Radioactive Waste from Transmutation of Technetium: a Model for Anticipating Characteristics of High Level Waste from Transmutation

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ABSTRACT

At this early stage in the conceptualization of fuel treatment and radioisotope transmutation for the disposition of nuclear wastes, it is possible to anticipate some characteristics of the waste stream resulting from the deployment of advanced technologies. Fission products and actinides cannot be completely destroyed by transmutation even with continuous purification and recycle. This is demonstrated for technetium in this analysis, but is true for all radioisotopes. Also, some of the reaction products are themselves long-lived radioactive isotopes. The purification and recycle steps produce nuclear wastes that must be planned for geologic disposal.

Five radioisotopes have been identified to be produced in abundance by transmutation of technetium using fast neutrons. Four of these isotopes may be more benign than the original technetium-99 because of their longer half lives. However, one isotope, molybdenum-93 with a half life of four thousand years, may be troublesome. All of the isotopes arising from the transmutation process that end up in high level waste must be examined in terms of their behavior in geologic disposal.

In selecting goals for chemical separations, the technologists must consider the entire cycle of separation and transmutation before applying the performance expected in a single separation to implications concerning a repository. A separation efficiency of 0.95 can translate into the disposal of as much as 30 to 60 percent of the technetium in the repository if down stream losses are not controlled. In this case, the treatment may have little impact on anticipated off site radiation from technetium. The destruction of technetium through continuous recycle requires the cost of increased neutron dose and increased space in reactors that must be considered in design of fuel treatment systems.

INTRODUCTION

The purpose of this analysis is to anticipate the types of radioactive waste that would result from the transmutation of technetium. Some of these wastes are directed to geologic disposal. The analysis for technetium is intended to be a model of the considerations that need to be made to deduce the characteristics of high level waste from any radioisotope that undergoes transmutation.

Transmutation schemes have been proposed using fast-spectrum reactors, light water reactors, and sub-critical reactors. Each of these reactors has neutrons in both the fast spectrum and in the thermal spectrum. Therefore, this analysis considers transmutation

by fast and thermal neutrons. Transmutation in an operating reactor is expected to be a combination of the results from both neutron spectra. The Global Nuclear Energy Partnership (GNEP) of the Department of Energy may find that the fast-spectrum reactors are the most favorable for transmutation. This will certainly be the case for higher atomic number actinides (Np, Am, Cm) that can only be consumed in fast-spectrum burner reactors. Additionally, technetium and other fission products are elements with isotopes that can be transmuted with thermal neutrons. So, wastes derived from the transmutation of technetium using both fast and thermal-spectrum reactors will be considered in this analysis.

This analysis will concentrate on technetium. The steps in the analysis conducted here are applicable to other elements such as iodine that are candidates for transmutation. Some waste elements, such as cesium, have both stable and radioactive isotopes and are not amenable to transmutation by either fast or thermal neutrons.

CHEMICAL PERFORMANCE

The research program of GNEP is examining chemical separation processes for both spent nuclear fuel and transmutation targets. The program has set process efficiency goals to be the removal of 99.9 percent of the transuranic isotopes and 95 percent of the technetium and iodine from the high level waste. This could lead to a 20-fold decrease in off-site dose reduction from these elements provided that the separated radioisotopes can be completely transmuted to other isotopes that do not require disposal as radioactive waste. [1]

One goal of the laboratory demonstration conducted at Argonne National Laboratory (ANL) [1] was to recover greater than 95 percent of the technetium. Because no specific mass balance is given in the reference for the laboratory demonstration, this analysis postulates that 95 percent of the technetium can be recovered for transmutation by the UREX process. This is consistent with the following analysis that indicates that a significant fraction (estimated to be at least 5 percent) of the technetium may be lost to the uranium and plutonium products of the separation.

Not accounted for in the ANL reference is that, generally, 20 percent of the technetium in spent nuclear fuel exists as insoluble metal and insoluble TcO_2 in spent nuclear fuel [2]. Based on experience with the UREX process, the insoluble metal and TcO_2 do not enter the aqueous solution and become part of the high level waste inventory for geologic disposal. However, for purposes of this calculation, we begin with the inventory of aqueous technetium and assume 95% separation efficiency. It should be considered that, based on the referenced experiment [1], the goal of 95% separation efficiency of the soluble technetium appears feasible.

A mass balance of technetium based on experience with the UREX process [1] regarding the separation of technetium from spent nuclear fuel is summarized in Table I.

Table I. Technetium Recovery Observed in the Lab Scale Demonstration for the UREX+2 Process Using Spent Fuel

Technetium Component	Technetium (percent of total technetium)
Insoluble Component from Spent Nuclear Fuel	Unspecified
Detected in the Np/Pu strip	0.35*
Detected in the uranium product	12.9*
Retained on the ion exchange column for subsequent recovery	86.7**

* Calculated from the data given in Table I of reference [1] using fuel with 4.4 % burnup and a concentration of 0.13 atomic percent technetium in the SNF.
** Calculated assuming that all technetium entered into solution and that 100 percent of the technetium will be recovered from the ion exchange column.

The fractions given in the table were calculated using data (weight percent cation in separation products) from Table I of reference [1]. No mass balance for technetium is provided in the reference. So, the total mass of technetium in the SNF was calculated using a 4.4 percent burnup of the SNF with a yield of 0.13 weight percent technetium in the fuel. The calculation indicates that a significant fraction of the technetium is lost to the plutonium and uranium products and will not be recovered for transmutation. This is consistent with the recovery of the technetium being no higher than 95 percent, and with the conclusion of the reference [1] that 95 percent of the technetium can be recovered by the UREX process. For the purposes of this analysis, we postulate that each chemical separation for technetium recovery will yield 95 percent of the technetium.

BURNER – TRANSMUTATION PROCESS

Wastes derived from transmutation by both thermal and fast-spectrum reactors will be considered in this analysis.

Transmutation in Fast Spectrum Reactors

For transmutation in a fast neutron spectrum, neutrons impact the nucleus and eject one or more nucleons (proton or neutron) from direct transfer of kinetic energy from the incident neutron. These nucleons can have kinetic energies up to the energy to the ejected nucleons. Additionally, evaporation neutrons are emitted from de-excitation of the target nucleus. So, the spallation reactions produce a variety of isotopes, some of which may be radioactive with very long half lives.

Spallation with technetium-99 is represented in the following reaction:

$$\text{Tc-99} + n \rightarrow \text{X-}(99\text{-}\nu) + \nu(n,p)$$

Where X is the chemical symbol of the product isotope that is dependent on the number of protons remaining in the nucleus, and ν is the number of nucleons, represented by

(n,p), ejected from the technetium nucleus. The number of nucleons ejected from the nucleus, ν, can be an integer from 1 up through 30 for a heavy isotope such as iodine-129 and an incident nucleon of up to 1 Gev energy. Additionally, many of the ejected nucleons can produce other spallation reactions leading to a cascade of reactions, each with decreasing energy of the incident particle.

To gain an estimate of the type of high level radioactive waste that may come from transmutation of isotopes by fast spectrum reactors, we modeled spallation reactions in simple terms. Fast neutrons from fission (with energies of about 1 Mev) produce spallation reactions that eject fewer than 30 nucleons. We chose to model the spallation reactions as emitting from 1 to 6 nucleons per reaction. Moreover, many of the ejected nucleons are not capable of producing spallation reactions; so, a cascade of reactions is less prevalent than for more energetic incident particles. In this estimate, we chose to consider the single reaction without subsequent reactions.

Table II presents the probability of the formation of specific isotopes by the spallation of technetium-99. The probabilities were calculated by statistically modeling the spallation interaction. The analysis used the probabilities for ejection of nucleons as follows [1 : 0.35; 2:0.25; 3:0.15; 4: 0.11; 5:0.09; 6:0.01], where the first number of each pair is the number of nucleons ejected and the second number is the probability for this reaction to occur for each neutron incident on a target nucleus. These probabilities represent an estimate based on experience with spallation reactions. For a more quantitative analysis, the probabilities could be derived from experimental data and would be expected to be dependent on the energy of the incident particle. The experimental data would be affected by secondary reactions that would make the experimental determination of these probabilities more difficult. The analysis performed here, additionally, uses the probability of ejection of a proton to be 0.4343 and the ejection of a neutron to be 0.5656. These are the abundances of protons and neutrons in the technetium-99 nucleus.

Table II. Probability of Formation of Specific Isotopes by the Spallation of Technetium-99 with Fast Neutrons

Atomic Weight	98	97	96	95	94	93	92
Element							
Technetium	0.1980	0.0800	0.0271	0.0113	0.0052	0.0013	0.0002
Molybdenum	0.1520	0.1228	0.0625	0.0346	0.0200	0.0060	0.0010
Niobium		0.0472	0.0480	0.0398	0.0307	0.0116	0.0023
Zirconium			0.0123	0.0204	0.0236	0.0119	0.0029
Yttrium				0.0039	0.0091	0.0068	0.0023
Strontium					0.0014	0.0021	0.0010
Rubidium						0.0003	0.0003
Krypton							0.0000

Table II shows that the probability of forming a specific isotopes is greatest for isotopes one or two mass units below techentium-99. At the lower portion of the table, the probability decreases with decreasing mass and element numbers of the resulting isotope.

Many of the resulting isotopes are radioactive and decay quickly to stable isotopes or long lived radioactive isotopes. As identified in this analysis, the stable isotopes of molybdenum are a major product of the transmutation of technetium by spallation.

Some of the resulting isotopes decay into the long-lived radioisotopes shown in Table III. The probabilities shown in Table III are the sum of the probabilities from Table II that lead to that isotope. For example, the production of molybdenum-93 shown in Table III (of 0.0176) results from the production of molybdenium-93 (at a probability of 0.0060) plus the production of niobium-93 (at a probability of 0.0116), which decays to molybdenum-93. The production of zirconium-93 in Table III includes a component from yttrium-93, which decays to zirconium-93.

Table III. Radioactive Products Resulting from the Transmutation of Technetium-99 and the Probability of Acquiring that Product for Each Spallation Reaction

Radioactive Product	Half Life (years)	Probability of Production
Technetium-98	4.20E+06	0.1980
Technetium-97	2.60E+06	0.0800
Molybdenum-93	4.00E+03	0.0176
Zirconium-93	1.50E+06	0.0187
Niobium-92	3.47E+06	0.0088
Total Probability		0.3231

This calculation shows that a significant fraction of the spallation reactions (32.3 percent) remains in the technetium target as long lived radioactive isotopes. Most of this radioactivity is in the form of technetium isotopes (27.8 percent of the 32.3 percent) and will be recycled with technetium-99 during reprocessing of the spent target. The other 5% of the long lived radioactive isotopes produced during technetium transmutation will be diverted to the nuclear waste stream during the reprocessing of the technetium target.

Reprocessing of the irradiated technetium targets is required to prevent the build up of additional long-lived radioactive isotopes from spallation reactions on stable isotopes. This effect is illustrated in Figure 1 which shows no decrease in long-lived radioactivity with continued neutron dose (after a dose of ~6.00E+23 neutrons/cm^2). The model used to develop Figure 1 is based on an ideal target in which none of the technetium atoms are shielded (thin target) and 100 percent of the incident neutrons produce transmutations (thick target). Actual targets will be less than ideal.

Figure 1 is derived considering that the irradiation is designed to destroy molecular quantities of long-lived radioisotopes. In practice, the irradiation may be designed to minimize another parameter, such as calculated dose to persons after geologic disposal. Many of the spallation products may have lower importance than technetium-99 due to longer half lives, lower energy emissions (lower dose conversion factors, or DCFs) and perhaps, different release and transport characteristics (solubility and retardation coefficients). This may permit longer irradiations solely to destroy technetium-99 before reprocessing.

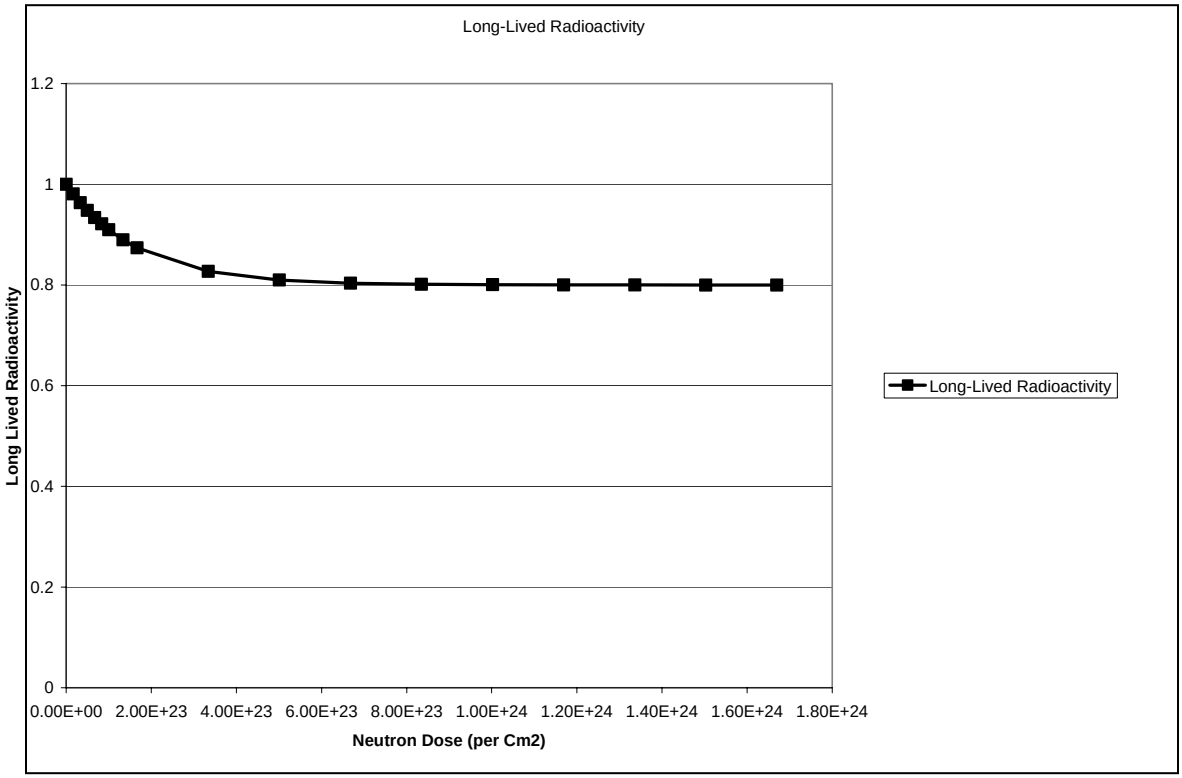

Figure 1. Decrease in long lived radioactivity with increasing neutron dose. The slowing of the decrease in radioactivity indicates that the technetium targets must be reprocessed, in the case shown, after a neutron dose of 4.0E+23 neutrons per cm^2.

The curve in Figure 1 was calculated using the cross section for the spallation of technetium-99 of 1.2 barns (1.2E-24 cm^2) and a buildup of radioactivity from reaction of the stable products. The curve indicates that the target should be reprocessed after a neutron dose of 4.0E+23 neutrons per cm^2 are incident on the target. Equilibrium between the radioactivity destroyed and the radioactivity created would occur at a neutron dose of 5.7E23 per cm^2 if the production of radioactivity from the stable isotopes (most notably the molybdenum isotopes) is the same as that for technetium-99.

Reprocessing the irradiated technetium targets 4 times would destroy 40 percent of the technetium and leave a waste product containing the activation products given in Table IV. The waste would have the components shown in Table IV.

Table IV. Waste Components from the Transmutation of Technetium by Irradiation with Fast Neutrons

Waste Component	Fraction of Original Tc Inventory (atom)
Fission product Tc-99 loss from initial processing	0.05
Tc-99 with Tc-98 and Tc-97 from losses during target reprocessing	0.12
Activation products (Mo-93, Zr-93, Nb-92) extracted during target reprocessing	0.03
Technetium and other activation products at the end of transmutation	0.41
Total inventory of radioactive isotopes destined to geologic disposal	0.60

Metal targets may be processed using pyrometallurgical techniques rather than portions of the UREX+ process. Alternatively, the research program of GNEP has explored the possibility of processing technetium by fluoride volatility separations. Technetium would have to be separated from fluorides of molybdenum, zirconium and niobium [3]. Technetium fluoride (TcF_5) has a boiling point of 480 degrees K and is very close to the boiling point of the major stable element from which it needs to be separated, molybdenum. (MoF_5 has a boiling point of 486 degrees K.) Efficient separations, therefore, would not be expected. Without having a demonstrated pyrometallurgical or volatilization process for the extraction of technetium, the analysis considered the process losses to be at least the same as those reported for the UREX+ process. So, the process loss of 5 percent was considered in assembling the data in Table IV.

Table IV shows that a substantial portion of the radioactivity in original technetium inventory could be destined for geologic disposal after transmutation by fast neutrons. This analysis indicates that 60 atom percent of the original technetium will be disposed as long lived isotopes of technetium, molybdenum, zirconium or niobium isotopes.

This transmutation process may produce radionuclides with little detriment to the repository. Four of the isotopes produced by transmutation and not significantly present in spent nuclear fuel may be more benign than the original technetium-99 because of their longer half lives (of 1.5 to 4.2 million years, compared to technetium-99 with a 213 thousand year half life). This is so because with their greater half lives, their specific activities are below that of the initial technetium-99. However, one isotope, molybdenum-93, has a half life of four thousand years that allows it to persist for a long time and provides a specific activity considerably greater than the original technetium-99. This isotope from the spallation of technetium may be the most troublesome. All of the isotopes arising from the transmutation process and ending in high level waste must be examined in terms of their behavior in geologic disposal, and their subsequent radiotoxicity.

An alternative strategy to the four cycles of irradiation of technetium is to continuously recycle the technetium by adding additional fission product technetium to the irradiated technetium that is separated from targets. This process is much more expensive in terms of the required neutron dose for transmutation but destroys more of the technetium than anticipated for four target recycles. Using this strategy, only 29 percent of the technetium, including long-lived radioactive transmutation products, is disposed in waste. However, recycling continues with some of the original technetium (1 percent) still present in the twentieth cycle. This strategy utilizes 7 times more neutrons than the 4 cycle approach. This requirement for additional neutrons may be prohibitive. A burner reactor with a neutron flux of 9.0E+15 neutrons per cm^2 per second at the technetium target will require 2 years for each irradiation. (The Petten High Flux Reactor exhibits 1.0E+15 neutrons per cm^2 per second at its core and would require 18 years for each irradiation. [5]) This means that, in an equilibrium case, burner reactors will host, at any one time, the inventory of technetium from 140 years of power production.

Transmutation in Thermal Spectrum Reactors

Technetium-99 has a relatively large cross section for adsorption of thermal neutrons (measured to be 22.9 barns [4] normalized at 0.0253 eV with significant resonance adsorption at 5.6 and 20.3 eV energies) and is not accompanied by other technetium isotopes in spent nuclear fuel. The transmutation process with thermal neutrons is one in which the technetium (Tc-99, possibly in the form of a metal target) is bombarded with neutrons to produce the short lived Tc-100 (half life = 16 seconds) which decays by beta decay to ruthenium (Ru-100). One disadvantage of this process is the need for a pure technetium target. Other fission products in the target will increase the activity of the irradiated target. Small traces of the minor actinides (such as americium and curium) will undergo fission to form fission products. Subsequently, the resultant contaminated target would have to be processed for all fission products, not just the products from the destruction of technetium.

The fraction of technetium undergoing transmutation in a thermal-spectrum reactor can proceed further than in a fast-spectrum reactor because of the slower build-up of long-lived reaction products. Transmutation in thermal spectrum reactors is likely to require reprocessing to avoid the build up of isotopes heavier than atomic mass 100, or to physically reconstitute the target. Given this need, process losses will accumulate in the waste stream comparable to that described for transmutation with fast neutrons. A detailed analysis, similar to that performed for transmutation with fast neutrons, can give an indication of the type and quantity of waste destined for geologic disposal from transmutation with thermal neutrons.

Consider that the transmutation in a thermal spectrum can proceed to 50 percent destruction of the technetium; then the fraction of technetium disposed in a geologic repository is calculated to be 9.7 percent. This calculation uses a separation efficiency of 0.95 and postulates that technetium is continuously recycled until it is destroyed or ends up in waste because of process inefficiency. (As in the fast reactor analysis, this

calculation does not specify that the 20 percent of technetium in spent nuclear fuel that may be undissolved also goes to high level waste.)

The destruction of 50 percent of the technetium in a target is high compared to that realized experimentally. For example, technetium targets irradiated for 193 effective full power days in the Petten High Flux Reactor transmuted about 6 percent of the technetium to ruthenium [5]. This reactor would require 4.4 years of continuous operation to effect 50 percent transmutation of technetium. In this reactor, non thermal neutrons comprise as much as 80 percent of the neutron flux so that significant spallation reactions may accompany the neutron adsorption reactions. This would imply that some of the radioisotopes predicted for transmutation by fast neutrons and exhibited in Table III may be present in the irradiated technetium targets. These targets were not examined for spallation products.

Given that transmutation can be performed with well-thermalized neutrons, the resulting waste stream will have no major long-lived reaction products if the targets are fabricated with extremely pure technetium. Contamination with actinides or other fission products will add to the long-lived radioactive products in the waste. Also, the loss of insoluble technetium during any phase of the operation will increase the quantity of technetium destined to geologic disposal. For example, the loss of insoluble technetium during the initial extraction could direct an additional 20 percent of the total inventory of technetium to geologic disposal.

INVENTORY OF TECHNETIUM

Technetium accumulates in nuclear fuel to a level of 0.11 percent with a burnup of 60 GWD/MTHM. The production rate of 26.6 kg/GW(e)·a is given in reference [6]. Therefore, 100 kg of spent nuclear fuel with this burnup will contain 0.11 kg of technetium. The annual production of technetium (in 2000 MTHM fuel at a burnup of 60 GWD/MTHM) is 2.48E+3 kg.

Technetium may be fabricated into targets as a metal. The annual yield of technetium (in 2000 MTHM fuel at a burnup of 60 GWD/MTHM) will produce 314 targets consisting of 4.06 meters long metal rods of 0.75 cm diameter (suitable for use in a pressurized water reactor). The total number of targets being irradiated will depend on the required irradiation time and the transmutation strategy (finite number of cycles or continuous recycle).[1]

DISCUSSION OF RESULTS

Even at this early stage in GNEP and AFCI programs, it is possible to anticipate characteristics of the waste stream resulting from the deployment of advanced technologies. The following results, demonstrated in this note, are characteristics of

[1] The inventories given here are referenced to an initial metric ton of heavy metal indicated by the symbol MTHM

advanced fuel treatment and transmutation processes now being considered in domestic and international research programs.

Fission products and actinides cannot be completely destroyed by transmutation even with continuous purification and recycle because reactions with stable products result in radioactive isotopes with long half lives. This is demonstrated for technetium in this analysis, but is true for all radioisotopes. Also, some of the reaction products are themselves long-lived radioactive isotopes. The chemical purification and nuclear recycling necessary to destroy radioactivity produce nuclear wastes that must be considered for geologic disposal.

Transmutation of technetium by fast neutrons produces radioactive wastes that previously have not been considered in the geologic disposal of spent nuclear fuel. Five radioisotopes have been identified to be produced in abundance by transmutation of technetium using fast neutrons. Four of these isotopes may be more benign than the original technetium-99 because of their longer half lives (of 1.5 to 4.2 million years, compared to technetium-99 at 213 thousand years). However, one isotope, molybdenum-93 with a half life of 4 thousand years may be troublesome. All of the isotopes arising from the transmutation process and ending in high level waste must be examined in terms of their behavior in geologic disposal.

In selecting goals for chemical separations, the technologists must consider the entire cycle of separation and transmutation before applying the performance expected in a single separation to implications concerning a repository. A separation efficiency of 0.95 can translate into the geologic disposal of 30 to 60 percent of the radioactivity in the initial inventory of technetium. This will produce as little as a 40 percent decrease in radioactivity at the repository and may have little impact on anticipated off site radiation from technetium. The improved destruction of technetium through continuous recycle comes at a price in terms of required increased neutron dose and increased space in reactors that must be considered in design of fuel treatment systems.

Fast-spectrum burner reactors have the advantage of consuming the higher atomic number actinides (Np, Am, Cm), therefore destroying some heat producers and long-lived radioactive isotopes in nuclear waste. However, the fast-spectrum burner reactors have limited advantage over thermal spectrum reactors in the transmutation of fission products such as technetium and iodine. The choice may be made to transmute fission products in thermal reactors and dedicate burner reactors to the destruction of the heavy actinide elements.

Experimental demonstrations of separations efficiency need to track rigorously the materials that are destined for geologic disposal. Accurate determinations of mass balance for all radioisotopes need to be an integral part of future experimental demonstrations.

CONCLUSION

Several factors determine the quantity of high level waste resulting from the transmutation of a radioisotope. The factors include the efficiency with which the element is separated from the fuel and the fraction of the element that can be consumed in an irradiation of the target. Also, the factors include the purity with which the element can be prepared in the target and the propensity of the destroyed atom to form other long-lived radionuclides. Estimates of the constituents of high level waste suggest that from 30 to 60 percent of the radioactivity of technetium in spent nuclear fuel can end up in high level waste after undergoing transmutation.

Transmutation of technetium in a fast spectrum reactor will reduce the quantity of technetium in long-lived radioactive waste in geological disposal, but will introduce other radioactive isotopes that must be considered in repository performance. The radioactivity of the high level nuclear waste resulting from the transmutation of radioisotopes can be different from that experienced in spent nuclear fuel. The geologic repository can expect to receive long-lived radioisotopes such as molybdenum-93, zirconium-93 and niobium-92 from transmutation of technetium-99 by fast-spectrum neutrons. Introducing these radioisotopes to the repository will require novel analysis and possible mitigation to control far field radiation dose.

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