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SOLID FORMS FOR SAVANNAH RIVER PLANT HIGH-LEVEL WASTE

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ABSTRACT

One option for long-term management of Savannah River Plant high-activity waste is solidification and storage in a retrievable surface storage facility to be located on the plantsite. This study was made to evaluate candidate solid waste forms and solidification processes, and to determine their applicability to engineered storage of Savannah River Plant waste. The study included: 1) characteristics of the present tank-stored waste, 2) criteria for acceptable long-term waste storage forms, 3) properties of potentially useful solid forms and the associated processes, and 4) evaluation of the potential product forms for Savannah River Plant waste.

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INTRODUCTION

One option for long-term management of Savannah River Plant (SRP) high-level radioactive waste is solidification and storage in a retrievable surface storage facility for 100 years or more. In similar facilities currently being designed for storing high-level waste from commercial reprocessing of power reactor fuel, the waste will be stored as a glass or calcine in steel or stainless steel cylindrical containers that will be cooled by either water or air. Over the last two decades, much work has gone into the development of various solid forms for power reactor waste. The purpose of this report is to examine the applicability of these forms to SRP waste.

The approach used in this study was first to investigate the characteristics of SRP wastes as they now exist and then to define tentative criteria for acceptable waste forms for engineered storage. A literature study was next made of the properties of potentially useful solid waste forms and of the processes that are used to prepare them. An evaluation of each of these waste forms was made by comparing their properties with the criteria for acceptance and by determining if the processes for making them were compatible with SRP waste.

SUMMARY

High-level radioactive waste solutions that originate in the two SRP separations plants are neutralized and stored in mild steel tanks as sludge, supernate, and salt cake. The sludge is composed principally of $Fe(OH)_3$ and MnO_2, but also contains many water-insoluble constituents such as HgO. The salt cake (formed when aged supernate is evaporated) and the supernate contain the water-soluble constituents, principally $NaNO_3$, $NaNO_2$, Na_2SO_4, $NaOH$, Na_2CO_3, and $NaAlO_2$.

^{90}Sr and ^{137}Cs are the major sources of radioactivity, toxicity, and heat generation in SRP wastes for the 100 years or more storage period, although smaller amounts of many other radio-

nuclides such as ^{106}Ru and ^{239}Pu will also be present. The ^{90}Sr resides mainly in the sludge, and the ^{137}Cs in the supernate and salt cake. For the purpose of this study, it has been assumed that the waste contains 200,000,000 Ci each of ^{90}Sr and ^{137}Cs and 17,000 Ci of ^{239}Pu, and that when the salt cake is dissolved and the resulting solution mixed with sludge, 80,000,000 gal of waste result. The average heat generation rate would be approximately 0.008 watt per liter.

The requirement for materials with good thermal properties in the solid form is not nearly as important for SRP waste as it is for power reactor waste because the power density in the former is much lower (by greater than one thousand times). Properties such as low leachability and high strength are more important.

Low leachability is important to the safety of a near-surface engineered storage facility because it reduces the consequences of any potential abnormal situation or accident in which a waste container might be breached and contacted with water. Additional properties of the solid that are important in relation to the safety of engineered storage include:

- Resistance to dispersion in air
- Chemical, thermal, and radiation stability
- Mechanical ruggedness
- Noncorrosiveness to container

Minimum volume is desirable only because it minimizes the cost of engineered storage.

Calcines ($NaNO_3$, Na_2SO_4, Na_2O) have undesirably high leach rates. Glasses are generally suitable products, but the presence of mercury, sulfate, and fluoride in SRP waste will interfere with the production of glasses: mercury will interfere because of volatilization and pluggage, and sulfate and fluoride because of corrosion. Glass production processes operate at high temperatures and require extensive off-gas treatment because of the production of volatile oxides of ruthenium as well as entrained radionuclides.

The leachability of devitrified phosphate glass is marginally acceptable. Borosilicate glasses will not dissolve sulfates, which float to the melt surface in processing and form a highly leachable separate phase. Aluminosilicates are the least leachable of the glasses, but techniques for their production are still under development. Production of glass from SRP waste would be facilitated if the sludge and supernate were separated and the cesium were sorbed on zeolite. Mercury, ruthenium, and possibly some sulfate in the sludge would still pose problems.

Asphalt can probably be used to incorporate radionuclides in sludges or other insoluble materials into highly unleachable solids. However, the asphalt matrix would soften and melt at low temperatures and is flammable. The radiation stability of asphalt beyond 10^9 rads is doubtful.

Cement can be used to solidify both sludge and supernate. The presence of large quantities of soluble salts in the supernate, however, will render the cement very leachable. If the sludge and supernate were separated and the cesium in the supernate was removed by sorption on zeolite, the sludge and the zeolite could be incorporated in the proper type of cement to yield a product of very low leachability. Such products could probably meet other anticipated criteria such as mechanical ruggedness, non-corrosiveness to the container, etc. Solidification with cement involves well-known low temperature mixing operations.

CHARACTERISTICS OF SAVANNAH RIVER PLANT WASTE

Origins

Most of the radioactive waste at SRP originates in the two separations plants; some waste is produced in the reactor areas, laboratories, and peripheral operations. The principal processes employed in the separations plants have been the Purex and the HM* processes, but others have been used to process a variety of fuel and target elements. The Purex process recovers and purifies uranium and plutonium from neutron-irradiated natural uranium. The HM process recovers enriched uranium from uranium-aluminum alloys used as fuel in Savannah River reactors. Other processes that have been employed include: recovery of ^{233}U and thorium from neutron-irradiated thorium, recovery of ^{237}Np and ^{238}Pu, separation of higher actinide elements from irradiated plutonium, and recovery of enriched uranium from stainless steel-clad fuel elements from power reactors. Each of these processes produces a characteristic waste.

Some processes at SRP incorporate a chemical decladding step to remove the protective aluminum jackets from fuel and target elements. Furthermore, many chemicals have been used in the separations processes. Hence, SRP radioactive waste contains large amounts of many different nonradioactive materials. The origin of much of this material will be illustrated by brief descriptions of the Purex and HM processes.

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* Process for recovering uranium from an aluminum-enriched uranium alloy.

In the Purex process, the aluminum cladding of the uranium metal fuel elements is dissolved in a solution of sodium hydroxide and sodium nitrate. The resulting solution (coating waste) contains only small amounts of radionuclides and is transferred to low-level uncooled waste tanks for storage. The irradiated uranium is then dissolved in nitric acid; at times a head-end step is used in which some of the ^{95}Zr and ^{95}Nb is removed by sorption on freshly precipitated manganese dioxide. The uranium and plutonium are separated from the fission products and each other by two cycles of solvent extraction with tri-n-butyl phosphate (TBP). During the solvent extraction processes, chemicals such as sodium nitrite and ferrous sulfamate are added to adjust the oxidation state of plutonium. These chemicals later appear in neutralized waste as sodium nitrate, sodium sulfate, and ferric hydroxide. The waste from the first cycle of solvent extraction (high-level waste**) contains the bulk of the fission products and small amounts of uranium, plutonium, and higher actinide elements. This waste is evaporated to reduce its volume, neutralized with sodium hydroxide, and transferred along with a slurry of the head-end manganese dioxide to cooled, high-level waste tanks made of mild steel. The waste from the second cycle, which contains only low levels of radioactivity, is also evaporated and neutralized but is transferred to either cooled or uncooled tanks, depending on the activity level. The uncooled tanks are also fabricated of mild steel.

In the HM process, fuel elements consisting of uranium-aluminum alloy clad in aluminum are dissolved in nitric acid with the aid of mercury as a catalyst. The uranium is recovered and decontaminated from fission products by two cycles of solvent extraction with TBP. Additional aluminum is added in the HM process to enhance the extraction of uranium; this adds considerably to the waste volume. The high-level and low-level wastes are evaporated, neutralized, and transferred to waste tanks as in the Purex process. After neutralization, most of the aluminum nitrate is converted to sodium nitrate and sodium aluminate.

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**High-level refers to wastes that originate in the first solvent extraction cycle and in the head-end step. These wastes initially produce decay heat of 0.04 to 0.4 w/l [0.5 to 5.0 BTU/(hr-gal)]. Low-level wastes have a fission product content of 1/1000 to 1/10,000 that of high-level wastes. Later in this report, the term high-level will be used in connection with power reactor wastes to refer to wastes with power densities of about 100 w/l.

Waste Management Practices

After waste is neutralized and transferred to tanks, manganese dioxide, ferric hydroxide, and other insoluble hydroxides and hydrous oxides (including those of fission products) settle to form a sludge layer. The volume of the sludge is about 10% of the total waste volume. The high-level wastes remain in cooled tanks for several years until the short-lived fission products decay. The supernatant solutions are then transferred to other tanks that contain little sludge. In recent years, aged supernatant solutions have been evaporated and returned to cooled tanks where much of the salt crystallizes. This procedure reduces the waste volume and conserves tank space; it also renders the waste less mobile and hence safer than if all liquid. Thus, the waste tanks contain sludge, water-soluble crystalline salts, and supernatant solutions. In further discussions on chemical and radiochemical composition, the crystalline salts and the supernate will be considered together because removal from the tanks will require dissolution of the salt in water and mixing with the existing supernate.

Transfers of waste from one tank to another have resulted in the mixing of the sludges and supernates of high- and low-level waste. Thus, for long-term management purposes the distinction between high- and low-level waste at SRP has almost vanished.

Chemical Composition

A completely valid generalization about the composition of SRP waste cannot be made because large variations in the composition of both the sludge and the supernate occur from tank to tank, within a tank, and with time. For present purposes, it is sufficient to list the components that are present and estimate their maximum and average concentrations. The major chemical components of the wastes are $NaNO_3$, $NaNO_2$, $NaOH$, Na_2CO_3, Na_2SO_4, $NaAlO_2$, $Fe(OH)_3$, and MnO_2. The iron and manganese compounds are insoluble in an alkaline medium and are found in the sludge layer. If there is insufficient $NaOH$ present to keep all of the aluminum in solution, a portion will precipitate as $Al(OH)_3$. The other compounds are found mainly in the supernate. An estimate of the average chemical composition of the waste is given in Table I. This composition assumes that all the sludge constituents are uniformly distributed through the waste, and all the supernate, sludge, and salt cake from all of the storage tanks are blended with enough water to dissolve the salt cake.

TABLE I. Average Chemical Composition of Waste

Constituent	Concentration, M
$NaNO_3$	2.2
$NaNO_2$	1.1
$NaAlO_2$	0.8
$NaOH$	0.5
Na_2CO_3	0.3
Na_2SO_4	0.3
$Fe(OH)_3$	0.15
MnO_2	0.02
NaF	0.02
Na_3PO_4	0.01
$NaCl$	0.01
KNO_3	0.01
$Ca(OH)_2$	0.006
$Hg(OH)_2$	0.002
$Mg(OH)_2$	0.001
NaI	0.0002

Table II lists elements that have been detected or are known to be in the sludge and estimates their maximum concentration. Table II does not represent an average sludge or even any particular one. Many of the components listed will not be present in most sludges. The concentrations shown are the highest found in any sludge or the highest calculated to be present from the amount of material known to have been placed in waste tanks.

Radioactivity and Toxicity

When waste is first transferred into the storage tanks, it contains a number of short-lived isotopes that make the waste highly radioactive. These nuclides decay on standing, rendering the waste less active. It is presumed that the waste will be at least ten years old before it is solidified, and thus only radio-nuclides that contribute significantly to the activity at that and later times have to be considered.

TABLE II. Maximum Concentration of Various Elements in Sludge

Element	Centrifuged Sludge, g/ℓ
Aluminum	53.6
Barium	6.1
Calcium	4.5
Cerium	4.7
Chlorine	0.2
Chromium	1.2
Cobalt	0.1
Copper	1.8
Iron	75.0
Lanthanum	1.9
Lead	11.1
Magnesium	1.3
Manganese	45.0
Mercury	30.0
Molybdenum	0.3
Neodymium	11.6
Nickel	21.0
Phosphorus	1.1
Potassium	0.2
Praseodymium	1.9
Promethium	0.9
Ruthenium	1.8
Silicon	4.0
Silver	0.045
Sodium	50.0
Sulfur	2.9
Tin	0.4
Titanium	0.3
Uranium	86.6
Yttrium	0.7
Zirconium	5.0

Table III contains a list of the radionuclides of concern in aged waste, their half-lives, the expected activity from each after ten years aging, and the relative toxicity of each.* The activities and relative toxicities shown in the table were calculated from data and by the procedure given in Reference 1. The isotopes are listed in order of their relative toxicity; mercury and nitrate-nitrite are included because their toxicity is actually greater than that of many of the radioactive nuclides.

^{90}Sr and ^{137}Cs are by far the most active and hazardous radionuclides. Based on maximum permissible concentrations given in Reference 1 for public zone water, strontium is more than fifty times as hazardous as cesium. Strontium will be found primarily in the sludge, while cesium will be primarily in the supernate. However, sludge is a gelatinous precipitate containing trapped supernate, and about 10% of the cesium will therefore accompany the sludge. Of the other elements, promethium, plutonium, cesium, samarium, mercury, zirconium, and terbium will probably be in the sludge; iodine, technetium, selenium, and niobium will probably reside in the supernate; and ruthenium and palladium will probably be distributed between the two phases.

Heat Generation

The heat release that accompanies radioactive decay causes the waste to be self-heating. The heat generation in fresh wastes may be as high as 0.4 w/l; over 90% of the heat generation is associated with the sludge because nearly all of the fission products except cesium and ruthenium are insoluble in alkaline solution. ^{137}Cs and ^{90}Sr are each present at an average concentration of approximately 0.66 Ci/l (2.5 Ci/gal). The average heat generation rate due to these nuclides is 0.0076 w/l [0.096 BTU/(hr-gal)], 60% of which occurs in the sludge.

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* Relative toxicity is defined as the ratio of the concentration of a given isotope in the waste to its maximum permissible concentration in public zone water. This analysis assumes that every radionuclide in the waste is distributed homogeneously and that the total volume of waste is 8 x 10^7 gal.

TABLE III. Amounts of Activity in Stored Waste and
Relative Toxicity Due to Radionuclides and Other Components

Isotope	Half-Life, years	Total Activity,[a] Ci	Relative Toxicity[b]
^{90}Sr	28.8	2.0×10^{8}	2×10^{9}
^{137}Cs	30.0	2.0×10^{8}	3×10^{7}
^{147}Pm	2.6	6.7×10^{7}	1×10^{6}
^{106}Ru	1.0	3.5×10^{5}	1×10^{5}
^{238}Pu	89	1.7×10^{5}	1×10^{5}
^{244}Cm	18.1	1.2×10^{5}	6×10^{4}
^{151}Sm	90	4.6×10^{6}	4×10^{4}
Hg (Inactive)	—	——	2×10^{4}
^{239}Pu	2.4×10^{4}	1.7×10^{4}	1×10^{4}
$NO_3^- + NO_2^-$ (Inactive)	—	——	6×10^{3}
^{129}I	1.6×10^{7}	31	1.7×10^{3}
^{99}Tc	2.1×10^{5}	3.0×10^{4}	300
^{79}Se	7×10^{4}	280	120
^{135}Cs	2.0×10^{6}	3.1×10^{3}	100
^{126}Sn	10^{5}	1×10^{3}	100
^{93}Zr	9.5×10^{5}	6.7×10^{3}	30
^{94}Nb	2×10^{4}	3.2	13
^{107}Pd	7×10^{6}	26	3
^{158}Tb	150	0.5	4×10^{-5}

a. These quantities were assumed as a basis for this report and do not represent the actual quantities (classified) to be processed
b. Ratio of concentration in waste to maximum permissible concentration in public zone water.

CRITERIA FOR ACCEPTABLE WASTE STORAGE FORMS

To provide a basis for evaluating the applicability of various solid waste forms for engineered storage, properties of solid waste forms related to the safety and economy of an engineered storage facility were identified and evaluated. This evaluation provided tentative criteria for the properties of solid waste forms; these criteria, however, give only the approximate magnitude desired for these properties and are not definitive requirements.

In a recent article, Schneider[2] listed the properties that are considered of primary importance to the safety or economy of solidified power reactor wastes. These are:

- High thermal conductivity
- Low leachability
- Good chemical and radiation stability
- Mechanical ruggedness
- Noncorrosiveness to container
- Minimum volume
- Minimum cost

Each of these properties will be discussed as they relate to the storage of SRP wastes. For the purposes of this discussion, it is assumed that the SRP storage facility will house cylindrical containers of waste cooled by air and/or conduction to the ground.

Thermal Conductivity

High thermal conductivity is not nearly as-important for SRP waste as it is for waste from power reactors. The power density in solidified power reactor waste is expected to be about 100 w/l.[3] Solidified SRP wastes, because of the large amounts of inert material, will have an average power density of only about 0.008 w/l (based on 2×10^8 Ci each of ^{137}Cs and ^{90}Sr in 8×10^7 gal).

High thermal conductivity is necessary in solidified power reactor wastes to keep the centerline temperature of cylinders below the melting point. The steady-state difference between the centerline and wall temperature $(T_c - T_w)$ of a self-heating cylinder is given by the equation:[4]

$$T_c - T_w = \frac{Ar^2}{4K}$$

where

A = heat generation rate/unit volume,

K = thermal conductivity, and

r = radius of the cylinder

A typical cylinder of glass made from power reactor waste[2] might have a radius of six inches (15 cm), a thermal conductivity of 1 Btu/(hr-ft-°F) or 0.0041 cal/(sec-cm-°C), and a power density of 100 w/l or 0.024 cal/(sec-cm^3), so that T_C-T_W = 330°C. SRP waste with a power density of 0.008 w/l made into the same glass would have a centerline to wall temperature differential, T_C-T_W, of 0.027°C. Even if the SRP waste (homogenized) were concentrated ten times and placed in a matrix with a thermal conductivity one-tenth that of glass, T_C-T_W would be only 2.7°C. High thermal conductivity is therefore not of primary importance with SRP waste unless the activity were concentrated by one thousand times.

Thermal stability is a more important requirement of solid forms for SRP waste than is high thermal conductivity. Thermal stability implies the ability of the solid form to withstand over long time periods the temperatures attained due to its own heat generation, or the ability to withstand higher temperatures that could be caused by external fires.

Leachability

Low leachability is important in case of an accident. Under normal operating conditions, the solidified waste would remain in its containers out of contact with water. For waste to be leached, the containers must be ruptured and the contents must come in contact with water, as in an explosion followed by a flood or rainstorm. Low leachability will improve safety by reducing the consequences of a major accident. With low-leachable forms, more time is available to take remedial action after an accident before activity release exceeds an acceptable level; as a corollary, the magnitude of an accident that can occur and not release unacceptable amounts of activity is increased.

An attempt was made to quantify these factors by relating leach rate to: 1) the amount of ^{137}Cs and ^{90}Sr activity released in a severe accident, 2) the time available to react to a severe accident before excessive amounts of activity are released, and 3) the numbers of containers that must be ruptured in a severe accident before releasing excessive amounts of activity. Pertinent equations are derived in the Appendix.

Leach rates are usually expressed in g/(cm^2-day). This definition presumes that the material being leached is uniformly distributed through the matrix and that it enters solution by dissolution of the matrix material. This presumption is not strictly true because leach rates usually decrease with time of exposure to water and depend on the substance being leached.

However, leach rates determined after long-exposure periods tend to be independent of time and less dependent on the substance being leached. [5,6] To a first approximation it may be assumed, therefore, that leaching depends only on the dissolution of matrix material and that leaching occurs at a constant rate.

If the solidified waste is assumed to be in the form of cylinders of initial radius r_0 and of sufficient length that end effects can be ignored, the radius r of the cylinder at time T after immersion in water is given by the expression:

$$r = r_0 (1-\beta T) \tag{1}$$

$$\beta = \frac{L}{\rho r_0}$$

where

L = leach rate and

ρ = density of the solid

The amount of activity in the environment, N_e, at the time T after immersion, caused by leaching from the cylinder is given by the expression:

$$N_e = N_0 \, 2\beta T \, (1 - \frac{\beta T}{2}) e^{-\lambda T} \tag{2}$$

where

N_0 = the total activity originally in the cylinder and

λ = decay constant of isotope involved.

The quantity β^{-1} is the lifetime of the cylinder, i.e., the time at which r goes to zero. The activity in the environment, N_e, in equation (2) goes through a maximum at time T_{max}.

$$T_{max} = \lambda^{-1} + \beta^{-1} - \sqrt{\lambda^{-2} + \beta^{-2}}$$

For sufficiently large values of β^{-1}, T_{max} approaches λ^{-1}.

Table IV contains the relations between leach rates and quantities, calculated from the above equations, that are directly related to safety. The first column contains leach rates in $g/(cm^2\text{-day})$. The range shown covers the leach rates of solid forms produced by present technology. The second column contains the lifetime in years of a cylinder exposed to water continuously, assuming the density to be 2 g/cm^3 and the initial radius r_0 = 30 cm

(2 ft in diameter). This is the size of waste form that might conveniently be made for SRP waste. Column 3 contains the maximum ^{137}Cs-^{90}Sr activity in Ci (N_e at T_{max}) leached from cylinders of the above dimensions, assuming all the containers are breached, and the initial activity of the SRP waste is 4×10^8 Ci. For leach rates of 10^{-3} g/(cm^2-day) or smaller, T_{max} is about 40 years.

Column 4 contains the amount of ^{137}Cs-^{90}Sr activity leached if the waste were involved in an accident in which all the containers are breached and the contents exposed to water for 150 days.

Column 5 gives the time required to leach 1000 Ci (500 Ci of ^{90}Sr and 500 Ci of ^{137}Cs)* if all containers are breached and exposed to water. This is essentially the time available to operating personnel to take remedial action before the 1000 Ci release would occur in the event of an accident resulting in the immersion of all waste containers.

TABLE IV.   Relation Between Leach Rates and Quantities Directly Related to Safety

Leach Rate, g/(cm²-day)	β⁻¹ Lifetime, years	Maximum Sr-Cs Activity In the Environment, Ci	Sr-Cs Activity Leached in 150 Days, Ci	Time to Leach 1000 Ci	Percent of Containers Breached to Leach 10³ Ci in 150 Days
1	0.17	4.0×10^8	4×10^8	6.6 sec	0.0003
10^{-1}	1.7	3.8×10^8	2×10^8	66 sec	0.0006
10^{-2}	17	2.7×10^8	2×10^7	10 min	0.005
10^{-3}	1.7×10^2	6.6×10^7	2×10^6	1.8 hr	0.05
10^{-4}	1.7×10^3	7.5×10^6	2×10^5	18 hr	0.5
10^{-5}	1.7×10^4	7.6×10^5	2×10^4	7.6 days	5.0
10^{-6}	1.7×10^5	7.6×10^4	2×10^3	76 days	50
10^{-7}	1.7×10^6	7.6×10^3	2×10^2	3.1 yr	100
10^{-8}	1.7×10^7	7.6×10^2	2×10^1	∞	100

* 1000 Ci was chosen as a release that would result in consequences significantly less than present guidelines for accident conditions. Based on calculations of Evans, Marter, and Reinig[7] an estimated 1000-curie release would lead to a whole body dose of less than 0.2 rem to an individual in the most exposed population at Savannah, Georgia. This dose is less than 1% of the present 25 rem guidelines for accident situations.[8]

Column 6 contains the percentage of the containers that could be breached and exposed to water for 150 days before leaching 1000 Ci. These numbers relate the magnitude of an accident to the potential consequences.

With leach rates of 10^{-8} g/(cm^2-day) or less, it is highly improbable that an accident will lead to serious consequences unless the waste forms are broken into small pieces. It therefore appears to be unprofitable to attempt to prepare less leachable forms.

With leach rates in the range from 10^{-8} to 10^{-6} g/(cm^2-day), the waste could survive severe accidents with little consequence. For example, with a leach rate of 10^{-6} g/(cm^2-day), all of the containers could be ruptured and all of the waste submerged in water for 76 days before 1000 Ci of ^{137}Cs-^{90}Sr activity would be leached. This should be ample time to take corrective action.

Leach rates of 10^{-5} to 10^{-4} g/(cm^2-day) provide protection against smaller accidents that have a higher probability. For example, at 10^{-4} g/(cm^2-day) all of the containers could be breached and the contents submerged for 18 hours before 1000 Ci of activity would be leached, or 10% of the containers could be breached and the contents exposed to water for 7.6 days before 1000 Ci would be leached.

Chemical and Radiation Stability

Good chemical and radiation stability are necessary if waste forms are to retain their original properties and if overpressurization of the container by radiolytic gas is to be prevented. The requirement for radiation stability is less stringent for SRP waste than for power reactor waste because of the lower power density of SRP waste. Solidified SRP waste will be required to survive an integrated dose of about 10^9 rad not correcting for concentration or dilution during fixation.

Mechanical Strength

Mechanical ruggedness is desirable to reduce the probability of waste forms breaking into smaller pieces. Breakage would result in more difficult retrieval and increased leach rates because of increased surface area; also it could lead to airborne dispersion if fine powders were formed. Although mechanical ruggedness is primarily of importance during transfer, it is also important after the waste is in storage to lessen the consequences of accidents such as airplane crashes or earthquakes. Mechanical strength is a more important property for SRP wastes than is high thermal conductivity.

Corrosiveness to Containers

Noncorrosiveness of waste to containers is necessary because integrity of the primary container is essential to the safety and feasibility of engineered storage. Corrosion rates will likely be lower with SRP wastes than with power reactor wastes because of the lower heat rate and thus lower temperature of SRP wastes.

Minimum Volume

Minimum volume is closely related to minimum cost and does not increase the safety of the stored waste. Actually, minimum volume wastes are more hazardous because of their high heat generation rate. A primary concern with high-level wastes from power reactors is the consequence of loss of cooling. A minimum volume waste with a power density of 100 w/l will heat at the rate of about 2000°C/day if not cooled; a more dilute waste, such as SRP waste with a power density of 0.008 w/l, will heat at a maximum initial rate of about 60°C/year. The minimum volume waste would melt rapidly after cooling is lost; the more dilute waste would not.

PROPERTIES OF POTENTIALLY USEFUL SOLID FORMS AND ASSOCIATED PROCESSES (From Literature)

The properties of solid waste forms reported in the literature and relevent to the present discussion are shown in Table V. The various forms that might be applicable to SRP waste fall into three categories: calcines, glasses and ceramics, and intermediate-level forms.

Calcines

Calcines are formed by simply removing water from the waste and perhaps thermally decomposing nitrates or converting to another anhydrous salt. The product that could be produced from SRP wastes would be mainly $NaNO_3$, Na_2O, Na_2SO_4, or $NaAlO_2$. Of these products, only $NaNO_3$ with its low melting point could be converted easily into a monolith; the others would probably exist as granules. All calcines that could be produced from SRP waste are characterized by high leachability.

Calcines are produced by pot calcination, spray calcination, or by the fluidized bed method.[2] The first two methods appear to be completely compatible with SRP supernates. However, there may be problems with mercury during processing of SRP sludges, because all mercury compounds decompose above 400°C; volatilization of metallic mercury would require special off-gas systems.[2]

TABLE V. Properties of Various Solid Waste Forms

Type of Solid	Form	Leachability, $g/(cm^2-day)$	Hardness	Friability	Reference
Calcines					
Low temperature melt $NaNO_3$-NaOH	Monolith Crystals	1 to 10^{-1}	Moderate	Moderately tough	
Pot calcine Na_2O	Calcine Cake Scale	1 to 10^{-1}	Soft	Crumbly	2,4
Fluid bed calcine Na_2SO_4	Granular	1 to 10^{-1}	Moderate	Moderate	2
Glasses and Ceramics					
WSEP phosphate glass	Monolith Glass	6×10^{-7} to 4×10^{-6}	Hard	Brittle	2,4
WSEP phosphate glass (devitrified)	Monolith Crystals	3×10^{-4} to 5×10^{-3}	Hard	Brittle	2,4
WSEP phosphate ceramic	Monolith Microcrystalline	6×10^{-5} to 8×10^{-3}	Hard	Tough	2,4
WSEP borosilicate glass	Monolith Glass	9×10^{-6} to 5×10^{-5}	Hard	Very brittle	4
French borosilicate glass	Monolith Glass	1×10^{-7} to 3×10^{-7}	?	?	9
Fingal phosphosilicate glass	Monolith Glass	3×10^{-7} to 1×10^{-6}	Hard	Brittle	5,10
Fingal phosphosilicate glass (Devitrified)	Monolith	3×10^{-6} to 1×10^{-5}	Hard	Brittle	5,10
Canadian alumino silicate nephelene-syenite-CaO glass	Monolith	3×10^{-8} to 2×10^{-7}	Hard	Brittle	11
Thermite alumino silicate glass	Monolith	3×10^{-8} to 4×10^{-7}	Hard	?	12
ARHCO thermalt alumino silicate glass	Monolith	1×10^{-7} to 2×10^{-7}	Hard	?	13
Intermediate-Level Forms					
Asphalt (Bitumen)	Monolith	1×10^{-4} to 3×10^{-4a}	Moderate	Tough	14,15
Cement	Monolith	10^{-1} to 2×10^{-9}	Hard	Tough	16,17

a. Asphalt incorporating 20 to 40 wt % $NaNO_3$.

Fluidized bed calcination is not compatible with wastes containing sodium nitrate because the low melting point of that salt causes particles in the bed to stick together. This process could be used if the waste were converted to the sulfate or aluminate.

Calcination methods, as do all high-temperature procedures, require elaborate off-gas treatment systems because of volatile ruthenium oxides and entrained matter. A solid waste form might be produced by simply evaporating the water and heating to melt sodium nitrate at a sufficiently low temperature to avoid ruthenium volatilization.

Glasses and Ceramics

Glasses and ceramics are produced by adding glass-forming agents to the waste and heating to form a melt, which is subsequently cast as a monolith and cooled. Glasses are generally characterized by low leachability, high thermal conductivity, hardness, and high friability.

There are three glasses that have been developed for waste fixation: phosphate, borosilicate, and aluminosilicate. Leachability generally decreases in the listed order; however, there are large variations within each class because of the wide variation of chemical composition possible. In general, low leachabilities are associated with high melting points.

All glasses are subject to a phenomenon known as devitrification (probably crystallization), which generally causes an increase in leachability. This problem is particularly severe in phosphate glasses because leachability can increase a thousandfold following devitrification.[6] Devitrification usually occurs when glasses are held at high temperature for prolonged periods. Since this is the usual condition for high-level wastes from power reactors, devitrification is almost certain to occur. Although SRP wastes would have much lower temperatures, it must be presumed that they would also devitrify in the very long storage periods required of them.

Glasses are produced by a variety of methods[2,3,9,18,19] that may differ in detail, but consist mainly of adding glass-forming agents to the waste before or after evaporation of the water and heating to a sufficiently high temperature to form a melt that is cooled to a glass. The process may be continuous as in the spray melt process or batch as in the pot glass process. The two products that have been studied in detail are phosphate and borosilicate glasses; aluminosilicate glasses are produced by methods[12,13] that have not been developed sufficiently to be of use at present.

Direct conversion of SRP waste to either phosphate or borosilicate glass would be difficult because of the presence of mercury, sulfate, and fluoride.[2,3] Mercury may require a special off-gas system, and sulfate and fluoride may cause excessive corrosion of the process equipment. In the case of boro-

silicate glasses, sulfates separate from the melt as a phase
that floats; such a phase is highly leachable after the glass
has cooled.

Intermediate-Level Forms

Forms for intermediate-level wastes are included in the
present discussion because these forms may be applicable to SRP
wastes. As already concluded, some of the properties required
for high-level wastes (high thermal conductivity, and the ability
to withstand high temperature and radiation doses) are not neces-
sary for SRP waste. Thus, solid forms for intermediate-level wastes
may be able to withstand the temperatures and radiation fields
likely to be produced by SRP wastes. Although a large number of
solidification schemes have been proposed for intermediate-level
waste solidification, recent work has concentrated on the use of
asphalt (bitumen) and cement.

Asphalt

Asphalt is currently used in Europe[15,20,21] to fix low-
and intermediate-level wastes, incorporating sludges as well as
sodium nitrate from evaporator concentrates. Up to 60% of
soluble salts ($NaNO_3$ + Na_2CO_3) have been incorporated into
asphalt.[15] A typical asphalt containing about 20% soluble salts
has a leachability of about 5×10^{-4} g/(cm^2-day);[14,15] those
containing more soluble salts are more leachable. Those that
contain less than 1% soluble matter, however, are "completely"
resistant to leaching.[15]

While incorporation of up to 60% $NaNO_3$ into asphalt would
seem to yield an explosive mixture, this does not appear to be
the case. Although incorporation of 40 to 60% $NaNO_3$ into asphalt
increases the flammability (samples spontaneously ignite at
330°C, compared to 450°C for untreated asphalt), the mixture
will not detonate.[14] There are indications, however, that
MnO_2-$NaNO_3$ combinations will lower the temperature of spontaneous
ignition dangerously.[15]

Russian workers[20] have studied a procedure in which radio-
nuclides are absorbed on vermiculite or zeolite, which is then
incorporated into bitumen. They report that very little activity
is leached by water, but do not give values for leachability.

From a production point of view asphalt appears to be quite compatible with SRP wastes. Sludges and even sodium nitrate-bearing wastes have successfully been incorporated into asphalt.[14,15,21,22] In processing, the waste is mixed with emulsified asphalt and evaporated in a wiped film evaporator at about 160°C. The product containing molten asphalt and anhydrous sludges and salts is then drained into a suitable container where it solidifies. There appears to have been little difficulty with the process, although one fire was reported[15] when sodium nitrate and manganese dioxide were simultaneously incorporated into asphalt in a laboratory test. Problems of mercury volatilization may occur, but have not been reported.

Cement

Cement has been studied extensively for the fixation of radioactive wastes.[15,16,17,22,23] It has been or is being used at several locations for fixing low- and intermediate-level wastes.[14,18-21] With few exceptions, solidification with cement consists simply of mixing liquid wastes containing large concentrations of soluble salts with cement and allowing the mixture to set. These salt-bearing cements are naturally highly leachable, particularly for highly soluble radionuclides such as ^{137}Cs. Russian workers[17,24] have measured leachability to be between 10^{-1} and 10^{-2} g/(cm²-day). Blanco,[23] by inference, reported leachabilities for sodium and cesium between 7.5×10^{-3} and 1.5×10^{-2} g/(cm²-day). (He actually reported that the leachability of asphalt was 1.5×10^{-4} g/(cm²-day) and that cement containing the same amount of waste was 50 to 100 times more leachable.) Other workers[25-28] reported that from 4.8% to 15% of the activity was leached from salt-bearing cemented wastes in 15 to 42 days, but they did not calculate leachabilities.

The leachability of cement containing no soluble salts is much lower than that of cement containing salts. French workers[29] investigated the leaching of radioactive sludges incorporated in cement and reported data from which were calculated average leachabilities of 2×10^{-4} to 4×10^{-5} g/(cm²-day) over a period of 45 days. Their data suggest that these rates will decrease substantially with time. Italian workers[30] reported data on leaching of mixed fission products from different types of cement, from which leach rates were calculated. Portland cement gave initial leachabilities of 1.7×10^{-3} g/(cm²-day), which dropped to 4.6×10^{-5} g/(cm²-day) after 119 days immersion in water. Pozzolanic cement gave an initial rate of 7×10^{-4} g/(cm²-day), which dropped to 2.6×10^{-6} g/(cm²-day) after 119 days.

Leach rates determined from leaching of actinides are smaller than those determined with mixed fission products. Workers at Los Alamos[16,31] incorporated wastes containing plutonium and americium as well as soluble salts in cement mortars and studied their leaching properties. Average leach rates calculated from these data are 1.1×10^{-7} g/(cm^2-day) during the first year. The instantaneous leach rate after about a year was 2×10^{-9} g/(cm^2-day). These values are probably smaller than the actual dissolution rate of cement because of adsorption of plutonium and americium on cement surfaces. The dissolution rate of concrete in the SRP disassembly basin is estimated to be 4.7×10^{-5} lb/(ft^2-day), or 2.3×10^{-5} g/(cm^2-day). The preceeding data indicate that, under some conditions, the leach rate of cement can be as low as that of glass.

Portland cement is thermally stable up to 300°C; prolonged heating at 500°C, however, causes a 50% or more loss in compressive strength, and complete failure occurs at 900°C.[32] It is highly resistant to gamma radiation; reactor shields composed of Portland cement showed a loss of compressive strength of only one half after an exposure of 3×10^{18} roentgens.[33]

From a production standpoint, cement is probably the most-convenient material with which to solidify waste; all that is required is that the material to be solidified is mixed with cement and water and the mixture is cast into the desired monolithic shape and allowed to set. Because cement mixing is a low-temperature process, there should be none of the off-gas treatment problems or corrosion problems associated with the high-temperature process for making glass.

EVALUATION OF PRODUCT FORMS FOR SRP WASTE

In this section, the waste forms previously discussed will be evaluated for application to SRP wastes. Two different bases will be used for the evaluation. First, it will be assumed that the sludge and supernate will be mixed together and converted to a solid form. In the second case, it will be assumed that the sludge and supernate are segregated and that the supernate is further decontaminated to remove the bulk of the cesium.

Combined Wastes

Calcines have the poorest properties of the solid waste forms considered. They are highly leachable, porous (except for the NaNO$_3$ low-temperature solid), and friable so that they provide no barrier to dispersion of activity via water or air. McElroy et al.[34] showed that 25% of the cesium in a calcine

made by the pot calcination process was leached within a week. Of the calcines, the low-temperature solidification product ($NaNO_3$) is probably the best (assuming radiation stability is adequate) because it can be cast into monoliths.

Calcines can be made from SRP wastes by a variety of processes. Large and expensive off-gas systems will be required to remove volatilized ruthenium and particulate matter. If the high-temperature calcination processes are used to convert SRP sodium nitrate wastes into sodium oxide, sulfate, or aluminate, means will be required to dispose of the tons of potentially contaminated nitric acid or oxides of nitrogen produced. Mercury in SRP sludges might require special off-gas systems.

Phosphate glass and ceramic are products of only moderate quality. The leach rate of the ceramic prepared by the spray melt process is initially high [10^{-3} to 10^{-4} g/(cm²-day)]; that of the glass, while initially low, becomes high when the glass devitrifies. These materials are superior to calcines because of their lower leach rates and because they form monolithic solids.

The phosphate products can be made with wastes containing sulfate, although its presence causes some problems. The introduction of appropriate chemicals can reduce the volatilization of sulfate in the spray melt process to less than 5%, but this residual sulfate as well as the fluoride in SRP waste would cause corrosion in the off-gas system; the mercury would require special design to avoid pluggage.[34]

Borosilicate glass is one of the best products that has been produced by well-developed technology. The leach rate is very low [10^{-6} to 10^{-7} g/(cm²-day)], although the material is very fragile and shatters easily. Borosilicate glass unfortunately cannot be made from wastes containing sulfate because of the formation of a separate phase that floats to the top of the melt and is very leachable. Even if adequate borosilicate glass could be made from SRP wastes, the mercury, fluoride, and ruthenium would present the same process problems as phosphate glass.

Aluminosilicates are probably the most insoluble materials that can be produced from waste. Unfortunately, the technology for their production has not been developed to the point where their compatibility with SRP waste can be adequately assessed. Since aluminosilicates melt at higher temperatures than the other glasses, it is probable that the same volatility problems would occur as with other high-temperature processes.

Asphalt can easily be incorporated into SRP waste to produce a product with a leach rate of about 10^{-4} g/(cm^2-day), which might be adequate. However, flammability of asphalt may make its use unacceptable to the public even though it is presently used in Europe to fix intermediate-level waste. It is also doubtful that asphalt could withstand the radiation dose (10^9 to 10^{10} rads) expected from SRP wastes.

Cement has adequate radiation stability, and its thermal stability is also adequate provided that the temperature does not greatly exceed 300°C. The presence of large amounts of soluble salts, however, renders cement physically weak, highly leachable, and therefore unsuitable for fixation of combined wastes.

There does not appear to be any entirely satisfactory process available to solidify combined SRP wastes. Mercury in the sludge would pose problems in all of the high-temperature processes, while sulfate and fluoride in the supernate would interfere with the glass-making processes because of corrosion or incompatibility with the product. Asphalt, which is already flammable, is rendered more so by the nitrates in the supernate: Cement is rendered too leachable by these salts.

Segregated Waste

Interference with most waste solidification schemes by the large volume of soluble salts in SRP supernate prompted consideration of alternatives involving partial segregation of the wastes. The simplest procedure is to separate the sludge from the supernate. This isolates much of the toxicity hazard (all of the ^{90}Sr and ^{239}Pu) in a relatively low volume and in a material of low solubility. Half of the activity (all of the ^{137}Cs) will remain in the supernate. However, the cesium can be removed from the salt-bearing supernate by sorption on ion exchange resin or zeolite,[34,35] and can be stored on zeolite. Thus, there will be three waste fractions: the sludge containing almost all of the strontium and the plutonium, zeolite containing almost all of the cesium, and the supernate containing the soluble salts but little long-lived radionuclides (the principal radionuclide remaining in the supernate will be ^{106}Ru).

Because the above procedures concentrate the bulk of the activity in insoluble solids, fixation should be simpler. Because zeolite is an aluminosilicate, it should be compatible with aluminosilicate, borosilicate, and perhaps phosphate glasses. It could also be incorporated as an aggregate in concrete. The sludge, however, would contain mercury and perhaps some sulfate, which present problems in high-temperature processes.

Because soluble salts are absent, sludge and zeolite could be incorporated into concrete to obtain a material with leach rates between 10^{-5} and 10^{-6} g/(cm^2-day). These rates are nearly as low as any obtained with glass, and much lower than some (phosphate glasses for example). Concrete mixing poses none of the production problems (mercury and ruthenium volatilization) of the high-temperature processes. Furthermore, concrete is physically strong and has proved its durability in Roman buildings and marine works that have lasted nearly two millennia.[32]

Sludge and zeolite could also be incorporated into asphalt, but fire hazards and uncertain radiation stability would seem to make asphalt as unacceptable for segregated waste as for salt-bearing waste.

A summary of the properties of the various solid waste forms and the evaluation of each are given in Table VI.

TABLE VI. Evaluation of Product Forms for SRP Waste[a]

	Various Concretes	Asphalt	Calcines — Sulfate	Aluminate	Oxides	Nitrate (Low-Temperature Solid)	Glasses — Borosilicate	Phosphate	Alumino-silicate
Leachability, g/(cm²-day)	0.1 to 10^{-9b}	$<10^{-6c}$	1 to 10^{-1S}	1 to 10^{-1S}	1 to 10^{-1S}	1 to 10^{-1S}	5×10^{-5} to 1×10^{-7}	4×10^{-5} to 6×10^{-7d}	4×10^{-7} to 3×10^{-6}
Product Form (Surface Area/Unit Volume)	Monolith (low)	Monolith (low)	Granular (high)[S]	Granular (high)[S]	Granular (high)[S]	Monolith (low)	Monolith (low)	Monolith (low)	Monolith (low)
Mechanical Strength	Good	Poor (soft)[D]	Poor[S]	Poor[S]	Poor[S]	Fair to Good	Fair (brittle)	Fair (brittle)	Good
Dispersibility in Air	Low	Low	High[D]	High[D]	High[D]	Low	Low	Low	Low
Radiation Stability	Adequate	Unknown (good to ~10^9 Rads)	Adequate	Adequate	Adequate	Unknown (gases when wet)[D]	Adequate	Adequate	Adequate
Thermal Stability: a. Normal Conditions	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate
b. Fire (<1,000°C)	Dehydrates and loses strength at >400°C[U]	Burns spontaneously at 425°C[S]	Melts at 884°C[U]	Stable	Stable	Decomposes to Nitrogen oxides and Na₂O[D]	Might melt	Might melt	Probably Stable
Corrosiveness to Container	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate	Adequate
Compatibility with SRP Waste	Adequate for salt-free waste	Adequate for salt-free waste	Requires addition of sulfate[D]; Problems with ruthenium volatilization[D]; Possible problems with mercury pluggage[D]	Requires addition of aluminum[D]; Problems with ruthenium volatilization[D]; Possible problems with mercury pluggage[D]	Requires high temperature[D]; Problems with ruthenium volatilization[D]; Possible problems with mercury pluggage[D]	Good	Poor[S]; Sulfates give phase separation and corrosion problems[S]; Hg causes pluggage problems[S]; Fluoride corrosion ruthenium volatilization[S]	Poor[S]; Sulfates give corrosion problems[S]; Hg causes pluggage problems[S]; Fluoride corrosion[S]; Ruthenium volatilization[S]	Technology not developed[S]; High process temperatures[S]; Would expect sulfate, mercury, and ruthenium problems[S]; Would expect cesium volatilization problems[S]
Processing	Low-temperature mixing operation; Simple, well-known technology	Mix and heat to ~160°C in wiped film evaporator; Well-known technology	Higher temperature process[D]; Requires fluid bed, spray, or pot process[D]; Off-gas treatment[D]	Higher-temperature process[D]; Fluid bed, spray, or pot process[D]; Off-gas treatment[D]	Highest calcination[D]; Fluid bed, spray, or pot process[D]; Off-gas treatment[D]	Moderate temperature; Melt and pour after evaporation	High-temperature glass making process[S]; Possibly preceded by fluid bed[S]; Expensive[S]; Off-gas treatment[S]	High-temperature glass making process[S]; Possibly preceded by fluid bed[S]; Expensive[S]; Off-gas treatment[S]	Higher temperature process[S]; Expensive[S]; Technology not developed[S]; Off-gas treatment[S]

a. U = Undesirable
   D = Disadvantage
   S = Significant Disadvantage
b. Higher rates for products high in nitrate.
c. Up to 3×10^{-4} with 20 to 40% NaNO₃.
d. 5×10^{-4} to 3×10^{-3} when devitrified.

APPENDIX
EQUATIONS FOR LEACHING

GENERAL EQUATIONS

A solid is assumed to leach ideally if in a given time period a uniform layer of solid dissolves from the surface, and any substance dispersed in the solid also enters solution in proportion to its concentration in the solid and the amount of solid dissolved.

The time rate of loss of mass of a leaching solid is given by

$$\frac{dm}{dt} = -LA \tag{1}$$

where

m = the mass in grams

t = the time in days

A = the surface area in cm^2

L = the leachability in $g/(cm^2\text{-}day)$

The rate of increase of volume of the solid per unit time is then given by

$$\frac{dv}{dt} = \frac{-LA}{\rho} \tag{2}$$

where

v = the volume in cm^3

ρ = the density in g/cm^3.

Since the solid dissolves uniformly, the volume dissolved in a short period can be represented as the product of the surface area and a uniform displacement vector, X, normal to the surface.

$$V = AX \tag{3}$$

The penetration rate, $\frac{dx}{dt}$, can be obtained by substituting Equation 3 into Equation 2.

$$\frac{dx}{dt} = \frac{-L}{\rho} \text{ cm/day} \qquad (4)$$

One way in which leach rates are measured is to incorporate a radioactive substance into the solid. The fraction f of the activity leached in a given time is measured, and the leachability is calculated as follows:

The increment of volume δV dissolving in a time interval δt is obtained from Equation 2.

$$\frac{\delta V}{\delta t} = \frac{LA}{\rho} \qquad (5)$$

If Equation 5 is divided by the initial volume of the solid, V

$$\frac{1}{V} \frac{\delta V}{\delta t} = \frac{LA}{V\rho} \qquad (6)$$

But $\frac{\delta V}{V} = f$, the fraction of the volume dissolved, which is assumed to be the same as the fraction of the activity dissolved. The leachability can then be calculated:

$$L = \frac{fV\rho}{(\delta t)A} \qquad (7)$$

LEACHING OF WASTE CYLINDERS

Consider a cylinder of initial radius r_0 and of sufficient length that the area of the ends (and thus dissolution of the ends) can be ignored compared to the cylindrical surface. Since the radius, r, of a cylinder is normal to the surface, Equation 4 becomes:

$$\frac{dr}{dt} = \frac{-L}{\rho} \qquad (8)$$

When Equation 8 is integrated, subject to the initial conditions that $r = r_0$ at $t = 0$, the following is obtained:

$$r = r_0 - \frac{L}{\rho} t$$
$$\text{or} \quad r = r_0 (1-\beta t) \qquad (9)$$

where
$$\beta = \frac{L}{\rho r_0} \qquad (10)$$

Since $r = 0$ when $t = \beta^{-1}$, β^{-1} is the life of the cylinders.

ACTIVITY IN THE ENVIRONMENT DUE TO LEACHING

Consider a cylinder of initial radius r_0, density ρ, and leachability L, and which initially contains N_0 curies of activity. Let the cylinder be placed in contact with water at time, t = 0. The rate at which activity accumulates in the environment is the difference between the rate at which it leaches from the cylinder into the environment and the rate at which it decays.

If N_e is the amount of leached activity accumulated at time t, then

$$\frac{dNe}{dt} = C\frac{dv}{dt} - \lambda Ne \qquad (11)$$

where

λ = decay constant

C = the concentration of activity in the cylinder in curies per unit volume at any time,

$\frac{dv}{dt}$ = the rate of decrease of the volume of the cylinder

Since

$$V = \pi r^2 h \qquad (12)$$

$$\frac{dv}{dt} = 2\pi h r \frac{dr}{dt} \qquad (13)$$

But from Equation 9,

$$r = r_0(1-\beta t) \qquad (9)$$

Differentation of Equation 9 and substitution into Equation 13 gives,

$$\frac{dv}{dt} = 2\pi r_0^2 h\beta(1-\beta t) \qquad (19)$$

Therefore

$$\frac{dv}{dt} = 2V_0\beta(1-\beta t) \qquad (15)$$

Substitution into Equation 11 yields

$$\frac{dN_e}{dt} = C2V_0\beta(1-\beta t) - \lambda N_e \qquad (16)$$

But

$$C = \frac{N_0}{V_0} \exp(-\lambda t)$$

Therefore $\qquad \dfrac{dN_e}{dt} = 2N_o\beta(1-\beta t)\exp(-\lambda t) - \lambda N_e$ $\qquad\qquad$ (17)

Equation 17 can be integrated with the initial conditions, $N_e = 0$ when $t = 0$, to give

$$N_e = 2N_o\beta t\left(1 - \frac{\beta t}{2}\right)\exp(-\lambda t) \qquad\qquad (18)$$

CALCULATION OF THE TIME, T_{max}, AT WHICH N_e IS MAXIMUM

If Equation 18 is substituted into 17 and $dN_e/dt = 0$

$$\frac{dN_e}{dt} = 2N_o\beta\exp(-\lambda\, t_{max})\,[1-\beta t_{max} - \lambda(t_{max} - \frac{\beta}{2}\,t^2_{max})] = 0$$

$$\frac{\beta\lambda}{2}\,t^2_{max}(\beta+\lambda) + 1 = 0 \qquad\qquad (19)$$

$$t_{max} = \lambda^{-1} + \beta^{-1} - \sqrt{\lambda^{-2} + \beta^{-2}} \qquad\qquad (20)$$

The positive root of Equation 19 is ignored because it occurs at times larger than β^{-1}, which is the lifetime of the cylinder.

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