# Evaluation of Waste Forms for Immobilization of $^{14}C$ and $^{129}I$

## Development of Novel Management Scheme for $^{14}C$ and $^{129}I$ in Utility LLW Streams

**TR-110096**

Final Report, August 1998

EPRI Project Manager
C. Hornibrook

EPRI • 3412 Hillview Avenue, Palo Alto, California 94304 • PO Box 10412, Palo Alto, California 94303 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com

## DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS REPORT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) NAMED BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS REPORT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS REPORT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS REPORT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS REPORT.

ORGANIZATION(S) THAT PREPARED THIS REPORT

**North Carolina State University**

## ORDERING INFORMATION

Requests for copies of this report should be directed to the EPRI Distribution Center, 207 Coggins Drive, P.O. Box 23205, Pleasant Hill, CA 94523, (510) 934-4212.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. POWERING PROGRESS is a service mark of the Electric Power Research Institute, Inc.

Copyright © 1998 Electric Power Research Institute, Inc. All rights reserved.

# CITATIONS

This report was prepared by

North Carolina State University
Department of Nuclear Engineering
1110 Burlington Laboratories
Raleigh, North Carolina 27695

Principal Investigator
Man-Sung Yim

This report describes research sponsored by EPRI.

The report is a corporate document that should be cited in the literature in the following manner:

*Evaluation of Waste Forms for Immobilization of* $^{14}$*C and* $^{129}$*I: Development of Novel Management Scheme for* $^{14}$*C and* $^{129}$*I in Utility LLW Streams,* EPRI, Palo Alto, CA: 1998. TR-110096.

# REPORT SUMMARY

---

$^{14}C$ and $^{129}I$ radionuclides can pose waste disposal challenges, since they are readily incorporated into bio-organic molecules and have half-lives that are substantially longer than most other radionuclides present in nuclear power plant low level waste (LLW). This study evaluated several techniques for separating $^{14}C$ and $^{129}I$ from LLW as well as a number of waste forms for immobilizing them. While the study did not result in any viable approaches for separating the waste, it did identify a number of waste forms warranting further investigation when operable separation techniques become available.

### Background

Long-lived radionuclides make up the majority of the dose projections from proposed LLW disposal facilities. Maintaining these doses at or below the 10CFR61 limit of 25 mrem/yr can be achieved by limiting the inventory of these radionuclides for disposal. However, limiting the inventory allowed will limit the operating life of the facility. To ensure that a disposal facility operates to the full extent of its potential life, EPRI is investigating methods for longer immobilization of these radionuclides.

### Objectives

To determine the feasibility of separating $^{14}C$ and $^{129}I$ from utility waste streams and identify advanced waste forms that would immobilize these nuclides for final disposal.

### Approach

Most $^{14}C$- and $^{129}I$-containing waste compounds in nuclear reactor coolant systems are captured by ion-exchange resins. Accordingly, project investigators attempted to identify techniques that could be used to separate $^{14}C$ and $^{129}I$ from ion-exchange resins. Next, they evaluated various potential waste forms for immobilizing the separated $^{14}C$ and $^{129}I$.

### Results

Developing cost-effective ways to separate and immobilize $^{14}C$ and $^{129}I$ radionuclides is important for encouraging the future use of the separation and immobilization approach by the nuclear power industry. Unfortunately, this study did not identify any techniques for separating $^{14}C$ from nuclear power plant ion-exchange resins, which could be integrated into current plant operations or waste handling approaches.

However, the study did determine potential intrinsic and matrix waste forms for immobilizing $^{14}C$ and $^{129}I$ if they could be successfully separated from LLW. Following are the key results of this study:

- Cement-based waste forms appear promising; however, the chemical forms of the carbon and iodine within the cement matrix and control of near-field chemistry are critical for long-term durability.
- Graphite, glassy carbon, and silicon carbide as engineered barriers (containers) appear to significantly improve long-term immobilization of $^{14}C$ and $^{129}I$, regardless of the intrinsic or matrix waste form used.

This study resulted in the development of a strategy to evaluate various waste forms, with and without the use of engineered barriers. The study also produced a design for a testing apparatus used to evaluate the performance of graphite as an engineered barrier.

**EPRI Perspective**

As investigation into separation techniques continued, it became clear that use of $^{14}C$ and $^{129}I$ separation technology at an operating nuclear power plant was neither feasible nor desirable at this time. Without the separation of these nuclides from the original wastes, the use of the proposed waste forms in this report would significantly increase the volume for final disposal as well as associated LLW management costs. It should be noted, however, that successful separation would result in relatively small waste volumes, which would be more cost-effective and technically feasible in the proposed advanced waste forms. Should separation technologies advance to the stage where their use is desirable and cost-effective, EPRI will reevaluate this research for further investigation.

**TR-110096**

**Interest Categories**

Low level radioactive waste management
Radiation field control

**Keywords**

Waste forms
Carbon-14
Iodine isotopes
Waste disposal

# ABSTRACT

Intrinsic waste forms are those that chemically bind a radionuclide.
Matrix waste forms microscopically encapsulate materials.
Engineered barrier, in this report, refers to containers and not structures.

This report presents interim findings for the EPRI research project, entitled, *Development of Novel Management Scheme for $^{14}$C and $^{129}$I in Utility LLW Streams*. The project's goal is to identify waste forms for $^{14}$C and $^{129}$I that are intrinsically durable when subjected to contact by ground water. Key findings to date include:

- The most widely accepted and studied waste form for $^{14}$C immobilization is calcite in a cement matrix. Long-term durability of this waste form depends not on its inherent durability, but rather on the ability of the cement to control the evolution of the ground water chemistry.

- Cement has been found to be the best matrix waste form for $^{129}$I. In this matrix, binding the $^{129}$I as silver iodide gives the best durability. Though having higher leachability than cement, other potentially suitable intrinsic waste forms include calcium iodate and barium iodate.

- Engineered barriers of graphite, glassy carbon, and silicon carbide appear to significantly improve long-term immobilization of $^{14}$C and $^{129}$I, regardless of the intrinsic or matrix waste form actually used. Uncertainty in predicting the environmental durability of graphite is very small.

- A strategy to evaluate various waste forms with and without the use of engineered barriers has been developed. A testing apparatus for evaluating graphite performance as an engineered barrier has been designed.

# CONTENTS

# LIST OF FIGURES

---

# LIST OF TABLES

# 1

# INTRODUCTION

10 CFR Part 61 [US NRC, 1982] ensures that the maximally exposed individual will not receive a dose greater than 25 mrem annually. This in practice requires limiting the inventory of long-lived highly mobile nuclides (i.e., $^{14}C$ and $^{129}I$) disposed in a site. Inventory control of $^{14}C$ and $^{129}I$ for the purpose of controlling the dose could be a major limiting factor in the operating life of LLW sites.

The majority of $^{14}C$ and $^{129}I$ in nuclear power plant wastes are found in Class C resins (used for reactor water cleanup) and Class B resins (used for processing liquid low level wastes). Commercial LLW processers have actively investigated alternative waste forms for use by the commercial nuclear power industry. Use of these waste forms have met with varying degrees of acceptance/use. EPRI was interested in researching the specific nuclide of interest ($^{14}C$ and $^{129}I$) to determine if they could be easily separated from our wastes (IX resins) and possibly captured in an alternate waste form of smaller quantity and lower leachability.

Phase 1 of this project was to identify: 1) methods for separating $^{14}C$ and $^{129}I$ from the wastes and 2) appropriate waste forms for stabilizing the separated $^{14}C$ and $^{129}I$. Phase 2 was to conduct leaching studies on the waste forms to determine which technique(s) is (are) reasonable from an operations, ALARA and cost standpoint. Phase 3 would test the selected waste form to determine the total cost and effectiveness of this unique approach.

Due to the complexity of separation of $^{14}C$ and $^{129}I$ from current waste resins it was determined that further investigation of this approach would not be desirable. Should more operable approaches be identified in the future, continued research would be proposed. Until that time, this report represents the research results of the first year's investigation and will serve as the final report for the project.

This report contains the following information. Section 2 briefly describes approaches for the separation of $^{14}C$ and $^{129}I$ from ion-exchange resins. Section 3 examines various concepts for waste forms and engineered barriers. Sections 4 and 5 provide a detailed review of candidate waste forms for $^{14}C$ and $^{129}I$, respectively. And Section 6 summarizes the findings of this report and describes the suggestions for further work.

# 2

# SEPARATION OF $^{14}$C AND $^{129}$I FROM ION-EXCHANGE RESINS

In this research project, separation of $^{14}$C and $^{129}$I from ion- exchange resins is the first step. The proposed approaches to separation are addressed below.

## 2.1 Incentive for $^{14}$C and $^{129}$I Separation

With current LLW practices, most of the $^{14}$C and $^{129}$I generated in nuclear reactor systems ends up in ion-exchange resins. For $^{14}$C, ion-exchange resins contain 60% of the total activity captured, with the balance accounted for by activated hardware (30%), dry active waste (5.4%), cartridge filters (3.2%), and filter media (1.6%). For $^{129}$I, about 50% of the activity is in ion-exchange resins, followed by about 30% in dry active waste and 10% in cartridge filters (based on the LLW manifests at Barnwell from 1989-1994).

Figure 1 shows the postulated release of $^{14}$C at the bottom boundary of a disposal unit in a LLW site. The release peak after about 300 years is largely attributed to the release from ion-exchange resins contained in high integrity containers [Yim, 1997]. Preventing the $^{14}$C release spike at about 300 years—by slowing down the release rate from the resins or preventing release altogether—will significantly lower long-term human radiation exposure from the disposal facility. This is shown in Figure 2 which shows the difference in the peak release between the case when no separation of $^{14}$C is performed and the case when the separation of $^{14}$C from Ion-exchange resins is performed (note that the figure has a different scale in the y axis from that of Figure 1 to clarify the difference). Separating $^{14}$C from ion-exchange resins and immobilizing it into a more stable waste form is found to lower the peak release by an order of magnitude. Similar release spikes will occur for $^{129}$I after waste container deterioration. From these projections, a waste disposal facility performance will be significantly improved if $^{14}$C and $^{129}$I can be separated from the waste and immobilized into a smaller, stable waste form.

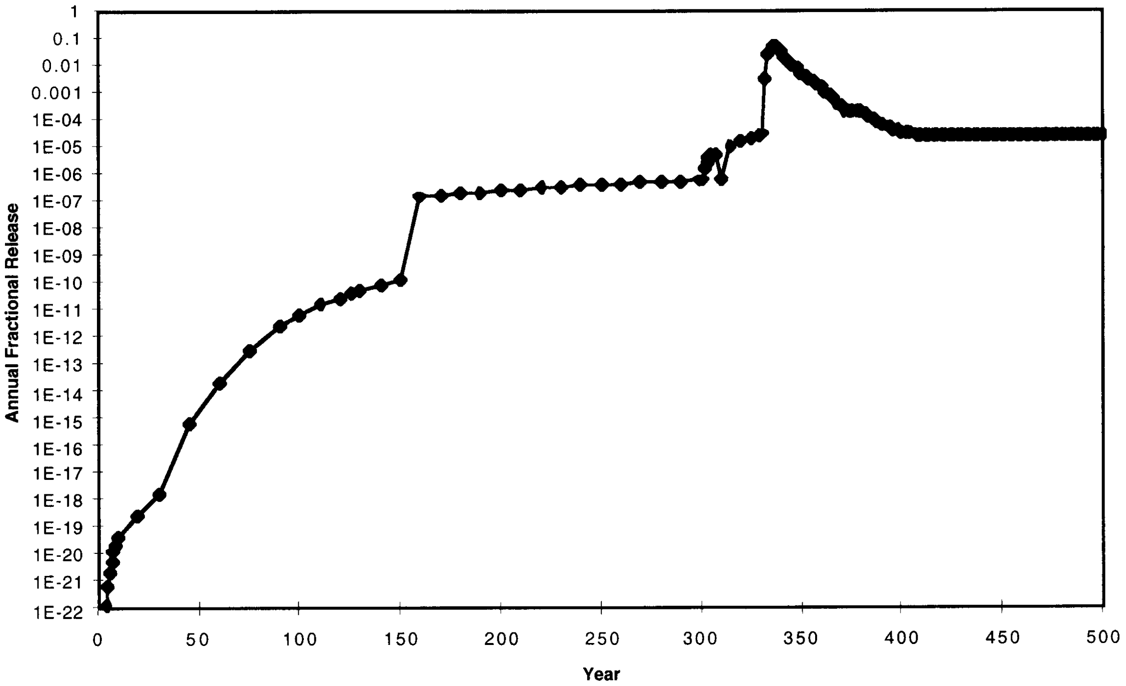


**Figure 2-1**
**Predicted release of $^{14}$C from a LLW disposal facility**

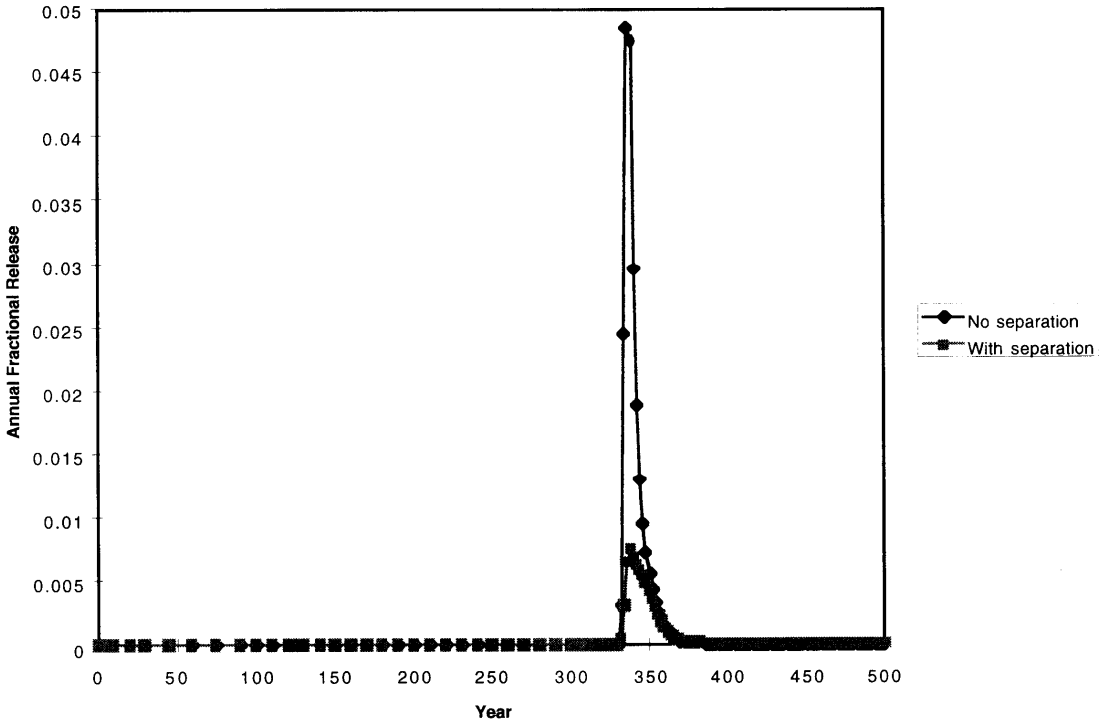


**Figure 2-2**
**Comparisons of predicted peak $^{14}$C release from a LLW facility ($^{14}$C separation from ion-exchange resins vs. no separation)**

## 2.2 Separation of $^{14}C$ and $^{129}I$ from Ion-Exchange Resins

The chemical form of $^{14}C$ in nuclear power plant primary coolant systems varies with reactor type. In PWRs it is primarily organic (58 - 95%), while in BWRs it is mostly inorganic (52 - 87%). In the inorganic form, $^{14}C$ mainly exists as carbonate [EPRI, 1995]. Organic $^{14}C$ has been found to be present in a wide variety of compounds, including methyl alcohol, ethyl alcohol, acetaldehyde, acetone, and acetic acid [Matsumoto, et.al., 1995]. In both PWRs and BWRs, the chemical form of $^{129}I$ is predominantly ionic, either as iodide ($I^-$) or iodate ($IO_3^-$) ions [Rudin, et.al., 1992]. Accordingly, anion-exchange resins are well known to be efficient at removing both $^{14}C$ and $^{129}I$ from nuclear plant waste streams. Ion-exchange resins are also believed to be efficient in capturing elemental carbon, non-ionic organics, or colloidal particles. Presumably these various forms of $^{14}C$ and $^{129}I$ adhere to the resins through the ion-exchange process for ionic forms, and physical adsorption or microfiltration for organic or colloidal forms.

Potential techniques identified for separating $^{14}C$ and $^{129}I$ from ion-exchange resins include water leaching, acidification, oxidation, and hydrogen reduction processes. Once separated from the waste, $^{14}C$ and $^{129}I$ can be captured through carbonate precipitation ($^{14}C$) and iodide precipitation ($^{129}I$).

Separation of $^{14}C$ in inorganic forms can be investigated using static leaching. If unsatisfactory, other alternative methods include:

- Starting with deionized water and adding progressively larger amounts of mild acids and alkalinity until the desired levels of release are attained.
- If the desired release levels are not attained, the above process can also be combined with gas-phase $CO_2$ stripping and capture.

Our goal is to use the least aggressive approach that provides a target separation of 90%. (That is, 90% removal of the activity initially present in the ion-exchange resin.) The separation process must also minimize the generation of secondary wastes. Accordingly, the use of strong acids needs to be avoided, as they are likely to release many secondary radionuclides.

Collection of gaseous $^{14}C$ from any of these separation techniques is also necessary. However, the collection technique will depend upon the ultimate waste form selected for immobilization. For example, $^{14}CO_2$ can be collected as a $CaCO_3$ precipitate in a $Ca(OH)_2$/methanol trap. The carbonate precipitate must be immobilized for disposal. This may involve processing it into cement or another matrix material, or perhaps processing into solid pellets of calcite.

In cases where $^{14}$C is in organic form in the waste (e.g., acetic acid, acetaldehyde), oxidation of organic $^{14}$C species into $CO_2$ or $CO_3^{2-}$ and subsequent capture as carbonate can be investigated.

For the separation of $^{129}$I, the remaining ion-exchange resins from the acidification process can be processed by hydrogen reduction, releasing iodine as HI. The released HI can be collected in NaOH solutions.

Generation of secondary waste is an important issue to be addressed along with separation of $^{14}$C and $^{129}$I. Processes viewed as successful should minimize the secondary waste generated.

Upon coducting this review the researcher concluded that separation of $^{14}$C and $^{129}$I from ion-exchange resins would be difficult due to 1) ALARA considerations; 2) secondary waste generated during processing; 3) processing of the secondary wastes; etc.

# 3

# WASTE FORM REVIEWS

Suitable waste forms for $^{14}C$ and $^{129}I$ are important aspects of the EPRI research. To establish the necessary level of performance, the waste form must be viewed as part of the entire waste disposal system, which includes components such as engineered structure, the container, the geochemistry, and hydrogeology of the site and its climate. The waste form/barrier, in this discussion, include those various components for disposal, i.e., the chemical form of the radionuclide, the solidification matrix, and the container. Waste forms can be divided into three types: intrinsic waste forms, matrix waste forms, and engineered waste forms (barriers). Intrinsic waste forms are those that chemically bind a radionuclide. Matrix waste forms microscopically encapsulate materials. Engineered waste forms (barriers) in this report refer to containers and not structures.

## 3.1 Development of Waste Forms

The primary function of a waste form is to miminize releases of contaminants to the environment [Franz, 1994].

Due to the difficulty in demonstrating the performance of a waste form this project uses a variety of existing tests to improve our understanding of the selected waste forms' suitability, integrity, and potential performance. These tests will provide a means for this study to quickly compare the performance of various waste forms and provides a basis for selecting the most suitable approach for a particular disposal application.

Various testing that can be employed to analyze the chemical durability of a waste form include:

- MCC-1 [Strachan, 1982], Product Consistency Test (PCT) [Jantzen, 1993], and ASTM test [ASTM, 1993], mainly to measure mass release by dissolution

- Accelerated Leach Test (ALT) [Fuhrmann, 1990] and ANS 16.1 test [ANSI/ANS, 1986] to assess diffusive release

## 3.2 Intrinsic Waste Forms

Intrinsic waste forms are those that chemically bind a radionuclide. Some potential intrinsic waste forms for $^{14}C$ and $^{129}I$ are discussed below.

### *3.2.1 Intrinsic Waste Forms for $^{14}C$*

#### Carbonate Minerals

Calcite (calcium carbonate) and dolomite (calcium + magnesium carbonate) are widely distributed forms of carbon in the natural environment, and generally have low solubility and good chemical and thermal stability. Calcite has a lower solubility over the largest range of naturally occurring waters, and is a strong candidate as an intrinsic waste form for $^{14}C$. Calcite has also been identified as the synthetic phase produced within cement waste forms, and has been extensively studied in this role [Dayal, 1992 & 1995; Krupka, 1995].

#### Carbon Allotropes

Elemental carbon can exist in a number of allotropic forms including graphite, glassy carbon, fullerenes, and diamond and are an intrinsic waste form option. Based upon limited data, graphite and glassy carbon have been shown to have far superior environmental durability over calcite or other similar waste forms. These materials, particularly graphite, also offer a unique approach to waste disposal because their durability does not depend upon maintaining a protective oxide film. They may also be less susceptible to non-uniform modes of attack for this same reason. Processing $^{14}C$ into graphite or glassy carbon is challenging because of the high temperatures required. Nonetheless, further investigations of these materials as both intrinsic waste forms and engineered barriers are worthwhile because of their outstanding durability (see Sections 4.3 & 4.4).

#### Metal Carbides

Metal carbides (carbides of silicon, titanium, tungsten, chromium, tantalum, etc.) have very good environmental durability. Silicon carbide is the least expensive and most well characterized of this group. Silicon carbide is expected to have outstanding durability over a broad range of environmental conditions, and may be able to be developed as a waste form or as an engineered barrier material.

### Organic Compounds

This includes a broad range of possible organic compounds (polyethylene, rubber, polystyrene, coal, bitumen, etc.). Desirability of these materials depends on the ease or difficulty in the synthesis of $^{14}C$ into the structure and the final chemical stability. Typically, organic materials are treated as matrix waste form materials rather than as an intrinsic waste form. Further discussions are provided in section 3.3.1.

## ***3.2.2 Intrinsic Waste Forms for $^{129}I$***

Since $^{129}I$ in ion-exchange resins is expected to be in iodate ($IO_3^-$) or iodide ($I^-$) form, it would be desirable to have intrinsic waste forms for iodine also in these forms. Relatively few elements can form highly stable, insoluble iodine compounds. The following were identified in this study.

### Metal Iodides

Relatively stable compounds of iodine include iodides of silver, bismuth, copper, mercury, lead, palladium, and thallium.

### Metal Iodates

Existing relatively stable metal iodates include iodates of silver, barium, bismuth, calcium, cerium, cobalt, copper, iron, mercury, indium, lanthanum, nickel, lead, plutonium, strontium, thorium, thallium, and zinc.

### Synthetic Minerals

A potentially excellent synthetic mineral for retaining $^{129}I$ is sodalite, a sodium aluminosilicate [Winters, 1980]. Iodide sodalite is prepared by reacting NaI, NaOH, and kaolinite clay in stoichiometric amounts at low temperature in an aqueous slurry. Complete incorporation of the iodine into the sodalite aluminosilicate lattice and densification of the product are accomplished by hot-pressing at 1,000°C and 34.5 MPa (5,000 psi) for 1 hr. (The heat-up at high pressure causes only a few percent loss of iodine.) The hot-pressed sodalites have near-theoretical iodine contents of ~19 wt%, with good thermal and radiation stability. However, iodine leachability does not show much improvement over cement as discussed in 3.3.2. Considering the complexity and cost of preparation, sodalite dose not appear to provide significant benefit.

Use of calcium-aluminate hydrates has also been suggested as an intrinsic waste form for $^{129}I$ immobilization in cement [Brown, 1985]. This approach is based on substituting iodine for sulfate in either ettringite or tetracalcium aluminate monosulfate, or both.

Iodine-substituted analogue phases were successfully synthesized in this approach within cement matrix. The leach rate of iodine was comparable to various metal iodates (barium, calcium, and mercury) in portland cement. However, iodine loading was much lower in the calcium aluminate hydrate analogue phase compared to other metal iodates [Brown, 1985].

## 3.3 Matrix Waste Forms

Matrix waste forms are microscopically encapsulated materials. That is, waste forms which are composite materials in which carbon or iodine compounds are embedded as a secondary phase.

### *3.3.1 Matrix Waste Forms for $^{14}C$*

Some potential composite matrix waste forms for carbon have a basis in naturally occurring ores in which carbonates or other carbon bearing forms are present as included minerals. Many materials that can incorporate carbon in various chemical forms within a solid structure are potential matrix waste forms. Some examples are addressed below.

#### Cement (Hydroxide Minerals)

Cements are a recent example of a matrix waste form that can hold inorganic carbonates (though some historical samples of cement which included calcite date back about 1,000 years [Miller, et.al., 1994]). Cements provide an alkaline environment as well as a physical encapsulation medium to prevent mass transport of carbon. Cement also serves as a physical barrier to fluid flow, at least in the short term. Cements have been extensively studied [Dayal, 1992 & 1995; Scheele, 1982] and the benefits have, to a large extent, been quantified. These literature results will be used as a baseline for comparing waste form durability and processing ease with other candidates. Therefore, no experimental work on cement encapsulated $^{14}C$ is included in this project.

#### Sulfate Minerals

Gypsum (Mg, Ca-$SO_4$) is a potential sulfate mineral matrix waste form. Calcite is often found as a minor phase in naturally occurring gypsum, suggesting a reasonable durability under a range of environmental conditions. Polymer modified gypsum cement has been investigated as a matrix waste form, however it requires acid conditions for solidification [Moghissi, 1986]. Since acid conditions promote conversion of $^{14}C$ species into $CO_2$ and subsequent gaseous release, this class of encapsulating matrix material may not meet the goals of this research.

### Phosphate Minerals

Calcite is also found as a major secondary phase in phosphate minerals, such as apatite ($CaPO_4$) which is the most abundant of the phosphate minerals [Krauskopf, 1982]. Certain phosphate minerals have excellent environmental durability and have even been considered for use as high-level waste forms [Lutze & Ewing, 1988]. Since this class of material is only in the early research stage, phosphate minerals would be considered only if other waste forms are found unsuitable.

### Zeolites

Zeolites are hydrated silicates of aluminum and sodium and/or calcium, with the general formula $Na_2O\ Al_2O_3\ nSiO_2\ xH_2O$ [Scott, 1980]. Zeolites occur in nature and are also produced by chemical synthesis. Their name (from the Greek "zeo" meaning boil, and "lithos" meaning stone) stems from their appearance when heated; they appear to melt or boil when heated as the water of hydration is driven off. Zeolites are also used as demineralizers along with resins for waste treatment purposes in nuclear power plants.

Molecular-sieve type of zeolites have a special crystalline structure which contain many interconnecting cavities of uniform size [Wright, et.al., 1973]. These cavities are connected by narrow openings and provide a tremendous internal surface area capable of retaining many different gases and liquids, including $CO_2$. Because of their inorganic crystalline structure, molecular sieve zeolites are extremely inert and stable, suggesting their use as a waste form. However, they have a very strong affinity for water. Thus, if molecular sieve zeolites holding $^{14}C$ are exposed to water or water vapor, release of $^{14}C$ is likely (controlled by the equilibrium loading capacity for $CO_2$ and water [Wright, et.al., 1973]. (At 21.1°C and a water partial pressure of 0.00123 MPa (0.178 psia), molecular sieves of 5A nominal pore size have an equilibrium loading capacity of 0.068 gm of $CO_2$ and 0.18 gm of $H_2O$ per gm.) Also, molecular sieve zeolites are susceptible to desorption of $CO_2$ from pressure reductions or temperature increases. Therefore, molecular sieve zeolites are not expected to be suitable for waste storage or disposal.

### Synthetic Polymers

Various synthetic organic polymers such as polyethylene, epoxy polymers, unsaturated polyesters, and urea-formaldehyde have been used as an encapsulating matrix material for low level or mixed waste solidification [Moghissi, 1986]. Use of urea-formaldehyde produces very acidic conditions in pore waters which may convert $^{14}C$ into $^{14}CO_2$. Polyethylene as matrix material requires heating above 120°C, suggesting loss of $^{14}C$ through volatilization is likely.

Use of epoxy polymers involves condensation of epichlorohydrim and diphenylolpropane using an alkaline catalyst, such as sodium hydroxide, with the waste material. The properties of the waste form are highly dependent upon the molecular weight of the polymer [Franz, 1994, Moghissi, 1986]. Unsaturated polyester is produced as the result of a condensation reaction between a polyhydric alcohol and polybasic acid [Frantz, 1994]. A class of unsaturated polyesters known as vinyl esters has also been used for LLW solidification. The vinyl ester monomer is diluted to about 45-50 wt% in styrene to form a low viscosity liquid which is polymerized through free radical initiators to form a three-dimensional network. The solidification of aqueous wastes with vinyl ester-styrene binder requires high shear-mixing to promote the formation of a waste water-monomer emulsion [Moghissi, 1986]. In case of dry waste, solid particulates can be suspended in the waste-monomer mixture and remain dispersed as the monomer polymerizes. Both epoxy polymers and vinyl esters are candidate $^{14}$C matrix waste forms. However, these materials have questionable chemical and radiation stability over long time periods and will not be considered as primary candidate waste forms in this study.

### 3.3.2 Matrix Waste Forms for $^{129}$I

Iodine is very reactive in the natural environment. Thus, there are few matrix materials that can incorporate and retain iodine within a solid structure. Some examples are addressed below.

#### Glass

Glasses based on fluoride are likely to be compatible with iodine compounds. These glasses have been examined in France at Rennes University but appear to be rather soluble in water [Burger, 1981]. This implies that vitrification is not preferrable for the production of advanced waste form for iodine. (Note: The glass matrix does immobilize the vast majority of remaining nuclides.)

#### Synthetic Polymers

Synthetic organic polymers, described above, may provide good short term protection. But potential problems with these materials include long-term chemical and radiation stability .

#### Bitumen

Bitumen is relatively impermeable to water and has a reducing, nonhydrolytic environment that promotes waste compound retention. Bitumen appears to be more resistant to degradation than synthetic organic polymers. But the process requires heating the waste and binders to over 145°C [Frantz, 1994], making iodine volatilized. Combustibility during packaging operation could be also a potential concern. (Note: Nuclear plant's use of this technology has not experienced this problem to date.) Bitumen is, however, less expensive than cement and has equal or improved stability.

### Cement

Cement (Portland cement) has been extensively studied as a matrix material for iodine compounds. Cement is inexpensive, simple to fabricate, stable in most environments, and has relatively good leachability (depending on the chemical form of iodine). Cement appears to be the material of choice for $^{129}$I immobilization.

## 3.4 Engineered Waste Forms (barriers)

Engineered barriers (containers) for $^{14}$C and $^{129}$I immobilization would use multiple engineered barriers to encapsulate the waste. Converting the carbon and iodine into stable chemical compounds is not required, though they still could be part of the engineered system.

An important element of engineered waste forms is the container, usually metal, that contacts the waste material. LLW containers currently used have short service lives, relative to the half lives of $^{14}$C and $^{129}$I. These include carbon steel drums and liners and various types of high integrity containers (HICs). In performance assessment, the NRC allows no waste retention credit for carbon steel drums (service life of zero years). Carbon steel liners are assumed to have a five year service life and HICs a 300 - 1000 year service life [NRC, 1993]. Of course, any proposed container material would have to be tested for compatibility with the waste form(s) selected for $^{14}$C and $^{129}$I. Another problem with relying on the container for waste retention is that all metallic containers are subject to uniform or localized corrosion, making long-term performance prediction uncertain.

Some preliminary assessments of new designs for engineered waste forms suitable for $^{14}$C and $^{129}$I retention are included in the next section based on waste form and barrier durability, process feasibility, cost, risk/safety issues, and secondary waste generation. Ultimately, the engineered waste form's performance during all phases of waste disposal needs to be assessed, including processing, storage, transportation, and ultimate disposition.

# 4

# DETAILED SUMMARY OF CANDIDATE WASTE FORMS FOR $^{14}C$

---

This section examines the most promising $^{14}C$ waste forms identified in Section 3, and evaluates their durability, producibility, licensability, and cost.

## 4.1 Alkaline Earth Carbonates (intrinsic waste form)

Among innumerable chemical compounds of carbon, inorganic carbonates are the chemical form most readily applicable to $^{14}C$ disposal as intrinsic waste form. A major part of the $^{14}C$ generated at nuclear power plants is in carbonate ($CO_3^{2-}$) or bicarbonate ($HCO_3^-$) form. Cement has been extensively studied as an immobilization matrix, and the chemical form of $^{14}C$ in cement would be as various alkaline earth compounds.

### *4.1.1 Environmental Durability*

The temperature in a LLW disposal facility is expected to be near the ambient temperature, thus thermal stability of carbonates is not expected to be a concern. Accordingly—since contact with water is the most likely release mechanism—environmental durability depends mainly on low solubility and slow chemical reactions in aqueous environments.

Carbonates are typically more soluble in acidic solutions. In addition, aqueous carbonate is in equilibrium predominantly with bicarbonate and $CO_2$ at pH less than 7. This "equilibrium" in an open system results in a continuous release of $^{14}C$ as $CO_2$. Accordingly, prior $^{14}C$ immobilization research has largely focused on cement as a matrix material in order to maintain an alkaline environment for very long times. When cement is used as the solidification matrix, the compound should be less soluble than the corresponding hydroxide or sulfate to prevent conversion to the corresponding metal hydroxide (oxide) or sulfate [Scheele, 1982]. The compounds with carbonate solubility less than the hydroxide and sulfate solubility are $PbCO_3$, $CdCO_3$, $MnCO_3$, $FeCO_3$, $SrCO_3$, $CaCO_3$, $BaCO_3$, and $Ag_2CO_3$ (see Table 1). In near-neutral solutions, bismutite, (BiO)2CO3, appears to offer the best solubility characteristics, with a wide region of stability (pH: 6~10) [Taylor, 1987]. The aqueous solution chemistry of bismutite, however, is complex and alteration of bismutite to other basic bismuth salts is possible depending on the conditions of the solution.

**Table 4-1**
**Solubility of Various Carbonate Compounds [Scheele, 1982**

| Compound | $[CO_3^{2-}]$, g-ion/L | $[OH^-]$ g-ion/L in corresponding hydroxide | $[SO4^{2-}]$ g-ion/L in corresponding sulfate |
|---|---|---|---|
| $(BiO)_2CO_3$ | ~$10^{-9}$ | | |
| $PbCO_3$ | $2.7x10^{-7}$ | $1.3x10^{-5}$ | $1.3x10^{-4}$ |
| $CdCO_3$ | $2.3x10^{-6}$ | $3.7x10^{-5}$ | 3.6 |
| $MnCO_3$ | $4.2x10^{-6}$ | $7.2x10^{-5}$ | 3.4 |
| $FeCO_3$ | $5.7x10^{-6}$ | $1.2x10^{-5}$ | slightly soluble |
| $SrCO_3$ | $1.0x10^{-5}$ | $8.0x10^{-2}$ | $5.7x10^{-4}$ |
| $CaCO_3$ | $5.3x10^{-5}$ | $2.2x10^{-2}$ | $3.0x10^{-3}$ |
| $BaCO_3$ | $7.1x10^{-5}$ | $2.1x10^{-1}$ | $1.0x10^{-5}$ |
| $Ag_2CO_3$ | $1.3x10^{-4}$ | $1.4x10^{-4}$ | $1.5x10^{-2}$ |

The reaction rates of some carbonate compounds have been studied by Scheele and Burger [Scheele, 1982]. Table 2 shows the results for $CaCO_3$, $BaCO_3$, and $SrCO_3$. The results are presented as normalized fraction leached, which is calculated by multiplying the fraction leached by the geometric volume-to-geometric surface area ratio. The test was performed by using a modified IAEA test (simulated dynamic test) with test duration up to 54 days [Scheele, 1982]. These data were obtained using cement-equilibrated distilled water. The data indicate that $CaCO_3$ has the best chemical durability under these test conditions.

Reaction rates of $CaCO_3$ and $PbCO_3$ (the least soluble carbonate compound) were also assessed by Scheele and Burger. Reaction rate was measured by a long term static test (up to 1 year) with the use of various aqueous solutions. Results showed that reaction rate of $CaCO_3$ is a factor of 100 less than that of $PbCO_3$.

These results suggest that calcium carbonate compound will be most suitable for $^{14}$C immobilization. Nonetheless, there are several possible concerns with $CaCO_3$, including:

- The leach rate is high during the first several days of water contact.
- Dissolved carbon dioxide in the system could have a deleterious effect of increasing carbonate leaching [Bush, 1984].
- $CaCO_3$ has low solubility in most natural water systems except in non-alkaline solutions.

The fact that the solubility of $CaCO_3$ increases significantly when pH is less than 11 limits the use of calcite in the alkaline environment. Therefore, the use of calcite as a $^{14}$C waste form requires additional means to control near-field chemistry such as a cemented environment.

**Table 4-2**
**Comparison of reaction rates of several alkali carbonates at 19-25°C**
**(average between 10 and 54 days)**

| | $SrCO_3$ | $BaCO_3$ | $CaCO_3$ |
|---|---|---|---|
| normalized leach fraction<br>(cm/day) | $1.3x10^{-5}$ | $3.4x10^{-7}$ | $1.6x10^{-7}$ |

### *4.1.2 Process Feasibility*

Assuming aqueous separation is successful, the feasibility of processing the dissolved carbonate into calcium carbonate is high because the process of carbonate precipitation is well known. The processing steps to take evolved $^{14}$C from the waste to a $CaCO_3$ precipitate ready for disposal can be summarized as:

1. Separation into an aqueous solution
2. Convert $CO_2$ or $HCO_3^-$ into a carbonate
3. Consolidation into a waste form or matrix
4. Cleanup of any secondary contamination or wastes during the process
5. Placement within engineered barriers.

This process uses a $Ca(OH)_2$ / methanol trap, which is a proven method in chemical processing industry. If $^{14}C$ exists as carbonate or bicarbonate in solution, $CaCO_3$ can be precipitated through reaction with $CaF_2$ or $CaCl_2$ in an alkaline solution.

Though several possibilities were identified in Section 3, the most likely waste form for $CaCO_3$ is cement, or direct processing of the precipitate into solid pellets.

The type and quantity of secondary wastes generated during $CaCO_3$ processing depends on the details of chemical processing steps. This needs to be further examined in the future with a bent toward minimization.

### 4.1.3 Licensability

Given what is known about $CaCO_3$ properties, long-term waste form performance will depend in part on the controlled degradation of the cement (or other matrix) and how that affects the chemistry of water that might contact the waste. Variables in how a waste repository might degrade make such chemistry assessments difficult. These uncertainties mean that modeling the release of $^{14}C$ from a cement or monolithic $CaCO_3$ waste form over geologic periods may require the use of very conservative approaches.

### 4.1.4 Cost

The costs associated with this waste form are due to the cost associated with process equipment chosen, the cost of carbonate compounds and the cost of cleaning up secondary wastes. The cost of carbonate compounds is generally very modest (see Table 3), and could be acceptable considering the benefits of the proposed approach (see section 2.1).

**Table 4-3**
**Cost of Various Metals**
**(from Chemical Market Reporter, November 3, 1997, except Ag is from Wall Street Journal, November 21, 1997)**

| Metal | Compound | Price, $/kg |
|---|---|---|
| Ag | Ag | 138 (5.22/troy oz) |
| Ba | $BaCO_3$ | 0.66 |
| Ca | $CaCO_3$ | 0.12 |
| Cd | $Cd(NO_3)_2$ | 8.27 |
| Cu | $Cu(NO_3)_2$ | 3.5 |
| Fe | FeO | 1.94 |
| Pb | $PbO_2$ | 4.0 |
| Mg | MgO | 1.9 |
| Mn | $MnO_2$ | 2.3 |
| Hg | HgCl | 14.3 |
| Ni | $Ni(NO_3)_2$ | 4.34 |
| Sr | $SrCO_3$ | 0.90 |
| Zn | $Zn(NO_3)_2$ | 0.79 |

## 4.2 Graphite (subset of "carbon allotropes")

Graphite (carbon allotropes) is a hexagonally crystallized allotrope of carbon that is widely used as a high-temperature refractory because of its thermal stability. Graphite also has excellent chemical stability. Graphite occurs naturally in large quantities. Its geochemical origin is thought to be either from carbon crystallizing from the molten magma which formed igneous rock, or as the "ultimate residue" in the carbonation and coking of hydrocarbons from vegetation.

Synthetic graphite can be manufactured from almost any organic material that leaves a high carbon residue on heating in the absence of air. Typical manufacturing processes involve pyrolysis of organic compounds where progressive thermal decomposition and polymerization is accompanied by the loss of foreign atoms, such as oxygen and hydrogen [Ubbelohde, 1960]. The detailed structure of the end product depends on the starting material and on the pyrolysis temperature.

### 4.2.1 Environmental Durability

Graphite is one of the materials most resistant to attack by the natural environment [Gray, 1980; Gray, 1982]. There is virtually no reaction between graphite and air at ambient temperatures. Graphite does not react with water, though the water will catalyze and accelerate a reaction with dissolved oxygen. Nevertheless, the reaction rate is at least 100 times lower than any other material that has been considered for waste isolation. The reaction rate of graphite in deionized water is 2 to $3x10^{-10}$ ($g/cm^2/day$) at 99°C and $1\text{-}3x10^{-8}$ ($g/cm^2/day$) at 250°C. Activation energy for oxidation of graphite in water is estimated to be 12.8 (kcal/mole). In the presence of a high-intensity gamma-radiation field, radiolysis of the water is enhanced by the presence of graphite. But no measurable effect on the reaction rate of graphite was detected.

Graphite is very insoluble in most acids and alkalis. It is known that graphite can be attacked by concentrated nitric acid with the formation of carbon dioxide, mellitic acid, hydrocyanic acid, or carbon dioxide and nitrous oxide, depending upon the conditions under which the reactions take place [Mantell, 1968].

Graphite has no apparent durability limitations. Processing difficulties (see next section) may prevent graphite's use as a waste form. However, the outstanding chemical durability makes it an excellent barrier material candidate.

### 4.2.2 Process Feasibility

Production of graphite as a waste form requires the separated $^{14}C$ to be converted to an organic form and pyrolyzed at process temperature of 2,000°C or higher. This temperature requirement appears to be too high for practical applications. Also, significant loss of $^{14}C$ through gaseous release would probably occur. Thus, the process feasibility of graphite as a carbon waste form appears low. Nonetheless, as noted above, graphite could well be used successfully as a radionuclide release barrier as an engineered waste form. This use is described further in Section 6.

### 4.2.3 Licensability

Due to its excellent environmental durability and well characterized properties, the licensability of graphite as an engineered waste form appears very high. Mass transport of radionuclides through graphite need to be better characterized however.

### 4.2.4 Cost

Cost estimates for graphite as an engineered waste form must wait on a specific design and process. The price of the raw material depends on the grade, and currently is about \$7.70/kg for medium grade graphite [Davis, 1997].

## 4.3 Silicon Carbide (subset of "metal carbides")

Silicon carbide (SiC) [Somiya, 1991] was accidentally discovered in 1891 by E. G. Acheson, an assistant to Thomas Edison, during an experiment on diamond synthesis. Natural SiC is rare, though it occurs in meteorites in very small amounts. SiC is strong and hard, with high thermal and electrical conductivity, low thermal expansion coefficient, and high thermal shock resistance. These properties have made SiC widely used as a grinding abrasive (it is the third hardest material after diamond and boron carbide). SiC is also used in heating elements, electrodes, and as a nozzle and cylinder material. Its strength and chemical resistance make it a candidate waste form.

### 4.3.1 Environmental Durability

Silicon carbide has a very high chemical stability and oxidation resistance due to the formation of a tenacious silica surface film. The film makes silicon carbide virtually insoluble in water at ambient conditions. SiC's reaction rate in deionized water is 1 to $5x10^{-7}$ (g/cm$^2$/day) at 250°C [Mantell, 1968]. Activation energy for oxidation of SiC in water is estimated to range between 8.2 and 15.3 (kcal/mole) [Mantell, 1968]. This yields an aqueous reaction rate at 25°C of $1.5x10^{-12}$ to $1.3x10^{-9}$ g/cm$^2$/day.

SiC corrodes at a low rate in acid or alkaline solutions. The reaction rates in various solutions at various temperatures are [Neffe, 1988]:

- $5x10^{-6}$ g/cm$^2$/day in 98% $H_2SO_4$ at 100°C
- $7x10^{-6}$ g/cm$^2$/day in 50% NaOH at 100°C
- < $5x10^{-7}$ g/cm$^2$/day in various other solutions, including 53% HF at 25°C, 85% $H_3PO_4$ at 100°C, 70% $HNO_3$ at 100°C, 45% KOH at 100°C, 25% HCl at 70°C, and 10% HF plus 57% $HNO_3$ at 25°C.

### 4.3.2 Process Feasibility

There are a number of techniques available for manufacturing silicon carbide. These include reaction forming process [Singh, 1994], chemical vapor infiltration process

[Kmetz, 1990], chemical vapor deposition [Emig, 1996; Zhao, 1994], sol-gel process [Raman, 1993], and reaction bonding process [Whitehead, 1992].

One possible way to utilize these techniques in $^{14}C$ immobilization is developing a SiC coating on the surface of a stabilized waste. In this case, the stabilized waste needs to be in a form suitable for one of the above processes. In that case the carbon atoms on the surface of the substrate would have to be strongly bound. For some potential substrates such as cement, this would be a problem since the carbon would be in the form of carbonate.

Another immobilization technique would be to use the reaction forming process or sol-gel process to cause the $^{14}C$ to react with silicon and be incorporated within the stable SiC. For this process to be applicable, $^{14}C$ needs to be incorporated into phenolic resins. This is possible through aqueous ion-exchange with phenolic resins in leachate water. Release of $^{14}C$ as gas (a secondary waste) during the high temperature processing is an important consideration in the feasibility of this process.

SiC could also be used as an engineered barrier material. Manufacturing of SiC in various shapes and sizes is commercially available.

### *4.3.3 Licensability*

Silicon carbide as an engineered waste form is likely to be licensable due to its high durability.

### *4.3.4 Cost*

As with graphite, it is difficult to estimate the cost of silicon carbide as an engineered waste form since this will be dependent on the specific design of the waste form. The price of silicon carbide material also depends on the process chosen, annual output, raw material and the final form of production. Raw material prices for SiC, graphite, and glassy carbon (discussed below) are summarized in Table 4. The price of silicon carbide is much higher than graphite.

**Table 4-4**
**Comparison of raw material prices**

| | **graphite**<br>**[Davis, 1997]** | **silicon carbide**<br>**(whisker form)**<br>**[Schoenung, 1991]** | **glassy carbon**<br>**[www.goodnet.com, 1997]** |
|---|---|---|---|
| Price | 7 to 20 ($/kg) | 50 to 500 ($/kg) | 50 ($/1000 cm$^3$)<br>(about 33 $/kg) |

## 4.4 Glassy Carbon

Glassy carbon (carbon allotropes) is an amorphous, gas-impermeable form of carbon with the appearance and fracture characteristics of glass. It is manufactured by the solid-phase pyrolysis and heat treatment of certain thermosetting polymers, typically phenolic resins. Glassy carbon has high temperature structural stability, chemical inertness, low gas permeability, high thermal shock resistance, and is electrically conductive and thermally insulating. Industrial applications include filtration, electrochemical cells, heating elements, electrodes, fuel cells, acoustics, and high-temperature insulation. With its low chemical reactivities and high strength, glassy carbon is a candidate $^{14}C$ waste form.

### *4.4.1 Environmental Durability*

Glassy carbon is nearly insoluble in water at ambient conditions. At higher temperatures, reaction rates in deionized water are found to vary with the temperatures of heat-treatment for the production of glassy carbon. These reaction rates are measured at about $3x10^{-8}$ (g/cm$^2$/day) for the glassy carbon heat-treated at 2,600°C and $2x10^{-7}$ g/cm$^2$/day for the glassy carbon heat-treated at 1,000°C [Gray, 1982] both at 200°C . Activation energy for oxidation of glassy carbon in water is estimated to be 10.8 (kcal/mole) for the glassy carbon heat-treated at 2,600°C.

There is no reaction between glassy carbon and air at ambient temperatures [Gray, 1982]. At elevated temperatures (above 200-300°C), glassy carbon may begin to oxidize, with the reaction rate depending upon the material's heat treatment temperature.

Glassy carbon functions satisfactorily in the strongest $H_2SO_4$ solutions at low current intensities [Lausevic, 1986]. However, it has been shown that anodic oxidation of glassy carbon in $H_2SO_4$ solution above the oxygen evolution potential causes electrochemical corrosion of the material [Neffe, 1988].

### 4.4.2 Process Feasibility

The formation of glassy carbon involves the slow carbonation of nonmelting cross-linked polymers, with or without applied pressure. In determining the morphology of the product, the chemical nature of the precursor is less important than the condition of pyrolysis. Similar products can be prepared from a variety of starting materials, including phenolic resins, acetone-furfural resin, polyfurfuryl alcohol, naphthalenediol, cellulose, cumarone, indene, cyclopentadiene, and pitch [McKee, 1973]. A method would have to be developed to incorporate $^{14}C$ into one of these starting materials. This would generally involve a reduction step to form a $^{14}C$ hydrocarbon. Methods to convert from $CO_2$ to $CH_4$ and other hydrocarbons have been identified [Calvin, et al., 1949], but the feasibility and practicality has not been fully assessed.

An alternative approach would be the capture of $^{14}C$ from water after leaching from the ion-exchange resins into phenolic ion-exchange resins. The efficiency of this process is expected to be very high. The resulting phenolic resins can be processed by slow pyrolysis above 1,000°C and be converted to glassy carbon. Required level of environmental durability will determine the maximum process temperature.

Structural changes with pyrolysis of phenolic resins has been studied [McKee, 1973; Ouchi, 1966; Lausevic, 1986]. The structure of the phenolic resin does not change much up to 300°C. Evolution of water begins above 100°C. This is perhaps due to dehydration of phenolic hydroxyl groups. Decomposition of aliphatic ether structures begins to occur near 350°C, initiating the evolution of various gases such as methane, hydrogen, carbon monoxide, and carbon dioxide. It is this latter stage of the processing that would have to be carefully controlled to capture and reprocess any $^{14}C$-bearing compounds. Although some changes occur, the polymer network remains essentially intact until about 500°C. At 500°C and above, drastic changes occur. The network collapses, aliphatic bridges are destroyed, hydrocarbonaceous residues are eliminated and those remaining are altered. Condensation of aromatic ribbon molecules starts above 600°C, followed by a large evolution of hydrogen. From about 700°C the dehydrogenation of aromatic hydrogens is accompanied by increased aromatization of the whole structure. Hydrogen evolution is complete at 700°C. With further increase in temperature, the network continues to shrink and pores formed by the previous gas evolution collapse [Morterra, 1985].

Total carbon yield of the final product is estimated to be between 80 and 85% [Fitzer, 1970]. Therefore about 15 to 20% of initial carbon content is expected to be released during the process. If it is assumed that the captured $^{14}C$ behaves the same as the structural carbon, about 80% of the initial $^{14}C$ would remain in the final glassy carbon product. Chemical durability of the product depends on the final process temperature.

The process of manufacturing glassy carbon is well developed. The phenolic resins as starting polymer material are widely used. However, the feasibility of using glassy carbon as a waste form depends on the selection of optimum required processing temperature. The properties of the final product are highly temperature dependent. The temperature could range from 1,000 to 3,000°C. With higher process temperatures, the waste form properties improve.

If $^{14}CO_2$ is released in the process of using glassy carbon as an intrinsic waste form, then secondary wastes are an issue. There is no secondary waste involved if glassy carbon is used as an engineered waste form. Even though the manufacturing of phenolic resins may involve exposures to phenol and formaldehyde, cured phenolic resins are completely innocuous [Knop, 1985]. The effluents from the glassy carbon process do not contain any hazardous substances. Safety issues involve handling high temperature equipment and materials if glassy carbon is used as an intrinsic waste form.

Using glassy carbon as an intrinsic or matrix waste form for $^{14}C$ immobilization, or as a container material, appears technically feasible. Cost and $^{14}C$ retention will likely become determining factors in the waste form application.

### 4.4.3 Licensability

Licensability of glassy carbon as an engineered waste form is likely to be high due to the material's durability. Its use as an intrinsic waste form will require that the $^{14}CO_2$ release and $^{14}C$ retention fraction be addressed.

### 4.4.4 Cost

Like many of the other processes, the cost of glassy carbon is very dependent upon the system used to fabricate the waste form and the specific design used. The cost of the precursor materials is not significant. The price of glassy carbon raw material is shown in Table 4 above.

# 5

# DETAILED SUMMARY OF CANDIDATE WASTE FORM FOR $^{129}$I

Cement has been extensively studied as a matrix material for iodine compounds. It has the advantages of low cost, processing simplicity, stability in most environments, and relatively good (i.e., slow) leachability (depending on the chemical fixation form of iodine). Accordingly, this section examines the single most promising $^{129}$I waste form: iodide/iodate compounds in a cement matrix.

## 5.1 Iodide/Iodate Compounds in Cement

Relatively few elements can form the stable, insoluble, inorganic compounds with iodine that are preferred for nuclear waste disposal. Since $^{129}$I in ion-exchange resins is expected to exist as iodate ($IO_3^-$) or iodide ($I^-$) ions, immobilizing the iodine in this form in a cement matrix offers a technically sound waste form.

### *5.1.1 Environmental Durability*

Since contact with water is the most likely release mechanism in the disposal environment, solubility of various iodine compounds was examined. Tables 5 and 6 show the solubility of various iodide and iodate compounds, respectively. Based on the data in Table 5 [Burger, 1982], the silver and monovalent mercury salts* are the most insoluble iodides, followed by palladium, copper, bismuth, thallium, and lead*. Among the iodates, similar elements show good solubility characteristics, as do the alkaline earth and rare earth elements such as barium, cerium, iron, thorium, lanthanum, zinc, uranium, and calcium.

Since cement is used as the solidification matrix, the iodine compounds should be less soluble than the corresponding hydroxide (oxide), to prevent conversion to hydroxide or oxide. The iodide compounds that are less soluble than the corresponding hydroxide

---

* These data are presented for background information. Due to the potential hazardous designation of these materials/elements they would not be considered for actual use.

are $Hg_2I_2$*, AgI and TlI. Among the iodates, the compounds that are less soluble than the corresponding

**Table 5-1**
**Solubility of various iodide compounds**

| Compound | Solubility of $[I^-]$, g-atoms/L | $[OH^-]$ g-atoms/L in corresponding hydroxide | Is the solubility of $[I^-]$ less than that of $[OH^-]$? |
|---|---|---|---|
| $Hg_2I_2$ | $9.7x10^{-15}$ | $1.4x10^{-12}$ | Yes |
| AgI | $9.1x10^{-9}$ | $1.4x10^{-4}$ | Yes |
| $PdI_2$ | $3.7x10^{-8}$ | $5.8x10^{-11}$ | |
| CuI | $1.0x10^{-6}$ | $1.0x10^{-7}$ | |
| $BiI_3$ | $3.9x10^{-5}$ | $3.0x10^{-8}$ | |
| $HgI_2$ | $1.3x10^{-4}$ | $7.4x10^{-5}$ | |
| TlI | $2.5x10^{-4}$ | 1.6 | Yes |
| $PbI_2$ | $2.4x10^{-3}$ | $1.3x10^{-5}$ | |

**Table 5-2**
**Solubility of various iodate compounds**

| Compound | Solubility of $[IO_3^-]$, g-mole/L | $[OH^-]$ g-mole/L in corresponding hydroxide | Is the solubility of $[IO_3^-]$ less than that of $[OH^-]$? |
|---|---|---|---|
| $Bi(IO_3)_3$ | insoluble | $3.3x10^{-8}$ | Yes |
| $Hg_2(IO_3)_2$ | $1.4x10^{-7}$ | $1.4x10^{-12}$ | |
| $Hg(IO_3)_2$ | $8.6x10^{-5}$ | $7.4x10^{-5}$ | |
| $Pb(IO_3)_2$ | $8.6x10^{-5}$ | $1.3x10^{-5}$ | |
| $AgIO_3$ | $1.7x10^{-4}$ | $1.4x10^{-4}$ | |
| $CuIO_3$ | $3.7x10^{-4}$ | $1.0x10^{-7}$ | |
| $Fe(IO_3)_3$ | $6.0x10^{-4}$ | $5.9x10^{-10}$ | |
| $Ce(IO_3)_4$ | $7.0x10^{-4}$ | - | |
| $Ba(IO_3)_2 2H_2O$ | $1.4x10^{-3}$ | $2.0x10^{-1}$ | Yes |
| $Th(IO_3)_4$ | $1.6x10^{-3}$ | $1.7x10^{-9}$ | |
| $TlIO_3$ | $1.8x10^{-3}$ | 1.6 | Yes |
| $La(IO_3)_3$ | $2.1x10^{-3}$ | $2.8x10^{-5}$ | |
| $In(IO_3)_3$ | $3.1x10^{-3}$ | $6.6x10^{-9}$ | |
| $Zn(IO_3)_2$ | $3.4x10^{-3}$ | $2.9x10^{-6}$ | |
| $UO2(IO_3)_2$ | $4.0x10^{-3}$ | $6.0x10^{-8}$ | |
| $Pu(IO_3)_4$ | $5.0x10^{-3}$ | - | |
| $Cu(IO_3)_2$ | $5.3x10^{-3}$ | $3.5x10^{-7}$ | |
| $Ce(IO_3)_3$ | $5.6x10^{-3}$ | $1.5x10^{-5}$ | |
| $Sr(IO_3)_2$ | $8.7x10^{-3}$ | $8.0x10^{-2}$ | Yes |
| $Ca(IO_3)_2 6H_2O$ | $1.1x10^{-2}$ | $2.2x10^{-2}$ | Yes |
| $Ni(IO_3)_2$ | $3.0x10^{-2}$ | $1.6x10^{-5}$ | |
| $Co(IO_3)_2$ | $5.8x10^{-2}$ | - | |

hydroxides are $Bi(IO_3)_2$, $Ba(IO_3)_2{\cdot}2H_2O$, $TlIO_3$, $Sr(IO_3)_2$, and $Ca(IO_3)_2{\cdot}6H_2O$. Solubility of these iodide or iodate compounds are given in Tables 5 and 6.

Reaction rates for iodine in aqueous solutions are available for only a few selected compounds: AgI, $Hg(IO_3)_2$, $Ca(IO_3)_2$, and $Ba(IO_3)_2$, as shown in Table 7 [Burger, 1982]. The leachability data in this table are presented as the normalized fraction leached, which is calculated by multiplying the fraction leached by the sample's geometric volume-to-surface area ratio, of 0.5 cm. All of the data are for the same test conditions: 8 wt% iodine in cement composite, static distilled water leachant, 25 days test duration, and temperature of 19-23°C. Among the compounds tested, silver iodide (AgI) exhibited the best leach resistance.

**Table 5-3**
**Comparisons of iodine leach data for various compounds in cement [Burger, 1982]**

| | **AgI** | **$Hg(IO_3)_2$** | **$Ca(IO_3)_2$** | **$Ba(IO_3)_2$** |
|---|---|---|---|---|
| Normalized fraction leached (cm) | $\sim 10^{-5}$ | $4\times10^{-3}$ | $6\times10^{-3}$ | $2\times10^{-3}$ |

Reduction of iodine compounds could be a source of iodine release during storage or disposal [Burger, 1982]. Reduction would not be expected by ordinary chemical reactions. However microbial induced anaerobic reduction could reduce the iodine compounds, forming $I^-$, $I_2$, or organic iodides.

### 5.1.2 Other Issues

The extensive work that has been done on iodine immobilization in cement has shown the process is feasible and licensability is likely. Costs would depend on the process equipment required, raw material prices, and secondary waste generation and cleanup. Based on environmental durability, AgI in cement is the leading candidate waste form. However, silver is by far the most expensive raw material ($138/kg) compared to other viable alternatives, including calcium ($CaCO_3$, $0.12/kg) and barium ($BaCO_3$, $0.66/kg).

# 6

# PROPOSED STRATEGY FOR $^{14}$C AND $^{129}$I WASTE FORM DEVELOPMENT

---

## 6.1 Summary of Findings

Various waste forms for immobilizing $^{14}$C and $^{129}$I were studied, and several approaches were found to warrant further investigation. For $^{14}$C the viable options include:

- Calcite and glassy carbon as intrinsic waste forms, with current judgment being that calcite is the better choice.
- Cement and phosphate minerals as matrix waste forms, with current judgment being that cement is the better choice.
- Graphite, glassy carbon, and silicon carbide as engineered barriers, with current judgment being that all three have attractive features and should be further investigated.

The most widely studied approach for $^{14}$C immobilization has been the formation of calcite in a cement matrix. While this approach is well established, the long-term durability of cement-calcite hinges not upon its intrinsic durability if exposed to ground waters, but on the long-term ability of the cement to control the evolution of the water chemistry, thereby maintaining low solubility of carbon from calcite. This approach is actively being investigated by other researchers [Dayal, 1992 & 1995]. The goal of this project is to identify intrinsically durable waste forms for $^{14}$C that do not rely on controlling water chemistry.

For $^{129}$I, cement was found to be the best matrix form, with silver iodide being the most durable iodine compound. Alternative intrinsic waste forms—with substantially higher leachability—include calcium iodate or barium iodate.

For both $^{14}$C and $^{129}$I, an engineered waste form approach using graphite, glassy carbon, or silicon carbide appears to provide significant promise, regardless of the types of intrinsic or matrix waste forms used. Figure 3 compares the ranges of environmental durability of various waste forms and barrier materials at ambient temperature. In this comparison, environmental durability is defined as the leaching rates of the matrix material in use. The materials compared include graphite, glassy carbon (GC), borosilicate glass (BG), silicon carbide (SiC), and cement. Graphite provides more than two orders of magnitude improvement over carbon steel, stainless steel, and cement, and about a order of magnitude improvement over SiC and glassy carbon. Also graphite has the smallest uncertainty in its durability.

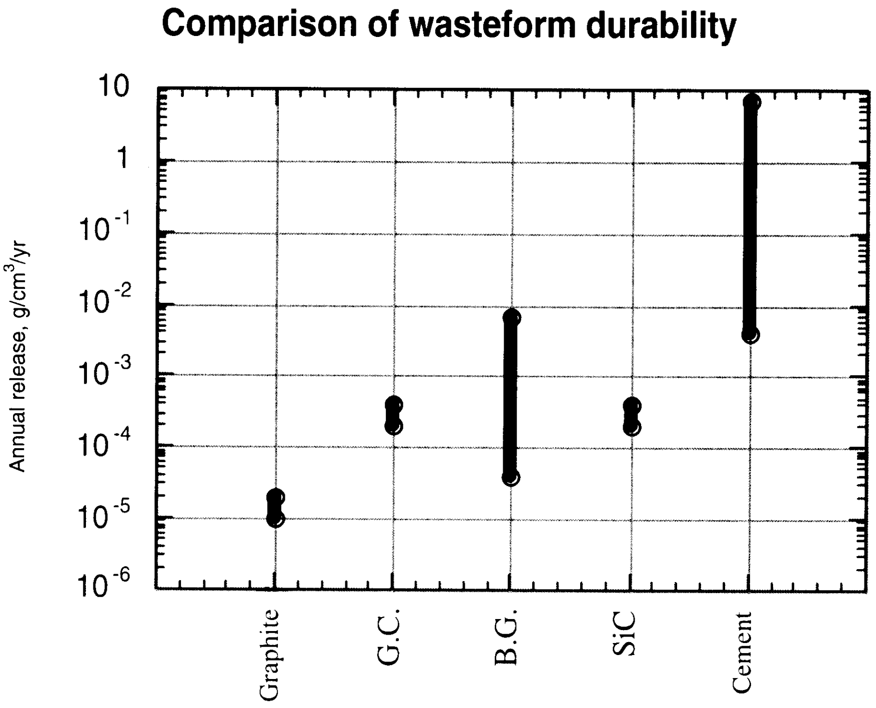


**Figure 6-1**
**Comparisons of environmental durability of various waste form materials at ambient temperature.**

## 6.2 Proposed Strategies for Investigating $^{14}$C and $^{129}$I Waste Form

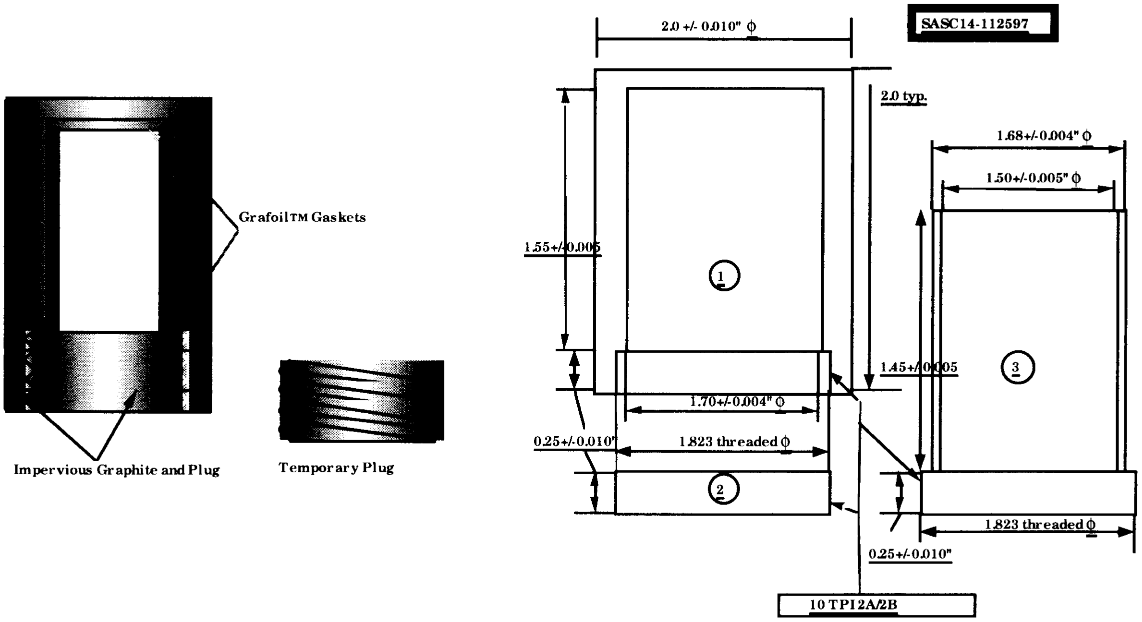
Based upon this preliminary study, the following strategies are proposed for further waste form research.

### *6.2.1 Engineered Waste Forms*

Engineered waste form approach appears to provide clear benefits for nuclear waste disposal if the volume of waste is relatively small. Since the total volume of materials of $^{14}$C and $^{129}$I separated from ion-exchange resins are expected to be small, the use of highly engineered barrier waste forms seems appropriate.

Since the environmental durability of graphite has been well documented, future work needs to focus on studying the permeability of $^{14}$C and $^{129}$I through the engineered barrier. For this, permeability of $^{14}$C and $^{129}$I species through graphite under various environmental conditions (e.g., aqueous environments at various pHs) needs to be investigated. This can be done using nonradioactive elemental carbon or iodine in the form of calcium carbonate or calcium iodate within the graphite barrier. This approach is viable because the permeability of $^{14}$C or $^{129}$I would be the same as other carbon or iodine species. Releases of carbon or iodine through the barrier are measured / detected through collection of $CO_2$ (and $I_2$) from a closed aqueous system using inert gas purging and gas chromatography analysis. By using a variety of experiments, the design of an engineered waste form can be optimized. If a more impermeable waste form than graphite is needed, resin-impregnated (impervious) graphite, glassy carbon, and silicon carbide can then be considered.

Figure 4 shows the suggested design of the graphite engineered waste form assembly for proof-of-principle testing. The final assembly would incorporate a larger dimension (about the size of a coffee can) for actual implemetation.



| | | |
|---|---|---|
| 1 | Capsule Body | POCO AXF -5Q |
| 2 | Cap #1 | POCO AXF -5Q |
| 3 | Cap #2 | POCO AXF -5Q |

All material must have certification of graphite grade

**Figure 6-2**
**Suggested design of the graphite engineered barrier assembly for proof-of-principle testing.**

### *6.2.2 Enhanced Waste Forms*

If any further improvement in performance is deemed desirable, additional waste form improvements may be investigated. For example, if the performance of graphite engineered barrier is not satisfactory, then additional matrix waste forms such as by using cement both for $^{14}C$ and $^{129}I$ within the graphite engineered barrier could be explored. For $^{129}I$, a intrinsic waste form of silver iodide within the cement could also be tested.

Other possibilities that may be investigated include:

- Glassy carbon as an intrinsic waste form for $^{14}C$ immobilization.
- Phosphate minerals and a polyethylene matrix waste form for $^{14}C$ immobilization.

## 6.3 Conclusion

Engineered barrier approach using graphite appears promising. A testing apparatus for evaluating graphite performance as an engineered waste form has been designed. If a more impermeable waste form than graphite is needed, resin-impregnated (impervious) graphite, glassy carbon, and silicon carbide could be considered. If any further improvement in performance is deemed desirable, additional waste form improvements using matrix and/or intrinsic waste forms may be investigated. Based on current funding, the proof-of-principle test on the graphite engineered barrier will not proceed in this project.

# 7

# REFERENCES

ASTM C 1220-92, "Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste," American Society for Testing and Materials, 1993.

ANSI/ANS-16.1-1986, "American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure," American Nuclear Society, 1986.

Brown, D. R. and M. W. Grutzeck, "Iodine Waste Forms: Calcium Aluminate Hydrate Analogues," Materials Research Society Symposium Proc., Vol. 44, pp. 911-918, 1985.

Burger, L. L., R. D. Scheele, and K. D. Wiemers, "Selection of a Form for Fixation of Iodine-129," PNL-4045, Pacific Northwest Laboratory, 1982.

Bush, R. P., G. M. Smith, and I. F. White, "Nuclear Science and Technology, Carbon-14 Waste Management," EUR 8749, Commission of the European Communities, 1984.

Calvin, M., C. Heidelberger, J. C. Reid, B. M. Tolbert, and P. F. Yankwich, "Isotopic Carbon," John Wiley & Sons, Inc., NY, 1949.

Clark, W. E., "The Isolation of Radioiodine with Portland Cement. Part I: Scoping Leach Studies," Nuclear Technology, Vol. 36, pp. 215-221, 1977.

Currie, L. M., V. C. Hamister, and H. G. MacPherson, "The Production and Properties of Graphite for Reactors," National Carbon Company, 1955.

6. F. R. Ribiero, A. E. Rodrigues, L. D. Rollman, and C. Naccache (eds), "Zeolites: Science and Technology," NATO ASI Series, Series E - No. 80, Martinus Nijhoff Publishers, 1984.

Davis, R., Private communications, Graphite Products Corporation, Nov. 1997.

Dayal, R. and E. J. Reardon, "Cement-Based Engineered Barriers for Carbon-14 Isolation," Waste Management, Vol. 12, pp. 189-200, 1992.

Dayal, R., "The Role of Cementitious Materials in Carbon-14 Waste Disposal," Proceedings of the 5th International Conference on Radioactive Waste Management and Environmental Remediation, pp. 1009-1013, American Society of Mechanical Engineers, 1995.

Emig, G. and N. Popovska, "Chemical Vapor Deposition of Silicon Carbide on Hollow and C-Shaped Carbon Fibre," Journal of Material Science, Vol. 31, pp. 4395-4399, 1996.

EPRI, "Characterization of Carbon-14 Generated by the Nuclear Power Industry," EPRI TR-105715, Electric Power Research Institute, 1995.

Fitzer, E. and W. Schafer, "The Effect of Crosslinking on the Formation of Glasslike Carbons from Thermosetting Resins," Carbon, Vol. 8, pp.353-364, 1970.

Frantz, E.-M., M. Fuhrmann, B. Bowerman, S. Bates, and R. Peters, "Proposed Waste Form Performance Criteria and Testing Methods for Low-Level Mixed Waste," BNL-52436, DOE/MWIP-30, U. S. Department of Energy, 1994.

Fuhrmann, M., J. Heiser, R. Pietrzak, E. M. Franz, and P. Colombo, "Method for Accelerated Leaching of Solidified Waste," BNL-52268, Brookhaven National Laboratory, 1990.

Gray, W. J., "Reaction of Graphite with Water and Its Implications for Radioactive Waste Storage," Radioactive Waste Management, Vol. 1 (1), pp. 105-109, 1980.

Gray, W. J., "A Study of the Oxidation of Graphite in Liquid Water for Radioactive Waste Storage Applications," Radioactive Waste Management and the Nuclear Fuel Cycle, Vol. 3 (2), pp. 137-149, 1982.

Haag, G. L., "Removal of Carbon-14," in Treatment of Gaseous Effluents at Nuclear Facilities, W. R. A. Goossens, et.al., ed., Harwood Academic Publishers, 1991.

Kane, R. D., "Prevent Corrosion of Advanced Ceramics," Chemical Engineering Progress, June 1991.

Kmetz, M. and S. Suib, "Silicon Carbide/Silicon and Silicon Carbide/Silicon Carbide Composites Produced by Chemical Vapor Infiltration," J. Amer. Ceramics Society, Vol. 73 (10), pp. 3091-3093, 1990.

Knop, A. and L. A. Pilato, "Phenolic Resins, Chemistry, Applications and Performance," Springer-Verlag, 1985.

Kosolapova, T. Ya., "Carbides, Properties, Production, and Application," Plenum Press, 1971.

Krauskopf, K. B., "Introduction to Geochemistry," 2nd edition, McGraw-Hill, 1982.

Krupka, K. M., R. J. Serne, and E. A. Jenne, "Geochemical Effects on the Behavior of Low-Level Waste Radionuclides in Soil/Groundwater Environments," 17th U.S. DOE LLW Management Conference, Phoenix, AZ, December 12-14, 1995.

Lausevic, Z. and G. M. Jenkins, "Anodic Oxidation of Glassy Carbon Surfaces," Carbon, Vol. 24, No. 5, pp. 651-652., 1986a.

Lausevic, Z. and S. Marinkovic, "Mechanical Properties and Chemistry of Carbonization of Phenol Formaldehyde Resin," Carbon, Vol. 5, pp. 575-580, 1986b.

Lutze, W. and R. C. Ewing, "Radioactive Waste Forms for the Future," North-Holland, Amsterdam, 1988.

Mantell, C. L., "Carbon and Graphite Handbook," John Wiley & Sons, Inc., 1968.

Matsumoto, J., T. Banba, and S. Muraoka, "Adsorption of Carbon-14 on Mortar," Mat. Res. Soc. Symp. Proc. Vol. 353, pp. 1029-1035, 1995.

McKee, D. W., "Carbon and Graphite Science," in Annual Review of Materials Science, Vol. 3, pp. 195-231, 1973.

Miller, W., R. Alexander, N. Chapman, I. McKinley, J. Smellie, "Natural Analogue Studies in the Geological Disposal of Radioactive Wastes," Elsevier, 1994.

Moghissi, A. A., H. W. Godbee, and S. A. Hobart, "Radioactive Waste Technology," The American Society of Mechanical Engineers, 1986.

Morterra, C. and M. J. D. Low, "I.R. Studies of Carbons - VII. The Pyrolysis of A Phenol-Formaldehyde Resin," Carbon, Vol. 23, pp. 525-530, 1985.

Neffe, S., "Electrochemical Corrosion of Glasslike Carbon in Sulfuric Acid Solution," Carbon, Vol. 26, No. 5, pp. 687-692, 1988.

Ouchi, K., "Infra-red Study of Structural Changes during the Pyrolysis of a Phenol-Formaldehyde Resin," Carbon, Vol. 4, pp. 59-66, 1966.

Raman, V., O. P. Bahl, U. Dhawan, "The Synthesis of Silicon Carbide Through the Sol-Gel Process from Different Precursors," Journal of Material Science, Vol. 30, pp. 2686-2693, 1993.

Rudin, M. J. and R. S. Garcia, National Low-Level Waste Management Program Radionuclide Report Series, Vol. 4: Iodine-129, DOE/LLW-120, 1992.

Scheele, R. D. and L. L. Burger, "Selection of Carbon-14 Fixation Form," PNL-4447, Pacific Northwest Laboratory, 1982.

Scheele, R. D., L. L. Burger, and K. D. Wiemers, "Leach Resistance of Iodine Compounds in Portland Cement," in Geochemical Behavior of Radioactive Waste, G. S. Barney et. al. (eds) American Chemical Society, 1984.

Schoenung, J. M., "The Economics of Silicon Carbide Whisker Fabrication," Ceram. Eng. Sci. Proc., Vol. 12 [9-10], pp. 1943-1951, 1991.

Scott, J., "Zeolite Technology and Applications," Chemical Technology Review No. 170, Noyes Data Corporation, 1980.

Singh, M. and S. R. Levine, "Low Cost Fabrication of Silicon Carbide Based Ceramics and Fiber Reinforced Composites," NASA Technical Memorandum 107001, 1994.

Somiya, S. and Y. Inomata (eds), "Silicon Carbide Ceramics -1, Fundamentals and Solid Reaction," Elsevier Applied Science, 1991

Strachan, D. M., R. P. Turcotte, and B. O. Barnes, "MCC-1: A Standard Leach Test for Nuclear Waste Forms," Nuclear Technology, Vol. 56, pp. 306-312, 1982.

Taylor, P., "Solubility and Stability of Inorganic Carbonates: An Approach to the Selection of a Waste Form for Carbon-14," AECL-9073, Atomic Energy of Canada Limited, 1987.

Ubbelohde, A. R. and F. A. Lewis, "Graphite and Its Crystal Compounds," Oxford University Press, 1960.

US NRC, Code of Federal Regulations, Title 10, Chapter 1, Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste," Fed. Registr. 47, 57446, 1982.

US NRC, "Source Term Implementation for Initial Performance Assessment Calculation," Technical Review of Performance Assessment Modeling Strategy," U.S. Nuclear Regulatory Commission, Rockville, MD, July 12-13, 1993.

Whitehead, A. J. and T. F. Page, "Fabrication and Characterization of Some Novel Reaction-Bonded Silicon Carbide Materials," Journal of Materiala Science, Vol. 27, pp. 839-852, 1992.

Winters, W. I., "The Effect of Hot-Pressing Conditions on the Properties of Iodide Sodalite," RHO-LD-153, Rockwell Hanford Operations, 1980.

Wright, R. M., J. M. Ruder, V. B. Dunn, and K. C. Hwang, "Development of Design Information for Molecular-Sirve Type Regenerative CO2-Removal Systems," NASA CR-2277, National Aeronautics and Space Administration, 1973.

www.goodnet.com/~richardm/homepage.htm, Nov. 1997.

Yim, M.-S., "Evaluation of Uncertainties in Low Level Waste Source Term Analysis," Proceedings of the 18th DOE LLW Management Conference, Salt Lake City, UT, May 20-22, 1997.

Zhao, G. Y., J. J. Thiart, D. Orlicki and V. Hlavacek, "Particle-Aided Chemical Vapor Deposition (PACVD) of Silicon Carbide Composites," Chemical Engineering Science, Vol. 49, No. 24B, pp. 4917-4938, 1994.