $1 B investment costs. Again, a large fraction of cost is Pu processing. Cost and schedule uncertainties are further discussed in Section 3.3.

2.9 Nonproliferation and Arms Control Assessment

The Nonproliferation and Arms Control Assessment was prepared by the DOE's Office of Arms Control and Nonproliferation with support from the OFMD. It contains a nonproliferation assessment of the various disposition alternatives using a set of technical and policy factors.

Technical factors included: how quickly an option could be initiated and finished, the degree of susceptibility to diversion during processing, the ease of international monitoring, and the ability to meet the Spent Fuel Standard (DOE 1997: ix).

Policy factors in the assessment were: the ability to impact Russian disposition activities (described as a "major motivation" for US action;) the support of arms reduction by ensuring irreversibility of the process; the commitment to US nonproliferation obligations such as the Nonproliferation of Nuclear Weapons Treaty; and the impact on fuel cycle choices of other nations.

As part of the Nonproliferation Assessment, a Proliferation Vulnerability Red Team report was solicited by the OFMD and produced by a Sandia National Laboratories led group. This Report provided a technical assessment of security vulnerabilities of the disposition options for the Assessment.

While the Assessment concluded that each alternative could provide high levels of security and none was clearly superior, several important findings were presented.

2.9.1 The Use of RGPu in Nuclear Explosives

The Red Team confirmed prior statements regarding the usability of various isotopic grades of Pu in weapons (Mark 1993). It issued a single summary statement on the matter (Sandia 1997: Ch.4 p.7):

> "All plutonium is good plutonium; some is better than other."

In the past there have been debates regarding the suitability of reactor-grade Pu (RGPu) for weapons use. RGPu has higher concentrations of Pu isotopes higher than Pu-239. This results in two potential problems for weapons designers: pre-initiation and heat dissipation.

Nuclear weapons contain cores of hollow Pu spheres termed ‘pits.’ The configuration of the Pu is initially subcritical but when the sphere is imploded, using high explosives, the system goes super-critical. Pre-initiation results when the fission chain reaction is initiated to soon, before the highest levels of compression are reached. This can cause the device to heat up too quickly and expand. This expansion force ultimately reduces the number of fission generations and thereby the ultimate yield.

Plutonium-240 has a higher spontaneous fission rates than Pu-239 and thereby increases the risk of pre-initiation. This isotope and the other shorter lived isotopes Pu-238 and Pu-241 also increase the heat generation in the weapon. High temperatures may be a problem with regard to the high explosives used in the weapon.

Despite the problems associated with RGPu, it’s ability to produce a nuclear explosion seems certain. “Even if pre-initiation occurs at the worst possible moment (when the material first becomes compressed enough to sustain a chain reaction), the explosive yield of even a relatively simple first-generation nuclear device would be of the order of a few kilotons” (DOE 1997: 38). It has also been noted that the issue of heat generation can be mitigated by heat sinks and/or delayed assembly of the weapon until just before use (NAS 1994: 33). Therefore the Assessment concluded that “reactor-grade plutonium is weapons-usable, whether by unsophisticated proliferators or by advanced nuclear weapon states” (DOE 1997: 39).

2.9.2 Radiation as an Accessibility Barrier

Another significant finding of the Red Team related to the effectiveness of the radiation barrier produced by each of the alternatives. In their estimation “none of the alternative final forms emit radiation fields large enough to require shielding for dedicated aggressors" (Sandia 1996: Ch.4 p.16). Therefore, the inherent radiation levels of the alternatives under investigation would not be a "significant accessibility barrier to unauthorized parties."

In assessing the radiation barrier of spent fuel the Red Team assumed a decay time of 10 years after irradiation. US BWR or PWR spent fuel would have a dose rate of 1000 rem/hr at 1 m from the surface. (As the can-in-can variants use older fission products the dose would be lower). They estimated that a successful overt theft would take roughly ten or twenty minutes in which case the accumulated dose would be about 300 rem. Based on dose/effect relationships taken from the reference "Sources, Effects and Risks of Ionizing Radiation" they determined that while such a dose would eventually produce radiation sickness effects, it "is unlikely to produce any symptoms during the course of the theft and is unlikely to result in death."

The Red Team accounted for the fact that a proliferator might have to touch the surface of the container for some period during the theft which would increase the dose rate. However, they made a distinction between extremity dose (e.g. to the hands) and that to the midline of the body. The extremities are less sensitive to dose than vital organs. They further noted that the midline dose might be much less than 300 rem as they would not need to be near the waste during the entire 10-20 minute period.

Nonetheless, the Assessment Report warned of underestimating the effort required to successfully divert a SFS form. While acknowledging the Red Team's devaluation of radiation as an accessibility barrier, it asserted that the *larger* barrier would be executing the theft, transportation, extraction and fabrication of a weapons without being detected and stopped (DOE 1997: 54). It went on to describe how the radiation field would make the transport vehicle easier to detect and that gaseous fission products would be released upon reprocessing that could be detected. The fact that the proposed immobilization alternatives do not contain volatile fission products was not noted in the Assessment.

Both the Assessment and the Red Team report stated that none of the alternatives make the plutonium impossible to recover. The Red Team Report further noted that only after the

Pu was emplaced in a geologic repository would proliferation resistance be dominated by intrinsic barriers rather than institutional ones (Sandia 1996: Ch.4 p.38). Safeguards would be necessary until the Pu was placed underground and sealed.

2.9.3 Strengths and Weaknesses of Individual Options

Some comments were made regarding specific alternatives. The reactor alternatives and can-in-can variants were noted for their ability to allow detailed accounting of Pu content during the production of fresh fuel and small cans , thereby easing verification. However, it was also noted that the can-in-can variants need additional research to prove that the individual cans could not be mechanically separated from the HLW without great effort.

On the issue of timing, the can-in-can variants provide some advantage as they could be initiated sooner. Conversely, it was remarked that the borehole option could possibly have large delays related to approvals for siting and construction. Similarly, it was stated that the electrometallurgical treatment option would be prone to delays as it is less technologically developed than the other immobilization options.

Finally, the Assessment urged caution in US participation in alternatives that would expand foreign MOX fabrication. It was recommended that financing for foreign MOX capability should be avoided to the extent possible (DOE 1997: xxi). If it were pursued, limits should be established such that the supported facilities would only be used for surplus WGPu disposition.

2.10 Record Of Decision

The Record of Decision (ROD) represented a formal statement of the DOE's strategy for WGPu disposition. It supports a "dual-track" approach in which both the reactor and immobilization options will be pursued. The ROD specifies that at least 8 MT of surplus Pu will be immobilized due to its impurity. Based on current evaluations the ROD concluded that the can-in-canister variant is likely to be used at the DWPF.

The remaining plutonium will either be immobilized or burned in a reactor depending on the results of further technical and non-technical feasibility studies. Reactor burning would occur in existing, US commercial reactors. To support this activity a government owned MOX fuel fabrication facility would be built at a DOE site. It was stressed that any MOX fabrication facility used during the program would be shut down upon mission completion and not used for any other purposes.

The ROD specified that the PEIS, Technical Summary Report, and the Nonproliferation Assessment were all taken into account in the decision making process. The ROD stated that reactor burning and immobilization were essentially environmentally comparable. Neither one of the alternatives appeared superior from a nonproliferation or arms control perspective as well. Each provided high level of security and were technically feasible.

While no weighting or even ranking of criteria was offered, several key issues were noted in the ROD. The importance of swift processing was stated repeatedly in the ROD. The impact on Russian processing was also highlighted. The ROD states that benefits of Pu disposition would be greatly increased if Russia took comparable steps with its own Pu (O'Leary 1997: 13).

The ROD justified the dual path strategy based on its ability to provide flexibility and insurance. By pursuing a hybrid approach the ROD contends that WGPu disposition could begin earlier and be completed faster. It was also argued that the two paths will serve as insurance for meeting schedule goals.

Additional support for the dual path strategy has been expressed. A letter, described in the ROD, from members of the U.S.-Russian Independent Scientific Commission on Disposition of Excess Weapons Pu supports the hybrid approach due to its impacts on Russia. They assert that the reactor burning option is needed in the US in order to influence Russian decisions related to the conditions and safeguards accompanying their Pu burning activities. It has also been argued that if the US pursued immobilization alone, hawks in Russia would stall disposition as US Pu would remain weapons-grade (Holdren 1997).

This statement is offered despite published US/Russian agreements to accept separate disposition approaches.

This chapter described the Pu disposition challenge today and the present US response. The following chapter provides a cost/benefit analysis for incremental Pu processing steps. The effectiveness of various disposition actions is combined with an understanding of the relevant risks to identify valuable components of any proposed disposition strategy. Using this framework a critique of the current US strategy is presented and an alternate strategy for WGPu disposition is proposed.

3.0 System Analysis

To design an effective disposition strategy it was necessary to understand the components of a successful outcome. In this chapter the desired objectives and the effect of material processing on those objectives are presented. The potential role for immobilization is further explored and an implementation strategy proposed.

The U.S. disposition program possesses many objectives. From its inception, the OFMD was tasked to evaluate "technical, nonproliferation, environmental, budgetary and economic" issues related to fissile material disposition. The 9 criteria chosen as a basis for comparison of disposition alternatives were identified in Section 2.7.

In this work, proliferation risk, cost, and (indirectly) timeliness were assumed to be the three most important attributes. The relative impact of the material form on each of these factors was explored to form the basis of strategy formulation.

The remaining criteria were treated separately. Public acceptance was viewed as adding uncertainty to any disposition schedule and will be discussed in Section 3.3. The issue of Russian reciprocity was recognized as important and the impact of US disposition is assessed in Section 3.4. A review of the PEIS shows all alternatives to possess somewhat similar environmental impacts. As environmental factors would not distinguish between disposition strategies they were not investigated further. The Technical Summary Report characterized each of the disposition alternatives as "viable" yet encouraged further research , especially for the immobilization alternatives. The technical feasibility of vitrification is explored in detail in Chapter 4.0.

It is proposed that an appropriate disposition strategy would reduce the proliferation risk from surplus plutonium to an acceptable level with an eye to cost. Flexibility for responding to future known and unknown uncertainties was identified as an additional attribute. This counters the oft stated U.S. goal of irreversibility. However, as none of the options under consideration achieve true irreversibility, and the potential downside risk is sizeable, reversibility was taken as a disposition asset. This point will be developed in detail later in this chapter.

The following section describes how proliferation risk was addressed in the analysis. The effect of material processing on risk is assessed for several credible categories of proliferators. In this way risk reduction over time can be compared with the associated cost profile. A disposition strategy that provides the greatest risk reduction in the near term at low project costs should be pursued.

3.1 Proliferation Risk

If proliferation risk reduction is desired, a comprehensive understanding of what is meant by risk is needed. Proliferation risk was taken to be dependent on three factors: desire, ability and opportunity. The greater the motivation and the ability of a group to divert fissile material given the opportunity, the greater the perceived risk.

Each of these factors is needed for proliferation risk to exist, however the relative risk contribution of each is unknown. The material form of Pu will affect each of these factors and thereby the perceived risk. In this section individual processing steps were evaluated to gauge their ability to minimize proliferation risk by attacking the individual risk factors. Issues other than material form are clearly capable of also affecting risk. However, the contribution of material form is the focus of this section.

3.1.1 Potential Diverters

In order to assess the impact of material processing on risk it is necessary to identify the proliferator. This is because processing has unique and disparate effects on individual proliferators. In this section four general classes of proliferators were selected and their potential proliferation motives and capabilities postulated. While the categories are complete in the sense that all proliferators could be placed in a class, the proposed motives are not likely to be exhaustive. The classifications were assumed to be sufficiently representative for use in this analysis.

Host Nations: Russia and US - Diversion amongst these parties would represent the "breakout" scenario referred to in the literature.[21] Given the size of their post-START II stockpiles and unspecified reserves they would appear to have little reason to seek addition fissile material. Only in a renewed arms race would this seem plausible. In such a case they would be seeking large quantities of Pu, preferably of the same isotopics found in present designs. Regarding capability, both countries posses warhead production experience. While material production capabilities are declining, both countries have vast experience and access to large industrial infrastructures.

Other Nuclear Weapon States (NWS) - In general this class would have little interest in Russian or US Pu as they have weapons capability of their own. Advancing their strategic nuclear position (to a superpower level) would require diversion of massive numbers of warheads. The risk of detection and conflict with another weapons state would seem an adequate deterrent. However, perhaps one or a few intact pits would be desired for their design information (particularly after the Comprehensive Test Ban Treaty). This may also introduce a new era of data espionage (even amongst allies).

Non-Nuclear Weapons States (NNWS) - These countries could desire any number of warheads, merely to gain entrance into the nuclear club. They have limited if any infrastructure for weapons production but could have access to a wide range of technical expertise.

Subnational Groups - These organizations have no fissile material production capability whatsoever. Their resources are likely to be smaller than a NNWS and their technical expertise more narrow. For this reason they may attach a premium to attaining the fissile material in pit form to avoid the manufacturing of a weapon altogether. However, they would desire Pu regardless of its material form.

21.See NAS (1994: 47) for example.

In the following section the effect of processing on the desire, ability and opportunity on the risk of proliferation for each class of threat is examined. From the perspective of a proliferator, surplus plutonium in a storage matrix represents:

- something I want to some degree (defined by my ability to use it and alternate sources of the fissile material);
- something I have some prospect of successfully obtaining (defined by degree of safeguards, physical form, tracking potential);
- and, given a degree of opportunity, I will acquire it.

The general material modifications assumed for this investigation are:

- pit processing - submitting the pit to an ARIES type process where its geometry is changed and perhaps transformed into oxide form;
- isotopic blending;
- chemical dilution with or without a radiation barrier, and
- increasing the unit size and mass.

Both desire and capability are directly affected by the material characteristics of the Pu. Opportunity is primarily a function of institutional control. However, if this is expressed as a function of time then the storage matrix may indirectly influence this factor as certain processing steps will take longer to implement and are more prone to delays than others. Such delays impede the application of direct verification and safeguards which are capable of reducing opportunities for diversion. The following sections describe the effect of each processing step on the proliferation risk from each class of proliferator.

3.1.2 Processing Effect on Desire

Altering the physical characteristics of the Pu can reduce its desirability in several ways. The processing may degrade the utility of the material or make alternate sources more attractive. Again the aspirations and capabilities of the proliferator determine the magnitude of the effect.

Host State

The only processing that could directly affect the utility of the material for the host state would be isotopic blending. This is not due to US or Russia's inability to use RGPu as a weapon - clearly they can. The affect is a logistical one. Both countries have a fleet of warheads designed for a particular grade of Pu. It may be that sufficient isotopic blending would make the Pu unusable in a significant portion of the designs (Sylvester 1996). While new designs could be utilized, the inability to test them due to the Comprehensive Test Ban Treaty (CTBT) could be an obstacle.[22] This may effectively demilitarize the Pu as the reliability of new designs may be insufficiently characterized.

The Vulnerability Report does not completely address this point. They noted that " a simple fission design would not require testing to *prove* that it would work," and "the only debate would be about the yield" (DOE 1997). This debate may be unacceptable for deployment in a military arsenal.

While the focus here is on arms control, the effect of pit processing on military readiness should also be noted. Nuclear weapons, if they were ever to be used, would most likely be launched in one or a few waves over a relatively short period of time. Any Pu that was not in pit form, would possess no military value as the time required to manufacture a weapon would be too long. If the Pu were processed out of pit form it would also greatly diminish the usefulness of the material from a military readiness perspective.

Processing the pit into an oxide would eliminate geometry information, force reduction to metallic Pu and require machining to reconfigure a weapon but the uncontaminated oxide material would still be attractive. While chemical dilution with a radioactive barrier may cause a delay, remote, industrial solvent extraction capability exists in both countries. This was how the Pu was initially produced.

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[22] The Comprehensive Test Ban Treaty bans all nuclear explosions. All declared weapon states have signed the treaty.

However, such dilution could reduce the desirability of the material if reversal were more expensive than alternatives such as uranium enrichment. The cost of retrieval will depend on the status of the host nation's reprocessing infrastructure as well as waste management policies. The cost would range from a low value representing operational reprocessing capability with no waste treatment and a high value for mothballed or decommissioned canyons and vitrification facilities.

Several observations were made regarding material processing effects on host state desire. A chemical barrier alone could result in the same degree of host state deterrence as a radiation barrier. The combination of an operational reprocessing facility and concerns over criticality safety may result in a "clean" storage form loaded with Pu to be processed in a remote facility. In that sense, a matrix that required the same processing should be viewed as equivalent to radioactive spent fuel.

In addition, the cost of reprocessing relative to uranium enrichment may also affect desirability. Roughly 200 SWU are required per kg of natural uranium feed enriched to 95 wt% U-235 (optimum tails).[23] At $100/SWU that equals $20,000/kg just for enrichment services. Each kg of enriched U would require 240 kg of natural U. At a cost of 16.50 per lb of uranium ore (U_3O_8) this results in $10,370/kg enriched U. Adding these costs together, the total cost is $30,370 for each kg of enriched uranium.

However, if the starting material is uranium from reprocessed spent fuel, as may be the case in Russia, the price of enrichment may be lower. Assuming a discharge enrichment of 1%, only 143 SWU would be required to reach 95% enrichment. This enrichment would cost $14,300/kg. The requisite 172 kg of 1% U-235 required may actually be viewed as free if the costs for retrieving it were assigned to reprocessing. If other contaminants (e.g. U-236) do not force additional processing, the total cost of HEU derived from reprocessed fuel would be $14,300 per kg.

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[23] SWU stands for Separative Work Unit in kg. It is a measure of the amount of enrichment services needed to achieved a desired isotopic concentration of fissile U-235 in U-238. Natural uranium has a concentration of 0.711 wt% U-235.

The OECD places a cost of 720 ECU/kg U on reprocessing and vitrification services.[24] Assuming a disposition loading of 5 wt% Pu, this results in a cost of $14,400/kg to retrieve Pu. The HEU derived from natural U is more than twice the price of Pu recovery. However if Russia has access to slightly enriched U from reprocessing the prices are comparable.

While either country might desire Pu for weapon design purposes, the economic incentive for retrieving Pu can be reduced by material processing, even when operational facilities exist. For Russia the accessibility to tonnes of separated RGPu from civilian operations could also lessen the attractiveness of safeguarded Pu. In any regard the host nation's fuel cycle choices and weapons design flexibility determine the potential impact of material processing on desirability.

Nuclear Weapons State

The CTBT could give some incentive for another NWS to obtain surplus Pu from US or Russia. However, merely altering the pit would eliminate any design information that might be available and thereby the desirability of this proliferator. Isotopic blending may effectively demilitarize the Pu as well. As mentioned above, the only other possible incentive another NWS may have would be to dramatically increase their stockpile in a short period. The prospect of attempting to steal large quantities of Pu even in concentrated form seems implausible given any reasonable safeguards. Further processing could make such an unlikely assault even more infeasible.

Non-Nuclear Weapons State

For a NNWS that wishes to develop some level of nuclear weapons capability, any of the processing steps would seem to have marginal effect on their desire for the material. The radiation barrier would be a nuisance, requiring additional time and personnel for Pu extraction. (The effect of radiation on the act of theft is discussed in Section 3.1 on

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[24] Reprocessing and vitrification cost taken from OECD (1994: 50). (1 ECU ~ 1 US$.)

page 40). But according to the Vulnerability Assessment only 2 additional weeks and 2 additional people would be needed to retrieve 8 kg of Pu (Sandia 1996: Ch.4 p.6).

This can be understood by examining the PUREX process for extracting Pu and U from spent fuel. Upon mechanically shearing the fuel rods, the fuel is dissolved in a hot nitric acid. Plutonium, uranium and fission products are all brought into solution. Dissolution times are on the order of minutes to hours. The pH of the aqueous mixture is then adjusted to around 2.5 and a reducing agent is added (e.g. sodium nitrite) to place Pu in a +4 state.

The Pu and U are then separated from 99% of the fission products by solvent extraction with TBP (tributyl phosphate) in an organic carrier (Benedict 1981: 484). Further processing is performed to separate Pu from U and further purify the product, however multiple order of magnitude reductions in radiation dose rate can be achieved in a single step. If a Pu SFS form could be subjected to a similar process, a radiation barrier could be swiftly removed.

If the production of many weapons was desired the loss of design information would perhaps have the greatest effect as this would prevent production of high quality replicas. If merely a few weapons were desired it would seem that any form of Pu would be attractive. Small batch sizes and shielded laboratory equipment could be employed to subvert a radiation barrier. Industrial size, canyon type facilities would not be needed if only one or two weapons were desired and the proliferator was patient.

The status and availability of enrichment technology would also be important for this proliferator. Cost is likely to be less a factor for a NNWS. If Atomic Vapor Laser Isotope Separation (AVLIS) technology were available and could be operated in a clandestine manner, the dispositioned Pu would become less appealing. A uranium weapon would also be simpler to design as only a gun-type assembly would be required.

Subnational Group

It appears that processing would have little effect on subnational desire as well. However, for certain groups Pu in pit form could be valued significantly more as weapon fabrication and design capability may be limited. Obtaining the Pu in pit form would also reduce the time needed after diversion to assemble a weapon which would reduce the chances for detection. As no stockpile ambitions would exist, one or two explosives of uncertain yields would be strongly desired. Therefore, as with the NNWS, the radiation barrier could be undermined.

The prevalence of uranium enrichment technology would also be important for determining the risk from this proliferator. The risk of immediate detection through uranium enrichment is likely to be lower than that of diversion of Pu from a safeguarded facility, particularly if the information and technology comprised in centrifuge and/or AVLIS enrichment becomes widely available.

Desirability Summary

The material processing of surplus WGPu would do little to reduce the ultimate desirability of the material to potential proliferators and then only under certain conditions. Pit conversion would eliminate design information eliminating any gain for a NWS proliferator. Isotopic dilution may be capable of demilitarizing the material for service in the host nation's existing weapon's infrastructure.

The most additional processing is capable of achieving is reduced attractiveness by forcing recovery and purification through chemical processing. If waste management is not a concern of the proliferator and it has the infrastructure for such processing or is willing to accept clumsy and slow laboratory scale reprocessing, the addition of a radiation barrier will not reduce the attractiveness of the material. In contrast, the nuclear fuel cycle infrastructure available to the proliferator can greatly affect desirability, particularly for the host state.

3.1.3 Ability to Divert

Another component of proliferation risk is the proliferators' estimated and actual capability to successfully transfer the Pu off-site. It is assumed that after disposition processing the Pu will be placed in a storage facility for monitoring. If all proliferators view removal from the site as virtually impossible there is no risk of proliferation as none will be attempted. The material form can affect the ease of safeguarding and/or off-site removal. This can dramatically decrease the proliferators expectations for success and thereby the proliferation risk. Clearly the level of institutional control (guns and guards) also affects diversion capability. However, as the same institutional controls may be applied to any Pu matrix, only the material contribution to deterrence was addressed in this work.

Host State

The host state would always be able to take possession of the material. The material form would have little if any impact. Access to military force, industrial equipment, knowledge of site operations, and the location of the storage site within the host nation's boundaries make removal or repossession of large quantities quite feasible. Inspectors could merely be forced to leave.

Verification would have some deterrence for the host state as the international community would be alerted. There have been some questions regarding the ability to adequately verify pit storage. The Nonproliferation Assessment stated that "acceptable verification and monitoring measures for pits in storage have not yet been resolved" (DOE 1997: Ch.5 p.51). Processing the Pu into non-pit form would allow the material to be accounted for directly and safeguarded by multinational parties. In this sense, ARIES processing could reduce the ability of the host state to reverse the disposition process.

Nuclear Weapons State

The addition of safeguarding and direct verification of processed pits would sufficiently deter diversion by a NWS proliferator. This is especially true if all design data were eliminated through ARIES processing. While military forces could be used, such an act would risk full scale confrontation with the host state. The severity of this outcome would seem adequate deterrence to NWS diversion.

Non-Nuclear Weapons State

The safeguarding of PuO_2 may not be sufficient to deter NNWS diversion attempts. However increases of unit size and mass would reduce the potential for diversion as detection would be much easier and transport more difficult. To the extent emitted radiation can be detected, the inclusion of HLW would provide an added reduction in proliferation risk. However, the radiation fields projected for the MOX and immobilization alternatives will not be capable of making the forms "self-protecting."

As noted in Section 2.9, the Red Team Report provides a detailed analysis of the self-protecting issue. To the extent a radiation field forces the use of heavily shielded equipment to move Pu containing material, it would hamper diversion. However, the Assessment notes "none of the alternative final forms emit radiation fields large enough to require shielding for dedicated aggressors" (Sandia 1996: Ch.4 p.16). An aggressor that is willing to take a non-incapacitating dose of a few hundred rem will not be deterred. The Assessment goes on to estimate that dose rates of several thousand rem/hr at 1 meter would be needed to produce lethal effects during the execution of a theft. They estimate 10 year old spent fuel to possess a dose rate of 1000 rem/hr at 1 meter.

Subnational Group

The analysis for the subnational group is identical to that for the NNWS. While a NNWS may have access to greater military resources and training, subnational groups have demonstrated their willingness to sacrifice their lives in execution of a terrorist act.

Ability Summary

There is virtually nothing to prevent retrieval by a host state. However, material processing may somewhat reduce the prospects for successful diversion by other proliferators. The most effective strategy would appear to be processing the material into an easily monitored form and safeguarding it. To the extent verification of pits is hampered due to the presence of classified data, at a minimum ARIES processing may be required. Beyond that the most import factor appears to be the use of unit/size and mass to hamper on-site manipulation and off-site transport by requiring industrial size equipment. However, the Assessment notes: "In all cases, it is estimated that intrinsic resistance to theft could be overcome in 15 to 30 minutes by one heavy lift helicopter and a few people on the ground" (Sandia 1996: Ch.5. p.40).

3.1.4 Opportunity

While form is important, when and where the Pu is processed also affects proliferation risk. This relates to the strength of institutional control. Much has been made of the documented smuggling attempts in Russia. This has been attributed to the relative economic and political turmoil in that nation. The lack of sufficient accounting also leads to vulnerability concerns. Therefore, it would appear that the greatest proliferation benefits would come from quickly securing Russian Pu. Additional gains could be had from moving Pu in Russia to a more stable country for processing.

Material processing could reduce the opportunity for proliferation. As execution of the present disposition alternatives will require decades, the near-term focus has been on safe, secure storage. However, as mentioned earlier, storage in pit form may not allow adequate verification. In addition, observer presence may be intermittent. For perhaps unrelated political purposes, inspectors may simply be forced out of storage facilities. Independent, direct verification would be desirable under such circumstances. Processing into non-classified forms would allow for such verification if the final form was suitable for non-destructive evaluation. If the present instabilities are believed to exist indefinitely, the benefits of a non-pit storage form over pit form become larger.

Pit conversion/Pu recovery operations could be initiated immediately if sufficient shipping/receiving facilities along with glove box and ventilation systems were available (LLNL 1996b: Ch.2 p.21). The availability of of such facilities in Russia is unknown. The ARIES process is currently being designed to process 250-500 pits per year (OFMD 1996c). Such a prototype could be replicated to increase throughput.

The operational start time for the ARIES process, combined with a vitrification step was estimated as 7 years (OFMD 1996c: Ch.5 p.10). For the immobilization alternative these processes were not individually evaluated as they would be treated as a single, integrated front-end process for combining the vitrified Pu with HLW. This estimate includes further R&D and licensing activities. It is possible that such processing could be done faster and cheaper in Russia.

For completeness the schedule for supplying a unit size and mass as well as radiation barrier is discussed. For the reactor alternative unit size and mass, and chemical dilution will be added in the MOX fabrication stage. If foreign fabrication facilities were utilized this would occur as Pu is extracted from pit form. Otherwise it is estimated that a domestic MOX facility could be operational in 10 yrs. It is estimated that reactors could be available in 9 yrs to provide a radiation barrier.

For the can-in-can and adjunct melter alternatives (described in Section 2.7), chemical dilution will occur in the first immobilization step. Unit size and mass, as well as a radiation barrier would be attained immediately after extraction from pits. This would occur through loading of the cans into a DWPF canister and filling the canister with HLW glass. The DWPF is already in operation.

While processing beyond ARIES may be pursued for other reasons (e.g. ability to divert), it would not reduce further the opportunity for proliferation. The potential benefits (in terms of reducing proliferator opportunity) of material processing are attained exclusively through processing the Pu into a directly verifiable form for storage in a safeguarded, international facility.

However if pit processing were delayed due to the unavailability of additional processing facilities, pursuing the SFS could increase the risk of proliferation as Pu would remain in pit form for an extended period. In addition if the rate of pit processing were constrained by MOX fabrication or HLW vitrification capacity, larger stocks of Pu would remain in pit form for longer periods. This too would increase the opportunity for proliferation. Given the limited benefits of a radiation barrier the risk of processing delay should be carefully assessed.

3.2 Costs

The potential proliferation benefits and detriments of material processing were identified above. The processing alternatives selected by the Secretary of Energy for surplus Pu disposition were then examined to determine the costs associated with each step of Pu processing. While other processes and forms are possible, cost estimates were not available. The data presented in the Technical Summary Report was used to form general conclusions regarding the relative marginal cost of processing Pu into various forms.

For both the reactor and immobilization alternatives the initial pit processing (common to both alternatives) was estimated to be the greatest contributor to life cycle costs. In the Existing LWRs - Existing Facilities alternative, a net life cycle cost of $1390 M was assigned to ARIES processing with Ga removal. The total undiscounted life cycle cost for this alternative was estimated to be $1920 M. For the vitrification can-in-can variant, front-end costs were $1340 M including the initial vitrification step. The total life cycle cost for this variant was $1830 M.

For the reactor alternative, chemical dilution in a large unit size and mass container is achieved at the price of MOX fuel fabrication. This results in an added life cycle cost of $1540 M. The addition of a radiation barrier would require $380 M in reactor related costs but result in a fuel displacement credit of $1390 M.

For the immobilization variants, chemical dilution would be achieved as the last stage of pit processing. A single facility would perform "all plutonium recovery operations and all immobilization operations not involving the final pour of the HLW glass" (LLNL 1996b: Ch.2 p.21). Therefore the marginal cost of chemical dilution for this alternative was included in the ARIES estimate above. This processing would "require similar glove box and ventilation systems as those used for the recovery operations and would not be contained in a separate facility in any reasonable implementation." The unit size and mass, and radiation barriers were estimated to cost an additional $490 M, $390 M for vitrification with HLW and $100 M for added disposal costs.

3.3 Relevant Uncertainties

Disposition strategies must recognize significant uncertainties and develop strategies for minimizing potential negative outcomes. Future events can dramatically affect Pu disposition activities and ultimate benefits. Several uncertainties are particularly important. These factors are identified and discussed in this section.

A particularly meaningful uncertainty is Russian Pu disposition activities. The Technical Summary Report noted that Russian reciprocity will be required for US disposition to proceed (OFMD 1996c: Ch.6 p.1). None of the disposition alternatives address this reciprocity issue. The disposition of US Pu will not reduce the obstacles Russia faces in burning its Pu. Without an accompanying strategy for effectively promoting Russian disposition, it is likely that US Pu will remain in pit form.

Each of the identified alternatives may face other scheduling delays. Licensing and public opposition may cause delays in the MOX alternative in the US. While licensing will be needed for all processing, opposition to MOX burning has already been organized (O'Leary 1997: 16). For immobilization options utilizing the DWPF, processing schedules will rely on its continuous availability. The risk of operational problems with such a complex, remotely-operated facility are possible. These factors weaken confidence in the proposed disposition schedule.

All of the immobilization alternatives may face delays due to waste form qualification issues. Even if Pu disposal forms meet disposal requirements at the beginning of processing, they may not be acceptable upon completion as standards are subject to change. Indeed, the performance requirements for Yucca Mountain have not yet been established. Nor has Yucca Mountain been selected as a nuclear waste repository. In the worst case scenario a reversal of disposition processing may be required.

Even if predicted schedules are met, uncertainties will also affect the realized proliferation benefits of disposition actions. As mentioned earlier, the diffusion of centrifuge and AVLIS technology over the several decades of disposition may dominate the long-term proliferation risk posed by surplus Pu. In addition, the subjective nature of the Spent Fuel Standard may result in the rejection of forms previously ruled as acceptable (e.g. the can-in-can variants).

Finally, the existence of a repository in the near and intermediate future is far from certain. This is relevant as all of the proposed alternatives rely on disposal in an underground repository for ultimate proliferation resistance. If such a facility is delayed or never materializes, the Pu will need to be safeguarded indefinitely. In such a scenario, the benefits realized from pursuing a Spent Fuel Standard matrix for Pu storage will be debatable.

3.4 Comments on the Present US Disposition Strategy

This section provides a critique of the present US disposition strategy. The expected proliferation gains and costs over time are discussed. The ability of the US strategy to manage the uncertainties described in Section 3.3 is also examined.

The Nonproliferation Assessment describes the impact on Russian programs for disposing of its surplus plutonium as a "major motivation for U.S. Action." From the perspective of proliferator opportunity the risk appears to be in Russia right now. In addition, the Red Team Vulnerability Report characterized the threat from unauthorized parties to be "the greater near-term concern," compared to host nation retrieval (Sandia 1996: Ch.2 p.1). Therefore it appears our strategy should be to encourage the secure storage of Russian Pu.

The current US approach is to clearly separate short term storage options and long term disposition options. Pit storage is viewed as the primary strategy for addressing near term risks. However, questions over the verification of pits in storage due to their classified form does exist. In addition the Nunn-Lugar facility (described in Section 2.5) is only designed for pits. Pu in other forms throughout Russia is of equal if not more concern. In any regard paving the way for long term storage of pits when other options exist seems undesirable.

The physical processing of Pu could allow direct verification and provide added security benefits. However, the current US disposition strategy seems incapable of providing near-term results. The current strategy has focused on processing Pu into a form that meets a proposed nonproliferation standard for an (optimistic) period of 100 years beginning 10-20 years from now. [25] While the impetus has been insecure Pu in Russia, our strategy has been to process US plutonium despite any indication that this will impact Russian action. All this when the long-term benefits of doing so are mixed at best, and significant down-side risks exist.

Some might argue that swift US disposition will indeed affect Russian action. As US Pu is processed, political pressure can be applied on Russia to do the same through prior reciprocity statements. Yet current US plans do not include a strategy for attaining such reciprocity and significant obstacles exist.

Russia has stated that it wishes to burn the Pu but lacks the funds to do so. This will be true whether US processes its Pu or not. Russia may also simply lack the desire to adopt our disposition schedule. The ability to process US plutonium without a parallel strategy for enabling or encouraging Russian action seems unproductive.

Contrary to encouraging Russian action, the US strategy is likely to impede it. The adoption of the Spent Fuel Standard as the only acceptable form for long-term Pu disposition seems certain to delay Russian processing. Such a standard *requires* Russia to either treat Pu as fuel or as waste. Russia flatly rejects treating the material as waste but has expressed a willingness to burn the Pu. As the US cannot financially support a Russian Pu fuel cycle due to its nonproliferation policies and Russia refuses to treat the material as waste, stagnation seems predictable. Even if burning did not run counter to US policy, the

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[25] The 10-20 year figure roughly represents the time when a large amount of Pu could be dispositioned. If at the time of fabrication the forms possess a 1000 rem/hr dose rate, in 100 years the rate will be below even the IAEA self-protecting standard of 100 rem/hr.

US has demonstrated an unwillingness to spend federal monies in Russia (see Section 2.5).

Setting aside for a moment the implementation problems associated with the SFS, the benefits of attaining it have been brought into serious question. The Red Team Report strongly challenges the nonproliferation benefit of the radiation barrier afforded by any of the alternatives. The radiation levels are simply not high enough. The impression that the alternatives under investigation leave plutonium in a "self-protecting" matrix is false. Indeed safeguards are required on all of the SFS forms until emplacement and ultimate closure in a repository. Regardless, whatever protection the SFS is proposed to provide will decay over time with fission product inventory.

The SFS form will also hamper if not prevent direct verification. The Nonproliferation Assessment notes that it will "no longer be possible with current technology to accurately measure the amount of Pu in the glass - just as it would not be possible to accurately measure Pu in spent fuel" (DOE 1997: 111). While this is also true for civilian spent fuel it is not a viewed as a beneficial trait. It appears the desire for uniformity in Pu storage matrices has exceeded the desire for acquiring meaningful nonproliferation tools.

The political debate has also produced confusion over what *can* be achieved by the Record of Decision alternatives. While irreversibility has been stated as a major political objective, it simply cannot be attained through the alternatives under investigation. Only through a deep-burn alternative (Pu elimination in a non-fertile matrix) or a similar approach would Pu disposition be entirely irreversible.[26]

For the alternatives examined, irreversibility is more a function of proliferator infrastructure and required retrieval rate. If irreversibility were truly desired each country could destroy its reprocessing facilities. This would greatly increase the time and cost of extraction and make uranium enrichment more attractive. In this scenario a radiation barrier

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[26] Virtually complete elimination of Pu can be achieved with existing reactors using non-fertile fuels and periphery assemblies (Chodak 1996).

would produce tangible benefits if a large amount of Pu were desired as expensive shielded facilities would necessarily be reconstructed.

The destruction of reprocessing infrastructures would also be a stronger statement of the US commitment to arms reduction than Pu disposition. If such capability is maintained, the world would recognize that relatively small investments in infrastructure would be needed to reverse any disposition action.

Cost issues related to Pu disposition are more difficult to judge. Each of the ROD alternatives were shown to possess somewhat comparable life cycle costs. The cost risks of each seem high. The MOX alternative will require significantly greater initial investments and rely on revenues from the use of fabricated fuel to reduce total costs. To rely on the availability of MOX burning capacity over an extended period appears risky.

There is significant cost risk associated with the immobilization alternatives as well. While investment and processing costs appear somewhat more controllable, if the final waste form is characterized as unacceptable, reprocessing charges could be enormous. The probability of this occurring could be minimized but it is nonetheless possible.

As a means of managing implementation risks the ‘hybrid’ alternative promoted in the ROD has limited effectiveness. By pursuing two paths, certain types of programmatic risk can be reduced somewhat. Having two alternatives does increase the odds of actual implementation. However, this does not eliminate the significant uncertainties facing the individual options as described in Section 3.3. In addition the individual options share common risks (e.g. delays due to the inability of Russia to reciprocate). In this sense the hybrid alternative is not robust as its components possess ‘common mode failures.’

It would appear that a shift in the focus of US disposition is needed. The next section describes a potential new direction for disposition.

3.5 Disposition Strategy Needs

An effective disposition strategy must be capable of responding to identified threats in a timely manner. Preference therefore should be placed on simple actions that can be executed in a short time period. Efforts should focus on incremental processing that can provide meaningful security while allowing for future improvements.

As lack of US/Russian consensus may hamper progress, options that do not require contentious fuel cycle commitments should be pursued. Incentives for Russian action, that can receive full US support, should also be formulated.

While the ultimate benefits are bounded, material processing is capable of meeting valuable nonproliferation objectives. However, strategy formulation must begin with well articulated nonproliferation objectives. What is the threat that is to be reduced? As described in Section 3.1 material processing has different effects on individual proliferators. Therefore, actions should be selected and implemented in a manner that minimizes this threat.

General conclusions regarding the effect of processing on individual classes of proliferators should be used to guide strategy formulation. The processing of Pu out of pit form for ease of verification and safeguarding reduces the opportunity for diversion by all would be proliferators. As this would be the first step for any disposition action it would appear that every effort should be made to achieve this action immediately.

For all but the host-state proliferator it appears on-site manipulation and removal is a major concern. If a proliferator successfully transports a Pu matrix off-site, security would rely on detection and interdiction. It has been said that "The current inability to locate a nuclear device without intelligence cueing is perhaps the greatest limitation of our neutralization capability" (Mullen 1996: 20). As noted in Section 2.9, the DOE's Nonproliferation Assessment stated that the primary benefit of the radiation barrier was its ability to aid the detection of Pu after a theft. This should be noted in strategy formulation.

The presence of significant uncertainties imply that disposition strategies should include insurance against future unknowns. In such conditions flexibility and reversibility are desirable attributes. Robust strategies capable of changing with evolving states of the world should be pursued.

Summarizing the above observations, it seems that the appropriate question that Pu disposition should answer is:

> What is the most easily safeguarded, verifiable, trackable and flexible form for storing Pu capable of being implemented in the near-term?

The following section presents an alternate Pu disposition strategy.

3.6 Proposal - Pu Material Bank

The following US strategy is designed to reduce the near-term risk of subnational or NNWS diversion in the near term. The US should propose the following processing steps be executed in coordination with Russia:

- initiate ARIES processing immediately;
- immobilize surplus Pu in a glass or ceramic phase without HLW;
- do not require the addition of HLW in the future;
- produce a high unit size/mass form via a can-in-can approach;
- add integral off-site tracking capability; and
- allow the conditional retrieval of Russian Pu in the future for use in energy production.

It is proposed that the US and Russia address their mutual proliferation concerns by initiating bilateral processing of their surplus WGPu immediately. Plutonium should be processed into a glass or ceramic matrix expected to be acceptable for repository disposal. The matrix would include sufficient neutron absorbers for long-term criticality control based on the present state of knowledge. High-level radioactive waste could be added at a later time but should not be required under any agreement.

Large unit size and mass would be achieved through small containers loaded into DWPF canisters. This would be identical to the can-in-can variants without the HLW glass. Glass or ceramic cans of the diameter of a DWPF canister would be produced in glove box facilities appended to the end of an ARIES processing line. The cans would be slid into a DWPF type canister and stored at an internationally safeguarded facility where it would be subject to periodic direct verification.

In addition, it is proposed that electronic devices allowing the tracking of individual cans be encapsulated during glove box operations. A 'beacon' from such a device could be used to locate and retrieve individual cans should they be diverted. The design of this device has not been explored in detail, however the absence of highly radioactive elements would appear to make this option feasible.

Plutonium would be processed in negotiated, incremental steps. Each host state would select the portion of the other's stockpile that it viewed as the most vulnerable, for immediate processing. In this way the most immediate security concerns of each nation could be addressed.

Russia could retain the option of retrieving the Pu but only if her energy needs demanded it. Russia would have to prove alternate stockpiles of RGPu were not available and Pu would be directly fabricated into MOX. The processed Pu would be treated as a safeguarded ore, much like a HLW repository. The US could financially support the production of this storage matrix as it would not contribute to the development of a Pu fuel cycle in Russia.

If Russia refused even this offer the US could propose a purchase of the material. The agreed upon Pu could be transferred directly for processing and storage in the US. Such proposals have been offered before but pricing has been an issue. A market based methodology for valuing Pu was developed and is described in detail in Chapter 5.

3.7 Discussion

The proposal would reduce the risk of subnational and NNWS diversion.

Processing Pu into a clean storage form would provide virtually all the proliferation risk reduction *attainable* by material processing. Removal from pit form and placement in a safeguarded facility would reduce the ability and opportunity of any proliferator to divert the material. Critical design information would also be lost.

Increasing the unit size and mass of the Pu host matrix would reduce the ability for NNWS and subnational groups (the primary target of the proposal) to successfully divert the material. The presence of off-site tracking capability would provide a new form of deterrence for these proliferators.

A detectable signal would probably be most useful during the initial transport off-site, before the transmitter could be removed. This capability would benefit the DOE's Nuclear Emergency Search Team (NEST) whose responsibility is to find nuclear materials both in the US and abroad under such conditions. The signal frequency could also be known by the international community, allowing any nation to independently monitor the location of Pu at any time. This would serve to further increase confidence in the arms control process.

The proposed processing would also prevent retrieval and subsequent direct use by the host nation. As noted in Section 3.1.2 , chemical dilution, combined with criticality concerns, could cause the Pu to be processed using shielded equipment. However, it is not clear whether this would meaningfully reduce the attractiveness of the Pu to the host state. The material may still be superior to other fissile sources such as HEU. The fact that it has been declared surplus and would be under international safeguards most likely provides the highest deterrent for host state retrieval. In any case, it is recognized that host state retrieval of Pu in any form is possible. It is for this reason that the proposal was largely designed to reduce the security risk from other proliferators.

By completely separating Pu disposition from other fuel cycle activities its execution can begin quickly. Processing could proceed at virtually any pace through the use of multiple process lines and/or higher capacity systems. This combined with the ability to process the most worrisome Pu first would produce tangible security gains in the near-term.

The possibility for direct verification would be retained by this proposal. Without the background radiation from HLW, isotopic and total Pu concentration in the matrix could be non-destructively determined. This was not developed in this work but it would appear that standard spectrometry techniques could be utilized.

It could be argued that given the marginal cost of adding a radiation barrier ($390 M for the can-in-can variants) is so low that we should add it even though the benefits are debatable. This would be true if there were no risks associated with the radiation barrier. If waste form qualification issues arise we run the risk of having to re-extract Pu, vitrify the HLW again and determine a suitable form for the Pu. This potentially immense cost must be weighed against the benefits of such processing.

Criticism of such an approach does exist. Previous work by this author and colleagues was referenced in the NAS's Reactor Related Options report. The CISAC committee dismissed non-radioactive storage forms as not providing enough of a barrier to be seriously considered as a long-term option (NAS 1995: 226). However they did note that it would be an "inexpensive and rapid method for transforming the existing metallic WGPu pits and ingots into a glass form" for storage until vitrification with HLW. Given the questionable benefits of the radiation barrier, the timeliness aspects of this approach may be more valuable.

If the presence of a radiation barrier were truly desired, the DWPF canisters could be stored alongside fully radioactive DWPF canisters. This would not differ appreciably from the can-in-can alternatives which have been promoted in the disposition Record of Decision.

The Nonproliferation Assessment also notes that anything less than the SFS would pose a unique risk “indefinitely.” However, this statement is not supported by the Assessment’s own investigations. The Report notes that SFS forms would not be ‘self protecting’ after 100 years according to IAEA’s standards. The US currently possesses several decades old spent fuel. By the middle of the next century we will have a growing inventory of non-SFS forms. Even if such a form was adopted for Pu disposition it is not clear what the penalty would be for having a ‘non-standard’ security threat.

Timely processing of both US and Russian surplus Pu would be possible.

Perhaps the biggest benefit of this alternative is its prospect for US/Russian cooperation. The proposal was designed to harmonize with Russian fuel cycle ambitions and yet allow for US financial support. The proposal represents a compromise between two polar alternatives for Pu disposition and in doing so provides a reasoned path forward for both countries.

Without a resolution to the Russian fuel value issue it appears no processing will move forward. By allowing retrieval or providing compensation, the proposal provides two means of addressing this concern. Either approach appears capable of being accepted.

The flexible nature of the strategy would reduce risks.

The modular nature of this design could provide valuable flexibility to address both technical uncertainties and political differences. If criticality control was deemed insufficient, the DWPF canisters could be repackaged to address regulatory concerns. (This is discussed further in Section 4.11.) In the extreme case the Pu could be reprocessed for other waste treatment without requiring the re-vitrification of HLW.

As time goes on, political tensions may cause intermittence in international oversight at Pu storage facilities. Confidence in treaty compliance may erode during such periods. The ability to directly verify Pu content would eliminate such uncertainties.

This approach would also buy time for each country to fully evaluate their respective Pu objectives. The US could further weigh disposal options and Russia could develop the necessary infrastructure to burn Pu. Neither would be forced to execute Pu programs requiring large industrial investments without thorough analyses.

The proposed form could be utilized in further Pu disposition initiatives.

The proposal could be formalized into a Surplus Plutonium Storage Standard which could be applied globally. The Red team noted that some non-weapons states may eventually want to disposition their excess Pu. This form would give them an alternative other than MOX fuel or mixing with HLW. Indeed the country may have neither alternative at their disposal. Such a form could be used to demonstrate a commitment to arms reduction, ease safeguarding and storage cost, and give verifiable proliferation resistance.

3.8 Future Work

Proposals of this nature warrant serious consideration for their ability to address stated disposition objectives while recognizing the limitations of all disposition alternatives and providing flexibility for dealing with future uncertainties.

The tracking capability must be developed and experimentally tested. To the extent possible the transmitter should be an integral part of the host matrix such that on-site separation would be infeasible. The system must be able to withstand the immobilization process environment and the power source should be long lived. Similarly, techniques for verifying the composition of an immobilized Pu matrix should be developed.

For countries such as Japan and Germany that possess separated RGPu but not burning capability, Pu storage forms that could easily be fed into a fuel fabrication process should be examined. For this purpose a UO_2/PuO_2 form would be more appropriate: a kind of rough MOX form, that contained mechanically separable reactivity control so the material could be moved directly into a fuel fabrication line or disposed of directly. Again, an alternative to fuel or processing with HLW would give these nations an alternate, less polar nonproliferation path.

The cost savings associated with storing Pu in an 'intermediate' form should be evaluated. With sufficient reactivity control, Pu could be stored in more dense configurations. Storing Pu in chemically stable, bulk particle matrix would reduce the risk of oxidation with exposure to air and dispersion. This may reduce the costs of installing and maintaining safety systems. Costs of safeguards could also be reduced.

Much would be gained by further investigation and quantification of the Spent Fuel Standard. The functional purpose of individual criteria embodied in the Standard should be further explored and alternate, potentially superior solutions evaluated (e.g. a trackable storage form). The focus should be on nonproliferation performance not the ability to mimic spent fuel. Indeed the verification questions posed by spent fuel are a concern.

The effect of future uncertainties could also be explicitly treated in the evaluation of disposition alternatives. Dynamic programming would be one approach. The probability of certain events could be altered to determine their impact on expected outcomes. In this way factors critical to programmatic success can be identified and robust strategies designed to reduce risk.

A major uncertainty of any Pu storage form is environmental performance. The next chapter addresses key technical issues for the vitrification of Pu both with and without fission products. The environmental performance of a Pu glass form is evaluated and the potential for a criticality event in a geologic repository is assessed.

4.0 Technical Feasibility

As significant quantities of plutonium have never been vitrified, the technical feasibility of such a proposal must be demonstrated. The feasibility of vitrification will require confidence in repository subcriticality. Neutron absorbers may necessarily be vitrified with Pu to control reactivity over geologic time periods. Rare earth elements have been identified for their neutron absorption capabilities and relative insolubility in groundwater. The homogeneous dissolution of these elements in glass is desired. The environmentally durability of the glass is especially important if Pu is to be vitrified with HLW. Each of these issues were investigated and the results are described in the following sections.

4.1 Introduction

The term glass is used to classify solids that possess an amorphous rather than a crystalline structure. While most liquids adopt a crystalline structure upon cooling, glasses do not. They become increasingly viscous until a rigid condition is obtained.

The most fundamental building block of silicates is the SiO_4 tetrahedron. As shown in Figure 2, this structure consists of a single Si atom at the center of four oxygen atoms. Both crystalline and amorphous silicates possess this tetrahedron structure.

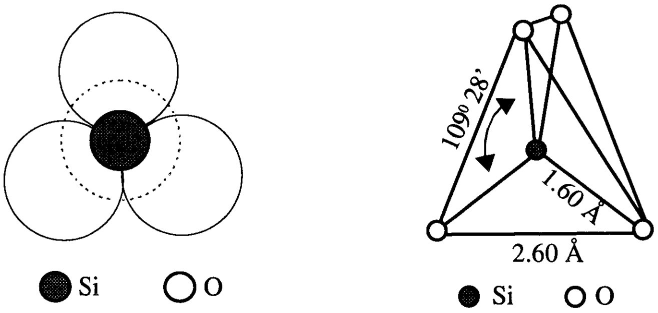
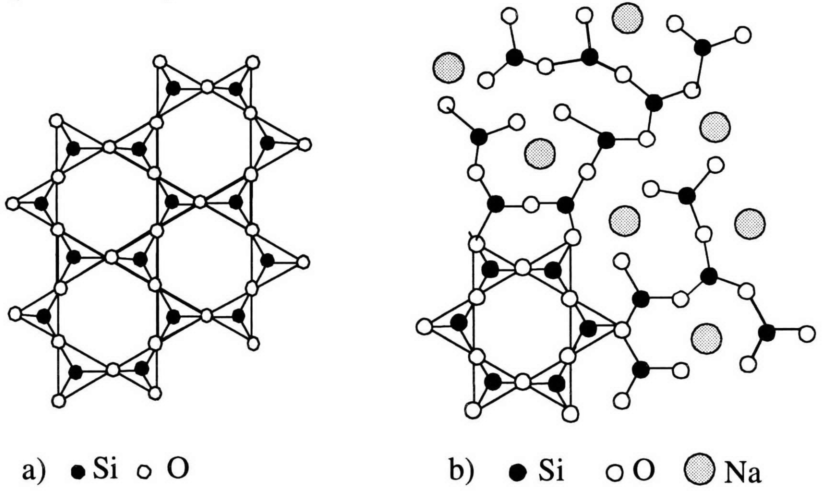


FIGURE 2. SiO_4 Tetrahedron (Vogel 1994: 35)

However, the two phases utilize this building block in different ways. The electron octet of silicates is formed by accepting electrons from adjacent metal ions or by linking the tetrahedra through what is termed "bridging oxygen." In both quartz and glass, oxygen link at most two tetrahedron and then only at the corners, not on the edges or faces. However, in quartz only two oxygen exist for every silica. In this matrix each and every oxygen link two tetrahedron together and a ridged crystalline structure is obtained. In amorphous silica, oxygen from added compounds free some SiO_2 oxygen from providing such linkage (Scholes 1974: 27). This results in a random structural arrangement. Figure 3 compares the ordered structure of SiO_2 with that of a Si-Na glass.



(not to scale)

FIGURE 3. Ordered and Random Arrangement of SiO_4 a) regular crystalline arrangement b) tetrahedrons in a sodium silicate glass (crystalline phase shown for comparison)

Zachariasen and Warren proposed a network theory for glass formation (Vogel 1994: 42). Amongst other requirements, for simple mixtures to enter the vitreous state polyhedral groups of less than 6 corners must be easily formed and anions should not bind more than two of the central atoms. These polyhedra are linked at their corners rather than their edges allowing a random structure to be formed.

The addition of other oxides can break the bridges between tetrahedra. The oxygen will share electrons at the free end of a tetrahedron with the cation occupying the space formed at the broken site. (See the Na atoms in Figure 3.) This produces what are termed “non-bridging oxygen" sites. These sites tend to be the first attacked when exposed to water and play a significant role in glass durability.

Cations that might exist in glass can be classified in three general categories: network-formers, network-modifiers and intermediates. Network-formers are capable of forming chains of polyhedra in the above described manner. These cations typically have coordination numbers of 3 or 4. Besides silica the oxides B_2O_3, P_2O_5 and As_2O_3 are examples of network-formers.

Network-modifiers typically have coordination numbers of greater than 6 and by themselves would form crystalline structures. Sodium, calcium and barium oxides are network-modifiers. Modifiers increase the number of non-bridging oxygen sites in the glass. This results in the decreased viscosity of the glass melt and aids in the fabrication process by lowering the required melting temperature.

Some elements form oxides that cannot be easily placed in either category. These "intermediates," while incapable of forming glass networks themselves, will adopt the coordination of network-formers in the glass. In this way they are capable providing linkage in the glass network.

Predicting the behavior of elements in glass is aided by inspecting the field strength of a particular cation. Field strength 'F' was defined by Dietzel to be:

$$F = \frac{Z_c}{a^2} \qquad \text{(EQ 1)}$$

where, Z_c is the valence of the cation, and

a is the sum of the cation and anion radii in the glass

This relation is analogous to Coulomb's law and roughly describes the electrostatic charge density of a single cation. Table 2 provides a comparison of several elements as published in Vogel (1994: 46) which was adapted from Dietzel.

TABLE 2. Field Strength of Various Glass Elements[1]

Element	Valence	Most Frequent Coordination Number	Ionic Distance for Oxides (Å)	Field Strength (1/Å^2)	Function in Glass
K	1	8	2.77	0.13	Network-Modifiers $F \approx 0.1 \ldots 0.4$
Na	1	6	2.30	0.19	
Li	1	6	2.10	0.23	
Pb	2	8	2.74	0.27	
Fe	2	6	2.15	0.43	
Mg	2	6 4	2.10 1.96	0.45 0.53	Intermediates $F \approx 0.5 \ldots 1.0$
Zr	4	8	2.28	0.77	
Fe	3	6 4	1.99 1.88	0.76 0.85	
Al	3	6 4	1.89 1.77	0.84 0.96	
B	3	4	1.50	1.34	Network-Formers $F \approx 1.5 \ldots 2.0$
Si	4	4	1.60	1.57	
P	5	4	1.55	2.1	

1. Table adapted from Vogel (1994: 46), based on data from Dietzel.

A correlation between field strength and participation in glass formation was observed by Dietzel. The compounds with relatively high field strength are capable of maintaining a glass network. Oxides with smaller field strengths tend to disrupt the network. The ability of intermediate elements such as Mg, Fe, and Al to increase their field strength through reduced coordination is displayed in the Table.

It has also been shown that, in binary melts, the difference between field strengths in the mixture is important (Vogel 1994: 49-50). Mixtures of glass formers and modifiers with field strengths that do not differ by large amounts will compete strongly for oxygen. The modifier is likely to be successful and form a stable oxide. However as the coordination of the modifier is higher it will not be structurally compatible with the glass former and crystallization will occur. This phase transformation is undesirable for waste glasses and will be discussed in Section 4.2.2.

If the difference between field strength is sufficiently high the modifier will be prevented from forming a separate phase. With field differences (> 1.33) homogeneous, ternary oxide compounds can be formed. The cation with the higher field strength will form an anion complex, charge balanced by the cation of lower field strength. This prevents the modifier from assuming its desired coordination and thereby disrupting the glass network.

4.2 Radioactive Waste Glasses

Glasses have been studied (and used) for the solidification of aqueous radioactive wastes.[27] In this application glass is used to sequester radionuclides in an environmentally durable matrix for disposal. Its non-crystalline structure will incorporate many dissimilar elements allowing diverse or poorly characterized waste streams to be treated. This was a major reason for its selection for radioactive waste management.

Design issues for waste glasses include: fabrication ease, loading (or elemental solubility) and repository performance.[28] Glass design is often a complex process of balancing between these desired attributes. The dependence of elemental behavior in glass on process parameters such as temperature adds to the complexity. The following sub-sections describe the relevant issues and how they were investigated for Pu immobilization.

4.2.1 Fabrication

Waste glass is fabricated by mixing a frit with the waste stream to be immobilized, heating to above the glasses' softening temperature and cooling to form a vitreous state. The melt temperature is a particularly important parameter for HLW vitrification as radionuclides such as Cs have relatively high vapor pressures. For Cs containing wastes, melt temperatures are typically kept below 1200°C in order to retain Cs in the glass.

To reduce softening temperatures and thereby processing temperatures, network-modifiers are added. Soda (Na_2O) is the principal flux used in glass making. Unfortunately soda also reduces the ultimate durability of glass. For this reason boria (B_2O_3) is often used in

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[27] For a comprehensive review of radioactive waste glass development see Lutze (1988).

[28] Other factors such as radiation effects, mechanical and heat transfer properties are also general concerns in waste glass production.

concert with soda in waste glasses. At low temperatures boron possesses a coordination number of 4 and is a glass former. However, at higher temperatures its coordination is reduced to 3 and it adopts a triangular, planar geometry. In this state it acts as a network-modifier thereby reducing the viscosity of the melt (Lutze 1988: 22). This dual property of boron is quite useful in waste glass design. Most HLW glass formations consist of a Na_2O-B_2O_3-SiO_2 ternary system.

The volatility of Pu or any rare earth neutron control element is not likely to force further reductions in process temperatures. While some volatilization is anticipated, requiring the use of critically safe off-gas filtering systems, the effect is small relative to Cs. In the can-in-can alternative the problem is avoided entirely with Pu being vitrified without Cs first, allowing for potentially higher temperature glasses to be pursued.

4.2.2 Waste Loading - Phase Transformation

If the concentration of a certain element is too high for a particular glass design devitrification may occur. The element itself may form a crystalline phase or, by disrupting the network, cause other elements to precipitate. Devitrification is a concern as crystallized regions of the glass can be depleted in amorphous silica and become less durable. Glasses may also phase separate into two distinct glasses of different compositions. This too may be detrimental to durability.

It should also be noted that process parameters such as the time/temperature profile of the glass during cooling can be as important as composition. If the glass is too fluid or cooling times are too long, diffusion of cations in the melt may produce nucleated crystalline regions. As glass is inherently a thermodynamically unstable phase, if viscous forces do not prevent it from doing so, glass will crystallize.

In HLW glasses, elements such as Mg and Ca are added to reduce devitrification or crystallization. These +2 cations aid vitrification by increasing the viscosity of glass at low temperatures (while allowing fluidity at melt temperatures) thereby reducing the potential for either phase transformation.

While borosilicate glasses have been used around the world for HLW vitrification there is virtually no experience with Pu vitrification. The solubility of Pu in borosilicate glass is somewhat unknown. The solubility of control elements in HLW glass is also uncertain but is expected to be fairly high.[29] This information is relevant from a cost and schedule perspective as well as environmental durability. It would appear that higher Pu loadings would reduce total costs as fewer additional logs would necessarily be produced and sent to a repository. Higher loadings would also lead to faster disposition rates.

For the can-in-can variant the relevance of Pu solubility is debatable. As PuO_2 is relatively insoluble in most groundwaters and other radionuclides are not present, devitrification in this glass may not be significant. To the extent that phase transformation affects rare earth release, solubility in glass may be important. The intimate mixing of fissile Pu with neutron absorbers is also important for stable, safe storage of Pu prior to disposal.

In any regard the behavior of Pu and rare earths in borosilicate glasses is of interest. Examining the field strength of these elements can give some indication of their behavior in glass. Plutonium atoms in the +3 and +4 state have ionic radii of 1.00 Å and 0.90 Å respectively (Cleveland 1979: 6). If the ionic radii of O^{-2} is taken to be 1.40 Å the distance between Pu and O in PuO_2 is 2.40 Å for Pu^{3+} and 2.3 Å for Pu^{4+}.[30] This produces field strengths of 0.52 $1/Å^2$ for Pu^{3+} and 0.76 $1/Å^2$ for Pu^{4+}.

It is not clear what valence Pu will exist. Although increasing alkali content and processing temperature results in increased oxidation, it is not expected to be sufficient to produce these high states (Paul 1990: 230). The reduction of Pu is a possible redox effect. One study had Pu competing with +3 cations in a waste glass (Plodenic 1995). However, in the present work Pu was assumed to exist in the +4 state in glass.

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[29] Mixtures of alkaline and rare earth oxides formed homogeneous glass at loadings of 20 wt% in borosilicate glasses with $Na_2O>7.5$ wt% (Lutze 1988: 35).

[30] The field strength calculation should actually be based on experimental measurements of Pu-O bonds in glass rather than using the ionic data.

Referring to Table 2, the field strength data indicates that Pu would act as an intermediate in glass. However, coordination is also important. As an empirical rule, Goldschmidt used the ratio of the radius of the cation to that of the anion to determine if an element's coordination could be sufficiently low to allow glass formation (less than or equal to 4) (Vogel 1994: 40).[31] In order for an element to posses the appropriate coordination in glass Goldschmidt suggested a range of 0.2 to 0.4 for this ratio.

If oxygen is assumed to have an ionic radius of 1.4 Å this means that cations greater than 0.56 Å cannot be network-formers or intermediates. All oxidation states of Pu have ionic radii greater than this value. Plutonium oxides also possess a cubic structure.[32] Therefore Pu is likely to exist in glass as a network modifier.

The solubility of rare earths in HLW glass is also unknown. Rare earths are expected to comprise >30 wt% of fission products in HLW (Lutze 1988: 438). However, the DWPF glass will contain less than 0.5 wt% of the rare earth elements (Baxter 1983: 28). For this reason the solubility limit for rare earths in borosilicate HLW glass has not been established.

An application of the glass metrics described above would imply that rare earth elements are likely to be network-modifiers. They all have ionic radii greater than the 0.56 Å limit set by Goldschmidt. As most exist in the +3 state their field strengths are lower than that of Pu. They are polymorphic, forming hexagonal, monoclinic, and body-centered cubic structures. The elements Gd, Sm and Eu exist in monoclinic structures at melting temperatures and tend to form BCC structures upon cooling (Gschneidner 1979: 341).

However in the +3 state they may exhibit intermediate behavior similar to that of alumina as described in the following section. Alumina is an important compound in borosilicate

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[31] Paul (1990: 10) shows this ratio can be correlated to various polyhedra based on geometrical considerations.

[32] Crystallographic data taken from Cleveland (1979: 296) and ionic radii from Cleveland (1979: 6).

glass fabrication. It transfers durability to the glass. The following section describes the role of Al in glass making.

4.2.3 Durability

In order to counter the weakening effects of Na, alumina (Al_2O_3) is typically included in waste glass formulations. Alumina's behavior in glass is complex. Alumina can work in concert with Na in glass to act as a network-former (forming the tetrahedron AlO_4) and increase glass durability. Soda donates oxygen, and Na increases the valence of the complex from -5 to -4 to mimic SiO_4 tetrahedra. However, in higher concentrations it tends to react more strongly, forming a separate crystalline phase (e.g. $NaAlSiO_4$) (Lutze 1988: 27).

Rare earth elements (REE) in borosilicate glass could exhibit behavior similar to that of aluminum. As with Al, excess network-modifiers (Na) could allow the rare earths to participate in the glass network. For Pu in the +4 state, excess network-modifiers could stabilize a soluble complex of the type described in Section 4.1. As both Pu and the REs' field strength are lower than Al, the prospect for devitrification should be lower. However, it is not clear. As with any multicomponent glass, elemental behavior must be experimentally tested and verified.

4.2.4 Experience with Pu, REE and Analogs in Glass

Walker and Riege observed a PuO_2 loading limit of 4.5 wt% in a particular German borosilicate glass.[33] This limit was reportedly not affected by the addition of 20 wt% loading of FP oxides. Plodinec (1995) found a similar loading limit of 4 wt% PuO_2 in a HLW glass but found solubility to be strongly affected by waste loading. Plodinec also noted that Pu solubility increased with increasing alkali content which would suggest the pres-

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[33] From Lutze (1988: 48) referring to: Walker, C., and U.Riege, Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, p.198 1979

ence of a stable $M_4Pu(SiO_4)_2$ compound of the type described in Section 4.1. The variability in these results displays the potential complexity of elemental solubility.

As Pu is a controlled and somewhat difficult radionuclide to work with, material analogs are often used. Given Pu's field strength and expected coordination it would appear that cerium would be a good analog for glass solubility. However Ce could exist in the +3 state in glass which would make its field strength much lower than Pu. Thorium, while a slightly larger ion, possess only the +4 valence. As it also possesses a face-centered cubic structure it seems a reasonable analog if we believe Pu to exist in the +4 state. Zirconium appears to be a promising analog as well with a nearly identical field strength. However, ZrO_2 is monoclinic in the expected temperature range (Benedict 1981: 325).

In previous work the author used thorium as a Pu analog in a borosilicate glass and tested the solubility of several rare earth elements as well (Sylvester 1994). Thorium was chosen not only for its approximation to Pu in glass but also for its ability to mimic Pu behavior in the primary decontamination stage of a PUREX type process. The glass formulation was also used in research designed to gauge the difficulty of re-extracting Pu from borosilicate glass in a solvent extraction process (Cerefice 1996).

The frit used in this study was the borosilicate glass Advanced Reference Material 1 (ARM1), distributed by the Materials Characterization Center at Pacific Northwest Laboratory. The glass was crushed and Th along with the rare earths Eu, Gd, and Sm were added and melted to form glass. A loading of 2 wt% of each of these oxides did not cause gross devitrification. However, visual indications and scanning electron micrographs showed that devitrification had occurred in a glass loaded with 10 wt% ThO_2. These results were in agreement with other studies involving Pu in glass (Plodinec 1995). The issue of solubility was not explored further in this work.

Examples of rare earths and thorium forming glass do exist. Various commercial optical glasses were designed to include La for its effect on optical properties of the glass. Some contain rare earth concentrations as high as 60 wt%.[34] ThO_2 has been added at concentrations as high as 22 wt% in a similar formulation. These glasses typically contain no Si. The initial frit uses TiO_4 and other compounds such as B_2O_3 to form the network. Lanthanum behaves in a manner similar to Al, complexing with soda to form stable tetrahedra.

A somewhat similar, lanthanide borosilicate (LaBS) glass is under evaluation for Pu disposition. Its composition is given in Table 14 in Appendix A. This glass is high in aluminum and contains no sodium. The result should be a more durable glass product. To reduce melting temperatures boron, barium and lead are added. At high molar ratios to Si, lead can act as an intermediate and reduce melt temperatures. Plutonium has been completely dissolved at concentrations of 15 wt% in this LaBS glass. This glass may have a higher softening temperature but it is not important as this glass is to be used in the first step of the can-in-can variant, without volatile Cs.

A low-temperature glass capable of dissolving Cs and Pu together is also under development. The glass is a B-Si-Na formulation with a composition also shown in Table 15 in Appendix A. The glass must maintain a low temperature, therefore soda and B_2O_3 are present in large concentrations. Rather than adding Al for durability, Sn, Ti, and Zr are used. Alumina was avoided because during glass reaction with groundwater, Al will precipitate Si in the form of various clays. As Si concentration in solution is the driving force behind glass dissolution, its precipitation will allow glass to react at a higher rate. This so-called ATS glass (for its alkali-tin-silica components) has been shown to dissolve 1 wt% CsO and 7 wt% PuO_2.

4.3 Actinide and Rare Earth Leaching Behavior

Relatively little Pu has been dissolved in glass, so there is little experience with its leaching characteristics. A French study investigated actinide leaching from the borosilicate glass R7T7 (Vernaz 1992). Actinides were loaded at 0.85 wt% and leached for one year in DI water at 90°C. After ultrafiltration the study determined that 90% of the Pu-239

34.See Vogel (1994: 16, 157, and 195).

leached from the glass was in colloid or particle form. However, 98% of Pu in the reacted glass remained in the alteration layer. The study also determined that release kinetics were controlled by the solubility of an actinide compound at the surface of the glass.

Colloids are suspended solids in a solution, ranging from a nanometer to one micron in diameter. Species may form (pure) colloids themselves or may adsorb onto other colloids (pseudo). Actinides have been shown to form both pure and pseudo colloids. The oxidation state of the actinide is important to the formation of pure colloids. The following order of colloid tendency is observed: $M^{4+}>MO_2^{2+}>M^{3+}>MO_2^{+}$(Kim 1991). The trend follows the decreasing charge on the central ion. Plutonium +4 has been shown to form oxide and hydroxide colloids but could form others (e.g. carbonates) in natural systems (Silva 1995: 390). Uranium +4 is expected to form similar colloids. Less information exists in the literature regarding the nature of uranium colloids.

Colloid formation appears to be path dependent. The process of colloid formation is thought to behave in a manner similar to precipitation which requires a solution to be supersaturated with respect to a solid phase prior to nucleation. In this case, rather than precipitate out of solution as the saturated phase, a portion is retained in colloid form. This increases the amount of an element available for transport.

In addition the nature of colloids affects their movement through porous media (Silva 1995). The flow velocity distribution across a channel in such a media can be taken to be parabolic with the velocity in the center being two times the average. Neutral colloids of sufficient size will not reach the walls where the velocity is slower and are therefore pushed to the middle. This serves to increase their velocity relative to the average velocity of the groundwater and reduce adsorption. Conversely, colloids possessing a charge opposite that of the media will move slower than average due to adsorption.

Uranium was also investigated in the French study. Uranium behavior is relevant to Pu disposition as Pu decays to U-235. Larger amounts of U were found in solution yet more than 80% remained either as part of the reacted glass or in colloid form. No information on the colloidal fraction was given for uranium.[35]

Another study of Pu release behavior by Pacific Northwest Laboratory (PNL) found similar results (Apted 1986). The plutonium was also loaded into a borosilicate glass but at a much lower loading, 0.03 wt% PuO_2. During static leach tests in 90°C DI water, 90% of the Pu released was found in colloids greater than 1.8 nm in diameter. An acid strip of the leachate container showed that roughly 10% of the dissolved Pu had adsorbed to its walls. The study also showed that the filtered concentrations of Pu in solution matched equilibrium with the amorphous phase $PuO_2 \bullet xH_2O$.

In the PNL study, the colloidal fraction of uranium was determined but for leach tests in brine and basalt waters. Uranium colloids were found in both solutions when Fe was added. Without Fe uranium was found entirely in solution in the case of basalt and nearly entirely sorbed on the vessel surface for the brine case. Normalized release data were not given.

While a durable glass is desired, Pu release is not likely to be a major concern from an EH&S perspective. Pu is relatively insoluble in groundwater and is not likely to migrate to the biosphere (unless perhaps in colloid form). However, the release of non-radioactive boron may be more important. Boron's inherent properties are a benefit to glass design, however its aqueous solubility may allow for a criticality event as the glass dissolves in a repository as it is the primary neutron absorber in borosilicate glass.

As noted in prior sections, the addition of insoluble rare earth elements is a potential strategy for addressing this criticality concern. Several rare earth elements possess strong neutron absorption characteristics. A list of relevant neutronic properties for boron and several REE is contained in Table 3.

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[35] Uranium leaching from glass was not experimentally investigated in this work. However, its potential effect on near- field criticality was explored inSection 4.9.

TABLE 3. Neutronic Poison Data[1]

Element	Isotope	atom% abundance	thermal neutron capture cross section, barns	resonance integral, barns
B	10	19.9	3,838	1722
Sm	149	13.8	5,900	4000
	152	26.7	208	3000
Eu	151	47.8	5,900	4000
	153	52.2	530	1500
Gd	155	14.8	61,000	1540
	157	15.65	255,000	800

[1] "Nuclides and Isotopes," 14th edition, General Electric Company 1989

Rare earth elemental release from glass is expected to be low as these elements are insoluble in groundwater. However, REE colloids are known to form in glass dissolution tests as well (Bates 1995: 377). Further investigation of Pu, U and REE leaching behavior is needed.

In order to assess the durability of a Pu glass, a borosilicate glass loaded with a Pu analog and several rare earths was leach tested. The release of neutronically relevant species was of particular interest. The following section describes the experimental approach and the results obtained.

4.4 Experimental Setup

As in the solubility study, the borosilicate glass ARM1 was used for durability testing. As the ARM1 frit contains simulated fission products this would be analogous to vitrifying Pu directly with HLW waste. The DOE's Record Of Decision suggests that the can-in-can variant is more likely to be utilized. However, if intimate commingling of Pu and fission products is required for nonproliferation purposes the ARM1 tests would be applicable for a borosilicate glass used for this purpose. The ARM1 glass contains nonradioactive Cs and possesses an Al concentration in between that of the ATS glass and the LaBS glass. In this respect it is roughly analogous to the two glass formulations under review.

An additional borosilicate glass frit SRL165 was also investigated. This is an actual frit designed to vitrify aqueous HLW at the defense waste processing facility (DWPF). The SRL frit without waste is not very durable. As Al is found in the waste stream, no alumina is present in the glass frit. This frit was used without additional alumina in order to examine the behavior of Pu and rare earth elements in a poor durability glass. The composition of the ARM1 glass is in Table 16 in Appendix A. The composition of the SRL165 frit is in Table 17 in Appendix A.

The performance of the ARM1 glass as well as the SRL165 provided a baseline for assessing the effect of Th and RE elements on glass durability. Their widespread use in experimental testing allowed the incremental effect of these elements to be more selectively evaluated. These glasses were not optimized for Pu disposition.

The glasses to be tested were prepared in the following manner. The ARM1 glass was crushed and weighed into fused silica crucibles. Nitrates of Th, Eu, Gd, and Sm were then weighed and added to produce glass frits with the desired loading. The SRL165 glasses were prepared in a similar manner although no crushing was necessary as a powdered frit was used.

The frits were then melted at 1150 °C and held at temperature for approximately one hour. The liquid was then poured into a preheated graphite mold in the shape of a bar and placed in a firebrick enclosure to cool. The mold was then annealed at 500 °C for periods ranging from several hours to overnight and allowed to oven cool.

After cooling the glass bars were sectioned and prepared for leach testing using the MCC-1P protocol. The samples were sanded, weighed and surface area measurements were made. They were then placed in a Teflon® container with a measured volume of deionized water such that a glass surface area to volume ratio of 0.01 1/mm was obtained. The containers were labeled and placed under controlled temperature for an extended period of time.

Upon completion of the tests, glass samples were removed from solution, rinsed and then dried. The pH of the leachate was taken immediately. The leachate was then filtered using 0.45 μm PTFE filters and acidified with nitric acid. This was done to remove suspended solids from solution that could clog analytical equipment. An acid strip test for colloid analyses was not performed.

The solutions were analyzed for elemental concentrations using inductively coupled plasma - atomic emission spectroscopy (ICP-AES). In this method a peristaltic pump generates a flow of leachant which is injected with argon gas to create a liquid-vapor mist. This mist is passed through an RF-induced argon plasma. The plasma excites elements in the passing mist. The de-excitation of these elements create photons of characteristic wavelengths. The intensity of the emitted photons varies linearly with the concentration of elements in the plasma. Standard solutions were prepared to provide three point calibration curves. When properly calibrated, solution concentrations can be determined.

The following elements were analyzed in solution: Si, Na, B, Th, Gd, Sm, Eu. The first three are major glass components and give an indication of overall glass durability. Silicon is likely to be partially held in what is termed the "alteration layer." This is a layer that forms on the surface of glass as is dissolves and is described in detail in Section 4.10. Sodium and boron are more soluble and are likely to be found entirely in solution. Thorium and the rare earth elements are the focus of the criticality study. The ICP-AES limit of detection for these elements are found in Table 4.

TABLE 4. ICP-AES Limits of Detection[1]

Element	Limit of Detection
Si	6.3 ppb
Na	16 ppb
B	1.5 ppb
Th	10.9 ppb
Eu	0.6 ppb

1. Limits taken from Spectro© (Gd and Sm limits not listed but expected to be similar to Eu)

The concentration of these elements in solution were combined with data related to the individual samples themselves to provide an estimation of a Pu-loaded glasses' inherent durability. The following section presents the results from the leach testing.

4.5 Leach Test Results

Knowing the concentration of the element in the leachant, the total mass of the leachant and the surface area of the glass allowed key parameters related to glass durability to be calculated. Elemental releases from glass are typically reported in units of normalized grams of element i per meter squared of glass. The mass of released element i is normalized by its concentration in the unreacted glass. The figures in this section display the normalized release data for the specific elements of interest.[36]

Leaching of the ARM1 glass at 90°C in deionized water agreed reasonably well with HLW glasses in the literature and accurately reflected trends in elemental leaching.[37] Figure 4 displays the normalized release behavior over a leaching period of one year. The glass reacts at a maximum initial rate, termed the forward rate. As glass components begin to enter into solution, glass reaction affinity begins to drop and the leach rate slows. During flow-through type tests borosilicate glasses will continue to react at the forward rate.

The $\sqrt{t}$ release behavior displayed in Figure 4 has led many to characterize glass dissolution as a diffusion controlled process. Indeed, diffusion models and models based on reaction affinity produce similar leach curves (Cunnane 1993). However, experiments have shown the affinity control hypothesis to be more plausible (Chick 1984). This issue as

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[36] A compilation of all leach data, including pH measurements, can be found in the Leach Test Record Book 1992-97 in the Radioactive Waste Management Laboratory in the Nuclear Engineering Department at MIT.

[37] See for example Lutze (1988: 105 and 122).

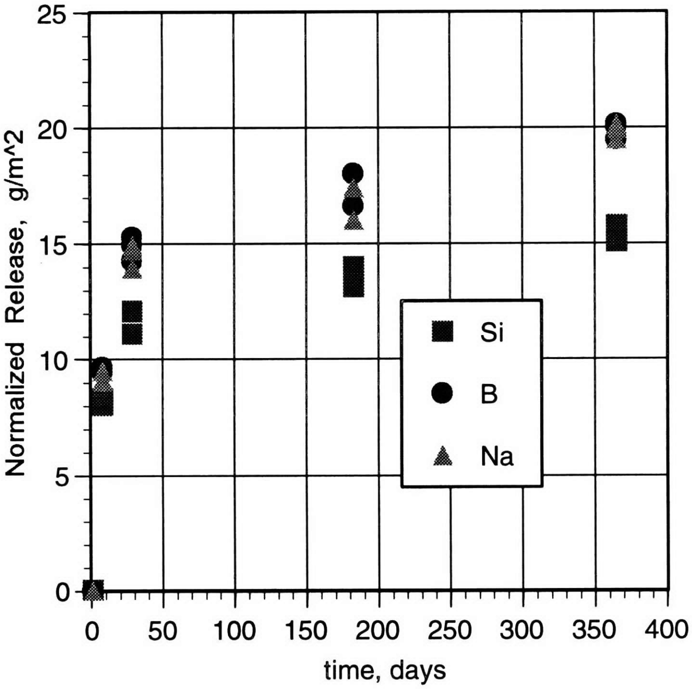

FIGURE 4. Silicon, Boron, and Sodium Release From Pure ARM1 Glass Leached in DI Water at 90°C

well as a more comprehensive discussion of glass reaction mechanics is contained in Section 4.8.

If every glass element entered into solution, their normalized release curves would be identical. The boron and Na release curves are nearly identical. Both elements are quite soluble in DI water. As shown in Figure 4, a portion of the Si (roughly 20 wt%) does not enter solution but remains, most likely as a constituent of the reacted glass. Boron and Na were assumed to represent the bulk reaction rate of the glass.

As expected the SRL165 frit had poor durability. As shown in Figure 5, elemental release was more than two orders of magnitude higher than that of the ARM1 glass at 90°C. After 364d, the pH values of the SRL165 samples were >11 while those of the ARM1 samples were <9. This demonstrates the greater Na^+ ion exchange with H^+ in solution for the

SRL165 glass. Without alumina, borosilicate glass can have extremely poor environmental durability.

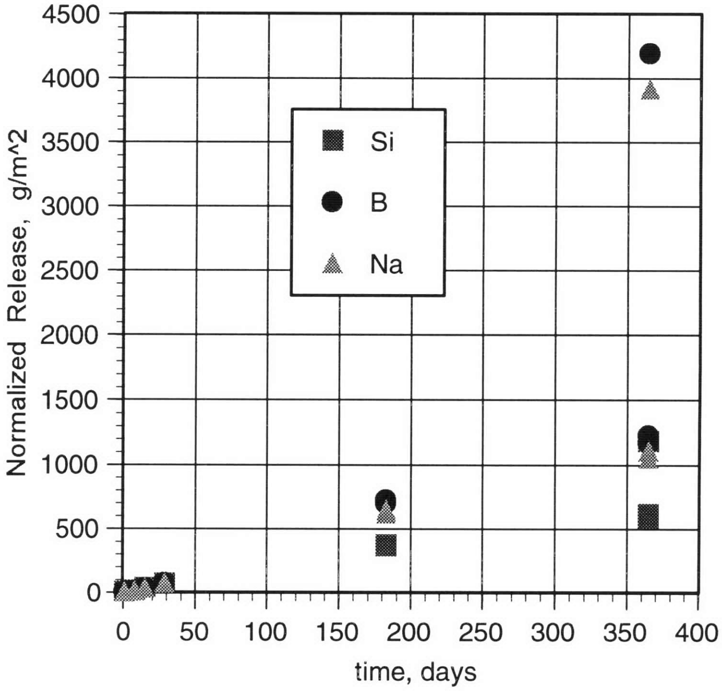

FIGURE 5. Silicon, Boron, and Sodium Release From Pure SRL165 Leached in DI Water at 90°C

Moreover, the release trends in the SRL165 glass do not follow the decreasing behavior demonstrated in the ARM1 tests. A potential explanation is that Si is forming a chemical complex or colloid in solution. This "removal" of Si activity keeps the SRL glass reacting at near the forward rate.

The nature of the colloid was not explored in detail. However, it is likely to be smaller than 45 μm as it was not affected by filtration at that level. When the leachate was acidified for analysis, the Si likely returned to solution. Pure SRL leachate that was not acidified formed a gelatinous cap on its surface upon cooling. Clearly Si had exceeded its solubility limit at room temperature.

A closer examination showed the two glasses initially reacting at nearly identical reaction rates. Figure 6 shows the elemental release of boron from the two glasses. While the ARM1 glass reaction rate diminishes shortly after 10 days, the SRL165 does not. This graph shows the potential importance of colloid formation in glass dissolution rates.

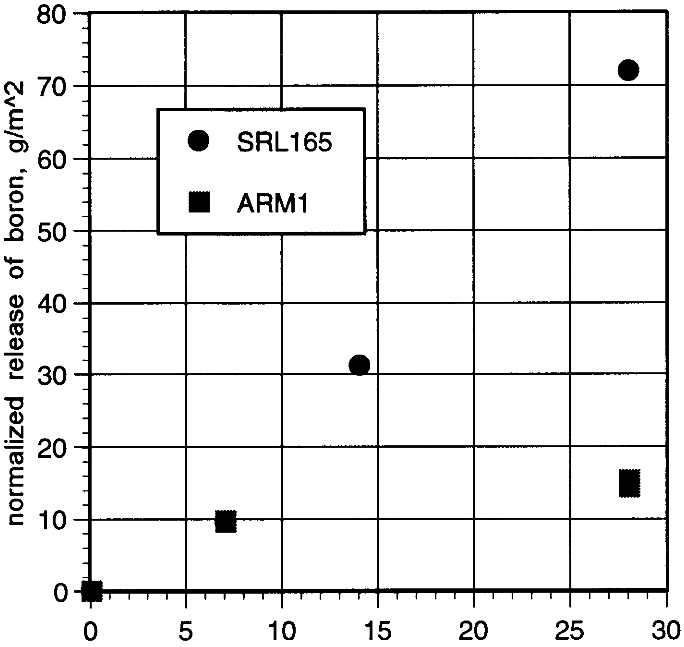

FIGURE 6. Initial Reaction Rates for ARM1 and SRL165 Glasses

The addition of Th and the rare earth elements to the ARM1 glass resulted in a product with roughly equivalent durability as pure ARM1. The release curves for Si, B, and Na are shown in Figure 7. While three of the samples had releases slightly higher than those for pure ARM1, two were lower. All releases were within a factor of two.

The ARM1 glass was effective at retaining the additional elements. The concentrations of Th, Eu, Gd, and Sm were below detection limits in three samples and within 1 ppb of the limits in the other two. (As the values were not corrected for elemental interference these value may actually be below detection limits as well.) Figure 8 shows the release data for the samples in which these elements were barely detectable. It is interesting to note the

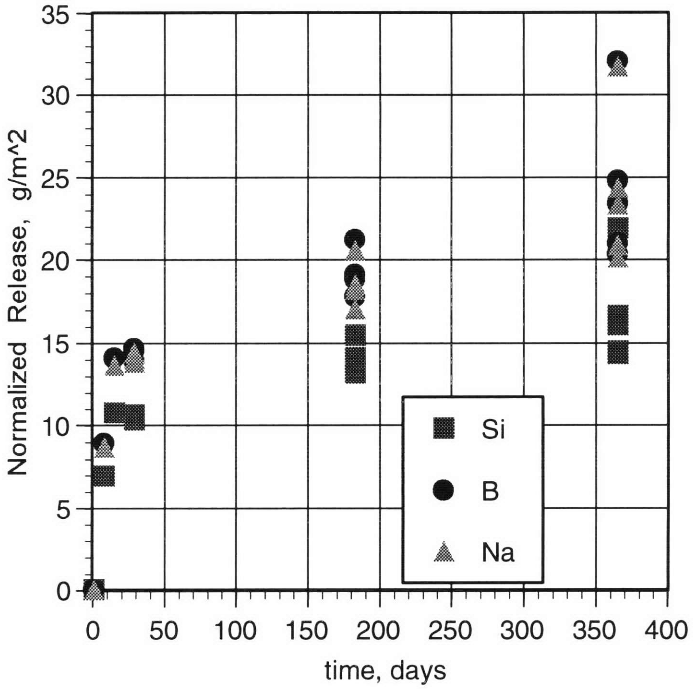

FIGURE 7. Silicon, Boron, and Sodium Release from ARM1 Glass Loaded with 2 wt% ThO_2, Eu_2O_3, Gd_2O_3, and Sm_2O_3 Leached in DI Water at 90°C

general order of elemental concentrations found either in solution or colloidal form. Thorium and Sm were the most soluble and Gd and Eu were the least. However, these concentrations are very near detection limits and should be viewed carefully.

In comparison with boron all the rare earth poisons exhibited superior performance. Figure 9 shows that while boron entered solution as the glass reacted, europium was much more resistant. This was the desired behavior for the added reactivity control. It is not known whether the rare earths remained in the alteration layer or were sorbed on container walls as strip tests were not performed. In the ARM1 glass the rare earths did not form colloids smaller than 0.45 μm. If they did form they would have been redissolved upon acidification and appeared in ICP analyses.

Figure 10 shows that the modified SRL frit did exhibit somewhat improved performance with the addition of Th, Eu, Gd, and Sm. The release trends of Si, B, and Na are lower and have less variability than those of pure SRL165. This may support the hypothesis that the

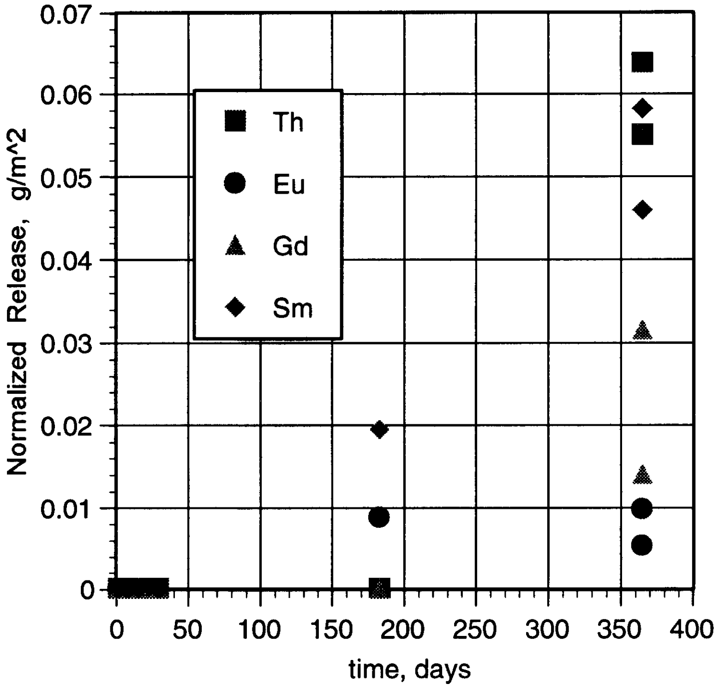

FIGURE 8. Detectable Thorium and Rare Earth Release From Modified ARM1 Glass at 90°C

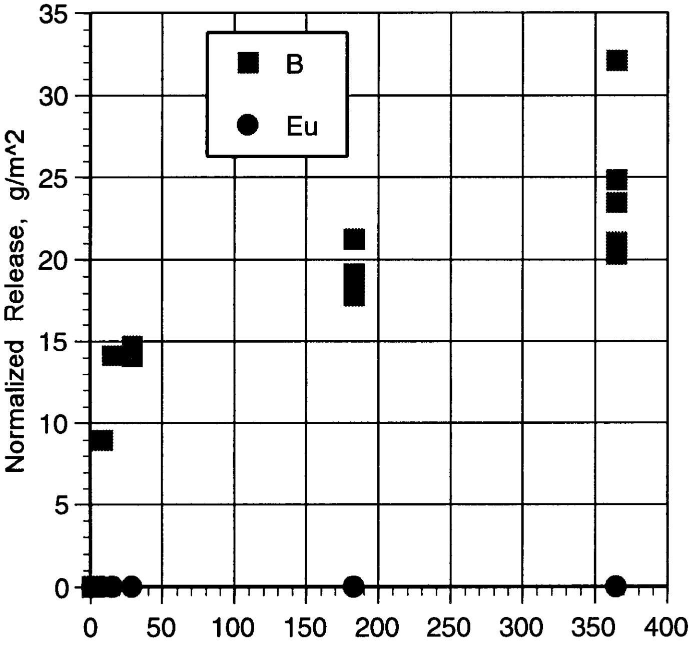

FIGURE 9. Reactivity Control Release in Modified ARM1 Glass at 90°C

RE elements act as Al does in the glass. As the rare earth elements are heavier, their molar concentrations in the SRL glass are below that of Al in the ARM1 glass (~1/4). Higher concentrations may have a more demonstrable affect on durability.

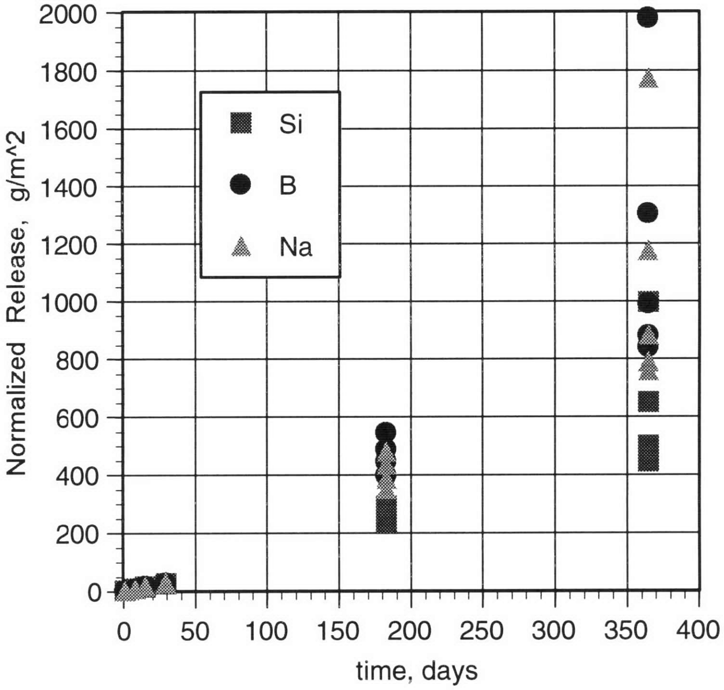

FIGURE 10. Silicon, Boron, and Sodium Release from SRL165 Glass Loaded with 2 wt% ThO_2, Eu_2O_3, Gd_2O_3, and Sm_2O_3 Leached in DI Water at 90°C

Regarding the release of Th and rare earths the results were mixed. These elements were below detection limits for three of the five SRL165 modified glasses. However the remaining two samples had 1-2 ppm of each element in its leachate. The Th and REE release behavior for these two samples is shown in Figure 11. These concentrations are much higher than the expected solubility limits of these elements in DI water.

This is an indication that as with the pure SRL165, colloids were formed in these two samples. However, only approximately 1 wt% of these elements actually went into solution. The rare earths had normalized releases on the order of 10 g/m^2 at 364 days. The normal-

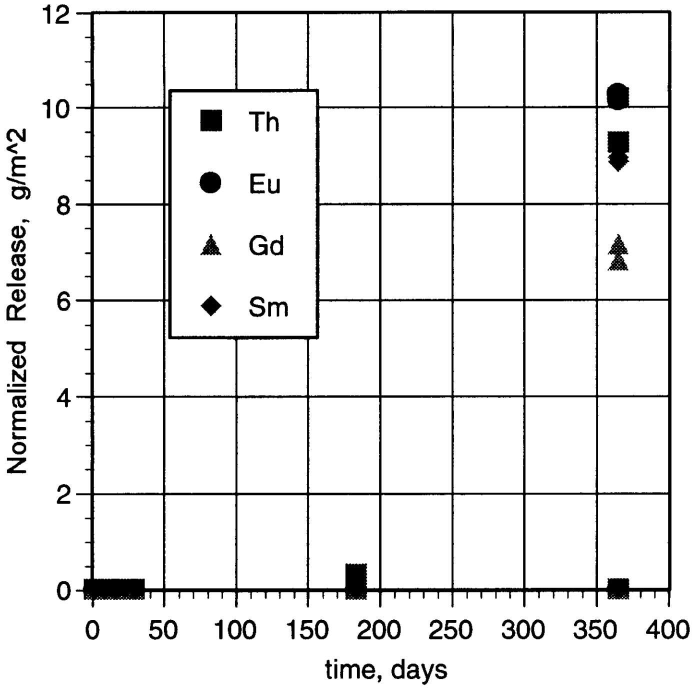

FIGURE 11. Detectable Thorium and Rare Earth Release From Modified SRL165 Glass at 90°C

ized releases from boron were two orders of magnitude higher. The REE and Th apparently both formed colloids. The Th did not separate from the REE.

The fact that boron releases in the glasses that did not form Th and RE colloids were lower than those for pure SRL implies that these elements increased the durability of the glass. The normalized boron release in these samples (where Th and RE releases were not detectable) ranged from 170 g/m^2 to more than 3200 g/m^2 lower than the pure SRL boron releases. The two samples that formed RE colloids had boron releases similar to pure SRL. All of these samples were more durable than the others. The difference between thorium loaded glasses could be a processing related effect.

For completeness, the Eu release relative to boron is displayed in Figure 12. Even in the relatively poor SRL glass, Eu release was much lower than boron over the time period investigated.

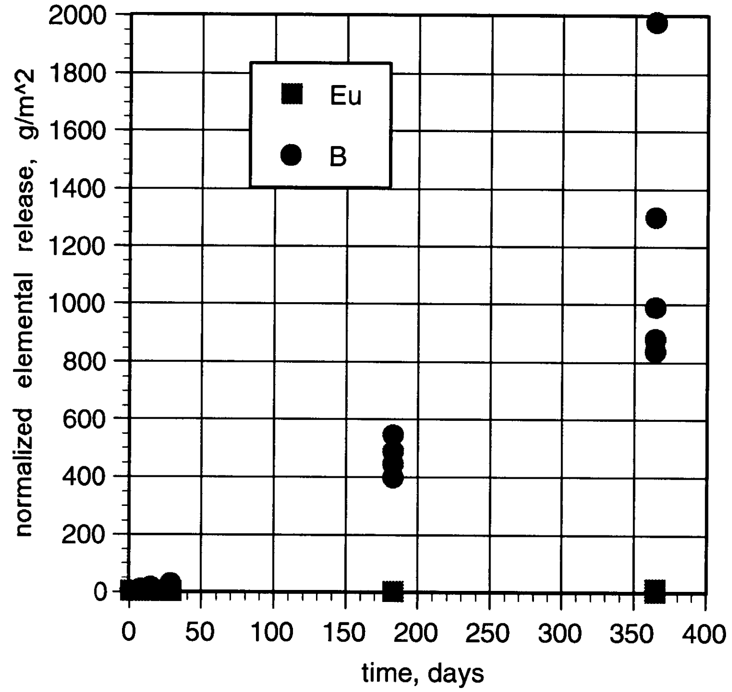

FIGURE 12. Reactivity Control Release in Modified SRL165 Glass at 90°C

4.6 Conclusions

The addition of Th and the REE does not harm glass durability and the potential exists for positive contributions. Further investigation is needed, but it appears that these elements were dissolved in the glass network and did not promote the formation of a less durable phase.

For glasses of reasonable durability it appears that Th will not enter solution. In this case Th is likely to be sorbed on surfaces or retained in reacted glass products. However, for a poor durability glass, dissolved species, high pH, or other factors allow Th to exist in colloid form. The Th could have formed a true colloid or sorbed on a Si or other colloid.

The rare earth elements had release characteristics virtually identical to that of Th in the tests performed. Regarding criticality control, the REE were always much more insoluble than boron. The formation of a colloid in the low durability glass is of concern as it may provide a release pathway for these elements. However, the data showed that ~99% of the Th and REE remained either sorbed on the container wall or in the reacted layer. When colloids were formed in the poor durability glass, both Th and the REE appeared to participate. This is significant as even in this case the neutronic poisons were demonstrated to mimic Th behavior.

4.7 Future Work

Further glass reaction testing should be performed on actual Pu loaded glasses in various concentrations. Upon selection of a glass formulation for Pu dispositioning, glasses with various ratios of Pu and REE should be fabricated to determine how these elements participate in the glass network. Any ternary compounds or stable complexes that form should be identified.

Devitrified products should also be produced and characterized. Devitrification may not be an important issue in glasses that do not contain HLW or Cs. However, the potential impact on neutronic control should be assessed. An attempt should be made to determine any differential behavior of the individual REE in glass formation. The suitability of Th as an analog should also be assessed.

Additional glass reaction experiments should be performed under a variety of aqueous conditions (e.g. flow-through tests) and include uranium. In particular regimes that generate colloids should be carefully examined. The nature and mechanisms for formation of the colloid produced during the SRL165 experiments should be determined. Their stability over a range of bulk environmental parameters (e.g. pH) and time should be characterized. Colloids that may be present in a geologic repository should also be assessed for their impact on actinide and rare-earth transport.

A variety of dissolved species should also be included in the leachate. The tests performed here utilized deionized water. Species in solution may be capable of forming complexes with the REE and thereby increase their concentration in solution. As this may provide a mechanism for REE and Pu separation, the conditions under which this might occur should be understood.

If credible scenarios for colloid formation are identified and it is shown that REE can be separated from Pu or U, alternate host phases for the control elements may be needed. Alternate glass or ceramic formulations should be assessed for their potential benefits in regard to colloid formation.

A mixed ceramic/glass form may have preferable characteristics. In these matrices, controlled devitrification is allowed as the glass formulation is tailored to provide durable host phases. Fabricated glass is reheated to encourage devitrification for this matrix. Glass ceramics have been shown to incorporate various REE in a durable sphene phase ($CaTiSiO_5$) (Lutze 1988: 427-469). Attention to Pu devitrification may not be necessary if it forms crystals of PuO_2 as this oxide is extremely insoluble.

Such a formulation may be especially useful in a can-in-can process where heat from the second stage vitrification may promote the uncontrolled devitrification of the present glasses under consideration. The LaBS glass is not a glass-ceramic formulation.

4.8 Glass Dissolution Model

In order to perform a near-field criticality assessment it was necessary to understand and model the physical mechanisms and spatial changes of an environmentally altered waste form. A model of this behavior was constructed and used to produce "snapshots" of system configuration during the reaction progress. This information was used to calculate the effective multiplication factor (k_{eff}) of the system as a function of time. This section describes glass reaction progress in aqueous environments and the assumptions used in this work.

4.8.1 Glass Reaction with Groundwater

Glass reaction is a complex process dependent on both glass and solution properties. In general, glass will react with water to release its soluble species and form more stable amorphous and crystalline phases. It is the redistribution of neutronically relevant nuclides during this process that is of primary interest in the work presented here.

Extensive research has been performed on glass reaction with water, the results of which have led to various descriptions of glass dissolution. One theory is that H^+ diffuses into the glass matrix and undergoes ion exchange, typically with alkali metals such as sodium (prevalently at the non-bridging oxygen sites). The alteration of the glass also allows soluble species (such as boron) to enter into solution. This produces a reacted layer that retains the amorphous silica structure of glass but with concentration gradients of alkali and soluble species. This layer has been termed the "diffusion layer."

Over time, the most depleted portion of the diffusion layer (its outer fringe) begins to hydrolyze. This results in a restructuring or repolymerization of the Si matrix into a more stable, hydrous "gel layer." This may or may not release Si into solution. The process apparently "kicks out" metals incapable of entering into a new amorphous phase (Bourcier 1991: 6). Eventually, the gel layer further reacts with water and is dissolved completely, releasing silica into solution. This reaction is termed "network dissolution."

This surface layer (the diffusion layer and gel layer combined) is typically less than a micron in thickness and moves into the glass as the bulk reaction proceeds. Following behind it is a layered region of amorphous and crystalline phases termed alteration layers.[38] This region has a complex elemental composition. Many of the metals that were either "kicked out" during gel layer formation or released as a result of network dissolution, quickly precipitate to form the alteration layers. These layers can be either amorphous or crystalline in nature. The retention of fissile nuclides in these layers is of interest here. Figure 13 provides a graphic description of the dissolution process.

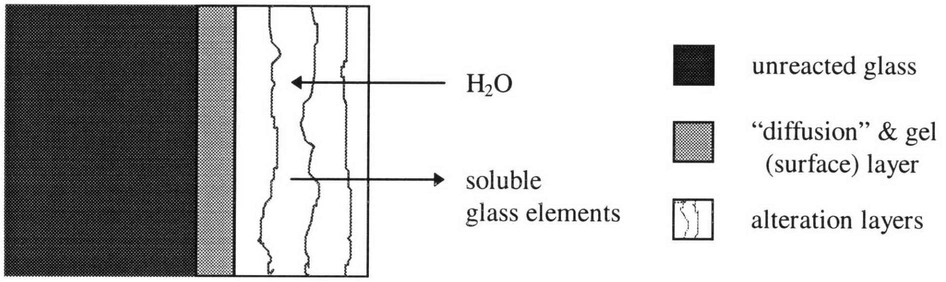

FIGURE 13. Dissolving Glass

Some experimental results have brought into question the importance of diffusion in glass reaction. Bunker et al demonstrated that there was no correlation between the solid-state diffusion coefficients for alkali elements and observed glass reaction rates (Strachan 1994: 130). The required interdiffusion coefficient (to support the assumption of a diffusion process) was several orders of magnitude higher than those measured for Na+ and K+. These results bring into question whether diffusion is occurring at all.

Results from experiments performed by Chick and Pederson demonstrate that if it is occurring, it is not a rate limiting reaction (Chick 1984). In one test a leached test sample was removed from its near saturation solution and placed (with alteration layers intact) into fresh leachate. If the layers (surface and alteration) were a diffusion barrier, the glass

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[38] There is inconsistent terminology in the literature as this region of alteration phases is often termed the gel layer.

reaction would continue at its slow pace. However, the sample exhibited dissolution behavior similar to its initial exposure to fresh leachate. The presence of layers apparently had no effect on glass reaction.

In any regard, it is the general consensus that the bulk dissolution rate of glass is primarily controlled by silica concentration in the leachate (Bourcier 1994: 8). Numerous glass reaction rate models use an affinity relationship of the form shown in Equation 2 to explain this behavior. This relationship is a simplified version of the general rate equation proposed by Aagaard and Helgeson (Strachan 1994: 136).

$$\vec{k} = k\left(1 - \frac{Q}{K}\right) \qquad \text{(EQ 2)}$$

where, $\vec{k}$ = dissolution rate[mol/(m^2*sec)];

k = rate constant (which actually depends on species activity) [mol/(m^2*sec)]

Q = reaction quotient (product of species formed raised to a power equal to their stoichiometric participation in the reaction)

K = equilibrium constant

The equation describes the reaction rate as a function of a constant material property, k, and the reaction affinity for some limiting glass dissolution reaction. The reaction quotient Q is related to chemical affinity in the following way:

$$affinity = \Delta G_{rxn} = RT\ln\frac{Q}{K}$$

or

$$\frac{Q}{K} = e^{\frac{\Delta G_{rxn}}{RT}} \qquad \text{(EQ 3)}$$

where, R = the gas constant(J/°K/mole)

T = temperature (°K)

As the glass reaction proceeds, Si species build up in solution and the Gibbs free energy of the system approaches its minimum (equilibrium) value. This "saturation" effect slows glass reaction rates. Other modeling approaches have included dependencies on solution species other than silicon, but the general approach is the same.

The adoption of an affinity model suggests an alternate role for the alteration layers. The alteration layers may control the concentration of the rate-limiting species in solution, which again is taken to be silica. Indeed, various silica phases have been assumed as controlling phases and used in reaction-rate modeling with relative success (Bourcier 1994: 18). In addition, the formation and dissolution of the alteration layer is reversible, therefore applying the rate law to the alteration layer is theoretically appropriate.[39] It is through this mechanism (rather than a transport barrier) that alteration layers could impact the long term dissolution rate.

The presence of alteration layers may explain why in closed system leach tests saturation is not reached. A "residual affinity" is observed that keeps the glass reacting, albeit at a relatively slow rate. It may be the case that the formation of the alteration layers and/or the nucleation and precipitation of a particular phase reduces solution concentration and maintains the residual affinity. In this case, as long as the phase can precipitate, the solution will never reach saturation with respect to the alteration layer.

4.8.2 Current Dissolution Models

A rate law associated with affinity control has been used in conjunction with a reaction path calculation to successfully model short-term glass performance (Bourcier 1994: 19). As the database of alteration phases is limited (making phase prediction difficult), analytical measurements of alteration layer composition on reacted glass are used . The solubility of a solid solution of phases chosen to reflect layer composition is then used in an affinity calculation. The rate constant is also determined experimentally. In this way the effect of rate-limiting reactions and alteration layer formation are accounted for in the models.

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[39] The irreversible glass dissolution reaction cannot possess an equilibrium constant.

While this approach has been successful at modeling glass reaction in the short-term, extending it to the long-term is difficult. The composition of alteration layers over time must be known in order to model the glass reaction rate. Short-term tests avoid this problem through direct measurement. This cannot be done over the long period of interest.

Yet formation of these phases can dramatically affect dissolution behavior. There is evidence that the eventual nucleation and precipitation of secondary phases rich in Si can dramatically increase glass reaction rate (Ebert 1991a). As with the alteration layers, the nucleation and precipitation kinetics of a rate limiting phase could control silica concentration, and thereby the long-term reaction rate. Accelerated leach tests have been performed in an effort to produce and thermodynamically characterize these Si phases (Ebert 1991b). However, predicting which phases form and when, requires assumptions about the evolution of repository chemistry over time.

The uncertainty concerning long-term rate control for glass reaction makes detailed modeling problematic if not impossible. Therefore the intent here was to utilize what is presently known about glass reaction mechanisms in aqueous environments to make both reasonable and bounding predictions of glass behavior over time. The following section describes the model used in this analysis.

4.8.3 A Glass Reaction Model

A simple model describing the composition and configuration of a single glass log in a repository was constructed. Available data on glass/groundwater chemistry were used to determine reacted glass and solution composition over time. System parameters were then varied to determine their effect on subsequent criticality calculations.

The following physical situation was modeled. The model assumes a glass log with the dimensions of a Defense Waste Processing Facility (DWPF) log (3m long x 60 cm diameter) and a nominal plutonium loading. The composition of the glass was the borosilicate glass used for HLW at the DWPF. This would represent the alternative of vitrifying Pu directly with HLW.

The canister was assumed to be emplaced in a horizontal drift at a repository with conditions similar to those expected to be found at Yucca Mountain in the state of Nevada. The mountain is under investigation as a potential high-level waste repository. A particular geologic formation known as "tuff" is taken to be the reference composition of the host rock.

As water infiltrates the region surrounding the glass, it reacts producing an annular region of alteration layers. This layer moves into the glass as reaction proceeds. The depletion of soluble poisons in this region may lead to a criticality event. Figure 14 is a graphical representation of the system as it evolves.

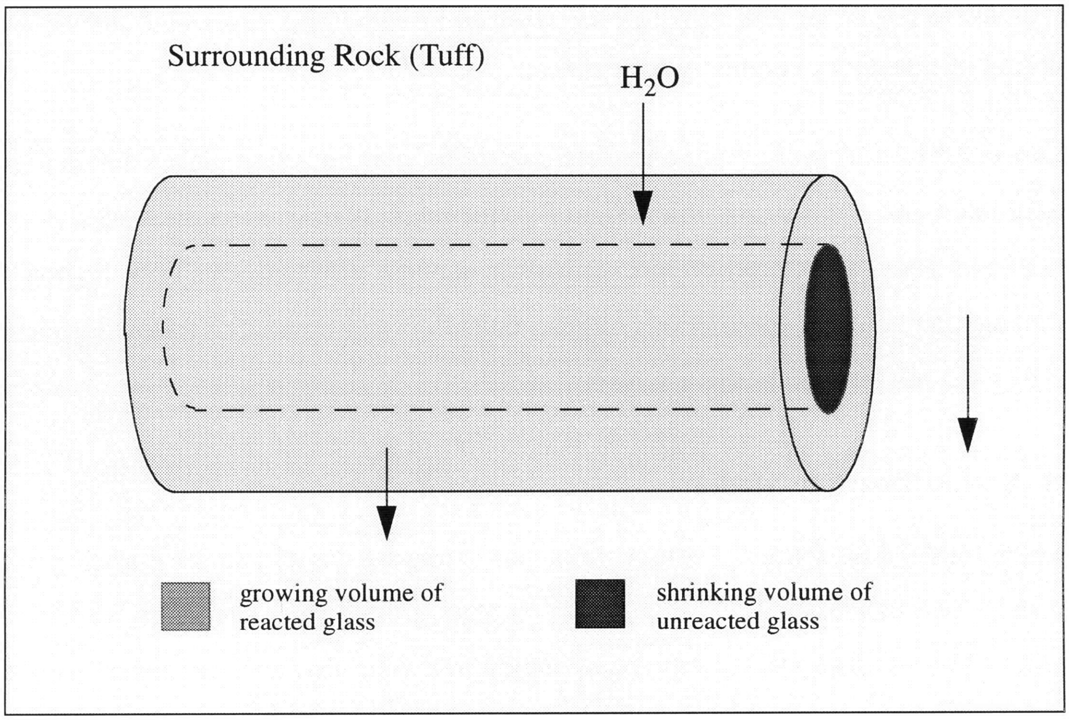

FIGURE 14. Hortizontal Drift Emplacement

Figure 14 shows the unreacted glass suspended concentrically within the alteration layers. This is not the most probable configuration. As the reacted glass will not provide mechanical support, the unreacted glass will more likely settle to the bottom of the drift. Uniform, cylindrical dissolution is also unlikely. Cracks in the glass, formed during cooling, could allow more homogeneous glass reaction. The configuration above was chosen for its low neutron leakage aspects. To perform a conservative criticality assessment, this was deemed to be appropriate.

Glass reaction was assumed to proceed in the following manner. As the glass reacts its constituents are released into the groundwater. The aqueous species react and insoluble phases are formed which make up the alteration layer. The composition of these phases was assumed to be those predicted using the speciation/solubility code EQ3/6, described in the next section.

The alteration layer is produced at an average bulk dissolution rate (BDR). The BDR was not calculated using an affinity model. As noted previously, the long-term reaction rate may be controlled by an unknown silica phase. The BDR was therefore taken as an exogenous input and varied to gauge its effect.

As reaction equilibrium is assumed, the predicted phases also determine the concentration of glass elements in solution. This concentration combined with the infiltration rate of water in the repository determines the removal rate of elements from the layer.

It is now possible to develop a set of mass balance equations for elements in the alteration layer. The radius of the unreacted log fixes the rate at which elements are added to the alteration layer, while decay and volumetric flow set the removal rate. Knowing the production rate and removal rate of elements in the layer, the following rate equation was constructed:

$$\frac{dN_i}{dt} = BDR(2\pi R(t)L)f_i(t) - IAC_{sol} - \lambda_i N_i \tag{EQ 4}$$

where: N_i = the mass of nuclide i in the alteration layer

BDR = bulk dissolution rate of the glass ($gm/cm^2/yr$)

R(t) = radius (cm) of the unreacted log at time t

L = the length of the log (cm)

$f_i(t)$ = the mass fraction of i in the log at time t

I = water infiltration rate ($cm^3/cm^2/yr$)

A = effective cross-sectional area of the region (cm^2)

C_{soli} = solubility limit of i (gm/cm^3)

$\lambda_i N_i$ = decay rate of i (gm/yr)

This general equation can be written for each glass component. For U-235, an additional buildup term due to the decay of Pu-239 is needed. The resulting set of equations can be solved using the elemental composition of fabricated glass as the initial condition to give a relationship for the mass of each nuclide in the alteration layer over time. The differential equations were solved numerically using a Runge-Kutta method. The details of this calculation are presented in Appendix B.

Equation 4 contains several variables that have yet to be discussed. The cross-sectional area is needed to determine the volumetric flow rate through the emplacement. An "interaction" thickness of 5 cm was added to the initial radius of the log for calculating this area. As the radius shrinks, a larger portion of water will "miss" the unreacted glass as it represents a smaller target. However, it is assumed that the initial "effective" borehole will provide a constant reaction volume for the glass/water mixture. This is conservative as a smaller volume of water would reduce neutron control removal rates. In addition, we are interested in removal of elements in the entire reacted region, not just the layers near the log.

The radius of the glass as a function of time is also needed. For simplicity, glass dissolution was assumed to occur only in the radial direction. With a constant BDR this gives the following function:

$$R_{\log} = R_o - \frac{BDRt}{\rho_s} \qquad \text{(EQ 5)}$$

where R_{log}= radius of the unreacted log

R_o = initial radius

BDR = bulk dissolution rate

ρ_s = density of the glass

The bulk dissolution rate, water infiltration rate and elemental loading can be varied to determine their effect on criticality. The remaining information needed is the solubility data. The following section describes how this information was attained.

4.8.4 Solubility/Phase Calculation

As the glass reacts, its components enter into solution. Whether elements remain in solution or precipitate is determined by the contacting groundwater conditions.[40] Over time, the glass reaction itself will alter solution chemistry. Available thermodynamic data were used to investigate the evolution of solution concentrations during glass reaction and the formation of precipitate phases. The composition of the phases over time will be used to determine if the near-field system approaches a critical condition.

Of primary interest for the criticality assessment were the neutronically relevant species in the glass and alteration layers. These included fissile, poison and moderating elements. While all major glass elements were used to determine the alteration layer phases, only the elements with significant neutron cross-sections were used to represent the layer in the criticality calculation. The remaining mass of alteration layer was assumed to be silica based. This procedure is discussed further in Section 4.9.1.

The behavior of the following elements was examined: Pu, U, B, Li and Eu. Plutonium and uranium are fissile elements. While no uranium is found initially in the glass, Pu-239 decays to produce fissile U-235 (half-life=24,100 yrs). Boron and lithium are neutron control elements that are normal components of the glass. It is the higher solubility of boron and lithium relative to Pu and uranium in solution that could lead to a criticality event.

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[40] Sorption or colloid formation may also occur.

Europium is a neutron absorber not used in the current DWPF glass frit that was evaluated for its neutronic control capabilities and its expected insolubility. Europium was identified in prior work by the author as being particularly detrimental to a Pu explosive device if not removed (Sylvester 1994). Lanthanide elements exhibit very negative equilibrium potentials and therefore act as reducing agents and in basic solutions form insoluble hydroxides (Pourbaix 1974: 192). Actinide elements behave similarly. It is hoped that their similar aquatic chemistry, as demonstrated in Section 4.5, will keep them commingled and thereby keep the near-field waste emplacement subcritical.

Actinide/Lanthanide Aqueous Chemistry

In aqueous solutions actinide ions exist in the trivalent and tetravalent states as simple hydrated ions An^{3+} and An^{4+}(Silva 1995). At higher oxidation states the actinides form oxygenated species called actinyl ions. For plutonium these ions are $PuO_2{}^+$ and $PuO_2{}^{++}$. Redox reactions between either of the two lower states and the two higher states will be pH dependent due to the formation of the actinyl ions. These pH dependent reactions also tend to be slower. The higher oxidation states are increasingly favored with increasing pH.

Oxygenation of the higher states reduces the charge on the central actinide to +3.2 or +2.2 and leads to a lower ionic potential. This explains why the +4 state is the most readily hydrolyzed and complexed of the oxidation states. Hydrolysis results in an insoluble hydroxide but if a ligand concentration is high enough (including OH^-), complexation will dominate and the actinide will be more soluble.

Actinides will form hydroxide, carbonate, fluoride, phosphate, and sulfate complexes. Chlorine and nitrate complexes can also be formed but are less favored (Silva 1995: 384). Other complexes (bromide, peroxide, oxalate, etc...) are known to form but are not concentrated in the glass or the groundwater (Cleveland 1979: 81 and 92). The actinide oxidation state is important for complexation. The following strength of complexation trend has been observed: $4+ > 3+ \approx 6+ > 5+$.

Lanthanides have similar chemical behavior but differ from actinides in certain respects. Under environmental conditions, lanthanides exist in the +3 state and behave chemically as the +3 actinides of similar ionic size (Gschneidner 1979: 554). Lanthanides do not exhibit the same robust redox behavior of the actinides. The hydration energy gain for +3 lanthanides is not sufficiently greater than the ionization energy for the 4f electrons to promote higher oxidation. The 5f electrons of the actinides are more shielded and therefore a wider range of oxidation states can be attained.

The oxidation state and the degree of complexation will depend on solution composition. As the assumed repository is Yucca Mountain, water from a well located at the site (J13) was taken as the reference solution. The composition of J13 well water is shown in Table 5.

TABLE 5. J13 Well Water[1]

Species	Concentration ppm
Na+	45.800
SiO2(aq)	60.970
Ca++	13.000
K+	5.0400
Mg++	2.0100
Li+	0.0480
H+	4.013e-5 (pH=7.41)
HCO3-	140.40
O2(aq)	5.6000
F-	2.1800
Cl-	7.1400
NO3-	8.7800
SO4--	18.400
B(OH)3(aq)	0.7660
Al+++	0.0080
Mn++	0.0120
Fe++	0.0400
Sr++	0.0400
HPO4--	0.1200

1. taken from EQ6 library

The J13 water is neutral pH and slightly oxidizing. It is a carbonate water with significant amounts of silica, sodium and calcium. Notably it also contains sulfate and fluoride species. These species were noted earlier for their ability to form complexes with actinides.

As glass dissolves, its constituents will alter solution chemistry, possibly hampering the formation of certain phases or promoting others. The relevance of glass composition has been noted in the literature. A study of particular interest performed a geochemical simulation of two types of dissolving glasses (Bruton 1987). In the glass used at West Valley, uranium complexed with the glass element phosphorus and remained at a relatively high concentration in solution. The DWPF glass contains no phosphorus and the uranium was predicted to precipitate as it could not form the soluble complex. Solution Eh and pH changes during glass reaction as well. All these factors influence elemental solubility and demonstrate the need for this type of analysis.

The reference glass used in the analysis was the DWPF glass (Savannah River frit 131). This represented the option of blending Pu directly with the sludge-supernate waste at Savannah River. This glass has a much higher soda loading than the ARM1 glass but is roughly comparable. Its composition is shown in Table 6 (Baxter 1995: 36).

Two scenarios were assumed to evaluate solution chemistry. First, reaction path issues were ignored and elemental solubility was calculated based on saturation in the J13 water alone. This was deemed to represent solution control dominated by simulated Yucca Mountain environmental conditions. Second, a calculation was performed to evaluate the effects of glass components. This combination of calculations was assumed to span the range of water chemistry that may contact the glass.

The speciation/solubility code EQ3/6 was used with its associated thermodynamic databases for both scenarios (LLNL 1992).[41] EQ3 uses mass action and redox relationships to

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[41] The composite data file ‘data0.com’ compiled and maintained by Lawrence Livermore National Laboratory was used for all solubility/speciation calculations.

TABLE 6. DWPF Sludge-Supernate Glass

Component	wt%	Component	wt%
Ag_2O	0.75e-02	MnO	1.73
Al_2O_3	3.35	$Na_2B_4O_7$	0.21e-03
B_2O_3	10.59	Na_2O	17.59
BaO	0.039	NiO	0.62
$Ca_3(PO_4)_2$	0.15	PbO	0.041
CaO	1.07	PuO_2	0.015
CoO	0.016	RhO_2	0.56e-02
Cr_2O_3	0.11	RuO_2	0.025
Cs_2O	0.073	SiO_2	45.09
CuO	0.036	SrO	0.029
Fe_2O_3	6.09	ThO_2	0.23
FeO	2.70	TiO_2	0.72
Group A[1]	0.11	UO_2	1.2
Broup B[2]	0.36	Y_2O_3	0.017
K_2O	0.19e-03	Zeolite	1.47
La_2O_3	0.36	ZnO	0.095
Li_2O	4.13	ZnO_2	0.36
MgO	1.59		

1. Group A: Radionuclides of Mo, Rb, Se, Tc, Te
2. Group B: Radionuclides of Ag, Am, Cd, Ce, Cm, Co, Cr, Eu, La, Na, Nd, Np, Pd, Pm, Pr, Sb, Sn, Tb, Tl, Zr

solve for the thermodynamic equilibrium state of a specified ground water, identifying species concentrations and supersaturated phases. The order of phase precipitation, which may allow initially supersaturated species to remain in solution, is not addressed. EQ3 was used to determine elemental concentrations for the environmental control scenario.

EQ6 models the addition of reactants to a solution allowing supersaturated phases to precipitate as reaction proceeds. The order of precipitation is determined by the degree of disequilibrium of the saturated phases. After the phases are removed, additional reactants are added and the process repeats. The onset of saturation can be observed in this way.

EQ6 was run in titration mode to model the effect of dissolving glass.[42] In the titration calculation glass components are stoichiometrically added to a constant volume of water where they are completely dissolved and new phases are allowed to precipitate. The calculation results in a description of the aqueous species and insoluble phases that form during reaction progress. Points along this reaction pathway were taken to represent alteration layer composition for various degrees of glass reaction. The associated phases and solution concentrations were then used in the analysis.

The major glass components (>1% by weight of the oxide) were used to determine the phases formed during reaction with simulated J13 groundwater. The remaining components were judged too small to impact phase formation. These trace elements (which include all the actinides and fission products) were ignored in the criticality assessment as well. They could provide additional neutron absorption, therefore eliminating them is conservative. This assumption also allows the results to be applied to a borosilicate glass without fission products.

The crystalline silica polymorphs (chalcedony, coesite, cristobalite(alpha), cristobalite(beta), quartz, and tridymite) were also suppressed in EQ6. This is a common procedure in reaction path modeling to prevent the formation of thermodynamically favored phases that are known through experiment not to form.

4.8.5 Solubility Results

Environmental Control

Under tuff control, EQ3 found boron to be soluble at concentrations greater than 5000 ppm. This confirmed that boron would not likely be present in the alteration layers.

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[42] There are three alternate methods for reaction path modeling in EQ6 : titration, closed system or fluid-centered flow-through system. The closed system differs in the way it treats saturation. At saturation in the closed system the reactant is reclassified as a secondary mineral with which equilibrium is reached. As the available reactant is now "gone," reaction stops. The titration model forces dissolution while the closed system reaction halts the reaction upon saturating.

Lithium however was predicted to precipitate in the petalite phase $LiAlSi_4O_{10}$. Equilibrium with this phase gave a concentration of 8.3E-9 M (moles/liter) in the J13 water. The groundwater was initially supersaturated. This Li concentration is therefore lower than the initial concentration. Europium formed the solid precipitate $Eu_2(CO_3)_3{:}3H_2O$. This gave a concentration of 4.5E-7 M. The insolubility of these phases would assist in criticality control.

The fissile elements plutonium and uranium were also predicted to precipitate. Plutonium in equilibrium with PuO_2 gave a concentration of 1.2E-15 M. Uranium precipitated as haiweeite, giving an equilibrium concentration of 8.6E-10 M.

Glass Control

Under DWPF glass control chemistry, elemental solubilities were calculated based on equilibrium with phases formed during various stages of glass reaction. The elements of 10 grams of DWPF glass were added stoichiometrically via a titration process into one kilogram of J13 water. The glass contained 8 wt% PuO_2 and one mole of Eu_2O_3 per mole of Pu.

EQ6 produced a history of phase production and solution chemistry during glass reaction. Figure 15 shows how the concentration of relevant elements changed over time. During the criticality analysis, points along the reaction pathway were chosen as the steady-state composition of the layer.

At no time during the reaction was boron predicted in the alteration layers. This confirms the EQ3 predictions.[43] However, the EQ6 results show Li follows B and is not insoluble as predicted by EQ3. During reaction, Li existed in solution as Li^+, not a complex. Its solubility therefore cannot be attributed to complexation with a glass component. Instead, as the glass reacts, aqueous Al is consumed (in stilbite and smectite) and pH rises as

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[43] The Bruton simulation of West Valley glass did predict the precipitation of B_2O_3 at the 10g glass/1 kg water mark.

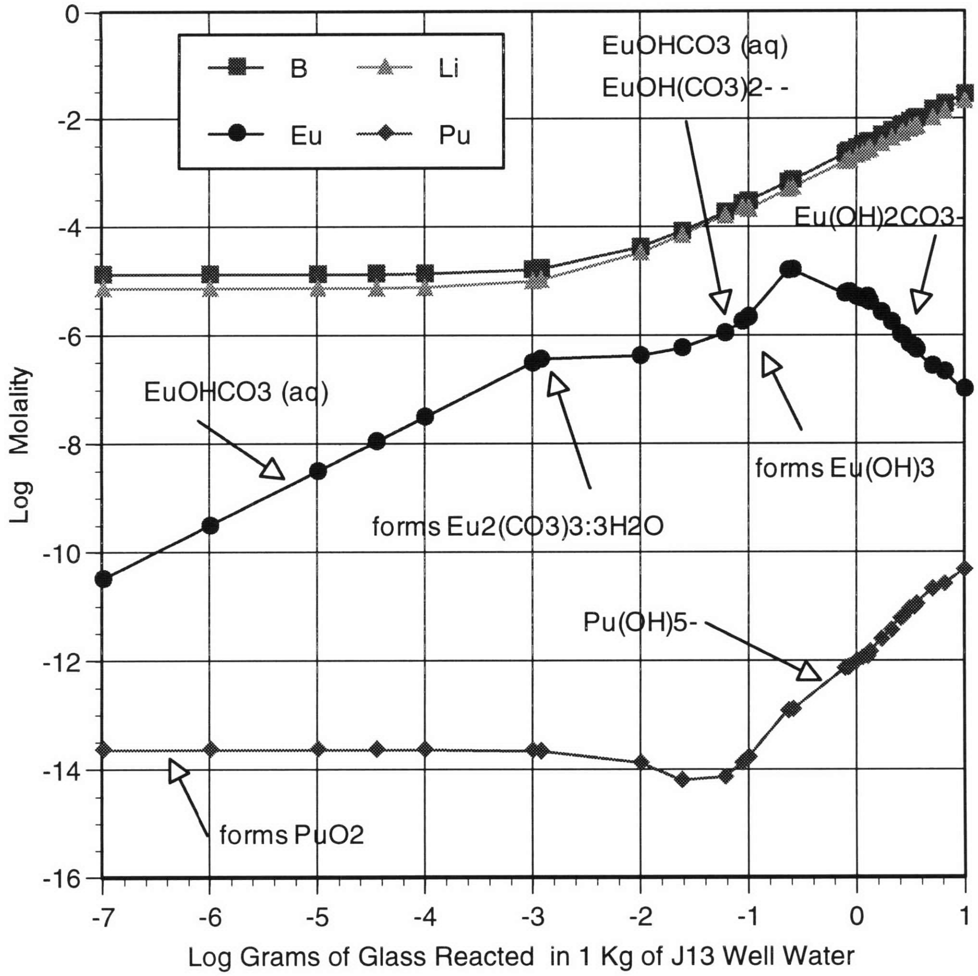

FIGURE 15. Reaction Path for DWPF Sludge-Supernate Borosilicate Glass in J13 Well Water from Yucca Mountain

shown in Figure 16. Both have the effect of hampering petalite formation. Therefore after an initial precipitation (~$10^{-2.5}$ moles) additional Li releases remain in solution.

The Li results demonstrate the potential importance of reaction kinetics. If the order of phase precipitation diverges from that predicted in the calculation, significant differences in solution concentration could be observed for elements such as Li. In this case this "common ion" determined whether Li would remain near the waste package or be solubilized. Kinetic issues were not addressed in this research but should be carefully investigated in future work.

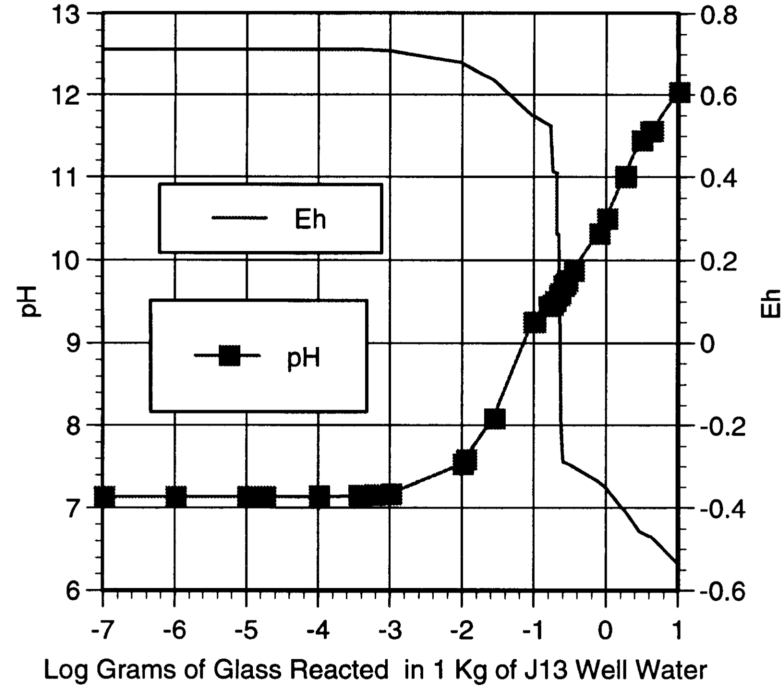

FIGURE 16. Solution Eh and pH Behavior for DWPF Sludge-Supernate Borosilicate Glass in J13 Well Water from Yucca Mountain

The remaining elements of interest evolved in the following way. Europium enters into solution as the carbonate species $EuOHCO_3$. It then precipitates as $Eu_2(CO_3)_3{:}3H_2O$, reaching the initial concentration predicted by EQ3. While the carbonate species appears important, at a pH of 7, Eu would have precipitated out at a slightly higher concentration due to solid $Eu(OH)_3$ formation. When HCO_3^- starts to drop , $Eu(OH)_3$ begins to form. Competition ensues between the formation of several carbonate complexes and precipitation. Ultimately Eu reaches a maximum concentration of 1.5E-5 M. Europium concentration is reduced with increasing pH. Eu remains in the +3 oxidation state throughout reaction.

Plutonium from the glass is immediately precipitated as PuO_2 (log K_{sp}=-7.36). The small amount remaining in solution exists in the +5 and +6 state (PuO_2^+ and $PuO_2F_3^-$). This is a slightly higher concentration than predicted by EQ3. As glass reaction continues, Pu concentration dips due to HCO_3^- reduction to a concentration of 5.8E-15 M. Eventually Pu is reduced to +4 and hydrolyzes (complexes with OH^-) causing the solubility of Pu to increase. This complexation allows the Pu to be more soluble under reducing conditions than earlier oxidizing conditions. Pu solubility is then controlled by pH.

Figure 17 shows the reaction path for the same glass but with uranium replacing Pu in equal molar quantities. As the glass reacts, the uranium concentration rises until haiweeite forms ($Ca(UO_2)_2(Si_2O_5)_3{:}5H_2O$) producing the uranium concentration predicted by EQ3. The carbonate complex $UO_2(CO_3)_3^{4-}$ keeps the U concentration initially at approximately 1E-9 M, otherwise the concentration would have been much lower. As pH drops and HCO_3^- is reduced, uranium concentration drops to a minimum value of 2.6E-10 M. As the glass continues to react, uranium is reduced to the +4 state and forms aqueous $U(OH)_4$, causing uranium concentration to rise. Eventually no carbonate complexes exist and uranium is in equilibrium with uraninite. Uranium concentration stabilizes as solution pH stabilizes. For determining U solubility, the initial U loading was not important.

4.8.6 Conclusions

Carbonate and hydroxide appear to be the most significant complexing agents in the system studied. While chloride and nitrates are present in J13 water, at no time do Pu or U form their complexes. This is consistent with the observed trend in complexation strength. It is the 'over' complexation of the actinides (hydroxide and carbonate) to produce negatively charged species that could increase solubility in the J13 water.

Glass components can have complex effects on elemental release. The consumption of dissolved oxygen due to Eu and Pu reactions produces species of lower oxidation states. Reduced species tend to be more insoluble. (While Pu^{3+} is soluble it was not formed here.) However the simultaneous increase in pH during glass reaction more than offsets the effect causing Pu solution concentrations to rise.

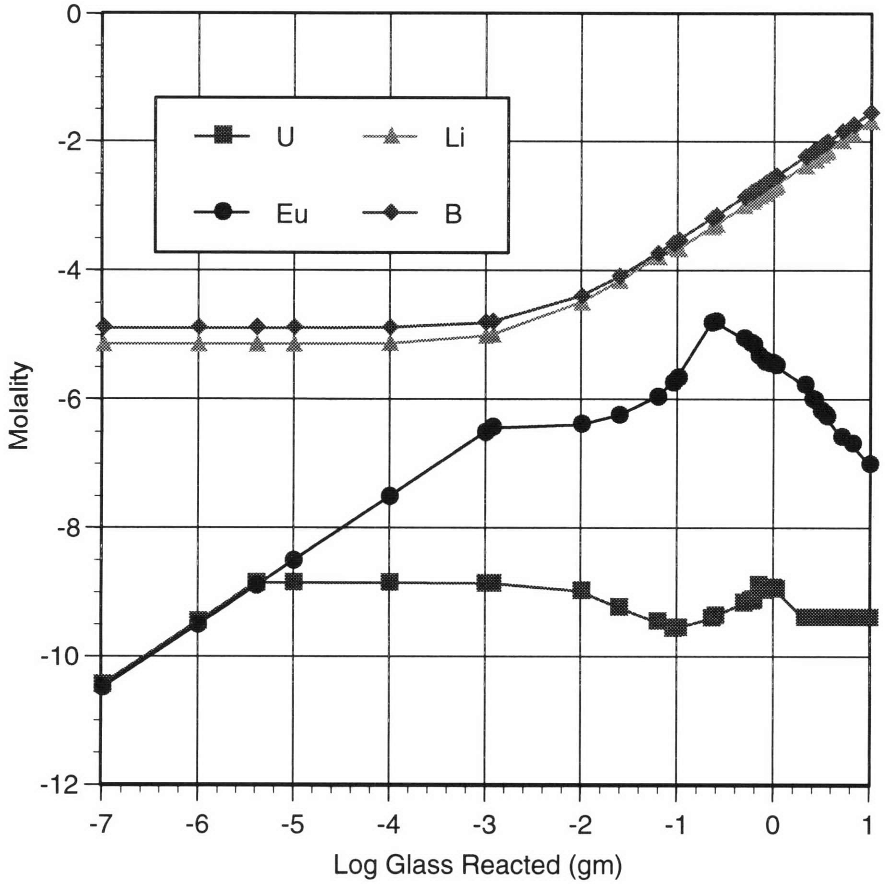

FIGURE 17. Reaction Path - Uranium and Lithium

The oxidation potential appears to be sensitive to the combined Eu and Pu loading. Without these elements the eH drops roughly 0.2 mV during glass reaction. With these elements it drops 1.2 mV. This reflects the strong reducing properties of rare earths and actinides. In contrast the loading of these elements does not affect pH.

The worst regime from a criticality perspective appears to occur when pH is around 9. This produces the greatest difference between Eu and Pu solubility. Uranium concentration is relatively constant throughout glass reaction. At higher pH Eu becomes less soluble, reducing this difference and the criticality concern. Due to the ion exchange reactions of dissolving glass, the groundwater closest to the surface is likely to be basic. However, the potential effect of radiolysis on pH due to actinide decay was not assessed.

This work based element solubility on precipitation and complex formation using available thermodynamic data. However, this data does not span all possible environmental conditions. Indeed thermodynamic data for all possible oxidation states does not exist for these elements (Silva 1995: 9). Other complexation (e.g. humic acids) may also affect solubility. In addition colloid formation (both true and pseudo) may provide an additional mechanism for neutron control removal. Radiation effects may be important but were not examined here. Sorption was also not considered but would tend to help matters in terms of near-field criticality.

Results from both the environmental and glass control scenarios will be used in the criticality calculations. For the glass control case the lowest solubility achieved by the fissile elements will be used with the highest calculated solubility for the control element. This was done to represent a worst case or highest degree of fissile/control separation. The details of this calculation are expressed in the following section.

4.9 Criticality Assessment

The result of the dissolution model was a description of the composition and thickness of the alteration layer as it replaced the dissolving glass. A description of how this data were used in the criticality calculation and a discussion of the additional assumptions made are presented in this section.

4.9.1 Problem Setup

The issue of WGPu disposal has sparked several repository criticality studies. These included an assertion by Dr. Charles Bowman et al of Los Alamos National Laboratory that the emplacement of large quantities of WGPu could result in underground nuclear explosions (Bowman 1995). Additional research on this issue claimed that such an explosion is impossible but that an underground criticality could occur (Sanchez 1996). Hence such explosions were not investigated in this work.

The Nuclear Engineering Department at U.C. Berkley has been investigating the possibility of a far-field criticality event (Kastenberg 1996a). Their work modeled the transport and eventual deposition of Pu and U-235. Scenarios were postulated for approach to criticality and a performance assessment was used to assess the risk of an auto-criticality event.

In this work, the potential for criticality to occur in the near-field was investigated. The system was modeled as three regions, the unreacted glass, the surrounding tuff, and the alteration layer. The unreacted glass was assumed to be comprised of the major components (>1 wt %) of the glass composition listed in Table 6. Various amounts of Pu and REE were added to this composition. The neglected components could contain neutron absorbers so their exclusion was deemed conservative. The density of the glass was taken to be 2.75 g/cc (Baxter: 1983).

The surrounding tuff was assumed to be of the composition given in Table 7. Its density was taken to be 2.2 g/cc (Kastenberg 1996b: 302). The porosity of the tuff was taken to be 0.3 While unfractured tuff is likely to posses a lower porosity, the tuff backfill would not due to disruption during emplacement. This value provided a upper bound on the amount of water that could be found in the tuff.

TABLE 7. Tuff Composition[1]

Element	wt%
Ti	0.06
Al	6.721
Fe	0.661
Mn	0.046
Mg	0.096
Ca	0.379
Si	35.99
O	49.2
K	4.126
P	0.00436
Na	2.7

[1] (Kastenberg 1996b: 302)

The uncertainty surrounding future phase nucleation, described in Section 4.8.1, added uncertainty regarding the exact elemental composition of the alteration layer. Without knowing the characteristics of each phase that nucleates, it is impossible to predict the exact makeup of the alteration layer. This unavoidable uncertainty provided another justification for tracking only neutronically important nuclides as the glass dissolves.

After determining the concentration of the relevant nuclides in the alteration layers (as described in Section 4.8.4), the remaining mass of alteration layer was assumed to be amorphous SiO_2. The total mass of the alteration layer was assumed to be 25% of the original glass. This also fixed the porosity of the alteration layers at 0.75.

Porosity was expected to be important as it determines the water concentration and thereby the degree of moderation under saturation conditions. The effective porosity could be increased if the specific densities of the alteration phases were higher than the density of the glass. However, in this analysis the densities of these phases were assumed to be equal to the bulk density of the glass.

After fully characterizing the system, the compositional information was used in the criticality code system SCALE-PC. The following section describes this code.

4.9.2 SCALE-PC

SCALE-PC is a modular code system for performing criticality safety analysis (ORNL 1992). It is comprised of various functional modules for cross section processing, criticality and shielding calculations. SCALE-PC uses a subset of the modules depending on the user specified sequence. For all the results presented below, the SCALE sequence CSAS1X was utilized. This control module used the functional modules BONAMI-S, NITAWL-S and XSDRNPM-S. These modules are described below.

A repository containing dissolving glass logs was modelled as a lattice of infinitely long, annular 'fuel' cells. However, the pitch was chosen large enough so that neighboring logs would not contribute to the neutron economy. The alteration layer, depleted of boron, was assumed to be analogous to the fuel region of a large annular fuel pin. The interior region contained the unreacted glass and the tuff represented the moderator portion of the unit cell.

Using the compositions specified, CSAS1X began by calling the BONAMI-S module. BONAMI assumes a simple expression for flux in an infinite homogeneous medium and applies the available Bondarenko factors to produce resonance corrected group cross sections for use in other modules. These factors are selected based on nuclide concentrations and temperature and used to modify infinitely dilute group cross sections. Dancoff factors are used to account for the additional self-shielding as a result of a heterogeneous lattice. Cross sections were taken from the Hansen-Roach library. This database contains 16 energy group data for the radionuclides used in the analysis.

Further self-shielding treatment is performed by the module NITAWL-S. The Nordheim Integral Treatment is a two-region (fuel and moderator) integral transport theory method for determining resonance corrected group constants. Energy variations of the flux are assumed and first-flight escape probabilities are used to account for coupling between the two regions.

NITAWL performs calculations for each resonance but does not include resonance overlap. As U-235 and Pu-239 have overlapping resonance there was some concern as to applicability.[44] In addition, thermal upscatter into the resonance region is not accounted for. This may lead to an over-statement of the resonance shielding and an underestimation of k_{eff}. While this effect is most notable at higher temperatures (such as in operating reactors) and may not be important, MCNP4A was used to gauge any impact. The results of this MCNP ‘benchmarking’ are discussed later.

Having generated the resonance-corrected cross-sections XSDRN-PM was used to calculate k_{eff} values. XSDRN-PM provides a 1-D, discrete ordinates, solution to the neutron transport equation. The discrete ordinates method represents the spectral dependence of

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[44] ORNL (1992: Part2 p.M7.2.6)

the neutron flux via Legendre polynomials. Due to the large, simple geometries of this problem, scattering order was taken to be 1. The angular quadrature used in the difference equations (S_n equations) in XSDRN-PM was of order eight. The unit cell had a reflected boundary condition on the left-hand side (center of the glass log) and a white boundary condition (isotropic return) on the right-hand side representing the tuff region.

4.9.3 Cases Investigated

For both environmental and glass control scenarios, model parameters were set at values most favorable for control removal and fissile element precipitation. The model parameters bulk dissolution rate and volumetric flow were set at high values in order to bound the concentration of Eu needed in the glass to maintain subcriticality. All together, these assumptions were assumed to represent a "worst case" scenario. These parameters as well as Pu loading were then varied to determine their relative importance in the model.

Initially, a glass loaded with 8 wt% PuO_2 was modeled. As 10 wt% ThO_2 was shown to devitrify this was assumed to limit the solubility of Pu in the glass. Europium was assumed to be dissolved in the glass at various concentrations. Europium was chosen for its high thermal cross section (and resonance integral) and, as noted in Section 4.8.4, its ability to complicate weapon design. The ratio of Eu/Pu was examined for its effect on repository criticality.

The bulk dissolution rate is the fundamental measure of glass performance and sets the growth rate of the alteration layer. It also determines whether the plutonium or uranium chemistry is relevant. A high BDR means the analysis will be concerned with both Pu and Uranium chemistry. For very low BDR, the problem is dominated by uranium chemistry. As uranium was predicted to be more soluble, thereby leaving the near-field more quickly, the case for a high BDR seemed to be of most concern. An initial value of 0.1 g/m2/yr for BDR was taken and then reduced to evaluate both Pu and U dominated scenarios.

It would appear that a high bulk dissolution rate would require a minimum water infiltration rate. This would continually expose the surface of the glass to fresh water, allowing the glass to react at its forward rate (i.e. a high BDR). However, under low flow conditions the nucleation and precipitation of a Si rich phase could allow glass to also react at the forward rate. This is the justification for independently varying the bulk dissolution rate and the water infiltration rate to gauge their impact. The current infiltration rate at Yucca Mountain is 0.001 $m^3/m^2/yr$.[45] For the bounding calculation, the flow was taken to be 0.01 $m^3/m^2/yr$, the highest expected rate under consideration at Yucca Mountain.[46] Moderation effects were investigated by changing the degree of saturation in the alteration layers and the tuff regions.

4.10 Results

The results using solubilities from the glass control chemistry are presented first. In all the figures in this section, solubilities for fissile elements were set at their lowest observed values during glass reaction and control elements at their highest. The evolution of k_{eff} is presented for the case of highest glass dissolution rate and volumetric flow (termed "worst case" conditions) for several Eu/Pu loadings. The results of modifying glass durability and groundwater flow are then presented.

4.10.1 Glass Control

"Worst Case" Conditions

Figure 18 shows the effect of control element removal for a glass log loaded with 8 wt% PuO2. Even at the assumed maximum Pu loading, only a relatively small concentration of Eu is needed to hold down reactivity. Both the thermal neutron cross section and resonance integral of Eu-151 are an order of magnitude higher than those of Pu-239. A mole ratio of 1/2 Eu to Pu kept the system subcritical for more than 800 thousand years. Due to the atomic mass differences between Pu and Eu, this corresponded to a loading of less than 3 wt% Eu_2O_3 (2.6 wt%).

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[45] Berkley paper

[46] Yucca Mt performance assessment.

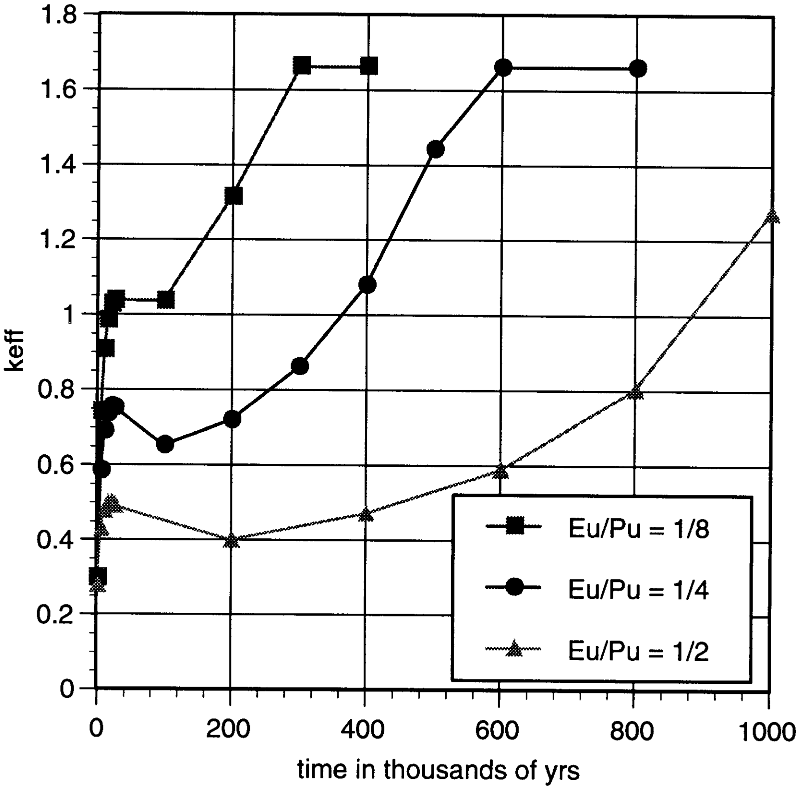

FIGURE 18. Europium Loading Effect (8 wt% PuO2)

As the Figure shows, while Eu was able to control criticality for hundreds of thousands of years, the critical state was ultimately reached. Europium eventually exited the near field entirely while sufficient U-235 remained. The system required only 0.014 g/cc U-235 to be present in the alteration layer to go critical. After 1 million years the U-235 concentration was 0.18 g/cc. Uranium's insolubility and 704 million year half-life assured that it would remain over the time period examined.

Europium loading can be thought of as an effective method for extending the time to criticality. However, if criticality at any time is viewed as unacceptable, this strategy may not be sufficient. If an absolute loading limit of 30 wt% Eu is assumed (i.e. a waste glass loaded only with Eu), for the worst case conditions, Eu will be gone after 13 M years. The concentration of U-235 will remain well above 0.014 g/cc at this time. If subcriticality must be assured over this time period, relying solely on dissolved Eu in the glass may not be sufficient.

The physical mechanisms affecting k_{eff} can be elucidated through a detailed examination of system behavior over time. Figure 19 shows the behavior of k_{eff} for a glass with a 1/4 mole ratio Eu/Pu and 8 wt% PuO_2 during glass reaction. Initial glass dissolution and removal of soluble poison increased the neutron multiplication of the system. After 23,000 years the entire glass had reacted and k_{eff} began to drop as Pu-239 decayed to U-235. This reduction was countered by the removal of Eu. Eventually, Pu-239 completed decayed and additional Eu losses caused k_{eff} to rise to its limiting level, slightly above 1.6.

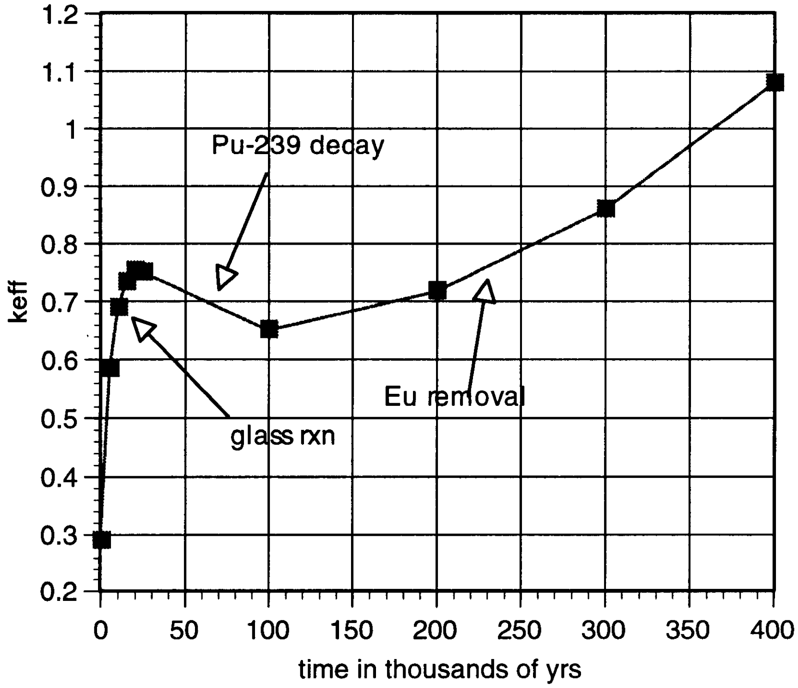

FIGURE 19. System Behavior (8 wt% PuO2 with an Eu/ Pu Mole Ratio of 1/4)

Reduced plutonium loading can also limit the k_{eff} of the system. Figure 20 displays the k_{eff} behavior of the glass at several PuO_2 loadings and 0.65 wt% Eu_2O_3 (1/8 mole Pu/Eu for 8% PuO_2 case). Reducing the Pu loading was effective in lowering k_{eff} throughout the reaction. It was the removal of Eu that allowed k_{eff} to rise and criticality to occur in each case.

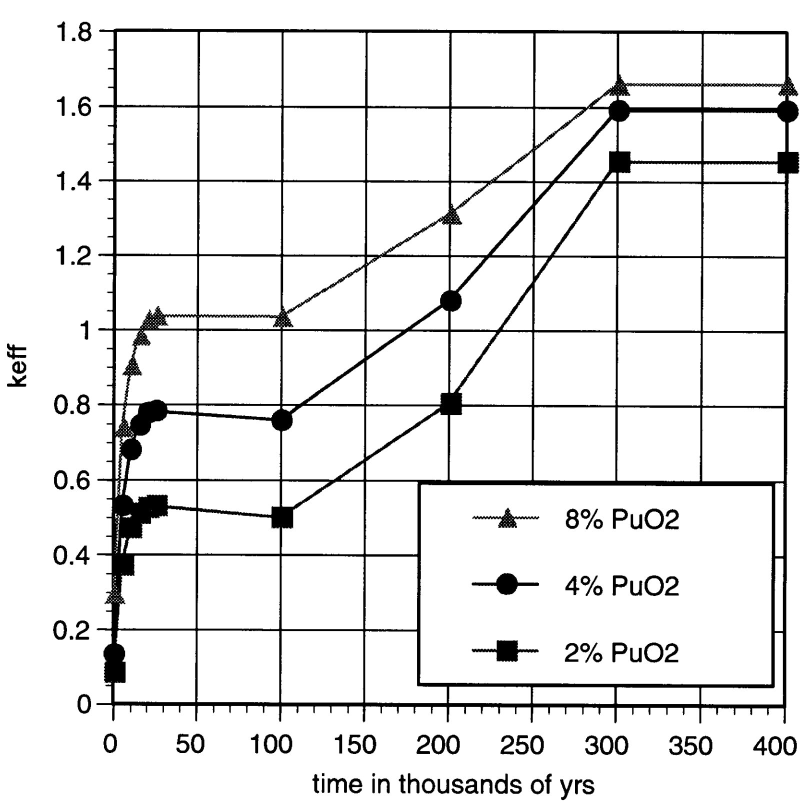

FIGURE 20. Pu Loading Effects(0.65 wt% Eu_2O_3)

While reducing the Pu concentration from 8 to 2 wt% pushed the time to criticality to roughly 225 thousand years, increasing the Eu concentration from 0.65 to 2.6 wt% pushed the time to criticality to approximately 900 thousand years. While Pu loading was effective at limiting the maximum reactivity possible, it was the Eu concentration that had the larger impact on *when* criticality occurred.

Nonetheless, the potential exists for diluting Pu to a level below which criticality cannot occur under the worst case conditions. If a radiation barrier were not required, a dilute waste form could be produced. It was determined that a loading of 0.45 wt% PuO_2 would keep the initial peak in k_{eff} below 1.0 without added reactivity control.[47] The benefits of this approach would have to be weighed against the increase in disposal costs as more than

6600 additional DWPF size canisters would be produced. The DWPF facility will produce 6105 canisters of vitrified HLW waste over 20 years of operation (McKibben 1993: 21).

Although not presently under consideration, Pu could be diluted directly with HLW from the Savannah River Site in order to reduce the total number of canisters produced. The quantity of Pu that could be diluted below 0.45 wt% would depend on when processing was begun, as well as the DWPF processing schedule. If DWPF processing were halted in 1997, roughly 5800 canisters would remain unprocessed. In this scenario 43 MT of WGPu could be diluted below the criticality limit in the remaining HLW and only 26 extra canisters would be needed.

This would exceed the 8 MT of Pu scheduled to be vitrified but not the 52.7 MT Pu declared excess. If the DWPF continued to operate, in 5 yrs approximately 4700 canisters would remain and roughly 35 MT of WGPu could be diluted. Rather than delay DWPF operations, which may be quite costly and undesirable for safety reasons, the future operation of a vitrification facility at Hanford, would provide additional HLW for dilution purposes.

In an effort to determine the boron contribution to control, k_{eff} was calculated with and without boron. Figure 21 shows the results for the 8% PuO_2 case with no Eu. Under the bounding conditions the glass went critical with only a fraction of the glass reacted. The boron in the unreacted glass did not provide significant criticality control. The hydrous alteration layer loaded with fissile elements was too reactive. It appears that the relevance of boron in the glass is low for criticality control purposes and additional control is needed.

47.The U-235 limit in the layer (~ 0.014 g/cc U-235) would produce a loading limit of 0.5 wt% U-235 in the glass. The Pu loading limit is lower as Pu-239 has a higher fission cross section and emits more neutrons per fission than U-235.

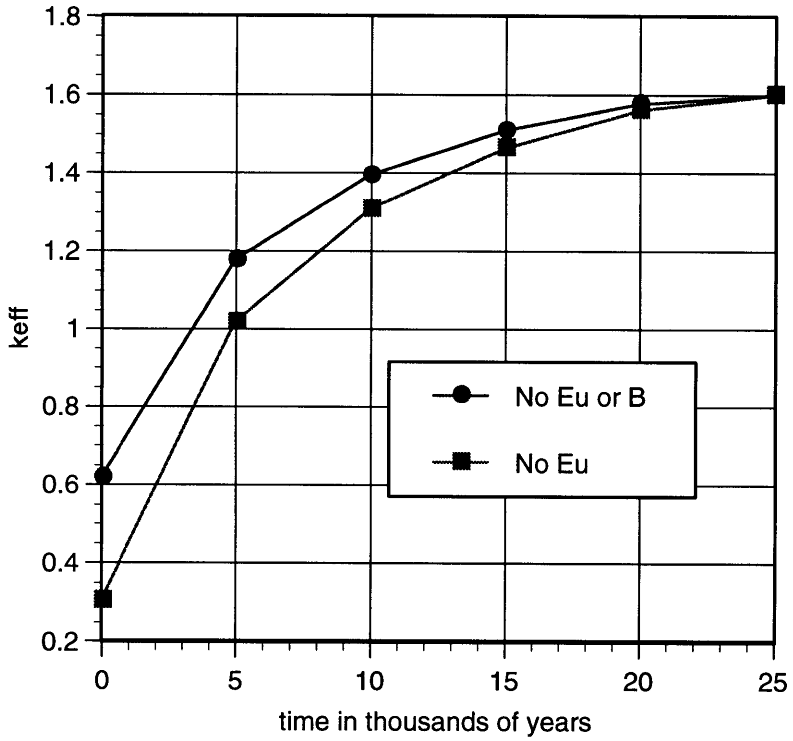

FIGURE 21. Boron Control (8 wt% PuO2)

In contrast the presence of a moderator had a greater impact on criticality. Figure 22 displays the k_{eff} evolution for the 8% Pu 1/8 Eu/Pu glass at several stages of saturation. This low Eu glass was chosen purely for illustrative purposes. The observed trend in k_{eff} showed the system to be undermoderated at all times. The spectrum benefits of added water outweighed the additional hydrogen absorption.

For spheres of Pu-239 and water, it has been shown that undermoderated conditions exist at concentrations between 0.03 g/cc and 5 g/cc (Knief 1992: 111). For the 8% PuO_2 case the alteration layer concentration was 0.18 g/cc Pu-239. By analogy to the sphere data, the PuO_2 would have to be reduced to less than 2 wt% for the macroscopic hydrogen absorption cross section to exceed that for fission.[48] The DOE estimated that the bulk loading in

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[48] Eta (the number of neutrons produced per fission) is also affected by neutron energy and impacts keff.

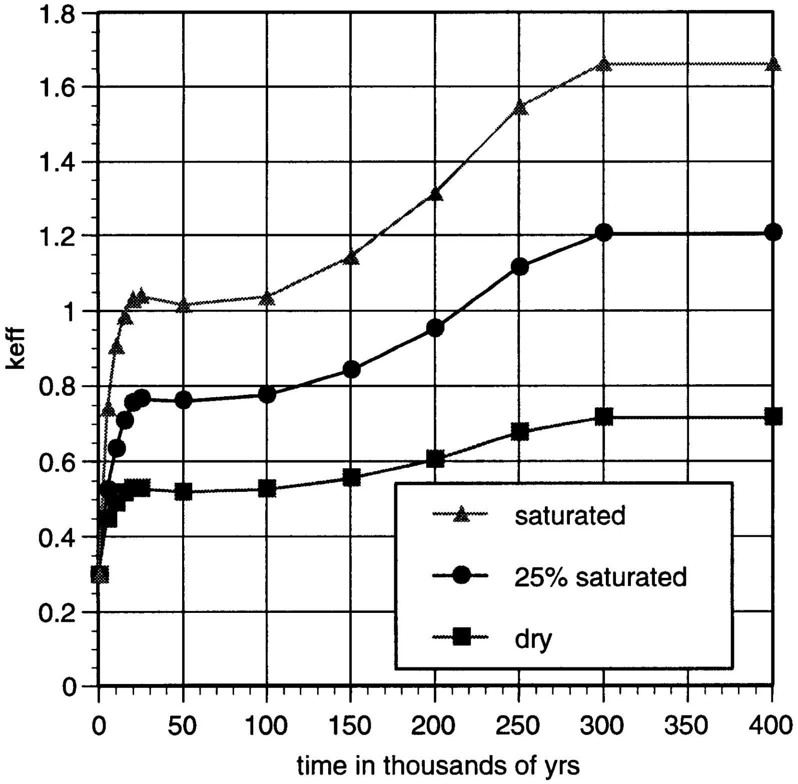

FIGURE 22. Saturation Effects on 8 wt% PuO2 with an Eu/Pu Mole Ratio of 1/8

the glass will be 5 wt % (DOE 1997: 108). Therefore, it is likely that the system will always be undermoderated.

Figure 22 shows that the alteration layers need not be fully saturated for criticality to occur. The additional of water produced a more thermal flux through hydrogen scattering. This spectrum effect is displayed in Figure 23. In the Figure, the group fluxes for the 16 energy groups were plotted. The lowest three groups are in the thermal region (0.003 - 3 eV). Virtually all of the fission occur in these groups. The addition of water sufficiently increased the thermal neutron flux, thereby causing the system to go critical.

The saturation results also highlighted the significance of bulk alteration layer components. As the effective porosity of the gel layer was calculated from the mass remaining after reaction (the alteration layer), the solubility of other glass components is significant.

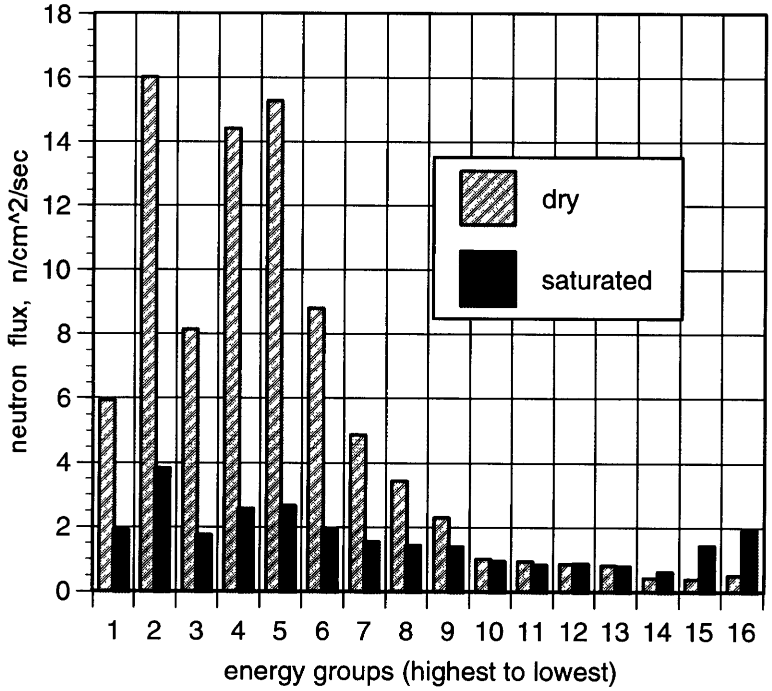

FIGURE 23. Neutron Spectrum at 300 thousand yrs (8 wt% PuO2 with an Eu/Pu Mole Ratio of 1/8)

The more glass components that are removed, the greater the effective porosity and potential degree of saturation.

The effect of reducing the bulk dissolution rate was also evaluated. This corresponded to the scenarios of improved glass performance. As shown in Figure 24, the better performing glass effectively eliminated the local k_{eff} maximum observed during the early stages of less durable glasses. The effect of Pu-239 decay to U-235 is also masked by the longer-lived glass. However, as shown in the Figure, even the best glasses of today can not guarantee subcriticality indefinitely.[49]

For the two less durable glasses Eu removal again dictates k_{eff} behavior. Figure 25 shows that as BDR was decreased, the formation of the alteration layers was slowed. As this increased the layer's exposure to flow, the concentration of Eu drops. For the most dura-

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[49] Typical values for long-term reaction rates at 90°C are between 0.01 and 0.001 $g/m^2/d$ (Lutze 1988: 143).

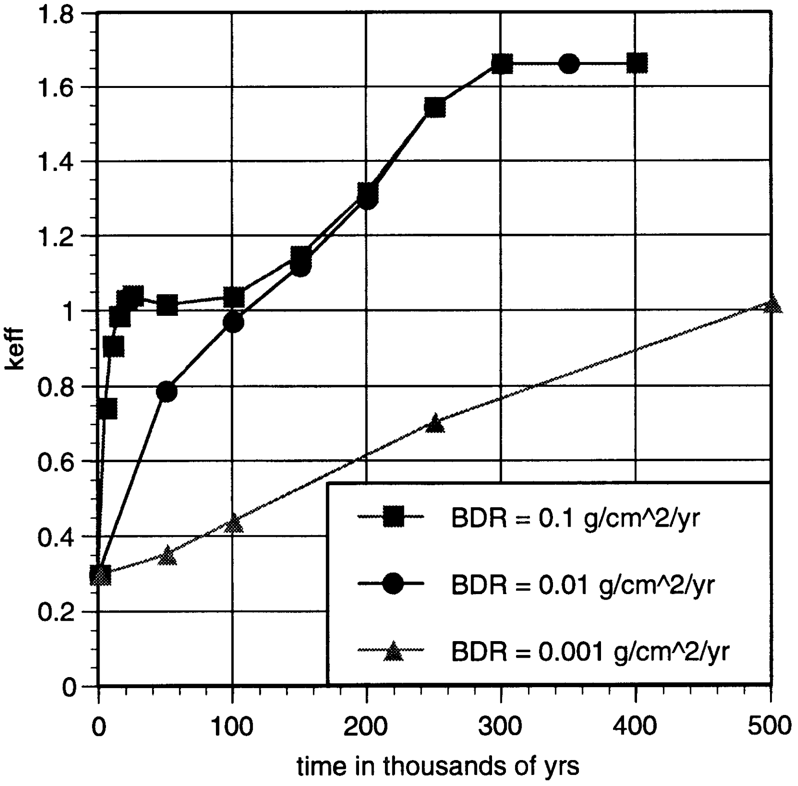

FIGURE 24. Durability Effects (8 wt% PuO2 with an Eu/Pu Mole Ratio of 1/8)

ble case (roughly the expected limit of today's glasses) Eu was completely eliminated from the layer. In this case it was the rate of reaction itself that limited the time to criticality.

Reducing the volumetric flow rate also had the effect of delaying the time to criticality. Figure 26 shows that Eu removal was slowed and a more dramatic dip in k_{eff} was observed. As Eu was more soluble than U or Pu, its concentration in the layer was most affected. As with the bulk dissolution rate, an increase in the time to criticality was observed with a decrease in this variable. If the volumetric flow is low enough, sufficient Eu will remain to ensure subcriticality until U-235 has decayed away. However, flow rates lower that those observed today would be required. .

"Expected" Conditions

Having explored system behavior with boundary conditions, calculations based on

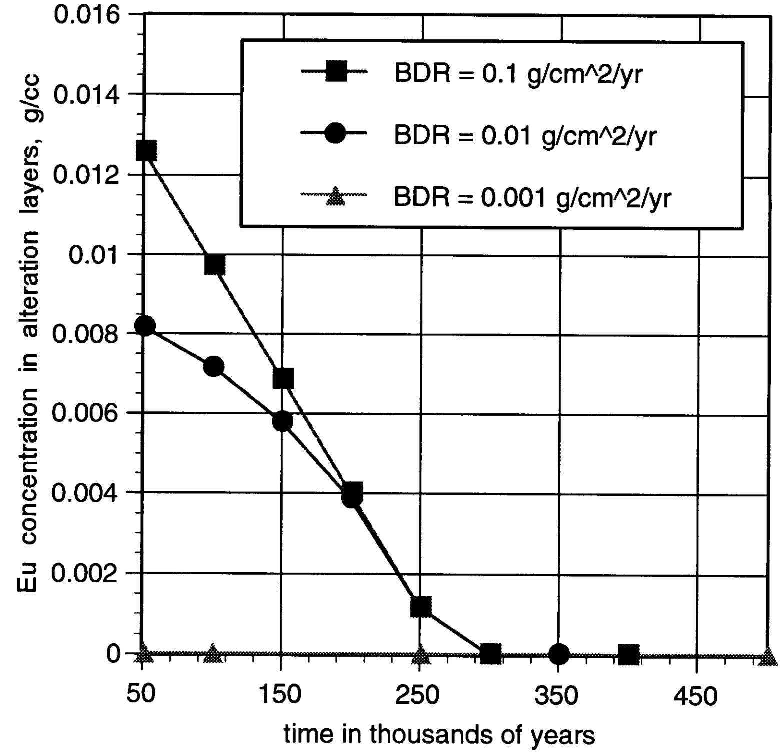

FIGURE 25. Europium Removal From Glasses With Different Durabilities (Initial Eu Loading of 0.65 wt% Eu_2O_3)

"expected" parameters were performed. The bulk dissolution rate was set at a value of 0.001 $g/m^2/d$. Today's flow rate of 0.001 m/yr was also used. The assumed solubilities were not changed. The reference loading for both the can-in-can alternative and homogenous alternatives have been set at a nominal 5 wt % PuO_2. Figure 27 displays the results from this Pu glass loaded with an equal molar quantity of Eu. While the time scale is shifted into the tens of millions of years, the system does go critical at approximately 13 million years. An even higher loading of REE could be used or other, stronger control elements utilized to push this time to criticality farther into the future.

As noted earlier other rare earth elements may be more suited for criticality control. Figure 28 shows the results from replacing Eu with equal molar amounts of Gd and Sm-149.[50] These isotopes are more effective at reducing k_{eff}. Europium was chosen as prior work identified it as relatively superior at increasing the compressed critical mass of

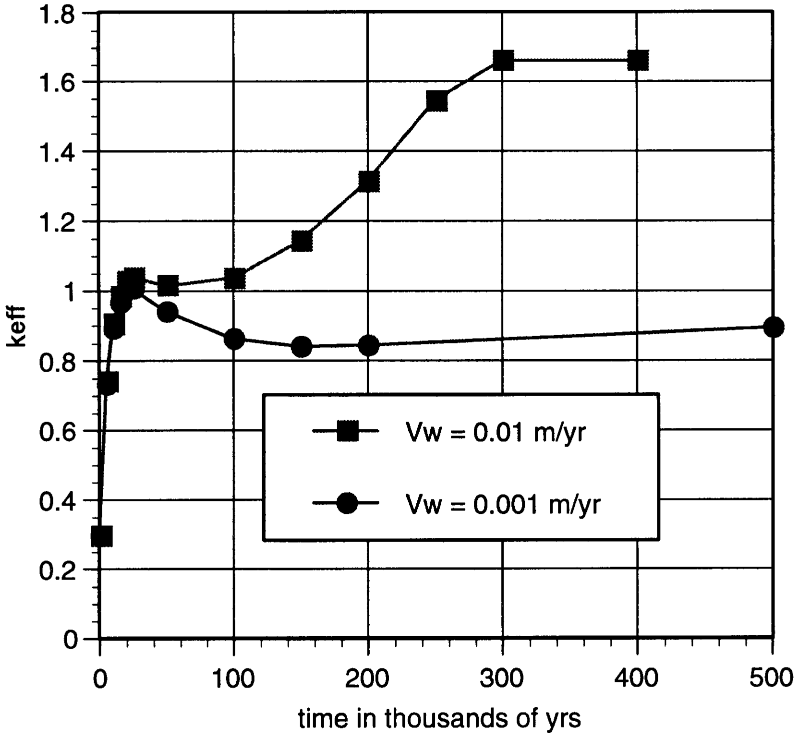

FIGURE 26. Flow Effects (8 wt% PuO2 with an Eu/Pu Mole Ratio of 1/8)

WGPu in an implosion type weapon (Sylvester 1994: 43). However, some combination of these rare-earths would most likely represent more a more robust solution for repository criticality control (and may be cheaper that acquiring the purified elements individually).

In order to assure the adequate treatment of resonance absorbers, several calculations were made using the Monte Carlo transport code MCNP4A. The Monte Carlo method traces individual particle movements through a specified material composition and geometry. Statistical distributions are used to predict interactions and thereby system behavior. As resonance assumptions are not used, MCNP4A was assumed to provide more accurate results (at a price of computational speed).

Figure 30 is a comparison between SCALE-PC and MCNP4A k_{eff} calculations for a dissolving glass loaded with 8 wt% PuO_2. The SCALE-PC results were consistently lower

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50.Sm-149 is the largest thermal and resonance absorber of the natural Sm isotopes. It only represents 13.8 wt% of natural Sm.

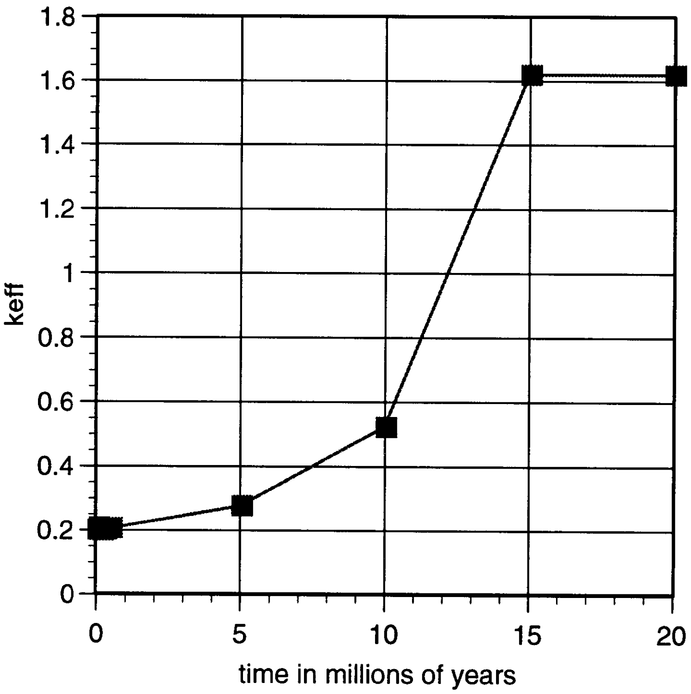

FIGURE 27. System Behavior Under Expected Conditions (5 wt% PuO_2 with an Eu/Pu Mole Ratio of 1/1)

than those for MCNP4A, but did not deviate by more than 5%. The lower values for SCALE-PC reflect the somewhat inadequate treatment of resonance absorption in Eu. Bondarenko factors did not exist for isotopes of this element. As the concentration of Eu decreased the SCALE-PC results converged to those from MCNP4A. The slight deviations were assumed to be acceptable for the analysis performed here.

4.10.2 Environmental Control

"Worst Case" Conditions

As noted in Section 4.8.4, individual glass components could exist at concentrations other than those predicted by EQ6 under glass control. Under the assumption of environmental control, it is assumed that glass elements do not affect solubilities, and phase precipitation effects on solution chemistry are ignored. This scenario predicted the added precipitation of Li, which contains the neutron absorber Li-6. In fact, the lithium is so insoluble that it remains in the alteration layer until U-235 decays.

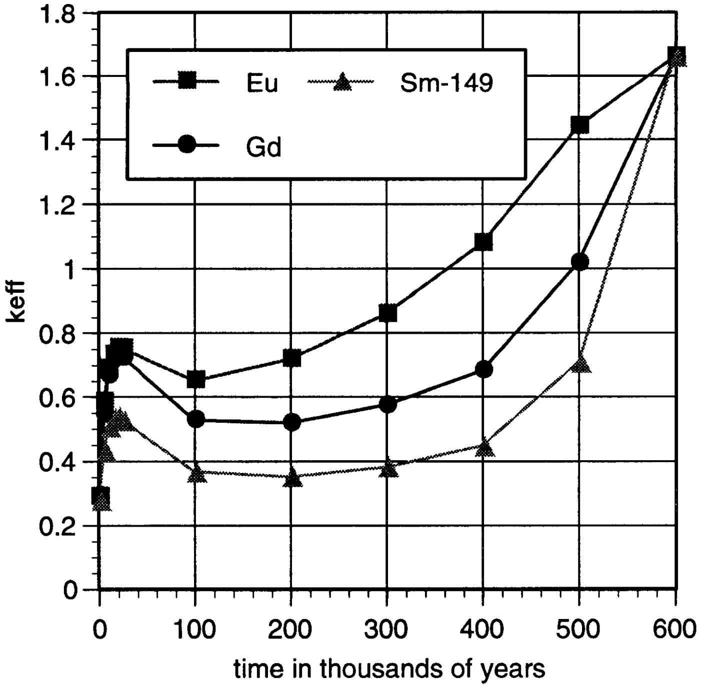

FIGURE 28. Gd and Sm-149 (8 wt% PuO_2 with an RE/Pu Mole Ratio of 1/8)

There is sufficient Li-6 in the glass to control long term criticality, but for a loading of 8% PuO_2 it is not enough to hold down the k_{eff} peak 25,000 yrs on its own. Therefore additional control elements were needed to get over the first maxima in neutron multiplication. Figure 30 shows the k_{eff} profile for a glass loaded with 8 wt% $PuO_2$and 1/8 mole ratio Eu, under environmental control. The same curve for tuff control is included for comparison.

"Expected" Conditions

Under "expected" conditions, the bulk dissolution rate and volumetric flow rates were low enough to avoid the early peak in k_{eff}. As Li-6 was taken to be insoluble in this scenario, criticality was never approached. Therefore the k_{eff} behavior of this system under "expected conditions" was not presented.

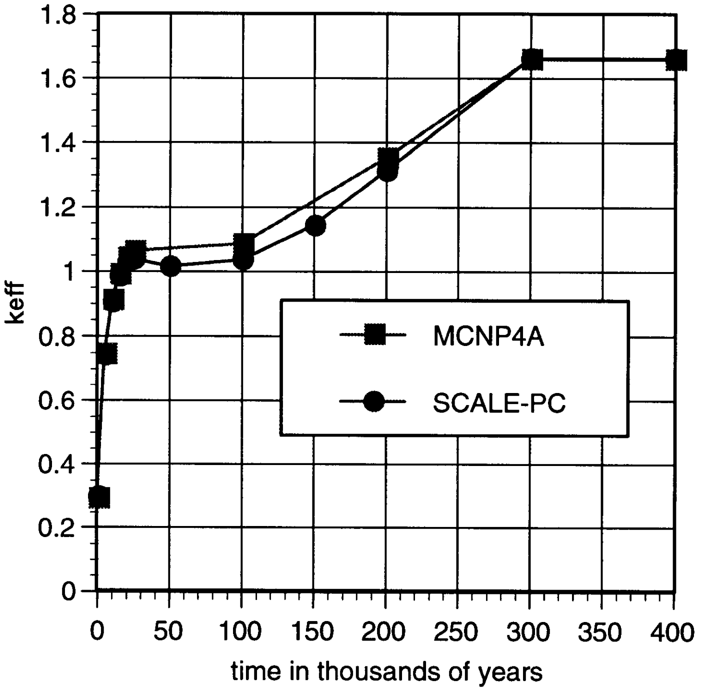

FIGURE 29. Benchmark with MCNP4A (8 wt% PuO_2 with an Eu/Pu Mole Ratio of 1/8)

4.11 Conclusions

The potential for a criticality event during borosilicate glass reaction in a repository environment does exist. Criticality may occur while much of the glass remains intact or long after the glass has completely reacted. However, several approaches for addressing criticality concerns can be pursued.

The most obvious approach is to limit the Pu loading in the glass. It is possible, given the quantity of HLW at Savannah River, to dilute a significant fraction of surplus WGPu to a concentration below that required for criticality, 0.45 wt% PuO_2. The DOE's Hanford site also contains quantities of HLW that could be used for this purpose. In this case, the addition of control elements to the glass would serve to provide added conservatism. Additional control elements may also be desirable for maintaining subcriticality in the case the Pu or U should transport and precipitate in the far field. As demonstrated in Section 4.5, the REE are capable of following actinide elements in such a scenario.

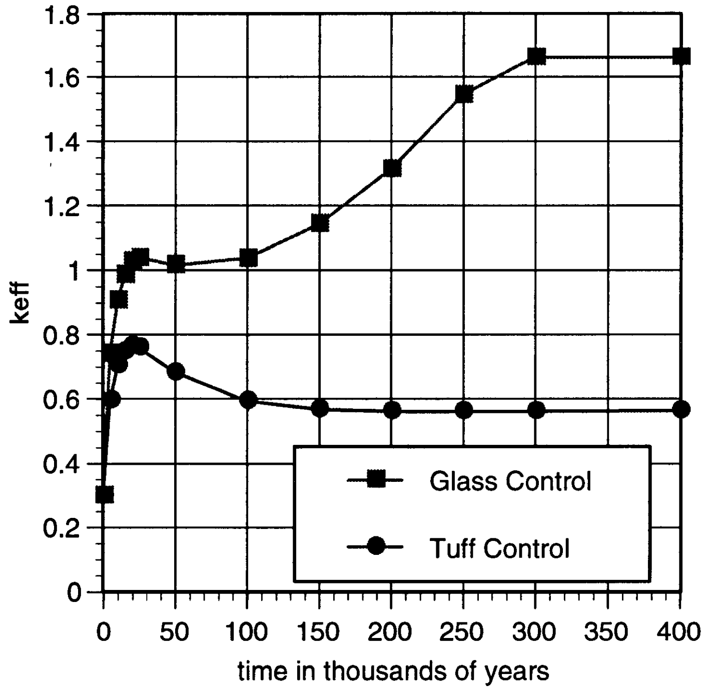

FIGURE 30. Chemistry Control (8 wt% PuO_2 with an Eu/Pu Mole Ratio of 1/8)

If higher loadings of WGPu are desired, Eu or other rare earths can effectively delay the onset of criticality. The model showed that relatively small amounts of an insoluble absorber can delay criticality for hundreds of thousands of years. At a minium, REE loading should be added in sufficient quantities to control reactivity through the early k_{eff} peak that could result under worst case conditions.

Additional REE could be added to meet regulated time requirements for subcriticality. While the time to criticality is an important glass design criteria there is no regulatory guidance on the matter.

> "There are no regulatory guides, DOE orders, or even any general agreement on the length of time for which criticality prevention must be guaranteed in a geologic repository. For groundwater contamination by radioactivity, EPA, and NRC regulations specify up to a 10,000-year period of contamination-free performance, but are silent on the subject of a

> required criticality-free period. At the other extreme, 2,000,000 years has been mentioned as a possible goal for criticality-free performance" (McKibben 1993:9).

The analyses presented here shows that even with Eu added to the glass, subcritcal conditions cannot be guaranteed indefinitely for the expected loading of Pu in glass. If multimillion year assurances of subcriticality are needed under worst case conditions, alternate strategies may be necessary. These strategies should incorporate what was demonstrated to be important neutronic factors in this system.

Of utmost importance for subcriticality of the reacted glass is the aqueous chemistry. For example, if the Li-6 already present in the glass were to form the insoluble phase petalite, even the 8 wt% PuO_2 glass would remain subcritical forever. The petalite would remain in sufficient quantities to control reactivity until the U-235 decays away - after approximately 7 billion years. Recognizing this, a high Al glass could be designed such that Li in the glass and the groundwater would be precipitated. In any regard solution chemistry will play a major role in the neutronic behavior of the system.

Other insoluble absorbers could be used in concert with or in place of Eu. Gadolinium and Sm-149 were briefly explored here. However, as noted in Figure 28, the ultimate effectiveness of all absorbers will be determined by their ability to remain commingled with the fissile elements.

To improve their effectiveness, REE could be dissolved in high concentrations in the glass. Alternatively, a mixed-phase ceramic of the type described in Section 4.7 could be utilized. A glass tailored to produce a more durable, crystalline host phase for the REE may be more desirable.

Complete reaction of the REE to form the crystalline phase in such a matrix may not be needed or desired. As shown in the analyses only small amounts of an absorber are needed to control reactivity in the near-field. Moreover, if colloids are shown to form as a result of glass reaction, an appropriate amount of REE may be needed in the amorphous phase in order to transport with Pu or U colloids.

Porosity is of equal importance. At the Pu concentrations expected and without thermal absorbers present, the system will be undermoderated. If the majority of the glass components remained in the near-field and/or swelled, water could be excluded from the region. This would reduce moderation and thereby k_{eff}.

This strikes upon another possible advantage of a non-HLW glass alternative of the type proposed in Section 3.6. If a can-in-can design were utilized, the remaining voids could be filled with a substance such as a monazite concentrate (from sand) which has high rare earth concentrations, rather than HLW glass. This would add both criticality control and weight to the container (added proliferation resistance). Monazite could also be used as a backfill material. Monazite concentrates from Florida beach sand (produced via a caustic soda process) contain about 70% monazite (Benedict 1981: 299). Of this 40% are REE oxides.

Such a design would provide regulatory benefits as well. As noted in Section 3.3, the regulatory acceptance of a vitrified Pu form is unknown. The analysis hear has shown that it could be dependent on the time frame of regulatory interest. The modular nature of a can-in-can variant, without HLW, could be use to address changing regulatory time requirements. For example, the ratio of Pu cans to REE filler could be easily modified to suit regulatory requirements.

In sum, near-field subcriticality of a Pu loaded glass could be assured over extremely long periods of geologic storage, but not indefinitely. High loadings of neutron absorbers expected to be insoluble over the range of groundwater conditions expected in a repository should be included in the glass or alternate host matrix. To complement such a strategy, fabricated REE host phases (or monazite sand) of known insolubility could be used both in the waste package and as backfill to address near-field criticality concerns. Implementation strategies that would simplify design modification should regulatory requirements change and/or new data becomes available, also appear valuable.

4.12 Future Work

The analysis presented here was an approach to model a complex system over extreme time periods. Many model parameters are important but elemental solubilities and identification of associated phases appear to be the most significant. The thermodynamic databases for each of the relevant radionuclides must be further developed to ensure completeness. The robustness of control solubilities must be examined over all ranges of pH, Eh and temperature. Additional complexation reactions as well as sorption and radiolysis effects should be investigated and included in the model. These processes and their order of reaction may produce meaningful differences in elemental behavior.

Continued investigation of colloid formation and transport should also be pursued. As Pu, U, and the REE have been shown to form colloids this could provide an important mechanism for control separation. While criticality has been shown to be possible without the presence of colloids, their formation could shorten the time to criticality. Of particular interest would be the re-wetting behavior of colloids. During dry periods, colloids may be sorbed on surfaces and their transport limited. This may reduce the impact of colloid formation.

While short-term glass dissolution modeling would benefit from basic research on the rate controlling reaction for glass dissolution, a more detailed assessment of alteration layer phase formation, composition and stability would be more beneficial for the criticality assessment. In the criticality assessment we are more interested in what remains in the near field and the robustness of alteration phase stability.

Bulk properties of the alteration layers should also be assessed. It was shown that porosity is an important criticality parameter. The void space in various glasses should be assessed. The mechanical properties of the layer are also important as they will impact the reacted glass geometry which will affect neutron leakage.

Criticality issues may also affect the emplacement of the logs themselves. The analysis performed here assumed a single log emplacement. If multiple logs are to be co-located reactivity may be increased. Calculations should be performed to ensure adequate control in such an array.

5.0 Financial Compensation for Russian Pu

The preceeding chapters have been devoted to the desirability and technical feasibility of the vitrification alternative. To be applied in Russia, vitrification will have to address a major political hurdle as well - the fuel value of WGPu.

Russia wishes to save her Pu for future use as reactor fuel. To burn the Pu, Russia will have to make additional investments in its nuclear infrastructure. It currently lacks the capital to do so. While the US favors processing the Pu into spent fuel, it is unwilling to contribute billions of dollars for facilities that, when operated as designed, run counter to the stated US policy of discouraging a Pu fuel cycle.

The vitrification alternative could be supported by the US but is flatly rejected by the Russian government as it treats the Pu as waste - ignoring its potential value as reactor fuel. It would appear that for vitrificiton to be implemented in Russia, Russia must be compensated for the fuel value of her WGPu. But what is WGPu worth?[51]

Recent evaluations place the present value of WGPu at zero due to the low price of uranium fuels and high price of plutonium fuel fabrication (Chow 1993: 75). It is simply cheaper to use uranium fuels. However, this may not always be the case. Perhaps Russia values Pu not for its current worth but for its potential value in the future. By adopting this view they are in effect valuing Pu as a call option on nuclear fuel. An asset of this type will produce a positive cash flow if the value of uranium fuel is above a certain price on a specified date. Realizing this, we have found an alternative, market based mechanism for valuing Pu that should be acceptable to Russia.

Assigning a derivative value to WGPu gives the US a *reasoned* mechanism to compensate Russia and thereby promote Pu disposition. Compensation may be in the form of a cash payment or a portfolio that replicates the potential cash flows from holding WGPu. The

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[51] Some might argue that a purchase of WGPu would not be an option as, unlike HEU, it cannot be denatured prior to delivery. However Russia offered to send HEU to the US as HEU if it would speed payment (Allison 1996).

latter allows Russia to retain her hedged position in the nuclear fuels market without stockpiling Pu. The former could provide Russia with hard currency. The remainder of this chapter focuses on the details of such a proposal and how it might fit into a surplus plutonium disposition strategy.

5.1 Plutonium Value Relative to Uranium

Assigning a market value to plutonium is difficult. Not only because Pu is not traded, but also because it can be used as fuel for nuclear weapons. This military value is virtually incalculable. The valuation performed here is for WGPu that has been retired from military service as a result of arms control agreements. It is assumed that these agreements effectively eliminate the weapon value of this material. It is the remaining commodity value of plutonium that is assessed in this work.

One approach could be to value Pu based on its ability to defer future reprocessing charges. As such charges are significant ($540-$720/kg uranium in spent fuel), a sizable value could be assigned to the Pu.[52] However, such an approach is problematic. The timing of reprocessing and thereby a schedule for plutonium burning would be needed. While the value of surplus Pu may indeed depend on such factors, agreeing on the valuation terms seems precarious. Virtually any schedule could be promoted. A reasoned approach that ties Pu value to market forces rather than a government's energy policy initiatives may be more attractive.

By relating the value of Pu to a traded commodity a market assessment can be made. If plutonium fuel is assumed to be a close substitute for uranium fuel, its worth in the market must be related to uranium.

To produce LEU fuel, uranium and a variety of services are needed. The cost components of LEU fuel are:

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[52] Cost data taken from OECD(1994: 50).

$$C_{LEU} = U_{LEU} + CON + SWU + FAB \tag{EQ 6}$$

where U_{LEU} is the cost of the required ore, CON the conversion cost (from U_3O_8 to UF_6 for enrichment), SWU the enrichment cost and FAB the fabrication cost. These factors are represented here in units of $/kg heavy metal of LEU. For 4% enriched fuel, enrichment services presently represent 40% of the unit costs with ore purchases contributing roughly 30%.

Today, fabricated plutonium fuel is most often burned as low-enriched, mixed-oxide (MOX) form. Equation 7 shows the cost of MOX fuel as a function of Pu production cost (Pu), the cost of uranium ore diluent (U_{MOX}), and MOX fabrication costs (MOX).

$$C_{MOX} = Pu + U_{MOX} + MOX \tag{EQ 7}$$

Assuming these commodities are close substitutes (i.e. 1 kg LEU is interchangeable with 1 kg of MOX fuel of the same fissile atom density), their price in the market place should be equal. This gives:

$$U_{LEU} + CON + SWU + FAB = Pu + U_{MOX} + MOX \tag{EQ 8}$$

or, rearranging,

$$Pu = U_{LEU} + CON + SWU + FAB - U_{MOX} - MOX \tag{EQ 9}$$

Equation 9 gives the value of the Pu contained in 1 kg HM of MOX fuel based on its ability to avoid uranium fuel expenditures. Its actual market value may be much lower due to supply and demand factors. This appears to be the case today as none of the world's plutonium burners have offered to purchase Russia's plutonium. This is true even though (as will be noted later) the equation assigns a present value to the plutonium.

A few notes should be made concerning the "interchangeable" assumption used to derive Equation 9. There are two aspects of this assumption. The first is neutronic in nature. Uranium 235 behaves differently in a reactor than does plutonium 239. Plutonium's higher fission cross section and eta factor (fission neutrons produced per neutron absorbed) may give it an initially higher reactivity worth. However, as the fuel is burned higher isotopes of Pu are produced. Buildup of parasitic Pu isotopes and the higher average cross section of Pu fission products combine to effectively eliminate any benefit (Correa 1979: 40-41 and 81-84). Therefore from a perspective of energy production in thermal reactors, Pu-239 and U-235 are essentially equal.

The second assumption relates to the actual use of MOX fuel and uranium fuel in reactors. It is assumed that reactors are available that can easily interchange Pu and U fuels. This is not presently the case. Most reactors today are not licensed for MOX fuel. Added reactivity control would be needed and, for partial MOX cores, care must be taken to avoid power peaking in the Pu rods caused by resonance absorption in Pu-239. The cost of these activities is not included in this evaluation.

The lack of demand for Pu can be explained by the relatively low numbers of MOX reactors and rising stocks of separated Pu. However, this situation could change. If MOX capacity rises and Pu stocks are reduced, Pu value could rise. It is this scenario that a strategy of holding Pu could produce revenues. While competition between future Pu producers may constrain the market price, the maximum payoff will be limited by the price of the substitute uranium fuel. If we can identify an asset that produces payoffs in exactly the same way, it must have the same price. A call option on uranium is such an asset.

5.2 Plutonium as a Uranium Derivative

A European call option gives the holder the right to purchase something for at a fixed price on a future date. (An American option may be executed any time prior to the 'strike' date.) If the price at that time is higher than this 'strike' price, the holder of the option receives the difference. Plutonium is equivalent to a call option on uranium fuel. Holding on to it pays off when the price of uranium fuel is above a certain level.

The future value of uranium fuel (and thereby Pu) will depend largely on the price of uranium and SWU. These two components are and will continue to be the greatest contributors to the cost of LEU fuel. Other costs are service charges which may change over time, but if Pu is to dramatically increase in value it will be due to increases in these two factors.

In this thesis plutonium is valued as a derivative on uranium only. Including enrichment costs would require valuing a "basket" option of uranium ore and enrichment services (Nelken 1996: 161). This is beyond the present scope of this work and SWU was therefore assumed constant with time. The potential effect of SWU volatility on option price is discussed qualitatively.

If SWU is held constant, the price of uranium ore alone will determine the future price of uranium fuel. Plutonium can therefore be valued as a call option on uranium ore. To price an option, the expected behavior of prices over time is needed. This information is used to assess the likelihood that an option will pay off. This section describes the common assumptions used in derivative theory.

5.2.1 A Price Path for Uranium

In order to value a derivative security it is necessary to understand how the price of the underlying asset moves (in this case uranium ore). One can then produce a distribution for the expected price of the asset at some future time. By combining the probabilities the asset will reach a certain price with information about how the market prices the risk associated with the asset, it becomes possible to value the derivative.

The economists Black and Scholes derived the equation for pricing derivatives on assets that follow geometric Brownian motions. Brownian motions possess three characteristics: a future value dependent only on its present value (Markov property); a probability distribution for the *change* in the process independent of any other separate period (independent increments); and changes in value of the asset are normally distributed with a variance that increases linearly with time (Dixit 1994: 63).

For stocks and other assets, this last aspect must be finessed as the price of a stock cannot fall below zero (normally distributed changes would allow for negative stock prices). It is therefore assumed that changes in price are *lognormally* distributed, or alternatively stated, changes in the logarithm of price are normally distributed. This is done by modelling the *logarithm* of price as a Brownian motion, not the price itself.

If we assume uranium ore follows a Brownian motion, we produce an equation for changes in the price of uranium ore (U \$/lb) of the following form:

$$dU = a(U, t)dt + b(U, t)dz \qquad \text{(EQ 10)}$$

The first term on the right hand side is the expected change in price over time and the second is a stochastic factor. The dz is the Wiener process $\varepsilon\sqrt{dt}$, where ε is a random drawing from a standardized normal distribution. It is this random sampling that makes the future price uncertain.

If we further assume that $a(U, t) = \mu U$ and $b(U, t) = \sigma U$ we produce the *geometric* Brownian motion:

$$\frac{dU}{U} = \mu dt + \sigma dz \qquad \text{(EQ 11)}$$

where μ is the expected return over dt, and σ is the volatility.

Volatility represents the uncertainty we have about the asset's price movement. Sigma squared is the variance 'rate' of the fractional change in price. The higher the volatility the greater the spread of possible future prices.

It has been argued that a geometric Brownian motion is an inappropriate path for a depletable natural resource. Indeed theoretical arguments have been made stating that, under realistic conditions, natural resources simply do not behave in such a manner (Lund 1993). A mean-reverting process may be more justifiable. Nonetheless, geometric Brownian motions are used in practice for pricing options on resources such as oil.[53] The objective here is to demonstrate a derivative pricing methodology for WGPu disposition, not to contribute to the debate on natural resource price paths.

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[53] Interview with Professor Vadeem Linetsky, University of Michigan Financial Engineering Program, June 6, 1996.

5.2.2 Pricing a Uranium Derivative

Having fixed the mechanism for the price movement of an asset it becomes possible to value a derivative asset. Black and Scholes were the first to derive and solve a pricing formula for a derivative security (Black 1973). Their approach, now considered the standard for option pricing, begins by expanding the instantaneous change in the value of a derivative using Ito's Lemma (the fundamental theorem of stochastic calculus). As the value of the derivative depends only on the underlying asset (U) and time (t) this gives:

$$'C = \left(\frac{\partial C}{\partial U}\mu U + \frac{\partial C}{\partial t} + \frac{1}{2}\frac{\partial^2 C}{\partial U^2}\sigma^2 U^2\right)dt + \frac{\partial C}{\partial U}\sigma U d{:} \qquad \text{(EQ 12)}$$

where C is the value of the derivative. This formula can be derived by taking a first-order Taylor's expansion of dC, inserting the geometric Brownian motion for dU, and rearranging terms.

The uncertainty in option value is reflected by the dz in the second term of Equation 12. By noting that the underlying asset is dependent on the same uncertainty (see Eq. 11), a portfolio of the derivative and the asset can be constructed such that this dz is eliminated. As the return on the portfolio is then certain, it should equal the risk-free rate of return. Equating the two produces a deterministic partial differential equation for the option value. Solving this equation with the appropriate boundary conditions gives the desired relationship.[54]

The Black-Scholes equation for a European call option is:

$$C = UN(d_1) - Xe^{-r(T-t)}N(d_2) \qquad \text{(EQ 13)}$$

where

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[54] The most important boundary condition sets the value of the option at the strike date equal to (U(T) - X) if U(T) is greater than or equal to X, or zero if U(T) is less than X. U(T) is the price of uranium at time T.

$$d_1 = \frac{\ln\left(\frac{U}{X}\right) + \left(r + \frac{\sigma^2}{2}\right)(T-t)}{\sigma\sqrt{T-t}}$$

$$d_2 = \frac{\ln\left(\frac{U}{X}\right) + \left(r - \frac{\sigma^2}{2}\right)(T-t)}{\sigma\sqrt{T-t}} = d_1 - \sigma\sqrt{T-t}$$

and $N(x)$ is the cumulative probability distribution function for a standardized normal variable.

These equations give the value of the call as a function of the stock's current price (U), its volatility (σ), the continuously compounded risk-free rate of return (r), and the terms of the contract - its strike price (X), and date (T) as measured relative to today's date (t).

The above equation is valid for any non-dividend-paying stock. However, a commodity held for consumption purposes (such as uranium) may posses an inherent dividend. This is because the holder of a commodity typically assigns an added value (or dividend) to physically holding the asset. The magnitude of this effect can be seen through an examination of forward prices for the commodity. A forward contract is a contract to sell the underlying asset at a fixed price on a future date. It is an obligation not an option.

The forward price (the price the asset will be sold for at time T) is related to the current price by (Hull 1996: 67):

$$F \leq Ue^{(r+s)(T-t)} \tag{EQ 14}$$

The right hand side of this relation is the cost of purchasing the commodity today and storing it until the execution date. (Storage costs (s) have been expressed as a cost proportional to the price of uranium). If this amount was less than the forward price, riskless profits could be made by entering into the short position of the forward agreement (i.e. agreeing to sell) and immediately covering your position by buying and storing the asset. As this arbitrage situation cannot hold for long, the forward price has an upper bound.

For commodities held only for investment, the relation in Equation 14 becomes an equality. Here storage costs are viewed as inevitable so that selling the commodity would produce an immediate dividend in the form of avoided storage costs. An amount equal to the revenue from the sale (and the present value of avoided storage costs) could be invested at the risk-free rate and used to fulfill the contract position. This too produces a risk-free profit and sets a lower bound. As this is the same price as the upper bound, a single forward price is determined.

However, for consumption commodities the inequality still holds as a lower bound cannot be fixed by an arbitrage argument. In this case storage costs are not a foregone conclusion (e.g. the commodity may be consumed) and the holder may assign additional benefits to physically holding the commodity. This convenience yield, by definition, represents the degree of inequality in Equation 14. Including this dividend (y) in the relation forces:

$$F = Se^{(r+s-y)(T-t)} \qquad \text{(EQ 15)}$$

The total dividend for consumption commodities is therefore q = -s + y. By looking at forward prices in the marketplace we can determine if indeed a dividend does exist.

A standard industry pricing practice allows us to determine uranium's dividend yield without dissecting recently inked forward contracts. In the uranium industry, forward prices are closely tied to spot prices. A standard approach, termed "base escalation", is to add $1-2 to the current spot price and escalate this value to the forward date (Fuller 1995: 16). If this initial increase is expressed as a fraction (B) of the current stock price we arrive at the following equation for the forward price:

$$F = (U + BU)e^{i(T-t)} \qquad \text{(EQ 16)}$$

The escalation factor (i) is typically taken to be the gross national product implicit price deflator.[55] If this factor is known, the following relation holds:

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[55] Separate communications with Dr. Thomas Neff and Ms. Treva Klingbiel of TradeTech in June, 1996.

$$(U + BU)\,e^{i(T-t)} = Ue^{(r+s-y)(T-t)}$$

or

$$\ln(1 + B) = (r + s - y - i)(T - t) \qquad \text{(EQ 17)}$$

If B is small and $(T - t)$ is large

$$(r + s - y - i) \approx 0 \qquad \text{(EQ 18)}$$

Therefore, inserting q into the relation gives;

$$q = -s + y = r - i \qquad \text{(EQ 19)}$$

Equation 19 shows that as long as the risk-free rate of return differs from the escalation rate, uranium will posses an inherent dividend.

Extending the Black-Scholes equation to cover dividend-paying stocks is straight forward (Hull 1996: 261). If the underlying stock pays a dividend over a time period, it effectively reduces the price the stock would have reached by the amount of the dividend. Therefore, if we deflate the current stock price by this amount we can value the derivative on a dividend-paying stock.

The Black-Scholes equation for a European call option on a dividend-paying stock becomes (for uranium):

$$c = Ue^{-q(T-t)}N(d_1) - Xe^{-r(T-t)}N(d_2) \qquad \text{(EQ 20)}$$

where

$$d_1 = \frac{\ln\left(\frac{U}{X}\right) + \left(r - q + \frac{\sigma^2}{2}\right)(T - t)}{\sigma\sqrt{T - t}}$$

$$d_2 = \frac{\ln\left(\frac{U}{X}\right) + \left(r - q - \frac{\sigma^2}{2}\right)(T - t)}{\sigma\sqrt{T - t}} = d_1 - \sigma\sqrt{T - t}$$

This version of the Black-Scholes equation uses the same variables described previously with U being the price of one pound of uranium ore. (The option can be sized to any amount of uranium.) If these variables are known a price for a uranium option can be calculated.

5.2.3 Terms of the Option

Having developed a theoretical basis, a uranium option can now be valued. What is needed are the required inputs. This section gives a description of the data used in the analysis and how it was determined.

5.2.4 Strike Price

The strike price should be set at the uranium ore price which makes $c_{LEU} = c_{MOX}$. This value was determined by varying the price of uranium ore until the cost of one kg of 4 wt% enriched uranium fuel equaled the cost of one kg of MOX fuel of the same enrichment (on a fissile atom density basis, assuming free WGPu). Using the values in Table 8 and Equation 9, the break even strike price was calculated to be \$8.84/lb U_3O_8. Having access to uranium ore at this price is equivalent to having access to free plutonium.

TABLE 8. Nuclear Fuel Cost data[a]

SWU ($/SWU)	**UF6 Conversion ($/kg U)**	**Fabrication ($/kg U)**	**Mixed-Oxide Fab ($/kg HM)**
110	8	275	1100

a. data taken from OECD (1994: 50)

The current price of U3O8 was taken to be \$16.50 per lb.[56] As this is higher than the break even price, this methodology assigns weapons grade plutonium a current value of \$4.87/g or \$244M for 50 tonnes. But this value could only be realized if the Pu could be used to offset uranium fuel purchases today, which it cannot. Again, WGPu will only have commercial value when it can be used as commercial fuel.

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[56] Interview with Ms. Treva Klingbiel of TradeTech.

Strike Date

The strike date for the option is open to negotiation. It should represent the time at which Russia is able to monetize the value of its Pu. For illustrative purposes I will choose 10 years from today. This number was chosen to represent the shortest time frame that global stockpiles of RGPu could be reduced to a point where Pu from Russia may be desired for fuel.

Volatility

Uranium volatility must be estimated from its price history. Volatility is the standard deviation of returns divided by the square root of the time period spanned. Monthly price data from NUEXCO were used for this calculation. Uranium's estimated volatility changes with time. Table 9 shows its volatility over several time periods. The price data from 1986 to 1996 were used to calculate the volatility in the base case analysis.[57]

TABLE 9. Uranium Ore Volatilities[a]

	1/70 - 1/96	1/86 - 1/96	1/76 - 1/86	1/91 - 1/96
volatility (1/sqrt yr)	14.7%	16.4%	11.6%	15.1%

a. volatilities calculated from Exchange Values published by TradeTech

Risk Free Rate and Inflation Rate

In order to price the option, estimates of the risk-free rate and inflation rate are also needed. The risk-free rate was assumed to be 8% per year. The escalation rate was taken to be 5%. By Equation 19, this gives a continuous dividend of 3%. These values are were assumed to be representative and will be varied to gauge their importance.

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[57] Hull (1996: 233) notes that the volatility should be calculated over a period of time equal to to the time period over which it is to be applied.

Summary of Base Case Values

Table 10 provides a summary of the base case values used in this analysis.

TABLE 10. Base Case Values Used in BS Equations

Current U3O8 Price	volatility	risk-free rate	strike price	strike date	escalation rate
$16.50/lb	16.4 %	8%	$8.84/lb	10 yrs	5%

5.2.5 Results

Using these inputs, the price of a call option on one pound of U3O8 was found to be $8.27. To convert this into a Pu value we must consider the size of the contract (i.e. the amount of ore covered). First we must calculate the uranium required to produce a quantity of LEU fuel equivalent to what the WGPu could have produced. We then subtract the amount of uranium ore that would have been needed in any regard for diluting the Pu in MOX fuel.

Fifty tonnes (MT) of WGPu could be used to produce approximately 1409 MT of MOX fuel (@ a fissile atom density equivalent to 4% U-235 enrichment). To produce 1409 MT of low enriched uranium fuel, 35.3 million lbs of U3O8 is needed. The MOX fuel would require 3.53 million lbs. This leaves a net amount of 31.8M lbs. The option contract should be sized to cover this amount of uranium ore. This gives a total value of $263M for 50 MT of WGPu.

Interestingly , for the base case values WGPu is more valuable as a potential fuel than if it were utilized today. If the WGPu could be substituted for 4% LEU fuel today it would have a current value of $244M. This is less than the option value calculated above. Therefore even if Russia could sell the fuel today, the expected revenue from the material would be greater is she stored it (assuming no storage costs).

However storing WGPu is not free. While the uranium option replicates the potential benefits from holding WGPu, it does not replicate all costs. Storage may be quite costly due to safety and security issues. The cost of storing WGPu must be subtracted from the calculated value of the option.[58]

Including the cost of WGPu storage has a dramatic effect. Cost estimates for Pu storage range from 430-2000 $/kg/yr.[59] If a storage cost of $400/kg/yr is assumed for ten years, a present value cost of $132M is incurred. This reduces the value of 50 MT of WGPu to $131M. If storage costs are assumed to be $1000/kg/yr, storage costs rise to $331M. This eliminates the entire value of the Pu. Therefore, unless storage costs are assumed to be low, the option value of plutonium is minimal. Figure 31 shows the value of the option relative to three low estimates for Pu storage costs.

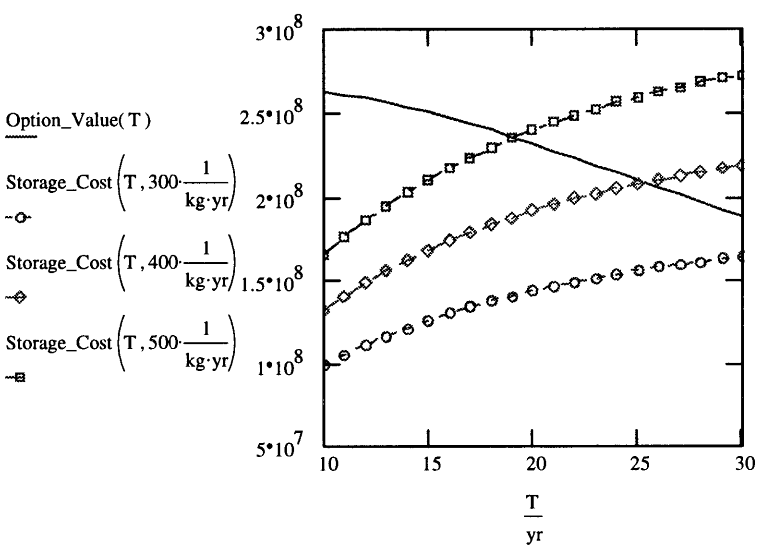

FIGURE 31. Storage Cost Effects on Option Value

Extending the duration of the option reduces its value while increasing the storage costs. As seen in Figure 31, for short term (10 year) contracts and low storage costs, the value of the uranium option exceeds storage costs. Eventually, however, storage costs dominate. Therefore the combination of strike date and storage costs are primary factors for valuing WGPu.

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58. I will assume no convenience yield for the plutonium. Convenience yields result from the ability to keep a production process running or profit from temporary shortages. Relative to the amount of RGPu the Russians have in stock the WGPu is a small fraction. It will not be a production factor. They also cannot profit from temporary shortages as there is currently no market for Pu sales.

59. Lower value taken from Chow (1993: 69), higher value take from OECD(1994: 40).

The way option value changes with duration is due to the market's estimation of future uranium prices as evidenced in the forward prices. These prices reflect uranium's inherent dividend. It is this dividend rate that determines the option response to duration.

The role of the dividend in calculating option value is shown in Equation 20. The equation shows that the dividend rate governs the reduction in the current stock price and alters the cumulative normal values. For the uranium option, q is estimated as r - i. For the reference case, q is greater than zero. The dividend therefore reduces the probability that the option will finish in the money by decreasing the cumulative normal values. However, the reduction is small as the low strike price virtually assures option execution.

The greater reduction in option value comes from the modification of uranium's current price. When calculating the value of the option, the stock price is discounted by the dividends paid over the life of the option. This reduces the expected payoff (relative to a non-dividend-paying stock) and thereby the value of the option. Increasing the duration of the option only magnifies the effect.

Figure 32 shows the value of the option for three escalation rates as a function of option duration for a constant r. This figure demonstrates the dividend effect. For the no dividend case (i.e. i=r), the option approaches an asymptotic value; the current price of the ore covered by the contract. The determination of the dividend rate (through estimations of r and i) is essential to determine the value of the option and the effect of option duration.

It may be the case that the escalation rate is found to be higher than the risk-free rate. This would give uranium a negative dividend. This would cause the value of the option to increase in an unbounded manner. The option evaluated here cannot possess this behavior. If Pu storage costs (which are higher than uranium storage costs) were expressed as a fraction of uranium price rather than an explicit fixed annual cost as it is treated here, the option would again be bounded. For this reason escalation values that would give a negative dividend were not evaluated.

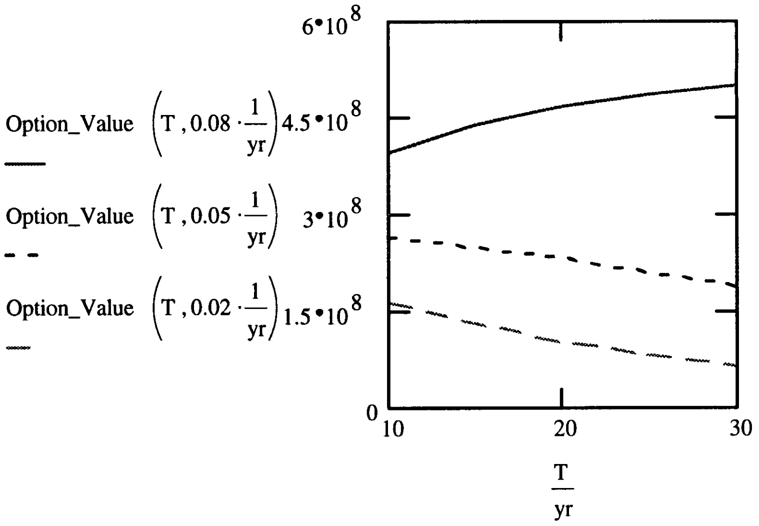

FIGURE 32. Option Value Dependence on Strike Date

The risk-free rate has multiple impacts on the value of the Pu. Figure 33 displays the effect of interest rate on option value and storage costs. As noted earlier, the dividend rate is proportional to the interest rate. Therefore as interest rates rise, dividends increase which has the effect of reducing the expected growth of uranium price. The payoff of the option at time T is also discounted at a higher level. This combination decreases the value of the uranium option as interest rates increase. Increasing interest rates cause storage costs to decrease as future costs are discounted at a higher level. However, the net effect is a reduced value of Pu as the value of the option is reduced by a larger amount. shows this effect for the base case values.

The value of the option is relatively insensitive to the volatility estimates as shown in Figure 34 (note the scale). The figure shows that as the volatility increases (over the range of values in Table 9), the value of the uranium option increases slightly with volatility . The effect is limited due to the low strike price which almost assures option execution. Relative to the selection of a strike date, the inflation rate, and the risk-free rate of return, volatility has a small effect on the value of the option.

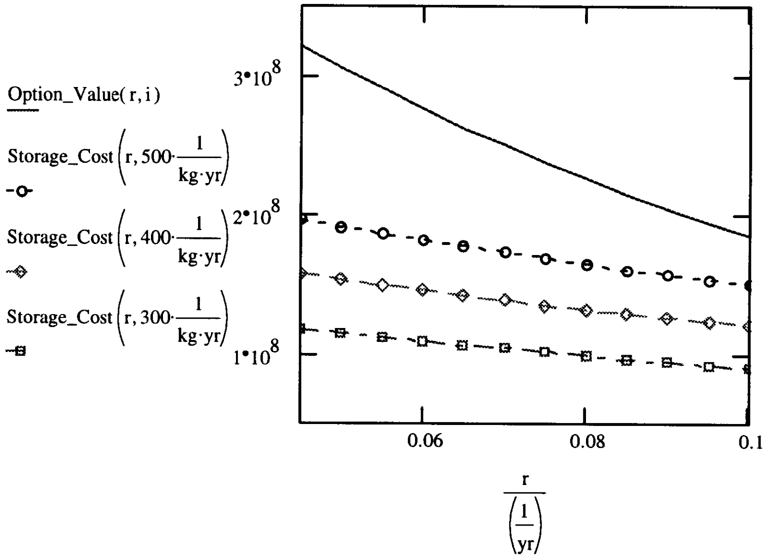

FIGURE 33. Risk Free Interest Rate Effects on Option Value

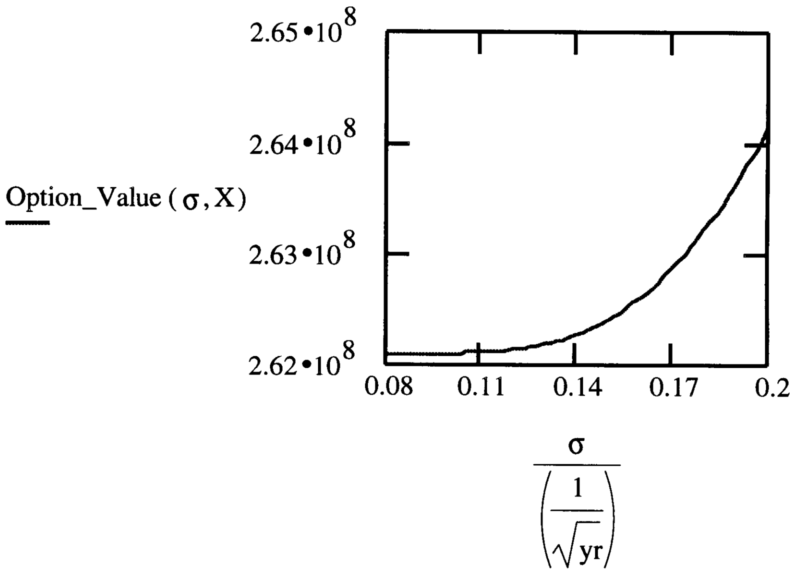

FIGURE 34. Volatility Effects on Option Value

5.3 Discussion

The derivative analysis reveals several significant facts. Depending on storage costs, surplus WGPu may have value even if it cannot be utilized today. What we do know is that this value is bounded. Figure 32 shows the option value heading towards an asymptotic limit. This value is $524 million for an option with an infinite strike date.

Storage costs are bounded as well but can be much higher than the option value. Assuming a low storage cost of $400/kg/yr, infinite storage would have a perpetuity cost of $250M. At a storage price of $1000/kg/yr the cost of storing WGPu exceeds the maximum value of the option. Storage costs are capable of eliminating any market value of the material.

The low strike price means the option will quite likely be executed. This means the price of the option is roughly the difference between the escalated price (from the forward prices) and the strike price, discounted at the risk-free rate. Unless the strike price is increased significantly the probability that the option will be exercised will remain high.

The strike price/break even price should be calculated using cost data valid *at the time of execution of the contract*. These values were assumed to be constant for this analysis. While these values will certainly change, there appears to be no reasoned way to inflate or deflate the values.

To account for shifting costs of other fuel inputs (namely the price of SWU) a different option should be valued. The payoff of this option would be a function of these costs as well as uranium. Such an option is termed a "basket option" as it represents a basket of assets rather than just one (Nelken 1996: 161).

It is not clear whether the basket option would assign a higher value to Pu or not. It will depend on the market's expectation of price movement for each individual cost and the correlations between them (Hull 1996: 305-307). A basket option for this problem is being pursued.

To obtain the rights to Russian WGPu, the US could write this call and give it to Russia or give her the cash equivalent. While the cash transfer would be the simplest to execute, the US would probably favor giving them the option contract. This would avoid arguments over the appropriate duration and storage costs needed to price the contract. However, the US would be accepting the risk of uranium price escalation. The next section will provide a discussion of how the US may reduce its exposure.

5.4 Hedging the US Position

If the US writes a call option on uranium it may desire a hedging strategy to avoid the associated risk. A simple solution would be to simply purchase the uranium call that they have bartered away. This would eliminate the risk (as the short position would be matched by the newly acquired long position). Unfortunately derivatives are not traded on uranium. This effectively eliminates this approach, but there are others.

5.4.1 Synthetic Hedge

When an option cannot be purchased directly it is necessary to “create a protective position through trading strategies that replicate the payoffs to the protective position” (Bodie 1993: 693). We again turn to Black and Scholes for assistance. Although the asset is not traded, we can use their equations to determine how the theoretical option’s price would behave if it did.

What we are interested in is how the option’s value would change as the price of uranium changes. This is termed the option’s “hedge ratio ”or “delta” and is found by differentiating Equation 13 with respect to the price of uranium. This yields the following equation:

$$\Delta = \frac{\partial C}{\partial U} = N(d_1) \qquad \text{(EQ 21)}$$

We then must create a portfolio that behaves in an equal and opposite manner. For example if a call option has a delta of 0.8, a $1 increase in the price of the underlying asset would cause the value of the option to increase by $0.80. We now must find a portfolio that would respond the same way to an increase in asset price. Holding that portfolio will be equivalent to holding the option itself.

Holding a specific amount of uranium today would provide the necessary hedge. The base case option has a delta of 0.735. To make its portfolio "delta neutral", the US must purchase 0.735 lbs of ore for every pound covered by the option.

Figure 35 shows the behavior of delta with changing price. The curve approaches an asymptotic value less than one. Therefore only a fraction of total ore is needed to entirely hedge the position. This is due to the implied dividend that will be realized by the holder of the uranium. These payments, invested over the life of the option, reduce the amount of material needed to assure adequate resources at the execution date. The corresponding amount of uranium is roughly equivalent to 47 reactor-yrs worth of fuel. Such a purchase would appear feasible as the market frequently deals in contracts of this size.[60]

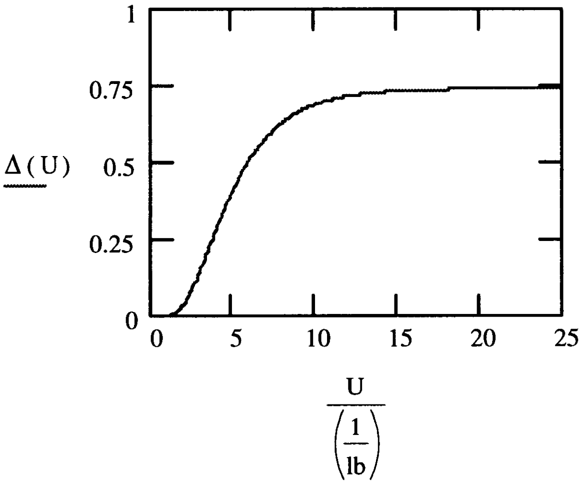

FIGURE 35. The Effect of the Price of Uranium on the Hedge Ratio

It should be noted that in practice, hedging any non-traded option can be difficult. It is a dynamic process. The delta of the option will change over the life of the option. As it

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[60] Near-term transactions in the US are typically on the order of 100,000 lb of ore. Long-term (> 1 yr but less than 10) contracts are typically for 1 million lbs of U_3O_8.

changes the portfolio must be rebalanced. In addition, merely holding the underlying commodity will not remove all risks. The value of the option is sensitive to volatility and interest rate changes that cannot be hedged using the underlying asset. Nonetheless, delta hedging is an important mechanism for reducing risk.

Fortunately the US may already possess the hedge it needs. It is in the form of another weapons usable material - highly enriched uranium (HEU). The prospect of using the material as a de facto hedge is explored in the following section.

5.4.2 A Highly Enriched Uranium Hedge

Arms control agreements have made available large amounts of HEU in both the US and Russia. Two hundred tonnes of HEU in the US arsenal is scheduled to be retired. In addition, the US has entered into a contract with Russia to purchase HEU from weapons, blended down to LEU fuel for reactors. As a result the US government already possesses or has contracted for vast quantities of uranium. In fact, either source alone can easily fulfill hedging requirements.

HEU of US Origin

In contrast to WGPu disposition, US plans for the disposition of surplus HEU have progressed rapidly. The US Department of Energy has issued a record of decision for the roughly 200 MT of HEU declared "surplus to defense needs" by President Clinton (DOE 1996a). The US plans to blend this material with natural uranium to denature the material. Approximately 85% of this HEU will then be sold on the commercial nuclear fuel market. The US is expected to net a profit of \$340 to \$770 million from the sale. The projected profit and technical ease of HEU disposition has put it on a fast track for implementation.

The government may nonetheless have to wait to receive this windfall. A provision in the United States Enrichment Corporation (USEC) Privatization Act requires the DOE to sell the fuel in a manner that has no adverse impacts on the domestic nuclear fuel industry.[61]

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[61] USEC Privatization Act (Pub. L. 104-134, SS 3112(d)(2)(B)

The DOE must also factor in the sale of blended Russian HEU in the US market when it decides to sell this fuel. As a result sales are likely to be spread over a 15 - 20 years and perhaps longer.

The delayed sale of fuel could serve as the hedge for the option contract. Storage of uranium fuel for decades is a long position in uranium. A cost comparison performed by the DOE estimated that the average enrichment of the 170 MT of HEU available for blending and commercial sale is 50% (DOE 1996b). This material could be blended to produce up to 2125 MT of LEU fuel of 4% enrichment. This is much more than the 1409 MT of LEU covered by the option contract. Incredibly, the surplus HEU the government already owns would completely cover this option contract.

HEU of Russian Origin

An even larger amount of uranium fuel will come under US government possession during the next two decades. In February of 1993 the US government agreed to purchase 500 MT of HEU (blended down to LEU) from Russia over a 20 year period (Allison 1996: 229). What the US really agreed to do was to allow an enrichment company it owned to buy and sell the fuel. The formal contract was signed the following year between Minatom and the United States Enrichment Corporation (USEC), the legislated broker of the deal. This contract gave USEC the exclusive right to purchase up to 10 MT annually for the first five years and 30 MT annually for the following 15 years. The objective of the deal is to increase US security by easing the way for Russia to denature her HEU.

Domestic concerns have hampered the execution of this agreement as designed. The increased sale of uranium from the former Soviet states produced fears over uranium price deflation. In 1991, US uranium producers petitioned for and attained anti-dumping laws restricting the sale of uranium and SWU of former Soviet origin (Allison 1996: 245). The sale of fuel derived from Russian HEU is restricted under these laws. A compromise designed to further the HEU deal while still protecting US companies will result in the long term storage of large quantities of natural uranium.

A Suspension Agreement was passed (and amended) that allows Russia to be partially compensated for her uranium fuel from HEU. The amended Agreement allows Russia to be paid for the SWU value of the material upon delivery to USEC. However, the feedstock value of the fuel will be held to the terms of the anti-dumping laws. (The feedstock manifests itself in the form of the uranium ore delivered to USEC but displaced by the Russian fuel). This means that USEC will only be able to sell a small amount of the Russian uranium on the US market.

Depending on global sales (allowed under the agreement), some fraction of the material will be stockpiled. Over the life of the current Agreement 1994-2003, USEC will have purchased 200 MT of HEU. Assuming 95% enrichment, this could produce 4750 MT of 4% fuel, displacing 53,967 MT of natural uranium. Under the terms of the Agreement during this same period only 16,517 MT of Russian uranium may be sold on the entire US market. Even if all of the quota were filled by HEU uranium, 53,967-16,517=37,450 MT of natural uranium will remain in storage. The option contract covers a mere 12,218 MT of natural uranium.

This natural uranium, contracted for purchase but not yet paid for, represents another hedging source. The problem is the nebulous terms of the Russian agreement. The price is subject to renegotiation every year. For this material to function as a hedge the US government should set the forward price (i.e. direct USEC to do so). However if one charges the risk to the HEU deal and not WGPu, (the HEU deal has progressed independently) the fact that an agreement exists to purchase the material is sufficient. Three hundred tonnes of HEU is scheduled to be purchased during the last 10 years of the HEU contract. If the sale of this material is limited as well, even more uranium will be in storage.

5.5 Conclusions

Viewing surplus WGPu as a derivative provides a fair, market based mechanism for valuation. The material has been removed from military service. Therefore the only value it can posses is of an economic nature. While current factors suggest the material is worthless, under certain future conditions the Pu may gain value. Derivative theory allows us to replicate this expected future value without assuming the inherent proliferation risk of storing WGPu.

Assigning WGPu a derivative value avoids polarizing statements regarding the Pu fuel cycle. While separated Pu may represent a future avoided cost for a projected fuel cycle project, the global market would be hard pressed to quantify this value as the expansion itself is based solely on governmental plans. The ability to discuss Pu's value as dependent on specific market variables provides bounded flexibility to negotiations. This flexibility may result in a successful disposition agreement.

The concept of bounding the value of the WGPu is important. As the option most certainly will be exercised (due to its low strike price), the US offer in effect compensates the Russians for the revenues from future sales. This is equivalent to saying "although you can't sell this material today, we'll pay you the present value of the revenues you could receive in the future." The most this could cost would be the current value of all the ore covered by the option. This ore could then be given to Russia today. As the convenience yield will at a minimum cover storage costs, this is the maximum value of the option. Any payment above this level would purely represent an incentive for action. This upper limit gives both parties a reference point for negotiation. Knowing when compensation ends and pure incentive begins should normalize the expectations of both parties and aid the formulation of an agreement.

Nonetheless, certain variables selected for this analysis may be challenged. Primarily the selection of LEU as the Pu substitute fuel. If the replacement fuel were of higher enrichment (e.g. fast reactor fuel), the strike price would be lower which would increase the value of the option. While this is true it should be noted that such reactors are not commercial entities today. We are in essence taking a non-tradeable asset (WGPu) and making it tradeable. It seems reasonable therefore to restrict the fuel to that which can be found in the market today and has a reasonable expectation for commercial demand in the next several decades.

The potential role of surplus HEU in WGPu disposition is intriguing. We have already decided not to sell the HEU for some time. Therefore we have decided to accept the associated interest and storage cost penalty. So the marginal cost of using it as a hedge is zero. Given the quantity of HEU available, the fuel option in exchange for Pu offer could be extended to other countries holding separated Pu. Used in this manner, HEU may do more to improve security than it did in warheads.

In summation, the derivative framework is a pragmatic response to legitimate Russian financial and US proliferation concerns. The proposal could clear the way for immediate processing or transfer of Russian WGPu to the US. Russia would receive reasoned compensation and the US would receive tangible movement on a security issue it views as critical. The implementation of this approach should be seriously considered.

6.0 Summary and Conclusions

Historic achievements in arms control were the catalyst for an international debate on surplus weapons-grade plutonium disposition. For the first time, superpowers are developing strategies for eliminating a portion of their nuclear stockpiles. While the reductions are welcomed, managing the fissile materials from retired warheads is a complex technical and political challenge. To be implemented, any proposal must satisfy constraints imposed in both areas.

6.1 Plutonium Disposition Problem

The total US inventory of all grades of Pu (both in the Department of Energy and Department of Defense) is 99.5 MT (OFMD 1996b: Ch.1 p.2). This includes 85 MT of WGPu (<7% Pu-240), 13.2 MT fuel grade (7-19% Pu-240), and 1.3 MT of RGPu (>19% Pu-240).[51] The US has declared a total of 52.7 MT of this Pu as surplus to security needs. Therefore at least this amount will be dispositioned in some manner.

The Russian inventory has been estimated at a total of 140 MT of Pu but Russia has not made public the true value. Of this, 25 MT are believed to be RGPu. While agreeing to disarm, Russia has not declared any of its Pu as surplus.

In a speech before the United Nations on September 27, 1993 President Clinton announced a series of initiatives designed to reduce the risk of nuclear weapons proliferation. The President stated that the US would "seek to eliminate where possible accumulation of stockpiles of highly enriched uranium or plutonium and to ensure that where these materials already exist they are subject to the highest standards of safety, security, and international accountability."[52]

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[51] The isotopic concentration of Pu-240 in Pu determines its classification as the spontaneous fission of this isotope increases the potential for predetonation in an explosive device.

[52] White House Press Release, Office of the Press Secretary, September 27, 1993

The President also called for "a comprehensive review of long-term options for plutonium disposition, taking into account technical, nonproliferation, environmental, budgetary and economic conditions." President Clinton invited Russia and other nations with relevant interests and experience to participate in the study. This set of initiatives was termed the U.S. Nonproliferation and Export Control Policy.

There has been much concern regarding the security of Russian Pu. During Senate testimony in 1996, John Deutch, then Director of the Central Intelligence Agency, described four confirmed thefts of weapons-usable material. This included thefts of 6 grams of Pu, a single gram of HEU, and approximately 500 grams of a Pu/U mixture (Deutch 1996: 9). The most significant was a case involving three kg of HEU in December of 1994. There have been numerous other unconfirmed reports of theft in Russia.

The underlying US objectives regarding WGPu disposition can be described as follows:

1. rapidly move Russian Pu into a form that provides sufficient barriers to unauthorized diversion and host-state retrieval;
2. as Pu storage in the US is more secure, dispose of US Pu in an environmentally sound manner with attention to cost (there is little imperative to act swiftly other than to encourage Russian action);
3. demonstrate US commitment to nonproliferation and in the process establish an international standard for Pu storage.

In order to aid decision making, a standard for Pu disposition was adopted and alternatives for meeting the standard were investigated. The standard, proposed by the National Academy of Science and subsequently revised by the DOE, identifies the goal of Pu disposition as: "to make the plutonium as unattractive and inaccessible for retrieval and weapons use as the residual plutonium in the spent fuel from commercial reactors" (OFMD 1996c: ES-1). The standard has been termed the Spent Fuel Standard (SFS).

The word *unattractive* was added ostensibly to avoid debate regarding the inaccessibility of various Pu matrices. The modification is widely interpreted as requiring a radiation barrier.[53] However, no specific measurable parameters were, nor have been, established to determine compliance with the Standard.

The NAS report stated that disposition options that did not meet this standard would represent “a unique safeguards problem indefinitely” (NAS 1994: 12). It was also noted that going beyond the standard would not be justified unless the same treatment was performed on the much larger stocks of Pu presently found in spent fuel. As this seemed unlikely, due to the enormous cost and complexities, the SFS was adopted. The Standard has become the basis for the administration’s disposition activities.

In her Record of Decision (ROD) for the disposition of US surplus WGPu, Secretary O’Leary described a dual path strategy for meeting the SFS. Both a reactor burning option and the immobilization with HLW would be pursued. By pursuing a hybrid approach the ROD contends that WGPu disposition could begin earlier and be completed faster. It was also argued that the two paths will serve as insurance for meeting schedule goals.

However the strategy appears prone to stagnation. The US has stated that it will require reciprocity from Russia before it processes any of its WGPu. Russia has expressed a desire to burn its Pu in reactors but presently lacks the infrastructure to do so. Russia has flatly rejected the other SFS alternative, mixing the Pu with HLW, as this treats the Pu as waste and does not extract the fuel value of the material.

It would appear that US security interests would be served if the US were to financially aid the processing of Russian Pu. However, to be consistent with the present US Pu fuel cycle policy the US cannot support Pu burning activities in Russia. The policy reads: “The United States does not encourage the civil use of plutonium and, accordingly, does not itself engage in plutonium reprocessing for either nuclear power or nuclear explosive purposes.”[54] An alternate strategy that approaches the functional capabilities of the SFS, yet is capable of being supported by both countries, is proposed in this thesis.

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[53] Actually a radiation barrier would not be required for the direct disposal of Pu in boreholes option or the space disposal option.

[54] White House Press Release, Office of the Press Secretary, September 27, 1993.

6.2 Proposed Strategy for Plutonium Disposition

6.2.1 Material Processing

The US should propose the following steps be executed in coordination with Russia:

1. immobilize surplus Pu in a glass or ceramic matrix without HLW;
2. do not require the addition of HLW in the future;
3. produce a high unit size/mass;
4. add integral off-site tracing capability; and
5. allow the conditional retrieval of Russian Pu in the future for use in energy production.

It is proposed that the US and Russia address their mutual proliferation concerns (primarily unauthorized diversion) by initiating bilateral processing of their surplus WGPu immediately. Plutonium would be processed into a glass or ceramic matrix expected to be acceptable for repository disposal. The matrix would include sufficient neutron absorbers for long-term criticality control based on the present state of knowledge and expected regulatory limits. High-level radioactive waste could be added at a later time but should not be required under any agreement.

A high unit size and mass product could be attained by immobilizing the Pu in canisters of the dimension of those being filled with HLW at the Defense Waste Processing Facility (DWPF) in South Carolina. These containers are approximately 3 meters in length and 60 cm in diameter. When filled with HLW glass they weigh approximately 2 tonnes. The size and weight would simplify safeguarding activities and provide barriers to unauthorized diversion. The canisters would be stored at an internationally safeguarded facility where they would be subject to periodic direct verification. Such verification would not be possible (using present technologies) if radioactive fission products were included.

In addition, it is proposed that an electronic device that would allow individual canisters to be tracked be encapsulated within the Pu matrix during glove box operations. A 'beacon' from such a device could be used to locate and retrieve individual cans should they be diverted. The design of this device has not been explored in detail, however the absence of highly radioactive elements would eliminate radiation damage concerns. Similar tracking devices are commercially available and have been used to aid the retrieval of stolen vehicles.

Russia could retain the option of retrieving the Pu but only if her energy needs demanded it. Russia would have to prove alternate stockpiles of RGPu were not available and Pu would be directly fabricated into MOX. The processed Pu would be treated as a safeguarded ore, much like a HLW repository. The US could financially support the production of this storage matrix as it would not contribute to the development of a Pu fuel cycle in Russia.

6.2.2 Financial Compensation for Russian Pu

If Russia refused even the material processing offer the US could propose an outright purchase of the material. The agreed upon Pu could be transferred directly for processing and storage in the US. Such proposals have been offered before but not pursued as a framework for pricing Pu has not been established.

Recent evaluations place the present value of WGPu at zero due to the low price of uranium fuels and high price of plutonium fuel fabrication (Chow 1993: 75). It is simply cheaper to use uranium fuels. However, this may not always be the case. It may be that Russia values Pu not for its current worth but for its potential value in the future. By adopting this view they are in effect valuing Pu as a call option on nuclear fuel. An asset of this type will produce a positive cash flow if the value of uranium fuel is above a certain price on a specified date. Realizing this, we have found an alternative, market-based mechanism for valuing Pu that should be acceptable to Russia.

Assigning a derivative value to WGPu gives the US a *reasoned* mechanism to compensate Russia and thereby promote Pu disposition. Compensation may be in the form of a cash payment or a portfolio that replicates the potential cash flows from holding WGPu. The latter allows Russia to retain her hedged position in the nuclear fuels market without stockpiling Pu. The former could provide Russia with hard currency. This proposal is discussed further in Section 6.5.

The issues related to the disposal of immobilized Pu in a repository (listed as the second objective in Section 6.1) are assessed in Section 6.4.

The following section describes the analyses that were performed to determine a reasoned strategy for Pu disposition.

6.3 Strategy Formulation

A system analysis was performed on the disposition problem. The marginal proliferation benefits and costs of processing were combined with an understanding of relevant uncertainties to identify components of an effective and robust disposition strategy. An effective strategy would meet the US disposition objectives outlined above.

To develop a strategy for meeting the US Pu disposition goals, it was necessary to develop a functional definition of these objectives. What specifically are the barriers to proliferation? How can these barriers be attained in the context of the present US/Russian disarmament process? How could they be extended to provide a Pu disposition standard for the international community ? At what cost? These questions are addressed in this section.

6.3.1 Proliferation Risk

To be considered a barrier to proliferation, a modification to the present Pu material form should result in reduced proliferation risk. A model for determining proliferation risk is proposed. Proliferation risk was assumed to be dependent on three factors: desire, ability and opportunity.

From the perspective of a proliferator, surplus plutonium in a storage matrix represents:

- something I want to some degree (defined by my ability to use it and alternate sources of the fissile material);

- something I have some prospect of successfully obtaining (defined by degree of safeguards, physical form, tracking potential);
- and, given a degree of opportunity, I will acquire it.

The greater the motivation and the ability of a group to divert fissile material given the opportunity, the greater the perceived risk. The 'ability' factor was taken to represent barriers to theft from a safeguarded storage facility. The 'desire' factor includes the ability to process the material into an explosive device once it has been transferred off-site. This factor also include the attractiveness of the Pu relative to other sources of fissile material (e.g. highly enriched uranium). Each of these factors is needed for proliferation risk to exist, however the relative risk contribution of each is unknown.

The strategy proposed in this work utilizes two approaches to reduce proliferation risk. The proposed material processing of Pu will affect each of the factors contributing to risk. As the opportunity for diversion of Pu exists primarily in Russia, the transfer of this material to the US via a purchase would also reduce proliferation risk. Both approaches are capable of dramatically reducing the risk posed by surplus Pu.

The Pu purchase, while amenable to implementation in stages, would in one step provide tangible security benefits. The benefits from material processing could be more incremental in nature. Individual processing steps were evaluated on the basis of their ability to minimize proliferation risk by attacking the individual risk factors.

In order to assess the impact of material processing on risk it was necessary to identify the potential proliferator. This is important because processing has unique and disparate effects on individual proliferators. A strategy that does not impact the class of proliferator that is of most concern would provide little benefit.

Four general classes of proliferators were selected and their potential proliferation motives and capabilities postulated. The classes of divertor were: Host Nation (US or Russia), other Nuclear Weapons State (NWS), Non-Nuclear Weapons State (NNWS), or a Sub-National Group.

The effect of processing on the desire, ability, and opportunity on the risk of proliferation for each class of threat was examined. The general material modifications assumed for this investigation were:

- pit processing - submitting the pit to a process where its geometry is changed and perhaps transformed into oxide form;
- isotopic blending;
- chemical dilution with or without a radiation barrier, and
- increasing the unit size and mass.

The means for achieving these modifications are presented in the context of immobilization activities as immobilization was the focus of this research.

General Findings

The political debate has also produced confusion over what *can* be achieved by the Record of Decision alternatives. While irreversibility has been stated as a major political objective, it simply cannot be attained through the alternatives under investigation. Only through a deep-burn alternative (Pu elimination in a non-fertile matrix) or a similar approach would Pu disposition be entirely irreversible (Chodak 1996).

For the alternatives examined, irreversibility is more a function of proliferator infrastructure and required retrieval rate. If irreversibility were truly desired, each country could destroy its reprocessing facilities. This would greatly increase the time and cost of extraction and make uranium enrichment more attractive.

The destruction of reprocessing infrastructures would also be a stronger statement of the US commitment to arms reduction than Pu disposition. If such capability is maintained, the world would recognize that relatively small investments in infrastructure would be needed to reverse any disposition action.

6.3.2 Material Processing - Benefits and Costs

Pit Processing

The processing of Pu out of pit form would reduce proliferation risk in several ways. There have been some questions regarding the ability to adequately verify pit storage. The Nonproliferation Assessment stated that “acceptable verification and monitoring measures for pits in storage have not yet been resolved” (DOE 1997: Ch.5 p.51). Processing the Pu into non-pit form would allow the material to be accounted for directly and safeguarded by multinational parties. This would reduce the opportunity for diversion by all would-be proliferators.

Pit conversion would eliminate weapon design information eliminating any gain for a NWS proliferator and would slightly reduce the attractiveness of the material for other proliferators. This material would also not be available for direct reinsertion in a host state warhead. As this would be the first step for any disposition action it would appear that every effort should be made to achieve this action immediately.

As the opportunity for proliferation is a function of time, the schedule for this step is especially important. Pit conversion/Pu recovery operations could be initiated immediately in the US if sufficient shipping/receiving facilities along with glove box and ventilation systems were available. The availability of of such facilities in Russia is unknown. The ARIES process is currently being designed to process 250-500 pits per year (OFMD 1996c: Ch.3 p.2). Such a prototype could be replicated to increase throughput.

The operational start time for the ARIES process, combined with a vitrification step was estimated as 7 years (OFMD 1996c: Ch.5 p.10). For the immobilization alternative these processes were not individually evaluated as they would be treated as a single, integrated front-end process for combining the vitrified Pu with HLW. This estimate includes further R&D and licensing activities. It is possible that such processing could be done faster and cheaper in Russia.

The cost of Pu processing in the US was identified as a major life cycle cost. In the Existing LWRs - Existing Facilities alternative, a net life cycle cost of $1390 M was assigned to ARIES processing with Ga removal. The total undiscounted life cycle cost for this alternative was estimated to be $1920 M. For the vitrification can-in-can variant, front-end costs were $1340 M including the initial vitrification step. The total life cycle cost for this variant was $1830 M.

Isotopics

The Red Team confirmed prior statements regarding the usability of various isotopic grades of Pu in weapons. It issued a single summary statement on the manner (Sandia 1996: Ch.4 p.7):

> "All plutonium is good plutonium; some is better than other."

In the past there have been debates regarding the suitability of reactor-grade Pu (RGPu) for weapons use. RGPu has higher concentrations of Pu isotopes above Pu-239. This results in two potential problems for weapons designers: pre-initiation and heat dissipation. Pre-initiation can reduce the expected yield of the weapon and the high heat rate can cause problems with regard to the high explosives and other materials in the weapon.

Despite the problems associated with RGPu, its ability to produce a nuclear explosion seems certain. "Even if pre-initiation occurs at the worst possible moment (when the material first becomes compressed enough to sustain a chain reaction), the explosive yield of even a relatively simple first-generation nuclear device would be of the order of a few kilotons" (DOE 1997: 38). It has also been noted that the issue of heat generation can be mitigated by heat sinks and/or delayed assembly of the weapon until just before use (NAS 1994: 33). Therefore the Assessment concluded that "reactor-grade plutonium is weapons-usable, whether by unsophisticated proliferators or by advanced nuclear weapon states" (DOE 1997: 39).

While the isotopic dilution of WGPu to approximate RGPu may not prevent its use in weapons *designed* for RGPu , it may be possible to demilitarize the material for service in the host nation's present designs. Both countries have a fleet of warheads designed for a particular grade of Pu. It may be that sufficient isotopic blending would make the Pu unusable in a significant portion of the designs (Sylvester 1996).

While new designs could be utilized, the inability to test them due to the Comprehensive Test Ban Treaty (CTBT) could be an obstacle.[55] This may effectively demilitarize the Pu as the reliability of new designs may be insufficiently characterized.

The schedule for isotopic blending is limited in the US by the availability of RGPu. The US halted its civilian Pu fuel cycle activities in the 1970's. However, approximately 14.5 MT of "non-WGPu" is available in the US for such a purpose. Russia has approximately 25 MT of RGPu. The schedule and cost for such blending is uncertain but would appear to be similar to that of the Pu processing described above.

Alternatively, the Reactor burning option would have to be utilized to achieve isotopic dilution. The US schedule for inserting Pu in reactors (should this alternative be pursued) is 9 yrs. One could argue that the marginal cost of isotopic dilution is negative as revenues are expected from fuel sales. However this is not appropriate as the total life cycle costs of this option are not completely offset by revenues.

Chemical Dilution With or Without Additional Radioactive Elements

The creation of a chemically mixed Pu product, by itself, has a minimal effect on proliferation risk. Producing a sufficiently radioactive mixture by commingling Pu with other radionuclides could in theory provide a diversion barrier if it required shielding to be used during an attempted theft from a safeguarded storage facility. This would complicate unauthorized on-site manipulation of the material.

However, in a report published by Sandia it was asserted that "none of the alternative final forms emit radiation fields large enough to require shielding for dedicated aggressors"

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[55] The Comprehensive Test Ban Treaty bans all nuclear explosions. All declared weapon states have signed the treaty.

(Sandia 1996: 16). Therefore, the inherent radiation levels of the alternatives under investigation would not be a "significant accessibility barrier to unauthorized parties."

The Assessment Report, while acknowledging the Red Team's devaluation of radiation barrier, asserted that the *larger* barrier provided by adding radionuclides would be related to detectability (DOE 1997: 54). (In the framework of this analysis, the ability to successfully divert the material would be reduced.) The Report asserted that a radiation field would make the transport vehicle easier to detect and that gaseous fission products would be released upon reprocessing that could be detected. (The fact that the immobilization alternative proposed in the ROD does not contain volatile fission products was not noted in the DOE's assessment.)

The ability of further chemical processing to hamper off-site activities (desirability) is also limited. Chemical processing could complicate the fabrication of a weapon or make alternate sources more attractive. The effect is dependent on the capabilities and options available to the proliferator.

Both host countries possess industrial size, operating, shielded separations facilities as well as uranium enrichment facilities. Therefore, the desirability of the material would depend on cost of retrieval of the Pu relative to alternative fissile sources (e.g. highly enriched uranium (HEU)). Plutonium extraction costs will be influenced by several factors. In addition to the processing infrastructure, the desired rate of Pu recovery and the waste management practices of the proliferator are also important.

For the host state the addition of a radiation barrier would not reduce the attractiveness of the material as it would still be cheaper to extract the Pu (roughly 1/2 the price per kg) than producing HEU. If the aqueous HLW produced from separating the Pu from a SFS was not vitrified the cost would be further reduced. In contrast if shielded separations facilities did not exist (and the desired recovery rate remained high), a radiation barrier would reduce the risk of host state diversion as such a facility would have to be constructed at great cost.

For a NNWS or sub national group that wished to develop some level of nuclear weapons capability, any of the processing steps would seem to have marginal effect on their desire for the material. Cost would not be relevant as they do not have an alternate source of fissile materials. These proliferators are likely to desire only one or a few weapons and would probably accept clumsy and slow laboratory reprocessing. The radiation barrier would be a nuisance, requiring additional time and personnel for Pu extraction. But according to the Vulnerability Assessment only 2 additional weeks and 2 additional people would be needed to retrieve 8 kg of Pu (a significant quantity of Pu as determined by the IAEA) (Sandia 1996: Ch.4 p.6).

A radiation barrier would also hamper if not prevent direct verification. The Nonproliferation Assessment notes that it will "no longer be possible with current technology to accurately measure the amount of Pu in the glass - just as it would not be possible to accurately measure Pu in spent fuel" (DOE 1997: 111). While this is also true for the much large quantities of civilian spent fuel it is not viewed as a beneficial trait.

For the immobilization variants, chemical dilution would be achieved as the last stage of pit processing. Therefore the schedule for dilution would mimic that of Pu processing. The marginal cost of chemical dilution for this alternative was included in the ARIES estimate above.

For the can-in-can variant, the radiation barrier would be simultaneously added with the unit size and mass step. The additional cost was estimated to be $490 M, $390 M for vitrification with HLW and $100 M for the disposal costs of the estimated 200 additional canisters produce by vitrifying 50 MT of WGPu.

For the reactor alternative, chemical dilution in a large unit size and mass container is achieved at the price of MOX fuel fabrication. This results in an added life cycle cost of $1540 M. The addition of a radiation barrier would require $380 M in reactor related costs but result in a fuel displacement credit of $1390 M.

It could be argued that given the marginal cost of adding a radiation barrier ($390 M for the can-in-can variants) is so low that we should add it even though the benefits are debatable. This would be true if there were no risks associated with the radiation barrier. If waste form qualification issues arise we run the risk of having to re-extract Pu, vitrify the HLW again and determine a suitable form for the Pu. This is identified as a relevant uncertainty in Section 6.3.3.

Unit Size and Mass

Unit size and mass is capable of reducing proliferation risk by reducing the likelihood of a successful theft from a safeguarded facility. While there is virtually nothing to prevent retrieval by a host state, the prospects for successful diversion by other proliferators may be reduced somewhat. The most important factor appears to be the use of unit size and mass to hamper on-site manipulation and off-site transport by requiring industrial size equipment.

Schedule and cost information for attaining high unit size and mass were included in the discussion of the chemical dilution step above.

6.3.3 Disposition Uncertainties

The disposition of WGPu is subject to programmatic risks due to uncertainty. This uncertainty goes beyond the uncertainties in detailed estimates of processing costs and other data. This uncertainty relates to the risk of negative outcomes resulting from disposition decisions today.

While the expected outcome of a strategy may be desirable, uncertainties may mean that a wide range of possible outcomes may be produced. Some of these outcomes may be quite undesirable. These uncertainties should be identified and an efforts made to reduce the probability of a negative outcome.

Schedule Uncertainties

Schedule uncertainties increase the risk of delay and the opportunity for diversion. A strategy that leaves Pu in an extremely secure material form yet cannot be implemented is of little value.

A particularly meaningful uncertainty is Russian Pu disposition activities. Russian reciprocity will be required for US disposition to proceed. None of the disposition alternatives explicitly address this reciprocity issue. The disposition of US Pu will not reduce the obstacles Russia faces in burning its Pu. Without an accompanying strategy for effectively promoting Russian disposition, it is likely that US Pu will remain in pit form as well.

All of the immobilization alternatives may face delays due to waste form qualification issues. Even if Pu disposal forms meet disposal requirements at the beginning of processing, they may not be acceptable upon completion as standards are subject to change. Indeed, the performance requirements for a repository have not yet been established. If disposition requires the operation of other facilities such as the DWPF, disposition will be dependent on its availability. The processing delays of the DWPF will become delays for Pu dispositioning.

External Uncertainties

Uncertainties also exist in the long-term benefits provided by Pu disposition. As described previously, proliferation risks were shown to be conditional on proliferator motives, capabilities and more importantly their alternatives. Over the several decades of disposition these factors are likely to change. The changes may reduce the marginal benefits of Pu processing in the long-term.

For example, the diffusion of centrifuge and AVLIS technology over the several decades of disposition may exceed the long-term proliferation risk posed by surplus Pu. Alternatively, options that are presently viewed as proliferation resistant may ultimately be viewed as unacceptable (e.g. the can-in-can variants). Given the uncertain benefit, alternatives that meet expected long-term goals should not be pursued over those that can reduce risks known to be present today.

The existence of a repository will also impact ultimate benefits. It has been noted that only when the SFS forms are placed in a geologic repository would proliferation resistance be dominated by intrinsic barriers rather than institutional ones. If such a facility is delayed or never materializes, the Pu will need to be safeguarded indefinitely. In such a scenario, the benefits realized from pursuing a Spent Fuel Standard matrix for Pu storage will be debatable.

As external uncertainties cannot be controlled by strategy formulation, emphasis is further placed on prioritizing near-term issues as uncertainty prevents us from knowing the long-term benefits of current decisions.

6.3.4 Conclusions

While the ultimate benefits are bounded, material processing is capable of meeting valuable nonproliferation objectives. However, strategy formulation must begin with well articulated nonproliferation objectives. The risk to be reduced must be identified. The benefits and costs of various actions must then be weighed to form an effective strategy that minimizes the programmatic risks of Pu disposition.

The proposal would reduce the risk of subnational and NNWS diversion.

Processing Pu into a clean storage form would provide virtually all the proliferation risk reduction *attainable* by material processing. Removal from pit form and placement in a safeguarded facility would reduce the ability and opportunity of any proliferator to divert the material. Critical design information would also be lost. Increasing the unit size and mass of the Pu host matrix would reduce the ability for NNWS and subnational groups (the primary target of the proposal) to successfully divert the material. This is the primary, near-term risk posed by this material.

The presence of off-site tracking capability would provide a new form of deterrence for these proliferators. It has been said that "The current inability to locate a nuclear device without intelligence cueing is perhaps the greatest limitation of our neutralization capability" (Mullen 1996: 20). The primary benefit of the radiation barrier was its ability to aid the detection of Pu after a theft.

The signal frequency could also be known by the international community, allowing any nation to independently monitor the location of dispositioned Pu at any time. This would serve to further increase confidence in the arms control process.

The possibility for direct verification would be retained by this proposal. Without the background radiation from HLW, isotopic and total Pu concentration in the matrix could be non-destructively determined. This was not developed in this work but it would appear that standard spectrometry techniques such as gamma-ray spectrometry could be utilized.

If the presence of a radiation barrier were truly desired the DWPF canisters could be stored alongside fully radioactive DWPF canisters. This would not differ appreciably from the can-in-can alternatives which have been promoted in the disposition Record of Decision.

The proposed processing would also prevent retrieval and subsequent direct use by the host nation. The fact that it has been declared surplus and would be under international safeguards most likely provides the highest deterrent for host state retrieval. In any case, it is recognized that host state retrieval of Pu in any form is possible. It is for this reason that the proposal was largely designed to reduce the security risk from other proliferators.

Timely processing of both US and Russian surplus Pu would be possible.

Perhaps the biggest benefit of this alternative is its prospect for US/Russian cooperation. The proposal was designed to harmonize with Russian fuel cycle ambitions and yet allow for US financial support. Contentious fuel cycle commitments are not required. The proposal represents a compromise between two polar alternatives for Pu disposition and in doing so provides a reasoned path forward for both countries.

Without a resolution to the Russian fuel value issue it appears no processing will move forward. By allowing retrieval or providing compensation, the proposal provides two means of addressing this concern. Either approach appears capable of being accepted and thereby reducing the risk of stagnation.

By completely separating Pu disposition from other fuel cycle activities its execution can quickly begin to reduce the opportunity for proliferation. Processing could proceed at virtually any pace through the use of multiple process lines and/or higher capacity systems. Schedule uncertainty would also be reduced by uncoupling Pu processing from other activities such as DWPF or reactor operations.

As the proposal is capable of providing security in the near-term, its benefits are not dependent on predictions of future proliferation risks. The most pressing dangers posed by the Pu can be addressed. In addition, the proposal does not prevent further processing should it be desired.

The flexible nature of the strategy would reduce implementation risks.

The modular nature of this design could provide valuable flexibility to address both technical uncertainties and political differences. If criticality control was deemed insufficient, the DWPF canisters could be repackaged to address regulatory concerns. In the extreme case the Pu could be reprocessed for other waste treatment without requiring the re-vitrification of HLW.

As time goes on, political tensions may cause intermittence in international oversight at Pu storage facilities. Confidence in treaty compliance may erode during such periods. The ability to directly verify Pu content would eliminate such uncertainties.

This approach would also buy time for each country to fully evaluate their respective Pu objectives. The US could further weigh disposal options and Russia could develop the necessary infrastructure to burn Pu. Neither would be forced to execute Pu programs requiring large industrial investments without thorough analyses.

The proposed form could be utilized in further Pu disposition initiatives.

The proposal could be formalized into a Surplus Plutonium Storage Standard which could be applied globally. Some non-weapons states may eventually want to disposition their excess Pu. This form would give them an alternative other than MOX fuel or mixing with HLW. Indeed the country may have neither alternative at their disposal. Such a form could be used to demonstrate a commitment to arms reduction, ease safeguarding and storage cost, and give verifiable proliferation resistance.

6.4 Technical Feasibility

As significant quantities of plutonium have never been vitrified, the technical feasibility of such a proposal must be demonstrated. The feasibility of vitrification will require confidence in repository subcriticality. Neutron absorbers may necessarily be vitrified with Pu to control reactivity over geologic time periods. Rare earth elements have been identified for their neutron absorption capabilities and relative insolubility in groundwater. The homogeneous dissolution of these elements in glass is desired. The environmental durability of the glass is especially important if Pu is to be vitrified with HLW. Each of these issues were investigated and the results are described in the following sections.

While a durable glass is desired, Pu release is not likely to be a major concern from an EH&S perspective. Pu is relatively insoluble in groundwater and is not likely to migrate to the biosphere (unless perhaps in colloid form). However, the release of non-radioactive boron may be more important. Boron's inherent properties are a benefit to glass design, however its aqueous solubility may allow for a criticality event as the glass dissolves in a repository as it is the primary neutron absorber in boro-silicate glass.

The addition of insoluble rare earth elements (REE) is a potential strategy for addressing this criticality concern. Several rare earth elements possess strong neutron absorption characteristics. A list of relevant neutronic properties for boron and several REE is contained in Table 11.

TABLE 11. Neutronic Poison Data[a]

Element	Isotope	atom% abundance	thermal neutron capture cross section, barns	resonance integral, barns
B	10	19.9	3,838	1722
Sm	149	13.8	5,900	4000
	152	26.7	208	3000
Eu	151	47.8	5,900	4000
	153	52.2	530	1500
Gd	155	14.8	61,000	1540
	157	15.65	255,000	800

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[a] "Nuclides and Isotopes," 14th edition, General Electric Company 1989

In order to assess the durability of a Pu glass, a borosilicate glass loaded with a Pu analog and several rare earths was leach tested. The release of neutronically relevant species was of particular interest. The following section describes the experimental approach and the results obtained.

6.4.1 Environmental Durability

The borosilicate glass ARM1 was used for durability testing. The glasses tested were prepared in the following manner. The ARM1 glass was crushed and weighed into fused silica crucibles. Nitrates of Th, Eu, Gd, and Sm were then weighed and added to produce glass frits with the desired loading. The modified ARM1 frit was then melted to form glass.

After cooling the glass bars were sectioned and prepared for leach testing using the MCC-1P protocol. The samples were sanded, weighed and surface area measurements were made. They were then placed in a Teflon® container with a measured volume of deionized water. The containers were labeled and placed under controlled temperature for an extended period of time.

Upon completion of the tests, glass samples were removed from solution, rinsed and then dried. Measurements of the concentration of elements in solution were then taken. Knowing the concentration of the element in the leachant, the total mass of the leachant and the surface area of the glass allowed key parameters related to glass durability to be calculated.

Elemental releases from glass are typically reported in units of normalized grams of element i per square meter of glass. The mass of released element i is normalized by its concentration in the unreacted glass. The figures presented here display the normalized release data for the specific elements of interest.

Leaching of unmodified ARM1 glass at 90°C in deionized water agreed reasonably well with HLW glasses in the literature and accurately reflected trends in elemental leaching.[56] The pure ARM1 tests were done to provide a baseline for comparison with modified glass behavior.

Figure 36 displays the normalized release behavior for pure ARM1 over a leaching period of one year. The glass reacts at a maximum initial rate, termed the forward rate. As glass components begin to enter into solution, glass reaction affinity begins to drop and the leach rate slows. During flow-through type tests borosilicate glasses will continue to react at the forward rate.

If every glass element entered into solution their normalized release curves would be identical. The boron and Na release curves are nearly identical. Both elements are quite soluble in DI water. A shown in Figure 36, a portion of the Si (roughly 20 wt%) does not enter solution but remains, most likely as a constituent of the reacted glass. Boron and Na were assumed to represent the bulk reaction rate of the glass.

The addition of Th and the rare earth elements to the ARM1 glass resulted in a product with roughly equivalent durability as pure ARM1. The release curves for Si, B, and Na are shown in Figure 37. While three of the samples had releases slightly higher than those for pure ARM1, two were lower. All releases were within a factor of two.

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[56] See Lutze (1988: 105 and 122) for example.

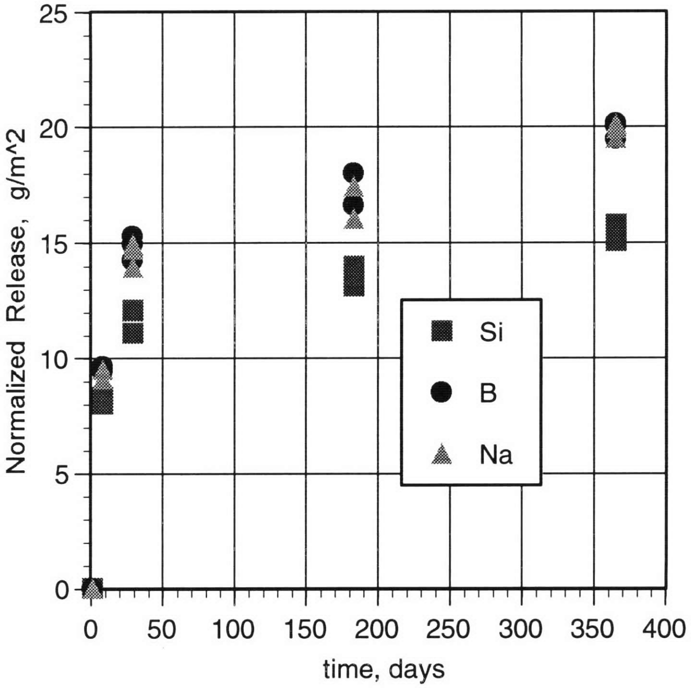

FIGURE 36. Silicon, Boron, and Sodium Release From Pure ARM1 Glass Leached in DI Water at 90°C

The ARM1 glass was effective at retaining the additional elements. The concentrations of Th, Eu, Gd, and Sm were below detection limits in three samples and within 1 ppb of the limits in the other two. (As the values were not corrected for elemental interference these value may actually be below detection limits as well.) Figure 38 shows the release data for the samples in which these elements were barely detectable. It is interesting to note the general order of elemental concentrations found either in solution or colloidal form. Thorium and Sm were the most soluble and Gd and Eu were the least. However, these concentrations are very near detection limits and should be viewed carefully.

In comparison with boron all the rare earth poisons exhibited superior performance. Figure 39 shows that while boron entered solution as the glass reacted, europium was much more resistant. This was the desired behavior for the added reactivity control. It is not known if the rare earths remained in the alteration layer or were sorbed on container walls as strip tests were not performed. In the ARM1 glass the rare earths did not form colloids

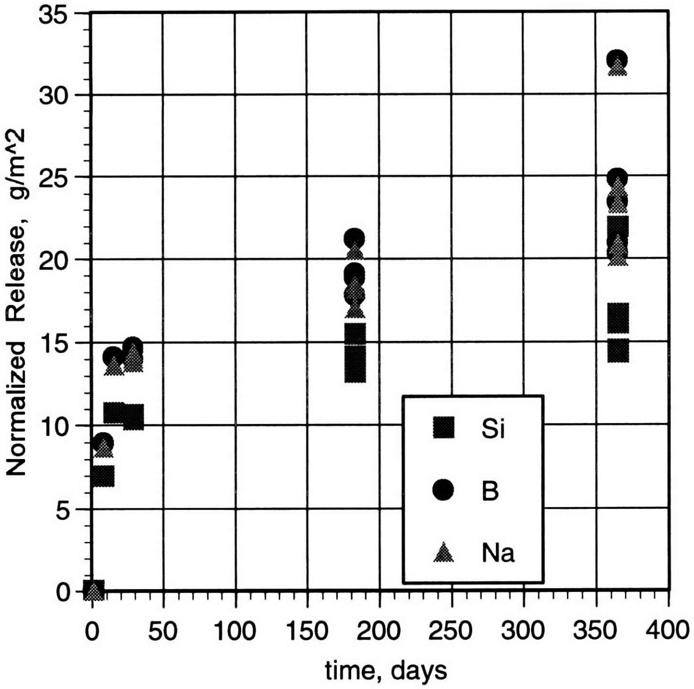

FIGURE 37. Silicon, Boron, and Sodium Release from ARM1 Glass Loaded with 2 wt% ThO_2, Eu_2O_3, Gd_2O_3, and Sm_2O_3 Leached in DI Water at 90°C

smaller than 0.45 μm. If they did form they would have been redissolved upon acidification and appeared in the measurements.

Another borosilicate glass formulation, known to possess low durability as it contains no Al, was also tested to examine Th and REE behavior in a poor performing glass. (This formulation would not be used in Pu or HLW vitrification.) In this glass, Th and REE releases were below detection limits for three of the five glass samples tested. However the remaining two samples had 1-2 ppm of each of these element in its leachate. These concentrations are much higher than the expected solubility limits of these elements in DI water and indicate the formation of colloids containing these elements.

Conclusions

The addition of Th and the REE does not harm glass durability and the potential exists for positive contributions. Further investigation is needed, but it appears that these elements

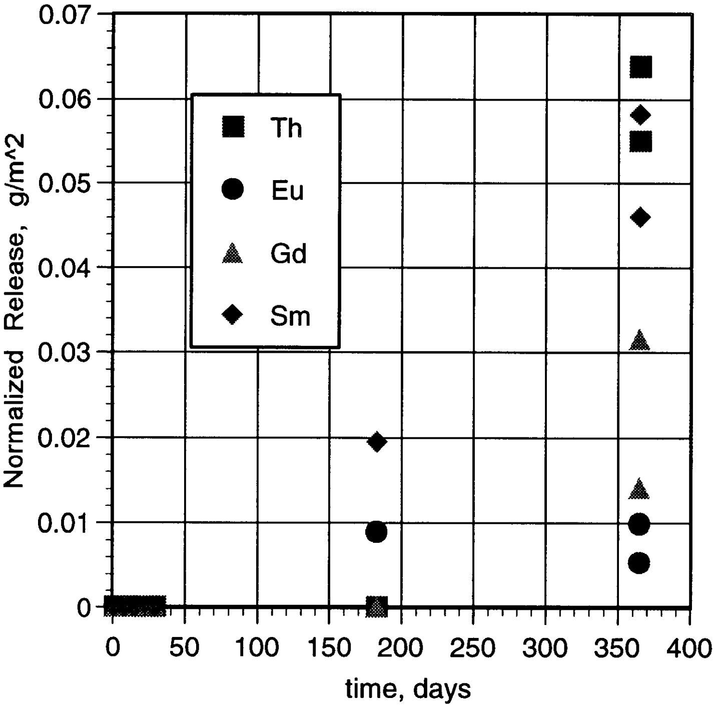

FIGURE 38. Detectable Thorium and Rare Earth Release From Modified ARM1 Glass at 90°C

were dissolved in the glass network and did not promote the formation of a less durable phase.

For glasses of reasonable durability it appears that Th will not enter solution. In this case Th is likely to be sorbed on surfaces or retained in reacted glass products. However, for a poor durability glass, dissolved species, high pH, or other factors allow Th to exist in colloid form. The Th could have formed a true colloid or sorbed on a Si or other colloid.

The rare earth elements had release characteristics virtually identical to that of Th in the tests performed. Regarding criticality control, the REE were always much more insoluble than boron. The formation of a colloid in the low durability glass is of concern as it may provide a release pathway for these elements. However, the data showed that ~99% of the Th and REE remained either sorbed on the container wall or in the reacted layer. When colloids were formed in the poor durability glass, both Th and the REE appeared to participate. This is significant as even in this case the neutronic poisons were demonstrated to mimic Th behavior.

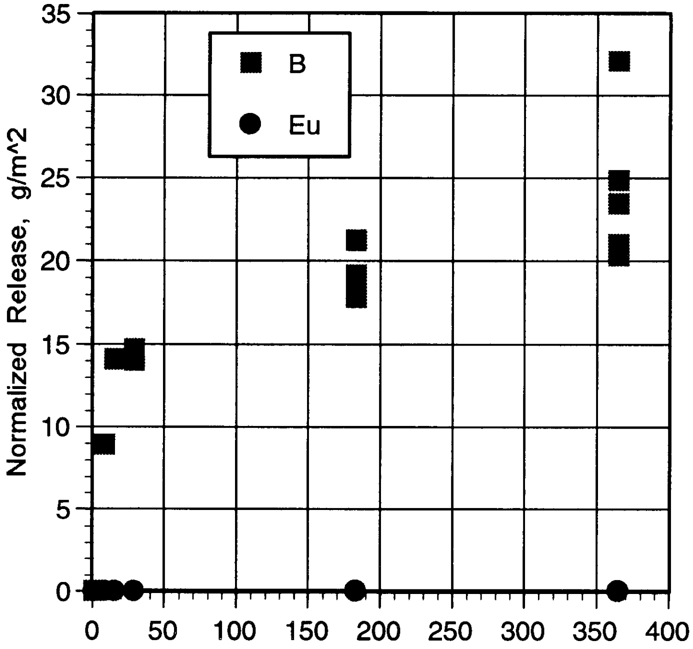

FIGURE 39. Reactivity Control Release in Modified ARM1 Glass at 90°C

6.4.2 Criticality Assessment

Over extended periods of exposure to groundwater, sufficient neutron absorbers could migrate from the near field to induce criticality. Plutonium has a half-life of 24,000 yrs and decays to fissile U-235 which has a half-life of 704 million years. Uranium can be relatively insoluble as well. Criticality is a concern as fresh fission products would be given an aqueous transport pathway, potentially to the biosphere.

Glass Reaction with Groundwater

Glass reaction is a complex process dependent on both glass and solution properties. In general, glass will react with water to release its soluble species and form more stable amorphous and crystalline phases. It is the redistribution of neutronically relevant nuclides during this process that is of primary interest in the work presented here.

Extensive research has been performed on glass reaction with water, the results of which have led to various descriptions of glass dissolution. One theory is that H^+ diffuses into the glass matrix and undergoes ion exchange, typically with alkali metals such as sodium (prevalently at the non-bridging oxygen sites). The alteration of the glass also allows soluble species (such as boron) to enter into solution. This produces a reacted layer that retains the amorphous silica structure of glass but with concentration gradients of alkali and soluble species. This layer has been termed the "diffusion layer."

Over time, the most depleted portion of the diffusion layer (its outer fringe) begins to hydrolyze. This results in a restructuring or repolymerization of the Si matrix into a more stable, hydrous "gel layer." This may or may not release Si into solution. The process apparently "kicks out" metals incapable of entering into a new amorphous phase (Bourcier 1991: 6). Eventually, the gel layer further reacts with water and is dissolved completely, releasing silica into solution. This reaction is termed "network dissolution."

This surface layer (the diffusion layer and gel layer combined) is typically less than a micron in thickness and moves into the glass as the bulk reaction proceeds. Following behind it is a layered region of amorphous and crystalline phases termed alteration layers. This region has a complex elemental composition. Many of the metals that were either "kicked out" during gel layer formation or released as a result of network dissolution, quickly precipitate to form the alteration layers. These layers can be either amorphous or crystalline in nature. The retention of fissile nuclides in these layers is of interest here. Figure 40 provides a graphic description of the dissolution process.

A Glass Reaction Model

A simple model describing the composition and configuration of a single glass log in a repository was constructed. Available data on glass/groundwater chemistry were used to determine reacted glass and solution composition over time. System parameters were then varied to determine their effect on subsequent criticality calculations.

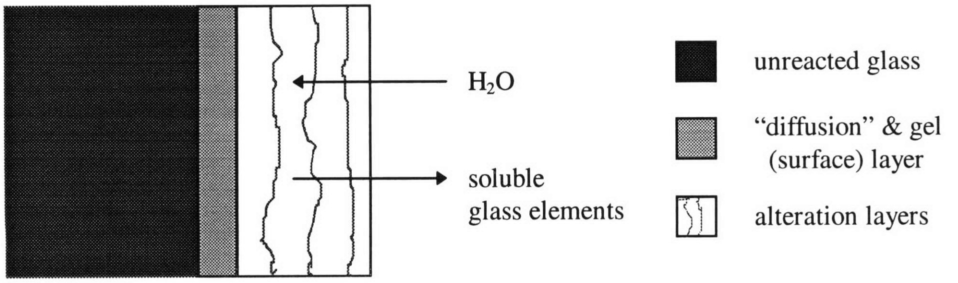

FIGURE 40. Dissolving Glass

The following physical situation was modeled. The model assumes a glass log with the dimensions of a Defense Waste Processing Facility (DWPF) log (3 m long x 60 cm diameter) and a nominal plutonium loading. The composition of the glass was assumed to be a borosilicate glass used at the DWPF. This would represent the alternative of vitrifying Pu directly with HLW.

The log was assumed to be placed in a horizontal drift at a repository with conditions similar to those expected to be found at Yucca Mountain in the state of Nevada. The mountain is under investigation as a potential high-level waste repository. A particular geologic formation known as "tuff" is taken to be the reference composition of the host rock.

As water infiltrates the emplacement it reacts with glass, producing an annular region of alteration layers. This layer moves into the glass as reaction proceeds. The depletion of soluble poisons in this region may lead to a criticality event. Figure 41 is a graphical representation of the system as it evolves.

As the glass reacts, its components enter into solution. Whether elements remain in solution or precipitate is determined by the contacting groundwater conditions.[57] Over time, the glass reaction itself will alter solution chemistry. Available thermodynamic data were used to investigate the evolution of solution concentrations during glass reaction and the

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[57] Sorption or colloid formation may also occur.

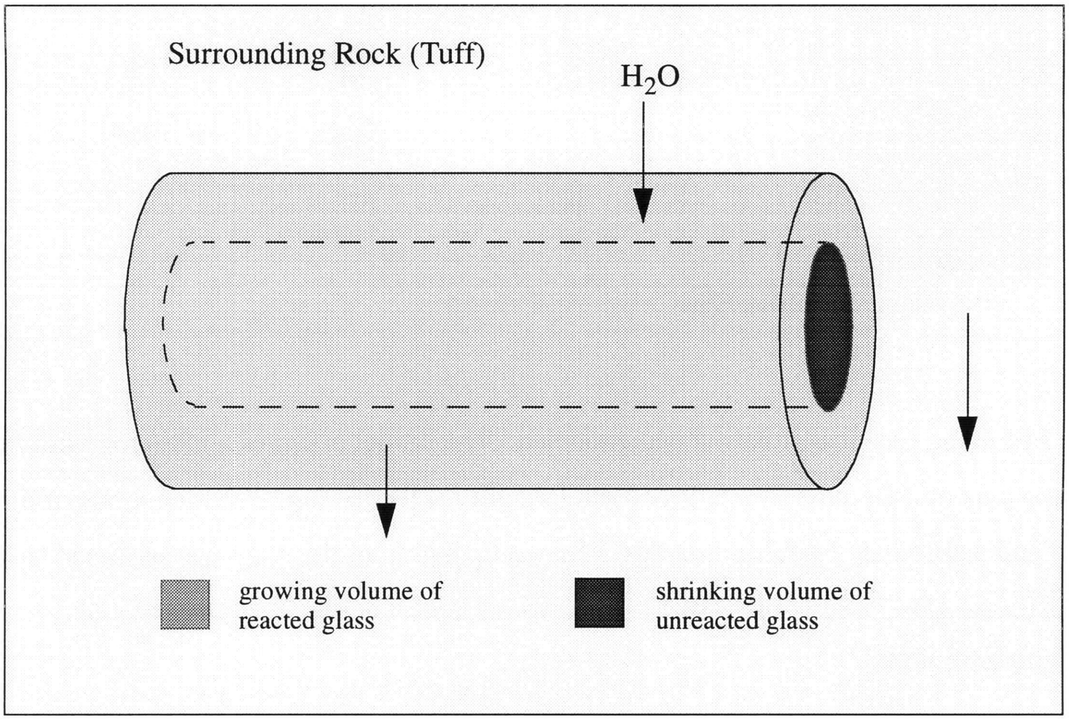

FIGURE 41. Hortizontal Drift Emplacement

formation of precipitate phases. The composition of the phases over time was used to determine if the near field system approaches a critical condition.

The durability of the glass can be described by its bulk dissolution rate (BDR). The BDR was not calculated as the long-term reaction rate may be controlled by an unknown silica phase. A range of BDR's was assumed. This was combined with a range of water infiltration rates to examine the dynamic behavior of elements entering and exiting the alteration layers.

The behavior of the following elements was examined: Pu, U, B, Li and Eu. Plutonium and uranium are fissile elements. While no uranium is found initially in the glass, Pu-239 decays to produce fissile U-235 (Pu-239 half-life=24,100 yrs). Boron and lithium are neutron control elements that are normal components of the glass. It is the higher solubility of boron and lithium relative to Pu and uranium in solution that could lead to a criticality event.

Europium is a neutron absorber not used in the current DWPF glass frit that was evaluated for its neutronic control capabilities and its expected insolubility. Europium was identified in prior work by the author as being particularly detrimental to a Pu explosive device if not removed (Sylvester 1994). It is hoped that their similar aquatic chemistry, as demonstrated in the leach tests, will keep them commingled and thereby keep the near field waste emplacement subcritical.

The oxidation state and the degree of complexation will depend on solution composition. As the assumed repository is Yucca Mountain, water from a well located at the site (J13) was taken as the reference solution. The J13 water is neutral pH and slightly oxidizing. It is a carbonate water with significant amounts of silica, sodium and calcium. Notably it also contains sulfate and fluoride species which are known to form complexes with actinides.

Solubility/Phase Calculation

The speciation/solubility code EQ3/6 was used with its associated thermodynamic databases to determine solution concentrations as the glass reacts (LLNL 1992).[58] EQ3 uses mass action and redox relationships to solve for the thermodynamic equilibrium state of a specified ground water, identifying species concentrations and supersaturated phases. The order of phase precipitation, which may allow initially supersaturated species to remain in solution, is not addressed.

EQ6 models the addition of reactants to a solution allowing supersaturated phases to precipitate as reaction proceeds. The order of precipitation is determined by the degree of disequilibrium of the saturated phases. After the phases are removed, additional reactants are added and the process repeats. The onset of saturation can be observed in this way.

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[58] The composite data file 'data0.com' compiled and maintained by Lawrence Livermore National Laboratory was used for all solubility/speciation calculations.

EQ6 was run in titration mode to model the effect of dissolving glass.[59] In the titration calculation glass components are stoichiometrically added to a constant volume of water where they are completely dissolved and new phases are allowed to precipitate. The calculation results in a description of the aqueous species and insoluble phases that form during reaction progress. Points along this reaction pathway were taken to represent alteration layer composition for various degrees of glass reaction. The associated phases and solution concentrations were then used in the analysis.

Elemental solubilities used in the dissolution model were calculated based on equilibrium with phases formed during various stages of glass reaction. The elements of 10 grams of DWPF glass were added stoichiometrically via a titration process into one kilogram of J13 water. The glass contained 8 wt% PuO_2 and one mole of Eu_2O_3 per mole of Pu.

EQ6 produced a history of phase production and solution chemistry during glass reaction. Figure 42 shows how the concentration of the relevant elements changed over time. At no time during the reaction were Li or B predicted in the alteration layers.

Europium enters into solution as the carbonate species $EuOHCO_3$ and eventually precipitates as $Eu_2(CO_3)_3{:}3H_2O$. When HCO_3^- starts to drop , $Eu(OH)_3$ begins to form. Competition ensues between the formation of several carbonate complexes and precipitation. Ultimately Eu reaches a maximum concentration of 1.5E-5 M. Europium concentration is reduced with increasing pH caused by the glass reaction itself. Europium remains in the +3 state throughout glass reaction.

Plutonium from the glass is immediately precipitated as PuO_2 (log K_{sp}=-7.36). The small amount remaining in solution exists in the +5 and +6 state (PuO_2^+ and $PuO_2F_3^-$). As glass

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[59] There are three alternate methods for reaction path modeling in EQ6 : titration, closed system or fluid-centered flow-through system. The closed system differs in the way it treats saturation. At saturation in the closed system the reactant is reclassified as a secondary mineral with which equilibrium is reached. As the available reactant is now "gone," reaction stops. The titration model forces dissolution while the closed system reaction halts the reaction upon saturating.

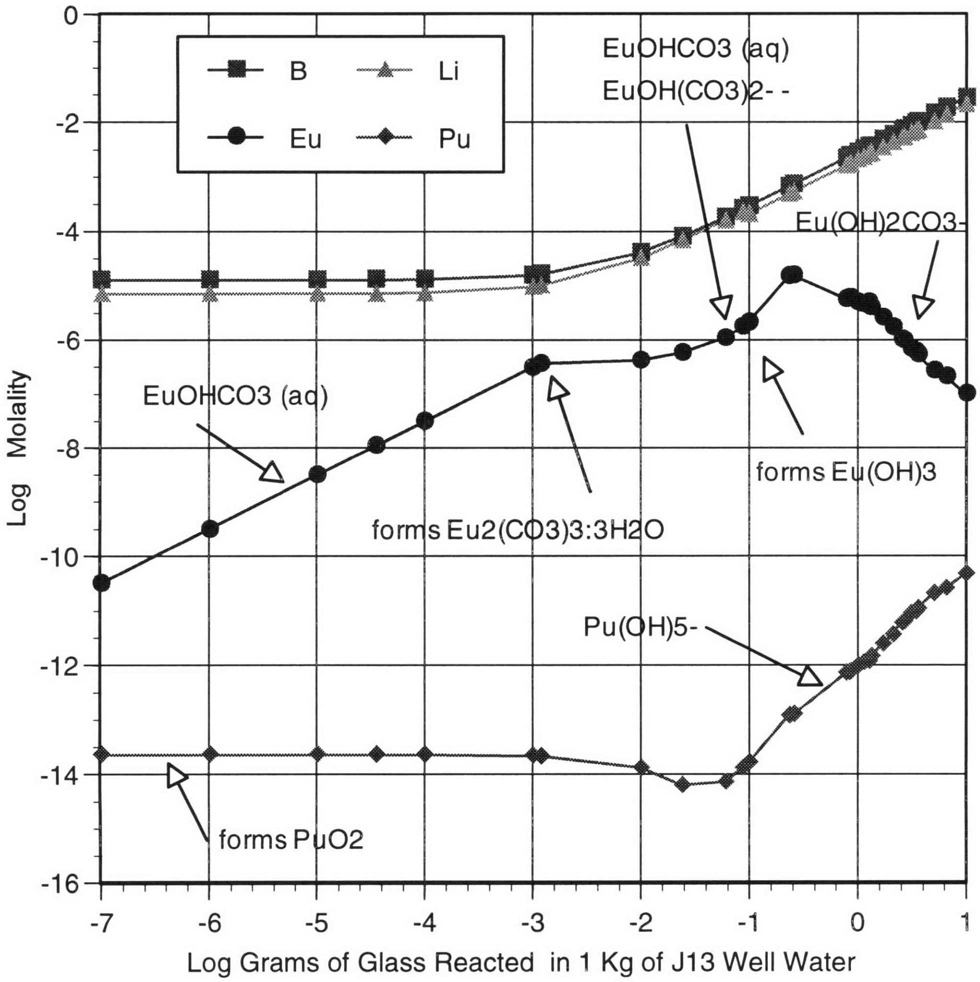

FIGURE 42. Reaction Path for DWPF Sludge-Supernate Borosilicate Glass in J13 Well Water from Yucca Mountain

reaction continues, Pu concentration dips due to HCO_3^- reduction to a concentration of 5.8E-15 M. Eventually Pu is reduced to +4 and hydrolyzes (complexes with OH^-) causing the solubility of Pu to increase. This complexation allows the Pu to be more soluble under reducing conditions than earlier oxidizing conditions. Pu solubility is then controlled by pH.

Replacing the Pu with equal molar U in glass provided similar information. As the glass reacts, the uranium concentration rises until haiweeite forms ($Ca(UO_2)_2(Si_2O_5)_3:5H_2O$). The carbonate complex $UO_2(CO_3)_3^{4-}$ keeps the U concentration initially at approximately

1E-9 M, otherwise the concentration would have been much lower. As pH drops and HCO_3^- concentration is reduced, uranium concentration drops to a minimum value of 2.6E-10 M. As the glass continues to react, uranium is reduced to the +4 state and forms aqueous $U(OH)_4$, causing uranium concentration to rise. Eventually no carbonate complexes exist and uranium is in equilibrium with uraninite. Uranium concentration stabilizes as solution pH stabilizes. For determining U solubility, the initial U loading was not important.

Conclusions

Carbonate and hydroxide appear to be the most significant complexing agents in the system studied. While chloride and nitrates are present in J13 water, at no time do Pu or U form their complexes. This is consistent with the observed trend in complexation strength. It is the 'over' complexation of the actinides (hydroxide and carbonate) to produce negatively charged species that could increase solubility in the J13 water.

The oxidation potential appears to be sensitive to the combined Eu and Pu loading. Without these elements the eH drops roughly 0.2 mV during glass reaction. With these elements it drops 1.2 mV. This reflects the strong reducing properties of rare earths and actinides. In contrast the loading of these elements does not affect pH.

The worst regime from a criticality perspective appears to occur when pH is around 9. This produces the greatest difference between Eu and Pu solubility. Uranium concentration is relatively constant throughout glass reaction. At higher pH Eu becomes less soluble, reducing this difference and the criticality concern. Due to the ion exchange reactions of dissolving glass, the groundwater closest to the surface is likely to be basic.

Criticality Calculation

For the criticality assessment the lowest solubility achieved by the fissile elements was used with the highest calculated solubility for the control element. This was done to represent a conservative estimate of the highest potential for fissile/control separation. This information was combined with various estimations of bulk dissolution rate and water infiltration rate to examine the potential for criticality to occur in the near-field.

The system was modeled as three regions: the unreacted glass, the surrounding tuff and the alteration layer. The unreacted glass was assumed to be comprised of the major components (>1 wt %) of the glass. Various amounts of Pu and REE were added to this composition. The neglected components could contain neutron absorbers so their exclusion was deemed conservative.

The porosity of the tuff was taken to be 0.3. While unfractured tuff is likely to posses a lower porosity, the tuff backfill would not due to disruption during emplacement. This value provided a upper bound on the amount of water that could be found in the tuff. After determining the concentration of the relevant nuclides in the alteration layers the remaining mass of alteration layer was assumed to be amorphous SiO_2. The total mass of the alteration layer was assumed to be 25% of the original glass. This also fixed the porosity of the alteration layers at 0.75.

After fully characterizing the system, the compositional information was used to determine the system k_{eff} over time using the criticality code system SCALE-PC. SCALE-PC is a modular code system for performing criticality safety analysis (ORNL 1992). It is comprised of various functional modules for cross section processing, criticality and shielding calculations. The XSDRN-PM module was used to produce 1-D, discrete ordinates, solutions to the neutron transport equation.

A repository containing dissolving glass logs was modelled as a lattice of infinitely long, annular 'fuel' cells. However, the pitch was chosen large enough so that neighboring logs would not contribute to the neutron economy. The alteration layer, depleted of boron, was assumed to be analogous to the fuel region of a large annular fuel pin. The interior region contained the unreacted glass and the tuff represented the moderator portion of the unit cell.

Results under “Worst Case” Conditions

In the interest of bounding the criticality problem a set of criticality calculations were performed using values most favorable for control removal and fissile element precipitation. The model parameters bulk dissolution rate and volumetric flow were set their highest values, 0.1 $g/m^2/d$ and 0.01 $m^3/m^2/yr$. These assumptions were assumed to represent a “worst case” scenario.

Initially, a glass loaded with 8 wt% PuO_2 was modeled. As 10 wt% ThO_2 was shown to devitrify this was assumed to limit the solubility of Pu in the glass. Europium was assumed to be dissolved in the glass at various concentrations.

Without additional Eu, the glass log was shown to go critical well before it was completely reacted. Figure 43 shows the results for the 8% PuO_2 case with no Eu under the “worst case” conditions of extremely low durability and high water infiltration rate. The boron in the unreacted glass did not provide significant criticality control. The hydrous alteration layer loaded with fissile elements was too reactive. It appears that the relevance of boron in the glass is low for criticality control purposes and additional control is needed.

Figure 44 shows the effect of control element removal for a glass log loaded with 8 wt% PuO_2. Even at the assumed maximum Pu loading, only a relatively small concentration of Eu is needed to hold down reactivity. Both the thermal neutron cross section and resonance integral of Eu-151 are an order of magnitude higher than those of Pu-239. A mole ratio of 1/2 Eu to Pu kept the system subcritical for more than 800 thousand years. Due to the atomic mass differences between Pu and Eu, this corresponded to a loading of less than 3 wt% Eu_2O_3 (2.6 wt%).

As the Figure shows, while Eu was able to control criticality for hundreds of thousands of years, the critical state was ultimately reached. Europium eventually exited the near field entirely while sufficient U-235 remained. The system required only 0.014 g/cc U-235 to be present in the alteration layer to go critical. After 1 million years the U-235 concentra-

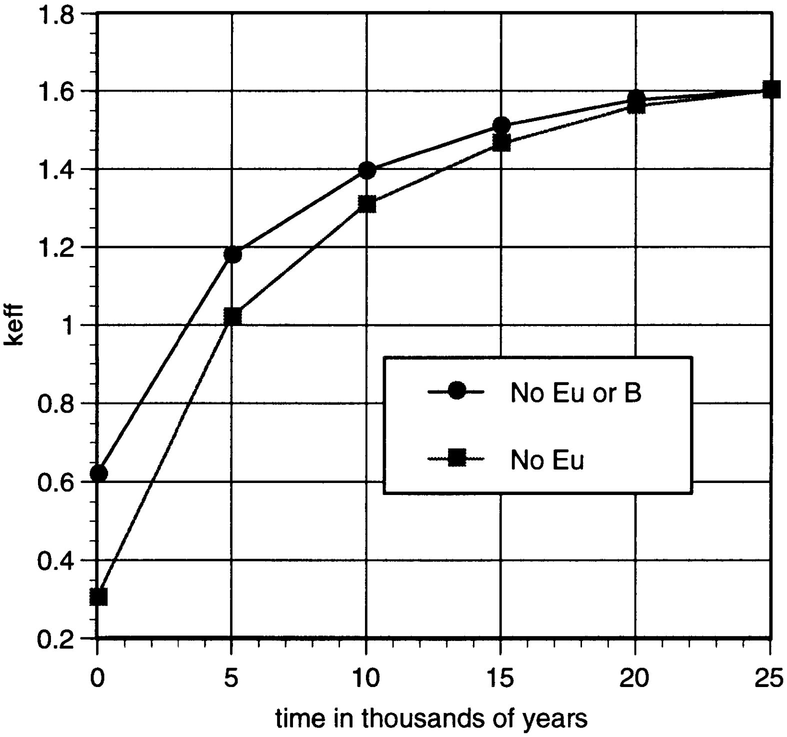

FIGURE 43. Boron Control (8 wt% PuO2)

tion was 0.18 g/cc. Uranium's insolubility and 704 million year half-life assured that it would remain over the time period examined.

Europium loading can be thought of as an effective method for extending the time to criticality. However, if criticality at any time is viewed as unacceptable, this strategy may not be sufficient. If an absolute loading limit of 30 wt% Eu is assumed (i.e. a waste glass loaded only with Eu), for the worst case conditions, Eu will be gone after 13 M years. The concentration of U-235 will remain well above 0.014 g/cc at this time. If subcriticality must be assured over this time period, relying solely on dissolved Eu in the glass may not be sufficient.

The physical mechanisms affecting k_{eff} can be elucidated by a close examination of Pu/Eu/U system behavior over time. Initial glass dissolution and removal of soluble poison increased the neutron multiplication of the system. After 23,000 years the entire glass had reacted and k_{eff} began to drop as Pu-239 decayed to U-235. However, this reduction was

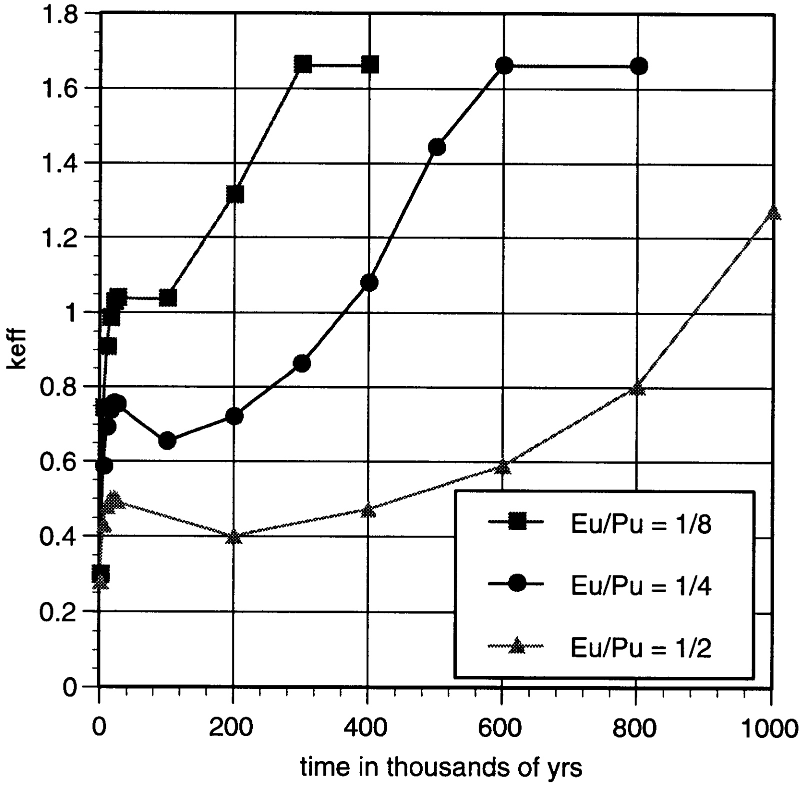

FIGURE 44. Europium Loading Effect (8 wt% PuO2)

countered by the removal of Eu. Eventually, Pu-239 completed decayed and additional Eu losses caused k_{eff} to rise to its limiting level, slightly above 1.6.

Reduced plutonium loading can also limit the k_{eff} of the system. Reducing the Pu concentration from 8 to 2 wt% pushed the time to criticality to roughly 225 thousand years. However, increasing the Eu concentration from 0.65 to 2.6 wt% pushed the time to criticality to approximately 900 thousand years. While Pu loading was effective at limiting the maximum reactivity possible, it was the Eu concentration that had the larger impact on *when* criticality occurred.

Nonetheless, the potential for diluting Pu to a level below which criticality cannot occur under the worst case conditions would be possible. If a radiation barrier were not required, a dilute waste form could be produced. It was determined that a loading of 0.45 wt% PuO_2 would keep the initial peak in k_{eff} below 1.0 without added reactivity control.[60]

The benefits of this approach would have to be weighed against the increase in disposal costs as more than 6600 additional DWPF size canisters would be produced. The DWPF facility will produce 6105 canisters of vitrified HLW waste over 20 years of operation (McKibben 1993: 21).

The presence of a moderator was shown to have a significant impact on criticality. Calculation showed the system to be undermoderated at all times. The spectrum benefits of added water outweighed the additional hydrogen absorption. Full saturation of the 0.75 porosity alteration layer was not required for the system to go critical. Less than 25% saturation was needed for a glass loaded with 8 wt% PuO_2 and an Eu/Pu mole ratio of 1/8.

The effect of reducing the bulk dissolution rate was also evaluated. This corresponded to scenarios of improved glass performance. The better performing glass effectively eliminated the local k_{eff} maximum observed during the early stages of less durable glasses discussed above. The effect of Pu-239 decay to U-235 is also masked by the longer-lived glass. However, even glasses possessing the best expected long-term durability can not guarantee subcriticality indefinitely.

Reducing the volumetric flow rate also had the effect of delaying the time to criticality. As with the bulk dissolution rate, an increase in the time to criticality was observed with a decrease in this variable. If the volumetric flow is low enough, sufficient Eu will remain to ensure subcriticality until U-235 has decayed away. However, flow rates lower that those observed today at Yucca Mountain would be required.

"Expected" Conditions

Having explored system behavior under limiting conditions, calculations based on "expected" parameters were performed. The bulk dissolution rate was set at a value of 0.001 $g/m^2/d$. Today's flow rate of 0.001 m/yr was also used. The assumed solubilities

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60.The U-235 limit in the layer (~ 0.014 g/cc U-235) would produce a loading limit of 0.5 wt% U-235 in the glass. The Pu loading limit is lower as Pu-239 has a higher fission cross section and emits more neutrons per fission than U-235.

were not changed. The reference loading for both the can-in-can alternative and homogenous alternatives have been set at a nominal 5 wt% PuO_2 (DOE 1997). Figure 45 displays the results from this Pu glass loaded with an equal molar quantity of Eu. While the time scale is shifted into the tens of millions of years, the system does go critical at approximately 13 million years. An even higher loading of REE could be used or other, stronger control elements utilized to push this time to criticality farther into the future.

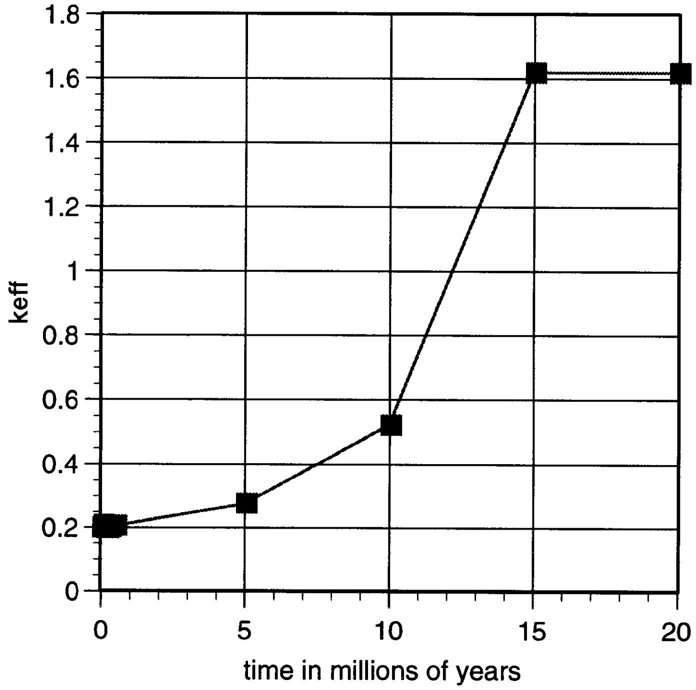

FIGURE 45. System Behavior Under Expected Conditions (5 wt% PuO_2 with an Eu/Pu Mole Ratio of 1/1)

6.4.3 Conclusions

The potential for a criticality event during borosilicate glass reaction in a repository environment does exist. Criticality may occur while much of the glass remains intact or long after the glass has completely reacted. However, several approaches for addressing criticality concerns can be pursued.

The most obvious approach is to limit the Pu loading in the glass. The coupled dissolution/criticality model developed in this work predicts that if the reference borosilicate glass were loaded with 0.45 wt% PuO_2, or lower, criticality would not occur. If higher loadings of WGPu are desired, Eu or other rare earths could effectively delay the onset of criticality.

The model showed that relatively small amounts of an insoluble absorber can delay criticality for hundreds of thousands of years. At a minium, REE loading should be added in sufficient quantities to control reactivity through the early k_{eff} peak that could result under worst case conditions.

Additional REE could be added to meet regulated time requirements for subcriticality when they are established. The analyses presented here show that even with Eu added to the glass, subcritcal conditions cannot be guaranteed indefinitely for the expected loading of Pu in borosilicate glass. If multi-million year assurances of subcriticality are needed under worst case conditions, alternate strategies may be necessary.

The proposed non-HLW storage matrix may have additional criticality benefits. If a can-in-can design were utilized, the remaining voids could be filled with a substance such as a monazite concentrate (from sand) which has high rare earth concentrations, rather than HLW glass. Monazite concentrates from Florida beach sand (produced via a caustic soda process) contain about 70% monazite (Benedict 1981: 299). Of this 40% are REE oxides. This would add both criticality control and weight to the container (added proliferation resistance). Monazite could also be used as a backfill material.

Such a design would provide flexibility benefits as well. The time requirement for subcriticality in a repository is presently unknown and when it is established becomes subject to change. The modular nature of a can-in-can variant, without HLW, would allow modifications to meet new requirements. For example, the ratio of Pu cans to REE filler could be easily modified in response to the time frame subcriticality would be required. This capability would appear valuable given the present regulatory uncertainty.

6.5 Financial Compensation

The preceding chapters have been devoted to the desirability and technical feasibility of the vitrification alternative. To be applied in Russia, vitrification will have to address a major political hurdle as well - the fuel value of WGPu.

By relating the value of Pu to a traded commodity a market assessment can be made. If plutonium fuel is assumed to be a close substitute for uranium fuel, its worth in the market must be related to uranium.

Assuming these commodities are close substitutes (i.e. 1 kg LEU is interchangeable with 1 kg of MOX fuel of the same fissile atom density), their price in the market place should be equal. This gives:

$$U_{LEU} + CON + SWU + FAB = Pu + U_{MOX} + MOX \qquad \text{(EQ 22)}$$

or, rearranging,

$$Pu = U_{LEU} + CON + SWU + FAB - U_{MOX} - MOX \qquad \text{(EQ 23)}$$

where U_{LEU} is the cost of the required ore for low-enriched uranium fuel, CON the conversion cost (from U_3O_8 to UF_6 for enrichment), SWU the enrichment cost and FAB the fabrication cost. These factors are represented here in units of $/kg heavy metal of LEU. Today, fabricated plutonium fuel is most often burned in low-enriched, mixed-oxide (MOX) form. Equation 22 shows the cost of MOX fuel as a function of Pu production cost (Pu), the cost of uranium ore diluent (U_{MOX}), and MOX fabrication costs (MOX).

Equation 23 gives the value of the Pu contained in 1 kg HM of MOX fuel based on its ability to avoid uranium fuel expenditures. Its actual market value may be much lower due to supply and demand factors. This appears to be the case today as none of the world's plutonium burners have offered to purchase Russia's plutonium. This is true even though (as will be noted later) the equation assigns a present value to the plutonium.

6.5.1 Plutonium as a Uranium Derivative

A European call option gives the holder the right to purchase something for at a fixed price on a future date. (An American option may be executed any time prior to the 'strike' date.) If the price at that time is higher than this 'strike' price, the holder of the option receives the difference. Plutonium is equivalent to a call option on uranium fuel. Holding on to it pays off when the price of uranium fuel is above a certain level.

The future value of uranium fuel (and thereby Pu) will depend largely on the price of uranium and SWU. These two components are and will continue to be the greatest contributors to the cost of LEU fuel. Other costs are service charges which may change over time, but if Pu is to dramatically increase in value it will be due to increases in these two factors.

In this thesis plutonium is valued as a derivative on uranium only. Including enrichment costs would require valuing a "basket" option of uranium ore and enrichment services (Nelken 1996: 161). This is beyond the present scope of this work and SWU was therefore assumed constant with time. The potential effect of SWU volatility on option price is discussed qualitatively.

If SWU is held constant, the price of uranium ore alone will determine the future price of uranium fuel. Plutonium can therefore be valued as a call option on uranium ore. To price an option, the expected behavior of prices over time is needed. This information is used to assess the likelihood that an option will pay off. This section describes the common assumptions used in derivative theory.

6.5.2 A Price Path for Uranium

In order to value a derivative security it is necessary to understand how the price of the underlying asset moves (in this case uranium ore). One can then produce a distribution for the expected price of the asset at some future time. By combining the probabilities the asset will reach a certain price with information about how the market prices the risk associated with the asset, it becomes possible to value the derivative.

If we assume uranium ore follows a Brownian motion, we produce an equation for changes in the price of uranium ore (U \$/lb) of the following form:

$$dU = a(U,t)\,dt + b(U,t)\,dz \qquad \text{(EQ 24)}$$

The first term on the right hand side is the expected change in price over time and the second is a stochastic factor. The dz is the Wiener process $\varepsilon\sqrt{dt}$, where ε is a random drawing from a standardized normal distribution. It is this random sampling that makes the future price uncertain.

If we further assume that $a(U,t) = \mu U$ and $b(U,t) = \sigma U$ we produce the *geometric* Brownian motion:

$$\frac{dU}{U} = \mu dt + \sigma dz \qquad \text{(EQ 25)}$$

where μ is the expected return over dt, and σ is the volatility.

Volatility represents the uncertainty we have about the asset's price movement. Sigma squared is the variance 'rate' of the fractional change in price. The higher the volatility the greater the spread of possible future prices.

Having fixed the mechanism for the price movement of an asset it becomes possible to value a derivative asset. However we must recognize that uranium possesses an inherent dividend. This is because the holder of a commodity typically assigns an added value (or dividend) to physically holding the asset. The magnitude of this effect can be determined by examining the forward prices for the commodity.

The Black-Scholes equation for a European call option on a dividend-paying stock is (for uranium) (Hull 1996: 261):

$$c = Ue^{-q(T-t)}N(d_1) - Xe^{-r(T-t)}N(d_2) \qquad \text{(EQ 26)}$$

where

$$d_1 = \frac{\ln\left(\frac{U}{X}\right) + \left(r - q + \frac{\sigma^2}{2}\right)(T-t)}{\sigma\sqrt{T-t}}$$

$$d_2 = \frac{\ln\left(\frac{U}{X}\right) + \left(r - q - \frac{\sigma^2}{2}\right)(T-t)}{\sigma\sqrt{T-t}} = d_1 - \sigma\sqrt{T-t}$$

and $N(x)$ is the cumulative probability distribution function for a standardized normal variable.

These equations give the value of the call as a function of the stock's current price (U), its volatility (σ), the continuously compounded risk-free rate of return (r), a factor accounting for the dividend (q), and the terms of the contract - its strike price (X), and date (T) as measured relative to today's date (t). If these variables are known a price for a uranium option can be calculated.

6.5.3 Terms of the Option

Having developed a theoretical basis, a uranium option can now be valued. What is needed are the required inputs. Table 12 provides a summary of the base case values used in this analysis. (The quantity 'q' was found to be equivalent to the risk-free rate minus the escalation rate used in pricing forward uranium contracts.)

TABLE 12. Base Case Values Used in BS Equations

Current U3O8 Price	volatility	risk-free rate	strike price	strike date	escalation rate
$16.50/lb	16.4 %	8%	$8.84/lb	10 yrs	5%

The volatility was calculated based on uranium ore price history over the last ten years. The strike price was set at the uranium ore price which made $C_{LEU} = C_{MOX}$ for 4 wt% enriched fuel (assuming free WGPu). Using the values in Table 13 and Equation 23, the break even strike price was calculated to be $8.84/lb U_3O_8. Having access to uranium ore at this price is equivalent to having access to free plutonium.

TABLE 13. Nuclear Fuel Cost data[a]

SWU ($/SWU)	UF6 Conversion ($/kg U)	Fabrication ($/kg U)	Mixed-Oxide Fab ($/kg HM)
110	8	275	1100

a. data taken from OECD(1994: 50)

6.5.4 Results

Using these inputs, the price of a call option on one pound of U_3O_8 was found to be $8.27. To convert this into a Pu value we must consider the size of the contract (i.e. the amount of ore covered). First we must calculate the uranium required to produce a quantity of LEU fuel equivalent to what the WGPu could have produced. We then subtract the amount of uranium ore that would have been needed in any regard for diluting the Pu in MOX fuel.

Fifty tonnes (MT) of WGPu could be used to produce approximately 1409 MT of MOX fuel (@ a fissile atom density equivalent to 4% U-235 enrichment). To produce 1409 MT of low enriched uranium fuel, 35.3 million lbs of U_3O_8 is needed. The MOX fuel would require 3.53 million lbs. This leaves a net amount of 31.8M lbs. The option contract should be sized to cover this amount of uranium ore. This gives a total value of $263M for 50 MT of WGPu.

Interestingly, for the base case values WGPu is more valuable as a potential fuel than if it were utilized today. If the WGPu could be substituted for 4% LEU fuel today it would have a current value of $244M. This is less than the option value calculated above. Therefore even if Russia could sell the fuel today, the expected revenue from the material would be greater is she stored it (assuming no storage costs).

However storing WGPu is not free. While the uranium option replicates the potential benefits from holding WGPu, it does not replicate all costs. Storage may be quite costly due to safety and security issues. The cost of storing WGPu must be subtracted from the calculated value of the option.[61]

Including the cost of WGPu storage has a dramatic effect. Cost estimates for Pu storage range from 430-2000 \$/kg/yr.[62] If a storage cost of \$400/kg/yr is assumed for ten years, a present value cost of \$132M is incurred. This reduces the value of 50 MT of WGPu to \$131M. If storage costs are assumed to be \$1000/kg/yr, storage costs rise to \$331M. This eliminates the entire value of the Pu. Therefore, unless storage costs are assumed to be low, the option value of plutonium is minimal. Figure 46 shows the value of the option relative to three low estimates for Pu storage costs.

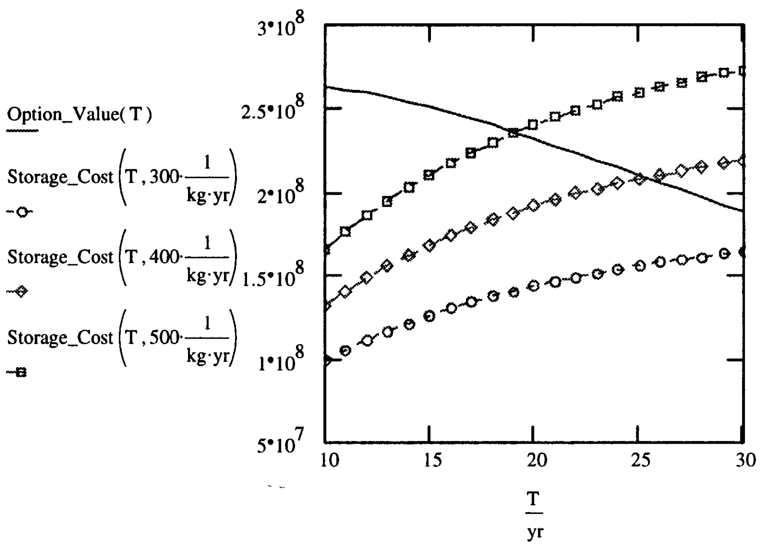

FIGURE 46. Storage Cost Effects on Option Value

Extending the duration of the option reduces its value while increasing the storage costs. As seen in the Figure, for short term (10 year) contracts and low storage costs, the value of the uranium option exceeds storage costs. Eventually, however, storage costs dominate. Therefore the combination of strike date and storage costs are primary factors for valuing WGPu.

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[61] I assume no convenience yield for the plutonium. Convenience yields result from the ability to keep a production process running or profit from temporary shortages. Relative to the amount of RGPu the Russians have in stock the WGPu is a small fraction. It will not be a production factor. They also cannot profit from temporary shortages as there is currently no market for Pu sales.

[62] Lower value taken from Chow (1993: 69), higher value take from OECD(1994: 40).

The way option value changes with duration is due to the market's estimation of future uranium prices as evidenced in the forward prices. These prices reflect uranium's inherent dividend. It is this dividend rate that determines the option response to duration.

Discussion

The derivative analysis reveals several significant facts. Depending on storage costs, surplus WGPu may have value even if it cannot be utilized today. What we do know is that this value is bounded at $524 million for an option with an infinite strike date.

Storage costs are bounded as well but can be much higher than the option value. Assuming a low storage cost of $400/kg/yr, infinite storage would have a perpetuity cost of $250M. At a storage price of $1000/kg/yr the cost of storing WGPu exceeds the maximum value of the option. Storage costs are capable of eliminating any market value of the material.

The low strike price means the option will quite likely be executed. This means the price of the option is roughly the difference between the escalated price (from the forward prices) and the strike price, discounted at the risk-free rate. Unless the strike price is increased significantly the probability that the option will be exercised will remain high.

The strike price/break even price should be calculated using cost data valid *at the time of execution of the contract*. These values were assumed to be constant for this analysis. While these values will certainly change, there appears to be no reasoned way to inflate or deflate the values.

To account for shifting costs of other fuel inputs (namely the price of SWU) a different option should be valued. The payoff of this option would be a function of these costs as well as uranium. Such an option is termed a "basket option" as it represents a basket of assets rather than just one (Nelken 1996: 161).

It is not clear whether the basket option would assign a higher value to Pu or not. It will depend on the market's expectation of price movement for each individual cost and the correlations between them (Hull 1996: 305-307). A basket option for this problem is being pursued.

To obtain the rights to Russian WGPu, the US could write this call and give it to Russia or give her the cash equivalent. While the cash transfer would be the simplest to execute, the US would probably favor giving them the option contract. This would avoid arguments over the appropriate duration and storage costs needed to price the contract. However, the US would be accepting the risk of uranium price escalation. The next section will provide a discussion of how the US may reduce its exposure.

Hedging the US Position

If the US writes a call option on uranium it may desire a hedging strategy to avoid the associated risk. A simple solution would be to simply purchase the uranium call that they have bartered away. This would eliminate the risk (as the short position would be matched by the newly acquired long position). Unfortunately derivatives are not traded on uranium. This effectively eliminates this approach, but there are others.

Arms control agreements have made available large amounts of HEU in both the US and Russia. Two hundred tonnes of HEU in the US arsenal is scheduled to be retired. In addition, the US has entered into a contract with Russia to purchase HEU from weapons, blended down to LEU fuel for reactors. As a result the US government already possesses or has contracted for vast quantities of uranium. In fact, either source alone can easily fulfill hedging requirements.

Conclusions

Viewing surplus WGPu as a derivative provides a fair, market based mechanism for valuation. The material has been declared surplus for military purposes. Therefore the only value it can posses is of an economic nature. While current factors suggest the material is worthless, under certain future conditions the Pu may gain value. Derivative theory allows us to replicate this expected future value without assuming the inherent proliferation risk of storing WGPu.

Assigning WGPu a derivative value avoids polarizing statements regarding the Pu fuel cycle. While separated Pu may represent a future avoided cost for a projected fuel cycle project, the global market would be hard pressed to quantify this value as the expansion itself is based solely on governmental plans. The ability to discuss Pu's value as dependent on specific market variables provides bounded flexibility to negotiations. This flexibility may result in a successful disposition agreement.

The concept of bounding the value of the WGPu is important. As the option most certainly will be exercised (due to its low strike price), the US offer in effect compensates the Russians for the revenues from future sales. This is equivalent to saying "although you can't sell this material today, we'll pay you the present value of the revenues you could receive in the future." The most this could cost would be the current value of all the ore covered by the option. This ore could then be given to Russia today. As the convenience yield will at a minimum cover storage costs, this is the maximum value of the option. Any payment above this level would purely represent an incentive for action. This upper limit gives both parties a reference point for negotiation. Knowing when compensation ends and pure incentive begins should normalize the expectations of both parties and aid the formulation of an agreement.

6.6 Conclusions

Separated weapons-grade plutonium in insecure storage represents a global security risk. Unfortunately, the option of swift elimination is not available. Complete Pu elimination options could be developed but would be hard to justify if only applied to separated plutonium and extremely costly to implement for Pu presently in spent fuel. Even if we could eliminate every atom of Pu on earth, institutional measures would be needed to assure that additional Pu or HEU were not being produced covertly.

Accepting that institutional controls will play a role in global security under any conditions, and that Pu elimination appears impractical, the relevant question for surplus WGPu disposition becomes "How do we ease the safeguarding burden posed by surplus Pu?" As all disposition alternatives under investigation transfer Pu from one form (e.g. pits) to another, this question accurately reflects the nature of the Pu disposition mission.

In order to answer the question, a practical understanding of what secure storage truly means is necessary. The Spent Fuel Standard must be understood in terms of its functional components. The rational for processing Pu into any form should be based on precise security objectives not standardization of Pu storage forms.

The work presented here concludes that the focus of US disposition activities should be: identifying and swiftly moving insecure Pu into verifiable, internationally safeguarded, and trackable forms around the world. The notion of "which Pu and when" is important. The reason Pu disposition has become so urgent is that difficult economic conditions in Russia have raised questions about the control of its weapons material. Therefore, the US disposition strategy should be designed primarily to address the risk of theft of Pu in Russia today.

Alternatives that can be implemented quickly and in cooperation with Russia should receive first priority. This implies that as many obstacles to implementation should be removed as possible. Plutonium storage issues should not be intermixed with contentious Pu fuel cycle issues. They can and should be separated. The work presented here has shown that mechanisms for addressing Russia's concerns regarding Pu's energy value do exist. Such proposals should be carefully considered as they may provide valuable flexibility to US/Russian negotiations.

Flexibility is a valuable disposition asset for numerous reasons. The Pu storage matrix should allow for the option of direct disposal. It has been shown that criticality could occur in a repository under certain conditions. While engineered barriers have been proposed to address this problem, given the uncertainty, the penalty for reprocessing the Pu into a safer or perhaps more secure form in the future should be low. This would aid timely decisionmaking as the probability of a costly outcome would be reduced. Our inability to know the optimum final form for Pu should not prevent us from addressing near-term security issues.

6.7 Future Work

Continued evaluation of Pu storage forms should be pursued. The addition of off-site tracking capability appears to be valuable from a safeguards perspective. The feasibility and effectiveness of including transmission devices as an integral part of a Pu storage matrix should be investigated. The system must be able to withstand the immobilization process environment and the power source should be long-lived. Similarly, techniques for verifying the composition of an immobilized Pu matrix should be developed.

The cost savings associated with storing Pu in such a form should be evaluated. With sufficient reactivity control, Pu could be stored in more dense configurations. Storing Pu in a chemically stable, bulk matrix would reduce the risk of oxidation with exposure to air and subsequent dispersion. This may reduce the costs of installing and maintaining safety systems. Costs of safeguards could also be reduced.

For the vitrification alternative a detailed understanding of how Pu and added neutronic control elements participate in the glass network is needed. Any ternary compounds or stable complexes that form should be identified. Mechanisms for separating Pu/U from rare earth elements during and after glass reaction must continue to be evaluated. Colloid formation is a particularly interesting process and its potential impact should be evaluated under a variety of potential repository conditions.

If credible scenarios for colloid formation are identified and/or it is shown that current forms allow unacceptable quantities of REE to be separated from Pu or U, alternate matrices may be needed. A mixed ceramic/glass form may have preferable characteristics. In these matrices, controlled devitrification is allowed as the glass formulation is tailored to provide durable host phases. Fabricated glass is reheated to encourage devitrification for this matrix. Glass ceramics have been shown to incorporate various REE in durable phases. Attention to Pu devitrification may not be necessary if crystals of PuO_2 are formed as this oxide is extremely insoluble.

The use of neutron absorbers outside the immobilized matrix itself could be effective. Fabricated or mined rare earth phases could be added in a can-in-can type system or used as backfill for the waste emplacement area. Monazite ores should be explored for this purpose.

The potential impact of a repository criticality should also be assessed. The behavior of the system during and after the predicted criticality should be investigated to determine radionuclide production over time. From this information a calculation of the risk to the environment and to human health can be made.

Appendix A - Glass Compositions

TABLE 14. Lanthanide Boro-Silicate Glass(LaBS)*

Oxide	wt %
SiO_2	25.8
B_2O_3	10.4
Al_2O_3	19.04
ZrO_2	1.15
Gd_2O_3	7.61
La_2O_3	11.01
Nd_2O_3	11.37
SrO	2.22
PuO_2	11.39

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*. Composition from Dr. Henry Shaw, LLNL August 1997

TABLE 15. Alkali-Tin-Silicate Glass (ATS)*

Oxide	wt%
SiO_2	47.3
B_2O_3	13.7
Al_2O_3	2.6
ZrO_2	6.0
Gd_2O_3	3.5
Cs_2O	0.8
K_2O	5.9
Li_2O	4.6
Na_2O	10.4
TiO_2	2.3

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*. (Plodinec 1995: 235)

TABLE 16. ARM1 Composition *

Oxide	wt%
SiO_2	46.50
Al_2O_3	5.59
CaO	2.23
TiO_2	3.21
Na_2O	9.67
B_2O_3	11.3
Nd_2O_3	5.96
Li_2O	5.08
ZnO	1.46
P_2O_5	0.65
ZrO_2	1.80
BaO	0.66
MoO_3	1.67
CeO_2	1.51
Cs_2O	1.16
SrO	0.45

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*. Materials Characterization Center, Pacific Northwest Laboratory, Richland, Washington

TABLE 17. SRL165 Compositoin*

Oxide	wt%
SiO_2	68.0
B_2O_3	10.0
Li_2O	7.0
Na_2O	13.0
MgO	1.0
ZrO_2	1.0

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*. Savannah River Laboratory, Aiken, South Carolina

Appendix B - Dissolution Model

Introduction

This Appendix contains a description of the glass dissolution model used in the criticality analysis. Each calculation step is explained in detail below.

Problem Setup

DWPF Reference Waste Form parameters (Baxter 1983):

Length $L \equiv 3 \cdot m$ Radius $R_{log} := 0.3 \cdot m$ Glass density $\rho_s := 2.75 \cdot \frac{gm}{cm^3}$

Emplacement hole radius (sets the effective cross section and volume of the near-field):

$R_{hole} := 0.35 \cdot m$

Mass of the log: $M_{log} := \rho_s \cdot \pi \cdot R_{log}{}^2 \cdot L$ $M_{log} = 2.333 \cdot 10^3 \cdot kg$

Unreacted Glass Radius

Bulk Dissolution Rate of the Glass (BDR): $BDR := 0.1 \cdot \frac{gm}{m^2 \cdot day}$

First order approximation for radius of the unreacted log :

$$R(t) := if\left(R_{log} - \frac{BDR \cdot t}{\rho_s} - epsilon > 0, R_{log} - \frac{BDR \cdot t}{\rho_s} - epsilon, 0\right)$$

(IF/THEN statement is used to avoid negative values.)

$epsilon \equiv 0.0001 \cdot cm$ (epsilon needed to avoid division by 0)

Surface area of log (less the top and bottom): $A_{log}(t) := \pi \cdot 2 \cdot R(t) \cdot L$

Volume of the unreacted log: $Vol_{log}(t) := \pi \cdot R(t)^2 \cdot L$

Alteration layers occupies this volume (taking no credit for gap dilution) :

$$V(t) := L \cdot \pi \cdot \left(R_{log}{}^2 - R(t)^2\right)$$

Elemental Solubilities and Loading in Glass

Now we input the solubility limits (CL) and loadings in the glass for the elements of interest (Concentrations shown are for the Glass Control case as calculated by EQ3/6.)

BORON

Boron solubility is more than 5000 ppm according to EQ3

$CL_b := 5000 \cdot \frac{gm}{10^6 \cdot cm^3} \quad CL_b = 5 \cdot 10^{-3} \cdot \frac{gm}{cm^3}$

Boron loading (g B/g glass): $fo_b := 0.113 \cdot \left(\frac{2 \cdot 10.81}{2 \cdot 10.81 + 3 \cdot 16} \right) \quad fo_b = 0.035$

PLUTONIUM

$CL_{pu} := \left(10^{-14.2194} \right) \cdot \frac{mole}{liter} \cdot 239 \cdot \frac{gm}{mole} \qquad CL_{pu} = 1.442 \cdot 10^{-15} \cdot \frac{gm}{cm^3}$ phase: PuO2

Plutonium loading (g PuO2/g glass) $PuO_2 \equiv 0.0045$

loading (g Pu/g glass): $fo_{pu} := PuO_2 \cdot \frac{239}{239 + 2 \cdot 16} \qquad fo_{pu} = 3.969 \cdot 10^{-3}$

WGPu Isotopics (wt%):

$Pu_{238} := 0.00012 \quad Pu_{239} := 0.939 \quad Pu_{240} := 0.0581 \quad Pu_{241} := 0.0023 \quad Pu_{242} := 0.00022$

EUROPIUM

$CL_{eu} := \left(10^{-4.8165} \right) \cdot \frac{mole}{liter} \cdot 151 \cdot \frac{gm}{mole} \qquad CL_{eu} = 2.304 \cdot 10^{-6} \cdot \frac{gm}{cm^3}$ phase: Eu(OH)3

Mole ration Eu/Pu: $Ratio_{mole} := \frac{1}{8} \qquad fo_{eu} := fo_{pu} \cdot Ratio_{mole} \cdot \frac{151.96}{239}$

Europium loading (g Eu/g glass): $fo_{eu} = 3.154 \cdot 10^{-4}$

URANIUM

$CL_u := \left(10^{-9.5857}\right) \cdot \frac{mole}{liter} \cdot 235 \cdot \frac{gm}{mole} \qquad CL_u = 6.101 \cdot 10^{-11} \cdot \frac{gm}{cm^3}$

phase: haiweeite Ca(UO2)2(Si2O5)3:5H2O

The loading of uranium will depend on the decay of Pu-239. The following section provides the input for relevant decay processes.

Radioactive Decay

Decay parameters

$$\lambda_{238} := \frac{\ln(2)}{87.8 \cdot yr} \qquad \lambda_{239} := \frac{\ln(2)}{24100 \cdot yr} \qquad \lambda_{240} := \frac{\ln(2)}{6.56 \cdot 10^3 \cdot yr} \qquad \lambda_{241} := \frac{\ln(2)}{14.40 \cdot yr}$$

$$\lambda_{242} := \frac{\ln(2)}{432.70 \cdot yr} \qquad \lambda_{235} := \frac{\ln(2)}{7.04 \cdot 10^8 \cdot yr}$$

(239 and 240 are the only Pu isotopes that will remain after a few thousand yrs)

Isotopic loading per g glass as a function of time

$$P_{238}(t) := Pu_{238} \cdot e^{-\lambda_{238} \cdot t} \cdot fo_{pu} \qquad P_{241}(t) := Pu_{241} \cdot e^{-\lambda_{241} \cdot t} \cdot fo_{pu}$$

$$P_{239}(t) := Pu_{239} \cdot e^{-\lambda_{239} \cdot t} \cdot fo_{pu} \qquad P_{242}(t) := Pu_{242} \cdot e^{-\lambda_{242} \cdot t} \cdot fo_{pu}$$

$$P_{240}(t) := Pu_{240} \cdot e^{-\lambda_{240} \cdot t} \cdot fo_{pu} \qquad U_{235}(t) := \frac{Pu_{239} \cdot fo_{pu} \cdot \lambda_{239}}{\lambda_{235} - \lambda_{239}} \cdot \frac{235}{239} \cdot \left(e^{-\lambda_{239} \cdot t} - e^{-\lambda_{235} \cdot t}\right)$$

$f_{pu}(t) := P_{239}(t) + P_{240}(t)$ <--- approximation as we are mainly past a few thousand yrs

$Pn_{239}(t) := \frac{P_{239}(t)}{f_{pu}(t)}$ <--- normalize Pu concentrations

$Pn_{240}(t) := \frac{P_{240}(t)}{f_{pu}(t)}$

Groundwater Flow

This is the groundwater flux through the repository (volume per unit area per unit time):

$v_w := \frac{10 \cdot mm^3}{yr \cdot mm^2}$ $v_w = 0.01 \cdot \frac{m}{yr}$ (today's flow is 0.001 m/yr)

Cross sectional area of near-field (taking credit for gap): $XArea := 2 \cdot R_{log} \cdot L$

Volumetric flow rate through the near-field: $FR := XArea \cdot v_w$

Alteration Layer Composition Over Time

The concentration of relevant isotopes in the reacted glass region was calculated via mass balance relations. The BDR determined the rate of addition of glass elements to the growing volume of alteration layers. Equilibrium of the glass elements with groundwater was then assumed, fixing solution concentrations. The volumetric groundwater flow determined the rate of element removal from the alteration layers. Decay was accounted for in both the glass and the alteration layers.

Vector solution for coupled differential equations

D(t,N) is a vector of 1st order differential equations. Each vector element describes the change of mass of a radionuclide in the alteration layer per unit time. N is a vector of the initial conditions for Pu-239, Pu-240 and U-235 which were based on the initial loading in the glass.

$$N := \begin{bmatrix} P_{239}(0) \cdot \rho_s \cdot V(0) \\ P_{240}(0) \cdot \rho_s \cdot V(0) \\ 0 \end{bmatrix} \text{ <---Initial conditions for Ni variables (Pu-239, Pu-240 and U-235)}$$

$$D(t,N) := \begin{bmatrix} BDR \cdot 2 \cdot \pi \cdot R(t) \cdot L \cdot P_{239}(t) - v_w \cdot XArea \cdot CL_{pu} \cdot Pn_{239}(t) - \lambda_{239} \cdot N_0 \\ BDR \cdot 2 \cdot \pi \cdot R(t) \cdot L \cdot P_{240}(t) - v_w \cdot XArea \cdot CL_{pu} \cdot Pn_{240}(t) - \lambda_{240} \cdot N_1 \\ BDR \cdot 2 \cdot \pi \cdot R(t) \cdot L \cdot U_{235}(t) - v_w \cdot XArea \cdot CL_u - \lambda_{235} \cdot N_2 + \lambda_{239} \cdot N_0 \cdot \frac{235}{239} \end{bmatrix} \text{ <-- Rate Equations}$$

(The variables "Ni" in D are elements of the vector N.)

The differential equations were solved via a Runge-Kutta technique (the *rkfixed* function in Mathcad PLUS). For this calculation a time period of interest is needed as well as a fixed time step for calculating solutions.

Time period of interest in yrs: $T := 2.5 \cdot 10^4$

Step size in yrs: $S := 0.5 \cdot 10^3$

Z is this matrix of solutions: $Z := \mathrm{rkfixed}\left(N, 0, T, \frac{T}{S}, D\right)$

The result of the calculation is a matrix (Z) of solutions to D giving the mass of the individu radionuclides in the alteration layers at various times in the future. A similar calculation is performed for the stable elements Eu and B. This mass data can then be combined with the calculated volume of the alteration layers as a function of time to give the concentration of elements in the alteration layers.

Unreacted glass compositions were calculated using the decay parameters specified above. Combined with the alteration layer data, and the surrounding rock composition, this provide complete model of the near-field environment.

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