Investigation of Alternative Waste Forms for GTCC ^{14}C Filters

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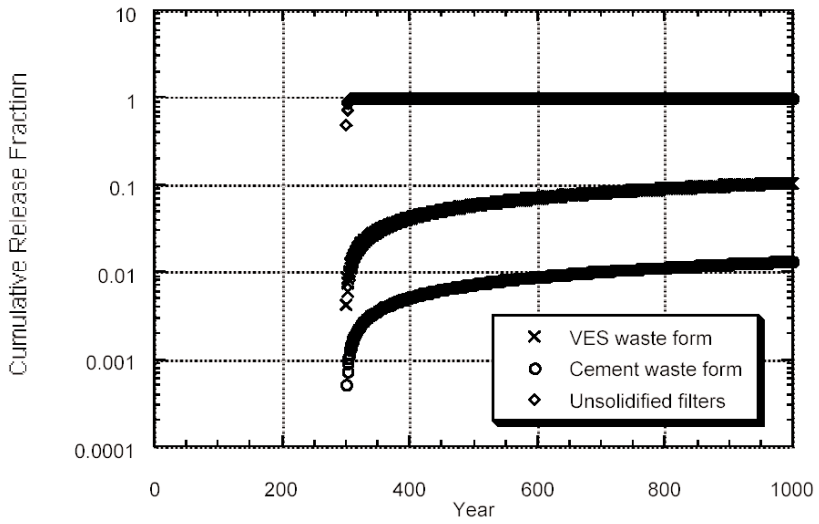

INVESTIGATION OF ALTERNATIVE WASTE FORMS FOR GTCC ^{14}C FILTERS

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Final Report, November 2001

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REPORT SUMMARY

This report demonstrates that both cement and vinyl ester-styrene (VES) are viable engineering solutions for the immobilization of Greater than Class C (GTCC) ^{14}C filters. The number of power plants installing submicron-size cartridge filters has increased with the incentive of radiation dose reduction. However, utilities are experiencing difficulty disposing of these filters due to significant increases in ^{14}C concentrations. By implementing the concentration averaging recommendations of this study, nuclear plant operators will reduce Greater than Class C filter disposal costs and avoid the storage of high-radiation filters.

Background

The development of good waste forms has been an interest in the nuclear power industry for successful radioactive waste management. Utilities can reduce or slow radionuclide release from waste by implementing proper immobilization, leading to a reduction in potential human health risk. The current regulatory approach to low level waste disposal is to limit the annual peak dose. Therefore, slower release of radionuclides can lead to an increase in the allowable inventory of radionuclides within a given volume of waste, for the same performance limits.

PWRs use cartridge filters extensively to remove insoluble materials in the coolant, and BWRs often use them in the processing of reactor cavity liquids and for spent fuel pool vacuuming. However, experiences with these submicron-size cartridge filters showed that concentrations of ^{14}C are much higher than would normally be expected. Since ^{14}C is the capacity-limiting nuclide in a low level waste disposal facility, an increase in the allowable inventory of this long-lived highly mobile radionuclide may lead to a service life extension.

Objectives

To examine the use of encapsulation techniques for the immobilization of waste cartridge filters to reduce the potential leaching of ^{14}C in waste disposal.

Approach

The research team qualitatively and quantitatively analyzed the impact of VES encapsulation on leaching of ^{14}C from the cartridge filter waste, and compared the results with cement encapsulation. They also reviewed the differences in the ^{14}C leaching mechanisms between grouted and ungrouted cartridge filters, and investigated changes in grouted cement due to the chemical interactions and evolutions in the system. The project team also examined the chemical forms of ^{14}C expected in the dewatered cartridge filters and used the DUST model to make predictions about ^{14}C release for the two waste forms. Uncertainties in the predicted ^{14}C release were addressed through careful characterization of key input parameters and examination of the model uncertainty issues.

Results

Spent cartridge filters have recently emerged as a very important radioactive waste stream for ^{14}C. Most high activity cartridge filters are currently disposed of after dewatering in poly HICs without immobilization. The source term analysis indicated that reductions in ^{14}C release with implementation of the cement or VES waste form would be significant enough for these two waste forms to be useful in ^{14}C immobilization and concentration averaging. Results indicate that VES reduces the peak annual release of ^{14}C by a factor of 15-144, and cement reduces it by a factor of 122-3025. Both cement and VES are viable engineering solutions for the immobilization of GTCC ^{14}C filters.

EPRI Perspective

In 2000, EPRI research examined the use of cement for the encapsulation of ^{14}C filters, and suggested an investigation of alternative waste forms for performance comparison. This year's research focused on VES as an alternative to cement and this report describes the comparison of the two waste forms. This study provides an important technical basis for concentration averaging of these filters with the encapsulation of filter waste. The concentration averaging with cement or VES encapsulation will reduce Greater than Class C filter disposal costs and avoid the storage of high-radiation filters.

Keywords

Low level waste disposal
Carbon-14
Filter waste
VES encapsulation
Cement encapsulation
Source term analysis

ABSTRACT

The objective of this research is to examine the use of encapsulation techniques (cement, polymer) for the immobilization of ^{14}C in cartridge filter waste to reduce the potential leaching of ^{14}C in waste disposal. For this purpose, the differences in the ^{14}C leaching mechanisms between the encapsulated and dewatered cartridge filters were reviewed. The chemical forms of ^{14}C expected in the dewatered cartridge filters and their changes in the encapsulating agent due to the chemical interactions and evolutions were also examined.

Carbon-14 in the cement encapsulated waste form experiences the mineralogic changes of the waste form with carbonation of cementitious materials. With the reduction of the permeability and porosity, mass transfer through the waste form becomes diffusion-controlled. The behavior of ^{14}C release from a cementitious waste form is also attributed to the solubility of the host phase for ^{14}C (mainly calcite). As long as the near-field is dominated by alkaline chemical conditions, the solubility of ^{14}C remains very low and the release of C-14 from the cemented waste is significantly inhibited. Due to the reaction between SiO_2 and CaO contained in the cementitious composition, the originally negatively charged (SiO^-) SiO_2 surface sites become positively charged, thus inorganic ^{14}C in the cement waste are adsorbed onto these surfaces by an electrostatic force. This enhanced sorption also reduces the release of ^{14}C from the cement waste form. This indicates that cement is a very good waste form for the immobilization of ^{14}C.

The polymer matrix is chemically cross-linked, structurally rigid, and of very limited permeability to water, thus providing a good physical barrier to mass transport. The structural rigidity means that the pore structure of the polymer matrix remains intact even though the waste may dissolve out of or otherwise be removed from the waste form. The impermeability of the polymer matrix to water means that mass transport of waste substances out of the waste form occurs through, and is constrained by, the pore structure of the polymer matrix. Thus ^{14}C leaching from VES encapsulated waste is diffusion-controlled through these pores. During the process of polymer encapsulation of ^{14}C filters, it may be possible for ^{14}C species in the filters to be chemically trapped in the polymer structure. However, ^{14}C in the VES waste form is not expected to undergo major chemical reactions.

Predictions of ^{14}C release were made for the three waste forms with the DUST computer model. Calculations indicated that encapsulation provides a substantial reduction in ^{14}C leaching from cartridge filters. Reductions in the ^{14}C release (as peak annual release) was by a factor of 15-144 using VES and 122-3025 with cement encapsulation. It is judged that the uncertainties in the source term analysis will not have major impact on the estimates made in this study. These indicate significant benefits of cement and VES encapsulation to immobilize ^{14}C on filters versus standard dewatering. Comparisons of other waste form characteristics showed that both cement and VES are relevant for the intended application. Therefore both cement and VES are viable

engineering solutions for the immobilization of GTCC ^{14}C filters. Findings from this research also support the position of the NRC guidance on concentration averaging over stable encapsulation agents for Class B/C waste. The concentration averaging with cement or VES encapsulation will reduce of Greater than Class C filter disposal costs and avoid the storage of high-radiation filters. There is no technical reason to disallow averaging activity over the waste and stable encapsulation agent for ^{14}C filters.

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1
INTRODUCTION: UTILITY AND REGULATORY BASIS FOR THIS WORK

Numerous power plants have employed sub micron filters. Disposal of some of these filters has been difficult due to high concentration of ^{14}C. In some cases the high ^{14}C concentrations have resulted in cartridges being "Greater than Class C" by more than a factor of 10 of the Class C limit (i.e., >80uCi/cc). These cartridges cannot be disposed of at the Barnwell, SC site because that site only allows concentration averaging over the waste filters without encapsulating agent.

NRC regulations allow the activity of solidified waste to be averaged over the waste and the solidification agent for purposes of waste classification when the agent has been approved for stability of Class B and C waste. The NRC Branch Technical Position on Concentration averaging and Encapsulation addresses activity averaging when solidifying solid objects (e.g., cartridge filters) in section C 3.7. This section reiterates the position that the activity on filters may be averaged over the final solidified mass so long as the encapsulation agent is approved for stability of Class B and C waste and the waste to encapsulation agent ratio complies with Appendix C of this BTP. Appendix C basically limits the amount of encapsulation agent the activity can be averaged over to no more than 0.2 m^3 (a 55 gallon drum) per filter.

The practice of encapsulating a single filter per drum has largely been abandoned in the U.S. in favor of placing numerous filters into large containers. The last Topical Report the NRC approved for waste form stability was for the encapsulation of filters with Vinyl Ester Styrene(VES) in March, 2000. This process has a waste packaging efficiency of at least 30% for filters that have not been volume reduced prior to encapsulation. The NRC found that this waste loading far exceeded the 13.6% packaging efficiency of a single filter per drum and was therefore in compliance with the BTP for concentration averaging. Should filters be volume reduced prior to encapsulation the waste loading would only increase and thus, still be in compliance with the BTP for concentration averaging.

The NRC never approved any of the cement encapsulation processes submitted for waste form stability under their Topical Report program. That program is now defunct. At least one cement encapsulation process has been submitted to the States for waste form stability approval. DOE Idaho is conducting the waste form testing program for the States. The State of South Carolina has already approved this process for Class B and C stability, although averaging the waste activity over the encapsulation agent is not allowed at Barnwell.

This report compares the ability of cement and VES encapsulation to immobilize ^{14}C on filters versus standard dewatering. The results demonstrate that encapsulation does immobilize ^{14}C

sufficiently to prove that there is no technical reason for any State to disallow averaging activity over the waste and stable encapsulation agent.

Concentration averaging also allows individual objects that exceed Class C to be grouped with other objects from the same waste stream. If the resultant group average does not exceed Class C, the waste can be disposed of as low level waste. When filters that exceed Class C are packaged with other filters for concentration averaging in a large container, not all of the filters are necessarily in the group being averaged. For example, there may be 200 filters in a large container and only 50 of these are grouped together for concentration averaging. The NRC BTP does not address what portion of the stable encapsulation agent can be applied to the 50 filters being concentration averaged. To comply with the spirit of the BTP, only the proportional amount of encapsulation agent (in this case 25%, assuming all the filters have the same geometry) should be added to the group of 50 filters to determine waste classification.

The use of stable encapsulation agents for filters that exceed Class C by more than a factor of 10 of the limit in concert with the application of concentration averaging with other filters of the same waste stream provides a method for disposal of such filters as low level waste. The results from this report demonstrate that there is no technical basis for any State to disallow averaging the ^{14}C activity on such filters over stable encapsulation agents. Similarly, filters that exceed Class C due to ^{63}Ni or TRU nuclides should also be allowed to have that activity averaged over the waste and stable encapsulation agent.

This report should serve to convince any new LLW Class B/C disposal site to adopt the NRC guidance as is and allow activity averaging over stable encapsulation agents.

2
CHEMICAL FORM OF ^{14}C IN FILTER WASTE

Carbon-14 is produced in reactor coolant systems from the reactions of neutrons with oxygen in the water molecules ($^{17}O(n, \alpha)^{14}C$), nitrogen dissolved in the water ($^{17}O(n, \alpha)^{14}C$), and carbon dioxide organic compounds in the water $^{13}C(n, \gamma)^{14}C$ [Vance, Cline, and Robertson, 1995]. After generation, Carbon-14 can exist in various chemical forms in the nuclear reactor systems [Rosset and Desbarres, 1993; Yim and Simonson, 1999]. Although the exact specification and the distributions are unknown, the following has been found for ^{14}C:

C-14 exists in PWR coolant systems mainly as organic carbon (58 to 95%) whereas in BWRs mainly as inorganic carbon (13-48% organic) [Vance, Cline, and Robertson, 1995].

The major forms of organic carbon compounds in PWR coolant systems are acetaldehyde, methylalcohol, ethyl-alcohol and acetone [Matsumoto, et al., 1995].

The chemical forms of ^{14}C captured in the cartridge filters could be different from those existing in the coolant system. Capture of ^{14}C in cartridge filters suggests that the activity is associated with particulates or chemical complexes in the system.

The chemical forms of ^{14}C also change as the temperature and redox potential of the system environment changes. When the cartridge filters reach their service lifetime and are withdrawn from the system, they are exposed to the ambient atmosphere. As the temperature of the system is lowered and the system becomes more oxidizing, ^{14}C could experience a series of oxidation processes. Plant experiences and observations suggest that the ^{14}C activity, at the time of withdrawal from the system, is in a pure particulate form or inorganic form tied to the iron [Miller, 2000].

Based on these understandings and observations, ^{14}C in cartridge filters is expected to be in mostly inorganic forms such as the insoluble reduced forms of carbon (elemental C) and the aqueous species carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). This is in agreement with the chemical species that are most commonly found in the natural environment and typical waste [Krupka and Serne, 1998; Dayal and Reardon, 1992; Jeffries, 1990; Gruhlke et al., 1986; Kunz, 1985; Martin, 1986; Cline et al., 1985; Impell Corp., 1985]. Existence of ^{14}C in organic forms however is still possible.

3
ENCAPSULATION OF FILTERS INTO CEMENTITIOUS WASTE FORM

3.1 Fundamental Understanding of Grouted Cement

Grouting is defined as an injection of appropriate materials under pressure into certain parts of structures in order to fill and seal voids, cracks or other cavities in the system [Bowen, 1981]. This results in water-tightness in the structure by establishing very low or negligible permeability. Grouting has been widely used in geotechnical engineering to improve the strength of various structures.

Portland cement mixed in a slurry with water is commonly used for grouting. This results in a cementitious waste form. Cements are not a single material but comprise a class of materials whose properties can be tailored to specific requirements [Atkins, et al, 1994]. The chemically active portion of Ordinary Portland cement (OPC) is termed paste. It comprises (>95%) six oxides: CaO, Al_2O_3, Fe_2O_3, SiO_2, SO_3 and H_2O. Smaller amounts of MgO, Na_2O and K_2O are also present. In order to achieve complete hydration, a water/cement ratio of 0.22-0.24 (by weight) is required. Grouts are typically made to the ratios of 0.3-0.5; the excess water after the hydration of materials is eventually entrapped in pores, and is termed 'pore water.'

The hydrate phases commonly found in cement pastes are both crystalline and amorphous. The crystalline components include portlandite ($Ca(OH)_2$), ettringite ($3CaO.Al_2O_3.3CaSO_4.36H_2O$), monosulphate ($3CaO.Al_2O_3.CaSO_4.12H_2O$), hydrogarnet ($3CaO.Al_2O_3.6H_2O$-$3CaO.Al_2O_3.SiO_2.4H_2O$), and hydrotalcite ($4MgO.Al_2O_3.10H_2O$). Calcium silicate hydrogel (C-S-H: $(0.9\text{-}1.7)CaO.SiO_2.xH_2O$) is the amorphous component (actually as a nearly-amorphous gel containing CaO, SiO_2, and water) and is very important in characterizing the cement pore/paste chemistry. Its Ca/Si ratio can vary and under higher Ca/Si conditions, anionic sorption is favored. The paste chemistry is also much influenced by additives, if additives are used. Typically fly ashes or slags are used to reduce heat of hydration and reduce viscosity of the mixtures, making processing easier [Malek and Roy, 1987].

All hydrated cement components of concrete, mortars, and grouts are unstable in the presence of carbon dioxide, converting ultimately to an assemblage of calcium carbonate, silica gel, etc. The reaction of carbon dioxide with the principal hydrated calcium-bearing components of cements results in mineralogic transformations as shown in the following reactions [Dayal and Reardon, 1992]:

Portlandite:

$$Ca(OH)_{2(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)}$$

Calcium silicate hydrate (C-S-H):

$$C\text{-}S\text{-}H_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + SiO_2,nH_2O_{(s)} + H_2O_{(l)}$$

The calcium carbonate that forms as a result of carbonation reaction is typically in the form of calcite, aragonite, or sometimes vaterite. The rate of carbonation of cementitious materials is affected by the cement type, porosity, permeability and water/cement ratio, and is typically very fast.

Physically, the amorphous phases and pore spaces present in a well-made cement entrap liquid. This aqueous phase is in intimate contact with high specific surface solids with which it is in a steady-state, quasi-equilibrium. A well-made cement may contain 2-25% porosity, much of which is present in fine pores, <1~2um effective pore entry diameter [Atkins, et al., 1991]. These pores contribute significantly to the mass transport properties of the cement matrix.

The principal factors that affect the long-term retention of radionuclides as a waste form (thus affecting the release of radionuclides) are pH and redox potential (or Eh). The pH and Eh will in turn affect the solubility and the sorption of chemical species. The structural incorporation of nuclides in the structure of more crystalline cement components is also important [Atkins, et al., 1991].

The dissolution of excess amounts of portlandite and alkali present in hydrated cement maintains high pH conditions in cement. Studies on the evolution of pH over time indicated that the pH will remain above 10.5 for very long time periods, (e.g., millions of years) [Atkinson, 1985; Bradbury and Sarott, 1995; Berner, 1992]. The exact time period will be dependent on the cement content of the system and infiltrating water flow. Initially the pH will be controlled by the alkali hydroxides in the pore fluid and can be above 13 in a high alkali cement lasting for the first 100 to 10,000 years. Following the dissolution of the alkali hydroxides, the pH will be buffered by the solubility of portlandite at about 12.4 until all the free $Ca(OH)_2$ has undergone dissolution. This environment may last from 100-10,000 years to 1,000-100,000 years [Berner, 1992]. After this phase, the C-S-H gel material controls the pH maintaining the pH at about 10.5 until all the gel material has dissolved. Although the cement waste form may develop cracks and structurally degrade in relatively short time periods, the cementitious materials continue to provide chemical functions in maintaining a high pH environment.

The redox potential of the cement internals was found to be positive, i.e., oxidizing, as most Portland cements are produced under oxidizing conditions. When additives are used, the redox potential is found to be less positive than for the normal cements, but still indicating slightly oxidizing conditions [Malek and Roy, 1987]. The Eh values inside the waste form were found to range from +100 mV to 200 mV in Portland cement [Atkins, et al., 1991].

3.2 Benefits of Cement Encapsulation for ^{14}C Disposal

The cementitious waste form provides both physical barriers to fluid flow and chemical barriers to the mass transport of waste constituents. Although the durability or integrity of the cementitious waste form is not maintained for long enough time periods to prevent fluid flow for the long-lived nuclide ^{14}C, the chemical interactions and reaction-induced chemical conditions are likely to last very long periods to make it an effective long-term chemical barrier for the immobilization of ^{14}C [Dayal, 1995].

As the filters are solidified in cementitious grout, the environment surrounding the filters becomes highly basic/akaline. Under these high pH conditions, various organic carbon species that may exist in the filter (i.e., methane, methanol, formaldehyde, etc.) are oxidized to carbonate [Rosset and Desbarres, 1993]. This applies to both oxidizing and slightly reducing conditions at various temperatures (25 ~ 300°C). An example of the applicable Eh-pH diagram is shown in Figure 3-1 for the 25°C conditions [EPRI, 1983]. This implies that regardless of the original chemical forms of ^{14}C in the cartridge filter waste, the ^{14}C will exist in inorganic forms (mainly as carbonate) in the encapsulated waste form.

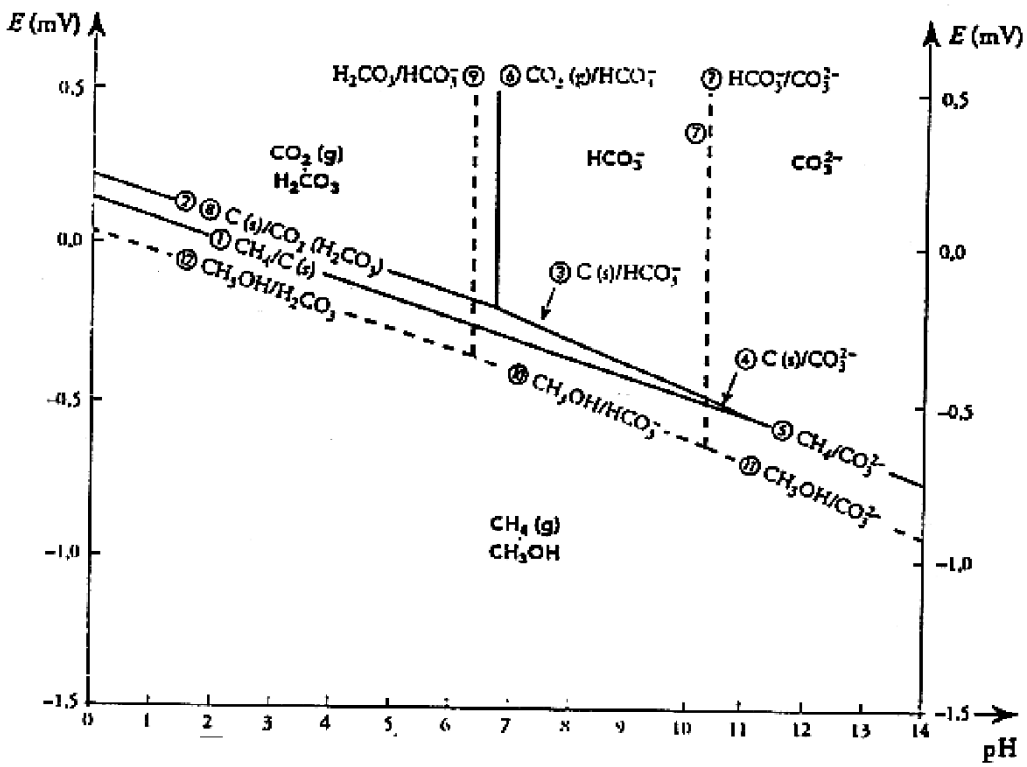

Figure 3-1
Eh-pH Diagram of Carbon Species at 25 °C

At pH above 12, calcite is more insoluble than portlandite and any carbonate molecules present in the solution will combine with the enriched calcium from the dissolution of portlandite to form a carbonate precipitate [Krupka and Serne, 1998]. Thus, the carbonate/bicarbonate ions that contain ^{14}C in the waste are expected to be exchanged with hydroxyl ions in the grout slurry, followed by localized precipitation of solid calcium carbonate in the filter/grout interface

[Dayal and Reardon, 1994]. Therefore, large amounts of inorganic carbons can be removed from aqueous solutions in a freshly hardened cement paste. Almost complete incorporation of ^{14}C into the cementitious material is expected by the precipitation of calcite ($CaCO_3$) within the pores of the cement [Serne et al., 1992; Allard et al., 1981; Dayal and Klein, 1987; Hietanen et al., 1985; Bayliss et al., 1988].

The mineralogic changes with carbonation of cementitious materials also induce changes in material properties such as permeability and porosity of the waste form by clogging of pores with the precipitation of calcite and other carbonation reaction products in the pore network and reducing average pore size [Dayal and Klein, 1987]. Reduced water flow will impede waste leaching and subsequent transport of radionuclides escaping from the waste package. This results in diffusion-controlled mass transfer through the system even under high flow conditions [Dayal, 1995; Dayal and Reardon, 1992]. Therefore the simple release mechanisms such as surface wash-off or rinse are not applicable to describe the release of ^{14}C from the grouted filter waste form.

A cemented waste form provides benefits of reducing ^{14}C release beyond the precipitation in the form of calcite by the increased sorption capacity for ^{14}C [Noshita, et al., 1996]. The SiO_2 is originally negatively charged in cement, but becomes positively charged through the interaction with CaO. These positive sites on the SiO_2 surface adsorb inorganic ^{14}C by an electrostatic force. The net effect of this increased sorption will be the much reduced effective diffusion coefficient of ^{14}C in the cement waste form.

The benefits of cement encapsulated filter waste for disposal are:

- The chemical forms of ^{14}C activity captured in filter waste become inorganic as the waste is solidified in the high pH, oxidizing environment in cement.
- The mineralogic changes associated with carbonation of hydrated cement in grout yield a calcite end product that immobilizes inorganic ^{14}C.
- The chemical buffering provided by the dissolution of cementitious materials will ensure low solubility of calcite, thereby minimizing the possibility for the remobilization of ^{14}C and contributing to the retention of ^{14}C in the solid phase in the waste form for an extended time period.
- As a result of carbonation, the permeability and porosity of the waste form are reduced. This will reduce mass transport through the waste form. Thus even under advective flow conditions, mass transfer through the waste form is diffusion-controlled.
- Due to the reaction between SiO_2 and CaO contained in the cementitious composition, the originally negatively charged (SiO^-) SiO_2 surface sites become positively charged. Thus inorganic ^{14}C in the cement waste is adsorbed onto these surfaces by an electrostatic force [Noshita, et al., 1996]. This enhanced sorption reduces the effective diffusion coefficient for the release of ^{14}C from the cement waste form.
- Although the cement waste form may develop cracks and structurally degrade, the cementitious materials continue to provide chemical functions in maintaining a high pH environment. Thus the cement waste form will remain effective for very long periods of time to immobilize ^{14}C.

4
ANALYSIS OF ^{14}C RELEASE FROM CARTRIDGE FILTER WASTE

4.1 Mechanisms of ^{14}C Release

The waste form has a considerable impact on the manner and degree to which radionuclides are retained following disposal. With cement encapsulation of cartridge filters, the mechanism of ^{14}C leaching drastically changes from that of the dewatered filters.

4.1.1 C-14 Release from Dewatered Filters

Cartridge filters are made of cotton, polymers, fiberglass, and epoxy-impregnated paper, many with metal cores and end caps. The radioactivity in cartridge filter waste is captured and retained in very small pores through filtration, impingement, and adsorption.

If the radioactivity is retained at the surface of the waste material through surface phenomena such as adhesion or sorption, the radionuclides can be easily released through surface-wash by water [Sullivan and Suen, 1989]. In this case, the surface-wash (rinse release) model is applicable. If the radionuclides are bound to the matrix material and can only be released through the dissolution or corrosion of the matrix material, the dissolution model is appropriate.

In the case of dewatered cartridge filters, some portion of activity would be released through surface-wash. However, if the majority of activity is mechanically bound in the tight pore structures, the activity will not be readily released but slowly released as the filters become dissolved or degraded. Unfortunately current understanding of the release of radionuclides from this particular waste form is very limited. Given this uncertainty, the current practice of modeling nuclide leaching from dewatered filters is to use the surface wash-off model. When using the surface wash-off model, the key modeling issue is the selection of proper distribution coefficient (K_d) value [Yim and Simonson, 2000; Yim and Su, 2000]. Distribution coefficient (K_d) represents the equilibrium state between the solid and aqueous phase and is defined as the ratio of concentration in the solid phase to that in the liquid phase.

4.1.2 C-14 Release from Encapsulated Filters

As described previously, the mineralogic changes of the waste form with carbonation of cementitious materials reduce the permeability and porosity of the system. This means the mass transfer through the waste form is diffusion-controlled. Diffusion will take place mainly through the pores where excess water or carbonation product water is being trapped. In a microscopic

scale, this diffusional mass transport process can be affected by dissolution, ion exchange, corrosion, and surface effects [Colombo, et al., 1985]. In a macroscopic scale, the combined effects of these mechanisms can be represented by the effective diffusion coefficient of the system.

The behavior of ^{14}C release from a cementitious waste form is also attributed to the solubility of the host phase for ^{14}C (mainly calcite). As long as the near-field is dominated by alkaline chemical conditions, the solubility of ^{14}C will remain very low and the release of ^{14}C from the cemented waste form is inhibited.

Surface-wash could also be important for cemented waste form for the early time periods if initial washing-off removes enough surface activity [Arora and Dayal, 1986]. However, this surface effect can be ignored in this study because ^{14}C surface contamination by grouting operation would be negligible.

4.2 Values of Key Parameters for Leach Modeling

Selecting proper values of the key parameters is critically important in modeling radionuclide leaching. Selection of these values should be based on a consistent technical basis with the understanding of the uncertainty and variability of each parameter.

To characterize the uncertainty of the key input parameters, probabilistic modeling was performed by constructing parametric distributions. The two key parameters of importance examined with this approach were K_d of ^{14}C in dewatered filter waste and the effective diffusion coefficient of ^{14}C in grouted filters.

4.2.1 Data for K_d Value of ^{14}C in the Dewatered Filter Waste

In modeling the release of ^{14}C by using the surface-wash model, the distribution coefficient (K_d) of ^{14}C in the dewatered filters is the most important parameter. The surface-wash model assumes the entire inventory is "rinsed" off the wastes upon contact with water with the water being subject to equilibrium partitioning between the solution and the waste form. The K_d value represents this equilibrium partitioning.

Unfortunately, data for the measured values of ^{14}C K_d in the dewatered filter waste do not exist. Estimates of ^{14}C K_d in the soils, sediments, or rocks are however available from various studies of radioactive waste management. These includes studies by a number of government agencies in U.S., Canada, the United Kingdom, Switzerland, Germany, and Finland compiling databases of ^{14}C Kd values [McKinley and Sholtis, 1993]. By assuming that the geochemical conditions within the dewatered/ ungrouted filter waste are similar to those of the soils or sediments, the databases from these studies were used in this research, except for the data for the carbonate-rich sediments (where large sorption is expected). These data are summarized in Table 4-1. Some of the data collected were measurement data obtained from field experiments although most of the data were drawn from databases. The ^{14}C K_d values obtained from databases represented both best estimates and two different sides of conservatism, i.e. those used for calculating transport in the near-field environment and those used in biosphere transport models. In the near-field transport studies, a low K_d is conservative by minimizing retardation. However, in biosphere transport studies, a high K_d is conservative by maximizing accumulation in the biosphere. All of these data are included in the Table 4-1.

Table 4-1
Data Used for the Characterization of C-14 K_d in Waste

Study	Kd Value	Environment	Nature of data
US NRC LLW performance assessment [NRC, 1993; Looney, et al., 1987]	0.01	Humid site	Estimated from database (“conservative”)
US EPA [EPA, 1988]	0.01	Soil/waste	Conservative
Sandia/US NRC study [Beyeler, et al., 1999]	1.89	Soil	Estimated from database (“mean”)
UK, LLW study, NRPB [Pinner et al., 1984]	0	Soil/surface sediment	Conservative
UK Biosphere database study [Ashton and Sumerling, 1988]	100	Soil/surface sediment	Estimated from database (“maximum”)
UK DOE study [Nacarrow, et al., 1988]	2	Clay	Best estimate
UK Nirex [Lever and Woodwark, 1990]	1	Clay mudstone	Best estimate
Swiss, NAGRA [McKinley and Hadermann, 1985]	50	Soil/surface sediment	Estimated from database
Swiss, NAGRA [McKinley and Hadermann, 1985]	5	Bentonite	Best estimate
Swiss, NAGRA [NAGRA, 1985]	1	Soil/surface sediment	Estimated from database
Swiss, NAGRA [McKinley and Hadermann,1985]	5	Granite	Best estimate
Swiss, NAGRA [NAGRA, 1988]	50	Clay	Best estimate
German PSE study [Butow, et al., 1985]	0	Sediment	Best estimate
Golder [Golder Associates, 1988]	0	Porous media	Conservative
AECL LLW study [Guvanasen, 1985]	2	Soil/surface sediment	Estimated from database (“conservative)
RIVM study [Glasbergen, et al, 1989]	2	Sand clay	Best estimate
GSF study [Buhmann et al., 1991]	5	Sediment	Best estimate
Finnish TVO study [Peltonen et al., 1985]	100	Soil/surface sediment	Estimated from database

Table 4-1
Data Used for the Characterization of C-14 K_d in Waste (Continued)

Study	Kd Value	Environment	Nature of data
Finnish TVO study - Biosphere analysis for the VLJ repository [Vieno and Suolanen, 1991]	10	Soil/surface sediment	Maximum estimate
Finnish TVO study [Peltonen et al., 1985]	6	Crystalline rock/reducing	Best estimate
Finnish TVO study [Vieno and Nordman, 1991]	1	Crystalline rock	Best estimate
AECL study [Sheppard and Thibault, 1990]	5	Sand	Geometric mean
AECL study [Sheppard and Thibault, 1990]	20	Loam	Geometric mean
AECL study [Sheppard and Thibault, 1990]	1	Clay	Geometric mean
AECL study [Sheppard and Thibault, 1990]	70	Organic soil	Geometric mean
EPRI C-14 Study [Vance, et al., 1995]	3	Bicarbonate in sands,	Measurement
EPRI C-14 Study [Vance, et al., 1995]	0	Bicarbonate in sediment	Measurement
EPRI C-14 Study [Vance, et al., 1995]	57	Citric acid in sands	Measurement
EPRI C-14 Study [Vance, et al., 1995]	6	Citric acid in soil	Measurement
EPRI C-14 Study [Vance, et al., 1995]	7	Palmitic acid in sands	Measurement
EPRI C-14 Study [Vance, et al., 1995]	0	Palmitic acid in soil	Measurement

Although the existing database on the K_d value of ^{14}C in soil/rocks is primarily for the inorganic form of carbon, some experimental data for organic forms of carbon were also included in the table. Even though the number of data points for the organic carbon is small compared to the total data point number, the values observed for organic carbon are in agreement with the range of the data values indicated by the rest of the database. Therefore combining these two pieces of information appears reasonable.

Because these combined data in Table 4-1 represent the mixture of large numbers of best estimates, two different sides of conservatism of estimated values, and the realism of experimental data for both the organic and inorganic chemical forms, the data can be assumed representative of the uncertainty range of ^{14}C K_d values.

4.2.2 Data for Diffusion Coefficient of ^{14}C in the Encapsulated Waste Form

Data for effective diffusion coefficient of ^{14}C in cement encapsulated waste form were available from several experimental studies [Serne, et al., 1992; Habayeb, 1985; Krishnamoorthy, et al., 1993]. These data are summarized in Table 4-2. These data were obtained from the experimental studies of ^{14}C mass transport using grouted liquid waste forms, immobilized resins in cement, and through artificial loading of ^{14}C onto cement. Although none of these represents grouted cartridge filters, they are expected to serve the purpose of this study well. This is because the behavior of ^{14}C in the grouted waste form is dominated by the physico-chemical conditions of

the cement environment rather than by the original chemical form of ^{14}C or the materials immobilized.

Table 4-2
Data Used for the Characterization of Diffusion Coefficient of C-14 in Grouted Waste (All measured Data)

Study	Effective Diffusion Coefficient	C-14 chemical form/Environment
PNL grouted LLW study [Serne, et al., 1992]	$5x10^{-14}$	C-14 in phosphate-sulfate liquid waste from decontamination process, solidified in cement with fly ash and clay, leaching with Hanford groundwater
PNL grouted LLW study [Serne, et al., 1992]	$2x10^{-13}$	C-14 in dissolved clad liquid waste, solidified in cement with fly ash, calcium hydroxide and clay, leaching with Hanford groundwater
PNL grouted LLW study [Serne, et al., 1992]	$<10^{-11}$ assumed 10^{-11}	C-14 in liquid LLW from reprocessing, solidified in cement with fly ash and furnace slag, leaching with Hanford groundwater.
Ontario Hydro study [Habayeb, 1985]	$1.23x10^{-13}$	C-14 in resins immobilized in cement (24% water, 29% PC) and 18% polymer, leaching with deionized water
Ontario Hydro study [Habayeb, 1985]	$3.20x10^{-14}$	C-14 in resins immobilized in cement (24% water, 29% PC) and 18% polymer, leaching with cement water
Ontario Hydro study [Habayeb, 1985]	$2.36x10^{-14}$	C-14 in resins immobilized in cement (23% water, 39% PC) and 23% polymer, leaching with deionized water
Ontario Hydro study [Habayeb, 1985]	$7.28x10^{-15}$	C-14 in resins immobilized in cement (23% water, 39% PC) and 23% polymer, leaching with cement water
Ontario Hydro study [Habayeb, 1985]	$2.06x10^{-14}$	C-14 in resins immobilized in cement (21% water, 54% PC) and 11% polymer, leaching with deionized water
Ontario Hydro study [Habayeb, 1985]	$1.12x10^{-14}$	C-14 in resins immobilized in cement (21% water, 54% PC) and 11% polymer, leaching with cement water
Ontario Hydro study [Habayeb, 1985]	$3.23x10^{-14}$	C-14 in resins immobilized in cement (23% water, 39% PC) and 23% polymer, leaching with deionized water
Ontario Hydro study [Habayeb, 1985]	$1.28x10^{-14}$	C-14 in resins immobilized in cement (23% water, 39% PC) and 23% polymer, leaching with cement water
Bhabha Atomic Center study [Krishnamoorthy, et al., 1993]	$1.54x10^{-14}$	CO_3^{-2} in hardened cement, leaching with deionized water
Bhabha Atomic Center study [Krishnamoorthy, et al., 1993]	$7.87x10^{-13}$	CO_3^{-2} in hardened cement, leaching with deionized water

4.3 Characterization of Uncertainty of Key Parameters

The characterization of the probability distributions of the parameters using the data given in Tables 4-1 and 4-2 are described in this section. To examine the characteristics of the data with respect to the fitting by parametric probability distribution models, summary statistics of the data were calculated for the two data sets as following:

Data for ^{14}C K_d in waste:	1.77 (coefficient of variation)
	1.90 (skewness)
	5.34 (kurtosis)
Data for ^{14}C diffusion coefficient:	3.14 (coefficient of variation)
	3.14 (skewness)
	11.0 (kurtosis)

These summary statistics indicated that the best parametric model for both of the data sets could be the beta distribution according to the suggestions on the selection of probability model in the literature [Hahn and Shapiro, 1967]. Since both the K_d data or diffusion coefficient data were highly skewed representing environmental phenomena, the lognormal distribution could also be considered as an alternative to the beta distribution.

The following normalized beta distributions were constructed based on the parameter estimation using the methods of moments [Ang and Tang, 1975; Morgan and Henrion, 1990]:

Probability density function for ^{14}C K_d in dewatered filter waste:

$$f(x) = \frac{x^{-0.8977}(1-x)^{-0.4815}}{\Gamma(0.1023)\Gamma(0.5185)/\Gamma(0.6208)} \qquad 0 \le x \le 1 \qquad \text{(Eq. 1)}$$

where x is the normalized value for the given range of K_d data.

Probability density function for ^{14}C effective diffusion coefficient in cement:

$$f(x) = \frac{x^{-0.9874}(1-x)^{-0.8685}}{\Gamma(0.0126)\Gamma(0.1315)/\Gamma(0.1441)} \qquad 0 \le x \le 1 \qquad \text{(Eq. 2)}$$

where x is the normalized value for the given range of diffusion coefficient data.

The following probability distribution functions were also obtained for the lognormal model based on the estimation of parameters using the maximum likelihood methods.

Probability density function for ^{14}C K_d in dewatered filter waste:

$$f(x) = \frac{1}{\sqrt{2\pi} \cdot x \cdot 2.0938} \exp\left[-\frac{(\ln x - 1.1999)^2}{2(2.0938)^2} \right] \qquad 0 < x < 100 \qquad \text{(Eq. 3)}$$

where x is the given K_d data.

Probability density function for the ^{14}C Effective Diffusion Coefficient in Cement:

$$f(x) = \frac{1}{\sqrt{2\pi} \cdot x \cdot 1.848} \exp\left[-\frac{(\ln x + 30.3074)^2}{2 \cdot (1.848)^2} \right] \qquad 5 * 10^{-17} < x < 10^{-11} \qquad \text{(Eq. 4)}$$

where x is the diffusion coefficient data.

These estimated probability distribution models (the beta and lognormal model) were compared based on a goodness-of-fit test. Since the number of data points are relatively small, the Kolmogorov-Smirnov test [Ang and Tang, 1975; Cullen and Frey, 1999] was used in this study.

The analysis for the fitted K_d data showed that the maximum difference (D_n) between the cumulative distribution function (CDF) for the hypothesized distribution and the stepwise empirical CDF was 0.69 for the beta distribution and 0.22 for the lognormal distribution. Both of these values are less than the critical Dn value of 0.24 at a significance level 0.05 indicating the lognormal distribution is acceptable with respect to the goodness-of-fit test. Thus, the lognormal distribution was selected as a probabilistic model to describe the uncertainty of the ^{14}C K_d.

The analysis for the fitted diffusion coefficient data showed that the maximum difference (D_n) between the cumulative distribution function (CDF) for the hypothesized distribution and the stepwise empirical CDF was 0.41 for the beta distribution and 0.20 for the lognormal distribution. The critical D_n value for the data set at significance level 0.05 was 0.38 indicating again that only the lognormal model is acceptable with respect to the goodness-of-fit test. Therefore the lognormal distribution was selected to describe the uncertainty of ^{14}C diffusion coefficient in cement.

From these two selected probability models, the following percentile values can be obtained:

C-14 K_d in waste (in ml/g) – lower end is conservative:

5th percentile	0.10
10th percentile	0.23
50th percentile (median)	3.3
Mean	30

C-14 effective diffusion coefficient in cement (in cm^2/sec) – upper end is conservative:

95th percentile	1.4×10^{-12}
90th percentile	7.1×10^{-13}
50th percentile (median)	6.8×10^{-14}
Mean	3.1×10^{-13}

Typically the 50th percentile value serves as a better average statistic than the mean for a skewed distribution. The 10th percentile (or 90th percentile) is considered a prudently conservative upper end of the distribution. In the following analysis, only the 10th and 50th percentile values were used to represent the uncertainty of the ^{14}C release estimates.

4.4 Analysis of ^{14}C Release Between the Dewatered and Encapsulated Filters

To examine the differences in the estimated ^{14}C release between the dewatered and encapsulated filter waste, the DUST code was used. The DUST code represents the NRC's state-of-the-art source term analysis computer model for low level waste. It has been validated through field testing and has been used for licensing purposes.

Since the code does not feature the probabilistic analysis capability, the uncertainties in the estimated release were analyzed by performing several case calculations considering the uncertainties of key input parameters, i.e., K_d in the dewatered filter waste and the effective diffusion coefficient in grouted filters. Based on the results of uncertainty characterization, the 90th (or 10th) and 50th percentile values were separately used for the calculation with DUST. The predicted ^{14}C releases between the two waste forms were compared to quantify the range of differences in the ^{14}C release. This difference can be considered as the quantitative measure of benefits of the grouting technology for the cartridge filters. The predicted release for the different percentile values were also combined to examine the range of difference in the predicted release.

Figures A-1 and A-2 show the predicted cumulative release of ^{14}C for different percentile input values for the ungrouted and grouted waste form at the end of 1000 years after the emplacement of waste in a disposal site. The numbers in the figures represent the fraction of ^{14}C released at the surface of the waste form in comparison to the total inventory in a container. The waste container was assumed to be a cylinder with a radius of 0.25m and a height of 1 m. It was also assumed that the wastes were disposed of in high integrity containers (HICs) and that the HICs had a lifetime of 300 years.

Both of the figures indicated that the rate of release of ^{14}C was slower with grouting of filters. The cumulative release of ^{14}C at 1000 years was much lower with the grouted filters for both of the 90th and 50th percentile cases (a factor of 73 and 234, respectively). The difference was smaller with the 90th percentile case since the cumulative release with the diffusion model was much higher in the 90th percentile value case.

Although the difference in the predicted cumulative release provides useful insight, more important insights come from the prediction of annual fractional release and the annual peak release rate. The predicted annual peak release rate reflects the projection of the peak annual dose to the members of the public. The peak release rate leads to the peak dose to humans after the geosphere and biosphere transport. The current regulatory approach to low level waste disposal uses the peak annual dose as a basis for protecting public health (25 mrem per year) [U.S. NRC, 1982]. Thus the compliance decisions in performance assessment deal mainly with the projected peak annual dose.

Comparisons of the predicted annual release rates for the 90th and 50th percentile values are shown in Figures A-3 and A-4. In the 90th percentile value case, the predicted peak annual release was a factor of 938 lower with the grouted filters compared to the ungrouted dewatered filters. In the 50th percentile value case, the difference was by a factor of 395. If the results of the two cases were combined to form a range, the difference in the predicted peak annual release was a factor of 122.

5
ENCAPSULATION OF FILTERS INTO POLYMERIC WASTE FORM

Polymeric waste forms have physical and chemical properties which make them compatible with different types of radioactive wastes over a wide range of conditions including wet and dry wastes. When compared with cement, the polymeric waste form has, in general, the benefit of improved leach resistance [IAEA, 1991]. Polymers also possess compatibility with other organic based wastes (e.g., organic ion exchange resins) and chemical inertness. Polymeric waste forms have been used by a number of nuclear power plants for the immobilization of LLW.

A number of different polymer systems have been investigated in the past for radioactive waste immobilization. Apart from urea formaldehyde systems which are no longer used (due to difficulties with excessive free water and container corrosion), the main groups include thermosetting polymers and thermoplastic polymers. Thermoplastic polymers are materials used as fully formed matrices which soften when heated. Only one thermoplastic polymer – bitumen – is in use as a binding medium for LLW [Cowgill, 1991].

Thermosetting polymers are materials polymerized *in situ* from monomers or pre-polymers by the action of heat, catalysts, ultraviolet lights, etc. The principal thermosetting polymers used in solidifying LLW are vinyl ester-styrene (VES) (often referred to as Dow binder, after the Dow Chemical Co. which developed the process), polyester resins and epoxy resins. Heating, however, volatilizes and releases ^{14}C in the processing of waste. VES process, unlike other polymeric waste forms, does not require heating. VES also exhibits increased chemical resistance and better performance in the presence of water over other polyesters. VES has been implemented at a number of nuclear power plants. VES encapsulation has received approval from the NRC in March 2001 as a stable waste form. The impact of VES encapsulation on the leaching of ^{14}C from cartridge filter waste was analyzed both qualitatively and quantitatively. Uncertainties in the predicted C-14 release were addressed through careful characterization of key input parameters and examination of the model uncertainty issues.

5.1 VES Waste Form

Vinyl-esters are a subclass of polyesters in which double carbon-carbon bonds are introduced by using an unsaturated acid monomer [IAEA, 1991]. Vinyl-esters are used as proprietary formulations in which a pre-polymer is dissolved in styrene as a suitable solvent. This solvent takes part in the polymerization process by modifying the repeating structural unit or altering the degree of cross-linking.

DOW Chemical Company developed a proprietary vinyl ester styrene (VES) for use as a radioactive waste solidification agent. VES uses three or four components: the binder, a catalyst, a promoter, and (in some processes) an extender or a wetting agent [Tucker, et al., 1983]. The polymerization reaction is started by adding a catalyst to the waste/binder mixture. A catalyst or an initiator is a relatively unstable material that decomposes to form free radicals. Typically benzol peroxide is used as initiator. A promoter is later added. Polymerization is complete in 1 hour. The polymerization of the unsaturated monomers is a chain reaction after being initiated by the action of free radical on a monomer molecule. The mechanism of polymerization initiated by a free radical is:

Free radicals are formed by the decomposition of an initiator.

The free radical is capable of reacting in such a way as to open the double bond of a monomer and to add to it, thus regenerating the unpaired electron.

Monomers add successively to the growing chain in a matter of seconds.

The growth of the chains ends when all the monomer is consumed or when the growing chains meet end to end. The rate of polymerization, the molecular weight and the molecular weight distribution can be controlled by varying the initiator (catalyst) concentration. Promoters can be used along with catalysts. Promoters are chemical compounds that can induce the decomposition of a peroxide type initiator by breaking the O-O bond. Typically cobalt naphthenate or dimethyl aniline is used for this [IAEA, 1988]. The promoter-catalyst combinations allow for a reasonable working time before the mixture sets. The polymerized thermosets form permanent cross-links between the linear chains, creating a very rigid three-dimensional chain structure.

VES must be used with some care to achieve satisfactory results, but the solidified product is very stable [Moghissi, et al., 1986]. The process works equally well for aqueous wastes in the pH range of 2.5 – 11.0, for aqueous wastes containing dispersed solids such as ion-exchange resins or filter aid materials and for dry solid wastes. In each case, the wastes are encapsulated by the binder and a homogeneous hard monolith is obtained.

In the solidification of aqueous wastes as an emulsion with comonomers, liquid or slurry wastes are stirred with a low viscosity liquid solution of vinyl ester in styrene monomer (the vinyl ester monomer is diluted to about 40-50 wt% in styrene) until a stable water-in-oil type emulsion is formed [Dougherty, et al., 1986]. The mixture is cured by the addition of a free radical, yielding a peroxide catalyst and a tertiary amine promoter. The emulsion is formed under high-shear mixing of the comonomers with the aqueous waste which is polymerized to form the solid waste form. Dry wastes are simply mixed with the comonomers, which then polymerize to form hard, solid monolith waste form. Polymerization is normally accomplished using a catalyst and promoter system which is added to the comonomer solution along with the waste to be solidified. When a liquid waste is processed, it is dispersed in the binder and, when the binder hardens, the waste becomes trapped in the small cells that are formed.

Advantages of vinyl-esters over other polyesters are increased chemical resistance and better performance in the presence of water [IAEA, 1991]. Vinyl esters are less polar than polyesters

and thus are less prone to the effects of water when cured by organic peroxides [Franz, et al., 1994]. This is particularly significant for the solidification of aqueous wastes. A drawback is the use of styrene which poses potential health and fire risks.

VES has been used in the USA and abroad to solidify radioactive wastes from nuclear power plants [IAEA, 1988]. Wastes that have been treated with the VES include:

- BWR evaporator concentrates
- PWR evaporator concentrates
- Ion exchange bead resins
- Powdered ion exchange resins
- Decontamination wastes (chelating agent solutions)
- Volume reduced dry salts and incinerator ash.

For the VES solidification process, wastes from the plant collection and storage tanks are transferred to the system waste batch tank. After thorough mixing, a representative sample is withdrawn and subjected to the solidification process. Waste characteristics are checked to insure that they are within the original design criteria. Also, variations are detected and accounted for. Solidification chemicals must not exceed their useful life. A small scale solidification test is also required to verify that the proper proportions of waste and binder are used and to ensure that a satisfactory product will be produced.

The waste volume for solidification is controlled by batch processing. The metering tank is filled to a predetermined level by pumping the wastes from the waste batch tank, with the overflow returning to the waste batch tank by gravity. The solidification container is loaded with a predetermined quantity of binder at the mixing station. Measured amounts of waste and binder are combined, and the catalyst and promoter are sequentially blended with the waste-binder mix to initiate the curing process. Interlocks prevent the use of the catalyst and promoter equipment before waste and binder are mixed. The materials are stored separately and the equipment is designed such that direct mixing of these materials is prevented. The mixture is put on a conveyor where it remains until it is cured. The temperature is controlled to remain below 100°C [IAEA, 1988].

Properties of polymers are affected by the incorporation of wastes into the waste form matrix. The degree to which these changes occur depends on the type and amount of waste incorporated, the chemical interactions between the waste components and the monomer or polymer system, and the processing parameters used to produce the waste forms [IAEA, 1988]. Solidification of the VES/waste mixture can be verified by monitoring the temperature of the mixture (there is a significant temperature rise when the binder solidifies) and/or by performing an impact test upon the surface of the solidified matrix [Tucker, et al., 1983].

5.2 C-14 Release from VES Encapsulated Filters

VES is a solidified emulsified material that has been reported to consist of droplets of waste enveloped in polymer [Colombo, et al., 1985]. The polymer matrix is chemically cross-linked, structurally rigid, and of very limited permeability to water, thus providing a good physical barrier to mass transport. The structural rigidity means that the pore structure of the polymer matrix remains intact even though the waste may dissolve out of or otherwise be removed from the waste. The impermeability of the polymer matrix to water means that mass transport of waste substances out of the waste form occurs through, and is constrained by, the pore structure of the polymer matrix. Expected mechanism of ^{14}C leaching from VES encapsulated waste is diffusion through these pores [Vejmelka and Sambell, 1984].

During the process of encapsulation of ^{14}C filters, it may be possible for ^{14}C species in the filters to be chemically trapped in the polymer structure. However, ^{14}C in the VES waste form is not expected to undergo major chemical reactions that lead to the reduction in leaching other than the crossed-linked polymer working as a low permeability barrier. Interactions between the polymer matrix and the waste is also possible through sorption or ion-exchange. These effects can be included in the effective diffusion coefficient [Dougherty, 1986].

Diffusion as the leaching mechanisms for radionuclides from VES waste form has been confirmed experimentally. The work performed at BNL [Soo, et al., 1988] using ^{60}Co containing ion-exchange resins in the VES showed that observed release closely followed the classic behavior of diffusion. The experimental results also showed that VES-based waste form does not exhibit a 'wash-off' effect during early leaching. An experimental work performed at AECL [Speranzini and Buckley, 1983], which specifically dealt with the issue of ^{14}C leaching, has also confirmed that ^{14}C leaching from polymer waste forms follows the diffusion behavior.

5.3 Values of Diffusion Coefficient for VES Waste Form for Leach Modeling

Since the release of radionuclides from the VES waste form is diffusion controlled, the key parameter for the modeling of ^{14}C release is the diffusion coefficient. Strictly speaking, the diffusion coefficient (as effective diffusion coefficient) is not generally constant but may be expected to vary with the concentrations of diffusant, porosity and other factors [Colombo, et al., 1985]. To characterize the uncertainty of ^{14}C diffusion coefficient, probabilistic modeling was performed by constructing parametric distributions based on existing literature data.

Most of the data on the diffusion coefficient of radionuclides in VES are for ^{60}Co and ^{137}Cs and not for ^{14}C. Use of these data to represent ^{14}C leaching is questionable. The closest one available for ^{14}C diffusion in VES is from an AECL study where ^{14}C leaching from a polyester waste form was analyzed [Speranzini and Buckley, 1983]. The waste used was slurries of barium carbonate mixed with ^{14}C as tracer. Leaching of ^{14}C from the waste was measured for 120 days. The study includes leaching data from cement, bitumen, and polyester.

Given these limitations of the data, two different statistical approaches were employed to determine the diffusion coefficient of ^{14}C:

1. Frequentist Approach (using the ^{14}C leaching data from polyester waste form) - Since the polyester is very close to the VES waste form, the observed ^{14}C leaching data was considered appropriate to represent ^{14}C diffusion in VES.

2. Bayesian Approach (combining the ^{14}C leaching data from the polyester waste form and the cement waste form) – As more experimental data are available, the uncertainty of the ^{14}C diffusion in cement is better characterized. Thus, utilization of these data is desired given the very limited nature of the ^{14}C diffusion data in polymers. Since the AECL study provides data on ^{14}C leaching in both polymers and cement, the ratio of the diffusion coefficient between polymers and cement can be developed. This ratio can be used with the ^{14}C diffusion coefficient in cement to produce a distribution of ^{14}C diffusion data in polymer. The resulting distribution is additional information. The results from (1) provide prior information. Combining these two by Bayesian updating provide a new distribution for ^{14}C diffusion coefficient in VES.

Figure 5-1 presents the leaching data from the AECL study. The following expression was used to determine the diffusion coefficient from the reported cumulative leaching data (as (CFR) times volume to surface area ratio),

$$(CFR)*\left(\frac{V}{S}\right)=2\left(\frac{D}{\pi}\right)^{1/2}t^{1/2} \qquad \text{(Eq. 5)}$$

where, (*CFR*) is the cumulative fractional release, (*V/S*) is the volume to surface area ratio, *D* is the diffusion coefficient, and *t* is time.

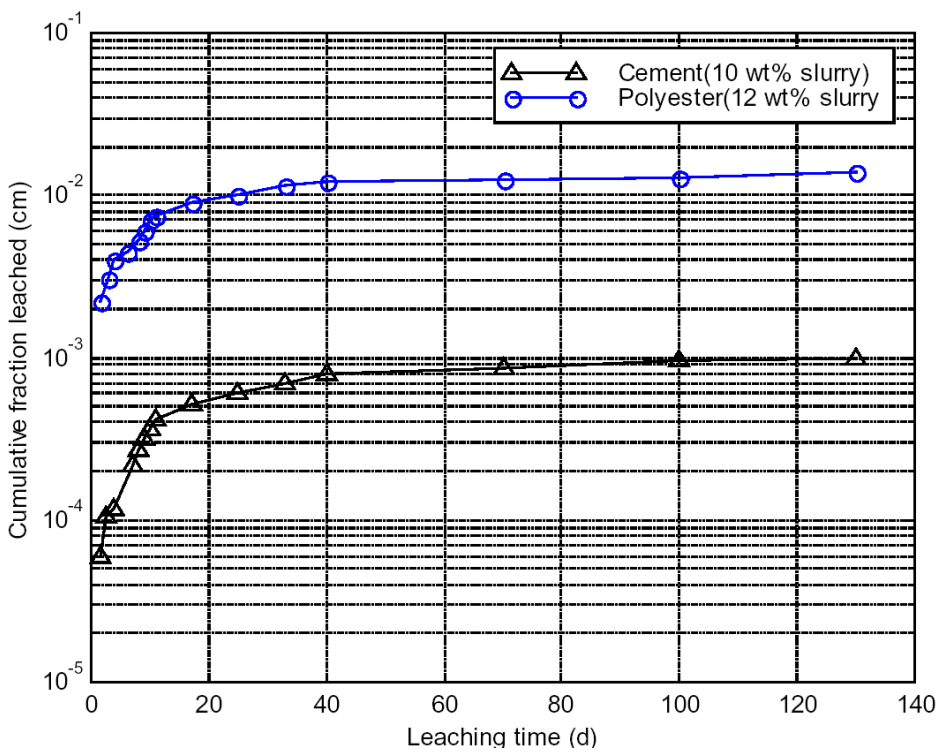

Figure 5-1
C-14 Leaching Data from Polyester and Cement Waste Form (in Cumulative Release Fraction Times Volume/Surface Area) [Speranzini and Buckley, 1983]

Based upon the moments analysis of the resulting diffusion coefficient data, lognormal distribution was selected to fit the data [Cullen and Frey, 1999]. Using the method of matching moment, the following lognormal probability distribution function was developed (This is the final result in Approach #1& the prior information in Approach #2):

$$f(x) = \frac{1}{\sqrt{2\pi} \cdot x \cdot 0.349} \exp\left[-\frac{(\ln x + 24.22)^2}{2 \cdot (0.349)^2} \right] \qquad \text{(Eq. 6)}$$

The goodness-of-fit testing based on the Kolomorov-Smirnov test showed that the maximum difference (D_n) between the cumulative distribution function (CDF) for the hypothesized distribution and the stepwise empirical CDF was 0.251. This was smaller than the critical D_n value of 0.3512 at a significance level 0.05 indicating the fitted distribution is acceptable with respect to the goodness-of-fit test.

From this pdf, the following percentile values are determined:

95th percentile:	5.4e-11 (cm^2/sec)
90th percentile:	4.8e-11
50th percentile:	3.0e-11
mean:	3.2e-11

The pdf of the ^{14}C diffusion coefficient in cement was determined to be also lognormally distributed as described in section 4: By using the ratio of the diffusion coefficient between polymers and cement from the AECL data, the following pdf is constructed as representing the diffusion coefficient of ^{14}C in VES (Additional information in Approach #2).

$$f(x) = \frac{1}{\sqrt{2\pi} \cdot x \cdot 1.848} \exp\left[-\frac{(\ln x + 24.82)^2}{2 \cdot (1.848)^2} \right] \qquad 10^{-15} < x < 10^{-10} \qquad \text{(Eq. 7)}$$

Combination of the two pdfs using Bayesian updating is shown in Figure 5-2. The corresponding percentile values of the combined distribution are:

95th percentile:	4.7e-11 (cm^2/sec)
90th percentile:	4.1e-11
50th percentile:	2.7e-11
mean:	2.8e-11

Typically the 50th percentile values serve as a better average statistic than the mean for a skewed distribution. The 90th percentile is considered a prudently conservative upper end of the distribution. The results indicated that the values from Approach 1 are more conservative. These values are used in the subsequent source term analysis to ensure the conservatism of the analysis.

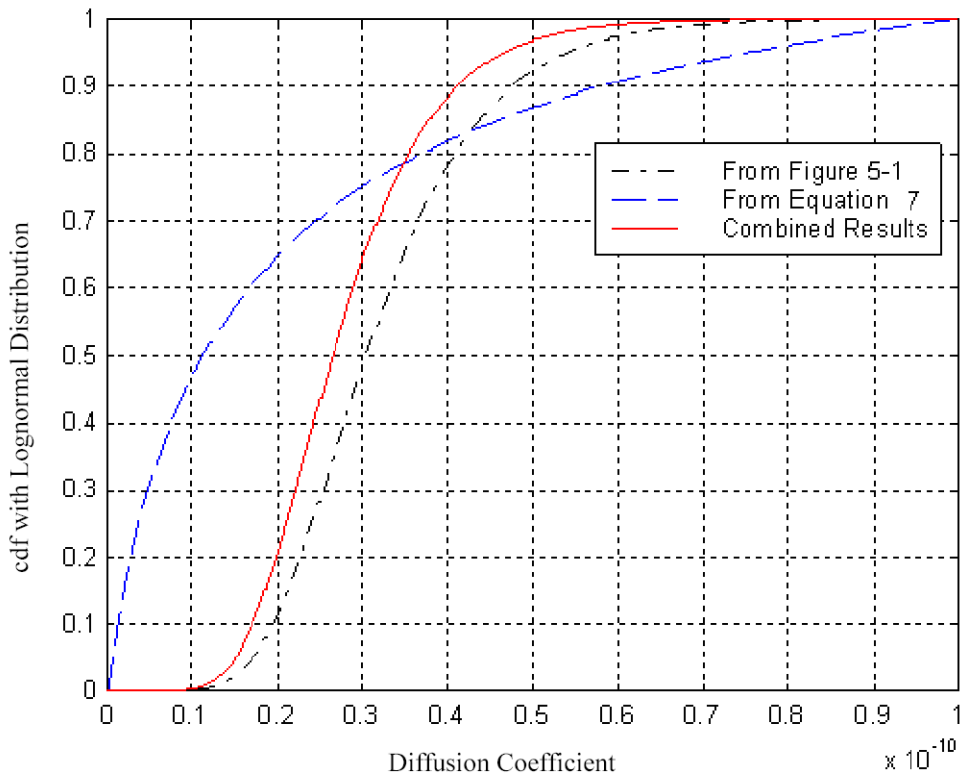

Figure 5-2
Results of Combinations of Two PDFs for ^{14}C Diffusion Coefficient in VES

5.4 Comparisons of C-14 Release Between Waste Forms

To examine the differences in the estimated ^{14}C release between the VES and cement waste form, the DUST code was used. Since the code does not feature probabilistic analysis capability, uncertainties in the estimated release were analyzed by performing several case calculations by using the 90th and 50th percentile values of the (effective) diffusion coefficient in the respective waste form. The predicted ^{14}C release between the two waste forms were compared to quantify the range of differences in the prediction of ^{14}C release.

Figures A-1 and A-2 show the predicted cumulative release of ^{14}C for different percentile input values for different waste forms at the end of 1000 years after the emplacement of waste in a disposal site. The numbers in the figures represent the fraction of ^{14}C released at the surface of the waste form in comparison to the total inventory in a container. The assumptions and scenarios described in section 4.4 were also used for this analysis. As shown in these figures, the release of ^{14}C was lowest with the cement encapsulated waste form. The release from the VES waste form was much lower than that of the unsolidified filters but higher than that from the cement encapsulated waste. In comparison to the VES waste form, the cement waste form showed a factor of 8 (90th percentile case) to 20 (50th percentile case) benefit in reducing the total cumulative release. Table 5-1 presents the summary of these comparisons.

Table 5-1
Comparisons of the Reductions in the Predicted ^{14}C Release Between the Cement and VES Waste Forms (in Reference to the Predicted Release from the Unsolidified Dewatered Filter Waste Form)

	Cement	VES
Cumulative release – 90th percentile	1/73	1/9
Cumulative release – 50th percentile	1/234	1/11
Cumulative release – combined range	1/73 ~ 1/235	1/9 ~ 1/11
Peak annual release – 90th percentile	1/938	1/115
Peak annual release – 50th percentile	1/395	1/19
Peak annual release – combined range	1/122 ~ 1/3025	1/15 ~ 1/144

Although the difference in the predicted cumulative release provides a useful insight, a more practically important insight comes from the prediction of annual fractional release, in particular, the annual peak release rate. The predicted annual peak release rate reflects the projection of the peak annual dose to the members of the public, should any human exposure take place from the release of radioactivity. The peak release rate leads to the peak dose to humans after the geosphere and biosphere transport. The current regulatory approach to low level waste disposal uses the peak annual dose as a basis for protecting public health (25 mrem per year) [NRC, 1982]. Thus the compliance decisions in performance assessment deal mainly with the projected peak annual dose.

Comparisons of the predicted annual release rates for the 90th and 50th percentile values are shown in Figures A-3 and A-4. In the 90th percentile value case, the predicted peak annual release was a factor of 938 lower with the cement encapsulated filters and 115 with the VES filters compared to the unsolidified dewatered filters. In the 50th percentile value case, the difference was a factor of 395 with cement and 19 with VES. If the 50th and 90th percentile results were combined to form a range, the difference of the predicted peak annual release would be by a factor of 122 to 3,025 with cement and 15 to 144 with VES.

6
COMPARISONS OF WASTE FORM CHARACTERISTICS

Solidification based on portland cement is well established and involves relatively simple operations carried out at room temperature. The level of worker exposure to radioactive waste is dependent on the amount of cleanup needed after the solidification process [Cowgill, 1991]. This is affected by such factors as whether or not the cement/waste mixing operation is performed in the disposal container. The cementation process itself is sensitive to the physical and chemical characteristics of the waste streams. However, for the solidification of filter wastes which are expected to be chemically simple, this may not be a concern. To assure that the formulations used are producing successful solidifications, it is required that verification and surveillance specimens be prepared.

The thermosetting processes involve several ingredients, thus the solidification processes have to be closely controlled. The VES encapsulation process is easy to use as the mixing solidification agent (and the subsequent blending of catalyst and promoter) are all accomplished in binder feed tank, thus minimizing worker exposure to radioactivity during cleanup operations. Because the vinyl ester resin is classified as a flammable liquid in the unsolidified state, all areas containing the unsolidified binder must comply with fire protection codes. The waste form itself is not a fire hazard. The chemicals used in the VES Process are more expensive than either cement or bitumen. The shelf life of the binder is about 6 months, but can be extended with proper storage procedures.

VES polymers have superior mechanical properties such as compressive strength and tensile strength. This allows for higher waste loads than can normally be incorporated into cement without compromising the integrity of the waste forms. Polymeric waste forms are very resistant to most acids, bases and organics that can be found in waste streams. The effect of weak acids and alkalies on the waste form is nil although strong acids can attack the material [IAEA, 1988]. Resistance to organic solvents is also considered good for VES polymers. The cross-linked thermoset polymers retain their properties up to temperatures as high as 175°C or until they reach decomposition temperatures. The decomposition temperature depends on molecular structure and bonding [IAEA, 1988]. Since a polymer has a higher density than its monomers, shrinkage can occur upon polymerization. Shrinkage can create stresses to the waste form and poor binding between the polymer and the waste. Also there is a significant temperature rise when the binder solidifies which can result in the cracking of the polymers. Usually these problems can be minimized through the use of additives and by controlling the polymerization reaction. Adding bead resins into the polymer matrix is suggested as a remedy to this cracking. NRC has approved the VES encapsulation method with addition of bead resins to the container.

A summary comparison of advantages and disadvantages of cement and VES waste forms are provided in Table 6-1.

Table 6-1
Summary Comparison of Advantages and Disadvantages Between Cement and VES Waste Form

	Cement	VES
Advantages	- A superior mass transport barrier for ^{14}C due to ^{14}C chemical reactions in cement. - Ready availability. - Low cost - Long shelf life - Relatively safe and easy to handle	- Compatible with different types of radioactive wastes over a wide range of conditions including wet and dry wastes. - Superior mechanical properties such as compressive strength and tensile strength, allowing for higher waste loads than can normally be incorporated into cement without compromising the integrity of the waste forms. - Possibility of co-disposal of IX resins and filters. - Less worker radiation exposure during cleanup operations - Approved by NRC
Disadvantages	- Worker radiation exposure can be higher depending upon the amount of cleanup efforts needed after the solidification process. - Not compatible with IX resins.	- Solidification processes have to be closely controlled. - Potential concern for cracking – can be avoided by adding bean resins. - Higher cost than cement. - The shelf life of the binder is about 6 months. - Use of styrene poses potential health and fire risk in the unsolidified state.

BNL [Neilson, 1981] produced acceptable solidified products with the Dow Binder using Dow's proprietary procedure and waste/binder ratio recommended by Dow. No free water was observed. The BNL work also confirmed that the binder is largely insensitive to chemical composition of the waste. Dow has performed extensive tests upon the product and the NRC has reviewed and accepted the Dow Topical Report, DNS-RSS-001-P-A [Tucker, et al., 1983]. The last NRC Technical Report to be approved was the VES Encapsulated Process.

Other properties of cement and polyester waste forms based upon the immobilization of ion exchange resins are summarized in the following table [IAEA, 1985]. The values of VES should be similar to those of polyester.

Table 6-2
Comparisons of Waste Form Properties [IAEA, 1985]

Properties	Cement	Polyester
Compressive Strength (kg/cm2)	100-300	380-420
Density (g/cm3)	1.3-2.0	1-1.1
Thermal conductivity (W/m-K)	Not significant	0.23
Thermal decomposition (C)	>400 C	300-450
Radiation stability (Gy)	Up to ~10^8	>10^6
Radiolysis	Negligible	Yes

7
DISCUSSION

LLW performance assessment emphasizes 'prudent conservatism' in the analysis methodology. If the deterministic approach is employed in performance assessment, the 10th percentile values are likely to be used for prudent conservatism. Therefore, the predicted difference of the peak annual ^{14}C release of 516 for the 10th percentile value case can serve as a representative measure of benefits of grouting for the deterministic approach. The difference of 408 from the 50th percentile value case can be considered more realistic considering the overall uncertainty of the inputs. The difference of 67 for the combined range would represent an unlikely case. The reduction in ^{14}C mobility from the use of cementitious grout can be viewed to range between 67 and 516 with 408 representing a more realistic case.

Assumptions made in the source term analysis scenario and the capabilities of the DUST code can also contribute to the uncertainty in the results. In the analysis of diffusional release with the DUST code, it was assumed that solubility is not limiting the release of ^{14}C. In reality, the solubility of ^{14}C in a high pH cement environment is expected to be very low and can inhibit the mass transport significantly. Thus the predicted ^{14}C release for the grouted filter waste could be overestimated.

The DUST code, in its modeling for the surface-wash release from the dewatered filter waste and the diffusional release for solidified waste, uses conservative approaches. For example. DUST surface-wash model assumes that all the rinsable mass inventory is washed out as the water contacts the waste regardless of the water flow rate. DUST diffusion model uses zero-concentration boundary condition which ignores the decrease in the concentration gradient with continued leaching at the waste form boundary. With the consistent use of conservative modeling approaches, the uncertainty in the relative difference of the source term between the two waste forms is expected to be insignificant.

In the DUST analysis, it was assumed that the waste container completely failed at a given single finite lifetime. In reality the failures of waste containers are more progressive than being catastrophic. Impact of this single lifetime assumption is higher release rate of ^{14}C than the realistic case. This higher release will occur with both the surface-wash and diffusional release. Thus, this assumption is not expected to be a major source of uncertainty.

This report showed that a cemented waste form provides a good encapsulation medium for ^{14}C filters with the benefits of reducing ^{14}C release by the reduction in permeability/ porosity, precipitation in the form of calcite with reduced solubility, and with increased sorption capacity for ^{14}C. Also a VES waste form was shown to provide a rigid, cross-linked, impermeable mass transport barrier for ^{14}C leaching. It is also noted that the VES waste form with the addition of bead resins has been approved by the NRC for the encapsulation of filters.

Discussion

Given the level of reduction in the predicted source term due to waste form encapsulation to be higher than by a factor of 10, concentration averaging for filters with the use of cement or VES encapsulation is a very feasible approach. Concentration averaging would allow individual objects that exceed Class C to be grouped with other object from the same waste stream. If the resultant group average does not exceed Class C, the waste can be disposed of as low level waste. Thus the use of stable encapsulation agents for filters that exceed Class C by more than a factor of 10 of the limit in concert with the application of concentration averaging with other filters of the same waste stream provides a method for disposal of such filters as low level waste (see Appendix B).

The results from this report demonstrate that there is no technical basis to disallow averaging the ^{14}C activity on such filters over stable encapsulation agents. Similarly, filters that exceed Class C due to other nuclides could also be allowed to have that activity averaged over the waste and stable encapsulation agent, if the nuclide's source term behaves similarly to ^{14}C.

8
SUMMARY AND CONCLUSIONS

This research investigated the cement/VES encapsulation of cartridge filters to reduce the potential leaching of ^{14}C in waste disposal. For this purpose, the chemical forms of ^{14}C expected in the dewatered cartridge filters and their changes in the grouted cement or VES due to the chemical interactions and evolutions in the system were examined. Based on this the following observations were made:

- The chemical forms of ^{14}C activity on filter waste encapsulated in cement become inorganic as the waste is solidified in the high pH, oxidizing environment in cement.
- The mineralogic changes associated with carbonation of hydrated cement in grout yield a calcite end product that immobilizes inorganic ^{14}C.
- The chemical buffering provided by the dissolution of cementitious materials will ensure low solubility of calcite, thereby minimizing the possibility for the remobilization of ^{14}C and contributing to the retention of ^{14}C in the solid phase in the waste form for an extended time period.
- As a result of carbonation, the permeability and porosity of the waste form are reduced. This will reduce mass transport through the waste form. Thus even under advective flow conditions, mass transfer through the waste form will be diffusion-controlled.
- Due to the reaction between SiO_2 and CaO contained in the cementitious composition, the originally negatively charged (SiO^-) SiO_2 surface sites become positively charged, thus inorganic ^{14}C in the cement waste are adsorbed onto these surfaces by an electrostatic force [Noshita, et al., 1996]. This enhanced sorption will further reduce the effective diffusion coefficient for the release of ^{14}C from the cement waste form.
- Although the cement waste form may develop cracks and structurally degrade, the cementitious materials continue to provide chemical functions in maintaining a high pH environment. Thus the cement waste form will remain effective for very long periods of time to immobilize ^{14}C.
- During the process of polymer encapsulation of ^{14}C filters, it may be possible for ^{14}C species in the filters to be chemically trapped in the polymer structure. However, ^{14}C in the VES waste form is not expected to undergo major chemical reactions.
- The polymer matrix is chemically cross-linked, structurally rigid, and of very limited permeability to water, thus providing a good physical barrier to mass transport. The structural rigidity means that the pore structure of the polymer matrix remains intact even though the waste may dissolve out of or otherwise be removed from the waste. The impermeability of the polymer matrix to water means that mass transport of waste substances out of the waste form occurs through, and is constrained by, the pore structure of the polymer matrix.

With these understandings, the differences in the ^{14}C leaching mechanisms between the dewatered and grouted filter waste were identified: The surface-wash release although conservative was accepted for the dewatered filter waste due to the uncertainties in describing ^{14}C leaching. For the encapsulated filter waste, diffusion through water in the pore spaces was the dominant mass transport mechanism. Carbon-14 release through these mechanisms was analyzed using the DUST code. Since the results of estimated ^{14}C release are predominately controlled by the values of K_d for the surface-wash release and the effective diffusion coefficient for the diffusional release, these two parameters were carefully characterized for their uncertainty. For this, parametric probability distribution model fitting was performed for these two parameters based on existing literature data. For the effective diffusion coefficient of ^{14}C in VES, Bayesian approach was adopted to utilize all available information given the very limited nature of the available experimental data.

From this probability model, various percentile values of the two parameters were obtained. In the DUST analysis, the 90th and 50th percentile values were used. Results of the DUST analysis indicated that the reductions in the ^{14}C release with the implementation of cement or VES waste form would be significant enough for these two waste forms to be useful for ^{14}C immobilization and concentration averaging. The peak annual release of ^{14}C was reduced by a factor of 15-144 using VES and 122-3025 with cement. It is judged that the uncertainties in the source term analysis will not have major impact on the estimates made in this study.

In conclusion, this research compared the ability of cement and VES encapsulation to immobilize ^{14}C on filters versus standard dewatering and found that both cement and VES are viable engineering solutions for the immobilization of GTCC ^{14}C filters. The results showed the reduction in the ^{14}C source term due to waste form encapsulation to be more than by a factor of 10. With the use of cement encapsulation, the reduction was higher than by a factor of 100.

This study provides important technical basis for concentration averaging of these filters with the encapsulation of filter waste. The concentration averaging with cement or VES encapsulation will reduce the greater than Class C filter disposal costs and avoid the storage of high-radiation filters. The findings also support the position of the NRC guidance on concentration averaging over stable encapsulation agents for Class B/C waste. There is no technical reason to disallow averaging activity over the waste and stable encapsulation agent for ^{14}C filters.

9
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A
APPENDIX

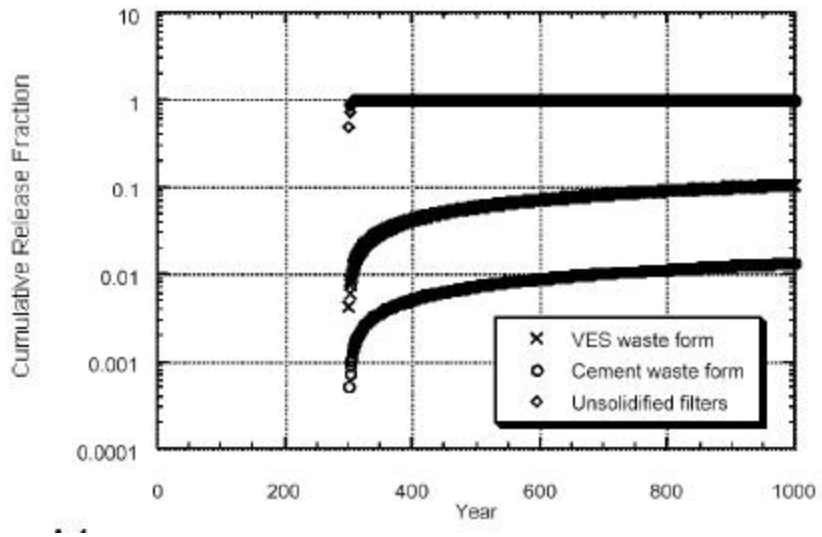

Figure A-1
Comparisons of Cumulative ^{14}C Release between Different Waste Forms (90th Percentile Case)

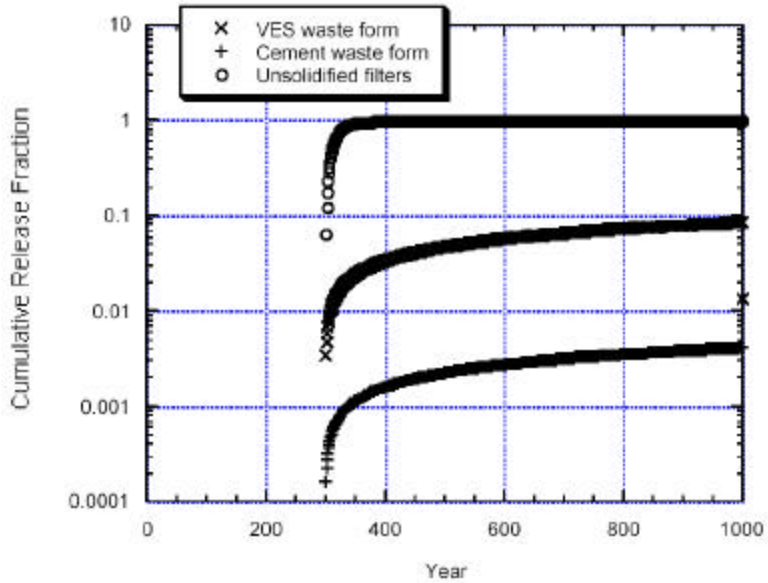

Figure A-2
Comparisons of Cumulative ^{14}C Release between Different Waste Forms (50th Percentile Case)

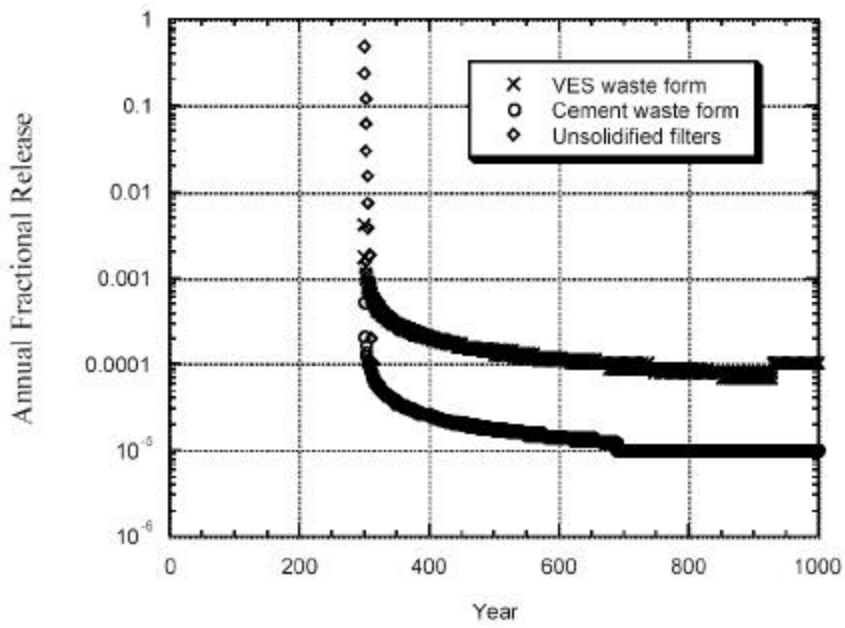

Figure A-3
Comparisons of Annual ^{14}C Release Between Different Waste Forms (90th Percentile Case)

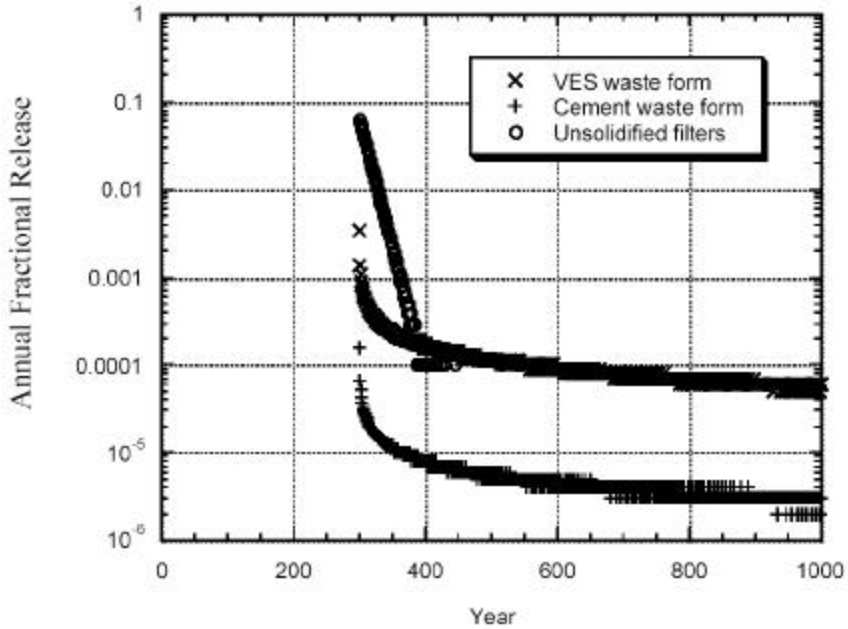

Figure A-4
Comparisons of Annual ^{14}C Release Between Different Waste Forms (50th Percentile Case)

B
APPENDIX

Nuclear Regulatory Commission Branch Technical Position on Concentration Averaging and Encapsulation, January 1995

This Appendix is a revision of the discussion of the NRC technical position on the averaging of waste radionuclide concentrations for packaged radioactive wastes published in *Low Level Waste Characterization Guidelines,* EPRI TR-107201, November 1996. The revisions are clarifications to the earlier version particularly relevant to concentration averaging for encapsulated filter cartridges. Actual excerpts from the NRC BTP relevant to this discussion are included in Appendix C.

This BTP expands upon, provides additional definitions, and replaces guidance provided in the section of the previous BTP on "Concentration Volumes and Masses". It also provides corrections to the 1983 BTP changing the *biannual requirement for analysis of Class A waste streams to biennial, and removing the requirement to classify wastes shipped to processors.* The BTP describes a rather complex set of criteria and rules for determining the classification of packages containing wastes from multiple streams. The rules differ for gamma-emitting nuclides and the others. They also differentiate between "conventional" waste streams and contaminated or irradiated metal hardware and mixtures of cartridge filters introducing definitions and rules for averaging over "discrete" components.

B.1 Mixing of Homogeneous Waste Types or Streams

Mixing of homogeneous streams is not considered mixing if done for a designed collection of homogeneous waste types from a number of sources within a licensee's facility, for purposes of operational efficiency or occupational dose reduction. In these cases concentration averaging can be over the entire volume of the waste in the container, providing the individual contributors are within a factor of 10 of the average concentration of the mixture. Otherwise the classification must be based from analyses of the concentrations of the highest contributor to the mixture.

Utility waste streams usually qualifying as homogeneous are filter sediments and powdered demineralizer resins, evaporator bottoms and DAW. Most mixtures of bead demineralizer resins qualify as homogeneous under the criteria as resulting from purposes of operational efficiency or occupational dose reduction.

The classification of the homogeneous streams in utility wastes is usually controlled in Class A and B wastes by the beta-emitting nuclide ^{63}Ni or the gamma-emitting nuclide ^{137}Cs. Averaging of different streams of homogeneous wastes must follow the rules for the nuclides that dominate.

B.2 Solidified and Absorbed Liquids

Concentrations of these wastes may be averaged over the volume or mass of the solidified waste if the binder is approved for the stability requirement. If not, e.g., in the case of absorbed liquid, the concentration must be averaged over the volume of the preabsorbed liquid.

B.3. Mixing of Activated Materials or Metals

Concentrations may be averaged over the volume of a single component, even if cut into sections, providing the entire component is included in the container sections. Different components are considered as discrete pieces. An individual section or piece is also defined as discrete if:

- The volume of the piece is less than 0.01 ft^3 or 0.00028 m^3 (typically less than 10 lb., 4.5 kg) and has nuclide concentrations greater than 700 Ci/m^3 ^{60}Co (not applicable for Class C), 1 mCi/m^3 ^{94}Nb, or 3 mCi/m^3 (30 Ci/m^3 for Class C) ^{137}Cs.
- The piece is a section cut from a larger component where the entire component is not included in the container and whose concentrations exceed 8 Ci/m^3 ^{3}H (not applicable for Class C), 1 Ci/m^3 ^{14}C (10 Ci/m^3 for Class C), 4Ci/m^3 ^{59}Ni (40 Ci/m^3 for Class C), 7 Ci/m^3 ^{63}Ni (1500 Ci/m^3 for Class C), or 3 mCi/m^3 TRU with half lives greater than five years (30 mCi/m^3 for Class C). Averaging is always allowed if the total gamma-emitting concentration of a discrete piece of component is less than 1 mCi/m^3.

Averaging is allowed for contents of a container where the pieces are all from a single component although the component itself is too large to fit inside a single container.

Concentrations may be averaged over mixtures of components or discrete pieces only if the classification-controlling concentrations of the individual components or discrete pieces are within a factor of ten of the average for DTM nuclides and a factor of 1.5 for the controlling gamma emitters, e.g., $^{6°}Co$, ^{94}Nb, ^{137}Cs. These comparisons may be done independently and apply only for waste classification-controlling radionuclides.

Else it is necessary, and always possible, to base a container classification on the highest classification of any discrete piece, section or component within the container.

Much irradiated hardware is either Class C or Greater-Than-Class C. The classification-controlling nuclides in these items are usually ^{63}Ni in the beta-emitting category and ^{94}Nb as a gamma emitter. Either or both of these nuclides can affect the averaging rules.

B.4. Contaminated Materials

For a single contaminated component, concentrations may be averaged over the volume of the component.

An individual section or piece is defined as discrete if:

- The volume of the piece is less than 0.01 ft^3 or 0.00028 m^3 (typically less than 10 lb., 4.5 kg) and has nuclide concentrations greater than 700 Ci/m^3 ^{60}Co (not applicable for Class C), 1 mCi/m^3 ^{94}Nb, or 3 mCi/m^3 (30 Ci/m^3 for Class C) ^{137}Cs.
- The piece is a section cut from a larger component where the entire component is not included in the container and whose concentrations exceed 8 Ci/m^3 ^{3}H (not applicable for Class C), 1 Ci/m^3 ^{14}C (10 Ci/m^3 for Class C), 4 Ci/m^3 ^{59}Ni (40 Ci/m^3 for Class C), 7 Ci/m^3 ^{63}Ni (1500 Ci/m^3 for Class C), or 3 mCi/m^3 TRU with half lives greater than five years (30 mCi/m^3 for Class C). Averaging is always allowed if the total gamma-emitting concentration of a discrete piece of component is less than 1 mCi/m^3.

Concentrations for a mixture of discrete contaminated components may be averaged over the entire volume if the concentrations of the DTM nuclides in each discrete piece do not differ from the average by more than a factor of ten or the concentrations of the gamma emitters in each component do not differ from the average by more than a factor of 1.5, or their concentrations are less than 700 Ci/m^3 ^{60}Co (not applicable for Class C), 1 mCi/m^3 ^{94}Nb, or 3 mCi/m^3 (30 Ci/m^3 for Class C) ^{137}Cs.

Else it is necessary, and always possible, to base a container classification on the highest classification of any discrete piece, section or component within the container.

B.5. Mixing of Cartridge Filters

Concentrations for a mixture of filter cartridges may be averaged over the entire volume if the concentrations of the non-gamma emitters in any filter do not differ from the average by more than a factor of 10 or the concentrations of the c*lassification-controlling* gamma emitters in each filter do not differ from the average by more than a factor of 1.5, or their concentrations are less than 700 Ci/m^3 ^{60}Co (not applicable for Class C),1 mCi/m^3 ^{94}Nb, or 3 mCi/ m^3 (30 Ci/m^3 for Class C)^{137}Cs.

Else it is necessary, and always possible, to base a container classification on the highest classification of any individual (discrete) filter within the container.

The exterior (envelope) volume of a cartridge may be used for classification as may the non-radioactive mass (including the end cap). The volume of the cartridge air space cannot be used if the filters are compacted or sheared before packaging.

B.6. Waste in High-Integrity Containers

Concentration averaging should only be over the volume and mass of the waste rather than that of the container, providing that the waste meets the criteria for a homogeneous waste stream.

B.7. Encapsulation of Solid Material

Concentration averaging may be over the volume or mass of the encapsulated waste providing that:

- A minimum amount of encapsulation is present to "increase the difficulty of an inadvertent intruder moving the waste by hand",
- The maximum amount of encapsulation is 0.2 m^3 unless a specific rationale is provided,
- The maximum amount of gamma-emitting concentration is that which, if credit is taken for a 500-year decay period, would result in a dose rate less than 0.02 mrem/hr on the surface of the encapsulating media,
- The classification of the encapsulated package does not exceed Class C,
- The discrete activity source is reasonably centered in the encapsulation, and
- The structural form meets the requirements of lOCFR61.56 for Class B and C waste.

When two different waste streams are together in a grouted container, the fraction of grout volume used for each stream in concentration averaging should be the same fraction as that waste volume in the mixture.

B.8. Mixing of Dissimilar Streams (Different Waste Types)

Averaging is allowed if the classification of the mixture is not lower than the classification resulting from any individual component of the mixture**.** Excluded from this requirement are small check sources (less than 100μCi).

C
APPENDIX

Excerpts from the Nuclear Regulatory Commission Branch Technical Position on Concentration Averaging and Encapsulation, January 1995

C.1 Mixing of Cartridge Filters

The classification of cartridge filters should be based on the nuclide activity contained on the filter divided by the displaced volume (interstitial space within the filters may be included) or weight of the filter. Because of the typical distribution of activity within cartridge filters, the envelope volume would generally be expected to be an appropriate volume for determining filter classifications.

Mixing of multiple cartridge filters in a disposal container or liner is permissible. In determining the classification of the multiple filters, it is always permissible to conservatively base the classification on the highest classification associated with any single filter. It is also permissible, under the following constraints, to average the concentrations of radionuclides listed in 10 CFR 61.55, Table 1 and Table 2. Because of the potential non-homogeneity of the filters, the classification of the combined filters may be affected by whether the waste contains the primary gamma-emitting nuclides (typically, Co-6O or Cs-137/Ba-137m). However, the classification of many higher class cartridge filters could be controlled by C-14 or transuranic concentrations. In determining the classification of a container of filters, one or more of the following paragraphs may apply.

C.1.1 Averaging Involving Primary Gamma-Emitters

For the purpose of classifying multiple cartridge filters containing the primary gamma-emitters (i.e., if these nuclides dictate the classification of the waste), their individual nuclide concentrations may be based on the volumetric-averaged concentration of combined filters, provided that the concentrations within the individual filters of the mixture in the disposal container or liner are within a factor of 1.5 of the respective averaged concentration values of each nuclide. This factor of 1.5 does not apply if the classification of the combined filters, as a result of other nuclides, is higher than the class derived from the primary gamma-emitter concentrations.

C.1.2 Averaging Involving Radionuclides other than Primary Gamma-Emitters

For the purpose of classifying multiple cartridge filters, the concentrations of all the 10 CFR 61.55 tabulated radionuclides in the disposal container or liner, other than the primary gamma-emitters, may be based on the volumetric or weight-averaged concentrations of the combined materials. In this case, all the concentrations of the “classification-controlling” individual

materials. In this case, all the concentrations of the "classification-controlling" individual nuclides within all the individual filters should be within a factor of 10 of their respective averages over all filters in the mixture.

C.1.3 Mixtures Containing Multiple Radionuclides

For cartridge filters containing combinations of tabulated nuclides, the sum-of-the-fractions rule described in 10 CFR 61.55(a)(7) would apply. For cartridge filters, this rule could involve summing the fractions of the appropriate 10 CFR 61.55, Table 1 or Table 2 concentration values associated with the primary gamma-emitting nuclides and the fractions of tabulated concentrations associated with the other nuclides. The respective fractions contributing to the sum can be calculated by using the "highest concentration associated with any filter or, if applicable, the concentration determined by using the "averaging" methods described previously.

Independent of whether the "highest concentration" or "averaging" method is used to classify multiple filters in a disposal container/liner, in accordance with Section III of Appendix F to 10 CFR Part 20, the licensee classifying the mixture of filters must have in place a quality control program to ensure compliance with the waste classification provisions of 10 CFR 61.55. As part of this quality control program, if the classification of the mixture of filters is based an the volumetric- or weight-averaged nuclide concentrations of the disposal container/liner contents, as allowed above, the licensee responsible for classification of the waste should prepare, retain with manifest documentation, and have available for inspection, a record documenting the licensee's waste classification analyses. It is generally expected that this record or analysis, in and of itself, should be sufficient to show that the averaging of concentrations over all the contents in the disposal container/liner was undertaken under the provisions of this position.

C.1.4 Illustrative Example

Example: A liner contains four cartridge filters. Note: In actual cases, more than this number could be contained in a liner. The filter volumes, weights, and principal "classification-controlling" nuclide activities are shown below (rounded), along with the nuclide's concentration expressed as a fraction (frac) of appropriate Table 1 concentration value. A Cs-137 concentration is also presented.

	Fuel Pool				**Reactor Coolant**			
	Filter #1		**Filter #2**		**Filter #1**		**Filter #2**	
Volume (m^3)	0.024		0.024		0.0127		0.0127	
(ft^3)	0.85		0.85		0.45		0.45	
Weight (kg)	9.08		9.08		4.09		4.09	
(lbs)	20		20		9		9	
Nuclide	Ci	frac	Ci	frac	Ci	frac	Ci	frac
V-14	0.01	0.052	0.009	0.047	0.005	0.05	0.002	0.02
Pu-241	0.008	0.25	0.007	0.22	0.01	0.71	0.004	0.28
Transuranic	0.0004	0.44	0.0003	0.33	0.0005	1.24	0.0002	0.49
10 CFR 61.55								
Table 1 Total Cs-137 =	0.74 concentration 1.5×10^{-2} Ci/m^3		0.60 concentration 1×10^{-2} Ci/m^3		2.00 concentration 1×10^{-1} Ci/m^3		0.79 concentration 4×10^{-2} Ci/m^3	

The Cs-137/Ba-137m activity in all the filters is sufficiently small such that the classification of the filters will not be determined by this gamma-emitting nuclide. Similarly, other nuclides to which 10 CFR 61.55, Table 2 values may apply have not been listed since their values will not affect cartridge filter classification. Thus, the four filters listed could be placed in a single disposal container/liner, since all the listed nuclide concentrations are within an order of magnitude of the averaged concentrations. The sum-of-the-fractions for the three nuclides would be: C-14, (0.04) + Pu-241, (0.32) + Transuranic (TRU), (0.53) = 0.89, indicating that the multiple filters could be classified as Class C waste.

C.2 Waste in High-Integrity Containers (HICs)

In the case of cartridge filters or other discrete item waste stabilized by emplacement within HICs, the volume or weight used to determine waste classification should be calculated over the displaced volume (interstitial space within the filters may be included - envelope volume may be appropriate) or weight of the cartridge filter or discrete item itself, rather than the gross volume or weight of the container. Similarly, the volume and mass considered for purposes of waste classification of dewatered ion-exchange resins, filter backwashes, and filter media placed into HICs should be the volume and mass of the contained waste. In both these cases, disposal in a HIC is not considered to alter the as-buried concentrations of radioactivity.

C.3 Encapsulation of Solid Material

For routine wastes such as filters, filter cartridges, or sealed sources centered in an encapsulated mass, classification may be based on the overall volume of the final solidified mass, provided that: (1) the volume and attributes of the encapsulated waste comply with the constraints established in Appendix C of this technical position; (2) the solidified mass meets the waste form structural stability criteria of 10 CFR 61.56 for Class B and Class C waste; and (3) the disposal unit containing the encapsulated mass is segregated from disposal units containing Glass A wastes, that do not meet the structural stability requirements in 10 CR 61.56(b). Under the above provisions, additional protection is provided through the shielding, lack of dispersibility, or identifiability of the encapsulated mass and, for Class C encapsulated waste, by the land disposal facility operational requirements in 10 CR 61.52(a)(2). This additional protection has been considered in the classification position developed in Appendix C and has been balanced against the hypothetical radiological impact caused by potential interactions between assumed intruders and the encapsulated mass.

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