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LONG-TERM EFFECTS OF NEUTRON ABSORBER AND FUEL MATRIX CORROSION ON CRITICALITY

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ABSTRACT

Proposed waste package designs will require the addition of neutron absorbing material to prevent the possibility of a sustained chain reaction occurring in the fuel in the event of water intrusion. Due to the low corrosion rates of the fuel matrix and the zircaloy cladding, there is a possibility that the neutron absorbing material will corrode and leak from the waste container long before the subsequent release of fuel matrix material.

An analysis of the release of fuel matrix and neutron absorber material based on a probabilistic model was conducted and the results were used to prepare input to KENO-V, an neutron criticality code. The results demonstrate that, in the presence of water, the computed values of k_{eff} exceeded the maximum of 0.95 for an extended period of time.

I. INTRODUCTION

Nuclear criticality is a situation that must be avoided in any proposed waste package intended for the long term storage of high-level nuclear waste. 10 CFR 60.131 requires that the effective neutron multiplication factor must show at least a 5% margin after allowance for calculation and code uncertainty. This must be ensured unless "two unlikely, independent, and concurrent or sequential changes have occurred in the conditions essential to nuclear criticality safety." Previous studies have shown that, in the presence of water, critical conditions can exist in spent fuel waste canisters at relatively low values of initial fuel enrichment[1,2], even when the effect of fuel burnup is included.[3]

In current waste package designs, it is assumed that low values of k_{eff} will always be ensured by adding a suitable neutron absorber, boron, in an aluminum or steel matrix. Unfortunately, significant changes in criticality will take place over time if the boron absorber material is removed from the waste package by corrosion and leaching at a rate faster than that of the fuel matrix.

In this study, a probabilistic model was used to predict the breaching of the waste package canister, resaturation of the interior, and dissolution of an aluminum-boron or steel-boron absorber as well as the zircaloy clad uranium ceramic fuel pellets. For a typical waste package design, the results indicate that differential removal of poison and fuel will lead to calculated supercritical conditions in the presence of water.

II. DESCRIPTION

A. Probabilistic Approach

The release of radionuclides and poison from a spent fuel canister is influenced by many variables including the mean lifetimes of the canister wall and the cladding, release times for poison and fuel matrix, and resaturation times. A reasonable approach to the combination of these effects to predict the loss rate of fuel and poisons from the waste package was presented by Wilson[4] in an analysis employing probability distribution functions to represent canister failure, cladding failure, and leaching rates. By assuming appropriate values for the corrosion rate of aluminum-boron alloy and uranium fuel, the release times for these two materials were computed. For example, the probability that a single container may fail during the

time interval of t_c to dt_c with a mean container lifetime of τ_c can be represented by an exponential distribution as shown in equation 1.

$$P = \frac{1}{\tau_c} e^{-t_c/\tau_c} dt_c \qquad (1)$$

Other assumed and computed values are listed in Table 1. The analysis was repeated by using a 304L-boron alloy as the neutron absorber.

B. Corrosion of the Fuel Matrix

Wilson and Burton[5] documented experimental data that showed release rates of actinides from spent fuel in J-13 water. The results agreed favorably with results from the EQ3/6 computer program and predictions were included for the dissolution of 33,000 MWD/MTU fuel exposed to a water flow of 20 l/yr. Based on the 1,000 year inventory of radionuclides, the release rate of uranium amounted to 0.0184% per year and 0.0123% for plutonium. The data was based on experiments conducted over a 6 month period.

Wilson[4] indicated a steady state leach rate of 0.003 mol/m^2-yr for uranium fuel.

C. Corrosion of the Cladding Material

Wilson computed corrosion rates for zircaloy cladding from data by Rothman[6] based on the rate of oxidation expected under repository thermal conditions. The 600 μm thickness of the cladding decreased very little as the calculations showed an oxidation depth of only 0.03 μm after 10,000 years assuming a container breach at 300 years. The oxidation rate was very temperature dependent and a container breach at 1,000 years decreased the 10,000 year oxidation loss to 0.006 μm. These values gave zircaloy cladding failure times of 9 x 10^6 years. Wilson suggested a conservative cladding failure time of 10,000 years to due oxidation. It was noted that swelling of the uranium fuel pellets from oxidation could cause early cladding failure. This was not expected to be an important factor for at least 10,000 years.

D. Corrosion of Al/B Neutron Absorber

Aluminum/Boron alloys have been proposed as potential neutron absorbing material in the multipurpose containers due to their light weight and strength.

Brubacker and Phipps[7] included plots of material loss from various corrosion-resistant aluminum alloys in heated water. Converted into units of (μm/yr), alloy A288 containing 1% Ni in refreshed water at 533 K experienced a steady loss of material at a rate of 39.2 to 58.1 μm/yr. Alloy X8001 with 1% Ni also in water at 533 K lost 33.8 μm/yr. Finally, the aqueous corrosion of alloy A288 (aluminum with 1% Ni, 0.5% Fe, and 0.1% Ti) showed a maximum loss rate of 21.4 μm/yr when immersed in water at 792 K and 10.3 μm/yr for immersion at 623 K.

Due to the lack of corrosion data for aluminum/boron alloys, alternative data was sought for composites of the two materials. Pohlman[8] noted that the addition of boron increased the corrosion rate of aluminum-boron composites and a regression fit of the available data yields:

$$R(\mu m/yr) = 22.665 + 1.605\,(\%\,Boron) \qquad (2)$$

This data was obtained by placing samples in a 3.5% NaCl solution at 294 K. In spite of this more corrosive environment, the minimum corrosion rate of 22.665 μm/yr fell within the range of data discussed earlier for corrosion-resistant aluminum alloys in heated water.

E. Corrosion of Steel/Boron Poison Material

Beavers, et al[9] measured the corrosion rates of steels in aerated simulated J-13 well water at 363 K. After a period of 13,000 hours, the electrochemical measurements showed corrosion rates of 1 to 4 μm/yr for alloy 825 and 2 - 3.4 μm/yr for 304L stainless steel. This data was accumulated over a period of 13,000 hours. Actual measurements of material loss indicated corrosion rates of less than 0.005 μm/yr for 304L at the end of this period of time.

Wilson suggested rates of 0.15 μm/yr in J-13 for candidate steels for nuclear waste containers. In the absence of accurate data for borated steels, the corrosion rate of 304L stainless steel was chosen for the criticality calculations.

F. Calculation of Criticality

Based on estimated times for the breaching and subsequent flooding of the waste package, cladding failure, and corrosion rates of the fuel matrix and neutron absorbing material, a computer program was written using the probabilistic approach suggested by Wilson. The program predicted the fraction of fuel matrix material and neutron absorber remaining as functions of time.

Based on these fractions, number densities were calculated for use in the nuclear criticality Monte Carlo computer code KENO V. The code predicted the value of the effective neutron multiplication factor, k_{eff}. When this value exceeds 1.0, the generation rate of neutrons is increasing. This supercritical condition must be avoided in spent fuel.

The simulation used a 4 m long, 1.38 m diameter canister containing 21 PWR fuel assemblies, placed horizontally in the drift of a geologic repository. The package was completely surrounded by saturated tuff in this simulation. To decrease the initial value of k_{eff} to 0.95 (assuming flooded conditions), 10% boron was added to both the aluminum-boron and steel-boron alloys.

In all runs, it was assumed that water was present in the container after the resaturation period and that the flowrate was sufficient to remove surface corrosion products from the fuel and absorber material.

III. RESULTS

The results showed that calculated values of k_{eff} exceed 1.0 at some time after the neutron absorber began to corrode and leave the container, but before the fuel matrix has begun to corrode. During these "supercritical" events, it is expected that the spent fuel will behave in a fashion similar to the natural fuel studied at the Oklo site in West Gabon, Africa.[3] This event occurred over 2 billion years ago when natural uranium became critical in the presence of water. In this "natural reactor", an equilibrium situation was reached where evaporation caused by fission heat balanced the need for water is a moderator to continue the fission process. The reactor is reported to have operated for several thousand years and released heat and radioactive fission products, including Pu^{239}.

A. Unirradiated Fuel, Aluminum/Boron Absorber

As shown in figure 1, rapid release of Al-B occurs at 700-1000 years shortly after canister breaching and resaturation of the interior. Zircaloy cladding has an expected lifetime of approximately 10,000 years[4] and this postpones the release of fuel matrix. After 100,000 years, virtually all poison and fuel have been removed from the waste package canister.

The resulting values of k_{eff} are shown in figure 2 for 3% unirradiated fuel. The effect of the early removal of the Al-B was dramatic. It should be noted that the uranium fissile mass decreased by only 0.01% over 100,000 years due to decay. By year 700, the waste package has became critical and this condition was sustained until the uranium content began to decrease. By year 50,000, the waste package contents again returned to subcritical conditions and after 100,000 years, the inventory of fuel was almost completely removed from the package.

Although the neutron absorber and fuel removal rates will vary depending upon the local flow rates and chemical environment, the differential removal was most dependent upon the rather long period of protection that the cladding offered the fuel matrix.

B. Unirradiated Fuel, Steel/Boron Absorber

Figure 3 shows the fractional releases of neutron absorber and fuel matrix material where a 304L stainless steel with 10% boron is used as the absorber. A nominal corrosion rate of 0.5 μm/yr was assumed for this run. The much lower corrosion rates of steel postpone the release of the neutron absorber and 50% of the material is removed from the waste canister after 10,000 years.

As noted in figure 4, the slower corrosion of the steel absorber causes critical conditions to occur at year 10,000 and end at 55,000 years. The reduced corrosion rates postpone the onset of criticality, but do not attenuate the effect.

C. Effect of Fuel Burnup

Although the rise in k_{eff} observed in unirradiated fuel would not be as significant in spent fuel, similar effects are expected. In addition, any corrosion mechanism that might lead to the separation of fusion product neutron absorbers such as samarium will exacerbate the problem.

D. Effect of Other Parameters

From the previous results for aluminum/boron and steel/boron alloy neutron absorbers, it was observed that criticality events occurred after neutron absorber removal began and before a substantial amount of the fuel was removed. Plots of the fractional release of neutron absorber and fuel material were useful in predicting when these criticality events would occur.

Variations in mean cladding lifetime, the container lifetime, and corrosion rates also affect the occurrence of these criticality events and these are demonstrated through fractional release plots.

In figure 5, the mean lifetime of the zircaloy cladding was decreased from 10,000 years to 1,000 years. The relative release rates still showed a substantial period of time during which the spent fuel remained in the container with very little neutron absorber remaining.

Figure 6 demonstrates the effect of extending the mean container lifetime from 300 years to 1,000 years. The same gap in fuel and neutron absorber fractions existed from 10,000 to 40,000 years.

In figure 7, the effect of neutron absorber corrosion rate was examined. The rate was decreased from a nominal value of 0.5 μm/yr to the lowest reported value of 0.005 μm/yr. The neutron absorbing material remained long after the fuel was removed from the container. In this case, there remained the possibility of a critical event occuring outside of the container wall due to the accumulation of fissionable material in the absence of a neutron absorber.

IV. CONCLUSIONS

The results demonstrate that the differential removal of poison and fuel from proposed waste packages can eventually lead to criticality events in the presence of water. The simple addition of a neutron poison only ensures the control of criticality in the short term.

We suggest that techniques be used to prevent the early corrosion of poison material, either by using poisons with low corrosion and solubility rates or by protecting the poison material in a manner similar to the protection offered the fuel matrix by the zircaloy cladding. Alternative techniques should be explored to provide long-term control of criticality, including:

1. Addition of more neutron absorber (B).
2. Use of more stable, corrosion-resistant absorber.
3. Match neutron absorber removal rates to fuel matrix removal rates.
4. Provide mechanical protection to the absorber material and minimize losses by corrosion.
5. Diversify the choices of neutron poisons. (e.g. Hf, Cd, Gd)

ACKNOWLEDGMENTS

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NOMENCLATURE

k_{eff}	effective neutron multiplication factor
$L_{r\text{-}NA}$	release rate for the neutron absorbing material
P	probability of failure between t and t+dt
t	time
τ_c	mean container lifetime
R	corrosion rate

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Table 1

Parameters Used to Predict
Fuel and Poison Release Rates

Parameter	Description	Value Used	Notes
t_m	Release Time for Fuel Matrix	55,459 yr	c
t_p	Release Time for Neutron Absorber	438 yr	c
t_z	Release Time for Cladding	10,000 yr	c
τ_b	Lower Limit for Resaturation	150 yr	1
τ_b	Upper Limit for Resaturation	300 yr	1
τ_c	Mean Canister Lifetime	300 yr	1
τ_f	Mean Cladding Lifetime	10,000 yr	1
$L_{r\text{-}UO2}$	Removal Rate of UO2	0.003 mol/m^2-yr	2
$L_{r\text{-}NA}$	Removal Rate of Neutron Absorber	23 μm/yr, 0.5 μm/yr	3
Notes:			
c	- indicates a computed value.		
1	- see ref [4] for applicable range of values.		
2	- range: 0.003 to 2 mol/m^2-yr, ref [4].		
3	- aluminum/boron, 304L SS/boron alloys.		

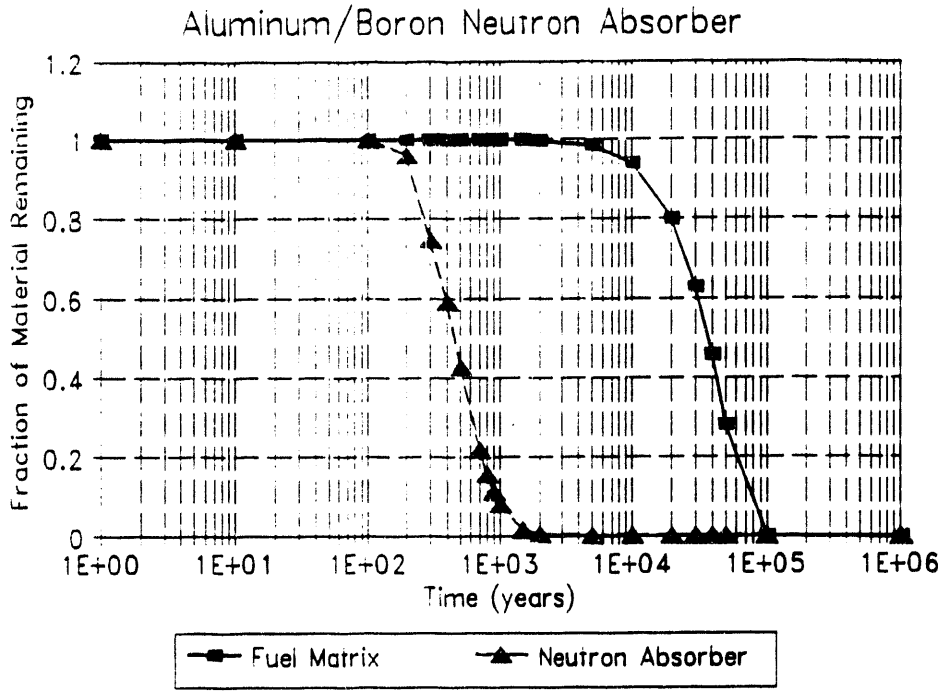

Fig. 1 Fractions of Fuel and Neutron Absorber Remaining in the Waste Container versus Time

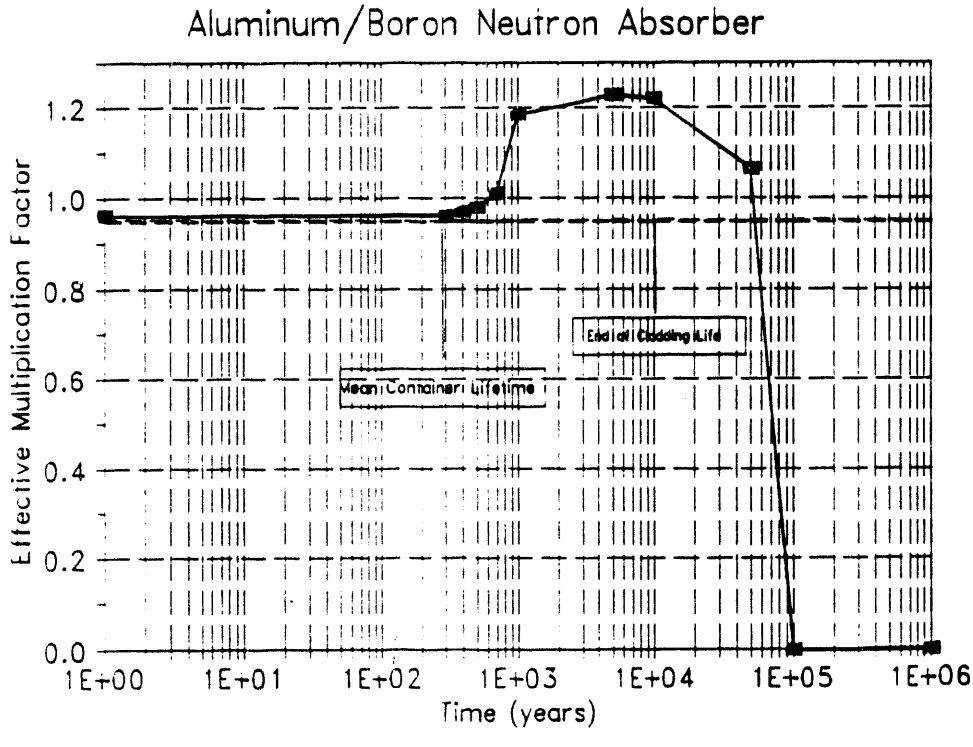

Fig. 2 Effective Multiplication Factor versus Time

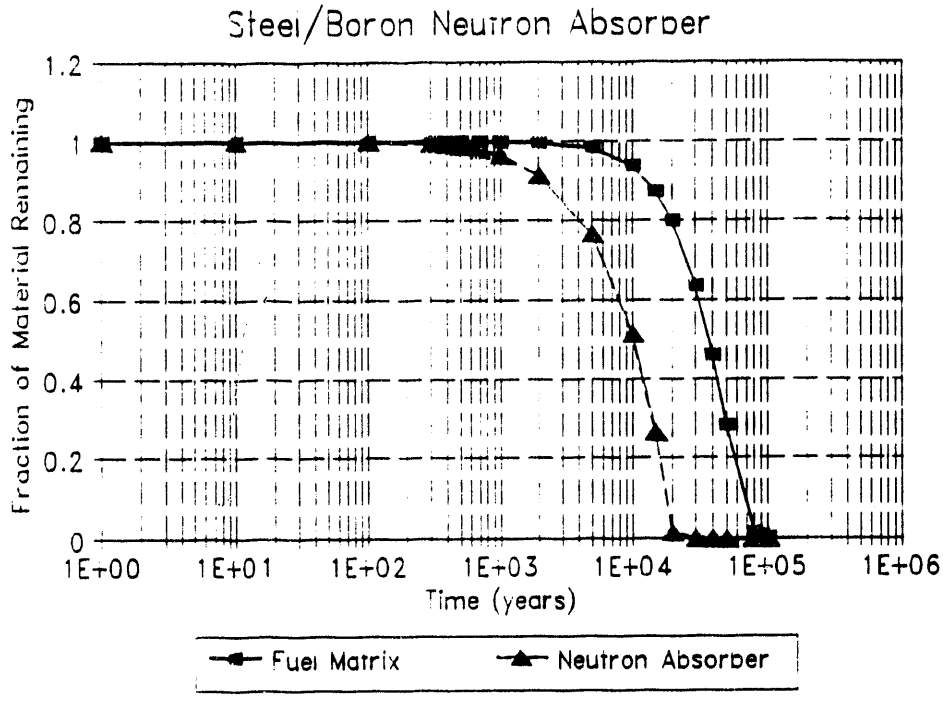

Fig. 3 Fractions of Fuel and Neutron Absorber Remaining in the Waste Container versus Time

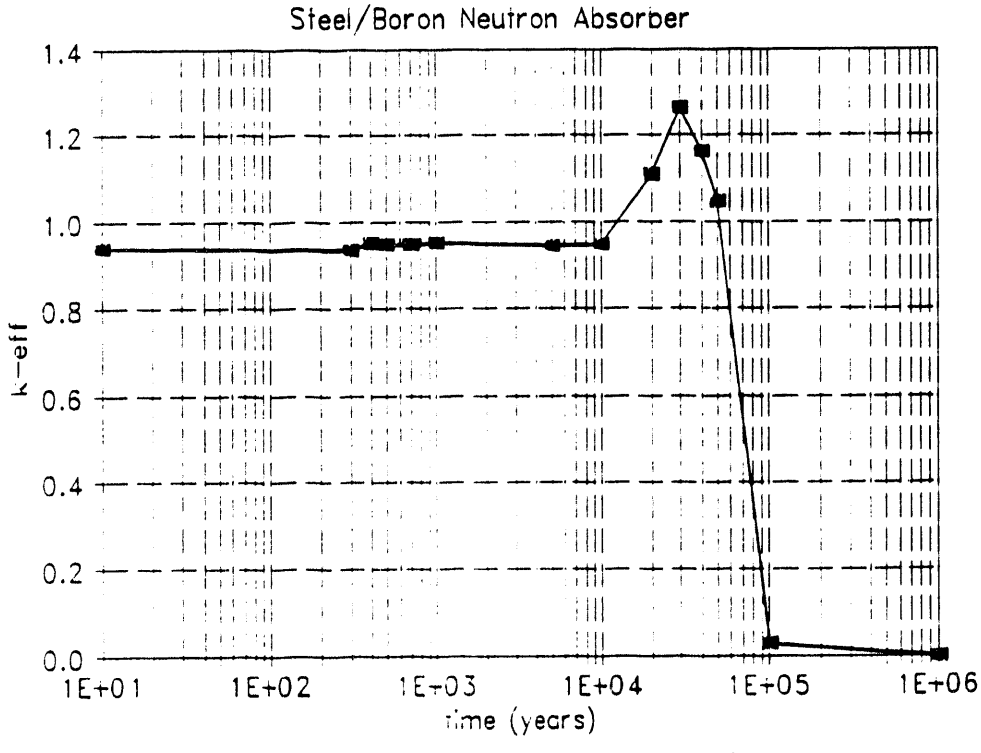

Fig. 4 Effective Multiplication Factor versus Time

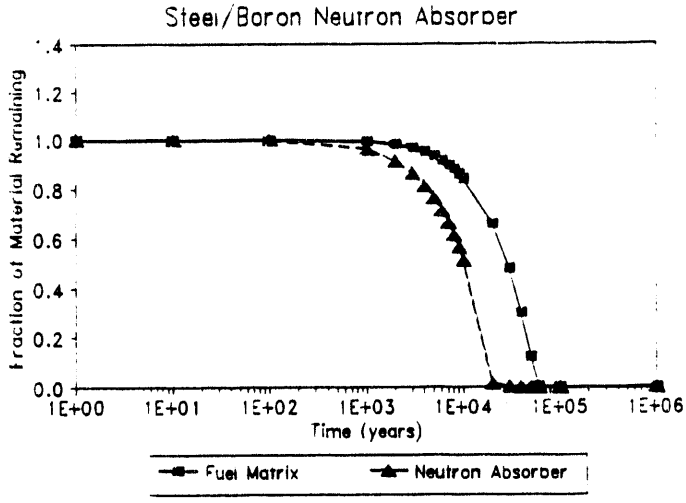

Fig. 5 Effect of Cladding Lifetime on Fractional Releases

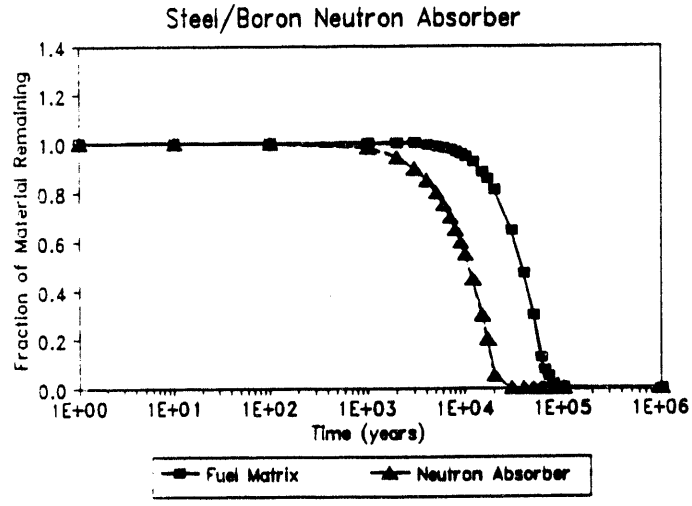

Fig. 6 Effect of Container Lifetime on Fractional Releases, (τ_c = 1,000 years)

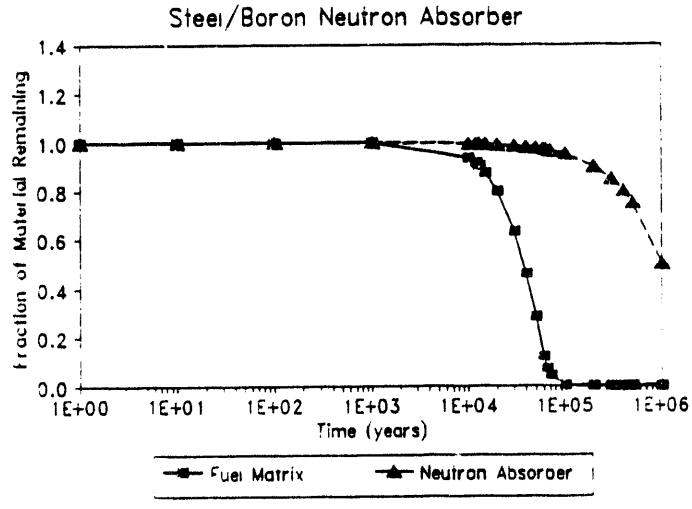

Fig. 7 Effect of Absorber Corrosion Rate on Fractional Releases, 304L-SS/Boron, ($L_{T\text{-}NA}$ = 0.005 μm/yr)

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