Use of Ceramic Materials in Waste-Package Systems for Geologic Disposal of Nuclear Wastes

H. T. Fullam

December 1980

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

The views, opinions and conclusions contained in this report are those of the contractor and do not necessarily represent those of the United States Government or the United States Department of Energy.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from:
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$_____ * Microfilm \$3.00

*Pages	NTIS
	Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

3 3679 00054 5147

USE OF CERAMIC MATERIALS IN WASTE-PACKAGE
SYSTEMS FOR GEOLOGIC DISPOSAL OF NUCLEAR
WASTES

H. T. Fullam

December 1980

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RL0 1830

Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

A program is currently under way at Pacific Northwest Laboratory to develop durable, long-lived packages for the containment of nuclear wastes under conditions of deep geologic disposal. One phase of the program consists of a study to investigate the potential use of ceramic materials as components in the waste package systems. The initial objective of the study was to screen and compare a large number of ceramic materials and identify the best materials for the proposed application. The principal method used to screen the candidates was to subject samples of each material to a series of leaching tests and to determine their relative resistance to attack by the leach solutions.

A total of 14 ceramic materials, plus graphite and basalt were evaluated using three different leach solutions: demineralized water, a synthetic Hanford ground water, and a synthetic WIPP brine solution. The ceramic materials screened were Al_2O_3 (99%), Al_2O_3 (99.8%), mullite ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), vitreous silica (SiO_2), BaTiO_3 , CaTiO_3 , CaTiSiO_5 , TiO_2 , ZrO_2 , ZrSiO_4 , Pyroceram 9617,[®] and Marcor[®] Code 9658 machinable glass-ceramic. Five leaching tests were used to screen the candidates:

- a static leach test at 100°C,
- a hydrothermal static leach test at 150°C,
- a hydrothermal static leach test at 250°C,
- a dynamic (flow) leach test at 90°C, and
- a dynamic (flow) leach test at 250°C.

Average leach rates for the materials tested were determined from analyses of the leach solutions and/or sample weight loss measurements.

Averaged leach rate measurements provide one method of screening the candidates, but the results obtained can be misleading because they provide no information on the extent to which localized attack or alteration reactions may occur with a given material. Therefore, additional analysis of the specimens is needed after testing, such as ceramographic examination and scanning electron microscopy. Because of the limited scope of the present study, evaluation of the specimens was limited to ceramographic examination.

Whenever possible the materials tested were obtained as dense, impervious shapes from commercial sources. Test specimens were cut from the commercial shapes using a diamond saw. Some material could only be obtained in powder form. These materials were compacted into dense pellets at PNL by hot-pressing or cold-pressing and sintering.

Based on an overall evaluation of the leach rate data, five of the materials tested--namely graphite, TiO_2 , ZrO_2 , and the two grades of alumina--exhibited much greater resistance to leaching than did the other materials tested. Some of the other materials exhibited good leach resistance in one or two tests, but on an overall basis they were inferior to the five

[®]Corning Glass Works, Corning, New York

materials mentioned above. In addition, most of the materials having poor leach resistance were also susceptible to alteration reactions (especially at 250°C), which was not a problem with the more leach-resistant materials.

Based on all the experimental data obtained, and considering other factors such as cost, availability, fabrication technology, and mechanical and physical properties, graphite and alumina are the preferred candidates for the barrier application. The secondary choices are TiO_2 and ZrO_2 .

CONTENTS

SUMMARY	iii
FIGURES	vii
TABLES	viii
1.0 INTRODUCTION	1
2.0 OBJECTIVES	3
3.0 EXPERIMENTAL	5
3.1 TESTING CRITERIA	5
3.2 TEST PROCEDURES	5
3.3 MATERIALS EVALUATED	9
3.3.1 Material Selection	9
3.3.2 Sample Preparation	10
3.4 LEACH SOLUTIONS	11
3.5 ANALYTICAL PROCEDURES	12
4.0 RESULTS AND DISCUSSION	13
4.1 LEACH RATES	13
4.1.1 Static Leach Tests at 100°C	14
4.1.2 Dynamic Leach Tests at 90°C	17
4.1.3 Dynamic Leach Tests at 250°C	17
4.1.4 Static Leach Tests at 150°C	21
4.1.5 Static Leach Tests at 250°C	26
4.1.6 Relative Leach Rates	30
4.2 REACTIONS WITH REPOSITORY MEDIA	32
4.3 EVALUATION OF CANDIDATE MATERIALS	34
4.3.1. Graphite	34
4.3.2 Al ₂ O ₃	37
4.3.3 ZrO ₂	40
4.3.4 TiO ₂	42
4.3.5 Mullite (2Al ₂ O ₃ •SiO ₂)	42
4.3.6 Vitreous Silica (SiO ₂)	44
4.3.7 CaTiO ₃	44

4.3.8	CaZrO ₃	.	.	.	.	.	.	.	.	.	.	.	.	48
4.3.9	CaTiSiO ₅	.	.	.	.	.	.	.	.	.	.	.	.	48
4.3.10	Basalt	.	.	.	.	.	.	.	.	.	.	.	.	51
4.3.11	ZrSiO ₄	.	.	.	.	.	.	.	.	.	.	.	.	51
4.3.12	BaTiO ₃	.	.	.	.	.	.	.	.	.	.	.	.	54
4.3.13	BaZrO ₃	.	.	.	.	.	.	.	.	.	.	.	.	54
4.3.14	Pyroceram 9617	.	.	.	.	.	.	.	.	.	.	.	.	57
4.3.15	Marcor 9658	.	.	.	.	.	.	.	.	.	.	.	.	57
4.4	ESTIMATES OF LONG-TERM ATTACK	.	.	.	.	.	.	.	.	.	.	.	.	57
5.0	CONCLUSIONS AND RECOMMENDATIONS	.	.	.	.	.	.	.	.	.	.	.	.	63
6.0	REFERENCES	.	.	.	.	.	.	.	.	.	.	.	.	65
7.0	ACKNOWLEDGMENTS	.	.	.	.	.	.	.	.	.	.	.	.	67
APPENDIX - DESCRIPTION OF CERAMIC MATERIALS STUDIED		.	.	.	.	.	.	.	.	.	.	.	.	A.1
	Al ₂ O ₃ (99%)	.	.	.	.	.	.	.	.	.	.	.	.	A.1
	Al ₂ O ₃ (99.8%)	.	.	.	.	.	.	.	.	.	.	.	.	A.1
	MULLITE (2Al ₂ O ₃ •SiO ₂)	.	.	.	.	.	.	.	.	.	.	.	.	A.1
	BASALT	.	.	.	.	.	.	.	.	.	.	.	.	A.2
	BaTiO ₃	.	.	.	.	.	.	.	.	.	.	.	.	A.2
	BaZrO ₃	.	.	.	.	.	.	.	.	.	.	.	.	A.2
	CaTiO ₃	.	.	.	.	.	.	.	.	.	.	.	.	A.3
	CaZrO ₃	.	.	.	.	.	.	.	.	.	.	.	.	A.3
	CaTiSiO ₅	.	.	.	.	.	.	.	.	.	.	.	.	A.4
	VITREOUS SILICA (SiO ₂)	.	.	.	.	.	.	.	.	.	.	.	.	A.4
	TiO ₂	.	.	.	.	.	.	.	.	.	.	.	.	A.5
	ZrO ₂	.	.	.	.	.	.	.	.	.	.	.	.	A.5
	ZrSiO ₄ (ZIRCON)	.	.	.	.	.	.	.	.	.	.	.	.	A.6
	GRAPHITE (TOYO)	.	.	.	.	.	.	.	.	.	.	.	.	A.6
	PYROCERAM 9617	.	.	.	.	.	.	.	.	.	.	.	.	A.6
	MARCOR MACHINABLE GLASS-CERAMIC	.	.	.	.	.	.	.	.	.	.	.	.	A.6

FIGURES

1	Equipment Used in the Static Leach Tests at 100°C	6
2	Equipment Used in the Dynamic Leach Tests at 90°C	8
3	Photomicrographs of Graphite Specimens Before and After Testing	36
4	Al ₂ O ₃ (99%) Specimens Before and After Leaching	38
5	Al ₂ O ₃ (99.8%) Specimens Before and After Leaching	39
6	ZrO ₂ Specimens Before and After Leaching	41
7	TiO ₂ Samples Before and After Leaching	43
8	Micrographs of Mullite Test Specimens	45
9	Micrographs of Vitreous Silica Specimens Before and After Leaching	46
10	CaTiO ₃ Specimens Before and After Leaching	47
11	CaZrO ₃ Specimens Before and After Leaching	49
12	Micrographs of CaTiSiO ₅ Specimens Before and After Leaching	50
13	Basalt Specimens Before and After Testing	52
14	Photomicrographs of ZrSiO ₄ Specimens	53
15	BaTiO ₃ Samples Before and After Leaching	55
16	Micrographs of BaZrO ₃ Specimens Before and After Leaching	56
17	Micrographs of Pyroceram 9617 Specimens	58
18	Marcor Specimens Before and After Testing	59
19	The Effect of Temperature on the Leaching of Various Materials	64

TABLES

1	Materials Evaluated in the Screening Tests	9
2	Composition of Solutions Used in the Leaching Experiments	11
3	Detection Limits for Cations Using the Induction-Coupled Plasma Spectrometer	12
4	Average Leach Rates for Ceramic Materials in Demineralized Water at 100°C--Vented Static System	15
5	Leaching of Pyrex Glassware in Demineralized Water at 100°C	17
6	Leaching of Ceramic Materials in Flowing Demineralized Water at 90°C	18
7	Average Leach Rates for Ceramic Materials Exposed to Flowing Demineralized Water at 250°C	20
8	Extent of Localized Attack or Alteration Reactions in Ceramic Materials Exposed to Flowing Demineralized Water at 250°C	22
9	Leaching of Ceramic Materials in Demineralized Water at 150°C--Static Tests in Sealed Gold Ampules	23
10	Leaching of Ceramic Materials in Hanford Ground Water at 150°C--Static Tests in Sealed Gold Ampules	25
11	Leaching of Ceramic Materials in Brine at 150°C--Static Tests in Sealed Gold Ampules	27
12	Leaching of Ceramic Materials in Demineralized Water at 250°C--Static Tests in Sealed Gold Ampules	29
13	Leaching of Ceramic Materials in Hanford Ground Water at 250°C--Static Test in Sealed Gold Ampules	31
14	Leaching of Ceramic Materials in Brine at 250°C--Static Tests in Sealed Gold Ampules	33
15	Relative Resistance of Ceramic Materials to Leaching Under Various Test Conditions (in Order of Decreasing Resistance)	35
16	Estimated Worst-Case Corrosion of Ceramic Material Exposed to Flowing Demineralized Water at 250°C	61
17	Corrosion Rates of Metals and Alloys in Deoxygenated Solutions	62

1.0 INTRODUCTION

A study is under way at Pacific Northwest Laboratory (PNL) to develop long-lived waste-package systems that can be used in the geologic disposal of nuclear wastes. The waste-package barrier system study represents one phase of PNL's High-Level Waste Immobilization Program, which is funded by the Department of Energy's Division of Waste Products.

The primary objective of the current study is to develop a waste-package engineered-barrier system that would serve to isolate the nuclear waste from the geologic repository environment for a period of 1000 years. The waste could be in the form of spent fuel or solidified high-level waste from a fuel reprocessing plant (i.e., glass, supercalcine, etc.). The 1000-year period would ensure that before the waste came in contact with the geologic medium the heat-producing, short-lived radionuclides in the waste would have decayed to very low levels, and that the heat output would have decreased accordingly.

A waste package is currently defined as 1) the waste form, 2) the canister surrounding the waste form, 3) any canister overpack, 4) the hole sleeve, if any, and 5) the backfill medium. The term "engineered barrier" generally refers to any of the foregoing except for the waste form. A number of engineered-barrier system options are available. The simplest system would consist of the waste canister and the backfill material used to fill the hole in which the canister is placed. Additional barrier elements, such as an overpack or a hole sleeve, can be added to increase the reliability and integrity of the system. Ceramic materials are being considered for possible use as elements in the engineered-barrier systems. This report summarizes the results of some initial scouting experiments that were carried out to screen and compare a large number of ceramic materials and identify the best materials for the barrier application. The screening tests were not intended to demonstrate the usability of the ceramic materials in engineered-barrier systems, but simply to identify those ceramic materials that provide the best chance of developing acceptable barrier elements. Additional experimental work will be required to demonstrate that ceramic materials can be successfully used in engineered-barrier systems.

In addition to ceramics, metallic and polymeric materials are being investigated at PNL for potential use in engineered-barrier systems.

2.0 OBJECTIVES

The primary objective of the ceramic materials investigation is to determine if practical ceramic-barrier elements can be developed that will provide protection of the primary waste canister for 1000 years under the conditions that would be encountered in a geologic repository. The current study is divided into two phases. The first phase consists of initial scouting studies whose basic objective is to screen and compare a large number of candidate ceramic materials and to select the best materials for detailed evaluation. The second phase is to carry out detailed experimental evaluation of the materials identified in Phase 1 and to determine if practical ceramic barrier elements can be developed. Continuation with Phase 2 of the study depends on the results obtained in Phase 1 and on the results obtained in the investigation of barriers made of other materials--i.e., metals and polymers.

3.0 EXPERIMENTAL

Screening of the candidate ceramic materials was carried out through a series of leaching experiments conducted under various temperature and pressure conditions. Solid-solid reactions between the candidate materials and repository media were studied to a limited degree. Initial comparisons were based on experimentally determined leach rates and observed interactions. Other factors, such as availability, fabricability, mechanical and physical properties, and cost were considered in the final comparison and in selecting the best materials for detailed evaluation.

3.1 TESTING CRITERIA

Criteria and design parameters for geologic waste repositories have not been defined. Geologic media still under consideration for use as a repository include bedded salt, salt domes, granite, basalt, shale and volcanic tuffs. Various repository design considerations such as the age of the waste at the time of disposal, heat-loading, temperature limitations, backfill materials, etc., remain unclear. In this study it was impossible to consider all geologic alternatives and design parameters that enter into the construction of an engineered-barrier system and waste repository. In order to reduce the degree of experimental testing to an acceptable level, it was necessary to make a number of assumptions in designing the test matrix:

- Only two repository types were considered: 1) bedded salt of the type found at the Waste Isolation Pilot Plant (WIPP) site in New Mexico, and 2) basalt typical of that found at Hanford.
- Aqueous solutions used in the leach tests were limited to: 1) demineralized water, 2) salt brine similar to that found at the WIPP site, and 3) a typical Hanford ground water.
- The maximum temperature for the hydrothermal leach tests, corresponding to a "wet" repository, was limited to 250°C.
- The temperature in a "dry" repository would not exceed 375°C.
- The possible effects of backfill materials on the reactions between the ceramic materials and repository environs was not considered.
- The effects of the radiation field on the reactions between the ceramic materials and repository environs was not considered.

3.2 TEST PROCEDURES

The ceramic materials to be screened were subjected to five different leach tests:

1. a static leach test at 100°C
2. a static leach test at 150°C
3. a static leach test at 250°C

4. a dynamic (flow) leach test at 90°C
5. a dynamic (flow) leach test at 250°C.

In addition, the direct reaction of the ceramic material with the repository media was studied at 375°C. Each of the test procedures is described in the following paragraphs.

Figure 1 shows the equipment used in carrying out the static leach test at 100°C. The ceramic test specimen was measured to determine its geometric surface area and then weighed on a calibrated semi-microbalance (accuracy = ± 0.01 mg). The weighed specimen was placed in a one-liter Pyrex flat-bottom flask and a known volume of demineralized water was added. The ratio of the geometric surface area of the test specimen to water volume (S/V) was maintained constant at 0.02 cm^{-1} for all of the tests. A water-cooled Pyrex condenser was connected to the Pyrex flask, and a short section of Pyrex capillary tubing was placed on the outlet of the condenser. The water in the flask was heated to boiling on a hot plate and held at boiling for up to 49 days. Samples of the solution were taken at periodic intervals for analysis. The test specimens were also removed from the flask periodically, vacuum-dried, and weighed to monitor the weight change. The solution samples were collected through a 0.3- μm Millipore filter using a polypropylene syringe and filter holder. The filter holder was placed in the solution and brought to the solution temperature before the sample was taken. As the solution entered the syringe, it was acidified to 2N H^+ with triply distilled nitric acid. The

FIGURE 1. Equipment Used in the Static Leach Test at 100°C

condenser and its capillary outlet reduced evaporation of water from the flask, but some water had to be added periodically to maintain the level. Blank tests, without ceramic specimens present, were also run in order to determine how much leaching of the Pyrex glassware occurred during testing. It is estimated that leach rates as low as $2 \times 10^{-8} \text{ g/cm}^2\text{-d}$ could be measured by this procedure.

The static leach tests at 150° and 250°C were carried out in sealed gold ampules. The following procedure was used for the tests. A weighed ceramic specimen of known geometric surface area was placed in a gold ampule, and a known volume of the leach solution was added. The gold ampule was then sealed by welding. The sealed ampule was placed in an autoclave filled with demineralized water. The autoclave was heated to 150° or 250°C , held at temperature for the required time, cooled, and the ampule was then removed and opened. The test specimen was removed from the ampule, washed, vacuum-dried, and weighed. The solution in the ampule was acidified with 2M high-purity hydrochloric acid and allowed to stand for several hours. After the solution was transferred to a sample bottle, the ampule was washed with more 2M hydrochloric acid. The original solution and wash solution were combined and analyzed for dissolved species. The test was then repeated for a different time period using the same test specimen and fresh leach solution. Each specimen was tested for four time periods (1 day, 7 days, 14 days, and 21 days) using fresh leach solution for each test. The tests were carried out using the three leach solutions described in Section 3.4. An attempt was made to use the same S/V ratio of 0.4 cm^{-1} (based on the specimens' geometric surface area) in all of the tests, but some minor variations in the ratio were inevitable with the different ceramic materials. The gold ampules used in the tests had an inner diameter of 0.50 in., and could hold up to 15 ml of leach solution. After the final test, the ceramic specimen was subjected to ceramographic examination. It is estimated that leach rates as low as $5 \times 10^{-8} \text{ g/cm}^2\text{-d}$ could be measured with the procedure.

The dynamic (flow) leach tests at 90°C were carried out using the equipment shown in Figure 2. The weighed test specimen, of known geometric surface area, was placed in a Teflon flask. The flask was placed in a water bath held at 90°C . Demineralized water was pumped through the flask at a controlled rate using a peristaltic metering pump. The solution exiting the flask was filtered through an in-line $0.3\text{-}\mu\text{m}$ Millipore filter and collected in a flask, which was also contained in the water bath. The average water-flow rate was approximately 0.2 ml/min, and the residence time in the flask was about 20 hours. Samples of the solution in the collection flask were taken on a periodic basis and analyzed for dissolved species. The samples were taken using the syringe-Millipore filter technique described earlier. The ceramic specimen was also removed from the flasks at specific intervals, vacuum-dried, and weighed to monitor weight change as a function of exposure time. A multichannel peristaltic pump was used for the experiments, which allowed as many as ten tests to be carried out at one time. Leach rates as low as $1 \times 10^{-7} \text{ g/cm}^2\text{-d}$ could be measured.

FIGURE 2. Equipment Used in the Dynamic Leach Tests at 90°C

The dynamic (flow) leach tests at 250°C were carried out in demineralized water within a Hastelloy C[®] autoclave. The weighed ceramic specimens, of known geometric area, were placed in the autoclave. Demineralized water was pumped through the autoclave at a controlled rate while the temperature was raised to 250°C and held at the temperature for the duration of the run. At specific intervals the autoclave was cooled and opened, and the ceramic specimens were removed, vacuum-dried and weighed. The specimens were then returned to the autoclave for additional testing. Each specimen was exposed for intervals of 1 day, 7 days, 14 days, and 21 or 23 days--giving a total exposure of 43 or 45 days. After the conclusion of the tests, the specimens were subjected to ceramographic examination. Eight ceramic materials were tested at one time and no attempt was made to analyze the demineralized water leaving the autoclave. The volume of the autoclave was ~6.5 L and the water-flow rate was about 1.9 L/h, giving a residence time of approximately 3.4 hours. Leach rates as low as 2×10^{-8} g/cm²-d could be measured. The scope of the study did not permit each material to be tested individually in the autoclave. The possibility exists that interactions between each group of materials tested could affect the results obtained, but these effects should be minimal considering the high water-flow rate and the low leach rates of the materials tested.

In addition to the leaching tests, the ceramic materials were subjected to one additional test. This test was intended to determine if any reaction might occur between a ceramic material and the repository medium--either basalt or salt. In these tests a weighed ceramic specimen was packed in crushed basalt or salt within a silica ampule. A small amount of water sufficient to give a partial pressure of 4 mm Hg (STP) was added to the mixture and the ampule was sealed. The ampule was then heated to 375°C in a muffle furnace and held at temperature for the required time. At the conclusion of the test the ampule was cooled and opened. The test specimen was visually examined for possible reaction with the basalt or salt and then was weighed. The tests lasted 2200 and 4500 hours.

[®]A corrosion-resistant nickel-base alloy produced by Cabot Corporation, Kokomo, Indiana.

3.3 MATERIALS EVALUATED

3.3.1 Material Selection

A wide variety of inorganic materials can be considered for use in an engineered-barrier system. For a variety of reasons, the materials considered for evaluation in this study were limited to inorganic oxides and graphite. A literature search was conducted to determine what oxide materials might be expected to be most resistant to attack by the aqueous solutions that could be encountered in the two types of geologic waste repositories under consideration. In addition, recommendations on the types of materials to test were solicited from various individuals at PNL and Rockwell-Hanford who have the appropriate expertise. The materials finally selected for evaluation are listed in Table 1. The basalt evaluated in the study was taken from Flow E of the Sentinel Bluffs-Grande Ronde Formations in south-central Washington. One grade of graphite was included in the screening tests. The graphite studied was Toyotanso® IG-11, which was developed for use in high-temperature, gas-cooled reactors and is reported to have a low permeability. Some naturally occurring, complex oxide minerals were seriously

TABLE 1. Materials Evaluated in the Screening Tests

Material	Method Used to Fabricate Dense Test Specimens
1. Al_2O_3 (99%)	Commercial ^(a)
2. Al_2O_3 (99.8%)	Commercial
3. Mullite ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$)	Commercial
4. Basalt	Naturally Occurring
5. BaTiO_3	Cold-Press and Sinter ^(b)
6. BaZrO_3	Cold-Press and Sinter
7. CaTiO_3	Hot-Press ^(c)
8. CaTiSiO_5	Cold-Press and Sinter
9. CaZrO_3	Cold-Press and Sinter
10. Vitreous Silica (SiO_2)	Commercial
11. TiO_2	Hot-Press
12. ZrO_2	Commercial
13. ZrSiO_4	Hot-Press
14. Graphite	Commercial
15. Pyroceram 9617 ^(d)	Commercial
16. Marcor Glass-Ceramic ^(d)	Commercial

(a) Obtained from a commercial source as a high-density shape.

(b) Powder cold-pressed into pellets and sintered.

(c) Powder hot-pressed into pellets.

(d) Corning Glass Works.

®Toyo-Tanso Co. Ltd., Osaka, Japan.

considered for evaluation but were dropped because they are being studied in other PNL programs. These include materials such as zirconolite, hollandite, and certain types of feldspars.

3.3.2 Sample Preparation

Wherever possible, the materials to be screened were obtained from commercial sources in the form of dense, impervious shapes. Several of the materials could only be obtained as powders and had to be compacted into dense test specimens. Depending on the material, hot-pressing or cold-pressing and sintering was used to fabricate the powders into dense pieces. Descriptions of the materials tested, including purity and method of densification, are given in the Appendix.

Fabricated shapes obtained from commercial sources and the naturally occurring basalt were sectioned into test specimens using a diamond saw. No attempt was made to polish the cut surfaces of the specimens before testing.

Hot-pressing was used to compact several of the powdered materials into high-density pellets. The hot press utilized an induction-heated graphite die and hydraulic press. The maximum temperature capability of the press was approximately 1700°C, while the graphite die limited the maximum pressure to about 5800 psi. Pellets up to 1 in. in dia could be prepared by varying the die diameter. The maximum pellet length was about 1 in. Very little interaction was observed between the oxide pellets and the graphite die. The surface of the pellet, after removal from the die, was discolored with graphite that was easily removed by heating the pellet in air at about 1200°C for several hours.

The average densities of the hot-pressed pellets varied from about 86% of theoretical density for ZrSiO_4 to 94% for CaTiO_3 . Density variations for pellets of a given material were about $\pm 0.5\%$.

Attempts to hot-press BaTiO_3 , BaZrO_3 , CaZrO_3 , and CaTiSiO_5 in graphite dies were unsuccessful. High-density pellets of the four materials were prepared by cold-pressing and sintering. One-inch-diameter pellets of each material were prepared by cold-pressing the powder at 50 tons/in.² in a hardened split-sleeve steel die. The "green" pellets were then fired at approximately 1200°C for 90 h in an air-atmosphere muffle furnace. Average densities of the cold-pressed and sintered pellets ranged from 89% of theoretical density for BaTiO_3 to 92% for BaZrO_3 . Density variations for pellets of a given material were about $\pm 1\%$.

The pressed pellets were sectioned to the desired size using a diamond saw. The test specimens were cleaned, rinsed with demineralized water, and vacuum-dried at 180°C. The specimens were then weighed on a semi-microbalance before testing.

Some of the test specimens (such as graphite) had considerable internal porosity and some were permeable. The surface areas of the specimens were determined by the Brunauer Emmett Teller (BET) method using krypton.

3.4 LEACH SOLUTIONS

The candidate ceramic materials were leached in three different solutions: demineralized water, a synthetic Hanford ground water, and a synthetic brine solution. The compositions of the last two solutions are given in Table 2.

The demineralized water used in the leach tests was prepared using a Corning Model LD-5 water purifier. The treated water had a resistivity greater than 2 MΩ, and its pH was approximately 6.2. Analysis of the demineralized water by induction-coupled plasma spectroscopy (ICP) showed that cation concentrations in the water were below the detectable limits for the instrument except for silicon, which averaged about 0.03 ppm.

The synthetic ground water used was based on the analysis of a ground water sample taken from the Umtanum basalt flow on the Hanford Reservation (Ames 1978). Analysis of groundwater samples taken from various sites on the reservation show significantly different compositions, but the composition used represents the one that has been widely used in various experimental programs at PNL, including radionuclide adsorption studies.

TABLE 2. Composition of Solutions Used in the Leaching Experiments

Solution Constituents	Solution Types	
	Synthetic Hanford Ground Water (pH = 8.0), mg/L	Synthetic Brine Solution (pH = 6.5), mg/L (a)
Na ⁺	33	115,000
K ⁺	9	18
Ca ⁺²	6.5	900
Mg ⁺²	1	10
Sr ⁺²		15
Rb ⁺		1
Cs ⁺		1
Fe ⁺³		2
Cl ⁻	16	175,000
SO ₄ ⁻²	23	4,200
I ⁻		10
HCO ₃ ⁻	63	12
F ⁻	0.7	
Br ⁻		400
BO ₃ ⁻³		10

(a) Synthetic solution density @ 22°C = 1.18 g/mL.

The synthetic salt brine used was a predominantly NaCl brine whose composition was representative of the brine encountered in the bedded salt at the WIPP site (Braithwaite and Molecke 1978). Brine of this composition has been and is being used in a variety of leaching tests at PNL and Sandia Laboratories.

3.5 ANALYTICAL PROCEDURES

Average leach rates were determined using the weight change measurements and solution analysis. The weight changes were monitored by weighing the test specimens on a semi-microbalance before and after testing. The various aqueous samples were analyzed for dissolved cations using an induction-coupled plasma spectrometer (ICP). Table 3 lists the detectable limits for various cations using the ICP. Analysis of the brine samples was complicated by their high NaCl content, but analysis of the samples at various dilutions gave fairly reproducible results.

After testing, the ceramic test specimens were subjected to ceramographic examination using standard techniques. The photomicrographs were used to determine if localized attack or alteration reactions had occurred during leaching.

TABLE 3. Detection Limits for Cations Using the Induction-Coupled Plasma Spectrometer

<u>Element</u>	<u>Detection Limit, ppm</u>	<u>Element</u>	<u>Detection Limit, ppm</u>
Al	0.013	Mg	0.005
As	0.032	Mn	0.001
B	0.004	Mo	0.003
Ba	0.001	Na	0.17
Ca	0.005	Nd	0.005
Cd	0.002	Ni	0.007
Ce	0.009	P	0.047
Co	0.002	Pb	0.009
Cr	0.006	Ru	0.007
Cu	0.001	Sb	0.016
Dy	0.001	Si	0.005
Eu	0.001	Sr	0.001
Fe	0.003	Te	0.02
Gd	0.004	Ti	0.001
K	0.041	U	0.04
La	0.020	Zn	0.004
Li	0.002	Zr	0.001

4.0 RESULTS AND DISCUSSION

A primary objective of this study was to screen a large number of candidate ceramic materials to determine which materials would be most resistant to attack in the repository environments. The principal method of material screening involved subjecting test specimens of each material to a variety of leach tests and determining their relative resistances to attack. An initial comparison of the materials can be obtained by determining their average leach rates under the various test conditions. The average leach rates can be determined from weight change measurements and from analyses of the leach solutions. Average leach rates can be misleading, however; localized attack of the test specimens, such as the leaching of impurities from grain boundaries, can result in far more serious attack than is evident from average leach rate determinations. In addition, alteration reactions at the specimen's surface can result in extensive attack that may not be apparent from either the solution analyses or the weight change measurements.

Determining if localized attack or alteration reactions are a problem requires that the ceramic specimens be subjected, after testing, to additional analyses such as ceramographic examination and scanning electron microscopy (SEM). Because of the large number of specimens tested it was necessary to limit the analyses to ceramographic examination of selected specimens--primarily those tested at the higher temperatures.

The photomicrographs obtained showed that several of the ceramic materials were susceptible to localized attack or alteration reactions. For this reason, the average leach rate data presented in Section 4.1 should not be used as a final basis for ranking the candidate materials. The final comparison and ranking of the materials must consider the effect of localized attack and alteration reactions, as well as a number of other factors including:

- cost
- availability
- mechanical and physical properties, and
- the availability of demonstrated techniques for fabricating dense, impervious shapes of the size required for an engineered-barrier system.

A detailed literature search on the properties of the ceramic materials under consideration was not carried out, and the comparison of the candidates was limited to the data given in various handbooks, such as Engineering Properties of Selected Ceramic Materials (Lynch, Ruderer and Duckworth 1966). Each of the ceramic materials is discussed individually in Section 4.3.

4.1 LEACH RATES

The average leach rates for the ceramic materials tested were determined from the solution analysis data and/or weight loss measurements. Calculation of the leach rates was based

on the geometric surface areas of the test specimens. With some of the materials there were differences in the leach rates determined from the two types of data. In general, the discrepancies were relatively greater for the more leach-resistant materials such as aluminum oxide than for the more soluble materials such as Pyroceram 9617. In most cases the leach rates determined from weight loss measurements were greater than those calculated from the solution analyses. Unless otherwise noted, the leach rates given in the following tables represent the maximum values determined from the two methods.

Two other factors affect the average leach rate data given in the tables. All of the test specimens had some porosity. Some were impervious; others, however, were somewhat permeable and the effective areas available for leaching were much greater than were the respective geometric surface areas of the test specimens used to calculate the average leach rates. For example, the effective surface area of a typical graphite test specimen, as determined by the BET method, was about 7000 cm², while the geometric surface area was about 3 cm².

The permeability of the specimens presented an additional problem when they were leached in the brine solution. At the conclusion of a test, it was very difficult to completely wash the brine solution from the interstices of the permeable specimens--especially the graphite. When the specimens were vacuum-dried before weighing, the dissolved solids in the residual brine precipitated in the voids, affecting the final weight measurement. In some cases, it was necessary to wash the specimens several times before a constant weight was attained, and even then there was no assurance that all of the dissolved solids in the brine had been completely removed from the specimens. Since the leach rates were usually very low, the presence of a small amount of residue from the brine would have an effect on the weight change measurements.

4.1.1 Static Leach Tests at 100°C

The average leach rates for ceramic samples exposed to demineralized water at 100°C in a static vented system are given in Table 4. The leach rates were determined from weight loss measurements. Analysis of the leach solution proved to be an unreliable method for determining the leach rates in most instances because of the leaching of material from the glassware used in the tests.

The tests were carried out in Pyrex glassware. The exposed surface of the glassware was many times greater than the geometric surface area of the ceramic test specimen, and leaching of the glassware could have had a marked effect on the leaching of the ceramic sample. In a typical leach test the S/V ratio for the ceramic sample was about 0.02 cm⁻¹, whereas the S/V ratio for the glass ware was about 1.0 cm⁻¹. The principal cation leached from the Pyrex glassware was silicon, together with lesser amounts of boron, sodium, aluminum, potassium, and calcium. Table 5 shows the range of results obtained when blank leach tests were run with the glassware alone. The cations leached from the glassware were also present in most of the ceramic materials tested either as primary constituents or impurities. This could affect the

TABLE 4. Average Leach Rates for Ceramic Materials in Demineralized Water at 100°C--
Vented Static System

Material	Exposure, days	Average Leach Rate, ^(a) g/cm ² -d ^(b)	
		Overall ^(c)	Differential ^(d)
Graphite	14	6.8×10^{-7}	6.8×10^{-7}
	24	5.3×10^{-7}	3.2×10^{-7}
	36	5.3×10^{-7}	6.3×10^{-7}
	43	5.9×10^{-7}	9.1×10^{-7}
Al ₂ O ₃ (99.8%)	14	2.0×10^{-6}	2.0×10^{-6}
	24	1.6×10^{-6}	0.9×10^{-6}
	36	1.5×10^{-6}	1.6×10^{-6}
	43	1.4×10^{-6}	1.1×10^{-6}
Al ₂ O ₃ (99%)	14	7.5×10^{-6}	7.5×10^{-6}
	24	7.0×10^{-6}	6.4×10^{-6}
	36	5.7×10^{-6}	3.0×10^{-6}
	43	5.3×10^{-6}	3.2×10^{-6}
Pyroceram 9617	14	1.7×10^{-5}	1.7×10^{-5}
	24	1.4×10^{-5}	1.1×10^{-5}
	36	1.4×10^{-5}	1.4×10^{-5}
	43	1.4×10^{-5}	1.3×10^{-5}
Vitreous Silica (SiO ₂)	14	2.6×10^{-5}	2.6×10^{-5}
	28	1.2×10^{-5}	1.0×10^{-6}
	35	1.0×10^{-5}	1.4×10^{-6}
	49	8.2×10^{-6}	1.3×10^{-6}
TiO ₂	14	5.2×10^{-5}	5.2×10^{-5}
	28	2.6×10^{-5}	1.1×10^{-6}
	35	2.1×10^{-5}	4.5×10^{-7}
	49	1.5×10^{-5}	7.8×10^{-7}
Basalt	14	5.8×10^{-5}	5.8×10^{-5}
	28	4.9×10^{-5}	4.0×10^{-5}
	35	3.5×10^{-5}	3.9×10^{-6}
	49	3.9×10^{-5}	3.7×10^{-5}
CaTiO ₃	14	5.4×10^{-5}	5.4×10^{-5}
	28	$2.8 \times 10^{-5(e)}$	2.2×10^{-6}
	35	2.3×10^{-5}	3.9×10^{-6}
	49	1.8×10^{-5}	3.2×10^{-6}
ZrO ₂	14	6.2×10^{-5}	6.2×10^{-5}
	28	5.5×10^{-5}	4.8×10^{-5}
	35	4.8×10^{-5}	3.1×10^{-5}
	49	4.2×10^{-5}	1.5×10^{-5}
ZrSiO ₄	14	7.3×10^{-5}	7.3×10^{-5}
	28	4.9×10^{-5}	2.4×10^{-5}
	35	4.5×10^{-5}	3.1×10^{-5}
	49	4.3×10^{-5}	3.3×10^{-5}
Marcor	14	7.5×10^{-5}	7.5×10^{-5}
	28	5.8×10^{-5}	4.1×10^{-5}
	35	5.4×10^{-5}	3.8×10^{-5}
	49	4.8×10^{-5}	3.2×10^{-5}

TABLE 4. (contd)

Material	Exposure, days	Average Leach Rate, ^(a) g/cm ² -d ^(b)	
		Overall ^(c)	Differential ^(d)
BaTiO ₃	14	13.0 x 10 ⁻⁵	13.0 x 10 ⁻⁵
	28	7.6 x 10 ⁻⁵	2.0 x 10 ⁻⁵
	35	6.3 x 10 ⁻⁵	1.3 x 10 ⁻⁵
	49	4.8 x 10 ⁻⁵	1.1 x 10 ⁻⁵
BaZrO ₃	14	13.0 x 10 ⁻⁵	13.0 x 10 ⁻⁵
	28	8.5 x 10 ⁻⁵	3.5 x 10 ⁻⁵
	35	7.0 x 10 ⁻⁵ (e)	1.4 x 10 ⁻⁵
	49	5.5 x 10 ⁻⁵	3.3 x 10 ⁻⁵
CaTiSiO ₅	14	2.8 x 10 ⁻⁴	2.8 x 10 ⁻⁴
	28	1.9 x 10 ⁻⁴	8.9 x 10 ⁻⁵
	35	1.6 x 10 ⁻⁴ (e)	6.1 x 10 ⁻⁵
	49	1.6 x 10 ⁻⁴	1.4 x 10 ⁻⁴
Mullite (2Al ₂ O ₃ ·SiO ₂)	14	3.1 x 10 ⁻⁴	3.1 x 10 ⁻⁴
	24	3.2 x 10 ⁻⁴	3.2 x 10 ⁻⁴
	36	3.0 x 10 ⁻⁴	2.8 x 10 ⁻⁴
	43	2.6 x 10 ⁻⁴	1.2 x 10 ⁻⁶
CaZrO ₃	14	3.2 x 10 ⁻⁵	3.2 x 10 ⁻⁵
	28	1.5 x 10 ⁻⁴ (e)	3.0 x 10 ⁻⁴
	35	1.7 x 10 ⁻⁴	1.9 x 10 ⁻⁴
	49	2.5 x 10 ⁻⁴	4.5 x 10 ⁻⁴

(a) Determined from weight loss measurements.

(b) Based on the geometric surface area of the test specimen.

(c) Average leach rate for the exposure time shown.

(d) Average leach rate for specific time interval.

(e) Solution turned cloudy.

leaching of some materials--especially the vitreous silica, mullite, ZrSiO₄ and CaTiSiO₅. Leaching of components from the glassware would also affect the pH of the leach solution, which could affect the leaching of the different materials.

The leach rates for the materials tested varied by about a factor of 500, with graphite exhibiting a significantly lower leach rate than any of the other materials. In several of the tests the leach solutions turned cloudy, indicating that some disintegration of the test specimen had occurred. When the specimens from these tests were vacuum-dried, they exhibited a powdery surface texture. All of the tests in which the solutions turned cloudy involved specimens that had been prepared at PNL by hot-pressing or cold-pressing and sintering. Time did not permit a detailed study to determine if the leach resistance of the materials could be increased by using different or improved procedures for fabricating the test specimens.

One surprising factor was the relatively high leach rate exhibited by the mullite. Overall, it exhibited the highest leach rate of any of the materials tested. In all of the other leach tests, however, mullite was average or better than average in leach resistance. No reason for the high leach rate of the mullite at 100°C in demineralized water was identified.

TABLE 5. Leaching of Pyrex Glassware in Demineralized Water at 100°C

1. Static Vented System
2. Leaching Time - 43 d (1032 h)
3. Exposed Glass Surface Area/Solution Volume ($S/V \cong 1.0 \text{ cm}^{-1}$)
4. Final Analysis of Leach Solutions (range of values for triplicate experiments):

Si = 20 to 50 ppm	Al = 1 to 2 ppm
B = 2 to 5 ppm	K = 0.2 to 1 ppm
Na = 1 to 3 ppm	Ca = 0.1 to 0.5 ppm.

In most of the tests the leach rates were initially high but decreased with time. This is to be expected with static leach tests involving materials whose components have a low solubility in water.

4.1.2 Dynamic Leach Tests at 90°C

The average leach rates for ceramic materials exposed to flowing demineralized water at 90°C are given in Table 6. The leach rates were determined from the weight loss measurements. The concentrations of dissolved species in the leach solutions leaving the reaction vessels were too low to permit reliable determination of the leach rates.

The leach rates for the various materials varied by a factor of about 250, with graphite exhibiting the lowest leach rate. Overall, the materials exhibited slightly lower leach rates in the dynamic tests at 90°C than in static tests at 100°C. The mullite, however, exhibited a leach rate about one hundred times lower than the rate at 100°C. Most of the materials exhibited a high initial leach rate that decreased with time, and some appeared to achieve a relatively constant rate after prolonged exposure. One material, the Marcor machinable glass-ceramic, exhibited a leach rate that appeared to be increasing with time.

4.1.3 Dynamic Leach Tests at 250°C

Samples of the ceramic materials were exposed to flowing demineralized water at 250°C in an autoclave. The sixteen materials were tested in two groups of eight. Each group of specimens was tested for four time periods. The testing sequence for the first group was 7 days, 14 days, 21 days, and 1 day; for the second group it was 23 days, 7 days, 14 days, and 1 day. After the final test each specimen was subjected to ceramographic examination. Limited autoclave availability and other scheduling problems made it necessary to change the testing sequence for the second group of materials. The differences in the testing sequences for the two groups of materials should have little effect on relative leach rates of the materials. Possible interactions between each group tested should have little effect on the results obtained.

The average leach rates were calculated from the weight loss measurements, and the results obtained are given in Table 7. The concentrations of dissolved species in the leach solution leaving the autoclave were too low to permit reliable determination of leach rates from solution analyses. In addition, eight materials--all of which contained common cations either

TABLE 6. Leaching of Ceramic Materials in Flowing Demineralized Water at 90°C

Material	Time, days	Average Leach Rate, ^(a) g/cm ² -d ^(b)	
		Overall ^(c)	Differential ^(d)
Graphite 2.2	7	5.8 x 10 ⁻⁷	5.8 x 10 ⁻⁷
	14	3.8 x 10 ⁻⁷	2.3 x 10 ⁻⁷
	21	4.1 x 10 ⁻⁷	2.7 x 10 ⁻⁷
	28	4.0 x 10 ⁻⁷	2.6 x 10 ⁻⁷
	35	4.0 x 10 ⁻⁷	2.7 x 10 ⁻⁷
Al ₂ O ₃ (99.8%) 4.0	7	16.0 x 10 ⁻⁷	10.0 x 10 ⁻⁷
	14	11.0 x 10 ⁻⁷	11.0 x 10 ⁻⁷
	21	8.9 x 10 ⁻⁷	5.5 x 10 ⁻⁷
	28	6.9 x 10 ⁻⁷	5.7 x 10 ⁻⁷
	35	7.4 x 10 ⁻⁷	10.0 x 10 ⁻⁷
Mullite (2Al ₂ O ₃ ·SiO ₂)	7	4.3 x 10 ⁻⁶	4.3 x 10 ⁻⁶
	14	2.9 x 10 ⁻⁶	1.4 x 10 ⁻⁶
	21	2.3 x 10 ⁻⁶	1.4 x 10 ⁻⁶
	28	2.1 x 10 ⁻⁶	1.4 x 10 ⁻⁶
	35	2.4 x 10 ⁻⁶	3.5 x 10 ⁻⁶
Al ₂ O ₃ (99%)	7	5.4 x 10 ⁻⁶	3.4 x 10 ⁻⁶
	14	4.0 x 10 ⁻⁶	2.7 x 10 ⁻⁶
	21	3.6 x 10 ⁻⁶	2.7 x 10 ⁻⁶
	28	3.4 x 10 ⁻⁶	2.7 x 10 ⁻⁶
	35	3.5 x 10 ⁻⁶	4.0 x 10 ⁻⁶
TiO ₂ 4.25	7	11.0 x 10 ⁻⁶	11.0 x 10 ⁻⁶
	14	6.7 x 10 ⁻⁶	2.8 x 10 ⁻⁶
	21	5.0 x 10 ⁻⁶	1.9 x 10 ⁻⁶
	28	4.3 x 10 ⁻⁶	2.1 x 10 ⁻⁶
	35	3.8 x 10 ⁻⁶	1.8 x 10 ⁻⁶
ZrO ₂ 5.5	7	3.6 x 10 ⁻⁵	3.6 x 10 ⁻⁵
	14	2.3 x 10 ⁻⁵	0.96 x 10 ⁻⁵
	21	1.7 x 10 ⁻⁵	0.48 x 10 ⁻⁵
	28	1.4 x 10 ⁻⁵	0.43 x 10 ⁻⁵
	35	1.1 x 10 ⁻⁵	0.25 x 10 ⁻⁵
Pyroceram 9617	7	0.47 x 10 ⁻⁵	0.47 x 10 ⁻⁵
	14	1.6 x 10 ⁻⁵	2.7 x 10 ⁻⁵
	21	1.4 x 10 ⁻⁵	0.95 x 10 ⁻⁵
	28	1.3 x 10 ⁻⁵	1.2 x 10 ⁻⁵
	35	1.2 x 10 ⁻⁵	0.62 x 10 ⁻⁵
CaTiO ₃	7	6.4 x 10 ⁻⁵	6.4 x 10 ⁻⁵
	14	5.3 x 10 ⁻⁵	4.1 x 10 ⁻⁵
	21	4.5 x 10 ⁻⁵	2.9 x 10 ⁻⁵
	28	4.0 x 10 ⁻⁵	2.5 x 10 ⁻⁵
	35	3.5 x 10 ⁻⁵	1.5 x 10 ⁻⁵
CaZrO ₃	7	6.5 x 10 ⁻⁵	6.4 x 10 ⁻⁵
	14	5.7 x 10 ⁻⁵	4.9 x 10 ⁻⁵
	21	4.8 x 10 ⁻⁵	2.9 x 10 ⁻⁵
	28	4.5 x 10 ⁻⁵	3.5 x 10 ⁻⁵
	35	4.7 x 10 ⁻⁵	5.6 x 10 ⁻⁵

TABLE 6. (contd)

Material	Time, days	Average Leach Rate, (a) g/cm ² -d(b)	
		Overall (c)	Differential (d)
Basalt	7	7.7 x 10 ⁻⁵	7.7 x 10 ⁻⁵
	14	6.7 x 10 ⁻⁵	5.8 x 10 ⁻⁵
	21	4.6 x 10 ⁻⁵	0.35 x 10 ⁻⁵
	28	3.6 x 10 ⁻⁵	0.69 x 10 ⁻⁵
	35	3.4 x 10 ⁻⁵	2.4 x 10 ⁻⁵
Vitreous Silica (SiO ₂)	7	7.1 x 10 ⁻⁵	7.1 x 10 ⁻⁵
	14	5.3 x 10 ⁻⁵	3.5 x 10 ⁻⁵
	21	5.5 x 10 ⁻⁵	5.9 x 10 ⁻⁵
	28	5.1 x 10 ⁻⁵	4.1 x 10 ⁻⁵
	35	4.9 x 10 ⁻⁵	3.8 x 10 ⁻⁵
Marcor	7	5.4 x 10 ⁻⁵	5.4 x 10 ⁻⁵
	14	5.1 x 10 ⁻⁵	4.7 x 10 ⁻⁵
	21	4.9 x 10 ⁻⁵	4.4 x 10 ⁻⁵
	28	5.5 x 10 ⁻⁵	7.6 x 10 ⁻⁵
	35	6.3 x 10 ⁻⁵	9.2 x 10 ⁻⁵
ZrSiO ₄	7	8.9 x 10 ⁻⁵	8.9 x 10 ⁻⁵
	14	7.8 x 10 ⁻⁵	6.8 x 10 ⁻⁵
	21	7.3 x 10 ⁻⁵	6.3 x 10 ⁻⁵
	28	7.0 x 10 ⁻⁵	6.0 x 10 ⁻⁵
	35	6.8 x 10 ⁻⁵	5.8 x 10 ⁻⁵
BaTiO ₃	7	11.6 x 10 ⁻⁵	11.6 x 10 ⁻⁵
	14	11.0 x 10 ⁻⁵	10.3 x 10 ⁻⁵
	21	9.2 x 10 ⁻⁵	6.4 x 10 ⁻⁵
	28	8.9 x 10 ⁻⁵	7.8 x 10 ⁻⁵
	35	8.6 x 10 ⁻⁵	7.3 x 10 ⁻⁵
CaTiSiO ₅	7	11.1 x 10 ⁻⁵	11.1 x 10 ⁻⁵
	14	8.7 x 10 ⁻⁵	6.2 x 10 ⁻⁵
	21	8.6 x 10 ⁻⁵	7.7 x 10 ⁻⁵
	28	8.1 x 10 ⁻⁵	6.7 x 10 ⁻⁵
	35	7.8 x 10 ⁻⁵	6.7 x 10 ⁻⁵
BaZrO ₃	7	13.0 x 10 ⁻⁵	13.0 x 10 ⁻⁵
	14	11.0 x 10 ⁻⁵	9.2 x 10 ⁻⁵
	21	10.0 x 10 ⁻⁵	9.4 x 10 ⁻⁵
	28	9.9 x 10 ⁻⁵	8.2 x 10 ⁻⁵
	35	9.6 x 10 ⁻⁵	8.0 x 10 ⁻⁵

(a) Determined from weight loss measurements.

(b) Based on the geometric surface area of the test specimen.

(c) Average leach rate for the exposure time shown.

(d) Differential leach rate for the specific time interval.

as primary constituents or impurities--were tested in the autoclave at one time, which precluded the use of solution analysis to determine leach rates.

Leach rates for the materials tested varied by about a factor of 1500, with graphite exhibiting the lowest leach rate. Titanium dioxide also exhibited a very low rate. In fact, the leach rate for TiO₂ at 250°C in flowing demineralized water was about the same as was its rate at 90°C. The other materials tested at 250°C had much higher leach rates than did the

TABLE 7. Average Leach Rates for Ceramic Materials Exposed to Flowing Demineralized Water at 250°C^(a)

Material	Exposure, days	Average Leach Rate, ^(b) g/cm ² -d ^(c)		Remarks
		Overall ^(d)	Differential ^(e)	
Graphite	7	2.0 x 10 ⁻⁶	2.0 x 10 ⁻⁶	
	21	5.7 x 10 ⁻⁶	7.6 x 10 ⁻⁶	
	42	6.9 x 10 ⁻⁶	8.1 x 10 ⁻⁶	
	43	7.0 x 10 ⁻⁶	9.0 x 10 ⁻⁶	
TiO ₂	23	9.6 x 10 ⁻⁶	9.6 x 10 ⁻⁶	Radial Cracks
	30	7.5 x 10 ⁻⁶	1.0 x 10 ⁻⁶	
	44	6.3 x 10 ⁻⁶	3.9 x 10 ⁻⁶	
	45	6.7 x 10 ⁻⁶	22.2 x 10 ⁻⁶	
ZrO ₂	7	3.0 x 10 ⁻⁴	3.0 x 10 ⁻⁴	
	21	1.6 x 10 ⁻⁴	9.2 x 10 ⁻⁵	
	42	1.0 x 10 ⁻⁴	3.9 x 10 ⁻⁵	
	43	1.0 x 10 ⁻⁴	1.0 x 10 ⁻⁵	
Al ₂ O ₃ (99.8%)	7	1.4 x 10 ⁻⁴	1.4 x 10 ⁻⁴	Localized Attack
	21	1.2 x 10 ⁻⁴	1.1 x 10 ⁻⁴	
	42	1.3 x 10 ⁻⁴	1.5 x 10 ⁻⁴	
	43	1.3 x 10 ⁻⁴	1.6 x 10 ⁻⁴	
Al ₂ O ₃ (99%)	7	2.5 x 10 ⁻⁴	2.5 x 10 ⁻⁴	Localized Attack
	21	1.9 x 10 ⁻⁴	1.5 x 10 ⁻⁴	
	42	1.7 x 10 ⁻⁴	1.5 x 10 ⁻⁴	
	43	1.8 x 10 ⁻⁴	2.6 x 10 ⁻⁴	
Vitreous Silica (SiO ₂)	7	6.9 x 10 ⁻⁴	6.9 x 10 ⁻⁴	
	21	5.3 x 10 ⁻⁴	4.5 x 10 ⁻⁴	
	42	4.9 x 10 ⁻⁴	4.4 x 10 ⁻⁴	
	43	5.0 x 10 ⁻⁴	5.1 x 10 ⁻⁴	
CaZrO ₃	23	3.5 x 10 ⁻⁴	3.5 x 10 ⁻⁴	Alteration Reaction
	30	4.8 x 10 ⁻⁴	9.0 x 10 ⁻⁴	
	44	4.4 x 10 ⁻⁴	3.5 x 10 ⁻⁴	
	45	4.4 x 10 ⁻⁴	4.8 x 10 ⁻⁴	
CaTiSiO ₅	23	4.5 x 10 ⁻⁴	4.5 x 10 ⁻⁴	Alteration Reaction
	30	5.3 x 10 ⁻⁴	8.0 x 10 ⁻⁴	
	44	6.1 x 10 ⁻⁴	7.7 x 10 ⁻⁴	
	45	7.0 x 10 ⁻⁴	46.0 x 10 ⁻⁴	
BaTiO ₃	23	3.6 x 10 ⁻⁴	3.6 x 10 ⁻⁴	
	30	5.2 x 10 ⁻⁴	10.0 x 10 ⁻⁴	
	44	5.1 x 10 ⁻⁴	4.9 x 10 ⁻⁴	
	45	Sample Shattered		
CaTiO ₃	23	5.8 x 10 ⁻⁴	5.8 x 10 ⁻⁴	Alteration Reaction
	30	6.5 x 10 ⁻⁴	8.9 x 10 ⁻⁴	
	44	6.7 x 10 ⁻⁴	6.9 x 10 ⁻⁴	
	45	7.2 x 10 ⁻⁴	32.0 x 10 ⁻⁴	
Mullite (2Al ₂ O ₃ ·SiO ₂)	7	0.14 x 10 ⁻³	0.14 x 10 ⁻³	Alteration Reaction
	21	1.6 x 10 ⁻³	1.8 x 10 ⁻³	
	42	1.3 x 10 ⁻³	1.0 x 10 ⁻³	
	43	1.3 x 10 ⁻³	1.0 x 10 ⁻³	

TABLE 7. (contd)

Material	Exposure, days	Average Leach Rate, ^(b) g/cm ² -d ^(c)		Remarks
		Overall ^(d)	Differential ^(e)	
ZrSiO ₄ 1.5	23	1.7 x 10 ⁻³	1.7 x 10 ⁻³	
	30	1.6 x 10 ⁻³	0.68 x 10 ⁻⁴	
	44	1.1 x 10 ⁻³	0.26 x 10 ⁻⁴	
	45	1.1 x 10 ⁻³	0.29 x 10 ⁻⁴	
BaZrO ₃ 1.6	23	2.0 x 10 ⁻³	2.0 x 10 ⁻³	Alteration Reaction
	30	1.6 x 10 ⁻³	0.40 x 10 ⁻³	
	44	1.4 x 10 ⁻³	0.84 x 10 ⁻³	
	45	1.4 x 10 ⁻³	0.29 x 10 ⁻³	
Basalt 2.6	23	4.1 x 10 ⁻³	4.1 x 10 ⁻³	Alteration Reaction
	30	3.6 x 10 ⁻³	1.9 x 10 ⁻³	
	44	3.0 x 10 ⁻³	1.7 x 10 ⁻³	
	45	3.0 x 10 ⁻³	2.5 x 10 ⁻³	
Marcor 3	7	6.6 x 10 ⁻³	6.6 x 10 ⁻³	Alteration Reaction
	21	5.4 x 10 ⁻³	4.8 x 10 ⁻³	
	42	3.5 x 10 ⁻³	1.6 x 10 ⁻³	
	43	Sample Shattered		
Pyroceram 9617 7	7	10.0 x 10 ⁻³	10.0 x 10 ⁻³	Alteration Reaction
	21	9.6 x 10 ⁻³	9.2 x 10 ⁻³	
	42	8.2 x 10 ⁻³	6.8 x 10 ⁻³	
	43	8.3 x 10 ⁻³	9.4 x 10 ⁻³	

(a) Tests carried out in a 6.5-L autoclave at a water flow rate of 1.9 L/h. Geometric surface area of the test specimens varied from 5 to 15 cm².

(b) Calculated from weight loss measurements.

(c) Based on initial geometric surface area of the specimen.

(d) Average leach rate for exposure time shown.

(e) Average leach rate for specific time interval.

graphite and TiO₂. In addition, most of the materials suffered localized attack or alteration reactions, which affected the samples to considerable depths. Estimates of the extent of the localized attack or alteration reactions, as determined from photomicrographs of the specimens, are given in Table 8. The TiO₂ specimen developed radial cracks to a considerable depth, but there is evidence that indicates the cracks may have resulted from fabrication problems, rather than attack by the leach solution. Additional discussion of how localized attack or alteration reactions affect the various materials is provided in Section 4.3.

4.1.4 Static Leach Tests at 150°C

The static leach tests at 150°C were carried out in sealed gold ampules that were heated in autoclave. Samples of each material were tested with each of the three leach solutions for four different exposure times. A single ceramic sample was used for the four exposures, but the leach solution was replaced after each exposure. The candidate materials were tested in two groups of eight. The testing sequence for one group was 7 days, 14 days, 21 days, and 1 day, and for the second group was 7 days, 14 days, 1 day, and 21 days. After the final tests, the ceramic samples were subjected to ceramographic examination. The change in the

TABLE 8. Extent of Localized Attack or Alteration Reactions in Ceramic Materials Exposed to Flowing Demineralized Water at 250°C(a)

Material	Total Exposure, days	Depth of Material Affected, μm	
		Localized Attack	Alteration Reactions
Graphite	43	0	0
TiO ₂	45	(b)	0
ZrO ₂	43	0	0
Al ₂ O ₃ (99.8%)	43	25	0
Al ₂ O ₃ (99%)	43	50	0
Vitreous Silica (SiO ₂)	43	0	0
CaZrO ₃	45		360
CaTiSiO ₅	45		200
BaTiO ₃	45		50
CaTiO ₃	45		100
Mullite (2Al ₂ O ₃ ·SiO ₂)	43		>800
ZrSiO ₄	45		100
BaZrO ₃	45		150
Basalt	45		550
Marcor	43		>850
Pyroceram 9617	43		>1000

(a) Estimated from photomicrographs.

(b) Specimens exhibited radial cracks to a considerable depth.

testing sequence for the second group of materials was again dictated by autoclave availability and other scheduling problems. The differences in the testing sequences might have some effect on the absolute values of the individual leach rates but should have only minimal effect on the relative leach rates.

The average leach rates for the ceramic materials in the three leach solutions at 150°C are given in Tables 9 through 11. Erratic results were obtained in some tests. Replicate experiments were not performed, and the values given in the tables should only be considered as approximations. The data are adequate, however, for determining the relative leach resistances of the materials tested.

In the tests with demineralized water and Hanford ground water the leach rates, except for graphite, were determined from the weight loss measurements and from the analysis of the leach solutions (graphite leach rates could only be determined by weight loss measurements). In most of the tests, the leach rates calculated from the weight loss measurements were higher than those determined from the solution analyses. The leach rates given in the tables are the

TABLE 9. Leaching of Ceramic Materials in Demineralized Water at 150°C--Static Tests in Sealed Gold Ampules(a)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Graphite	7	0.078	1.1×10^{-5}	
	14	0.055	3.9×10^{-6}	
	21	0.019	0.9×10^{-6}	
	1	0.002	2.0×10^{-6}	
Al ₂ O ₃ (99.8%)	7	0.055	7.9×10^{-6}	
	14	0.046	3.2×10^{-6}	
	21	0.055	2.6×10^{-6}	
	1	0.029	2.9×10^{-5}	
Al ₂ O ₃ (99%)	7	0.10	1.4×10^{-5}	Localized Attack
	14	0.13	9.3×10^{-6}	
	21	0.13	6.2×10^{-6}	
	1	0.045	4.5×10^{-5}	
Mullite (2Al ₂ O ₃ ·SiO ₂)	7	0.15	2.1×10^{-5}	
	14	0.15	1.1×10^{-5}	
	21	0.15	7.2×10^{-6}	
	1	0.073	7.3×10^{-5}	
Vitreous Silica (SiO ₂)	7	0.18	2.6×10^{-5}	
	14	0.23	1.6×10^{-5}	
	21	0.28	1.3×10^{-5}	
	1	0.12	1.2×10^{-4}	
ZrO ₂	7	0.34	4.9×10^{-5}	
	14	0.30	2.1×10^{-5}	
	21	0.38	1.8×10^{-5}	
	1	0.15	1.5×10^{-4}	
Pyroceram 9617	7	0.27	3.9×10^{-5}	
	14	0.42	3.0×10^{-5}	
	21	0.56	2.7×10^{-5}	
	1	0.19	1.9×10^{-4}	
TiO ₂	7	0.64	9.1×10^{-5}	
	14	0.52	3.7×10^{-5}	
	1	0.23	2.3×10^{-4}	
	21	0.72	3.4×10^{-5}	
CaTiSiO ₅	7	1.18	2.6×10^{-4}	
	14	1.32	9.4×10^{-5}	
	1	1.1	1.1×10^{-3}	
	21	1.28	6.1×10^{-5}	
ZrSiO ₄	7	0.88	1.3×10^{-4}	
	14	1.24	8.9×10^{-5}	
	1	0.38	3.8×10^{-4}	
	21	2.6	1.2×10^{-4}	
CaTiO ₃	7	0.84	1.2×10^{-4}	
	14	1.46	1.0×10^{-4}	
	1	0.50	5.0×10^{-4}	
	21	3.1	1.5×10^{-4}	

TABLE 9. (contd)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Basalt	7	2.7	3.9 x 10 ⁻⁴	
	14	2.2	1.6 x 10 ⁻⁴	
	1	1.5	1.5 x 10 ⁻³	
	21	2.6	1.2 x 10 ⁻⁴	
Marcor	7	1.8	2.6 x 10 ⁻⁴	
	14	2.9	2.1 x 10 ⁻⁴	
	21	2.2	1.0 x 10 ⁻⁴	
	1	1.3	1.3 x 10 ⁻³	
CaZrO ₃	7	0.19	2.7 x 10 ⁻⁵	Alteration Reaction
	14	4.6	3.3 x 10 ⁻⁴	
	1	2.9	2.9 x 10 ⁻³	
	21	5.8	2.8 x 10 ⁻⁴	
BaZrO ₃	7	9.8	1.4 x 10 ⁻³	
	14	7.3	5.2 x 10 ⁻⁴	
	1	4.1	4.1 x 10 ⁻³	
	21	12	5.7 x 10 ⁻³	
BaTiO ₃	7	14	2.0 x 10 ⁻³	
	14	68	4.9 x 10 ⁻³	
	1	8	8.0 x 10 ⁻³	
	21	Sample Shattered		

(a) $S/V \cong 0.4 \text{ cm}^{-1}$ based on geometric surface area of specimen.

(b) Based on geometric surface area of specimen.

(c) Average leach rate for exposure time shown.

larger of the values determined by the two methods. In general, there was better agreement in the two sets of values for materials exhibiting moderate and high leach rates than for materials having very low leach rates (i.e., Al_2O_3 , TiO_2 , ZrO_2).

In the tests with the brine solution, the leach rates could only be determined from the weight loss measurements. Solution analyses could not be used because the brine initially contained large concentrations of cations that were present in the ceramic materials, either as primary constituents or impurities, and which leached from the materials during testing.

In almost all of the static tests at 150°C the leach rate decreased with increasing exposure time. This is to be expected in static tests where the leach solution can become saturated with the dissolved species, especially in the tests under consideration where the solution volume is small and the S/V ratio high. Analysis of the leach solutions indicated that saturation effects did serve to control the leach rates of most of the ceramic materials tested at 150°C .

Most of the materials tested exhibited a higher leach rate in the demineralized water than in the other two solutions. The data indicate that this is due in part because the saturation concentrations of most of the dissolved species appear to be higher in the demineralized water than in groundwater and brine solutions.

TABLE 10. Leaching of Ceramic Materials in Hanford Ground Water at 150°C--Static Tests in Sealed Gold Ampules^(a)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Al ₂ O ₃ (99.8%)	7	0.048	6.9 x 10 ⁻⁶	
	14	0.034	2.4 x 10 ⁻⁶	
	21	0.058	2.8 x 10 ⁻⁶	
	1	0.016	1.6 x 10 ⁻⁵	
Graphite	7	0.086	1.2 x 10 ⁻⁵	
	14	0.074	5.3 x 10 ⁻⁶	
	21	0.075	3.6 x 10 ⁻⁶	
	1	0.063	6.3 x 10 ⁻⁵	
Al ₂ O ₃ (99%)	7	0.15	2.1 x 10 ⁻⁵	
	14	0.094	6.7 x 10 ⁻⁶	
	21	0.13	6.2 x 10 ⁻⁶	
	1	0.062	6.2 x 10 ⁻⁵	
Mullite (2Al ₂ O ₃ ·SiO ₂)	7	0.12	1.7 x 10 ⁻⁵	
	14	0.17	1.2 x 10 ⁻⁵	
	21	0.18	8.6 x 10 ⁻⁶	
	1	0.11	1.1 x 10 ⁻⁴	
ZrO ₂	7	0.20	2.9 x 10 ⁻⁵	
	14	0.20	1.4 x 10 ⁻⁵	
	21	0.25	1.2 x 10 ⁻⁵	
	1	0.093	9.3 x 10 ⁻⁵	
Pyroceram 9617	7	0.15	2.1 x 10 ⁻⁵	Alteration Reaction
	14	0.19	1.4 x 10 ⁻⁵	
	21	0.25	1.2 x 10 ⁻⁵	
	1	0.16	1.6 x 10 ⁻⁴	Specimen Cracked
CaZrO ₃	7	0.45	6.4 x 10 ⁻⁵	
	14	0.62	4.4 x 10 ⁻⁵	
	1	0.43	4.3 x 10 ⁻⁴	
	21	0.45	2.1 x 10 ⁻⁵	
ZrSiO ₄	7	0.86	1.2 x 10 ⁻⁴	
	14	0.65	4.0 x 10 ⁻⁵	
	1	0.16	1.6 x 10 ⁻⁴	
	21	0.88	4.2 x 10 ⁻⁵	
CaTiO ₃	7	1.15	1.6 x 10 ⁻⁴	
	14	0.96	6.9 x 10 ⁻⁵	
	1	0.5	5.0 x 10 ⁻⁴	
	21	1.7	8.1 x 10 ⁻⁵	
TiO ₂	7	1.1	1.7 x 10 ⁻⁴	
	14	0.56	4.0 x 10 ⁻⁵	
	1	0.8	8.0 x 10 ⁻⁴	
	21	1.3	6.2 x 10 ⁻⁵	
CaTiSiO ₅	7	1.0	1.4 x 10 ⁻⁴	
	14	1.3	9.3 x 10 ⁻⁵	
	1	0.8	8.0 x 10 ⁻⁴	
	21	1.8	8.6 x 10 ⁻⁵	

TABLE 10. (contd)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Vitreous Silica (SiO ₂)	7	1.7	2.4 x 10 ⁻⁴	
	14	1.5	1.1 x 10 ⁻⁴	
	21	1.9	9.0 x 10 ⁻⁵	
	1	1.3	1.3 x 10 ⁻³	
BaTiO ₃	7	2.2	3.1 x 10 ⁻⁴	
	14	3.6	2.6 x 10 ⁻⁴	
	1	0.3	3.0 x 10 ⁻⁴	
	21	4.3	2.0 x 10 ⁻⁴	
Basalt	7	2.9	4.1 x 10 ⁻⁴	
	14	3.8	2.7 x 10 ⁻⁴	
	1	1.5	1.5 x 10 ⁻³	
	21	3.6	1.7 x 10 ⁻⁴	
Marcor	7	2.8	4.0 x 10 ⁻⁴	
	14	4.4	3.1 x 10 ⁻⁴	
	21	3.9	1.9 x 10 ⁻⁴	
	1	1.7	1.7 x 10 ⁻³	
BaZrO ₃	7	16	2.3 x 10 ⁻³	
	14	4.4	3.1 x 10 ⁻⁴	
	1	1.5	1.5 x 10 ⁻³	
	21	12	5.7 x 10 ⁻⁴	

(a) $S/V \cong 0.4 \text{ cm}^{-1}$ based on geometric surface area of the specimen.

(b) Based on geometric surface area of specimen.

(c) Average leach rate for exposure time shown.

Localized attack or alteration reactions did not appear to be a major problem with most of the materials tested at 150°C. A few specimens did exhibit a powdery surface after testing, and some developed cracks. Additional information on the subject is provided in Section 4.3, where the test materials are discussed individually.

4.1.5 Static Leach Tests at 250°C

The static leach tests at 250°C were also carried out in gold ampules inside an autoclave. Test procedures were identical to those used in the 150°C static tests. The materials were tested in two groups of eight: the testing sequence for one group was 7 days, 14 days, 21 days, and 1 day, and for the second group was 23 days, 7 days, 14 days, and 1 day. After the final tests, the ceramic specimens were subjected to ceramographic examination. The change in the testing sequence for the second group of materials was again dictated by autoclave availability and other scheduling problems.

The average leach rates measured at 250°C in the three leach solutions are given in Tables 12 through 14. As was the case with the 150°C tests, erratic results were obtained in several of the 250°C tests. Leach rates in the demineralized water and ground water were determined from weight loss measurements and from analysis of the leach solutions--except for

TABLE 11. Leaching of Ceramic Materials in Brine at 150°C--Static Tests in Sealed Gold Ampules^(a)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Graphite	7	wt. gain	---	
	14	wt. gain	---	
	21	wt. gain	---	
	1	wt. gain	---	
TiO ₂	7	wt. gain	---	
	14	wt. gain	---	
	1	wt. gain	---	
	21	wt. gain	---	
Al ₂ O ₃ (99.8%)	7	0.018	2.6 x 10 ⁻⁶	
	14	0.018	1.3 x 10 ⁻⁶	
	21	0.028	1.3 x 10 ⁻⁶	
	1	0.009	9.0 x 10 ⁻⁶	
Al ₂ O ₃ (99%)	7	0.077	1.1 x 10 ⁻⁵	
	14	0.046	6.6 x 10 ⁻⁶	
	21	0.050	2.4 x 10 ⁻⁶	
	1	0.038	3.8 x 10 ⁻³	
Mullite (2Al ₂ O ₃ ·SiO ₂)	7	0.082	1.2 x 10 ⁻⁵	
	14	0.060	4.3 x 10 ⁻⁶	
	21	0.095	4.5 x 10 ⁻⁶	
	1	0.057	5.7 x 10 ⁻³	
Vitreous Silica (SiO ₂)	7	0.12	1.7 x 10 ⁻⁵	
	14	0.047	4.5 x 10 ⁻⁶	
	21	0.095	2.6 x 10 ⁻⁶	
	1	0.086	8.6 x 10 ⁻⁵	
Pyroceram 9617	7	0.071	1.0 x 10 ⁻⁵	
	14	0.10	7.1 x 10 ⁻⁶	
	21	0.19	9.0 x 10 ⁻⁶	
	1	0.061	6.1 x 10 ⁻⁵	
ZrO ₂	7	0.010	1.4 x 10 ⁻⁶	
	14	0.070	5.0 x 10 ⁻⁶	
	21	0.28	1.3 x 10 ⁻⁵	
	1	0.041	4.1 x 10 ⁻⁵	
CaTiO ₃	7	0.92	1.3 x 10 ⁻⁴	
	14	0.80	5.7 x 10 ⁻⁵	
	1	0.5	5.0 x 10 ⁻⁴	
	21	5.9	2.8 x 10 ⁻⁴	
ZrSiO ₄	7	1.5	2.1 x 10 ⁻⁴	Alteration Reaction
	14	3.6	2.6 x 10 ⁻⁴	
	1	2.3	2.3 x 10 ⁻³	
	21	4.5	2.1 x 10 ⁻⁴	
Marcor	7	2.4	3.4 x 10 ⁻⁴	
	14	3.8	2.7 x 10 ⁻⁴	
	21	4.4	2.1 x 10 ⁻⁴	
	1	1.5	1.5 x 10 ⁻³	

TABLE 11. (contd)

<u>Material</u>	<u>Exposure, days</u>	<u>Specimen Weight Loss, mg/cm²(b)</u>	<u>Average Leach Rate, (c) g/cm²-d(b)</u>	<u>Remarks</u>
BaTiO ₃	7	16	2.3 x 10 ⁻³	
	14	8.6	6.1 x 10 ⁻⁴	
	1	1.3	1.3 x 10 ⁻³	
	21	17	8.1 x 10 ⁻⁴	
BaZrO ₃	7	0.9	1.3 x 10 ⁻⁴	Alteration Reaction
	14	6.2	4.4 x 10 ⁻⁴	
	1	9.9	9.9 x 10 ⁻³	
	21	Sample Shattered		

(a) $S/V \cong 0.4 \text{ cm}^{-1}$ based on geometric surface area of the specimen.

(b) Based on geometric surface area of specimen.

(c) Average leach rate for exposure time shown.

graphite, whose leach rates were determined only from the weight loss measurements. Leach rates in the brine solution were determined only from the weight loss measurements. Where there was a lack of agreement between the leach rates determined by the two methods, the higher values are reported in the tables.

Unlike the results obtained at 150°C, in many of the 250°C tests the leach rates determined from the solution analyses were higher than those calculated from the weight loss measurements. This was because several of the ceramic materials tested at 250°C suffered alteration reactions that affected the weight loss measurements. In several of the tests the specimens cracked or shattered into two or more pieces during testing, which invalidated the weight loss measurements.

In most of the static tests at 250°C the leach rates decreased with increasing exposure times because of saturation effects. In general, leach rates were higher in demineralized water than in the groundwater or brine solution. Except for two materials, graphite and TiO₂, the leach rates in flowing demineralized water at 250°C were much higher than were the rates measured in the static demineralized water tests at 250°C. This also illustrates the effect saturation limits can have on the leach rates of slightly soluble materials in static systems. It was not determined why the leach rate of TiO₂ was lower in the flowing demineralized water at 250°C than in the static test at 250°C. The higher leach rate of graphite in the static test at 250°C as compared to the dynamic test can probably be explained by the reaction of the graphite with dissolved oxygen, since the gold ampule was only partially filled with demineralized water and the remaining space with air (see Section 4.3.1).

As expected, the leach rates determined in the static tests at 250°C were generally higher than the corresponding rates measured at 150°C. Because of the erratic nature of some of the data, however, some anomalies were apparent. The increase in leach rates with temperature was not as great as one might anticipate. On an overall basis, the leach rates at 250°C were about three times higher than the rates at 150°C, although much greater increases were observed in some cases.

TABLE 12. Leaching of Ceramic Materials in Demineralized Water at 250°C--Static Tests in Sealed Gold Ampules^(a)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Al ₂ O ₃ (99.8%)	7	0.092	1.3 x 10 ⁻⁵	Localized Attack
	14	0.12	8.6 x 10 ⁻⁶	
	21	0.11	5.2 x 10 ⁻⁶	
	1	0.04	4.0 x 10 ⁻⁵	
Graphite	7	0.21	3.0 x 10 ⁻⁵	
	14	0.16	1.1 x 10 ⁻⁵	
	21	0.16	7.6 x 10 ⁻⁶	
	1	0.054	5.4 x 10 ⁻⁵	
Al ₂ O ₃ (99%)	7	0.30	4.3 x 10 ⁻⁵	Localized Attack
	14	0.34	2.4 x 10 ⁻⁵	
	21	0.44	2.1 x 10 ⁻⁵	
	1	0.082	8.2 x 10 ⁻⁵	
TiO ₂	23	0.38	1.7 x 10 ⁻⁵	
	7	0.36	5.1 x 10 ⁻⁵	
	14	0.64	4.6 x 10 ⁻⁵	
	1	0.27	2.7 x 10 ⁻⁴	
CaTiO ₃	23	0.24	1.0 x 10 ⁻⁵	
	7	0.066	9.4 x 10 ⁻⁶	
	14	0.14	1.0 x 10 ⁻⁵	
	1	1.3	1.3 x 10 ⁻³	
ZrO ₂	7	0.43	6.1 x 10 ⁻⁵	
	14	0.49	3.5 x 10 ⁻⁵	
	21	0.55	2.6 x 10 ⁻⁵	
	1	0.16	1.6 x 10 ⁻⁴	
Vitreous Silica (SiO ₂)	7	1.6	2.3 x 10 ⁻⁴	
	14	1.7	1.2 x 10 ⁻⁴	
	21	1.9	9.0 x 10 ⁻⁵	
	1	0.20	2.0 x 10 ⁻⁴	
Basalt	23	4.0	1.7 x 10 ⁻⁴	Alteration Reaction
	7	3.9	5.6 x 10 ⁻⁴	
	14	3.7	2.6 x 10 ⁻⁴	
	1	0.55	5.5 x 10 ⁻⁴	
CaTiSiO ₅	23	0.75	2.4 x 10 ⁻⁵	Alteration Reaction
	7	1.1	1.6 x 10 ⁻⁴	
	14	6.4	4.6 x 10 ⁻⁴	
	1	1.3	1.3 x 10 ⁻³	
Mullite (2Al ₂ O ₃ ·SiO ₂)	7	2.3	3.3 x 10 ⁻⁴	Alteration Reaction
	14	3.8	2.7 x 10 ⁻⁴	
	21	3.6	1.7 x 10 ⁻⁴	
	1	1.4	1.4 x 10 ⁻³	
CaZrO ₃	23	3.3	1.4 x 10 ⁻⁴	Alteration Reaction
	7	2.4	3.4 x 10 ⁻⁴	
	14	5.5	3.9 x 10 ⁻⁴	
	1	3.8	3.8 x 10 ⁻³	

TABLE 12. (contd)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
ZrSiO ₄	23	2.9	1.3 x 10 ⁻⁴	
	7	4.8	6.9 x 10 ⁻⁴	
	14	7.3	5.2 x 10 ⁻⁴	
	1	Sample Shattered		
Pyroceram 9617	7	4.7	6.7 x 10 ⁻⁴	Alteration Reaction Sample Cracked
	14	5.6	4.0 x 10 ⁻⁴	
	21	13	6.2 x 10 ⁻⁴	
	1	4.1	4.1 x 10 ⁻³	
BaZrO ₃	23	5.8	2.5 x 10 ⁻⁴	Alteration Reaction Sample Cracked
	7	7.3	1.0 x 10 ⁻³	
	14	16	1.1 x 10 ⁻³	
	1	28	2.8 x 10 ⁻²	
BaTiO ₃	23	1.0	4.0 x 10 ⁻⁵	
	7	4.8	6.9 x 10 ⁻⁴	
	14	23	1.6 x 10 ⁻³	
	1	Sample Shattered		
Marcor	7	17	2.4 x 10 ⁻³	Alteration Reaction Specimen Cracked
	14	23	1.6 x 10 ⁻³	
	21	28	1.3 x 10 ⁻³	
	1	12	1.2 x 10 ⁻²	

(a) $S/V \cong 0.4 \text{ cm}^{-1}$ based on geometric surface area of the specimen.

(b) Based on geometric surface area of specimen.

(c) Average leach rate for exposure time shown.

4.1.6 Relative Leach Rates

It is difficult to make precise rankings of the candidate materials based on the leach rate data obtained in the various tests. In most of the tests the leach rates of the ceramic materials varied with time. Additional long-term leaching tests are needed in order to make quantitative comparisons of the candidates. In some of the tests erratic results were obtained, and replicate experiments are needed in order to ensure the reliability of the leach rate data. Unfortunately, it was not possible to carry out the additional testing needed to allow quantitative ranking of the candidate materials for each leach test. It was possible, however, to make some qualitative comparisons of the materials tested based on the leach rate data obtained in the various tests. This has been done, and in Table 15 the candidate materials are listed in order of their estimated leach resistance for each of the leach tests. It must be remembered that the rankings given in Table 15 are not absolute. The leach resistance of any given materials should definitely be greater than that of a material several positions lower on the scale. In the case of adjacent materials, however, it is impossible in most cases to say that one is more leach-resistant than the other.

A cursory examination of Table 15 shows that five materials--namely graphite, TiO₂, ZrO₂, and the two grades of Al₂O₃--exhibit the highest leach resistance in most of the tests. Some

TABLE 13. Leaching of Ceramic Materials in Hanford Ground Water at 250°C--Static Test in Sealed Gold Ampules^(a)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Al ₂ O ₃ (99.8%)	7	0.14	2.0 x 10 ⁻⁵	
	14	0.09	6.4 x 10 ⁻⁶	
	21	0.15	7.0 x 10 ⁻⁶	
	1	0.03	3.0 x 10 ⁻⁵	
Graphite	7	0.21	3.0 x 10 ⁻⁵	
	14	Leach Solution Lost		
	21	0.15	7.1 x 10 ⁻⁶	
	1	0.046	4.6 x 10 ⁻⁵	
ZrO ₂	7	0.094	1.3 x 10 ⁻⁵	
	14	0.17	1.2 x 10 ⁻⁵	
	21	0.36	1.7 x 10 ⁻⁵	
	1	0.029	2.9 x 10 ⁻⁵	
Al ₂ O ₃ (99%)	7	0.34	4.9 x 10 ⁻⁵	Localized Attack
	14	0.38	2.7 x 10 ⁻⁵	
	21	0.56	2.7 x 10 ⁻⁵	
	1	0.097	9.7 x 10 ⁻⁵	
TiO ₂	23	0.75	3.3 x 10 ⁻⁵	
	7	0.46	6.6 x 10 ⁻⁵	
	14	0.70	5.0 x 10 ⁻⁵	
	1	32	3.2 x 10 ⁻²	Sample Cracked
CaTiO ₃	23	1.93	8.4 x 10 ⁻⁵	
	7	0.36	5.1 x 10 ⁻⁵	
	14	1.3	9.3 x 10 ⁻⁵	
	1	0.4	4.0 x 10 ⁻⁴	
CaTiSiO ₅	23	1.0	4.0 x 10 ⁻⁵	
	7	0.97	1.4 x 10 ⁻⁴	
	14	1.0	7.1 x 10 ⁻⁵	
	1	0.45	4.5 x 10 ⁻⁴	
BaZrO ₃	23	1.1	4.8 x 10 ⁻⁵	Alteration Reaction
	7	0.32	4.6 x 10 ⁻⁵	
	14	5.6	4.0 x 10 ⁻⁴	Sample Cracked
	1	1.9	1.9 x 10 ⁻³	
CaZrO ₃	23	0.8	3.5 x 10 ⁻⁵	Alteration Reaction
	7	2.7	3.9 x 10 ⁻⁴	
	14	3.4	2.4 x 10 ⁻⁴	
	1	1.1	1.1 x 10 ⁻³	
Mullite (2Al ₂ O ₃ ·SiO ₂)	7	2.3	3.3 x 10 ⁻⁴	Alteration Reaction
	14	3.0	2.1 x 10 ⁻⁴	
	21	3.7	1.8 x 10 ⁻⁴	
	1	1.3	1.3 x 10 ⁻³	
Basalt	23	4.3	1.9 x 10 ⁻⁴	Alteration Reaction
	7	2.7	3.9 x 10 ⁻⁴	
	14	4.3	3.1 x 10 ⁻⁴	
	1	2.3	2.3 x 10 ⁻³	

TABLE 13. (contd)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Vitreous Silica (SiO ₂)	7	6.0	8.6 x 10 ⁻⁴	
	14	7.2	5.1 x 10 ⁻⁴	
	21	5.5	2.6 x 10 ⁻⁴	
	1	2.0	2.0 x 10 ⁻³	
Pyroceram 9617	7	6.0	8.6 x 10 ⁻⁴	Alteration Reaction
	14	6.6	4.7 x 10 ⁻⁴	
	21	8.5	4.0 x 10 ⁻⁴	
	1	4.7	4.7 x 10 ⁻³	
ZrSiO ₄	23	17	7.4 x 10 ⁻⁴	
	7	20	2.9 x 10 ⁻³	
	14	13	9.3 x 10 ⁻⁴	
	1	3.3	3.3 x 10 ⁻⁴	
Marcor	7	20	2.9 x 10 ⁻³	Alteration Reaction Specimen Cracked
	14	22	1.6 x 10 ⁻³	
	21	27	1.3 x 10 ⁻³	
	1	3.5	3.5 x 10 ⁻³	
BaTiO ₃	23	16	7.0 x 10 ⁻⁴	
	7	35	5.0 x 10 ⁻³	
	14	19	1.4 x 10 ⁻³	
	1	Sample Shattered		

(a) $S/V \cong 0.4 \text{ cm}^{-1}$ based on geometric surface area of the specimen.

(b) Based on geometric surface area of specimen.

(c) Average leach rate for exposure time shown.

of the other materials may exhibit a high leach resistance in one or two tests, but on an overall basis they are much inferior to the five materials mentioned.

The rankings in Table 15 are based only on the measured leach rates. They do not take into account the effects that localized attack or alteration reactions can have on the stability of candidate materials. These factors are considered in Section 4.3.

4.2 REACTIONS WITH REPOSITORY MEDIA

A limited number of experiments were carried out to determine if the ceramic materials would react with the repository media in a "dry" system. In the tests a sample of the candidate material was contacted with the repository medium (either synthetic WIPP salt or crushed basalt) in a sealed silica ampule at 375°C. The tests lasted for 2200 and 4500 h. At the conclusion of the test the silica ampule was opened and the sample was carefully separated from the bulk of the salt or basalt. The sample was then examined visually for evidence of possible reaction with the salt or basalt, after which it was weighed. In none of the tests was there any visual evidence of reaction between the test specimen and the salt or basalt. None of the specimens exhibited any significant weight changes.

TABLE 14. Leaching of Ceramic Materials in Brine at 250°C--Static Tests in Sealed Gold Ampule^(a)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Graphite	7	wt. gain	---	
	14	wt. gain	---	
	21	wt. gain	---	
	1	wt. gain	---	
Al ₂ O ₃ (99.8%)	7	0.028	4.0 x 10 ⁻⁶	
	14	0.094	6.7 x 10 ⁻⁶	
	21	0.091	4.3 x 10 ⁻⁶	
	1	0.018	1.8 x 10 ⁻⁵	
ZrO ₂	7	0.10	1.4 x 10 ⁻⁵	
	14	1.3	9.3 x 10 ⁻⁵	
	21	0.10	0.48 x 10 ⁻⁵	
	1	0.11	1.1 x 10 ⁻⁴	
Al ₂ O ₃ (99%)	7	0.29	4.1 x 10 ⁻⁵	Localized Attack
	14	0.39	2.8 x 10 ⁻⁵	
	21	0.38	1.8 x 10 ⁻⁵	
	1	0.096	9.6 x 10 ⁻⁵	
TiO ₂	23	0.79	3.4 x 10 ⁻⁵	
	7	0.50	7.1 x 10 ⁻⁵	
	14	0.61	4.4 x 10 ⁻⁵	
	1	0.22	2.2 x 10 ⁻⁴	
CaTiO ₃	23	1.1	4.8 x 10 ⁻⁵	
	7	0.58	8.3 x 10 ⁻⁵	
	14	0.60	4.3 x 10 ⁻⁵	
	1	0.1	1.0 x 10 ⁻⁴	
Mullite (2Al ₂ O ₃ ·SiO ₂)	7	1.5	2.4 x 10 ⁻⁴	Alteration Reaction
	14	1.3	9.3 x 10 ⁻⁵	
	21	0.9	4.3 x 10 ⁻⁵	
	1	1.0	1.0 x 10 ⁻²	
BaZrO ₃	23	1.9	8.3 x 10 ⁻⁵	Alteration Reaction
	7	0.94	1.3 x 10 ⁻⁴	
	14	1.1	7.9 x 10 ⁻⁵	Specimen Cracked
	1	13.1	1.3 x 10 ⁻²	
Vitreous Silica (SiO ₂)	7	3.9	5.6 x 10 ⁻⁴	
	14		Ampule Leaked	
	21	5.1	2.4 x 10 ⁻⁴	
	1	1.0	1.0 x 10 ⁻³	
Pyroceram 9617	7	1.9	2.7 x 10 ⁻⁴	
	14	6.3	4.5 x 10 ⁻⁴	
	21	11	5.2 x 10 ⁻⁴	
	1	1.6	1.6 x 10 ⁻³	
ZrSiO ₄	23	7.6	3.3 x 10 ⁻⁴	Specimen Cracked
	7	10.7	1.5 x 10 ⁻³	
	14	13.3	9.5 x 10 ⁻⁴	
	1	2.4	2.4 x 10 ⁻³	

TABLE 14. (contd)

Material	Exposure, days	Specimen Weight Loss, mg/cm ² (b)	Average Leach Rate, (c) g/cm ² -d(b)	Remarks
Marcor	7	12	1.7×10^{-3}	Alteration Reaction
	14	16	1.1×10^{-3}	
	21	39	1.9×10^{-3}	
	1	3.8	3.8×10^{-3}	Specimen Cracked
BaTiO ₃	23	27	1.1×10^{-3}	
	7	14	2.0×10^{-3}	
	14	22	1.6×10^{-3}	
	1	53	5.3×10^{-2}	Specimen Cracked

(a) $S/V \cong 0.4 \text{ cm}^{-1}$ based on geometric surface area of the specimen.

(b) Based on geometric surface area of specimen.

(c) Average leach rate for exposure time shown.

4.3 EVALUATION OF CANDIDATE MATERIALS

4.3.1 Graphite

The properties of graphite can vary significantly, depending on the grade of graphite being considered. The material used in this study was a low-permeability graphite (Toyo-Tanso IG-11)[®] developed for use in high-temperature, gas-cooled reactors.

Overall, the graphite exhibited the greatest resistance to attack by the leach solutions of any of the materials tested. Photomicrographs of the graphite specimens before and after testing provided no visual evidence of attack by the leach solutions in the dynamic tests or in the static tests at 150°C and lower. In the static tests at 250°C, however, the micrographs do show some indication of corrosion (see Figure 3).

Analysis of leach solutions from the static tests showed that small quantities of aluminum, sodium, and silicon were leached from the graphite. The amount of impurities leached from the graphite samples, however, accounted for only 10% to 20% of the weight loss exhibited by the graphite in the various leach tests. The bulk of the weight loss in each case was probably due to the reaction of the graphite with dissolved oxygen in the leach solution. This could explain why the graphite exhibited slightly greater leach rates in the static tests at 250°C than in the tests with flowing demineralized water at 250°C. In the static leach tests the gold ampules were only partially filled with leach solution. The remaining space was filled with air, and during testing the oxygen in the air could dissolve in the leach solution and react with the graphite. Calculations show that the air contained in the sealed gold ampules could supply sufficient oxygen to account for up to 80% of the weight loss exhibited by the graphite samples in the static tests at 250°C, and all of the weight loss in the 150°C static tests. Gray (1980) studied the reaction of graphite powder with water at 200°C to 300°C and reported that his results indicated the carbon reacted with dissolved oxygen rather than with water.

[®]Toyo-Tanso Co. Ltd., Osaka, Japan.

TABLE 15. Relative Resistance of Ceramic Materials to Leaching Under Various Test Conditions (in Order of Decreasing Resistance)

Static Leach Test at 100°C, Demineralized Water	Dynamic Leach Test at 90°C, Demineralized Water	Dynamic Leach Test at 250°C, Demineralized Water	Static Leach Test at 150°C			Static Leach Test at 250°C		
			Demineralized Water	Hanford Ground Water	Brine	Demineralized Water	Hanford Ground Water	Brine
Graphite	Graphite	Graphite	Graphite	Al ₂ O ₃ (99.8%)	Graphite ^(a)	Al ₂ O ₃ (99.8%)	Al ₂ O ₃ (99.8%)	Graphite ^(a)
Al ₂ O ₃ (99.8%)	Al ₂ O ₃ (99.8%)	TiO ₂	Al ₂ O ₃ (99.8%)	Graphite	TiO ₂ ^(a)	Graphite	Graphite	Al ₂ O ₃ (99.8%)
Al ₂ O ₃ (99%)	Mullite	Al ₂ O ₃ (99.8%)	Al ₂ O ₃ (99%)	Al ₂ O ₃ (99%)	Al ₂ O ₃ (99.8%)	Al ₂ O ₃ (99%)	ZrO ₂	ZrO ₂
Pyroceram 9617	Al ₂ O ₃ (99%)	ZrO ₂	Mullite	Mullite	Al ₂ O ₃ (99%)	TiO ₂	Al ₂ O ₃ (99%)	Al ₂ O ₃ (99%)
Vitreous Silica	TiO ₂	Al ₂ O ₃ (99%)	Vitreous Silica	ZrO ₂	Mullite	CaTiO ₃	TiO ₂	TiO ₂
TiO ₂	ZrO ₂	Vitreous Silica	ZrO ₂	Pyroceram 9617	Vitreous Silica	ZrO ₂	CaTiO ₃	CaTiO ₃
Basalt	Pyroceram 9617	CaZrO ₃	Pyroceram 9617	CaZrO ₃	Pyroceram 9617	Vitreous Silica	CaTiSiO ₅	Mullite
CaTiO ₃	CaTiO ₃	CaTiSiO ₅	TiO ₂	ZrSiO ₄	ZrO ₂	Basalt	BaZrO ₃	BaZrO ₃
ZrO ₂	CaZrO ₃	BaTiO ₃	CaTiSiO ₅	CaTiO ₃	CaTiO ₃	CaTiSiO ₅	CaZrO ₃	Vitreous Silica
ZrSiO ₄	Basalt	CaTiO ₃	ZrSiO ₅	TiO ₂	ZrSiO ₄	Mullite	Mullite	Pyroceram 9617
Marcor	Vitreous Silica	Mullite	CaTiO ₃	CaTiSiO ₅	Marcor	CaZrO ₃	Basalt	ZrSiO ₄
BaTiO ₃	Marcor	ZrSiO ₄	Basalt	Vitreous Silica	BaTiO ₃	ZrSiO ₄	Vitreous Silica	Marcor
BaZrO ₃	ZrSiO ₄	BaZrO ₃	Marcor	BaTiO ₃	BaZrO ₃	Pyroceram 9617	Pyroceram 9617	BaTiO ₃
CaTiSiO ₅	BaTiO ₃	Basalt	CaZrO ₃	Basalt		BaZrO ₃	ZrSiO ₄	
Mullite	CaTiSiO ₅	Marcor	BaZrO ₃	Marcor		BaTiO ₃	Marcor	
CaZrO ₃	BaZrO ₃	Pyroceram 9716	BaTiO ₃	BaZrO ₃		Marcor	BaTiO ₃	

(a) Test specimens exhibited weight gains due to incomplete removal of brine prior to drying.

(a) AS-RECEIVED

(b) FLOWING DEMINERALIZED WATER,
43 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
43 d AT 250°C

(d) STATIC TEST - BRINE SOLUTION,
43 d AT 250°C

FIGURE 3. Photomicrographs of Graphite Specimens Before and After Testing

The graphite used in this study was permeable, and the test samples had total surface areas, as determined by the BET method, that were 2000 to 3000 times greater than their geometric surface areas. If the leach rates are calculated on the basis of total surface areas, the values for graphite under the various test conditions would range from 10^{-11} to 10^{-8} g/cm²-d. Gray (1980) reported reaction rates ranging from 5×10^{-11} to 5×10^{-8} g/cm²-d over the same temperature range.

Graphite possesses a number of properties that favor its selection as a barrier material over the other material tested. Graphite is readily available and relatively inexpensive. Some techniques are available for fabricating large shapes, and graphite is easily machined, which facilitates the use of special overpack canister closures. The permeability of the graphite can probably be reduced to an acceptable level using various impregnation techniques. Overall, the mechanical and physical properties of graphite are superior to those of the ceramic material tested. It has good thermal conductivity and thermal-shock resistance for a nonmetallic material--two properties that are critical to the development of barrier elements. Its mechanical properties should be adequate to permit its use as overpack or a hole sleeve.

The one major question that must be answered regarding the use of graphite as a barrier material is what effect radiation would have on the corrosion of the graphite by the liquids encountered in the repository. Detailed studies of graphite leaching in the presence of a radiation field are required to resolve this question. Some development work on the fabrication of large shapes of the size required for a barrier system would also be necessary.

4.3.2 Al_2O_3

Overall, the leach resistance of Al_2O_3 was lower than that of graphite but superior to the other ceramic materials tested. Two grades of alumina were evaluated, the principal difference between the two being the impurity content. One grade contained approximately 0.2 wt% impurities, while the second contained about 1 wt% impurities. In every leach test the Al_2O_3 having the lowest impurity content exhibited the lowest leach rate. Even at 250°C the aluminum concentration in the leach solutions was quite low and the dissolved alumina never accounted for more than 50% of the weight loss suffered by a test specimen. Analysis of the leach solutions showed that a number of cation impurities were leached from both grades of alumina with silicon, sodium, and calcium being the principal species removed. As would be expected, leaching of impurities from the 99% Al_2O_3 was much greater than from the 99.8% material. Ceramographic examination of the test specimens after leaching showed extensive localized attack that apparently resulted from the leaching of impurities from the grain boundaries of the alumina. Figures 4 and 5 show typical micrographs of Al_2O_3 before and after testing. It is obvious from the micrographs that, for a given leach test, grain boundary attack was substantially greater with the 99% Al_2O_3 than with the 99.8% Al_2O_3 .

At 250°C both grades of alumina exhibit much higher leach rates in the flowing demineralized water than in the static tests. In the static tests the aluminum concentration in the leach solution appears to reach saturation in a relatively short period of time. As the aluminum concentration approaches saturation, the leach rate decreases accordingly, although even

(a) AS-RECEIVED

(b) FLOWING DEMINERALIZED WATER,
43 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
43 d AT 250°C

(d) STATIC TEST - BRINE SOLUTION,
43 d AT 250°C

(e) STATIC TEST - GROUNDWATER,
43 d AT 250°C

FIGURE 4. Al_2O_3 (99%) Specimens Before and After Leaching

(a) AS-RECEIVED

(b) FLOWING DEMINERALIZED WATER,
43 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
43 d AT 250°C

(d) STATIC TEST - BRINE SOLUTION,
43 d AT 250°C

(e) STATIC TEST - GROUNDWATER,
43 d AT 250°C

FIGURE 5. Al_2O_3 (99.8%) Specimens Before and After Leaching

at aluminum saturation some attack occurs due to the leaching of impurities from the grain boundaries. In the dynamic test at 250°C the flow rate of the demineralized water was sufficiently great that the aluminum concentration in the leach solution leaving the autoclave was very low--far below the apparent solubility limit.

In the static leach tests at 150° and 250°C the apparent saturation concentrations for aluminum were highest in the demineralized water and lowest in the brine solution, with the ground water exhibiting intermediate levels. Reasons for the differences in apparent aluminum saturation concentrations for the different leach solutions were not determined.

Aluminum oxide possesses certain advantages that increase the potential for its use as a barrier element. It is relatively inexpensive, although the cost increases rapidly with increasing purity. Techniques are available for preparing dense impervious shapes of Al_2O_3 , and work in Sweden has shown that impervious canisters of the size required for an engineered-barrier system can be prepared by hot isostatic pressing.

Considerable data are available on the mechanical and physical properties of Al_2O_3 , and its properties appear adequate to permit its further consideration for the proposed application. Its thermal-shock resistance is superior to that of any of the other ceramic materials tested, except for the vitreous silica and possibly basalt; its thermal conductivity is also relatively high.

Two problems regarding the use of Al_2O_3 as a barrier material must be resolved. Additional development effort is needed on the fabrication of full-sized barrier elements, such as overpacks or hole sleeves, and the effect of radiation on the leaching of Al_2O_3 must be determined. The effect of radiation on leaching should be less critical in the case of alumina than in the case of graphite.

4.3.3 ZrO_2

Zirconium oxide did not excel in any of the leach tests, but on an overall basis it was clearly superior to all of the other materials tested except for graphite, the two aluminas, and TiO_2 . Analysis of the leach solutions showed that their zirconium contents were very low and that leaching of impurities accounted for almost all of the weight loss exhibited by the test specimens. Calcium, silicon and sodium were the principal impurities leached from the ZrO_2 . In the test with flowing demineralized water at 250°C and some other tests, the leach rate of ZrO_2 decreased rapidly with time, indicating that for very long-term exposures the leach resistance of ZrO_2 may exceed that of graphite and TiO_2 . Photomicrographs of the test specimens showed no visual evidence of attack by the leach solutions (Figure 6).

Zirconium dioxide possesses certain disadvantages that reduce its potential as a barrier material. Compared to graphite and alumina, it is relatively expensive and less readily available. Techniques for fabricating large, dense impervious shapes have not been developed. Zirconium oxide undergoes a transformation from a monoclinic to a tetragonal form when heated; the transition is accompanied by about a 9% volume change. By the addition of a stabilizer, such as CaO , MgO , or Y_2O_3 , it is possible to produce a cubic ZrO_2 that is stable above and below

(a) AS-RECEIVED

(b) FLOWING DEMINERALIZED WATER,
43 d AT 250°C

(c) STATIC TEST - GROUNDWATER,
43 d AT 250°C

(d) STATIC TEST - BRINE SOLUTION,
43 d AT 250°C

FIGURE 6. ZrO_2 Specimens Before and After Leaching

the monoclinic-tetragonal transformation temperature. The ZrO_2 used in this study was stabilized with CaO . The stabilized ZrO_2 is quite sensitive to thermal shock. The thermal conductivity of ZrO_2 is relatively low and its other pertinent physical and mechanical properties appear to be inferior to those of graphite and alumina.

4.3.4 TiO_2

On an overall basis, TiO_2 was less leach resistant than graphite, alumina, and ZrO_2 but was clearly superior to the other materials tested. In the test with flowing demineralized water at 250°C , TiO_2 exhibited a much lower leach rate than ZrO_2 and the two aluminas but had to be down-graded because the specimen exhibited several radial cracks (Figure 7). Some of the other TiO_2 samples also exhibited cracking. There is some indication, however, that the cracking was the result of fabrication problems rather than attack by the leach solutions.

TiO_2 appeared to be unusual in two respects: the leach rates did not appear to be especially sensitive to temperature, and the leach rates were higher in the static tests than in the dynamic tests. Analysis of the leach solutions showed that leaching of impurities from the TiO_2 accounted for the major fraction of the weight loss exhibited by the specimens in the various tests. Silicon, sodium, barium, calcium, magnesium, copper and iron were the principal impurities leached. Titanium concentrations in the various leach solutions were quite low.

Photomicrographs of the test specimens showed no visual evidence of attack by the leach solutions, except for the cracking observed with some samples (Figure 7). The localized attack apparent with Al_2O_3 was not obvious with TiO_2 , which is surprising, considering the quantity of impurities leached from the samples.

As a barrier material, TiO_2 appears to be inferior to graphite and alumina in almost every respect; it is less readily available and more expensive. Techniques for fabricating large impervious shapes are not well developed. The physical properties of TiO_2 , such as thermal conductivity and thermal-shock sensitivity, are inferior to those of graphite and alumina. Only a limited amount of data are available on the mechanical properties of TiO_2 , but the data available indicate TiO_2 is inferior to both graphite and Al_2O_3 . The one advantage of TiO_2 was the low leach rate exhibited in flowing demineralized water at 250°C .

4.3.5 Mullite ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$)

Evaluation of the leach rate data shows that, on an overall basis, mullite is much less resistant to leaching than are graphite, Al_2O_3 , ZrO_2 , or TiO_2 . In addition, ceramographic examination of the test specimens showed that at 250°C mullite undergoes alteration reactions with the leach solutions that affect it to much greater depths than is apparent from the leach rate data. Micrographs of the specimens tested at 250°C are shown in Figure 8 and the extent of the alteration reactions is obvious. In the test with flowing demineralized water the entire area shown in the micrograph (Figure 8b) has undergone the alteration reaction.

Analysis of leach solutions from the static tests at 250°C showed that the amount of material dissolved from a given sample was 2 to 3 times greater than the sample's measured weight loss. This indicates that some form of hydration reaction probably occurred at the sample sur-

(a) AS-FABRICATED

(b) FLOWING DEMINERALIZED WATER,
43 d AT 250°C

FIGURE 7. TiO_2 Samples Before and After Leaching

face. The analytical data showed that silicon was the principal cation leached from the mullite, together with minor amounts of aluminum, potassium, calcium, and sodium. The aluminum concentration in solution was usually less than 5% of the silicon concentration.

Ceramographic examination of mullite samples tested at 150°C provided no visual evidence that alteration reactions occurred with any of the leach solutions (see Figure 8f). Analysis of the leach solutions from the static tests at 150°C showed that silicon was the major species leached from the mullite. The aluminum concentrations in the leach solutions were low, amounting to no more than 10% of the silicon concentrations.

Mullite possesses many of alumina's attributes. It is readily available and relatively inexpensive. Techniques have been developed for preparing dense, impervious mullite shapes. The pertinent physical and mechanical properties of mullite, however, are generally inferior to those of alumina. Based on the results obtained in the various leach tests, there is little to recommend the further consideration of mullite as a barrier material.

4.3.6 Vitreous Silica (SiO_2)

The leach resistance of vitreous silica in the various tests ranged from slightly above average to below average. Analyses of the leach solutions showed that silicon was the principal species leached from the silica, together with small amounts of sodium and potassium. In the static tests at 150°C the silicon concentration in the leach solution continued to increase with increasing exposure time. In the static tests at 250°C the silicon in the leach solutions appeared to reach an equilibrium concentration in a relatively short period of time (≤ 7 days). At both 150° and 250°C the leach rate of silica was higher in the Hanford ground water than in the other two solutions. At 250°C the equilibrium silicon concentration in the Hanford ground water was about 220 ppm and was much lower in the other two solutions.

Ceramographic examination of the silica specimens tested at 250°C showed no indication of localized attack or alteration reactions (Figure 9). The specimen tested at 150°C with Hanford ground water, however, did show some evidence of cracking (see Figure 8d).

On an overall basis, the pertinent properties of vitreous silica are generally inferior to those of alumina and graphite. One advantage of silica over alumina is its superior resistance to thermal shock. Methods for casting dense impervious shapes of silica are well developed, although additional development work would be needed in order to fabricate silica canisters of the size needed in a barrier system.

Based on all of the data available, there appears to be little justification in giving further consideration to silica as a barrier material.

4.3.7 CaTiO_3

The results of the leach tests showed that the relative leach resistance of CaTiO_3 is near the medium of the materials tested. The sample exposed to flowing demineralized water at 250°C suffered some surface alteration, which was not apparent with the specimens subjected to the static tests at 150° and 250°C (Figure 10).

(a) AS-RECEIVED

(b) FLOWING DEMINERALIZED WATER,
43 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
43 d AT 250°C

(d) STATIC TEST - GROUNDWATER,
43 d AT 250°C

(e) STATIC TEST - BRINE SOLUTION,
43 d AT 250°C

(f) STATIC TEST - DEMINERALIZED WATER,
43 d AT 150°C

FIGURE 8. Micrographs of Mullite Test Specimens

(a) AS-RECEIVED

(b) FLOWING DEMINERALIZED WATER,
43 d AT 250°C

(c) STATIC TEST - HANFORD GROUNDWATER,
43 d AT 250°C

(d) STATIC TEST - HANFORD GROUNDWATER,
43 d AT 150°C

FIGURE 9. Micrographs of Vitreous Silica Specimens Before and After Leaching

(a) AS-FABRICATED

(b) FLOWING DEMINERALIZED WATER,
45 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
45 d AT 250°C

(d) STATIC TEST - BRINE SOLUTION,
45 d AT 250°C

FIGURE 10. CaTiO_3 Specimens Before and After Leaching

Analysis of the leach solutions showed that calcium was the principal species leached from CaTiO_3 , with calcium concentrations reaching 300 ppm in some tests done with Hanford ground water. Titanium concentrations were very low in all of the leach solutions, amounting to no more than 1 to 2 ppm. Impurities accounted for as much as 40% of the material leached from the CaTiO_3 samples in some tests.

The CaTiO_3 specimens used in this work were prepared by hot-pressing at 1600°C ; even so, the specimens exhibited considerable porosity. Decreasing the porosity of the CaTiO_3 should increase the leach resistance. Unfortunately, there is little information available on techniques for preparing large, dense impervious shapes of CaTiO_3 . The limited data available on the mechanical and physical properties of CaTiO_3 indicate that for the barrier application the properties of CaTiO_3 are generally inferior to those of Al_2O_3 and graphite.

4.3.8 CaZrO_3

The leach resistance of CaZrO_3 was lower than that of most of the materials tested, and it suffered alteration reactions when exposed to the leach solutions at temperatures of 150°C and above (CaZrO_3 was not tested with the brine solution). Figure 11 shows micrographs of specimens leached at 150° and 250°C in demineralized water and Hanford ground water, and the attack is obvious.

Analysis of the leach solutions showed that calcium was the principal species leached from the CaZrO_3 , with the calcium content of some solutions being as high as 400 ppm. The zirconium content of the solutions was very low--usually less than 0.5 ppm. Leaching of impurities from the CaZrO_3 (principally silicon, barium, aluminum, and iron) accounted for up to 10% of the weight loss suffered by the samples.

Only a limited amount of data are available on the physical and mechanical properties of CaZrO_3 . From the data that are available, there is nothing that recommends the use of CaZrO_3 as a barrier element over the more leach-resistant materials such as Al_2O_3 . Attempts to hot-press high-density CaZrO_3 pellets were unsuccessful and only moderate densities were achieved by cold-pressing and sintering. There is very little information available in the literature on fabricating dense impervious shapes of CaZrO_3 .

4.3.9 CaTiSiO_5

On the basis of overall leach resistance, CaTiSiO_5 was one of the poorer materials tested. In addition, surface alteration and cracking was evident in the specimen exposed to flowing demineralized water at 250°C (Figure 12). The CaTiSiO_5 was not tested with the brine solution.

Analysis of the leach solutions showed that at 250°C calcium was the principal species leached from the CaTiSiO_5 , while the silicon and titanium concentrations were low. At 150°C silicon was the principal species leached from the CaTiSiO_5 , and the titanium and calcium concentrations were low. Impurities (primarily sodium, barium and aluminum) accounted for up to 30% of the material leached from the CaTiSiO_5 species in the various tests.

Little data are available on the physical and mechanical properties of CaTiSiO_5 , and procedures for fabricating large, dense impervious shapes have not been developed. The specimens

(a) AS-FABRICATED

(b) FLOWING DEMINERALIZED WATER,
45 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
45 d AT 250°C

(d) STATIC TEST - DEMINERALIZED WATER,
43 d AT 150°C

FIGURE 11. CaZrO_3 Specimens Before and After Leaching

(a) AS-FABRICATED

(b) FLOWING DEMINERALIZED WATER,
45 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
45 d AT 250°C

(d) STATIC TEST - GROUNDWATER,
45 d AT 250°C

FIGURE 12. Micrographs of CaTiSiO_5 Specimens Before and After Leaching

used in this work were prepared by cold-pressing and sintering and had a relatively low density. Attempts to hot-press CaTiSiO_5 were unsuccessful. Limited quantities of relatively pure CaTiSiO_5 are available as the naturally occurring mineral sphene.

4.3.10 Basalt

The leach resistance of basalt was inferior to that of several of the other materials tested, and exposure to the leach solutions at high temperatures produced alteration reactions (the basalt was not tested with the brine solution). The alteration reactions appeared to begin at about 150°C and were quite rapid at 250°C (Figure 13).

Analysis of the leach solutions from the static tests showed that silicon was the principal cation species leached from the basalt, together with smaller amounts of sodium, potassium, and aluminum. The analytical data from the 250°C static tests showed that the amount of material dissolved from a given sample was substantially greater than the sample's measured weight loss, indicating that some form of hydration reaction(s) had probably occurred at the sample surface.

Basalt has two potential advantages as a barrier material: 1) it is inexpensive and readily available, and 2) if a basalt repository is developed, it could be advantageous to have a barrier element fabricated from the same material as the repository medium. Disadvantages, in addition to poor leach resistance, include: 1) lack of demonstrated technology for fabricating large, dense impervious shapes, and 2) mechanical and physical properties that are generally inferior to those of graphite and alumina. On an overall basis, there appears to be little justification for further consideration of basalt as a barrier material.

4.3.11 ZrSiO_4

On an overall basis the leach resistance of ZrSiO_4 was lower than that of most of the materials tested. The specimen exposed to flowing demineralized water at 250°C suffered an alteration reaction, but the specimens from the static tests at 250°C showed little evidence of attack by the leach solutions (Figure 14).

Analyses of the leach solutions showed that silicon was the principal species leached from the ZrSiO_4 . The zirconium content of the leach solutions was very low. Small amounts of sodium and calcium were also leached from the ZrSiO_4 .

In general, the pertinent mechanical and physical properties of ZrSiO_4 are inferior to those of Al_2O_3 , with two exceptions. The impact strength of ZrSiO_4 is much greater than that of Al_2O_3 , and its thermal expansion coefficient is lower. Dense shapes of ZrSiO_4 are reported to have poor thermal-shock resistance.

Examination of the micrographs in Figure 14 point out an additional problem with ZrSiO_4 . The test specimens used in this study were prepared by hot-pressing at $\sim 1600^\circ\text{C}$. Even so, the density of the specimens was low and they exhibited considerable continuous porosity. Zirconium silicate is reported to decompose at about 1675°C , which prevents hot-pressing at temperatures much above those used in this work. The limited information available in the literature indicates it is difficult to produce high-density shapes from ZrSiO_4 .

(a) AS-RECEIVED

(b) FLOWING DEMINERALIZED WATER,
45 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
45 d AT 250°C

(d) STATIC TEST - GROUNDWATER,
45 d AT 250°C

FIGURE 13. Basalt Specimens Before and After Testing

(a) AS-FABRICATED

(b) FLOWING DEMINERALIZED WATER,
45 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
45 d AT 250°C

(d) STATIC TEST - BRINE SOLUTION,
45 d AT 250°C

FIGURE 14. Photomicrographs of ZrSiO_4 Specimens

Zirconium silicate is available in limited amounts as the naturally occurring mineral zircon.

4.3.12 BaTiO_3

The leaching data indicate that BaTiO_3 is less resistant to leaching than are most of the materials tested. In the static tests at 150° and 250°C , however, there were large differences between the BaTiO_3 leach rates calculated from weight loss measurements and those determined from solution analyses. In every case the solution analyses gave much lower leach rates. Ceramographic examination of the test specimens indicated that alteration reactions did not occur to any extent even at 250°C (Figure 15). Most of the specimens tested at 150° and 250°C were either cracked or shattered into several pieces. The micrographs in Figure 15 show that the test specimens were very porous. It is possible that the high leach rates calculated from the weight loss measurements resulted from the spalling of small fragments from the specimen surface.

Analysis of the leach solutions showed that barium was the principal species leached from the BaTiO_3 . In the static tests at 150° and 250°C the barium concentration appeared to reach a steady-state level very quickly (~ 1 day). The titanium concentration in the leach solution was very low--usually less than 5% of the barium concentration. Impurities (primarily silicon, calcium, aluminum and sodium) accounted for up to 20% of the material leached from the BaTiO_3 .

Attempts to hot-press BaTiO_3 were unsuccessful and pellets prepared by cold-pressing and sintering were very porous. There is little data in the literature on methods for preparing dense impervious shapes of BaTiO_3 . Information on the physical and mechanical properties is limited, and the data that is available indicates that BaTiO_3 is generally inferior to Al_2O_3 and TiO_2 . It is possible that the leach resistance of dense impervious BaTiO_3 would be lower than the results obtained in this study, but even so there is little incentive to give additional consideration to BaTiO_3 as a barrier material.

4.3.13 BaZrO_3

Barium zirconate was one of the least leach-resistant materials tested. In addition, exposure of BaZrO_3 to the leach solutions at 250°C produced extensive alteration reactions (Figure 16). Most of the specimens tested at 150° and 250°C suffered some degree of cracking.

Analyses of the leach solutions showed that barium was the principal species leached from the BaZrO_3 (up to 500 ppm). Zirconium concentrations were much lower (up to 100 ppm), but were still much higher than in any of the other leach tests involving ceramic materials containing zirconium. Reasons for the increased zirconium concentrations were not determined. Impurities leached from the specimens, principally calcium and silicon, accounted for up to 20% of the weight loss suffered by the test samples.

Very little information is available in the literature on the mechanical and physical properties of BaZrO_3 . Techniques for fabricating BaZrO_3 into large, dense impervious shapes have not been developed. Based on its poor leach resistance and the lack of needed property data, BaZrO_3 is dropped from further consideration as a barrier material.

(a) AS-FABRICATED

(b) FLOWING DEMINERALIZED WATER,
45 d AT 250°C

(c) STATIC TEST - BRINE SOLUTION,
45 d AT 250°C

FIGURE 15. BaTiO₃ Samples Before and After Leaching

(a) AS-PREPARED

(b) FLOWING DEMINERALIZED WATER,
45 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
45 d AT 250°C

(d) STATIC TEST - BRINE SOLUTION,
45 d AT 250°C

FIGURE 16. Micrographs of BaZrO₃ Specimens Before and After Leaching

4.3.14 Pyroceram 9617

Pyroceram 9617 is a glass-ceramic developed by Corning Glass Works. It can be produced in large, dense impervious shapes and possesses a number of physical and mechanical properties that are desirable in a barrier element. The leach resistance of Pyroceram 9617 is relatively high at low temperatures, but decreases rapidly with increasing temperature. In addition, exposure of the Pyroceram 9617 to the leach solutions produced alteration reactions that appeared to start at temperatures as low as 150°C and become extensive at 250°C (Figure 17). After a specimen was dried, the reaction layer was powdery and very easily removed from the surface. Analyses of the leach solutions from the static tests at 150°C and 250°C showed very high concentrations of dissolved cations, especially silicon, lithium, and aluminum. The high aluminum concentrations (up to 40 ppm) were surprising because the tests with Al_2O_3 indicated that the saturation concentrations for aluminum in the leach solutions were much lower. The high aluminum concentrations observed in the Pyroceram 9617 tests may result from changes in pH of the leach solutions due to dissolution of various cations in the Pyroceram 9617 (i.e., Li, Na) or from the formation of soluble aluminum complexes.

Based on the experimental results obtained, there appears to be little incentive to consider Pyroceram 9617 for use as an element in an engineered-barrier system. One mitigating factor is the possibility that the repository might be designed to maintain the maximum temperature below 100°C. If this should happen, there is some incentive to evaluate Pyroceram 9617 in more detail.

4.3.15 Marcor 9658

Marcor 9658 is a machinable glass-ceramic developed by the Corning Glass Works. Marcor possesses a number of desirable properties that could make it a potentially useful barrier material if it had the necessary corrosion resistance. Unfortunately, Marcor rated at or near the bottom in all of the leach tests. In addition to its high leach rates, Marcor underwent alteration reactions when exposed to the leach solutions at 250°C (Figure 18). There were also indications that the alteration reactions occurred at temperatures as low as 150°C in the Hanford ground water (Figure 18f).

Analysis of the leach solutions from the static tests at 150°C and 250°C showed that the principal species leached from the Marcor were very soluble in the leach solutions. Thus, saturation effects in static systems would have less effect on the leaching of Marcor than on most of the other ceramic material tested.

Based on the results of the leach tests, the Marcor can be dropped from further consideration as a barrier material.

4.4 ESTIMATES OF LONG-TERM ATTACK

In order for a ceramic barrier element to be of use in a nuclear waste package, it must provide isolation of the primary waste canister from the repository environment for the required 1000-year period. It is impossible to estimate with any degree of accuracy the

(a) AS-RECEIVED

(b) STATIC TEST - DEMINERALIZED WATER,
43 d AT 250°C

(c) STATIC TEST - GROUNDWATER,
43 d AT 250°C

(d) STATIC TEST - BRINE SOLUTION,
43 d AT 250°C

FIGURE 17. Micrographs of Pyroceram 9617 Specimens

(a) AS-RECEIVED

(b) FLOWING DEMINERALIZED WATER,
43 d AT 250°C

(c) STATIC TEST - DEMINERALIZED WATER,
43 d AT 250°C

(d) STATIC TEST - GROUNDWATER,
43 d AT 250°C

(e) STATIC TEST - BRINE SOLUTION,
43 d AT 250°C

(f) STATIC TEST - DEMINERALIZED WATER,
43 d AT 150°C

FIGURE 18. Marcor Specimens Before and After Testing

long-term leach resistance of the materials tested using the limited amount of data obtained in this study. Extrapolation of the measured leach rates to very long exposure times is difficult because in almost all of the tests the leach rates varied with time. In some of the dynamic leach tests the leach rates continued to decrease with time, and steady-state conditions were not attained. In the static tests the leach rates varied with time as expected, and in many of the tests the concentrations of dissolved species in the leach solutions did appear to reach saturation levels. In a static system, however, the extent of attack of the ceramic material will depend upon the volume of aqueous phase present and the S/V ratio for the system, and this parameter is unknown for a geologic repository. In addition, ceramographic examination of the test specimens was limited to samples that had been exposed for a single time period. Therefore, it is not possible to reliably estimate from this work how localized attack or alteration reactions would vary with exposure time.

Some very conservative "worst-case" estimates of the attack expected in a repository environment over a 1000-year exposure period can be made. In general, the materials tested exhibited their highest leach rates and maximum localized attack and alteration reactions in the dynamic tests at 250°C. Therefore, extrapolation of the results from the short-term dynamic tests at 250°C should provide conservative estimates of long-term attack; this is especially true because the repository temperature would be much below 250°C for most of the 1000-year period. The estimates have been made and the results obtained are given in Table 16. The average corrosion of each material for a 1000-year exposure was estimated using the average leach rates given in Table 7 for the longest exposure time (43 or 45 days, depending on the material). The extent of localized attack or alteration reactions was estimated by linear extrapolation of the results given in Table 8.

The very conservative "worst-case" estimates presented in Table 16 show that, except for TiO₂ and graphite, all of the materials tested would suffer extensive corrosion when exposed to flowing demineralized water at 250°C for 1000 years. The estimated barrier thickness that would be required with most materials to provide the required level of isolation would probably be greater than could be fabricated with existing technology. In the case of TiO₂ the canister thickness required, based on the estimate of average corrosion, would not be a problem; but the problem of cracking observed with the TiO₂ specimens would have to be resolved before TiO₂ could be considered for barrier use.

In a static system the long-term corrosion of the candidate materials should be much less than the values given in Table 16. Decreasing the temperature would also decrease the corrosion rate markedly, and at temperatures below 150°C localized attack and alteration reactions should not be a major problem with most of the candidate materials.

Detailed experimental evaluation of the corrosion behavior of ceramic materials under the conditions expected in a geologic repository would allow more reliable estimates of long-term corrosion to be made. These estimates would probably show that the thicknesses of ceramic barrier elements needed to provide the 1000-year protection would be considerably less than the values given in Table 16.

TABLE 16. Estimated Worst-Case Corrosion of Ceramic Material Exposed to Flowing Demineralized Water at 250°C

Material	Corrosion, cm/1000 yr	
	Average(a)	Localized Attack or Alteration Reactions(b)
TiO ₂	0.6	(c)
Graphite	1.5	None
ZrO ₂	7.5	None
Al ₂ O ₃ (99.8%)	13	21
Al ₂ O ₃ (99%)	18	42
BaTiO ₃	35	42
CaZrO ₃	40	290
CaTiO ₃	70	85
CaTiSiO ₅	80	160
Vitreous Silica (SiO ₂)	85	None
BaZrO ₃	90	130
ZrSiO ₄	100	85
Mullite (2Al ₂ O ₃ •SiO ₂)	170	>700
Basalt	350	450
Marcor	500	>720
Pyroceram 9617	1200	>1000

(a) Based on the average leach rates obtained in the screening tests--Table 7.

(b) Based on linear extrapolation of results obtained in the screening tests--Table 8.

(c) Specimen used in the screening test exhibited radial cracks to a considerable depth, but the results could not be extrapolated to long exposure times.

Although tests have not been carried out under identical conditions, it is interesting to compare reported corrosion rates for potential metallic barrier materials with the results obtained using ceramic materials. Studies were conducted at Sandia Laboratories (Braithwaite and Molecke 1978) to measure the corrosion of various metals in seawater and two brine solutions. The tests with deoxygenated brines were carried out by sealing test coupons in Pyrex or quartz ampules along with an aliquot of solution and heating them in an autoclave at 250°C for 2 to 8 weeks. The two brines used were 1) a brine similar in composition to the brine used in this study (primarily NaCl) and 2) a high-KCl-NaCl-MgCl₂ brine (dissolved solids ~306 g/L). The results reported by Braithwaite and Molecke (1978) for the deoxygenated solutions are summarized in Table 17. A linear extrapolation of the data given in Table 17 shows that the more corrosion-resistant metals and alloys such as titanium, Zircaloy-2 and Ticode 12 (a titanium alloy) would suffer less attack in a 1000-year period than the best of the ceramic materials.

TABLE 17. Corrosion Rates of Metals and Alloys in Deoxygenated Solutions (250°C,
P = 5 MPa)

Alloy	Brine A, cm/yr	Brine B, cm/yr	Seawater, cm/yr
1018 Mild Steel	0.17	0.007	0.04
Corten A. Steel	0.09	0.005	0.02
2-1/4 Cr-1 Mo Steel	0.10 ^(a)	0.01 ^(a)	0.02
Lead	0.05	0.03	0.03
Copper	0.007	0.005	0.005
Naval Brass	0.1	---	0.10
90-10 Cupronickel	0.014	---	0.007
SS-304L	0.0018	0.001	0.0006
SS-316L	0.0015	---	0.0005
SS-Nitronic 50	0.0008	---	0.0003
SS-20Cb3	0.0007	---	0.0005
SS-Ebrite 26-1	0.0016	---	0.0005
Monel-400	0.003	---	0.01
Incoloy-825	0.0006	---	0.0004
Inconel-600	0.0009	0.0007	0.0005
Inconel-625	0.0005	0.0001	0.0012 ^(b)
Hastelloy C-276	0.0007	---	0.00015
Zircaloy-2	0.0001	---	---
Titanium C.P.	0.0003	---	0.0006
Ticcode-12	0.00006	---	0.0005

(a) Crevice corrosion

(b) Pitting corrosion

If one allows for the differences in the conditions under which the tests were conducted, however, it is impossible to say if the best metallic materials are more corrosion-resistant than are graphite and the best of the ceramic materials. In order to obtain meaningful comparisons of the corrosion resistance of the two groups of materials, the corrosion tests would have to be carried out under similar conditions.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Based on the results obtained in the various leach tests there are several general conclusions that can be reached regarding the leach resistance of the candidate materials evaluated in this study.

- On an overall basis, graphite exhibited the greatest leach resistance of the materials tested. Attack of the graphite appeared to depend primarily upon the dissolved oxygen in the leach solution.
- All of the ceramic materials tested suffered extensive attack in one or more of the leach tests. Overall, the two grades of alumina appeared to be the most leach-resistant of the ceramic materials tested. Titanium dioxide and ZrO_2 were the best of the remaining materials.
- Localized attack or alteration reactions presented a serious problem at temperatures of 150°C and above with most of the ceramic materials. Only ZrO_2 and TiO_2 did not appear to suffer from localized attack or alteration reactions, although some of the TiO_2 specimens exhibited cracking that may have resulted from fabrication problems rather than attack by the leach solutions.
- The leach rates increased with temperatures as expected. Direct comparisons are difficult because the leach rates varied with time. But in some cases the increase in leach rates with temperature were not as great as one might anticipate. Figure 19, for example, shows the effect of temperature on the average leach rates of several materials exposed to flowing demineralized water at 90° and 250°C . The values given in the figure are the average leach rates for the longest exposure time used in the tests (35 days at 90°C and 43 or 45 days at 250°C). For some materials, such as mullite and Pyroceram 9617, the leach rate increased 500 to 1000 times as the temperature increased from 90° to 250°C , whereas the leach rate of TiO_2 approximately doubled over the same temperature range. In the static tests, where the leach rates were limited by saturation effects, the increases in the average leach rates for the various materials were generally less than an order of magnitude over the temperature range of 150° to 250°C .
- In the static tests at 150° and 250°C the leach rates were generally highest in the demineralized water and lowest in the brine solution, with the Hanford ground water giving intermediate results.
- In most of the tests the leach rates varied with time, although in some of the dynamic tests it appeared that steady-state conditions were attained. In most of the static tests it was apparent that saturation of dissolved species in the leach solutions served to limit dissolution of the ceramic materials.

The conclusions stated above are based on an overall evaluation of the test results, and may not be valid for a specific repository environment where conditions could be quite different from those used in the leach tests.

FIGURE 19. The Effect of Temperature on the Leaching of Various Materials

The results obtained in this study are not adequate to demonstrate the feasibility of ceramic barrier elements. Additional research and development will be required to demonstrate that one or more of the materials tested can be used successfully in engineered-barrier systems. The results of this work do show, however, which of the materials offers the best chance of developing acceptable barrier elements. Based on the experimental results obtained, and considering other factors such as cost, availability, fabricability, mechanical and physical properties, graphite appears to be the primary choice for the barrier application, with alumina as the second choice. If the problem of cracking can be overcome, TiO_2 would also be a likely choice. Zirconium oxide appears to be quite resistant to the leach solutions, but does not appear to warrant further consideration as a barrier because of its thermal-shock sensitivity and fabrication difficulties. None of the other ceramic materials tested appear to warrant further consideration for the barrier application.

If the decision is made to continue with the development of nonmetallic barrier elements, it is recommended that graphite, alumina and possibly TiO_2 be the materials considered for detailed evaluation.

6.0 REFERENCES

- Ames, L. L. 1978. Low Temperature Radionuclide Kd Values for Basalt, Heulandite and Nontronite. PNL-2817, Pacific Northwest Laboratory, Richland, Washington.
- Braithwaite, J. W. and M. A. Molecke. 1978. High-Level Waste Canister Corrosion Studies Pertinent to Geologic Isolation. SAND 78-2111, Sandia Laboratories Albuquerque, New Mexico. (Presented at the Conference on High-Level Radioactive Solid Waste Forms, sponsored by the NRC, Denver, Colorado, December 19-21, 1978).
- Gray, W. J. 1980. Radioactive Waste Management. 1:105.
- Lynch, J. F., C. G. Ruderer, W. H. Duckworth (eds.). 1966. Engineering Properties of Selected Ceramic Materials. Compiled by Battelle Memorial Institute, Columbus, Ohio and published by the American Ceramic Society, Columbus, Ohio.

7.0 ACKNOWLEDGMENTS

Most of the experimental studies were performed by R. J. Elovich. Autoclave testing was provided by R. A. Clark. Ceramographic examination of the test specimens was provided by R. H. Beauchamp and F. T. Hara provided the analysis of the leach solutions.

R. E. Westerman was the Task Leader. The report was edited by M. H. Henry and reviewed by D. E. Larson, H. H. Van Tuyl and R. E. Westerman.

APPENDIX

DESCRIPTION OF MATERIALS STUDIED

DESCRIPTION OF MATERIALS STUDIED

What follows are general descriptions and lists of characteristics for each of the materials studied.

Al₂O₃ (99%)

Coors AD-99® high-purity impervious recrystallized alumina; test specimens cut from 1/4-in.-dia rod obtained from the manufacturer.

Porosity--gas-tight

Water adsorption--none

Micrographs--show some unconnected internal voids

Density-->90% of theoretical density

Surface area (BET) of test specimen--<10 cm²/g

Al₂O₃ (99.8%)

McDanel high-purity impervious alumina;® test specimens cut from 1/4-in.-dia rod obtained from manufacturer.

Porosity--gas-tight

Water adsorption--none

Micrographs--show some unconnected internal voids

Density-->92% of theoretical density

Surface area (BET) of test specimens--<10 cm²/g

MULLITE (2Al₂O₃·SiO₂)

Coors impervious Mullite® (Sillmanite); test pieces cut from 1/4-in.-dia rod obtained from manufacturer.

Porosity--gas-tight

Water adsorption--none

Micrographs--show some unconnected internal voids

Density-->90% of theoretical density

Surface area (BET) of test specimens--<10 cm²/g

®Coors Porcelain Co., Golden, Colorado

®McDanel Refractory Porcelain Co., Beaver Falls, Pennsylvania

BASALT

Test specimens cut from a sample of basalt taken from Flow E of the Sentinel Bluffs - Grande Ronde Formation.

Micrographs--show some slight internal porosity

Average density-- 3.17 g/cm^3

Surface area (BET) of test specimens-- $\sim 100 \text{ cm}^2/\text{g}$

BaTiO₃

BaTiO₃ powder obtained from Cerac, Inc.;^(a) test specimens were prepared by cold-pressing the BaTiO₃ powder into pellets at 50 tons/in.^2 and sintering the pellets at $\sim 1200^\circ\text{C}$ for 90 h.

Purity 98% analysis:

Al	= 0.01 - 0.1%
Ca	= 0.01 - 0.1
Co	= 0.001
Cu	= 0.005 - 0.005
Fe	= 0.005 - 0.05
Mg	= 0.01 - 0.1
Si	= 0.01 - 0.1
V	= 0.001 - 0.01

Particle size: -325 mesh + 5 microns

Micrographs of the pellets--show extensive connecting internal porosity

Average pellet density--89% of theoretical density

Surface area (BET) of pellets-- $\sim 320 \text{ cm}^2/\text{g}$

BaZrO₃

BaZrO₃ powder obtained from Cerac, Inc.; test specimens were prepared by cold-pressing BaZr₂O₃ powder into pellets at 50 tons/in.^2 and sintering the pellets at $\sim 1200^\circ\text{C}$ for 90 h.

Purity 99% analysis:

Al	= 0.03 - 0.3%
Ca	= 0.01 - 0.1
Cu	= 0.0001
Fe	= 0.01 - 0.1
Mg	= 0.01 - 0.1
Si	= 0.1 - 1.0
Ti	= 0.03 - 0.3

(a) Cerac, Inc., Milwaukee, Wisconsin

Particle Size: -325 mesh

Micrographs of the pellets--show extensive internal porosity

Average pellet density--~92% of theoretical density

Surface area (BET) of pellets--~700 cm²/g

CaTiO₃

CaTiO₃ powder obtained from Cerac, Inc.; test specimens were prepared by hot-pressing the CaTiO₃ powder into pellets at 1600°C and 5200 psi using graphite dies, then heating the pellets in air at ~1200°C for 24 h.

Purity 99% analysis: Al = 0.005 - 0.05%

Co = 0.01 - 0.01

Cu = 0.001

Fe = 0.001

Mo = 0.001

Pb = 0.005 - 0.005

Si = 0.001 - 0.011

Sr = 0.001 - 0.01

Zr = 0.001 - 0.01

Particle Size: -325 mesh

Micrographs of the pellets--showed some internal porosity

Average pellet density--~94% of theoretical density

Surface area (BET) of pellets--~450 cm²/g

CaZrO₃

CaZrO₃ powder obtained from Cerac, Inc.; test specimens prepared by cold-pressing CaZrO₃ into pellets at 50 tons/in.² and sintering the pellets at ~1200°C for 90 h.

Purity 99% analysis: Al = 0.01 - 0.1%

Ba = 0.003 - 0.03

Cu = 0.001 - 0.01

Fe = 0.03 - 0.3

Mg = 0.001 - 0.01

Si = 0.15

Ti = 0.03 - 0.3

Particle size: -325 mesh

Micrographs of the pellets--show some unconnected internal voids

Average pellet density--~91% of theoretical density

Surface area (BET) of pellets--too low to measure (<10 cm²/g).

CaTiSiO₅

CaTiSiO₅ was prepared by reacting CaTiO₃ and SiO₂ powders at high temperatures. The CaTiO₃ and SiO₂ powders were obtained from Cerac, Inc. The purity and analysis of the CaTiO₃ powder is given in a previous section. Purity of the SiO₂ was 99.9% and the particle size was -325 mesh. Analysis of the material was as follows:

Al = 0.003 - 0.01%

B = 0.001 - 0.01

Ca = 0.01 - 0.1

Fe = 0.005 - 0.05

Mg = 0.005 - 0.05

Mn = 0.001

Pb = 0.001

Ti = 0.01 - 0.1.

Stoichiometric quantities of the powders were wet-milled and then vacuum-dried. The mixed powders were fused in a platinum crucible at 1600°C. After cooling, the product was crushed to a fine powder. X-ray diffraction analysis of the powder showed it to be CaTiSiO₅ with no indication of other phases being present.

The test specimens were prepared by cold-pressing the powder into pellets at 50 tons/in.² and sintering the pellets at ~1200°C for 90 h.

Micrographs of the pellets--showed some connecting internal porosity.

Average pellet density--~90% of theoretical density

Average surface area (BET) of pellets--~900 cm²/g.

VITREOUS SILICA (SiO₂)

Amersil Infrasil vitreous silica glass;[®] test specimens cut from 1/4-in.-dia rod obtained from the manufacturer.

Porosity--gas-tight

Water adsorption--none

Micrographs--show no indication of internal porosity

Density--2.20 g/cm³

Surface area (BET) of test specimens--<10 cm²/g

[®]Thermal American Fused Quartz Co., Montville, New Jersey.

TiO₂

TiO₂ powder obtained from Cerac, Inc.; test specimens were prepared by hot-pressing the TiO₂ powder into pellets at 1600°C and 5200 psi using graphite dies, then firing the pellets in air at ~1200°C for 24 h.

Purity 99.9% analysis:

Al	= 0.01 - 0.1%
Ca	= 0.01 - 0.1
Co	= 0.001 - 0.01
Cr	= 0.01 - 0.1
Cu	= 0.001
Fe	= 0.05 - 0.1
Mg	= 0.01 - 0.1
Ni	= 0.001
Sb	= 0.001 - 0.01
Si	= 0.01 - 0.1
Sn	= 0.001
V	= 0.001
Zr	= 0.05 - 0.5

Particle Size: -325 mesh + 10 microns

Micrographs--show extensive internal porosity

Average pellet density--93% of theoretical density

Surface area (BET)--~220 cm²/g

ZrO₂

Degussit Zr-23 CaO-stabilized ZrO₂^(a) (>98% ZrO₂); test specimens were cut from impervious tubing obtained from the manufacturer.

Porosity--gas-tight

Micrographs--show extensive unconnected internal porosity

Density--91% of theoretical density

Surface area (BET) of test specimens--~20 cm²/g

(a) Supplied by Alpha Products, Donvers, Maine.

ZrSiO₄ (ZIRCON)

ZrSiO₄ powder obtained from Cerac, Inc.; test specimens were prepared by hot-pressing ZrSiO₄ powder into pellets at ~1600°C and 5200 psi using graphite dies, then firing the pellets in air at ~1200°C for 24 h.

Purity 99% Analysis: Al 0.03 - 0.3%

Fe 0.01 - 0.1

Mg 0.001

Ti 0.03 - 0.3

Particle Size: -200 mesh + 10 microns

Micrographs of the pellets--show extensive interconnected internal porosity

Average pellet density--85% of theoretical density

Surface area (BET) of test specimens--~1120 cm²/g

GRAPHITE (TOYO)

Toyotanso Graphite IG-11[®] for HTGR; test specimens cut from a block of graphite obtained from the manufacturer.

Density--1.80 g/cm³

Micrographs--showed extensive interconnected external porosity

Surface area (BET) of test specimens--~10,000 cm²/g

PYRO CERAM 9617

Pyrocera 9617 glass-ceramic from Corning Glass Works; test specimens cut from a block of material supplied by the manufacturer.

Porosity--gas-tight

Micrographs--show very little internal porosity

Density--2.52 g/cm³

Surface area (BET) of test specimens--<10 cm²/g

MARCOR MACHINABLE GLASS-CERAMIC

Marcor Code 9658 machinable glass-ceramic from Corning Glass Works; test specimens cut from 8-mm-dia rod obtained from the manufacturer.

Water adsorption--none

Micrographs--show only very slight internal porosity

Density--2.52 g/cm³

Surface area (BET) of test specimens--<10 cm²/g.

[®]Toyo-Tanso Co. Ltd., Osaka, Japan

DISTRIBUTION

<u>No. of Copies</u>	<u>No. of Copies</u>
<u>UNITED STATES</u>	
A. A. Churm DOE Chicago Patent Division 9800 South Cass Avenue Argonne, IL 60439	J. B. Whitsett DOE Idaho Operations Office 550 2nd Street Idaho Falls, ID 83401
R. E. Cunningham Deputy Director for Fuels and Materials Nuclear Regulatory Commission Silver Springs, MD 20910	E. S. Goldberg DOE Savannah River Operations Office P.O. Box A Aiken, SC 29801
T. C. Chee DOE Office of Nuclear Waste Management Washington, DC 20545	27 DOE Technical Information Center
C. R. Cooley DOE Office of Nuclear Waste Management Washington, DC 20545	J. R. Berreth Allied Chemical Corporation 550 2nd Street Idaho Falls, ID 83401
Sheldon Meyers DOE Office of Nuclear Waste Management Washington, DC 20545	Allied Chemical Corporation (File Copy) 550 2nd Street Idaho Falls, ID 83401
R. G. Romatowski DOE Office of Nuclear Waste Management Washington, DC 20545	A. Williams Allied-General Nuclear Service P.O. Box 847 Barnwell, SC 29812
C. A. Heath DOE Office of Nuclear Waste Management Washington, DC 20545	J. L. Jardine Argonne National Laboratory 9700 South Cass Avenue Argonne, IL 60439
G. Oertel DOE Office of Nuclear Waste Management Washington, DC 20545	M. M. Steindler/L. E. Trevorow Argonne National Laboratory 9700 South Cass Avenue Argonne, IL 60439
A. F. Perge DOE Office of Nuclear Waste Management Washington, DC 20545	Wayne Carbiener Office of Nuclear Waste Isolation Battelle Memorial Institute 505 King Ave. Columbus, OH 43201
R. D. Walton DOE Office of Nuclear Waste Management Washington, DC 20545	J. Kircher Office of Nuclear Waste Isolation Battelle Memorial Institute 505 King Ave. Columbus, OH 43201
J. Neff, Program Manager Department of Energy Columbus Program Office 505 King Avenue Columbus, OH 43201	Beverly Rawles Office of Nuclear Waste Isolation Battelle Memorial Institute 505 King Ave. Columbus, OH 43201
John Van Cleve DOE Oak Ridge Operations Office P.O. Box X Oak Ridge, TN 37830	

No. of
Copies

J. W. Voss
Office of Nuclear Waste Isolation
Battelle Memorial Institute
505 King Ave.
Columbus, OH 43201

Brookhaven National Laboratory
Reference Section
Information Division
Upton, NY 11973

M. D. Boersma
E. I. duPont DeNemours and Company
Savannah River Laboratory
Aiken, SC 29801

J. L. Crandall
E. I. duPont DeNemours and Company
Savannah River Laboratory
Aiken, SC 29801

H. L. Hull
E. I. duPont DeNemours and Company
Savannah River Laboratory
Aiken, SC 29801

D. E. Gordon
E. I. DuPont DeNemours and Company
Savannah River Laboratory
Aiken, SC 29801

R. G. Garvin
E. I. duPont DeNemours and Company
Savannah River Laboratory
Aiken, SC 29801

D. L. McIntosh
E. I. duPont DeNemours and Company
Savannah River Laboratory
Aiken, SC 29801

J. A. Kelley
E. I. duPont DeNemours and Company
Savannah River Laboratory
Aiken, SC 29801

S. Mirshak
E. I. duPont DeNemours and Company
Savannah River Laboratory
Aiken, SC 29801

A. S. Jennings
E. I. duPont DeNemours and Company
Savannah River Laboratory
Aiken, SC 29801

H. Henning
Electric Power Research Institute
3412 Hillview Avenue
P.O. Box 10412
Palo Alto, CA 94301

No. of
Copies

Environmental Protection Agency
Technology Assessment Division
(AW-559)
Office of Radiation Programs
Washington, DC 20460

R. G. Barnes
General Electric Company
175 Curtner Avenue (M/C 858)
San Jose, CA 95125

Los Alamos Scientific Laboratory (DOE)
P.O. Box 1663
Los Alamos, NM 87544

J. P. Duckworth
Plant Manager
Nuclear Fuel Services, Inc.
P.O. Box 124
West Valley, NY 14171

J. G. Cline, General Manager
NYS ERDA
Agency Building #2
Empire State Plaza
Albany, NY 12233

Oak Ridge National Laboratory (DOE)
Central Research Library
Document Reference Section
P.O. Box X
Oak Ridge, TN 37830

E. H. Kobisk
Solid State Division
Oak Ridge National Laboratory
Oak Ridge, TN 37830

R. Roy
Pennsylvania State University
Materials Research Laboratory
University Park, PA 16802

W. Weart
Sandia Laboratories
Albuquerque, NM 87107

J. O. Blomeke
Union Carbide Corporation (ORNL)
Chemical Technology Division
P.O. Box Y
Oak Ridge, TN 37830

R. E. Blanco
Union Carbide Corporation (ORNL)
Chemical Technology Division
P.O. Box Y
Oak Ridge, TN 37830

No. of
Copies

D. E. Ferguson
Union Carbide Corporation (ORNL)
Chemical Technology Division
P.O. Box Y
Oak Ridge, TN 37830

H. W. Godbee
Union Carbide Corporation (ORNL)
Chemical Technology Division
P.O. Box Y
Oak Ridge, TN 37830

4 DOE Richland Operations Office

P. A. Craig
R. B. Goranson
H. E. Ransom
M. J. Zamorski

8 Rockwell Hanford Operations

L. Brown
R. A. Deju
M. J. Kupfer
E. L. Moore
G. Reep
M. J. Smith
D. D. Wodrich
File copy

Exxon Nuclear Company

S. J. Beard

2 Westinghouse Hanford
Company

A. G. Blasewitz
D. A. Cantley

79 Pacific Northwest Laboratory

S. M. Barnes
W. J. Bjorklund
H. T. Blair
W. F. Bonner
R. A. Brouns
J. L. Buelte
L. A. Chick
R. D. Dierks
R. L. Dillon
H. T. Fullam (20)
M. S. Hanson
A. J. Haverfield
M. H. Henry (3)
L. K. Holton
J. H. Jarrett
A. B. Johnson

No. of
Copies

Pacific Northwest Laboratory
(contd)

D. E. Knowlton
C. A. Knox
M. R. Kreiter
W. L. Kuhn
D. E. Larson (2)
J. L. McElroy (3)
G. B. Mellinger
J. E. Mendel
M. D. Merz
F. A. Miller
T. Nelson
R. E. Nightingale
R. D. Nelson
D. E. Olesen
K. H. Oma
C. R. Palmer
P. J. Pelto
A. M. Platt
D. L. Prezbindowski (2)
W. A. Ross
J. M. Rusin
R. J. Serne
D. H. Siemens
S. C. Slate
C. L. Timmerman
R. T. Treat
R. D. Westerman (5)
Technical Information (5)
Publishing Coordination EI(2)