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6th I.H.L.R.W.M. Conf.

2 May 1995

Waste Form Alteration -- Vitrified Wastes

Radionuclide Releases from Borosilicate and Natural Glasses

**Don L. Shettel
&
Maury E. Morgenstein**

**Geosciences Mgt. Inst. Inc.
1000 Nevada Highway, Suite 106
Boulder City NV 89005**

**(702) 294-3064
FAX: (702) 294-3065**

**Acknowledgements:
Agency for Nuclear Projects
Nuclear Waste Project Office
State of Nevada**

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Geosciences Management Institute, Inc.
1000 Nevada Highway, Suite 106
Boulder City, NV 89005
(702) 294-3064; FAX -3065

Radionuclide Releases from Borosilicate and Natural Glasses

Don L. Shettel & Maury E. Morgenstein

Text of Presentation made at the 6th Annual International High Level Radioactive Waste
Management Conference & Exposition

Mirage Hotel & Casino, Las Vegas, NV
2 May 1995

Overhead # [Title of overhead]

1. [Title Page]

Before I begin I would like to acknowledge the support of the State of Nevada through the Agency for Nuclear Projects, Nuclear Waste Project Office.

The recent availability of experimental data for unsaturated drip tests on vitrified waste forms from the Argonne National Laboratory (ANL), permits one to make long term predictions regarding the release of radionuclides from the glassy waste forms.

2. [Radionuclide Release Model]

My rather simplistic radionuclide release model is based on the normalized leach rate equation given here. I read here what each of the parameters is in the equation. In general, the normalized leach rate is a function of temperature, pressure (fixed here), the waste form plus its degree of alteration, the chemistry of the solution contacting the waste form, and the flow or drip rate. Only one temperature and solution composition (equilibrated J-13 water) have been looked at so far, and one flow/drip rate has been used. The flow or drip rate used in the experiments by Bates group at ANL upon which our predictions are based is equivalent to an average of 0.5 mm/y infiltration at Yucca Mountain. Recent data from the USGS used in the 3D modeling of Yucca Mountain, shows that in individual columns of cells the infiltration rate could be a factor of 20 to 30 times this value. The ability to model leach rates requires more variations on these parameters.

One key assumption in our calculations is that the total elemental release is the sum of each individual isotope of that element released [blue equation at bottom]. Conversely, if we know the release rate for an individual radionuclide, then with the inventory for the waste form we can calculate the elemental release rate.

Radionuclide Release Model

$$(NL)_i = (A_i / A_o)(W_o / SA \cdot t)$$

where:

A_i = amount of nuclide or element i released

A_o = initial amount of i (inventory)

W_o = Weight of sample

SA = surface area

t = time interval

$(NL)_i$ = function of T, P, waste form + alteration, solution chemistry (including Eh & pH), flow rate

$$A_{Am} = A_{241Am} + A_{242Am} + A_{242mAm} + A_{243Am}$$

3. [Assumptions for Radionuclide Release Calculations]

We have to make several other assumptions to proceed with the long term predictions of radionuclide releases from vitreous waste forms. One of these is the surface area of the glass monolith, we have used 175 m², not 50 m² as stated in the paper. I must apologize because the figures in the paper are not for 50 m² as claimed, but for a somewhat higher surface area that would be more representative of fractured glass after it has been more completely hydrated (at some time after canister failure). The idealized unfractured and unhydrated glass monolith would have a starting surface area of 5 m², but due to tensile fracturing that forms upon cooling of the monolith the surface area may be from 10 to 35 times that of the ideal. We have chosen to start at the high end of the range, but we hold this constant during our predictions when in reality the surface area is increasing geometrically over time as the glass hydrates (after canister failure).

We also assume that the canister or multipurpose canister (MPC) fails at some time after emplacement; here we have used 1,050 years (50 years beyond the range mandated in 10 CFR 60). There are two ways to look at the data, we can assume one canister fails and scale the results up to 1,000 metric tonnes of heavy metal (MTHM), or assume the 594.2 canisters fail at the same time that are holding 1,000 MTHM. I must point out that we are not attempting to predict canister failure at all, but are merely using an arbitrary failure time; the results for the long-lived radionuclides are relatively unaffected by any canister failure time assumptions.

The radionuclide release rates assume that unsaturated drip conditions occur, the waste is just below boiling (90°C), and that the glass is initially unhydrated. However, depending on the thermal load employed and when canisters fail, glass could become hydrated before it comes in contact with liquid water; in this case, the radionuclide release rates would be considerably higher if one is starting with hydrated glass.

Finally, we realize that the DoE has not settled on a final glass composition and radionuclide inventory, but we will use that for SRL-165 with a characteristic radionuclide inventory.

4. [Photograph of Cross Section of Glass Pour Canister]

This is a photograph of a cross section of a glass waste form in a pour canister. Note the highly fractured nature of it and that there are voids in the glass (trapped air/gas bubbles). In addition there are fines on the highly rubblized surface of the canister. Clearly, the initial surface area of a glass monolith is not even close to the the idealized SA. The canister is also probably under tensile stress due to the difference in thermal expansion between the metal and the glass.

Assumptions for Radionuclide Release Calculations

- Surface area = ¹⁷⁵~~50~~ m² for fractured glass monolith
(SA increases geometrically with time as glass hydrates)
- Canisters all fail at some time after emplacement
- Radionuclide release rate assumes:
unsaturated drip conditions
below boiling temperatures
initially unhydrated glass
- There are 594.2 glass monoliths per 1,000 metric tonnes of heavy metal (MTHM)
- SRL-165 glass and a characteristic radionuclide inventory

fractures - rubblelized surface



Figure 3. Fractured Glass Waste Form, With Voids,
at Canister Center, 0.61 m from Bottom

Molecke et al. (1993)

Canister under tensile stress

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5. [SRL - 165 Radionuclide Inventory]

This overhead shows the radionuclide inventory of selected isotopes for SRL-165 glass; the data are from the Baxter reference (see paper). I merely show this to point out those few radionuclides that could potentially exceed regulatory limits, even remanded ones. From a radioactivity standpoint, the important isotopes are most of the plutonium ones, except for Pu-242, and Am-241. Neptunium does not appear important initially, but due to ingrowth from Am-241 could be significant. Notable for their absences are those radionuclides for which experimental data has not been published, such as technetium.

6. [Uranium Isotopic Inventory in SRL-165 Glass]

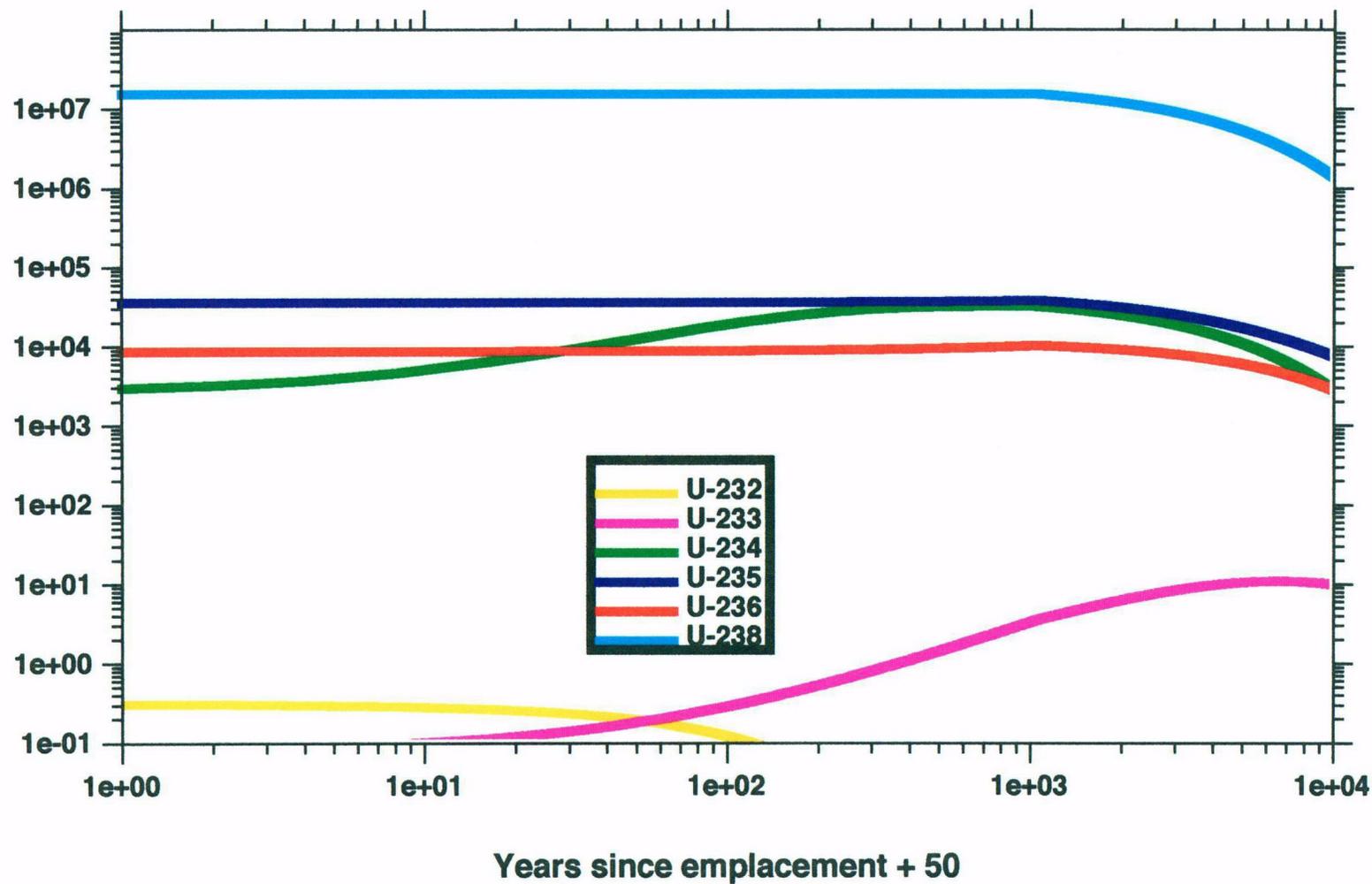
NOTE: Due to a bug in the plotting software, the label for the ordinate (the value or Y) axis had to be placed directly on the line below the title. SpyGlass Plot™ 1.01 would not plot rotated QuickDraw text correctly (at all).

This overhead shows the variation in the masses of the uranium isotopes in 1,000 MTHM up to and after the canister failure at 1,050 years. Note that the magenta curve for U-233 is increasing due to the addition of daughter product from the decay of Np-237 and that the green curve for U-234 exhibits a maximum due to ingrowth of daughter product from the decay of Pu-238. The point is that our program for computing long term predictions does take into account radioactive decay.

SRL-165 Radionuclide Inventory

| | Ci/1,000 MTHM | Half-life (y) |
|----------------|----------------------|----------------------|
| U-232 | 6.53 | 73.6 |
| U-233 | 7.70E-04 | 1.62E+05 |
| U-234 | 17 | 2.47E+05 |
| U-235 | 0.077 | 7.10E+08 |
| U-236 | 0.55 | 2.39E+07 |
| U-238 | 5.12 | 4.51E+09 |
| | | |
| Np-237 | 4.34 | 2.14E+06 |
| | | |
| Pu-238 | 723,635 | 86 |
| Pu-239 | 6,259 | 24,000 |
| Pu-240 | 4,233 | 6,580 |
| Pu-241 | 814,090 | 13.2 |
| Pu-242 | 6 | 3.80E+05 |
| | | |
| Am-241 | 5373 | 458 |
| Am-242 | 7 | 0.002 |
| Am-242m | 7.1 | 152 |
| Am-243 | 2.82 | 7,370 |

Uranium Isotopic Inventory in SRL-165 Glass grams per 1,000 MT



col

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7. [Uranium Isotopic Releases from SRL-165 -- Cumulative Curies]

This overhead shows the cumulative Curies of radioactivity released from the glass waste forms during the regulatory time period. Note that the old remanded EPA release limit of 100 Curies cumulative to the accessible environment over 10,000 years for each radionuclide is marked. The National Academy of Sciences is currently reevaluating this standard, and once they reach a decision, then the EPA must promulgate a new standard (probably based on dose).

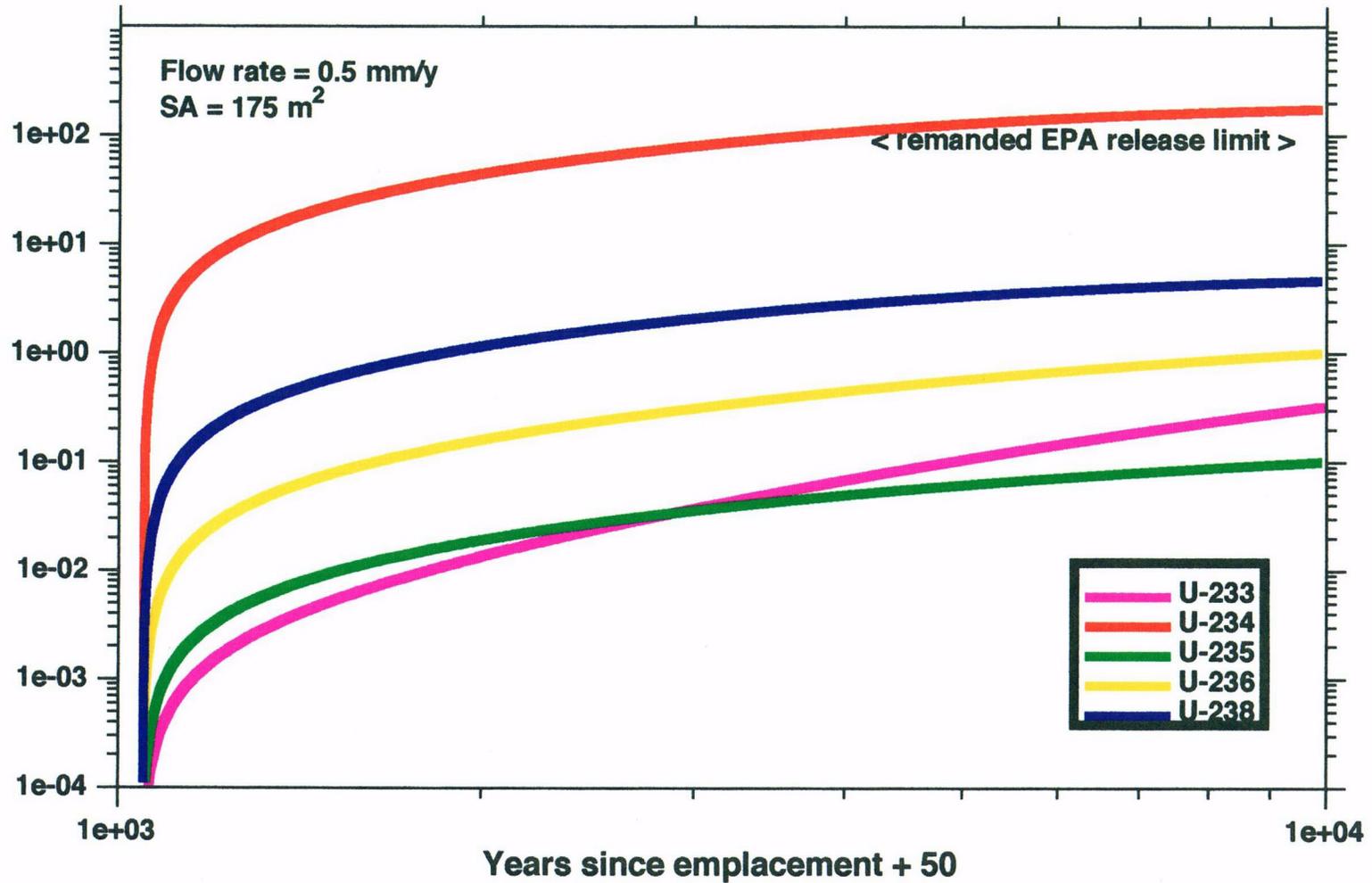
Only one uranium isotope potentially exceeds this limit: ^{234}U . However, one must keep in mind that these releases are only from the waste form and that the transport, solubility, and retardation (at least) of the radionuclides must be considered to determine what fraction of the releases actually would reach the accessible environment. However, if less than 100 Curies cumulative of each isotope were released from each 1,000 MT of the waste forms, then it would be impossible for more than 100 Ci to reach the accessible environment; conversely, if more than 100 Ci is released, then the possibility exists that the release limit could be attained.

8. [Fractional Releases of Uranium Isotopes from SRL-165 Glass]

Another measure of releases of radionuclides is specified in 10 CFR¹ 60 as less than 1 part in 100,000 per year, or less than a fraction of 10^{-5} per year relative to the inventory at 1,000 years. This overhead shows the model predicts that the fractional releases of five of the uranium isotopes is greater than the 10 CFR 60 release limit over the entire regulatory time period. However, the fraction for U-233 actually increases over time due to the ingrowth of daughter from the decay of Np-237.

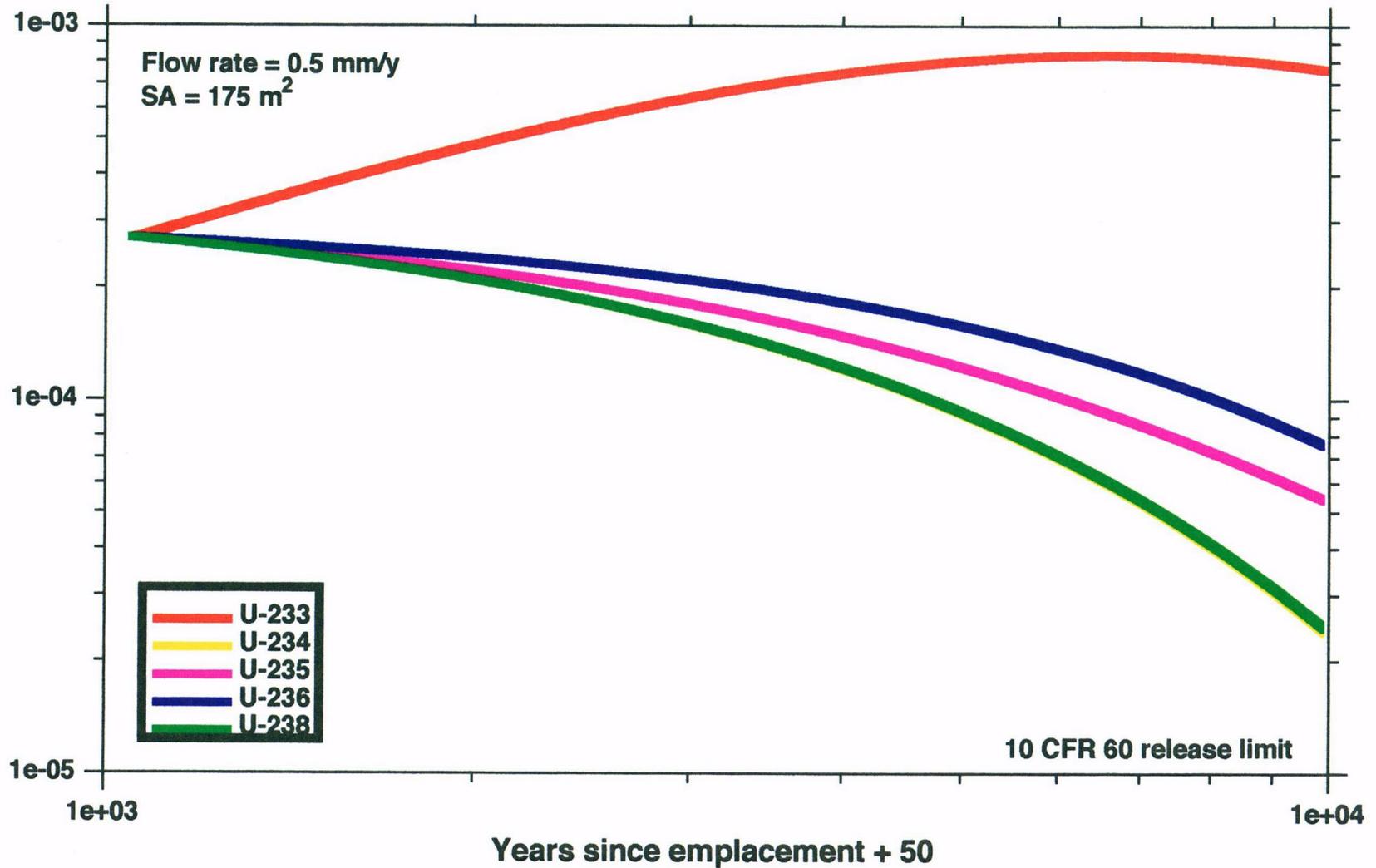
¹ CFR stands for "Code of Federal Regulations."

Uranium Isotopic Releases from SRL-165 Glass Cum. Curies released per 1,000 MTHM



602

Fractional Releases of Uranium Isotopes from SRL-165 Glass Ratio of yearly releases to inventory at 1,000 y



C03

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9. [Am & Np-237 Isotopic Inventory of SRL-165 Glass -- grams per 1,000 MTHM]

This overhead shows the masses of neptunium and americium isotopic inventory of the waste form over the regulatory time period both before and after canister failure at 1,050 years and the flow rate of 0.5 mm/y. Note that Np-237 increases gradually over time due to ingrowth of daughter product from the decay of Am-241. ²⁴¹Am shows a maximum due to ingrowth of daughter product from the decay of Pu-241. Am-242 also shows a maximum due to the isomeric transitional decay of ^{242m}Am. Both of these latter Am isotopes fall off rapidly due to simple radioactive decay.

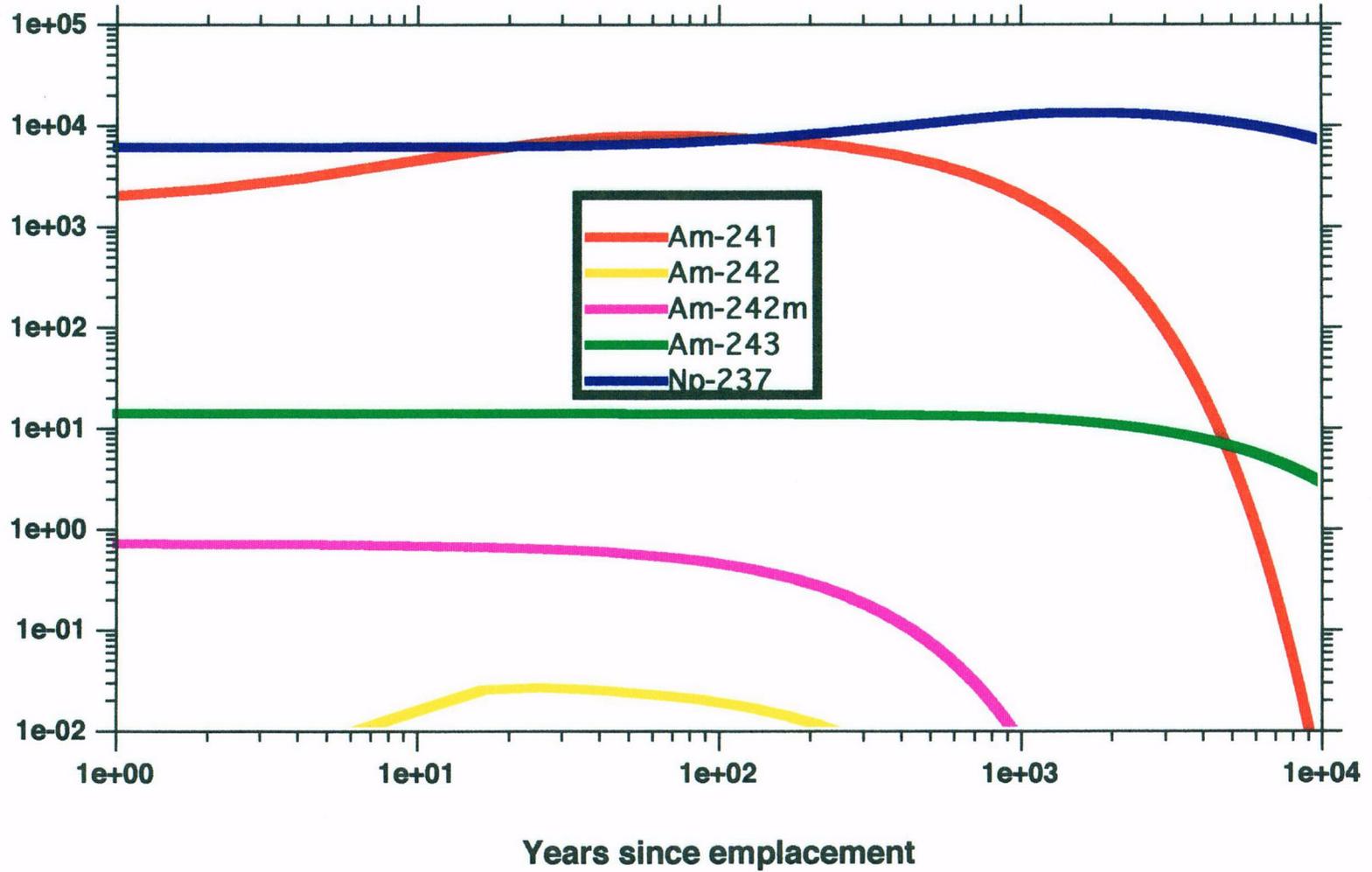
10. [Releases of Np-237 and Americium Isotopes from SRL-165 Glass -- Cum. Ci]

This overhead is a companion to the previous one, but the masses have been converted to radioactivity of the individual isotopes. None of the isotopes shown exceed the remanded EPA release limit of 100 cumulative Curies to the accessible environment over the regulatory 10,000 year time period.

11. [Fractional Releases of Np-237 & Am Isotopes from SRL-165 Glass]

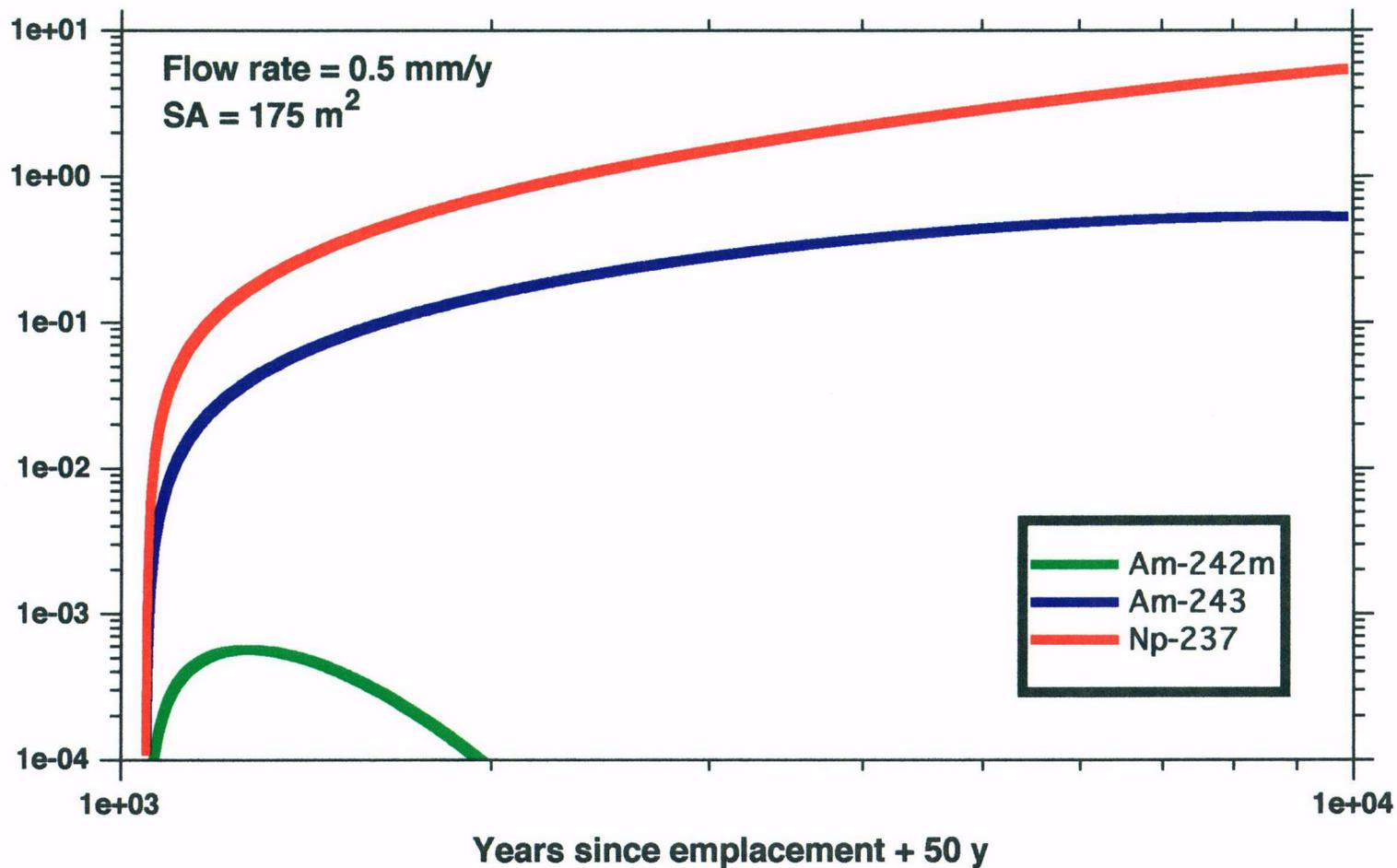
This overhead is part of the same set as the previous two. It shows the ratio of yearly releases of neptunium and americium isotopes to their inventory at 1,000 years; 10 CFR 60 requires that this release be less than 1 part in 100,000 per year or less than a fraction of 10^{-5} per year. Two of the important, long-lived isotopes (Np-237 and Am-243) exceed this standard. Releases of Am-242m are initially above the limit as well, but due to a rapid decrease in its amount resulting from a relatively short half life, it becomes a rapidly diminishing proportion of the total Am isotopes released from the waste form.

Am & Np-237 Isotopic Inventory of SRL-165 Glass grams per 1,000 MTHM



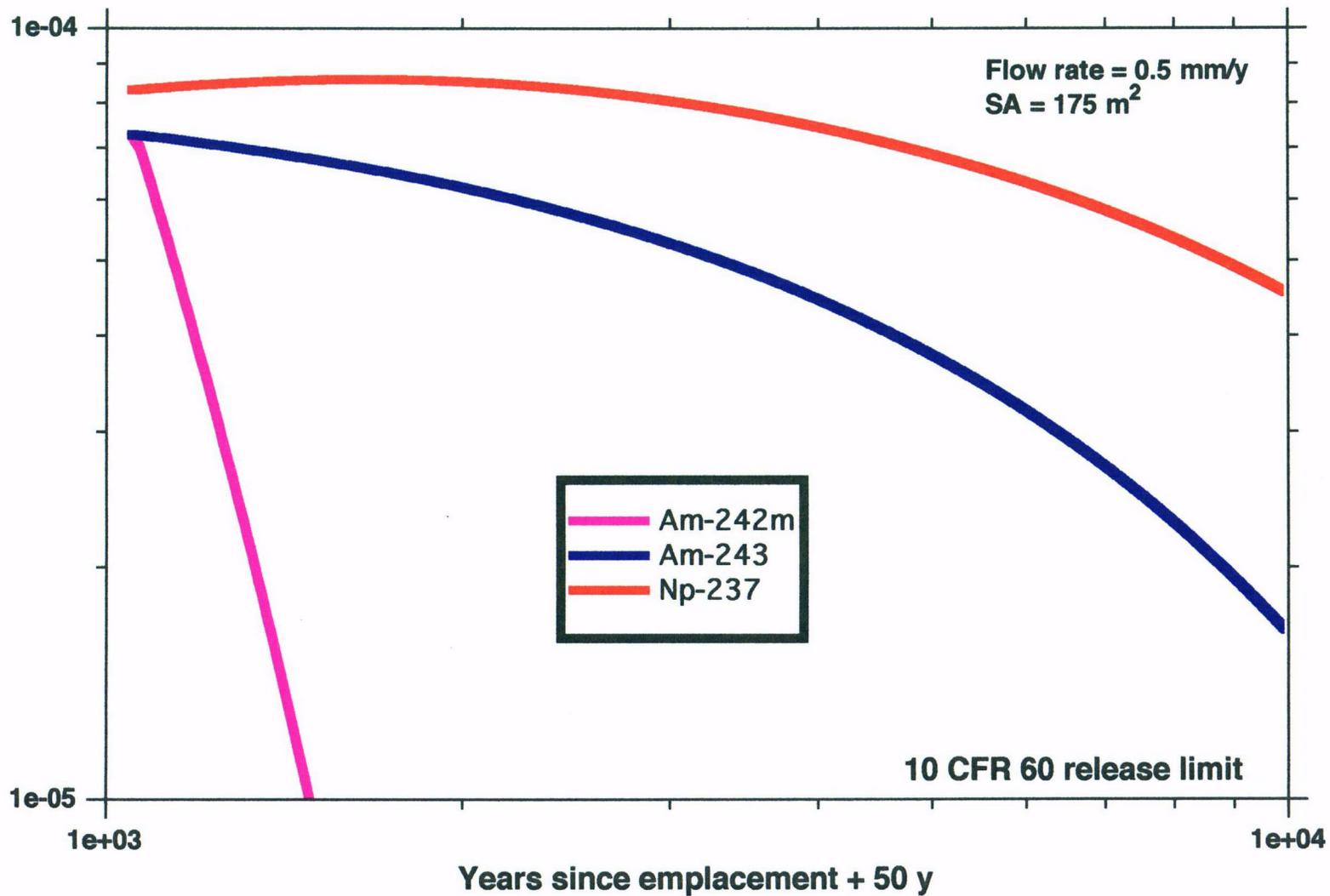
C04

Releases of Np-237 & Americium Isotopes from SRL-165 Glass Cum. Curies released per 1,000 MTHM



C05

Fractional Releases of Np-237 & Am Isotopes from SRL-165 glass Ratio of yearly releases to inventory at 1,000 y



C06

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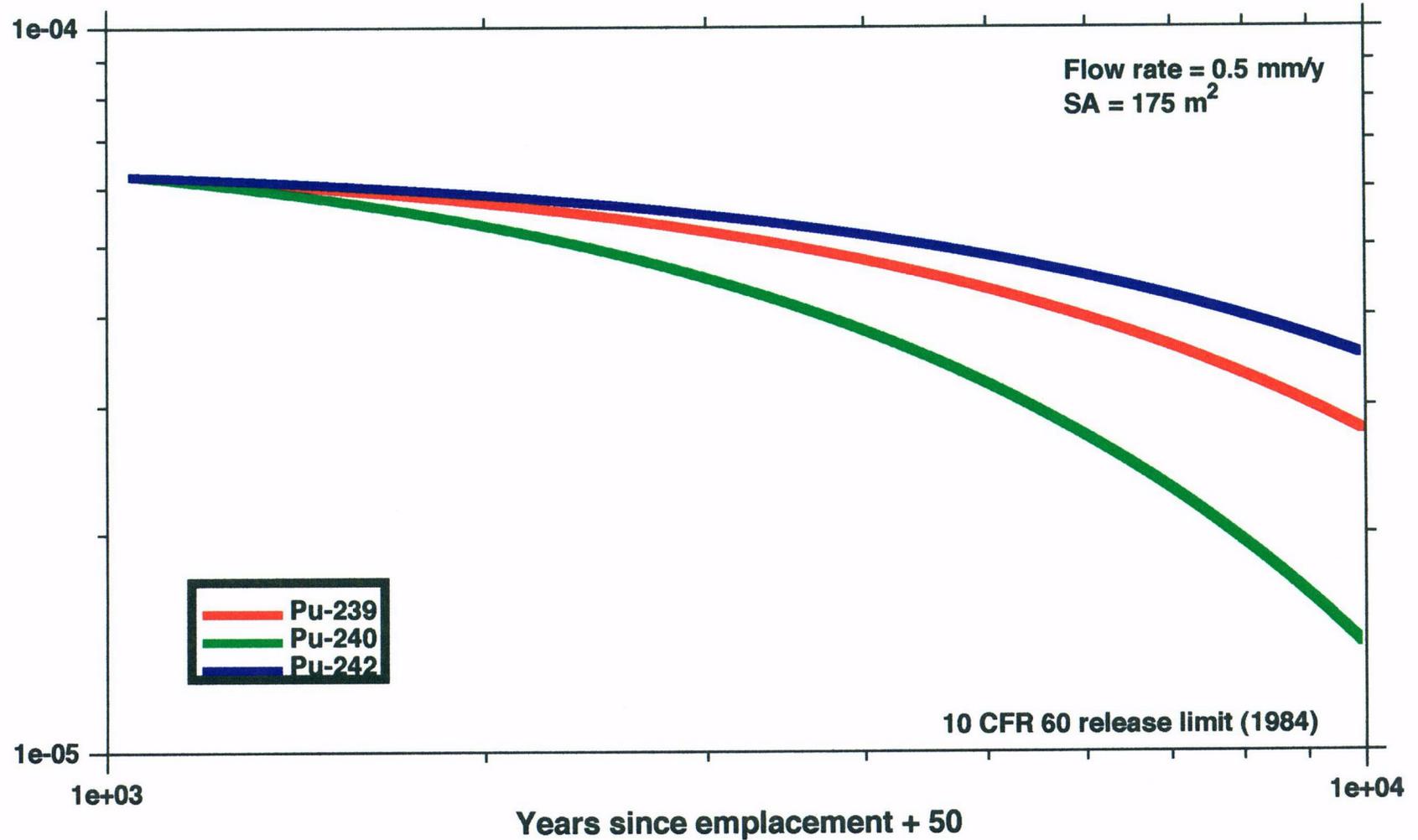
12. [Plutonium Isotopic Releases from SRL-165 Glass -- Cum. Curies]

The cumulative Curies of plutonium isotopes calculated to be released from SRL-165 glass under relatively low flow rate conditions (0.5 mm/y) is shown on this overhead. The remanded EPA release limit of 100 Curies cumulative to the accessible environment over 10,000 years is shown for reference purposes. Two plutonium isotopes (Pu-239 and Pu-240) exceed the EPA release limit.

13. [Fractional Releases of Plutonium Isotopes from SRL-165 Glass]

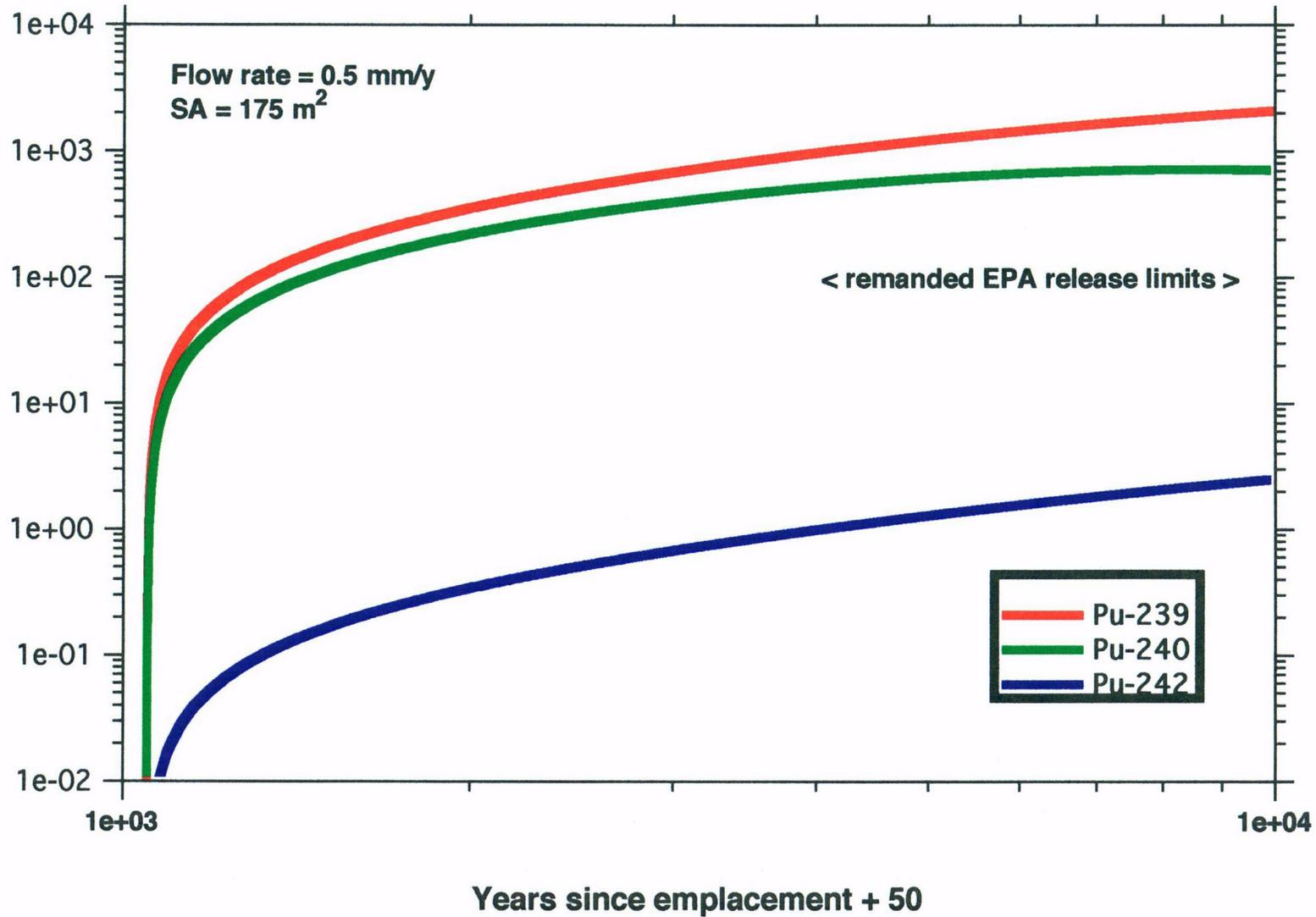
The 10 CFR 60 release limit for radionuclides from the waste form is one part in 10^5 per year, or on a fractional basis, should not exceed 10^{-5} per year relative to their inventory at 1,000 years after emplacement. The three plutonium isotopes plotted exceed this release limit over the regulatory time period of 10,000 years.

Fractional Releases of Plutonium Isotopes from SRL-165 Glass Ratio of yearly releases to inventory at 1,000 y



C07

Plutonium Isotopic Releases from SRL-165 Glass Cum. Curies Releases per 1,000 MTHM



C08

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14. [Problems with Borosilicate Waste Glass -- Part I]

Apart from the radionuclide releases I have just shown you, there are other problems with vitrified waste forms. From natural analog studies of glass we know the following: [read items from the overhead].

15. [Problems with Borosilicate Waste Glass -- Part II]

We also know from experimental studies of waste glass that [read items from the overhead].

16. [Problems with Borosilicate Waste Glass -- Part III]

Therefore, if a canister containing glass leaks for whatever reason, even a pinhole leak in the right place, the humid atmosphere (steam) will initiate glass hydration. Later contact with brines will continue hydration and begin releases of the waste form. However, the volume expansion of hydrating glass and the crystallization of alteration phases may cause the canister to rupture along its welds. This might be a catastrophic failure or perhaps gradual over time, but the result is increased exposure of the waste form to dripping vadose zone waters that have been modified by refluxing conditions.

Problems with Borosilicate Waste Glass Part 1

From Natural Analog Studies of Glass -

- Volume expansion upon hydration causes fracturing
Result: surface area increases geometrically
with time

- Fe and Mn increase hydration rate:
Sideromelane > Obsidian

- Hydration rate doubles for every 12C° increase

Problems with Borosilicate Waste Glass Part 2

From Experimental Studies of Borosilicate Glass -

- Pouring of glass produces extensive cavities and cooling fractures**
- Steam contact causes extensive and rapid hydration of borosilicate glass ("aging")**
- Radiolysis of thin films of water produces nitric, formic, and carboxylic acids which enhance hydration and leaching by lowering pH**
- Corrosion of glass-metal contact enhances hydration**

Problems with Borosilicate Waste Glass Part 3

Thereby Resulting In -

- Leak in canister containing glass will initiate glass hydration from steam, then brines**
- Volume expansion of hydrating glass and crystallization of alteration phases may cause further rupturing of canister**

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17. [Comparative Mineral Associations]

As part of our continuing research, we are investigating authigenic mineralogy of glass alteration. I will not go through this overhead in detail, but it is a compilation of the various alteration mineralogy of different glass types, including waste glass. There are obvious compositional differences but there are also similarities. Our interests are in authigenic minerals that might be retarders of radionuclides, other minerals that might coprecipitate radionuclides, and colloids that would promote transport of radionuclides.

18. [Mineral Colloids, Suspended Particles, and Precipitates ...]

This overhead is a schematic diagram comparing alteration of Yucca Mountain obsidian with waste glass in the near field. Again, I will not go through this in detail because we are still working on it, but the mineralogy of alteration starts out with differences and with time (aging) and increased temperatures it becomes more similar. Mineral stability appears to increase and there are decreased sorptive capabilities.

COMPARATIVE MINERAL ASSOCIATIONS

| Glass and Authigenic Minerals | Yucca Mountain Obsidian ^t Authigenics | Basaltic Glass Sideromelane ^{tt} Authigenics | Waste Glass Authigenics ^{ttt} |
|-------------------------------------|--|---|---|
| Glass | Glass | Glass | Glass |
| Nontronite | | Nontronite | Nontronite |
| Montmorillonite | Montmorillonite | Montmorillonite | |
| Beidellite | Beidellite | | |
| Saponite | | | Saponite |
| Smectite/Illite | Smectite/Illite | Smectite/Illite | |
| Smectite/Chlorite | | Smectite/Chlorite | |
| Chlorite | Chlorite | | |
| Kaolinite | Kaolinite | | |
| Phillipsite | | Phillipsite | Phillipsite |
| Heulandite | Heulandite | | |
| Clinoptilolite | Clinoptilolite | Clinoptilolite | |
| Mordenite | Mordenite | | |
| Harmotome | | Harmotome | |
| Erionite | Erionite | | |
| Chabazite | Chabazite | Chabazite | Chabazite |
| Analcime | Analcime | Analcime | Analcime |
| Albite | Albite | | |
| K-Feldspar | K-feldspar | | |
| Laumontite | Laumontite | | |
| Opal-CT | Opal-CT | Opal | |
| Cristobalite | Cristobalite | | |
| Tobormorite | | Tobormorite | Tobormorite |
| Xonotlite | | Xonotlite | |
| Herschelite | | | Herschelite |
| Quartz | Quartz | | |
| Hematite | Hematite | Hematite | Iron-oxides(?) |
| Maghemite | | Maghemite | |
| Goethite | | Goethite | |
| Lepidocrosite | | Lepidocrosite | |
| FeOOH.HOH | | FeOOH.HOH | |
| Birnessite | | | |
| (7A Manganite) | Birnessite | Birnessite | Mn-oxide (?) |
| Todorokite | | | |
| (10A Manganite) | Todorokite | Todorokite | |
| Psilomelane | | | |
| (Romanechite) | | Romanechite | |
| Hydrotalcite | | Hydrotalcite | Hydrotalcite |
| Calcite | Calcite | Calcite | Calcite |
| Dolomite | Dolomite | | |
| Apatite | | | Apatite |
| Fluorite | Fluorite | | |
| Barite | Barite | | |
| Pyrite | Pyrite | | |
| Brockite | | | Brockite |
| Weeksite (K & Na varieties) | | | K & Na Weeksite |
| Uranophane | | | Uranophane |
| Boltwoodite | | | Boltwoodite |
| Haiweeite | | | Haiweeite |
| Powellite | | | Powellite |
| Cerianite-type mineral | | | Cerianite-type |
| Soddyite | | | Soddyite |

MINERAL COLLOIDS, SUSPENDED PARTICLES AND PRECIPITATES FORMED FROM GLASS HYDRATION

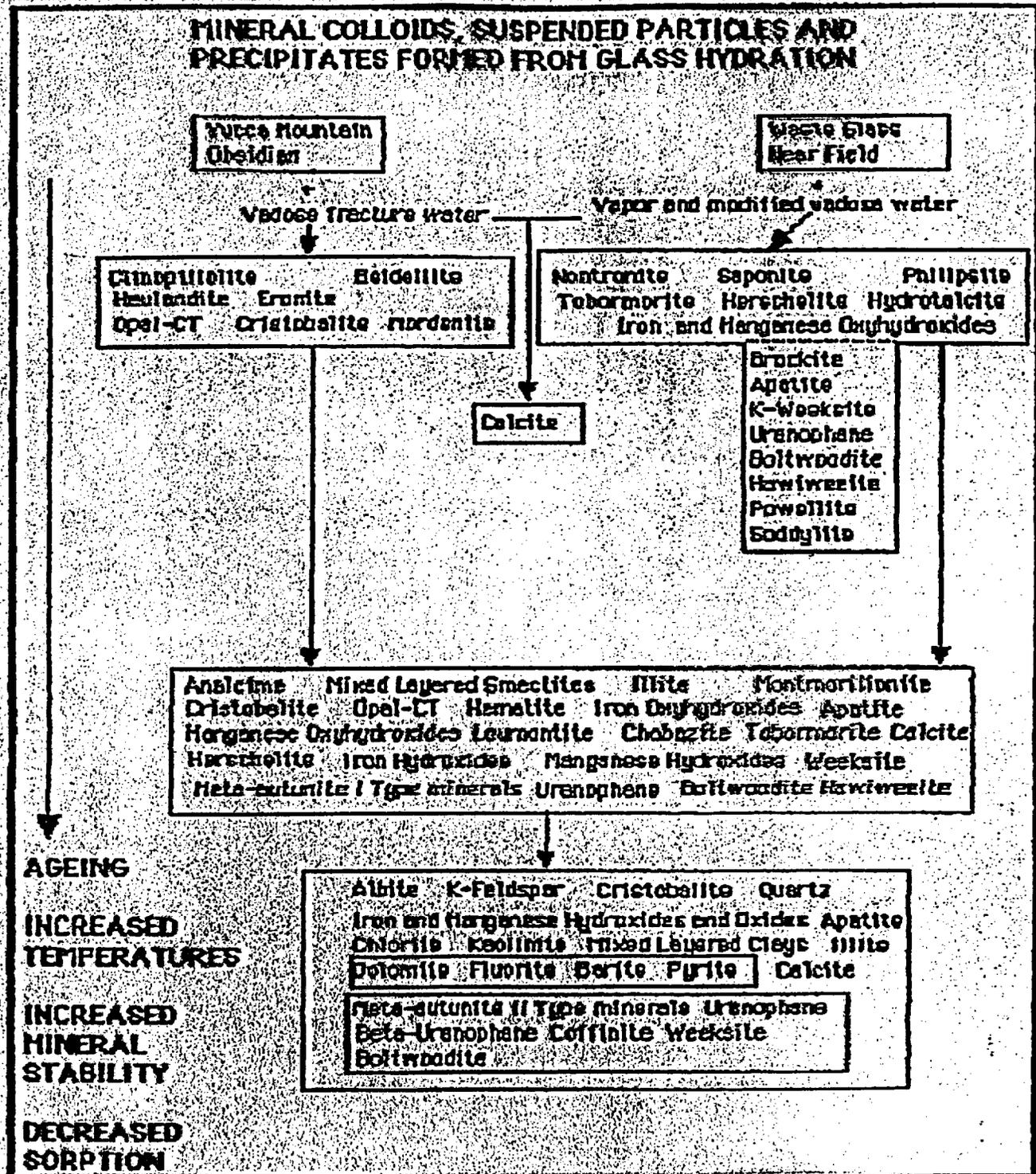


Figure 1: Diagram of Mineral Associations From Obsidian and Waste Glass.

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19. [Conclusions]

Some of the conclusions presented on this overhead are not unique to this talk and have been suggested by the cited workers at ANL. [Read the individual items.] However, on the last one I must emphasize that much more work is needed on the source term releases from the spent fuel waste forms under unsaturated conditions before we can get a firm grasp on the handle for modeling these under any of the projected conditions proposed for the Yucca Mountain repository.

20. [Conclusions (continued)]

Finally, I conclude that the vadose zone may not be the best place, and indeed may be the worst place, for a permanent geologic repository for nuclear waste due to the fact that the waste form and canister are simply incompatible with the oxidizing, humid environment of the vadose zone. Since the waste form and the engineered barrier system are incompatible with this environment, implying that they will degrade and corrode, the rates of these processes are extremely important to know for performance assessment purposes.

This environment has dripping water that results in thin films of water in which radiolysis is enhanced; radiolysis causes the formation of acids from the vapor phase which settle in the thin films and which lower the pH and thereby enhances canister corrosion and waste form degradation.

Galvanic effects may result from the seemingly increasing number of different metals proposed for the MPC and effects of microbially induced corrosion (MIC) are just beginning to be explored for the proposed conditions at Yucca Mountain. MIC apparently can exceed inorganic corrosion rates by 5 to 9 orders of magnitude. Both of these effects can enhance the waste container corrosion.

Under the high thermal loads being considered for the repository, the refluxing of fluids will cause high salinity fluids, or brines, to form, with an associated elevation in the boiling temperature, which increases the contact time between the waste form and engineered barrier system; the nature and composition of these brines and their effects on canister and waste form degradation need to be fully investigated.

CONCLUSIONS

- **Solubility calculations for PA not conservative**
- **Dynamic (flow) tests are more conservative than static ones (and more realistic)**
- **Much more work needed on source terms of waste forms:**
 - **other radionuclides**
 - **dynamic (flow / drip) testing**
 - **model (NL)_i as function of parameters**

Conclusions (continued)

- **Vadose zone is not best place for a permanent geologic repository:**
 - **humid, oxidizing environment with dripping water**
 - **radiolysis of thin films of water**
pH lowered by acid formation
 - **enhanced waste form & container corrosion**
MIC & galvanic effects
 - **high salinity fluids (brines?) will form under refluxing conditions**

HIGH LEVEL RADIOACTIVE WASTE MANAGEMENT 1995

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RADIONUCLIDE RELEASES FROM BOROSILICATE AND NATURAL GLASSES

D. L. Shettel and M. E. Morgenstein
Geosciences Management Institute, Inc.
1000 Nevada Highway, Suite 106
Boulder City, NV 89005 (USA)

ABSTRACT

The recent availability of experimental data for drip tests on borosilicate glasses permits the calculation of realistic and conservative radionuclide releases. Source terms based on these data are an improvement over those based on static closed-system saturated experiments and solubility calculations for Yucca Mountain, Nevada.

I. INTRODUCTION

Normalized leach rates, calculated from open-system unsaturated drip experiments¹ on radionuclide-doped borosilicate glass (SRL-165), have been used to model potential radionuclide releases from the glass waste form over the 10,000 year regulatory time period. Figures 1 through 3 show calculated results for plutonium radioisotopes, americium radioisotopes and ²³⁷Np, and uranium radioisotopes, respectively. Model assumptions included a characteristic glass radionuclide inventory,² reaction temperature fixed at 90°C, surface area fixed at 50 m² for each monolith, infiltration rate fixed at 0.5 mm/y in the vadose zone, and canisters containing 1,000 metric tons of heavy metal [MTHM] (594.2) all arbitrarily fail at 1,000 years after emplacement. The glass monolith as manufactured has an initial unhydrated, fractured surface area of approximately 10 to 35 times³ its "ideal" unfractured surface area (about 5 m²).

II. RESULTS

Radionuclide inventories in glass (Pu, Am, and U; and ²³⁷Np) closely approach depletion long before the end of the regulatory time period (10⁴ y) with any subsequent decline attributable to radioactive decay. Releases of the radionuclides ²³⁹Pu, ²⁴⁰Pu, and ²⁴¹Am from the waste form potentially exceed the old EPA release limits⁴ of 100 Curies cumulative per nuclide to the accessible environment over 10⁴ years, although physical transport and geochemical processes have not yet been considered. Although it might be expected that over time armoring by alteration reduces the reaction rate, hydration induces fracturing of the glass that results in a geometrical increase over time of fresh surface for increased reaction. In the absence of longer duration experiments, these data should be considered as a conservative starting point.

III. MINERALOGY

There are about 70 common authigenic minerals that have the potential to form during waste glass devitrification and associated near field reactions under a wide range of changing repository conditions. Many of these minerals can be responsible for retardation of some of the radionuclides. A much smaller list of authigenics have the potential to act as colloid transporters of portions of the radionuclide inventory. Waste glass composition, thermal history, rates of glass network *former, intermediate, and modifier* reactions with the repository environment, and environmental parameters present, help determine the production of authigenic mineral suites and their aging and transport histories. Histories of natural and anthropogenic glass-authigenic mineral associations are investigated.

IV. CONCLUSIONS

For a permanent high-level nuclear waste repository, the vadose zone may not be the best choice for a number of reasons. From natural analog studies, the rate of hydration of glass appears to double for every 12°C increase in temperature and the hydration of glass (both basaltic and borosilicate) causes a volumetric increase resulting in tensile fracturing with a geometric increase in reactive surface area with time. Radiolysis^{5,6} of thin films of water in the presence of atmospheric gases causes the formation of acids (nitric, formic, oxalic, and carboxylic) which lower solution pH and enhance waste form leaching (and presumably canister corrosion). Iron assimilated from the sensitized stainless steel-glass contact enhances borosilicate glass reaction and hydration. Solutions high in total dissolved solids may form in the high thermal gradients⁷ resulting from increased thermal loading; the effects of these "brines" on waste form and canister degradation need to be investigated. Steam hydration preceding liquid attack enhances glass degradation.⁸

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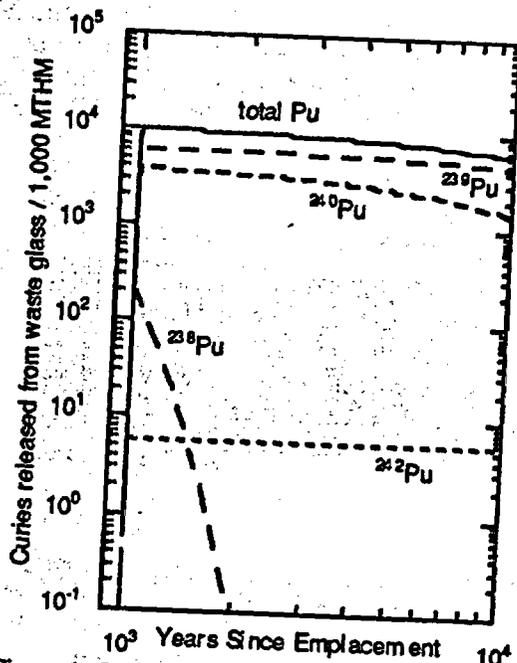


Figure 1. Calculated Pu isotope releases from waste glass under unsaturated drip conditions since time of canister emplacement.

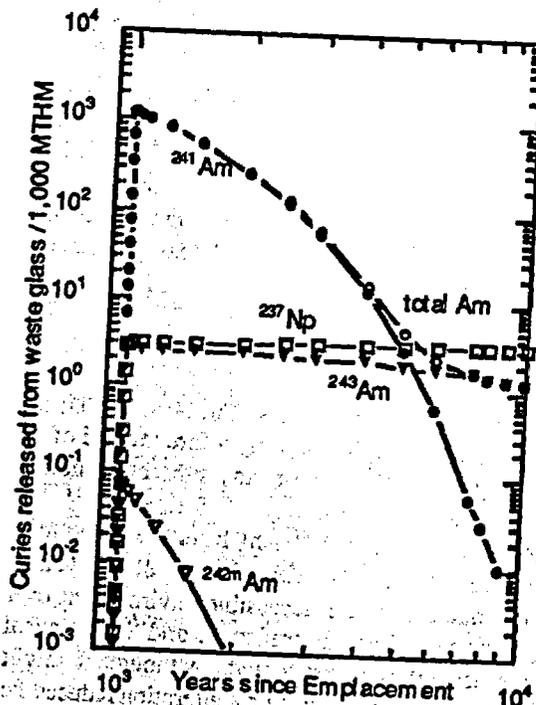


Figure 2. Calculated Am and ^{237}Np isotope releases from waste glass under unsaturated drip conditions since time of canister emplacement.

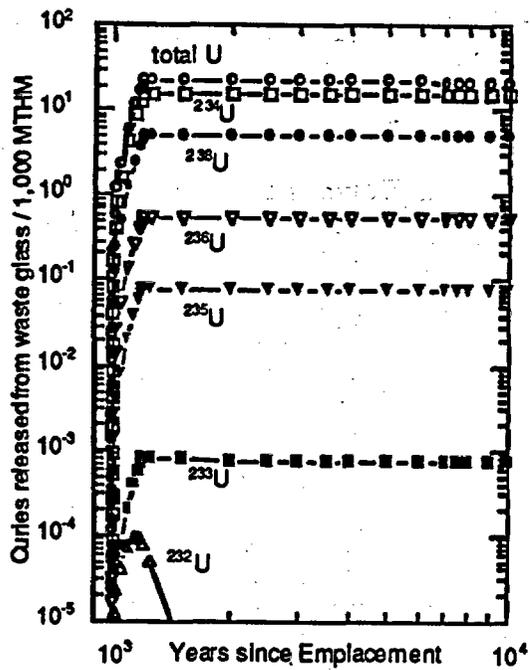


Figure 3. Calculated U isotope releases from waste glass under unsaturated drip conditions since time of canister emplacement.