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NRC NUCLEAR WASTE MANAGEMENT TECHNICAL SUPPORT IN THE DEVELOPMENT OF NUCLEAR WASTE FORM CRITERIA:

TASK 4: TEST DEVELOPMENT REVIEW

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NOTICE

ABSTRACT

This interim report concerns the development of testing procedures to assess the performance of waste packages to be used for high level waste disposal in geologic repositories. Single component testing of the waste package is determined to be a workable strategy for testing and evaluation in terms of NRC release rate criteria. An initial literature review has identified key tests and those variables which must be included in testing procedures to simulate repository conditions. The range of these conditions remains to be determined precisely. Methods for leach, corrosion, and sorption testing are reviewed and initial recommendations made for preferred procedures. A combination of static and dynamic tests are needed to evaluate waste package component performance. Additional research is necessary in certain areas both to establish reliable testing methods and to define the range of testing variables. Research recommendations are included in the report. Ancillary measurements will be required to ensure that key tests rigorously assess the durability of waste package components under anticipated repository conditions. In particular, radiation effects in the repository environment must be considered and, where necessary, simulated during critical testing. Research is recommended to aid in determining when and how this should be done.

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TEST DEVELOPMENT REVIEW

1. INTRODUCTION

Minimizing the release of radionuclides to the environment is a prime consideration in the design of a high level waste repository. Design emphasis in the past was placed on radionuclide containment by the geologic media. The concept of multiple engineered barriers to radionuclide migration[1,2] represents the current approach in considerations of repository design. In a repository, the "waste package" comprises the waste form (containing the radionuclides), the surrounding container or canister, the overpack-backfill, and any other engineered barriers placed around the canister. In order to include interactions with the immediate surrounding host rock, it is reasonable to consider that the waste package should also include the adjacent geologic media to a depth of at least several inches. We also assume that waters from the surrounding environment will contact the waste package after emplacement.

Radionuclide release rates for the waste package are being considered by the NRC as tentative operational criteria to be met by a proposed package. These "strawman" criteria at present are:

> "The waste package is required to contain the radioactive materials for 1000 years and as long thereafter as is reasonably achievable... Beyond that period of time, the engineered system is required to maintain releases as low as is reasonably achievable but less than one part in one hundered thousand per year."[1]

A proposed waste package must demonstrate compliance with these criteria before it can be put into use. Such a demonstration will involve extensive testing and evaluation.

Our initial veiws on the testing of the waste package components are based on two objectives:

1) to identify the types of tests required to evaluate waste package performance for compliance with NRC proposed criteria;

2) to recommend both specific tests to be used and, where required, the research needed to develop and implement these tests.

This study does not consider all types of quality assurance tests which should be used to characterize the components of the waste package. Only those tests which directly bear on radionuclide release are considered here.

The scope of this task will be to:

1) Identify the types of tests required. Single component testing of the waste package components will be considered initially.

2) Define the variables in testing methods that are needed to obtain the necessary data for evaluation. These include, for example, environmental parameters, radiation effects, problems of accelerated testing, and extrapolation of test results.

3) Anticipate and evaluate synergistic effects of test variables as well as physical chemical and mechanical interactions between individual components of the waste package.

4) Review the state of knowledge concerning the tests identified earlier and evaluate the existing methodology with respect to the needs identified in 1 and 2 above.

5) Make recommendations concerning specific test methods, and research necessary to fill technological gaps in test methods and interpretation identified in 1 and 3 above.

This draft will initiate a review on leach, corrosion, and sorption testing in terms of methodology and interpretation. Preliminary evaluation and recommendations will be presented in each section. Section six begins our evaluation of radiation effects. Recommendations presented in this draft are preliminary and consist of two types: (1) recommendations concerning testing strategy and methodologies and (2) research areas where effort should be placed to fill gaps identified in the state of knowledge. Testing methodology recommendations are discussed in each section and summarized in the final section. Section seven discusses research needed to support testing procedures identified previously and also summarizes general testing recommendations from the individual testing sections.

1.1 References

1. Code of Federal Regulations, 10CFR60, "Disposal of High-Level Radioactive Wastes in Geologic Repositories," (Proposed), Advance notice of proposed rule making. Available from the Nuclear Reuglatory Commission, Washington, D.C.

2. Interagency Review Group on Nuclear Waste Management, "Report to the President by the Interagency Review Group on Nuclear Waste Management," TID-28817 (Draft), October, 1978. Available for purchase from National Technical Information Service, Springfield, VA 22161.

2. GENERAL TESTING CONSIDERATIONS FOR WAST PACKAGE EVALUATION

2.1 Introduction

This section treats general aspects of testing. Major test areas for the package components are identified, and the question of selecting variables to simulate the natural environments of repositories are considered. Interpretation of the test results is also considered, with emphasis on the problems of scaling and extrapolation.

2.2 The Waste Package

A schematic of one form of a "waste package" is given in Figure 2.1. At the center is the waste form, which contains the radioactive waste. This component is enclosed in a container around which is placed an overpack consisting of one or more absorbent materials. The overpack and backfill insulate the container from direct contact with the walls of the emplacement cavities within the repository. The final component of the package is the repository host rock.

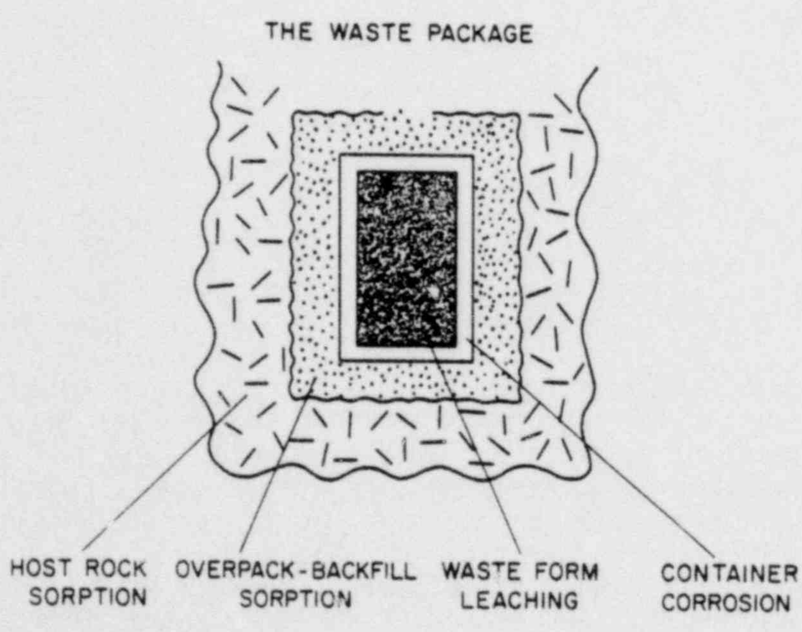

Figure 2.1. Schematic diagram of the waste package.

As presently considered, the waste package includes the repository host rock to a depth of several inches; but this depth is somewhat arbitrary. The host rock is included so that interactions between it and the remainder of the package will be part of any operational evaluation of package behavior.

The multiple barrier construction of the waste package serves two functions. First, the overpack and container shield the waste form from contact with water originating from the environment surrounding the package. Second, should any radionuclides be released from the waste form, these barriers and the host rock are designed to retard migration of radionuclides beyond the boundary of the package.

The various combinations of waste form-container-overpack and host rock which have been considered are given in Table 2.1. A final selection will be based on future research and development along with critical testing.

Table 2.1

Waste Package Component Options

Waste Form	Container	Overpack-Backfill	Host Rock
glasses	copper	clays	rock salt
calcines	lead	zeolites	granite
ceramics	steel	exchange resins	basalt
SYNROC	titanium	ground host rock	shale
coated particles	new alloys	cements	
cements			
matrix forms			

2.3 Whole Package Vs. Single Component Testing

The prime concern in testing the waste package is to determine the radionuclide release rate. At present, it is not practical to test entire packages under simulated repository conditions. Necessary information is lacking on both repository environmental parameters and on the large number of possible package combinations. At this time, single component testing offers a more manageable strategy in that individual component performance can be evaluated relatively rapidly. After elimination of unsatisfactory materials, *in situ* repository testing under actual field conditions would then be carried out on specific candidate packages.

2.4 Multicomponent Testing

Some mechanical and physical tests will require that combinations of components be tested together. Mechanical strength and thermal conductivity are two specific examples where multicomponent testing would be required. In particular, the mechanical strength of the container-waste form combination under stress is an important behavioral property since potential fracturing is of concern in repository engineering design, as well as radionuclide release.

The same reasoning applies to thermal conductivity measurements. Heat generated by the radioactive wastes may affect corrosion rates and sorptive behavior in the surrounding components. These tests are considered ancillary to the main testing areas to be described.

2.5 Single Component Testing

To evaluate package component behavior in terms of the proposed release rates, those tests which bear directly on radionuclide release or retention are of principal concern. Figure 2.1 lists the processes which result in release or retention of radionuclides for each of the package components. For the waste form, leachability is the prime concern. Other properties are of importance, but to a lesser degree. For example, the mechanical strength will determine if the waste form will fracture or disintegrate easily, thereby exposing more surface area for leaching.

For the container, the most important process is breaching by corrosion. How fast the container is breached will determine when the waste form is subjected to leaching by waters from the surrounding environment. Movement of released radionuclides away from the waste form will also be affected by the condition of the corroded container.

The sorptive properties of overpack-backfill and host rock materials will control retardation of radionuclides which escape the waste form and container barriers. As in the case of the waste form, other properties will have some influence in this process. The mechanical strength of the host rock is of some concern, since fracturing of the media will provide pathways for radionuclide bearing waters to rapidly escape beyond the package boundary, essentially short circuiting the sorptive barrier. Here again, the sorptive behavior is the area of prime concern.

In the final evaluation of the package performance, the "strong link" in the chain of components will determine the total release rate. For example, a particular waste form may have a higher leachability than another form, but still be acceptable for the package, if the other components can be shown to retard the migration of released radionculides to within the required limits. A conservative approach to package design would require that each of the individual package components meet or exceed proposed standards. This would assure that the entire package will readily satisfy performance requirements if no detrimental interactive effects occur. Such a conservative approach would require minimum leachability and corrosion rate standards for the waste form and containers respectively. Overpacks and geological media would have to show high sorption capacities, and selectivity for particular ions. The limits for these individual standards would be based on existing and future research.

The disadvantage of single component testing is that synergistic effects cannot be tested directly. These effects can only be anticipated (see section 2.6.4) and the test conditions modified accordingly.

2.6 Testing Variables and Interpretation

In our attempt to design testing methods, the two important immediate considerations are the selection of variables to be included, and interpretation of the resulting data. An ideal test would include all the pertinent variables at realistic magnitudes and time spans. However, this ideal test may be impossible, or extraordinarily difficult, to develop. For this reason, and for experimental convenience, leach, corrosion, and sorption tests reported in the literature were frequently performed with an arbitrarily limited number of variables. One parameter is varied at a time, often with little concern for simulating expected natural conditions. An examination of the literature in these test areas will reveal the most important variables to be included in a thorough testing method.

Interpretation of the test results is a more difficult problem. Test results should be evaluated in light of the variables used in the testing methods, as well as the test methods themselves. Interpretation also involves questions of analytical sensitivities in the measurements, as well as scaling and extrapolation of the data.[a] A more thorough study of the literature in these areas is required to deal with these questions.

2.6.1 Variables-Simulating the Natural Environment

In testing the waste package components, the samples should be subjected to conditions expected in the repository environment. A survey of the literature reveals the following areas of concern in this respect.

2.6.1.1 Media Composition

Comparison of test results using a variety of similar generic materials often show unacceptably wide variations. For example, corrosion study results (Table 2.2) showed as much as an order of magnitude variation when the liquid phase was changed from sea water to brine. Another example is given in Table 2.3 which lists sorption coefficient results (K_d) obtained for a variety of soil samples and "generic" groundwaters. The results show that the observed sorption varies as a function of both the liquid and solid phase compositions. Numerous other examples can be found where test results are apparently unknown functions of compositional variables such as pH, redox potential, particle size, etc.

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[a]Scaling involves prediction based on increased sample sizes, namely extending results from small laboratory samples to actual field size materials. Extrapolation is used here to denote predictions based on the extension of test result trends as a function of time.

Table 2.2[2]

Corrosion Rates of Candidate Alloys in Oxygenated Solutions

(250 °C and P = 7 MPa, t = 14 days)
(O_2) = 600 ppm in Brine A and 1750 ppm in Seawater

Alloy	Brine A (mm/yr)	Seawater (mm/yr)
1018 Mild Steel	7.0	11.0
Copper	1.2	5.0
Lead	1.2	1.0
90-10 Cupronickel	0.4	0.7
SS-Ebrite 26-1	0.24	---
SS-20CB3	0.1[b]	---
Inconel 600	---	0.1
Hastelloy C-276	0.06	0.2[a]
Ticode 12	0.0004	0.0006

[a]pitting and crevice corrosion.
[b]crevice corrosion.

Table 2.3[3]

Cesium K_d Values for Seven Glaciofluviatile Sediments
and Various Solutions (pH = 12)[a]

Sediments	Solution I	II	III	IV	V
1. Silt	13.41	6.00	1.80	0.85	12.02
2. Gravelly Sand	9.37	3.47	1.37	0.61	7.14
3. Sand	9.06	3.42	1.27	0.58	7.21
4. Silty Sand	8.11	3.08	1.37	0.73	.68
5. Caliche	10.93	3.70	1.83	2.92	11.30
6. Silty Sand	7.88	2.04	0.93	1.20	7.97
7. Gravel	8.74	2.79	1.14	1.47	9.49

[a]Data shown was determined by Serne, 1973, and reported in Ref. 3, p. 3-55.

For reliable test results, liquid phases should duplicate the expected ground waters in the repository environment. Samples of these natural waters should be used, or simulated groundwaters prepared based on reliable analytical data. The solid materials should be actual samples not "generic" simulations. The use of "generic" materials should be avoided whenever possible.

2.6.1.2 Flow Rates-Contact Time

Contact time variations will affect the release and subsequent movement of radionuclides from the package. In the repository, groundwaters will contact the package components for varying times depending on a number of environmental factors, such as permeability of the host rock, temporal variations in the thermal field, etc. The contact time, or flow rate, is the most difficult variable to estimate because it will be controlled by site specific conditions that are not easily predictable. Data from site-specific field tests may provide information useful for rough predictions of expected hydrologic conditions. Existing testing methods have not included adequate techniques to gauge this effect.

Test methodologies for leaching, corrosion, and sorption (discussed in more detail in the succeeding sections) involve static and dynamic procedures. Static tests maintain continual contact between the same solid and liquid phases during the duration of the test, while the dynamic tests involve contact with a continually renewed aqueous phase. A conservative approach to testing would require both static and dynamic testing to be performed on the package components. Dynamic tests should use flow rates which span the best available predictions of *in situ* rates.

An example of the potential effect of flow rate (contact time) on test results is illustrated in Table 2.4, for the results of a dynamic leaching test performed on a glass. For two flow rates, the differences in radionuclide activity (fractional) released ranged from insignificant (for cesium) to an order of magnitude (for cerium).

Table 2.4

Dynamic Leach Test Results on a Melt Glass
Taken from Coles, et al.(4)

Flow Rate (mL/day)	Test Duration (days)	$R \times 10^4$ ($M^{-2}d^{-1}$) - Fractional Release			
		Mn	Co	Cs	Ce
185	120	0.41 ± .05	.39 ± .04	3 ± 1	0.48 ±.09
35	120	.24 ± .03	.23 ± .03	2.5 ± .8	0.07 ±.04

2.6.1.3 Time

The duration of a test often determines the results observed. For example, sorption measurements (K_d) for cesium often show a pronounced time dependency (Table 2.5). Testing must be continued long enough for apparent steady state conditions to be established. Steady state results are also required for scaling and extrapolation of test results.

Table 2.5

Cesium Sorption Results - K_d vs. Contact Time
Taken From Erdal, et al.[5]

Sorption Test Duration (days)	Sorption Ratio (K_d,mL/g)
6.75	1320
16.75	1370
27.77	2350
58.77	2740

2.6.1.4 Temperature

As in the case of time, test results may also be affected to a significant degree by temperature. The temperature in and around the waste package will vary as some function of the component's thermal conductivities, the waste loading and decay rate. Consequently, leaching, corrosion, and sorption processes may take place above ambient repository temperatures. Sorption data listed in Table 2.6 illustrates the effect of increased temperature on technecium and cesium behavior.

It should be relatively easy to predict the likely temperature range in the immediate package environment, given initial waste loadings, thermal conductivity and heat capacities of the materials. However, it is not possible to predict at what point in the thermal history of the package it will be subjected to extensive leaching and corrosion, or at what temperature sorption reactions will take place. Consequently, testing should be performed at a number of temperatures to obtain data which span the best predictive estimates of the *in situ* conditions.

2.6.1.5 Radiation

Radiation is known to produce structural damage in a variety of materials, influence diffusion rates, and cause chemical reactions (radiolysis). These effects will be discussed in more detail in a later section. For testing purposes, it must be determined if a radiation field influences the results to a significant degree. Table 2.7 lists leach data for irradiated and unirradiated

Table 2.6

Technecium and Cesium Sorption Results at 20 °C and 70 °C
Taken From Erdal, et. al.[5]

Temperature	Sorption Ratio, K_d(mL/g)	
	Tc	Cs
20	16.2	2740
70	1.06	765

Table 2.7

Comparison of Leach Test Results for Gamma-Irradiated and Unirradiated Samples
(D.I. Water, ~ 90 °C, 209.5 hrs, V/SA Ratio = 10/1
Modified From Rusin, et al.[6]

Element	Gamma-Irradiated[a] 7668 Glass DIW[b] (87°C)	Unirradiated 7668 Glass DIW (89°C)	Gamma-Irradiated Supercalcine DIW (89°C)	Unirradiated Supercalcine DIW (89°C)
Si	40.5[c]	21.0	10.6	2.5
B	7.9	4.6	1.3	0.2
P	1	0.1	1	0.05
Al	1	0.1	1	0.1
Ca	4.3	1.0	1.8	0.1
Sr	0.7	0.2	4.1	0.4
Ba	0.7	0.1	3.0	0.6
Mg	0.5	0.05	0.5	0.1
Li	0.5	0.05	0.5	0.05
Na	60	18.5	30	1.9
Cs	1.8	2.4	2.7	1.6
Mo	4.0	2.6	16.6	1.5
Fe	1	0.1	1	0.1
Co	0.1	0.01	0.1	0.1
Ni	0.4	0.01	0.4	0.1

[a]Dose ratio was 2.4×10^6 R/hr; total dose was 7.4×10^8 R.
[b]Deionized water.
[c]All numbers are in ppm.

glass and supercalcine samples. This data indicates that irradiation causes differing leach behavior. Another significant question is how radiation effects can be simulated in testing procedures. The container, overpacks and host rock will be exposed primarily to gamma radiation while the waste form will also be exposed to alpha and beta radiation.

2.6.2 Analytical Sensitivities

The degree to which test results can be applied to the repository field situation depends upon how well the data can be scaled and extrapolated. These data manipulations in turn are dependent upon the analytical sensitivities of the test measurements. For example, Flynn, et. al. (7) state that leach rates as low as 10^{-8} g/cm^{2}day can be measured using a combination of neutron activation and gamma counting. They suggest that this limit can be extended to the range of 10^{-10} g/cm^{2}day by increasing sample size and/or neutron fluence. These leach rates are orders of magnitude lower than those measurable by other analytical techniques. In the case of sorption testing, radionuclides with either very high or low distribution coefficients will contain small concentrations in the liquid or solid phases respectively. Therefore, sample sizes and measurement techniques must be adjusted to give maximum analytical sensitivity. Clearly, the analytical methods used for measurements should be as sensitive as possible in order to produce the most useful data.

2.6.3 Scaling and Extrapolation

The questions of scaling and extrapolation are more difficult areas to address than variable selection or measurement sensitivities. For tests in which apparent steady state conditions are established for a given set of experimental conditions, it is a relatively simple matter to extend the data as functions of sample size (scaling) or time (extrapolation). However, applying these predictions directly to the field situation where many variables are operative is not as straightforward.

Two approaches to the scaling and extrapolation problem can be taken. The first is empirical in nature. A number of extrapolations can be made using experimental data sets. For example, leach tests performed as functions of temperature, flow rates, radiation doses, etc., can be individually extrapolated. These estimates will hopefully span the field situation with high and low estimates. A large amount of experimental data exists in the principal testing areas, and predictions based on the empirical approach can make use of this.

The alternative approach involves examining mechanisms for the leaching, corrosion, and sorption processes. By determining fundamental process parameters such as activation energies, diffusion coefficients, and adsorption isotherms, predictions can be made on a theoretical basis. For this approach, existing experimental data require evaluation in terms of the mechanistic information that can be obtained from these results. If values for the process parameters are shown to be consistent when derived via different sets of experimental data, the mechanisms operative in these experiments are the same. These parameters can be used in turn for theoretical predictions. Also, additional studies required to supply mechanistic information necessary for predictions can be more easily identified. Laboratory testing would still be required to check the predictions, but the large data base necessary for the emprical approach is not required.

Relatively little effort has been invested in this approach. This avenue should be pursued more closely not only as an alternative to the purely empirical approach, but also as a confirmatory tool for these predictions. For example, if mechanisms operative in leach tests performed as functions of temperature or flow rate are shown to be the same, extrapolation of results to other conditions are more reliable.

The large number of generic studies on leaching and sorption behavior can supply the data base necessary to test scaling and extrapolation methods. Results from short term leaching studies can be used to predict longer-term behavior and then compared against the results of longer duration leaching studies reported in the literature. In a similar manner, sorption studies using single mineral species, or generic soil and rock types, can be used to predict sorptive behavior under different conditions. These predictions can then be compared against published results for sorption experiments done under these conditions. Little effort has been directed along these lines, with the exception of sorption studies.[8] The extent of these scaling and extrapolation studies will be limited because many studies cannot be compared easily due to differences in experimental design. However, more effort should be directed into this area to make better use of the generic study results.

2.6.4 Synergistic Effects

Another aspect of testing and interpretation is the possibility of synergistic effects, not only between variables, but also between components of the waste package. For example, container corrosion and waste form leaching will release metallic ions to solution, which in turn may be sorbed by the overpack material preferentially, relative to the radionuclides . This preferential sorption would decrease the efficienty of the overpack in retarding radionuclide migration. In anticipation of this synergistic effect, the sorption test conditions, and their applications, would require the following modifications. The ions released to solution due to container corrosion and waste form leaching should also be included in the liquid phases used to measure the overpack sorption capacity and selectivity. Calcluations to determine the thickness of overpack material surrounding the container would have to consider the decreased retardation efficiency if sorption studies demonstrate that container corrosion products produce a significant effect. Another synergistic effect may result from helium generation in the waste form. Gas generation within the container may result in stress corrosion behavior.

Small "model" waste packages could be constructed and tested under simulated environmental conditions in an effort to identify any synergistic effects which may be operative (see research recommendation 7.1.3).

2.6.5 Summing the Parts

The final product of single component testing is a collection of data unique to each of the components. Corrosion and leach rates are reported (Table 2.8) as functions of time, while sorption results are only indirectly related to time. These results must then be combined to produce a release rate for the total waste package. Here again, more than one approach can be taken. In each of these approaches, an initial radionuclide loading in the waste form must be assumed before the data can be evaluated in terms of release rates.

Table 2.8

Units of Measure for Leach Corrosion and Sorption Testing

Component Test	Parameter	Units
waste form-leaching	mass leach rate volume leach rate fractional leach rate	$g/cm^2/day$ cm/day $(cm^2hr)^{-1}$
container corrosion	mass corrosion rate volume corrosion rate	g/day cm/day
host rock-overpack sorption	sorption coefficient (K_d)	mL/g

The most conservative approach would require that all of the components pass individual standards high enough to meet or exceed the total package relase rates. This would require waste form leachabilities to be low enough so that their release rates satisfy the total package requirements. Containers must resist breaching for a thousand years, and the sorptive capacity of overpacks and host rocks must be high enough to contain the entire waste package radionuclide inventory which must be known. This approach would assure that the whole package standards are met, and also avoids the problem of integrating single component test results into a whole package release rate. Such an approach may be excessively demanding however.

The "strong link" approach mentioned earlier (Section 2.5) would allow one or more of the components to fall below the standards for the whole package. The waste package would be acceptable as long as at least one component can be demonstrated to meet, or exceed, the total package release rate. This approach also avoids the problem of integrating data from component tests into a whole package release rate.

If the "strong link" approach cannot be used, the integration problem is unavoidable. In order to safely predict whole package behavior in this case, the testing of each component should be more extensive than otherwise necessary. For example, to integrate sorption results with container failure and leaching releases, the adsorption isotherms for overpack and host rock materials must be well defined. Leach rate data in terms of flow rates and temperature must be extensive. Also, container breaching by corrosion must determine not only the time necessary for failure, but also the dimensions of the resulting openings as a function of time. These openings will control the rate at which water leaches the waste form, and the rates at which radionuclides migrate into the sorptive barriers. Sorption calculations must assume a set of conditions for waste form and container behavior in terms of leaching and corrosion. The difficulty with these calculations is that the assumed conditions are very difficult to predict reliably. Various alternative scenarios would be required necessitating an extensive modeling effort. Modeling the behavior of the whole package based on experimental data for single component testing also requires an assumed waste form loading.

The conservative approach would be most desirable to assure compliance with the NRC criteria. However, if materials cannot be found to satisfy the requirements, more difficult modeling efforts are necessary. Such efforts can be initiated before all the experimental data is accumulated. (See recommendation 7.1.2.)

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3. LEACH TESTING

In terms of radionuclide release, leachability is a primary concern for evaluating the performance of candidate waste forms. This section concerns the methodologies, variables, and test result interpretations involved in leach testing.

3.1 Test Method Review

In this section, various test methods are reviewed and recommendations made concerning preferred testing procedures. The largest volume of leach data reported in the literature concerns glasses, comparatively little work has been done on other waste forms. A summary of leach rate data (Fig. 3.1) for most waste forms has been provided by McElroy and Burns.[1] Very little information is published on the leaching behavior of SYNROC[2] and coated particles, but their leach resistance is anticipated to be quite high.

3.1.1 Test Methods

Leach tests can be grouped loosely into two classes, either static or dynamic tests. Some methodologies contain elements of both static and dynamic procedures, namely the IAEA leach test and its numerous modifications. Particularly good summaries of leach test methods are given by Mendel[3] and Flynn, et al.[4]

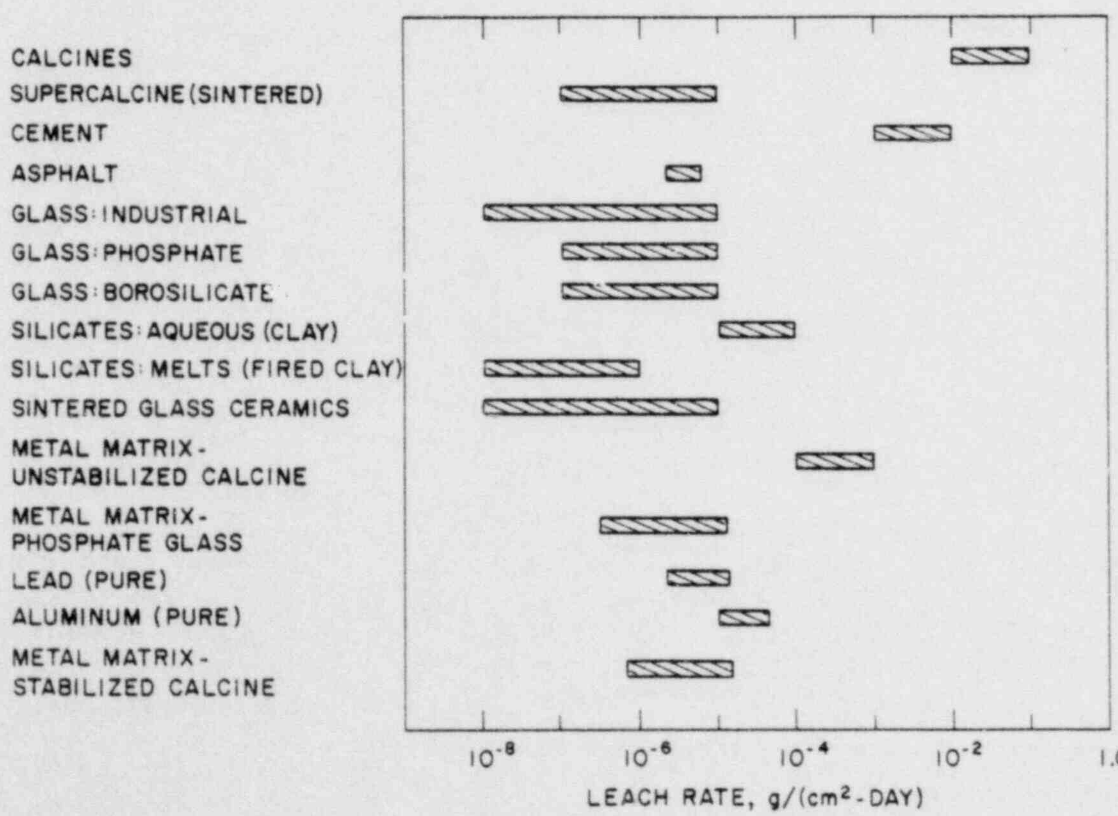

Figure 3.1. Comparison of leach rate data for various waste forms[1]

The various leach test procedures are briefly described below.

• Static tests - these tests involve leaching in a closed system where contact is maintained between the sample and the same leachant for the duration of the experiment. Static tests are frequently used as a screening device prior to more elaborate testing procedures.

• IAEA procedure - this is an essentially static system; however, the leachant is periodically replaced giving the test a dynamic aspect. The original procedure[5] has been modified many times in terms of operational aspects (sample sizes, leachant replacement intervals, etc.). In one form or another, this is the most widely used leach test, both in this country and abroad.[3]

• Soxhlet type tests - these are dynamic tests in a closed recirculating system wherein a continual stream of leachant contacts the sample. Two variations have been developed.

(1) The classical soxhlet apparatus collects leachant in a resevoir below the sample which is kept at the boiling point. Water vapor from the resvoir is condensed and drips over the sample continually. A modification of this apparatus employs a resevoir to collect the distillate before it is recirculated over the sample, allowing a measure of temperature control of the leachant.[6]

(2) In the Paige apparatus,[7] an airlift recirculator is used to cycle the leachant between the reservoir and the sample.

In the first case, the leachant is always distiled water; the leach products concentrate in the reservoir. In the Paige apparatus, the leachant plus leach products are recirculated over the sample.

• Continuous leaching - these are dynamic procedures of various types. A large resevoir of leachant is used and either a one-pass circulation system employed,[8] or a multi-pass system in which case exchange columns are put in line to remove material leached from the samples.[3,9] The leachates are analyzed directly in the one pass system, whereas in the multipass system, the leachates are flushed from the exchange columns for analysis. The general character of these tests are similar to the soxhlet type systems, except much larger in scale.

Most of these procedures involve a compromise between ideal simulations of natural conditions and experimental convenience. The thermally driven soxhlet and multi-pass continuous flow procedures, are of necessity restricted to distilled and deionized water leachants respectively, neither of which simulates natural conditions. The IAEA family of tests also uses pure waters frequently. In the IAEA tests, replacing the leachant solution is an attempt to simulate flow rate conditions in the natural situation and to accelerate the test. However, the flow rate simulation is very poor and the "acceleration" aspect of the test is impossible to quantify. Dynamic procedures, which involve recirculating leachates [air-lift (Paige) recirculating soxhlet and multi-pass continuous flow procedures] simulate flow conditions more closely, but the accumulated leach products are thought to have an inhibiting effect on further leaching.[3]

The single-pass continuous flow procedure[8] appears to have the most experimental flexibility for allowing realistic simulation of natural conditions. Resevoir waters can be tailored to match any composition expected in the repository, and flow rates can be as fast or slow, as desired. Temperature, pressure, and radiation conditions can also be included in the test. This procedure is recommended because of these strong points.

A number of proposed waste forms are of the multibarrier type, consisting of the radionuclide host and "barrier" overcoating and/or matrix phases. In testing these forms, the same strategy advanced for multi-component waste packages should be adopted. Namely, it is the penetration of the barrier phases which is significant, while leaching is expected to be the principal failure mode of the radioinuclide host phase of these composite waste forms. There is an interrelationship in that leaching behavior may depend upon the manner in which the barrier is penetrated. Adequate testing requires that the penetration modes of the barrier systems be understood. Following this, leach tests should be performed on the radionuclide host phases. This may require artificially penetrating the barriers before measuring the leachability.

3.1.2 Standardized Leach Tests

Attempts have been made to establish a standardized leach test,[5,10] but the proposed procedures are variation of the IAEA test method. Poor reproducibility has plagued these standardization attempts,[3] probably due to difficulties in experimental design, materials characterization, and understanding of the leaching mechanisms. However, these tests may be of use as screening devices prior to selecting materials for more extensive testing.

One standard leach test to evaluate candidate waste forms does not appear feasible, because conditions in the repository can be difficult to predict with certainty (particularly flow rates, see section 2). Environmental conditions will also change during the repository lifetime making it necessary to perform tests under a range of condtions for temperature, flow rates, etc. The flow rate problem is the most difficult variable to simulate. A static test would approximate the situation where water movement in the waste package is extremely slow, while dynamic procedures simulate faster flow conditions.

For evaluating waste form performance under the range of expected conditions, we recommended that a static test and a dynamic test be performed. The single-pass continuous flow procedure appears to be the most useful dynamic test. Test conditions should span those expected in the repository environment. The variables to be included in these tests are discussed in the following section.

3.2 Variables

The variables which may effect the leach rate behavior of candidate waste forms are the same as those already described in section 2. The recommendations in these catagories are given below.

3.2.1 Media Composition

Leach tests described in the literature use solutions varying in composition, from deionized water, through "generic groundwaters," to waters recoverd from specific natural environments. The form of the solids leached also varies from finely ground powders, through small blocks or clyndess of representative materials, to full size forms used in field tests. Inconsistencies in leachant compositions and the solid materials make extensive inter-comparisons of published test results very difficult. Without more controlled testing, only general comparisons can be made.

Leach rates for identical materials are known to be affected by the compositon of the leachant.[11,12] Leach rates for individual elements vary in the same material, and as functions of temperature.[4,8,11,13,14] In light of these observations, leachants should duplicate waters expected in the repository, and samples should be the actual waste form compositions. "Generic" waters and simulated waste form samples should be avoided whenever possible for final testing.

For the most reliable results, the waters should also be equilibrated with the overpack-backfill material prior to contacting the samples. In the field situation, invading waters must also pass through these materials which may alter the composition of local groundwaters before they contact the waste form. By pre-equilibrating the lechants, this effect can be simulated in the lab. However, this procedure assumes that the overpack-backfill material has been selected. For initial testing this step may be omitted, but for final testing an effort should be made to incorporate this procedure.

3.2.2 Time

Leach data typically show high leach rates for the initial portion of the test followed by a more gradual decrease, often approaching a constant rate with time. Some fluctuation in leach rates with time have also been observed,[11,12] and attributed to changes in leaching mechanisms or sample conditions. From studies of leaching behavior in glasses, it is believed that initial attack is not homogeneous, resulting in differential leaching, controlled by diffusion processes. Over the long term, the leaching behavior appears to be controlled by dissolution of the remaining glass framework.[12] Based on these observations, it is evident that leach tests be sufficiently long to establish steady state behavior.

Information on the long-term behavior of waste forms other than glass is not available at present. Such information is necessary before final testing of the forms can be performed. It is recommended that work be initiated on generic materials to supply the missing information. These studies must also attempt to illucidate leaching mechanisms. Once the general mechanisms are known some measure of assurance can be placed on long term predictions based on extrapolation of relatively short term laboratory tests.

3.2.3 Temperature

Increased temperature generally increases leach rate,[3,13] but this is not always the case[11]. It is recommended that leach tests be performed over the range of temperatures expected around the waste package during its lifetime.

Predicting the thermal properties of the waste package requires an initial assumption of the waste form loading, along with information on the thermal properties (thermal conductivities, heat capacities) of the form, container, overpack-backill and host rocks. Generic studies conducted in various areas may supply information useful in formulating these temperature predictions.

3.2.4 Flow Rate - Contact Time

This is the most difficult variable to predict for the reasons mentioned earlier. Single-pass continuous flow leaching of glass[8] showed unpredictable behavior when flow rates and temperature were varied. No information is avialable for other waste forms in terms of leachability and flow rate; however, their behavior should also vary in a similar manner. This aspect requires more detailed study.

Because of these uncertainties, a static test should be used to estimate the very low flow situation, and dynamic testing performed to measure the effects of higher flow. Flow rates for the dynamic testing should cover the range expected in the repository. This requires some assumptions concerning the waste package configuration (size, shape, loading, thermal behavior), and site-specific hydrologic characteristics around the repository site. Numerous regional geologic studies have been performed which may supply typical geohydrologic data useful for predicting expected flow rates.

3.2.5 Radiation

Radiation is known to produce damage in solids, and radiolysis in liquids, both of which may affect leachability (see section 6). Whether radiation effects can be simulated or not is still an open question. If radiation effects cannot be adequately simulated, the candidate waste forms would have to contain the actual radionuclide loading for reliable testing.

3.3 Test Result Interpretation

Measurements, sensitivities, and the units used to report the data will govern how the results are interpreted and the limits of extrapolation and scaling attempts.

3.3.1 Analytical Sensitivities and Units

Leach rate data are reported either as quantities of specific elements leached (g/cm^2 day), or as fractional releases relative to the waste form inventory. The element or elements measured must be unambiguously stated because leaching is an incongruent process. Fractional release rates are the most practical way of reporting data and easiest to use for comparison against quantitative release criteria rather than release rates.

The release rate data is normalized to the surface area of the test sample and equations to describe leaching behavior also contain a surface to volume term.[4,15,16,17] Typically, the geometric surface area is measured, which is lower than the actual surface area exposed to leachant solutions due to the microscopic irregularities in the sample surface. Part of the scatter in leach rate data may be due to this uncertainty. Various posimetry methods[18] may be useful for obtaining more accurate surface area data, rather than using geometric areas in the leach rate calculations.

In order to compare release rates with the NRC criteria, it will be necessary to obtain a measure of fractional inventory release. This may be obtained by multiplying laboratory leach rates by surface to volume ratios anticipated in the waste form <u>only</u> if the following conditions are met:

1. It is explicitly shown that the laboratory leach rate is sensibly independent of test sample surface area.

2. The same measure is used to obtain the surface area in test sample and waste form.

The appropriate measure for surface area is, by definition, that which leads to area independent leach rates. It is shortsighted to assume that the geometric area will provide such a measure in all cases. Leaching in crystalline waste forms could be dominated by grain boundary or dislocation related effects. Additional research is required to establish the appropriate measure for a particular waste form. (See recommendation 7.2.3.)

It has been suggested that leach test data be reported in terms of diffusion coefficients.[5] This assumes a mechanism which may not be operative in all cases (for example, glass vs. crystalline waste forms), or may change during the course of the test.[19] This idea may only be useful for comparisons of candidate materials of the same type.

Leach test data often shows wide variations for identical experimental runs,[3] particularly for glass samples. The most sensitive analytical techniques should be employed in any testing procedure along with statistical treatment of the test data. Rates as low as 10^{-8} g/cm^2 day can be measured in the laboratory with gamma counting. Flynn, et al.[4] report that neutron activation and gamma counting combined can extend this limit. The accuracy of measurements however, is greater than the reproducibility of testing results. Inductively coupled plasma (ICP), along with flameless atomic absorption techniques, are also possible analytical methods which may increase analytical sensitivities in situations where leach rates are very low.

3.3.2 Scaling and Extrapolation

Predictive models have been made to scale laboratory results to larger size samples.[15,16] These mode' have had only limited success, perhaps because they assume mechanisms which may not be operative.

Verification studies, using published results, would be useful to compare predicted results based on data from one study, with measured results from another. However, the uncertainty in leaching behavior and differences in the chosen variables and conditions may make this attempt very difficult or impossible. More effort is required in this area before laboratory results can be reliably scaled up to actual waste form sizes.

The fabrication process may also result n a full size product which differs from laboratory size samples in characte tics which may significantly affect !eachig behavior. For example, large si.. glass waste forms develop stress cracks during cooling.[20] This increase in exposed surface area may significantly affect leaching behavior, however, laboratory size samples cannot guage this effect. Scaling laboratory results without some means of evaluating this effect would produce questionable predictions. (See recommendation 7.2.3.)

For leach tests where apparent steady state conditions are established, it is a relatively simple matter to extend the results as a function of time, as long as the leach mechanism remains constant. The considerations of test duration (section 2.6.1.3), scaling and extrapolation (section 2.6.3) would apply.

Extrapolation of the test results also requires assumptions for the thermal history of the package, the behavior of other package components, and flow rates in the repository before long term release calculations can be attempted. Several calculations should be made based on a number of assumed values for these bounding conditions. Further research in this area is described in section 7.

Leaching measurements on waste glasses often indicate incongruent dissolution: relative release rates for radionuclides may be substantially lower than those for sodium or certain glassy matrix materials. The apparent retention of certain radionuclides in a relatively insoluble structure is encouraging; however, we feel that the consequences of incongruent dissolution have not yet been adequately addressed with regard to predicting long term radionuclide release. Taken to the limit, this incongruent dissolution process would result in a situation where the radionuclides are retained in a host phase altered by the selective removal of certain components. In such circumstances, it would be the properties of the altered phase, rather than the original glass, which would control radionuclide release. Very little is known about the properties of the insoluble structures resulting from the incongruent dissolution of waste glass (radiation damage susceptibility, for example, has never been studied to our knowledge). Actually, it is commonly anticipated that the incongruent dissolution will persist only up to a point at which time some dynamic balance is established; thereafter the relative release rates for all elements would be identical. However, it is not clear whether this would be achieved by a decrease in the release rate for host elements or an increase in the rate for radionuclides.

The observation of incongruent dissolution in waste forms implies that either the mechanism of leaching must change at some point, or the radionuclide inventory must be retained in an altered structure if extensive leaching occurs. Additional research is recommended (section 7.2.2) to determine which case is important in practice, and to investigate the durability of the altered structure. If such information is not obtained, one can not conservatively apply regulatory criteria to release rates for radionuclides measured in the presence of incongruent dissolution; the only alternative would be to regulate the release of the most volatile element in the waste form.

3.3.3 Acceleration

The IAEA procedure (section 3.1.1) and its various modifications are "accelerated" tests, but the effect is impossible to quantify because of flow rate uncertainties in the natural situation. Other means of accelerating leaching (increasing temperature, flow rates, agressiveness of the solution) also depend on the assuption of a mechanism and its constancy, which may be undemonstrable. Long term leaching experiments appear to be a more reliable alternative although time consuming. Durations in excess of a year are commonly required to determine the long range behavior of waste forms.

3.4 Recommendations

A combination of static and dynamic tests is recommended for reliable testing of the waste form leachability. Repeated testing would be required to cover the range of conditions expected in a repository. For example, the thermal behavior of the form will be a function of its loading primarily, as well as characteristics of the other package components. Consequently, a series of leach tests would be required, performed at temperatures which vary from ambient repository temperatures to slightly in excess of maximum levels. In a similar fashion, leach tests must be repeated for variation in flow rates and other variables to span the range of expected environmental conditions.

A survey of the literature reveals that the compositions of both liquid and solid phases affect leach rate behavior. For the most reliable results, the composition of the liquids should match that of the local groundwaters. If possible, they should also be pre-equilibrated with the overpack-backfill material before leaching is initiated. The solids should also be of the same composition as the actual candidate waste form. This implies that the form also incorporates actual waste loadings. Radioactive isotopes should be used in the loadings rather than nonradioactive substitutes for the most reliable results. However, nonradioactive elements may be used if radiation effects are shown to be insignificant for particular forms, or if radiation effects can be effectively simulated externally. The overwhelming majority of leach tests measure the release rates of fission products and other relatively short lived radionuclides. Only a small number of relatively recent studies measure the behavior of the long lived radionuclides. We recommend that these long half life isotopes be incorporated into future leach testing since these will be of major concern in terms of long term behavior of the waste package (see section 2.7, Task 1 draft report - R. Dayal, P. Soo, and K. Swyler).

The single-pass continuous leaching procedure appears to be the most realistic and flexible dynamic testing method. Liquid compositions can be tailored to duplicate any expected composition. Flow rates, temperature and radiation effects can also be incorporated into the experimental design relatively easily.

For static testing, a simple closed system is adequate as long as temperature and radiation conditions can be included. The same requirements for media composition described above apply to static testing also.

The duration of the leach tests must be long enough for steady state conditions to be established. These periods may well be in excess of one year, based on the long term leaching behavior of glasses. Little information is available concerning the long term leaching behavior of crystalline waste forms, however. Specifying the required length of a leaching test is not feasible without more detailed information in this area.

Laboratory leach tests commonly show initial leach rates (over the period of days to a few weeks) commonly two orders of magnitude higher than longer term leach rates after steady state conditions are established. Predictions of leach behavior are based on the steady state rates, however, rather than the higher initial rates. This is the proper approach for predictions of long term behavior over hundreds of thousands of years. However, after the container is breached, initial leach behavior may release radionuclides at levels which will exceed the 10CFR60 release rates for short periods - probably a period of several years or less. Such a sudden pulse will be of very short duration relative to the functional lifetime of the package and pose no serious environmental impact since the fractional release is high for a short time only. The sorptive barrier may contain the radionuclides released during the initial rapid leaching of the waste form, but this is a function of the whole package design. If this is the case, no pulsed release will escape the package. We recommend that the release rate criteria (either for whole pakage release on waste form leachabilities) be structured so that this short term rapid release does not violate the criteria.

Studies should be initiated on, (1) the long-term leaching behavior of crystalline waste forms (see research recommendation 7.2.1), (2) analytical methods for size scaling of test results from laboratory size samples to full size forms and, (3) confirmation studies comparing predicted results from short duration tests against measured results from long term tests (see research recommendations 7.2.2 and 7.2.3).

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4. CORROSION TESTING

Corrosion testing is the principal area of concern in evaluating the performance of potential container materials. The time at which the container is breached will determine the onset of waste form leaching, and the migration of radionuclides into the overpack and backfill.

- The container must have several basic requirements in order to meet the recent "strawman criteria" of near zero release for 1,000 years, as currently proposed by the NRC. These requirements were recently reviewed by Scott,(1) shown schematically in Figure 1 and summarized as follows:

- "Size - for spent fuel the containers will be about 5 m in length and 20 cm in diameter. For regular HLW the length may vary between 3-10 m and 20-30 cm in diameter.

- Sealing - container must be capable for being filled and sealed remotely. Sealing will probably be done by welding for metallic containers.

- Compatibility - the container must be compatible with the waste form and any transmutation products or volatile species which will contact the interior wall. The outer surface must be compatible with the interim storage environments and repository environments.

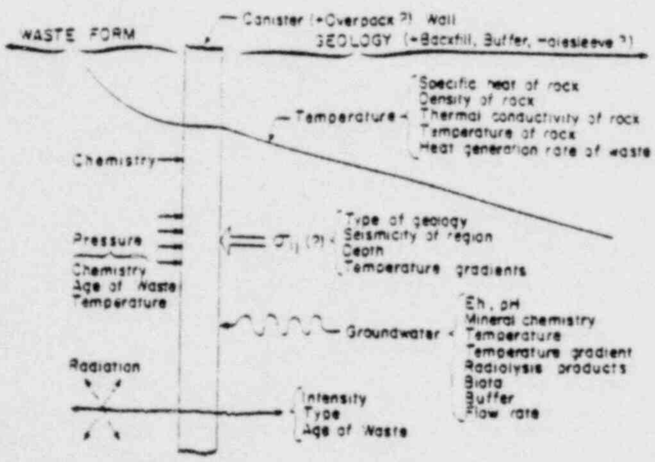

Figure 4.1. Schematic drawing of the contain r environment in a geologic repository.

• Temperature - for certain waste forms, such as glass, in-can melting temperatures will be approximately 1200°C for short times. Interim storage and repository temperatures will be much less and will depending on the waste loading and host rock.

• Mechanical strength and ductility - containers will be subjected to high thermal loads during in-can melting procedures and during welding. Metallic materials will usually possess ample ductility to accommodate deformation associated with these processes. Impact resistance is a necessary requirement for transportation accidents. For ceramic containers suitably designed packaging around the canisters must be employed to avoid impact failure."

In terms of the proposed release rates, if at least one of these components can prevent fission product migration from the waste package for the first 1000 years, the criterion will be met. Based on available data, it is anticipated that the container will be the principal means for meeting the 1000 year nearly zero release criterion. Lately, various types of waste forms, such as pyrolytic carbon coated waste also appear capable of meeting this criterion independently of the container(2).

Recent papers(3,4) have indicated that container materials are now available which may satisfy the 1000 year zero release criteria. Research in Sweden(3) indicates that either copper or lead can withstand the groundwater environment in igneous rock for periods of a thousand years or more. Results from tests performed at Sandia(4) indicate that a titanium alloy (Ticode A 0.3 Fe, 0.8 N, 0.3 Mo, bal. Ti) could withstand attack by some brine solutions for 300-600 years.

Corrosion tests performed on these materials were largely laboratory tests using solutions simulating those expected in a repository. The corrosion detected was generally a uniform attack, so that extrapolation to long times was readily made. In engineering applications, uniform corrosion is not always the case. More devastating types of corrosion can occur. Namely, pitting, intergranular, crevice or stress corrosion cracking. Because these corrosion modes are extremely penetrating and propogate rapidly once initiated, they are more severe. Conditions which could contribute to these types of corrosion may be stresses due to internal pressure generated by heat from the waste form, stresses from fabrication or transportation, crevices resulting from container manufacture or the presence of backfill, pit initiation sites from backfill, support members, impurities from the intruding water, etc.

To properly evaluate container materials, laboratory and in-situ tests must be devised to produce any of these severe corrosive conditions likely to be present in the repository. The test material's compositional homogeneity, surface roughness and cleanliness, as well as their condition of stress and heat treatment, must be considered since they can seriously effect localized corrosion. The corrosive media's chemical composition, temperature, gas content, and flow rate are a few of the factors which can effect localized corrosion.

4.1 Test Methods

Corrosion testing of high level waste container materials can be considered in two categories - laboratory tests, and scale-up or in situ tests.

4.1.1 Laboratory Tests

Laboratory tests are usually performed to select promising materials for further testing from a large number of candidate materials. In the testing procedure, attempts are made to simulate normal or extreme environmental conditions likely to be encountered. The laboratory tests are generally much simpler to run and the results easier to interpret than in situ tests. These tests can also be used to examine a great number of variables, at lower cost and in shorter time frames. Test conditions can also be chosen so that some degree of acceleration can be attained.

Test specimens may be in the form of rods, tabs or other suitable geometry which may represent the potential use of the material, or be in a shape that will facilitate the evaluation of the corrosion test. Specimens may have their surfaces carefully polished so that small amounts of corrosion may be readily detected, as well as structural and chemical anlaysis of the surface facilitated. Methods for evaluating specimens are many and largely depend on the type of corrosion, material or test environment. An ASTM standard for corrosion sample evaluation is referred to below. A popular method, although not usually the best, is to weigh the samples and calculate a corrosion rate. Several assumptions are made concerning the type and uniformity of the corrosion taking place. This method is attractive because the samples are not destroyed and the test can be continued. The weight change measurements are usually complemented by destructive examinations by the optical microscopy, x-ray diffraction, SEM, XES, etc.

Container materials corrosion tests have been carried out at temperatures ranging from 25° to 600°C, depending on the design of the overall waste package. Tests investigating materials at temperatures over 100°C are performed in stainless steel or nickel alloy autoclaves. Usually the autoclaves have metal or teflon liners for protection against the corrosive solution, or to prevent interaction between the autoclave and the specimens. In some cases, the specimens and corrosive media are encapsulated to prevent the interactions mentioned above. With proper assembly of specimens, crevice corrosion can also be studied in autoclave tests.

Typical results obtained from such tests are shown in Table 4.1[5] for corrosion rates obtained on a variety of materials in three different brine solutions. Crevice and pitting corrosion were detected in these tests.

4.1.1.1 Standardized Test Procedures

One of the problems encountered where laboratory tests are conducted by several laboratories is the difficulty in comparing results due to nonuniformity in materials, test apparatus, and procedures used. Such problems usually occur early in a testing program and are not resolved until after great expediture

Table 4.1

Corrosion Rates of Candidate Alloys in Deoxygenated Solutions
(250°C, P = 5 MPa, t = 28 days)[5]

Alloy	Brine A (mm/yr)	Brine B (mm/yr)	Seawater (mm/yr)
(1018 Mild Steel, 25°)	0.03	0.03	
(1018 Mild Steel, 70°)	0.07	0.036	
1018 Mild Steel	1.7	0.07	0.4
Corten A Steel	0.9	0.05	0.2
2-1/4 Cr-1 Mo Steel	1.0[b]	0.1[b]	0.2
Lead	0.5	0.3	0.3
Copper	0.07	0.05	0.05
Naval Brass	1.0	----	1.0
90-10 Cupronickel	0.14	----	0.07
SS-304L	0.018	0.01	0.006
SS-316L	0.015	----	0.005
SS-Nitronic 50	0.008	----	0.003
SS-20Cb3	0.007	----	0.005
SS-Ebrite 26-1	0.016	----	0.005
Monel 400	0.03	----	0.1
Incoloy 825	0.006	----	0.004
Inconel 600	0.009	0.007	0.005
Inconel 625	0.005	0.001	0.0012[a]
Hastelloy C-276	0.007	----	0.0015
Zircaloy-2	0.001	----	----
Titanium C.P.	0.014	----	0.012
Ticode 12	0.003	----	0.001

[a]pitting corrosion.
[b]crevice corrosion.

in time and funds. There are however, standard test procedures which have been developed to circumvent this problem. The ASTM has adopted many standards for corrosion testing, some of which are:

ASTM G1 - Preparing, cleaning, and evaluating corrosion test specimens.

ASTM G3 - Conventions applicable to electrochemical measurements in corrosion testing.

ASTM G5 - Standard reference method for making potentiostatic and potentiodynamic anodic polarization measurements.

ASTM G28 - Detecting susceptibility to intergranular attack in wrought nickel-rich, chromium bearing alloys.

ASTM G30 - Making an using U-bend stress corrosion test specimens.

ASTM G36 - Performing stress corrosi. cracking tests in a boiling magnesium chloride solution.

ASTM G41 - Determining cracking suscept:bility of titanium alloys exposed under stress to a hot salt environment.

ASTM G46 - Examination and evaluation of pitting corrosion.

These specifications are quite complete. For example, a sketch showing stressed U-Bends (ASTM G30) is shown in Figure 4.?. and the definitions of pit corrosion types are shown in Figure 4.3, (ASTM G46). Other organizations having corrosion standards are the National Association of Corrosion Engineers (NACE) and the International Atomic Energy Agency (IAEA).

4.1.1.2 Waste Form Container

While there is considerable interest in corrosion of container materials by the respository environment, tests are also being conducted to evaluate the corrosive effect of the waste form on the container during filling.[6] Currently, two alternative processes are being considered for incorporating high level radioactive waste forms into the containers, the continuous melter and the in-can melter. It is the latter process which presents the more serious corrosion problem, since the glass waste form is at higher temperature for a longer time in the container. A test assembly used to evaluate candidate materials are shown in Figure 4.4. These tests involve immersing samples of the test materials in the molten glass. In the coupon test, a ceramic crucible is used to contain the glass and the entire assembly is placed in a furnace. The coupon is exposed to the glass, air, and to air and molten glass. Since these all represent conditions to which the container is exposed examination is made on all three areas of the coupon. In a "thermocouple test", the container containing the glass is made of Type 304 stainless steel pipe, and the assembly holding specimens is again placed in a furnace in air. This test is used to evaluate the attack of the test materials only at the glass-metal interface. Results obtained from such tests are shown in Table 4.2.

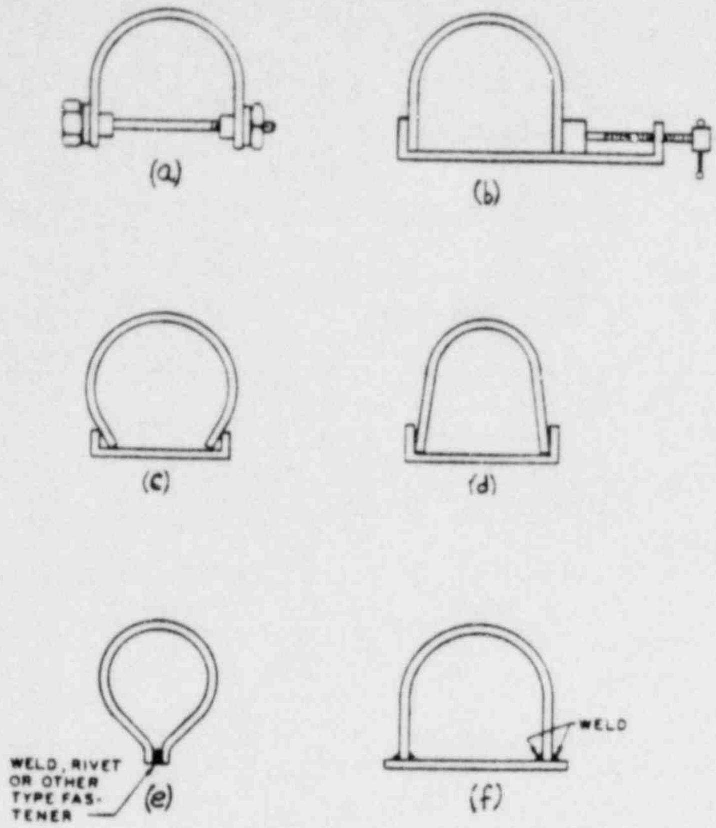

Figure 4.2. Typical stressed U-bends.

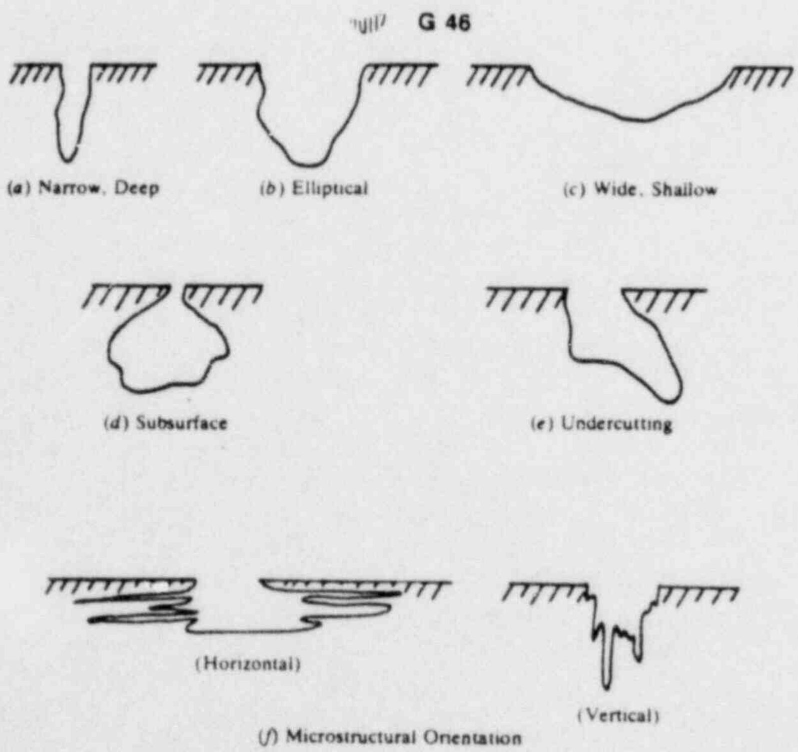

Figure 4.3. Variations in the cross-sectional shape of pits. (ASTM G-46).

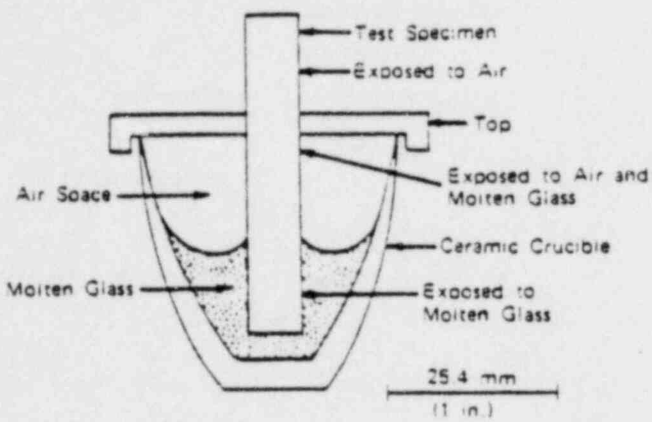

Figure 4.4. Coupon test assembly.(5)

Table 4.2

Penetration of Canister Alloys by Pure Frit 211 at 1150°C[6]

Alloy	Penetration, mils	Wt. % Cr	Test Condition	Remarks
Inconel 625	16.9	21	25 hr at 1150°C	
Hastelloy X	19.8	22		
Inconel 601	19.0	23		Little selective penetration as found in previous test[b]
Incoloy 801	>19.0	20		Specimen completely penetrated
Type 310 Stainless Steel	25.2	25		
Type 304L Stainless Steel	25.9	19		
Inconel 600	25.9	16		
Type 347 Stainless Steel	38.3	18		
Hastelloy C-4	110	16	7 hr at 1150°C[a]	15 wt.% Mo reduces resistance to penetration

[a]Hastelloy C-4 exposed to 65 wt.% Frit 21 and 35 wt.% composite sludge (with uranium).

[b]W. N. Rankin, "Compatability Testing of Vitrified Waste Forms," DP-MS-115 (Rev. 2/15/78), presented at Corrosion '78 Meeting, Houston, TX (March 6-10, 1978).

Tests such as these are quite specific for an application. The corrosiveness of the glass can be adequately determined if the glass waste form composition to be used in the final process is known. The contact time is short, so that no extrapolation is required and there does not appear to be any scaling required. These tests do not consider the long term effects of the waste form container interaction during storage in a repository. This area also requires evaluation.

4.1.1.3 Corrosion in Salt

Laboratory tests are also being conducted to study the interaction between salt from a potential storage location (Carlsbad) and candidate container materials (carbon steel and stainless steel)[7] Coupons of the materials in sealed and unsealed capsules are heated in furnaces at temperatures expected during storage (80°C and 225°C). Higher temperatures (600°C) are used to accelerate any reactions that may occur. The sealed capsule sample volume is approximately five cubic centimeters. Corrosive attack on the coupons is evaluated by visual appearance and optical microscopic examination. Dimensional changes of the specimens are measured with a traveling stage microscope. SEM, x-ray energy spectrometry (XES), and x-ray diffraction are used to analyze surface films on the specimens. Some of the corrosion data obtained in these tests is shown in Table 4.3. As with the waste form tests described previously, these tests are for a very specific set of conditions -the salt is from a specific potential storage location. The advantage of such capsule tests is that they are relatively easy to run and are not too costly, particularly for long term tests.

Table 4.3

Penetration (mils)[a] of Candidate Canister Alloys in Sealed Capsules with Salt from Carlsbad, NM[(7)]

Material	Temp °C	Time (hr) at 600°C: 1000 End in Vapor	1000 End in Salt	5000 End in Vapor	5000 End in Salt
	80	<2	<2	<2	<2
Type 304L	225	<2	<2	<2	<2
Stainless Steel	600	<2	<2	<2	<2
Low-Carbon	80	<2	<2	<2	<2
Steel	225	<2	<2	<2	<2
(ASTM-A-516)	600	3.3	2.8	20.1	9.3

[a] Penetration = $\frac{\text{Change in diameter}}{2}$

4.1.1.4 Electrochemical and Stress Corrosion Testing

Two other laboratory tests used to evaluate container materials are electrochemical studies and stress corrosion tests. The electrochemical tests are valuable in leading to an understanding of the corrosion processes which may be occurring. To some extent, there has been some standardization of these type tests in order to obtain better agreement between results obtained in different laboratories. ASTM G-5 is an example of such a standard. Electrochemical behavior of candidate titanium canister alloys have been performed by Braithwaite, et al. at Sandia.[(4)]

For many materials, the application of stress to the material in an aggresive environment will lead to early failure. There are several standard tests used to evaluate the susceptibility of materials to stress corrosion. These standards have been established by organizations such as ASTM and some of these specifications for stress corrosion testing have been referred to above. In most tests, specimens of a particular geometry have a stress applied by bending and maintaining the bend with a bolt or spring. The assembly is then exposed to an appropriate solution in a suitable vessel or autoclave. Stress corrosion can also be evaluated under slow strain conditions. In this case, a mechanical device which can control the strain rate is used. Again, the sample is in a vessel or autoclave during the test.

Fracture mechanics are studied in much the same manner except the specimen is usually precracked before testing in the corrosive environment. Results of stress corrosion tests and fracture mechanical tests on container materials have been recently reported.(4)

4.1.2 Scale-Up and In Situ Tests

Scale-up and in situ tests are most desirable since they represent testing at conditions closest to the field conditions. Normally, these tests are not performed routinely since they represent a considerable investment of time and money.

Some in situ testing of container materials has been done at Oak Ridge National Laboratory and the results recanlty summarized.(5) In these tests, the specimens were heaters that were placed in a salt mine. Both carbon steel and stainless steel were evaluated in this manner. Since the laboratory tests conducted in this program were run under somewhat different conditions than the in situ tests, it was difficult to determine any scale-up effects.

4.2 Test Variables

The purpose of conducting corrosion tests is to qualify a material which will contain the waste form for a defined period of time, which is 1000 years in the NRC strawman criteria. Interactions between the container and the waste form must be studied, and more importantly, interaction between the container and the isolation enviornment. In these studies, the conditions of the test should be governed by the waste form and the repository in which the container will be placed.

In a recent publication(5) Braithwaite and Molecke discussed the variables which can have an effect on container corrosion in a waste repository. They list some enviornment parameters for various repositories, Table 4.4, and discuss the effect of these variables as follows:

"Temperature: Increases in temperature generally increase the corrosion rates of metals.[4,5] However, as Shannon[6] noted for steel in geothermal brines, the corrosion retardant passivating film formed sometimes becomes more protective as temperature is increased and the observed corrosion rates

[4] H. H. Uhlig, Corrosion and Corrosion Control, John Wiley and Sons, NY, 1972.

[5] F. L. Laque, Marine Corrosion Causes and Prevention, John Wiley and Sons, NY, 1975.

[6] D. W. Shannon, "The Role of Chemical Components in Geothermal Brines on Corrosion," Paper 57, presented at Corrosion 78, NACE, Houston, TX, March 6-10, 1978.

Table 4.4

Repository Isolation Environments for High-Level Waste[5]

Geologic Formation and Waste Type	Maximum Interface Temperature	Lithostatic/ Hydrostatic Pressure	Chemistry
Bedded Salt:			
Spent fuel	70-100°C	18 MPa	Dry NaCl
Defense HLW	70-100°C	18 MPa	Dry NaCl
Reprocessed HLW	250°C[a]	18 MPa	Dry 98% NaCl, with dispersed 1/2% H_2O
Reprocessed HLW	150°C[a]	18 MPa	With potential inundation due to localized intrusion of NaCl-$MgCl_2$ brine or hydrologic flow
Subseabed Sediments:			
Reprocessed HLW	200°C	55 MPa	Seawater saturated sediments (40% solids)
Basalt, Shale, Tuff:			
Reprocessed HLW	250-300°C	Atmospheric	Air and steam for about 100 years, then possibly inundated with ground water

[a]Assumes 37 watts/m^2 (150 kW/acre) container spacing in repository; does not include radiolysis effects.

decrease. Also, increases in temperature in an open system will cause a depletion in dissolved oxygen in aqueous solutions. This will decrease the corrosion rate of metals whose rate is controlled by diffusion of oxygen (for example, 1018 mild steel).

Pressure: The restraining pressure which an HLW canister is subjected to in a waste repository affects the corrosion rate primarily in that it influences the physical state of intruding water and the concentration of dissolved gaseous species. The lithostatic (rock overburden) pressure, combined with low gas pereability, in a bedded salt repository or the hydrostatic pressure in the deep ocean sediment will prevent water vaporization even at high waste temperatures. HLW emplaced in hardrock formations will not be exposed to liquid water because of the lack of a confining pressure. These arguments, of course, depend upon the sealing and reflux properties of the formations.

Solution Chemistry: Waste canisters will be exposed to any thermal decomposition products of the geologic isolation formation (CO, SO_2, etc.) and any dissolved and gaseous species present (O_2, N_2, HCl, H_2, etc.). In general, species in solution which increase the oxidizing power of that solution (O_2, H^+, H_2S, NO_3, etc.) will increase the corrosion rate. Hydrogen ions can also reduce the thickness and therefore the effectiveness of a metal's passivating layer.[4] Basic pH conditions can cause caustic stress corrosion cracking or even rapid dissolution if the metal is ampnoteric.[4] Choride ion is potentially the most aggressive of the ions in that it promotes localized passive film breakdown (which leads to pitting), and is a key consituent in causing stress corrosion cracking of many alloys.[4] Large concentrations of chloride can inhibit the corrosion rates of many alloys by salting out dissolved oxygen and/or by adsorbing and blocking many active surface sites.[4]

Stress: The tensile stress present in the canister wall is one of the essential requirements for stress corrosion cracking in geologic isolation conditions. For the candidate alloys the environment-specific experimental study needs to be conducted. For susceptible alloys, the threshold tensile stress depends strongly on temperature, solution composition, and the presence of an aqueous phase.

Sensitization and Welding: Alloys containing carbon and chromium can be susceptible to sensitization. For example, sensitization in stainless steels refers to the thermally induced formation of chromium carbide at or near grain boundaries. This increases the susceptibility of the alloy to intergranular attack and intergranular stress corrosion cracking.[4,5] Welding, becasue of the high temperatures involved, often leads to sensitization and tensile stress in welded regions. Stainless steel 304, for example, undergoes sensitization at temperatures above 400°C.

Radiolysis Products: A study of gamma-radiolysis an hydrolysis in bedded salt brines was conducted by G. H. Jenks.[8] The following conclusions can be

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[4] Ibid.

[5] Ibid.

[8] G. H. Jenks, "Radiolysis and Hydrolysis in Salt-Mine-Brines," ORNL-TM-3717, March 1972.

drawn from his work: (1) the principal corrodant is HCL which forms from $MgCl_2$ hydrolysis, (2) 2/3 of the $MgCl_2$ present in the brine can hydolyze to produce HCl (only if the HCl is removed or consumed as it is formed), (3) important radiolysis products will include small amounts of H_2, O_2, H_2O_2, and OCl^-. Chlorates, bromates, and Cl_2 will not be stable at the high temperature and pH expected in HLW geologic repositories."

4.3 Test Specimens and Equipment

Specimens used in the corrosion tests should be representative of the materials to be used for the containers. That is, the coupons should be wrought, cast, etc., if that is the form to be used in container fabrication, and be subjected to similar heat treatments and surface finishes. In these tests, the corrosion rates are expected to be very small, so that it may be necessary to polish the surfaces in order to detect corrosion in the surface layers. However, the effect of surface polishing on the measured corrosion rates and process should be evaluated. If welds are to be used in container fabrication, their corrosion resistance must be evaluated because of the significant structural changes (cast structure, heat affected zone, etc.) produced by welding.

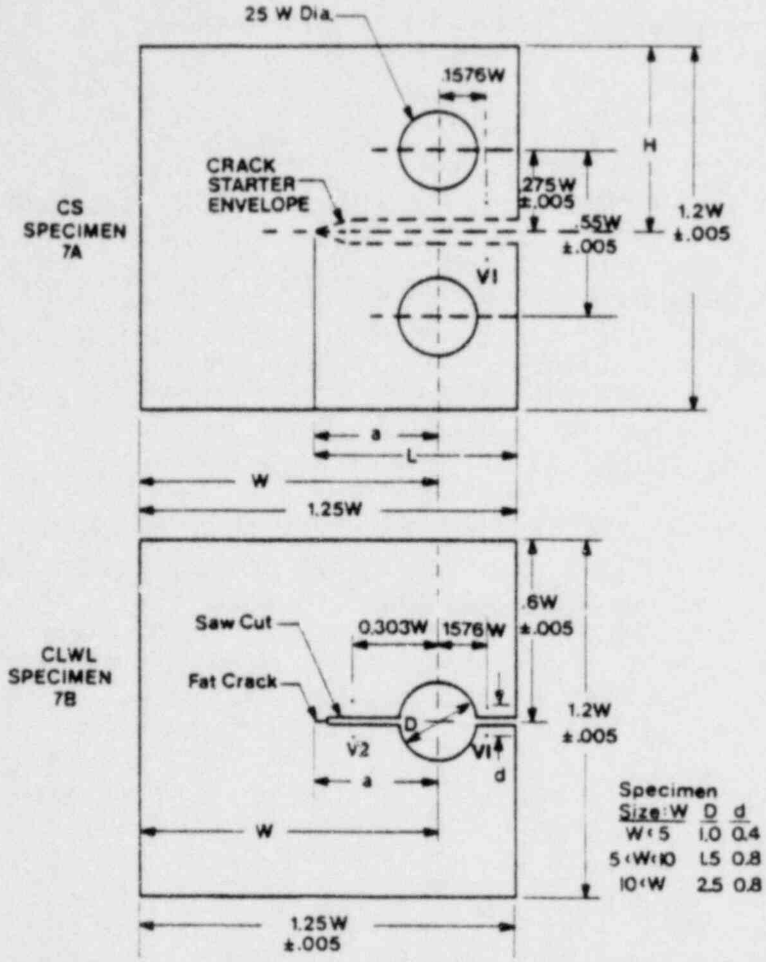
For laboratory testing, conventional speciments can be used. General corrosion, pitting, and crevice corrosion can be determined on specimens of almost any geometry determined by the test being performed and equipment used. Some tests such as stress corrosion, fracture mechanics and slow strain rate corrosion require specially shaped specimens. Some of these are shown in Figures 4.2 and 4.5. Specimens should always be made in standard shapes and from well characterized materials (fabrication history, composition, heat treatment, etc.).

Corrosion test apparatus can be glass or metallic vessels containing the specimen, or autoclaves (for normal or high pressures) which are sometimes modified to perform special types of tests. The apparatus used is largely governed by the test temperature and agressiveness of the test enviornment. Whatever apparatus is used, it geometric configuration and construction materials should not interfere with the corrosion test results. A simple resin flask recommended for immersion testing in ASTM G31 is shown in Figure 4.6.

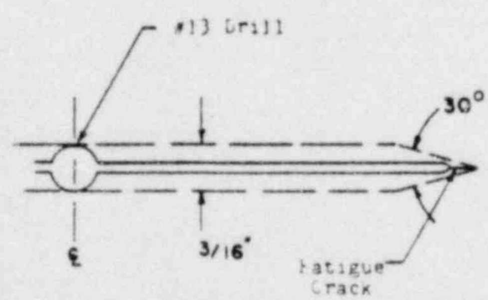
4.4 Test Result Interpretation - Accelerated Tests

Ideally, a corrosion test should be run under in-situ conditions and for as long as the expected life of the container. Unfortunately, in real life, the corrosion engineer does not have this option and must attempt some form of accelerated testing or extrapolation.

Two experimental variations are used to accelerate corrosion testing, namely increasing the temperature or, the corrosiveness of the solution. For example, to check the validity of the temperature acceleration, the data should include a significant number of different temperatures. When plotted, the test results should give a linear Arrhenius plot. Results deviating from linearity should be investigated for a possible change in the corrosion mechanism. A mechanism change with increased temperature would invalidate the acceleration test. Another method of test acceleration is to increase the corrosiveness of



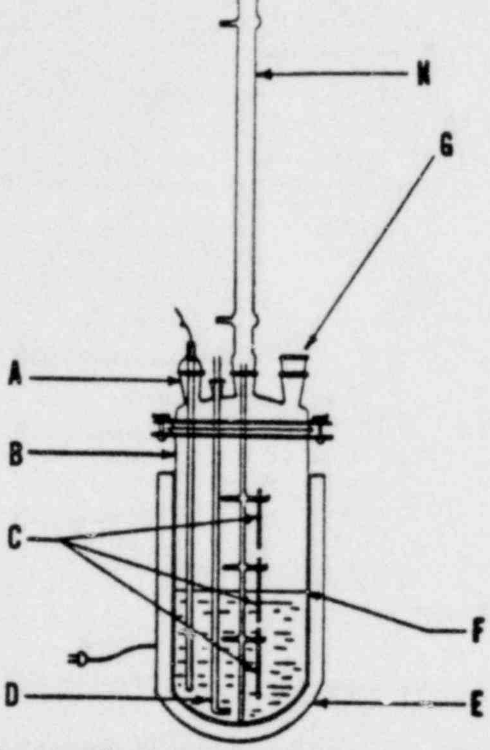
Compact and Crack-Line-Wedge-Loaded Specimens.



Enlarged View of the Right Half of the Permitted Notch Envelope in CCT Panels.

Figure 4.5. ASTM specifications for test specimen shapes (ASTM E 561).

the solution. However, interpretation of such tests is very difficult and their use for extrapolation purposes is questionable.



NOTE—The flask can be used as a versatile and convenient apparatus to cond... simple immersion tests. Configuration of top to flask is such that more sophisticated apparatus can be add... ...ired by the specific test being conducted. *A* = thermowell, *B* = resin flask, *C* = specimens hung on supporting ... – air inlet, *E* = heating mantle, *F* = liquid interface, *G* = opening in flask for additional apparatus that may b... ed, and *H* = reflux condenser.

Figure 4.6. Typical resin flask (ASTM G31).

Alternatively, it is possible to test materials at the highest anticipated temperature in the "worst case" corrosive media, and run the tests until the steady-state corrosion is well defined. Hopefully, the steady-state condition obtained will reflect anticipated long term behavior and produce conservative performance estimates.

An important consideration in extrapolating corrosion data is the nature of the corrosive attack. If the corrosion is uniform in nature, the extrapolation to some finite time is relatively simple. However; in the case of localized attack, such as pitting, crevice corrosion, intergranular or stress corrosion cracking, extrapolation is extremely difficulat since the initiation time and penetration rates for these corrosion types are difficult to determine. For applications such as waste containers, it would be best to select materials which do not exhibit these corrosion types or pursue a multibarrier container approach.

4.5 Recommendations

For the initial screening of container materials, it would be appropriate to conduct the corrosion tests in laboratory experiments. However, it is important to conduct these tests under close control and with standard test procedures wherever possible, so that results in different laboratories can be compared. The test materials should be well documented and the test media should be representative of repository environments. In the laboratory tests, the material should be subjected to tests which would inidicate its susceptibility to pitting, crevice, intergranular, or stress corrosion. The test environment should take into account changes in composition due to replenishment which may take place in a flooded repository, and the effects of radiation exposure.

In order to qualify as a container material for use in a repository a more extensive test must be made. The candidate material should be exposed to conditions that are expected to exist in a selected repository. These conditions should be determined from repository site-specific investigations or from information obtained from modeling. (See recommendation 7.1.3.) The former is preferred. The test should allow synergistic effects to be evaluated. (See recommendation 7.1.1.) Test conditions should have the material under the anticipated maximum temperature and stress expected. The selected backfill should be in contact with the material at the expected pressure and the environment should be that of the selected repository. Radiation levels and dose rates should be those expected at the container surface. Container surface area to environment volume should be scaled and replenishment rates duplicated. A sampling plan which allows the determination of the steady state corrosion rates, as well as the nature of the corrosive attack is required also.

The test described above should give adequate confidence in the performance of the container in the respository. Therefore, the <u>in situ</u> testing should consist of placing retrievable coupons of the container materials in the repository adjacent to the containers. These coupons would be then retrieved periodically to monitor the performance of the container.

Corrosion rates, (and thus the useful lifetime of a material) are most easily determined for materials which corrode uniformly. It may occur that a suitable uniform corroding material may not be developed in the container materials corrosion program. Materials susceptable to localized corrosion may then have to be used. One method of using such materials and improving the ability to predict their life would be to construct the container of multiple layers. Usually the time to initiate a local pit or crack is much longer than the penetration rate of the pit or crack. Knowing the time it takes for one of these pits or cracks to penetrate a thin layer of material, one can better estimate the life of a container fabricated of materials susceptable to localized corrosion.

4.6 References

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2. W. Newmann and O. Kofler, "Coating of Waste Containing Ceramic Granules," p. 150, in Ceramics in Nuclear Waste Management, U.S. DOE Conference Proceedings, CONF-790420, May 1979. Available from the National Technical Information Service, Springfield, VA 22161.

3. E. Mattson, "Corrosion Resistance of Canisters for Final Disposal of Spent Nuclear Fuel," in Scientific Basis for Nuclear Waste Management, G. J. McCarthy, Ed. (Plenum Press, NY, 1979), pp. 271-282, available in public technical libraries.

4. J. W. Braithwaite, N. J. Magnani, J. W. Munford, Sandia Laboratories, "Titanium Alloy Corrosion in Nuclear Waste Environment," Paper No. 213, presented at NACE Corrosion/80, Chicago, Illinois, March 3-7, 1980.[1]

5. J. W. Braithwaite and M. A. Molecke," Nuclear Waste Canister Corrosion Studies Pertinent to Geologic Isolation," Sandia Laboratories, to be published in Nuclear and Chemical Waste, An International Journal of Hazardous Waste Management, 1(2) 1980 Pergamon Press. Available from Pergamon Press.

6. W. N. Rankin, "Attack of High Strength, Oxidation-Resistant Alloys During In-Can Melting of Simulated Waste Glasses," Paper No. 215, presented at NACE Corrosion/80, Chicago, IL, March 3-7, 1980.[1]

7. W. N. Rankin, "Canister Compatibility with Carlsbad Salt," Paper No. 212, presented at NACE Corrosion/80, Chicago, IL, March 307, 1980.[1]

[1]Available from the National Association of Corrosion Engineers.

5. SORPTION TESTING

The sorptive barrier consists of the backfill-overpack material and the host rock. Sorption testing is the main area of concern for evaluating the performance of these package components.

5.1 Test Method Review

In this section, sorption test methods are reviewed, and preferred methods recommended. The parameter used to describe sorption properties is the distribution coefficient (K_d), which is simply the ratio of the activity in the solid phase (Ci/g) to that in the liquid phase (Ci/mL) for the solid-liquid system under consideration. According to its strict definition, the K_d is a thermodynamically derived distribution law, valid for single ions at trace level concentrations under ideal solution behavior. In practice, it is extremely difficult to determine a strictly valid K_d, and such a result has dubious value for predictions of non-ideal real system behavior. "Apparent" distribution coefficients are actually measured experimentally and commonly referred to as K_d numbers. Often the symbol R_d is used to avoid equilibrium connotations for the experimentally derived distribution coefficients. An excellent collection of recent work concerning sorption studies is compiled in reference 1.

5.1.1 Test Methods

Sorption tests are either static or dynamic in nature. The various procedures are outlined below.

- Batch tests - these static tests are the most widely used procedures largely due to their relative simplicity. Solids and spiked liquid phases are contacted in a closed system. Contact times are either arbitrarily selected, or based on the establishment of steady state conditions. The choice of liquid phase composition and solid phase form (powders, chips, or pellets) is made to simulate expected natural environments. Sorption during flow through porous media is simulated by using powdered solids. Chips or pellets of the solids are used to mimic sorption on fracture surfaces in hydrologic regimes dominated by fracture flow.

- Column tests - these dynamic tests involve percolating a spiked liquid phase through a column of either compacted granular material or unaltered material (rock or soil cores). The spike is applied either directly to the top of the column before liquid is percolated through (analagous to "spotting" samples for chromatographic analysis), or by spiking the liquid reservoir itself. In the first case, the apparatus functions as a chromatographic column, while in the second case, the percolating liquid maintains a constant radionuclide concentration entering the column. Breakthrough of the radionuclides in the column effluent is most frequently determined, but in some studies,[2,3] the distribution of radionuclides in the cores is examined after the test is completed. The column offers the most realistic means of simulating field conditions for natural materials, if liquid phase compositions and solids can be chosen adequately. The use of homogenized, repacked solids in the column to simulate flow through lithified materials negates this aim, but has been used to avoid the technical difficulties of using undisturbed material, and to simplify the experimental procedure. When the permeabilities of the undisturbed materials are exceedingly low, the use of high pressure heads is questionable in many situations, leaving little alternative except repacked columns. For studies involving the overpack-backfill material repacked columns are required.

• Soil chromatographic tests(4) - In these procedures a slurry of powdered solids is allowed to dry in a grooved surface. Spiked solutions are contacted with one end of the sorber "column." Under the influence of capillary draw, the solution migrates along the column. The solid and liquid phases are analysed at the conclusion of the experiment. Due to the rather drastic alteration of the solids, results of these tests are questionable and of little widespread application. This procedure may be of some use in measuring sorptive properties of solid material under field conditions in the unsaturated zone. No studies comparing field observations and experimental results have been reported in the literature.

• Axial filtration(5) - this is a variation of the flow through column test. The procedure involves centrifugation of a slurry and filtration of the liquid phase during rotation. As the test proceeds, the radionuclide content of the filtrate is monitored until steady state concentrations are established. Experimental conditions used in this procedure appear very unrealistic and difficult to interpret at best. Little work has been done to compare this procedure with other sorption tests.

The column test appears to be the most flexible in terms of simulating natural conditions. Liquid phases can be tailored to match those expected in the repository and flow rates can be as fast or slow as desired. Temperature, pressure, and radiation fields can also be included in these tests. "Chromatographic" column experiments appear to be unrealistic because once the container is breached, radionuclides escaping from the inner package components will do so at relatively constant concentrations depending on the leach rate of the waste form. A large, sudden input of radionuclides into the sorptive barrier appears unreasonable. For column tests of the overpack-backfill material, spiking the reservoir to maintain a constant radionuclide concentration for the inflowing water would be more realistic. Columns of packed granular material simulate flow through the relatively porous overpack-backfill, while columns consisting of rock cores (either fractured or unfractured material) simulate flow through the host rock. Columns containing fractured rock samples can be used to simulate flow through fractured host rocks, however this situation should be avoided in the repository by proper site selection. The column test is recommended because of these strong points.

Static tests would also be recommended to completely cover the range of environmental conditions possible in the respository. A batch test using powdered material would simulate a very low flow rate situation in the overpack-backfill. Using chips or pellets of the host rock in a batch test would simulate low flow rates in a fracture flow regime. Both static and dynamic testing are recommended to test candidate materials over the range of conditions possible in a repository.

5.1.2 Standardized Tests

Efforts are in progress to establish standardized batch tests. Reference materials have been characterized,[6] and interlaboratory comparisons of experimental results compiled.[7] No attempts have been made to standardize column testing. In order to obtain data to properly evaluate the components in the sorptive barrier, testing will require conditions which closely simulate those in the repository. A rigid standardized testing procedure can be contrary to these goals and should be avoided.

A data bank accumulation of sorption data is being established[8] and predictive models tested.[9] Information in this data bank is largely composed of generic studies upon which the modeling equations are based. Few sorption studies include all the pertinent variables which may affect the observed results, therefore the potential of the data cannot be fully realized. However, this information should be useful in narrowing the list of candidate host rocks, overpack and backfill materials, as well as determining the variables most important for predicting the sorptive behavior. For final selections, site-specific studies will be needed.

5.2 Variables

The variables which may effect sorptive behavior of candidate materials are those described in section 2. The recommendations in these areas are given below.

5.2.1 Media Composition

Numerous studies have shown sorption to be dependent on chemical variables in the liquid phase (pH, redox potential, dissolved species concentrations, etc.), as well as variations in compositions, particle size, surface area, etc., of the solid components. Reference 1 and the summary by Ames and Rai[10] contain the results of numerous studies which illustrate this.

Both the solid and solid phases must be well characterized in terms of parameters thought to influence sorptive behavior. The liquid phase should be analyzed in terms of major anions and cations, pH, Eh, and dissolved silica. Highly charged ions present at low concentrations may significantly alter sorptive properties and should be included in the descriptive data, as well as the concentrations of naturally occurring carrier ions.[a] Analysis of the liquid phase after the completion of sorption experiments would also aid in interpreting the results, but this is not as essential as the initial characterization. The solid phases also require extensive characterization. For the solids, the most important supporting data includes particle size distribution, surface area,[b] exchange capacity (cation and anion) and selectivity, as well

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[a]No specific methods are recommended for these determinations. Numerous standard procedures appear adequate for this purpose.

[b]For layer silicate minerals (clays), a surface area procedure using organic sorbers[11,12] is recommended so that inter-layer, as well as external surface area can be measured in these minerals.

as qualitative and quantitative mineralogy which must include amorphous and crystalline components. The recommended characterization data is listed in Table 5.1.

Table 5.1

Characterization Data Required to Supplement Sorption Test Results [Modified From Hostetter, Serne, and Brandstetter[8]]

Liquid Phase	Solid Phase
Major Cations	Cation Exchange Properties (capacity and selectivity)
Major Anions	Surface Area
Minor Ionic Species (strongly sorbing species and carrier species)	Particle Size Distribution
Pore Water SiO_2	Porosity
Eh	Permeability
pH	Hydraulic Conductivity
	Quantitative Mineralogy (crystalline and amorphous compounds)

Every effort should be made to use liquid phases identical to those expected in the repository. For the solid phases, the material should be the same composition and form as that to be used in the repository. For best results, site-specific samples of the host rock should be used. Generic materials are to be avoided whenever possible.

5.2.2 Contact Time

Contact time is the most difficult experimental variable to match with expected repository conditions,as mentioned earlier (section 2.6.1.3). Static tests would simulate very low flow situations, and dynamic testing would simulate the higher flow rate situations. A series of experiments should span the expected range to provide the necessary data for evaluation.

Because sorption is not an instantaneous process, the sorptive behavior of some elements, notably cesium (see Table 2.5), show a strong time dependence which must be known before test results can be interpreted properly. For a mined repository in crystalline rock, the water flow around the waste package will probably be quite slow. Therefore, the duration of a static test should be long enough for steady state conditions to be established. Flow rates for dynamic testing should be low also.

5.2.3 Temperature

Sorption has been shown to be influenced by temperature (see section 2.6.1.4). Testing should be performed at temperatures which cover the range of those expected in the repository.

5.2.4 Radiation

Little effort has been expended to measure the effects of radiation on sorptive behavior. Radiation can produce structural damage in solids[6] and radiolysis products, which may affect sorptive behavior (see section 6 for more information). With the exception of rock salt, little is known about radiation damage in geomedia. Some structural damage has been observed,[13-15] but the effects on sorption behavior remain to be determined. This area requires much more study before radiation effects on sorptive behavior can be assessed.

5.3 Test Results and Interpretation

Interpreting sorption test results is more involved than interpreting leach and corrosion results because sorption is a reversible process. Ions sorbed on surfaces can be desorbed with changes in the aqueous phase composition, either easily ("reversibly sorbed" ions), or with difficulty ("fixed" ions). For interpretive purposes, the desorption behavior of ions must also be known. Desorption experiments are done by the same procedures outlined previously, simply by changing the liquid phase composition and repeating the test.[1] Any number of aqueous phase changes can be used depending on the scenario to be simulated. Desorption experiments are recommended to compliment the sorption studies.

5.3.1 Analytical Sensitivities

For elements with very large or very small K_d numbers, only small amounts of activity will be in the liquid or solid phases respectively. Therefore, analytical sensitivities must be high, and sample sizes adjusted accordingly for best results.

5.3.2 Scaling and Extrapolation

Sorption data (K_d numbers) are directly applicable to the field situation if no significant variation in K_d is found for variations in solid/liquid ratios in batch tests, and porosity variations in column tests. This also assumes complete testing so that the data reflect the effects of all the environmental variables over the ranges expected in the repository.

Extrapolations with time require that desorption data be obtained so that predictions can be made for a variety of scenarios. Sorption data for particular elements as a function of time are also required for predictive purposes. For this reason also, sorption testing should be sufficient duration for steady state conditions to be established.

To determine the efficiency of the sorptive barrier, additional information is required describing the physical characteristics of the host rock, overpack and backfill configuration in the repository. Assuming water saturation and a given flow rate, the effective porosity, hydraulic conductivity and permeability of the sorptive barrier components must be known (Table 5.1). Assuming a given radionuclide release from the inner package components, the thickness of the sorptive barrier required to confine the radionuclides can then be calculated. The scenario described above also assumes porous flow hydrology. If fractures are present in the sorptive barrier components, radionuclide migration through the barrier would be greatly enhanced. This situation should be avoided whenever possible.

5.3.3 Acceleration

It does not appear feasible to accelerate sorption testing and obtain valid data. However, the time frames required to achieve steady-states in laboratory experiments are not so excessive as to be impracticable.

5.4 Recommendations

A combination of column and batch tests are recommended for sorption testing. The materials used, and experimental conditions, should duplicate those expected in the repository as closely as possible. To span the range of environmental conditions likely to be encountered, multiple testing of the candidate materials will be required. For example, tests must be repeated for a number of temperatures to determine sorptive behavior during the thermal history of the repository. For predictive purposes, desorption, as well as sorption tests are required, and the sorption behavior must be known as a function of concentration of the specific ions of concern, other chemical variables such as pH, Eh and other species concentrations, and surface area. Not only the sorption capacity, but the selectivity of the barrier components must be determined. Analysis of the liquid phases after contact with the solids may be helpful for predictive purposes.

For dynamic sorption tests, columns of the candidate host rock may be either fractured or unfractured depending upon the situation to be simulated. Columns made from ground repacked material are suited only for testing of the overpack-backfill material. The material used in the repacked columns should be the same form (particle size distribution, surface area, etc.) as that to be used in the repository, and the liquids should duplicate the expected composition of intruding waters as closely as possible. "Chromatographic" column tests (section 5.1.1) are not appropriate for either host rock or overpack-backfill testing, unless the technical difficulties of working with radionuclide bearing solutions cannot be overcome. The water entering test columns should have a constant radionuclide concentration rather than the sudden large concentration used in chromatographic procedure.

Radionuclide breakthrough in the column effluent should be measured not only as a function of initial radionuclide concentration in solution, but also other chemical variables such as Eh and pH (see Table 5.1). The sorptive capacity of the barrier components must also be determined in order to evaluate its ability to hold the waste form radionuclide inventory. Following the conclusion of sorption and desorption testing, the distribution of radionuclides on the column should be examined. Either autoradiography or detailed analysis of the column material may be used.

Batch tests can be used to simulate low water flow rates, or essentially stagnant conditions, around the waste package. Pellets or slabs of the host rock and actual samples of the overpack-backfill should be used in the tests. The duration of batch tests should be sufficiently long for steady-state conditions to be established. As in the case of column tests, the sorptive capacity and selectivity must be determined as functions of radionuclide concentration and other chemical variables so that the test data is sufficiently complete for predictive purposes. Recommended research areas dealing with the sorption testing of candidate overpack-backfills and host rocks, as well as radiation effects on sorption behavior are described in section 7.

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[2] Available in public technical libraries.
[3] Available from the National Technical Information Service, Springfield, VA.

6. RADIATION EFFECTS

6.1 Introduction

An important part of the present task is to establish realistic conditions for waste package component testing. The literature clearly indicates that radiation effects must be considered when formulating test conditions. What is less evident is how and when the radiation conditions anticipated in a repository should be simulated. This question merits immediate and systematic consideration - not only because of synergistic effects, but because of the additional operational complexities resulting where tests in a radiation environment are required.

In this section, we first describe the radiation conditions expected to exist in waste repositories, and the general effects which may result in the waste package components. The potential impact of these effects on leach, corrosion, and sorption testing is then discussed. At this point, certain preliminary conclusions concerning testing and interpretation can be drawn, and several questions defined. These are presented in the last section.

6.2 Radiation Environment in the Waste Package

Within the waste package, the radiation environment will vary with both space and time. Fission fragments in high level waste forms will decay primarily by beta-emmission, producing energetic electrons and gamma rays. These decays will account for most of the heat and radioactivity generated initially within the waste form.(1) However, the lifetimes for beta-decay are for the most part relatively short: substantial gamma ray, energetic electron and thermal fluxes within the waste package will largely be confined to the first several hundred years after burial.

Energetic electrons generated in fission fragment decay will be largely restricted to the immediate vicinity of the waste form - the range in typical materials is a few millimeters or less. Gamma-rays, on the other hand, are vastly more penetrating. All the components of a high level waste package may be subjected to a considerable gamma dose. Values on the order 10^{10} rad have been estimated for material immediately surrounding wasteforms.(2) Initial dose rates may be as high as 10^5 rad/hr.(2)

Unlike the situation for fission fragments, radiation effects due to transuranic (TRU) elements will be almost entirely confined within a single waste package component - the waste form. The important decay mode here is alpha particle emission. While other radiations are produced in the decay chains, the emitted alpha particle and recoil nucleus will produce most of the radiation damage. These particles interact quite strongly with matter, and the primary damage ranges are extremely small - typically a few hundred angstroms for recoil nuclei. Consequently, barring actual migration of the radionuclides, the primary damage from alpha decay will be restricted to the immediate vicinity of the waste form.

Both alpha and beta decay result in atomic transmutations. The decay products can be quite different chemically from the parent radionuclide. For example when ^{90}Sr is transmitted to ^{90}Zr by successive beta decays, the valence increases by + 2 and the ionic radius decreases by 38 percent. Such changes can defect the stability of the radionuclide host phase. Atomic transmutations should be considered as part of the radiation environment.

Alpha decay in TRU elements is an inherently long lived process, typically involving a number of intermediate species. Alpha decays will continue to accumulate waste forms for many thousands of years after the thermal and beta-gamma fluxes from cesium fragments have decayed. There is, however, a prompt component to the alpha-decay dose. Under typical conditions, roughly 5 percent of the million year alpha decay dose is produced during the first one hundred years. During this time, the beta-gamma dose from the decay of fission fragments will have reached 90 percent of its ultimate value. Comparative behavior for fission fragments and TRU decay in typical cases is illustrated in Table 6.1. It is evident that substantially different time scales should be used when considering the effects of beta/gamma irradiation and those of alpha decays.

Table 6.1

Build Up of Radiation Dose in Waste Glass

Time Since Vitrification (Years)	Cumulative α-Dose (α/g) x 10^{-17}	Cumulative β-Dose From Fission Fragments (β/g)[b]
2	1.1	3.8×10^{17}
6	1.9	1.09×10^{18}
10	2.5	1.75×10^{18}
10^2	7.1	7.7×10^{18}
10^3	14.6	8.5×10^{18}
10^4	29.5	8.5×10^{18}
10^5	61.3	8.5×10^{18}
10^6	19.5	8.5×10^{18}

[a]Data from ref. 1.
[b]Estimated from ref. 3.

6.3 Radiation Effects in the Waste Package

In the radiation environment described above, effects may occur which have a direct bearing on testing. In considering these, it is useful to draw a distinction between the ways in which gamma rays, electrons and heavy particles interact with matter.

Gamma rays lose energy in matter mainly by producing energetic electrons. Occassionally, these may cause atomic displacements by elastic collision. Far more frequently, however, the energetic electrons displace other electrons - chemical bonds may be ruptured, valence states modified, etc. These processes can be viewed as radiochemical or ionization effects fundamentally involving some kind of charge transfer. With certain notable exceptions, ionization is not very effective in displacing atoms in solids of the type considered for HLW packages.[4,5,6]

Energetic electrons (beta particles) resulting directly from beta decay interact with matter in the same way as the compton or photoelectrons due to gamma irradiation. Again, for most solids, the principal effect is ionization; Hall, et al.[3] have estimated that in a waste glass only about one atom is displaced for every eight beta particles emitted.

Atomic displacements, however, are readily provided by elastic collisions in internal alpha decay. The heavy recoil nucleus in particular can displace roughly 2000 atoms.[7] The number of atomic displacements produced in typical waste forms by internal alpha decay is estimated to be at least 100 times greater that due to other mechanisms. Helium is also formed when alpha particles are stopped in matter. When large numbers of stable displaced atoms are produced, the bulk physical properties of materials are altered, resulting in swelling, embrittlement, metamictization, etc. When the displaced atoms are produced by elastic collisions, the process is known as displacement damage. Both the radiation environment and the anticipated effects will be different for different components of the waste package. The general situation is depicted in Table 6.2.

6.4 Radiation Effects in Leach Testing

Leach testing applies primarily to the waste form. The radiation environment and those effects which must be considered are indicated in Table 6.2.

6.4.1 Displacement Damage in the Waste Form

Displacement damage can cause compaction of glasses, and metamictization of minerals, possibly accompanied by swelling and gas buildup.[5,8-10] Such effects may modify leach rates; a number of evaluations have been carried out for specific waste form candidates.[1,11-17] The time scale for displacement damage due to alpha decays is long enough so that laboratory evaluation commonly involves drastically accelerated testing-displacement doses which would accumulate over thousands of years in the repository environment are administered in a few years. Methods which have been employed to simulate internal alpha decay in waste forms include:

- Doping with short-lived alpha-emitters such as $^{244,242}Cm$, ^{238}Pu, and ^{241}Am.[1,11-16]
- Internal fission.[7]
- Neutron bombardment.[7,16,17]

Table 6.2

Radiation Conditions in the Waste Package[a]

Waste Package Component	Radiation Environment	Radiation Effects
Waste form	prompt accumulation of α and α recoils, ($\sim 10^{2-3}$ yrs), 10^{18} α/g followed by long term build-up ($\sim 10^6$ yrs) to levels of $\sim 10^9$ α/g Substantial β^- and γ flux over first $\sim 10^2$ yrs (10^{12} rad)	displacement damage; ionization; helium buildup, transmutation
Canister	α,α recoil and β^- at surface only. Substantial gamma flux ($\sim 10^{10}$ rad) possible	displacement damage at inner surface; ionization;
Overpack	Depending on shielding effect of inner components, gamma flux for a material within ~ 1 meter of wasteform	ionization (+ possible displacement if radionuclides migrate)
Environment (geomedia and liquids)	As in overpack	ionization; radiolysis of liquids;

[a]The numbers are typical of literature values. Displacement damage here is taken to mean that which results from atomic displacements caused by elastic collisions. Fast neutrons may also be produced within the wasteform; these have not been included here. While our assessment is continuing, fast neutron effects are visually considered negligible in comparison to those produced by alpha and beta decay.(6)

- Heavy ion bombardment (implantation).[7,12]

Doped waste forms may show only a relatively minor increase in leach rate in these accelerated tests (Table 6.3).

Table 6.3

Radiation Effects on Leach Rates[a]

Glass	Conditions	Leach Rate g/cm^2-day
Zinc Borosilicate[1] PNL 76-68	unirradiated	8.4×10^{-6}
	doped (244 Cm, 8×10^{17} α/g)	1.7×10^{-5}
Lithium Borosilicate[11]	doped (^{238}Pu, 9×10^{17} α/g)	1.6×10^{-3}
	doped (^{238}Pu, 1.8×10^{18} α/g)	2.3×10^{-3}
	doped (^{238}Pu, 2.7×10^{18} α/g)	2.6×10^{-3}
Borosilicate[12]	ion implanted to simulate 2×10^{18} α/g	increase in leach rate of $\sim 1.4 \times 10^{-3}$g/c calculated from data in ref. 12

[a]Since different leach tests are used in each case, only relative changes are meaningful.

[b]This leach rate is said to be equal to that in a control sample doped with ^{239}Pu.

However, the reliability of accelerated radiation effect tests with doped waste forms remains to be established. (See recommendation 7.5.1). In particular, it has been claimed that when alpha recoil damage is simulated by surface ion bombardment, drastically increased leaching can occur in waste storage glasses.[12] Data are included in Table 6.3.

It is not clear how well ion bombardment, in which heavy positive ions are nonstochastically implanted in a thin surface layer, realistically simulates internal alpha decay. Leaching is demonstrably sensitive to surface conditions. In glasses, for example, "...differences in chemical durability among various silicate glasses reflect differences in the porous structure of the surface films and consequent differences in the rates of diffusion processes taking place in these films..."[18] The thickness of these films is typically at least comparable to the range of an alpha recoil, or to the implantation depth of a heavy ion. We are not yet certain how much is known about displacement damage effects on surface film formation; it is possible that if an exposed structure of alpha recoil tracks exists, surface films will be less important in determining leach behavior.[19] In any event, it may be necessary to leach the material to a depth equivalent to several alpha recoil ranges in order to achieve steady-state conditions. It is doubtful that these conditions could be realistically achieved when recoil damage is simulated by heavy ion implantation if this process produces a damage layer which is essentially one recoil range thick.[12]

Certain waste forms such as multi-phase ceramics are inherently inhomogeneous on a macroscopic scale; others may be rendered locally inhomogeneous in the fabrication process, etc. If radionuclides are nonuniformly distributed on a scale which is large compared with the range of a recoil nucleus, spatial fluctuations in the alpha-recoil dose will occur. (In SYNROC, for example, displacement damage will presumably be concentrated in the zirconolite and perovskite phases.[20]) Under these conditions, differential effects such as local swelling could concievably affect the leach resistance of the waste form.[21] Each case requires individual assessment.

We do not feel that these differential effects in general can be properly simulated by irradiation with external sources. While techniques such as neutron or heavy ion bombardment may be quite useful in screening or initial assessment studies, it seems too much to expect these to reproduce the relatively fine-grained spatial distribution of alpha-recoil damage expected in certain waste forms. Thus, unless it can somehow be demonstrated, a priori, that the anticipated radiation effects are insensitive to the spatial dist bution of alpha emitters within a given waste form, critical evaluation wi involve testing with doped samples.

Table 6.4 lists the isotopes which are commonly used as dopants to simulate the effects of internal alpha decay in high level waste glass.

Table 6.4

Doping Isotopes for Testing Waste Glasses

Isotope	Half-Life
Pu-238	87.7 yr
Am-241	432 yr
Cm-242	162.8 day
Cm-244	18.1 yr

In order to achieve total alpha-decay doses equivalent to those anticipated in actual waste forms, doping levels of a few percent are commonly required.[1,3,11,13-15] Even at these loadings, a few years may be necessary to obtain dose levels in the range of 10^{18} α/g. [The virtues of a reliable screening procedure are apparent (see recommendation 7.5.1)]. The available evidence[1,7,16] suggests that the effects of internal alpha decay do not depend critically upon dose rate in these accelerated tests. This is encouraging in that a strong dose rate dependance might cast serious doubts on the ability of accelerated testing to reflect behavior under repository conditions. We feel, however, that this area should be investigated further. In particular, it should be determined whether accelerated testing with doped samples is expected to represent worst case conditions. Also, in studies with doped samples, most of the helium generated in internal alpha decay presumably remains in the sample as the damage builds up.[1,13,15,22,23] This may not be the case at the low dose rates anticipated in repositories. In certain instances, the presence of helium may (synergistically) affect radiation damage formation - by stabilizing voids, for example.[8] Here also additional comparison between accelerated tests and repository conditions is warranted. (See recommendation 7.5.3.)

Since leach tests typically probe only a thin surface region, steps must be taken to ensure that the spatial distribution of radionuclides and displacement damage in or near the region under test does indeed reflect the situation anticipated in actual wasteforms. This will require a certain amount of characterization; alpha autoradiography may be particularly useful here. It is not generally adequate to consider only the bulk effects of radiation on the individual components or phases of a complex waste form. Leach testing should be carried out on material which is characteristic of bulk and surface regions of the manufactured waste form. Very-near surface regions may not be entirely characteristic of bulk behavior since recoil nuclei can be ejected from surfaces during alpha decay.[24] There is also evidence that selective chemical attack occurs along recoil nucleus and heavy ion tracks at surfaces.[19,25] As a minimum requirement, the material should be leached to a depth of several recoil tracks.

6.4.2 Ionization in the Waste Form

Internal ionization within the waste form is expected to provide only a relatively small number of atomic displacements in comparison to the alpha recoil damage. Certain structural changes are said to occur in silicate based materials under very heavy doses of ionizing radiation. Quartz becomes amorphous upon heavy irradiation (10^{13} rad) with electrons whose energies are below the threshold for displacement damage.[4,26] Swelling or compaction of silicate glasses may also occur due to ionization. Typically, doses of 10^{12} rad are required to provide an observable effect.[27] These changes apparently do not involve large scale migration of displaced atoms. Of perhaps equal importance are effects associated with internal charge transfer. A relevant example is cerium, which when incorporated in glass can change its oxidation state under gamma irradiation.[28] If a glass or ceramic waste form changes color under irradiation, it is likely that changes in oxidation states have taken place; a leach test should assure that the charge states of radionuclides and other species in the waste form do in fact simulate those which are anticipated in the presence of radiation in the repository. (See recommendation 7.5.4.)

Leach tests to study the effects of alpha recoil damage are often carried out in waste forms which have not been subjected to gamma radiation. Under actual repository conditions, the waste form will have received a substantial gamma dose before alpha recoils build up to the values commonly used in tests (Table 6.3). The possible effects of gamma-ray "preconditioning" should be established in tests designed to study long term leaching. (See recommendation 7.5.4.) There is some evidence to indicate that ionization may tend to offset certain effects such as swelling which are produced by displacement damage.[29] We are not aware of any direct studies on waste form materials. It has been suggested[7] that ionization might play a role in radiation annealing. Of course, the ionization from fission fragment decay will persist for a relatively short time with respect to that required for the build-up of alpha decays. There are situations in which modified atomic species or defects exist in substantial numbers only during irradiation.[30,5] In others, however, atoms rendered mobile by irradiation may remain mobile after the irradiation has ended. Primak[31] has shown that sodium atoms in glasses can retain their irradiation induced mobility subsequent to electron bombardment.

6.4.3 Radiolysis of Leachants

The chemical nature of leachants may be modified by radiolysis. This effect has been studied in salt brines where both gaseous and liquid species may be produced by gamma radiolysis.[2,32] The quantity of radiolysis products formed is found to increase with total dose, concentration of dissolved solids and dose rate. Static leach tests on glass and ceramic wasteforms carried out during gamma irradiation indicate accelerated leaching in certain cases (Table 2.7). It is difficult to be more specific without a careful comparison of the techniques used at several different laboratories; such a comparison will be required to establish realistic test conditions. The accelerated leaching may involve radiolysis, as well as those possibilities discussed in the previous section. It is important that the question be settled - radiolysis might be important only during the first few hundred years after burial, (i.e., during the high gamma flux) while damage in the wasteform could remain stable for much longer periods.

6.5 Radiation Effects in Corrosion Testing

Corrosion testing is most directly applicable to waste canisters. Relevant effects which must be considered are indicated in Table 6.1.

6.5.1 Radiation Damage to the Container

Metals are quite resistant to bulk ionization damage. Under anticipated repository conditions, we do not expect that the bulk properties of heavy metal containers will be significantly altered by gamma irradiation. Prudence, however, dictates that this be confirmed by direct measurement at repository doses. This should be a straightforward matter, and tests in generic materials are considered acceptable at this point. (See recommendation 7.5.2.) Heavy displacement damage, if it occurs at all, should be largely confined to a thin interior layer next to the waste form. If multi-component canisters are used, radiation damage may occur in nonmetallic components; organics may be particularly susceptible. Ionization effects including charge buildup could presumably occur in insoluble insulating layers (e.g., corrosion films) on or near metal surfaces

The conductivity of highly insulating oxide layers such as TiO_2 can be increased by ionizing radiation which might affect electrochemical corrosion processes.[32] While the significance of these effects is doubtful in comparison to effects such as requirements on radiolysis, some assessment is warranted in view of the stringent requirements on containers and the localized nature of corrosive attack.

6.5.2 Radiolysis of Corrosive Agents

The chemical nature of corrosive agents may be altered by radiolysis. Measurements at Sandia Laboratories indicate that corrosion of metal canisters in salt brines under static conditions is accelerated by gamma radiolysis. To quote:[33]

"...Effect of Radiation: Several alloy specimens were exposed to 90 °C brines in the presence of gamma radiation (10^7 R/hr, integrated dosage 1-2 x 10^{10} R) from a ^{60}Co source. A number of preliminary conclusions can be drawn: (1) the principal effect on corrosion is due to the production of radiolysis products; (2) the quantity of radiolysis products formed increases with increases in the dose rate, the total dose, and the concentration of solids dissolved into the irradiated solution; and (3) at dose rates typical of high level waste, the corrosion rate of 1018 mild steel is doubled, while that of stainless steel, Inconel 625, and Ticode-12 are just detectably increased. The increases in rate are probably due to a slight increase in the oxidizing potential of the solution..."

It is interesting that the quantity of radiolysis products (as well as corrosion rates) is said to depend upon dose rate as well as total dose; apparently the test can be accelerated by increasing the dose rate. We assume that most radiolysis products will be created in material within about 1 meter of the wasteform during the first thousand years. These may be lost to back reactions, scavenging, etc., during and after irradation. When this occurs, the concentration of radiolysis products at any given time will depend upon dose rate, as well as total dose. This is apparently the case in the Sandia experiments. Under these conditions, a dilemma arises -should one test at realistic dose rates or realistic total doses? The answer depends on which method demonstrably provides worst-case conditions. To address this question, information will be needed on the time required to build up radiolysis products and on their stability in the absence of radiation. This information will also be necessary to determine how often corrosive or leaching solutions should be changed. (See recommendation 7.5.2.)

6.6 Radiation Effects in Sorption Testing

Sorption tests will apply primarily to overpack and host rock materials. Again, the radiation environment and effects of potential importance are indicated in Table 6.1. Both the solid and liquid phases may be influenced by radiation.

6.6.1 Ionization in Overpack and Host Rock Materials

Typical overpack materials include clays, zeolites, and exchange resins. There is little radiation damage information available on some of these materials.[34] Hydrated minerals such as clays might be modified to some extent by internal radiolysis. (Radiolysis has been observed in concretes, for example.[35]) Should some radiation damage occur, it is not clear that it would be harmful. For example, dehydration may expose more surface area for sorption; our knowledge here is quite incomplete. The basic constituents of many overpack and host rock minerals are oxides which are relatively resistant to bulk ionization damage. Sorption, however, may involve surface effects in aggregate materials. Workers in the U.S.S.R.[36] have found that radiation influences the surfaces of alumnosilicate minerals, and changes sorption properties. Again, little information is available; however, the effects may be rather modest. (See recommendation 7.4.2.)

Rock salt has been studied in some detail.[4,5,37,38] This material, however, is not expected to be useful in terms of its sorptive properties. Rather, radiation effects in rock salt may in part establish the environmental conditions under which sorption testing should be carried out. We have previously mentioned radiolysis of rock salt brines.[2] In addition rock salt is, without question, the most susceptible of the candidate host rocks to radiation damage. The extent of the radiation damage is governed by factors such as temperature, radation dose rate, and total dose.[4,5,37] Under certain conditions, radiation induced defect concentrations might approach 0.1% or more in material within about a foot of waste containers.

When irradiated rock salt dissolves in water, gaseous hydrogen and hydrochloride ions are produced, in addition to the usual sodium and chloride ions.[38] The possible presence of these species should be taken into account in assessing the capacity of those materials (if any), which might be used as sorption barriers in rock salt. Such barriers, however, might effectively shield the salt from radiation.

6.6.2 Radiolysis Effects on Liquid Media

As in leach and corrosion testing, radiolysis may modify the chemistry of the media which transport radionuclides through the overpack. In certain cases, radiolysis effects are said to increase sorptive capacity slightly.[36] Radiolysis is particularly efficient in liquid media (such as rock salt brines) which contain bromide ion as a scavenger.[2] There is apparently some evidence that radiation effects can influence the oxidation states of plutonium in aqueous solution.[39] The relevance of these and other results toward formulating realistic test conditions needs to be established. For example, valence changes in aqueous species will probably be overwhelmed by the redox potential of the geochemical environment. (See recommendation 7.5.2 and 7.4.2.)

6.7 Conclusions

In this section we summarize our initial review and offer certain preliminary conclusions bearing on radiation effects in waste package testing.

6.7.1 Establishing the Radiation Environment in High Level Waste Packages

The radiation environment is inherently complex and will depend sensitively on waste package design. Alpha recoil damage may be inhomogeneously distributed in complex waste forms; gamma dose rates at the outer surface of the waste form or container will depend on the waste form loading and the shielding properties of these components. Realistic estimates of the anticipated radiation environment within specific waste packages will be an absolute necessity in establishing test conditions for individual components. The current task will assemble the available information as promptly as possible. When this is complete, certain tests may prove demonstrably unnecessary. Our initial evaluation indicates for example that radiolysis effects on container corrosion will not require study if heavy containers of the type proposed by Swedish researchers are used.(40) However, some of the data apparently remain to be developed for the newer candidate waste package configurations.

6.7.2 Simulation of Radiation Damage in Waste Forms

• We feel that at some point in the waste package evaluation it will be necessary to test waste forms or waste form materials which have received radiation doses at least as large as those anticipated under repository conditions. This will require either that the test form be doped or externally irradiated; both may be required. No waste form should be considered in which realistic radiation doses cannot be administered without using highly atypical test specimens. Such waste forms are inherently untestable. It is conceivable that such a situation might arise if, due to solubility limitations, a multiphase waste form could not be doped with active alpha emitters without producing an atypical internal structure. We do not see this as a problem for any of the waste forms currently under study by DOE. It may, in some cases, be difficult to administer realistic gamma doses to internal components embedded in heavy matrix material. However, as long as the process of embedding does not drastically influence the properties of the radionuclide host, external testing of the host phase under gamma irradiation would appear adequate.

• There is no standard method for simulating the alpha recoil damage anticipated in wasteforms. Doping is commonly used, but external irradiation has also been suggested. In at least one case surface ion implantation is said to accelerate leach rates to an extent not commonly observed in materials doped with alpha emitters. It is extremely important that this result be understood. (See recommendation 7.5.1.) In the absence of standard test conditions, it is not immediately clear how significant the difference is (Table 6.3). The situation is being reviewed; we will not speculate here except to say that it is our present feeling that external irradiation may be a useful technique for screening waste forms by comparison, but should not be entirely relied on to produce a realistic absolute measure of waste form durability. Neutron irradiation cannot be considered an acceptable simulation technique for critical evaluation unless it can be demonstrated either that the anticipated spatial distribution of alpha-emitters in the waste form is sensibly uniform or that the radiation damage is insensitive to the details of the radionuclide distribution.

Although radiation may modify bulk properties, it is often only a region near the surface which is actually tested. It is important that the test region be adequately characterized to ensure, as well as possible, that the spatial distribution of radiation damage and radionuclides corresponds to that of the actual waste form. We recommend that the leach testing be carried out on samples obtained from both interior and exterior regions of monolithic waste forms. Research will be necessary to determine how best to characterize the radionuclide distribution. (See section 7.5.1.)

- The different time scales involved for fission fragment and TRU decay chains suggest that the important effects of beta decay and alpha recoil might be simulated separately or sequentially. The validity of such a procedure remains to be established, however, since a prompt buildup of alpha recoil to a certain level may precede the slow long term accumulation. We will require an accurate estimate of the temporal evolution of alpha, beta, and gamma fluxes within the waste form, as in section 6.7.1. Except for transmutations, internal beta decay can probably be adequately simulated by external gamma irradiation, or in thin samples by energetic electron bombardment.

- If necessary, preconditioning effects of gamma irradiation on long term alpha decay damage could be simulated by first subjecting doped samples to a heavy gamma dose before leach testing is carried out. This would approximate conditions for times greater than about 300 years. It is quite possible that screening experiments can be carried out which show that such a simulation is not required for critical waste form evaluation. For example, in certain cases, the majority of the ionization damage may not be sufficiently stable to have a significant effect on the long term buildup of alpha-decay damage. Also, as mentioned earlier, it appears that the effect of ionization may be to supress certain effects due to displacement damage, rather than to enhance them. A few measurements of the effects of simultaneous gamma irradiation and internal alpha decay on candidate waste form materials would be useful in establishing worst case conditions, as discussed in recommendation 7.5.4.

6.7.3 Simulation of Radiolysis Effects

- The available evidence indicates that leaching, corrosion, and sorption can be modified by radiolysis of the liquid media. Consequently, we anticipate a need for standardized radiolysis/leaching, radiolysis/corrosion, and radiolysis/sorption tests. If the chemical composition of radiolysed solution can be established, it may be possible to carry out simulations without irradiation. However, testing during gamma irradiation has the advantage that the component under test is also irradiated. This distinction could be unimportant in some corrosion tests; in leach and sorption testing however, we have seen that gamma irradiation might affect the component being tested. Testing during irradiation is generally recommended. If worst case conditions can be confidently established, only a limited amount of testing during irradation may be required. Additional research required to establish these conditions is recommended in section 7.5.2.

6.7.4 Simulation of the Effects of Internal Transmutations

• The effects of internal transmutation due to beta decay may be the most difficult to simulate for test purposes. Realistic simulation would seem to require doping the waste form with active beta-emitters with the same chemical characteristics as cesium and strontium. It is important, in view of the complexities which accurate simulation would entail, that some initial screening be undertaken promptly, possibly by neutron induced transmutations. We must learn as soon as possible if transmutation effects need to be accurately simulated in waste form testing (recommendation 7.5.5).

6.7.5 Additional Questions

In addition to certain points explicitly discussed above, several other questions remain to be addressed. These include the effects of temperature and dose rate on radiation damage simulation, and a stipulation of which tests must be performed during irradiation and which can be carried out in irradiated material. These topics will be taken up in subsequent reports, as a necessary prelude to formulating final test recommendations. Proposed research in certain of these areas is described in Section 7.

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7. SUMMARY OF TESTING RECOMMENDATIONS AND RECOMMENDED RESEARCH AREAS

In this section, we will enumerate areas where research is needed to fill information gaps identified in the testing areas discussed in previous sections. These areas have been identified during our limited review of state-of-the-art technology in testing methodology, as well as the state of knowledge concerning the predictive interpretation of test results. These recommendations are, of course, subject to modifications if newer information comes to our attention which may in part resolve the questions posed here. Both areas must be integrated in order to recommend specific tests and performance requirements necessary to assure that a waste package or packages will meet the proposed release rate requirements.

Much of the research described in the following discussions is closely interrelated. The discussions presented are somewhat arbitrary in this regard. A very tightly coordinated research plan is required to interrelate the efforts in these areas as described, so that a larger, coherent, and useful body of information is developed to support the formulation of specific testing procedures to evaluate waste package candidates for compliance with the 10CFR60 proposed criteria.

7.1 General Research Areas

7.1.1 Repository Environmental Conditions

For this report, it was assumed that environmental conditions around the waste package could be predicted with a fair degree of accuracy so that initial efforts in this task could concentrate on assessing test methodology and the identification of variables requiring inclusion in a testing scheme. However, a directed effort is needed to define precisely the range of environmental conditions (temperature, radiation fields, groundwater compositions, etc.) to which the waste package will be exposed during its functional lifetime. This information is necessary so that bounding conditions for testing can be established. This will require analysis of many repository scenarios based on combinations of host rocks and package components. We recommend that this work be initiated as soon as possible so that formulating detailed testing schemes can be completed. We plan to incorporate at least a portion of this work in our future efforts in the test development review task. However, we feel that this problem will require a greater effort for best results.

7.1.2 Modeling Package Behavior-Summing the Parts

If the "strong link" approach to predicting package behavior (Section 2.6.5.) cannot be applied to particular package designs, it will be necessary to integrate laboratory results for single component testing to produce whole package release rates. This is by no means an easy task. A modeling effort is required in which various failure modes are assumed and consequent whole package release rates developed from existing test data on single component behavior. The conditions under which failure scenarios are developed will be based on the following assumptions:

1. Failure modes for the container must be assumed in terms of the type of corrosion breaching developed, i.e., uniform attack, crevice corrosion, stress corrosion cracking, etc., and the extent to which the waste form is exposed to intruding waters as a function of time. This prediction on corrosion behavior assumes environmental conditions which require definition (see recommendation 7.1.1), test data on corrosion behavior and leach rates, some of which are available.

2. Leach rate behavior under a variety of conditions must be assumed where adequate experimental data are not existant. This requires many scenarios for environmental flow rates to be used which are based on predictions of canister behavior (assumption 1 above) environmental conditions, (recommendation 7.1.1) and leach rate data as a function of flow rate (Sections 2.6.1.2 and 3.2.4). In this latter area, little information is available (see recommendation 7.2.1.).

3. Sorption behavior of the overpack-backfill and host rock must be well defined since this is the final barrier preventing radionuclide migration out of the package (see recommendation 7.4.1). Here again, assumptions must be made for each failure scenarior investigated, in terms of sorptive behavior as a function of flow rates (in this case, the contact time-Section 5.2.2) and other environmental conditions (liquid media composition, temperature, etc.).

• We recommend that this modeling effort be initiated as soon as possible. It is not necessary to wait until a large data base of testing results is assumed since the purpose of this research area is to determine <u>how</u> to integrate test results into whole package release rates. Methods for doing this can be developed for assumed scenarios and refined as more reliable test data becomes available.

7.1.3 <u>Whole Package Testing and Synergistic Effects</u>

Synergistic effects cannot be adequately tested in the single component testing strategy (Section 2.5 and 2.6.4). We recommend that research be initiated to focus on the identification of synergistic effects in specific waste package combinations.

• Small "model" waste packages can be manufactured using candidate waste forms, containers, and overpack-backfill materials. These packages can be exposed to leachant solutions tailored to simulate site-specific waters from several repository environments. For these tests, the containers can also be artificially breached to allow leachant solutions access to waste forms, and to accelerate the testing. The "model" can also be tested in a radiation field. After a period of time, the package can be recovered and examined to determine the effects of the various components on each other.

The purpose of this experiment is to identify synergistic effects only. These synergistic effects cannot be quantified easily because of the many compromises required to make a small, easily tested, waste package. If unexpected results are observed (such as relatively increased corrosion rates on one side of the container) testing under more realistic conditions can be designed to quantify the observed effect. For these scoping tests, we do not recommend that fully loaded waste forms be used, in order to make the experimental procedure relatively simple in these early experiments.

Information on potential synergistic effects is necessary to support any detailed testing plan proposed for evaluating single component performance. Without assurance that synergistic effects will not result in unexpected failure of the barriers, testing results for single components can always be questioned, and these questions cannot be answered reliably.

7.2 Leach Testing

Research is necessary in the area of leach testing concerns systematic testing of candidate waste forms under realistic repository conditions, methods of scaling and extrapolating laboratory results to field conditions and time scales, and studies to illucidate the relationship of surface to leach behavior.

7.2.1 Long Term Leach Behavior of Crystalline Waste Forms

Most of the leach data existent relevant to waste form behavior concerns glass waste forms. Little information is presently available concerning other waste forms and certainly an insufficient data base to allow their performance to be evaluated reliably in terms of the proposed release rates. Information on leach rate behavior for specific radionuclides as a function of flow rate is particularly lacking and should be collected for glass, as well as crystalline waste forms.

- We recommend that long term leaching studies be initiated immediately on non-glass waste forms. The static and dynamic test methodologies have been recommended (Section 3.4) along with the variables to be included in these studies. The range of conditions should be determined by studies of potential repository-waste package scenarios as discussed earlier in this section (recommendation 7.1.1). The duration of leach testing must be sufficiently long so that steady state behavior can be determined. Based on the results of glass leaching behavior, this may well require periods in excess of one or two years. The long term tests should also include data analysis which provides mechanistic information. Test samples must be examined in detail to determine the effects of grain boundaries, lattice defects and dislocations, etc. on the observed leach behavior in the crystalline forms. Without this type of information, prediction based on laboratory tests, cannot be extended with confidence to the time frames needed to assure radionuclide isolation from the biosphere.

7.2.2 Extrapolation of Leaching Data

The problems of extrapolation of test data have been discussed previously (Sections 2.6.3 and 3.3.2). Methods for scaling and extrapolating test results must be proven before any waste package can be relied upon to contain the radionuclide load for the periods of time required. A considerable data base exists for leach behavior of glasses which can serve as a testing ground for scaling and extrapolation models. Laboratory results for short duration leach tests (in the order of days to a month of two) should be used to predict the behavior of the glasses in longer duration tests. These predictions can then be checked against the results of long duration laboratory tests. This approach is feasible for glass, but it should also be applied to laboratory leach data collected for crystalline waste forms during the course of research recommended on these forms (recommendation 7.2.1).

- Laboratory results for leaching experiments which show incongruent dissolution cannot be extrapolated reliably to time periods approaching the functional lifetime repositories. We recommend that research be carried out to investigate the conditions under which congruent dissolution is obtained in the leaching of glassy and crystalline waste forms. Specific emphasis should be directed toward establishing whether radionuclide release rates increase to become commensurate with matrix dissolution rates, or vice versa. We also recommend that, where possible, all long term extrapolation of fractional release rates be based on those for congruent dissolution. These, by definition, will be the same for all radionuclides. We feel that waste forms which achieve congruent dissolution after a reasonable time period will probably be much easier to test reliably. However, this assertion must be substantiated by additional research.

- In particular, we recommend that procedures be developed to quantitatively assess the mechanical, chemical, and radiation durability of the radionuclide-rich altered structures that often arise as a result of incongruent leaching. These structures first appear as films or layers, which protect the unaltered inside form; fracture of these films is commonly invoked to explain a pulsed increase in measured leach rates. This however, requires direct verification. Consequently, the durability of the altered structures is important because they may control the long term leach behavior. Ultrasonic and shock testing may be useful in establishing the relative durability of surface films. These tests would simulate shocks or stresses anticipated in the repository which may remove the protective layer.

7.2.3 Surface Area Effects on Leach Rates and Scaling

In standardized leach testing, geometric surface areas are typically measured (see Section 3.3.1), but this measure is not indicative of the actual area in contact with the leachant. The relationships between the surface/volume ratio and leach behavior must be more precisely defined so that scaling and extrapolation methods can be applied to laboratory results with more reliability (see recommendations 7.2.2 and 7.2.3).

- At present, there is no generally acceptable method by which to relate laboratory leach rates to fractional release of radionuclide inventory in actual waste forms. Laboratory leach rates are often expressed as a surface mass flux, i.e., in g/cm^2day. These may be multiplied by a surface-to-volume ratio anticipated in a waste form to obtain fractional release rates for that waste form only if certain conditions are met, specifically:

1. It must be shown that the laboratory leach rate is sensibly independent of the test sample surface area.

2. Pursuant to 1 above, it must be shown that the same methods are used to arrive at the surface area in test samples and waste forms, i.e., equivalent measures must be used.

3. The appropriate measure for surface area is that which leads to area independent leach rates. One commonly used measure is the geometric surface area; this may fail to provide an appropriate measure if the leaching occurs selectively at microcracks, grain boundaries or dislocations. We expect that leaching in crystalline waste forms might be influenced by the latter two mechanisms (References 1 and 2).

Additional research is recommended both to (1) determine the appropriate surface measure to use for leach testing in different waste forms, and (2) to determine, by this measure, the anticipated surface-to-volume ratios in actual waste forms. Other surface measures beside geometric area which may require consideration include: (a) dislocation density in ceramics, (b) grain boundary area in ceramics or devitrified glass, (c) microfracture density, and (d) BET area.

- The nature of the reactive surface is also important in leaching behavior. Internal cracks developed in a waste form (Section 3.5, Reference 20) may not be as susceptable to leaching as outer surfaces. Strained material produced in the actual waste package may also leach quite differently than unstrained laboratory samples if selective attack occurs at dislocation. In addition, where waste forms are enclosed in containers and subsequently leached in the field situation, the waste form surfaces in contact with the container walls may well behave differently than those on small laboratory scale samples. These surface relationships require additional study. A series of relatively simple tests can answer these questions. These experiments are described below:

1. Several sets of leaching experiments would have to be performed using samples of identical composition (both crystalline and glass waste forms), but different surface-to-volume ratios. The leaching, of course, would be performed under identical conditions. The surface areas should be measured by several methods (geometric, BET, and gas porosimetry methods, and liquid sorbers of various types). Test results can then be compared in terms of measured surface area to determine the measurement technique which produces the most reliable results. This information is necessary in both (1) formulation of specific testing procedures, and (2) in developing reliable methods for scaling and extrapolation of laboratory test results to the field situation.

2. Evaluating the relative importance of fractured and unfractured waste forms to leach behavior can be studied by performing tests on fractured and unfractured samples under identical experimental conditions.

3. A study should be initiated to determine the relative leach behavior of waste form surfaces on laboratory samples in direct contact with leachant solutions, as opposed to surfaces in contact with container walls. This can be done in several ways by performing leach tests under identical conditions. Using glass or crystalline waste forms, samples, one or more sides of which are in contact with container material and the remaining sides in contact with the solution, the surfaces can be examined to determine differences in the modes of attack between the two surfaces after a period of leaching. Another approach would employ samples that are essentially laboratory scale waste form and container combinations, as well as samples of the waste form material alone. The container-waste form would have to be artificially breached to allow access by the leachant. Both sample types would be leached under identical experimental conditions. Leach rate results can then be compared directly (in terms of fractional releases for specific radionuclides), and the samples examined at the conclusions of the experiment to determine the mode and extent of surface attack.

4. The leachability of strained or compacted materials should be studied by performing leach tests using identical samples under stressed and stress free conditions. One dimensional stress can be applied to the samples (for experimental simplicity) and the leach rates measured relative to unstressed samples. The surfaces of stressed and unstressed samples should also be examined to determine the mode of surface attack under both conditions. If an effect is observed with uniaxial strain, more realistic stress fields can be applied and the tests repeated.

Information from these studies is necessary for several applications concerned with evaluating package performance, as follows:

1. Determining the synergistic effects of the container on the leaching behavior of the waste form. This knowledge is necessary in order to formulate specific testing procedures.

2. Determine reliable surface-to-volume relationships for use in scaling applications (Sections 2.6.3 and 3.3.2, recommendation 7.2.3).

These experiments should be initiated as soon as possible so that the information can be available to evaluate the performance of potential materials in terms of the proposed release rate criteria.

7.3 Corrosion Testing

A relatively small amount of effort in the Nuclear Waste Management Program has been devoted to the evaluation of materials for waste containers. This is probably due to the only recent emergence of the "strawman" criteria in 10CFR60. Since such a small amount of effort has been spent on container corrosion studies, more research is needed in this area to qualify a container for use in a high level waste repository.

7.3.1 Standardized Corrosion Testing of Candidate Container Materials

• Laboratory tests now being conducted on container materials need to be expanded. These tests are essentially screening devices which evaluate a large number of materials and test conditions such as the effects of temperature, solution chemistry radioactivity, and stress on material performance. The tests also determine the nature of corrosive attack i.e., uniform corrosion or localized attack, such as pitting, crevice, stress, or intergranular corrosion. These tests should be performed in a uniform standardized manner so that results from the various laboratories could be compared. An expanded effort in the small laboratory screening tests is necessary and recommended. This will allow further effort to focus on selected materials for extensive testing.

7.3.2 Loop Testing for Corrosion Tests

• The shortcoming of laboratory screening tests lies in not testing materials at conditions close enough to the final application. The advantage of small laboratory tests, are their simplicity, reasonable cost, screening function, insight into the corrosive processes occurring. To evaluate materials under more realistic conditions, a more sophisticated test such as a "loop" is required. A loop test is usually used when flow of the corrosive media is present. These loops are complex since they must supply a source of flow, heat transfer, corrosive media chemistry control, sample evaluation, surface-to-volume ratio, etc. Such a loop test is costly, but comes closest to testing materials under conditions of actual use. A test program should be initiated to design, build, test, and operate such a loop facility. When adequate information is available from modeling studies and the repository environment detemined on actual selected repository sites (see recommendations 7.1.1, 7.1.2, and 7.1.3), materials can then be evaluated in the test loops under almost identical repository conditions.

7.3.3 In Situ Testing

• While testing in the laboratory loop facilities will evaluate container materials under expected repository conditions, there is always the possibility that during the storage of the container in the repository, the conditions will change from those predicted. It is recommended that an approach used in industry be incorporated into the canister corrosion program. This would be to initiate a research effort to evaluate the feasibility of using retrievable test coupons placed adjacent to or as part of the containers. These coupons would be removed periodically from the repository for evaluation. Corrosive attack, mechanical properties, and physical measurements would be made on the retrieved coupons. The use of such coupons would permit the assessment of container materials performance during the life of the container. It would indicate whether changing repository conditions are affecting the life of the container and give assurance of the container performance.

7.3.4 Multilayered Containers

• Another area of research recommended is associated with the type of corrosion which takes place on container materials. As was suggested previously, the corrosion test program should seek to identify materials which are least likely to suffer from localized corrosion, since the performance prediction of materials subject to localized corrosion is extremely difficult. If the corrosion program shows that there are no materials which meet the uniform corrosion criteria, then another approach is needed. It is recommended that a research program be initiated to evaluate the design of containers using materials which can be susceptible to a localized attack. A suggested approach would be to make the container of multilayers. This would take advantage of the nature of most localized corrosion in that in that the time for pit, crack, etc. initiation is usually much greater than their penetration rate. Once the time to completely penetrate a thin layer of container materials has been established, the container can then be fabricated with the number of layers needed to meet the proposed life of the container. There are many types of multilayer constructions which can be considered. The container layers could be of similar or dissimilar materials, they can be metallurgically bonded, or they can be insulated, they can be sacrificial, etc. Materials selected and the geometric designs, would be chosen depending on the type of corrosion taking place and the environmental conditions. The successful development of a multibarrier container would permit a more accurate prediction of container life, and may also be necessary if a material showing uniform, low corrosion rates is not found.

7.4 Sorption Testing

7.4.1 Overpack-Backfill Material Sorption Behavior

As discussed previously (Section 5.2.1), the sorptive properties of materials are affected by the environmental conditions (media composition, temperature, pH, Eh, etc.). Little information is available on the sorptive properties of potential overpack-backfill material determined under site-specific conditions, largely because these conditions are not precisely defined.

- We recommend that a systematic testing program be initiated to determine the sorptive properties of candidate materials under very precise sets of conditions designed to duplicate those expected in the respository during its functional lifetime. These conditions can be defined from site specific studies (recommendation 7.1.1). The recommended test methodologies are described previously (Sections 5.1.1 and 5.4). Variables included in such tests were also described at length previously (Section 5.2). In addition to simply measuring adsorption, desorption behavior must also be determined so that this information can be used as a predictive tool for assessing long term behavior of the waste package, as well as efforts to "sum the parts" (Section 2.6.5 and recommendation 7.1.2). We recommend that this effort be initiated as soon as possible.

7.4.2 Radiation Effects on Sorptive Properties

Little information exists on the effects of radiation exposure on sorptive properties. The components of the waste package will be exposed to radiation (Section 6), the degree and nature of which is a function of the waste loading and package component design. It remains to be determined if radiation exposure will adversely affect the performance of the sorptive barrier. Such information is required so that any adverse effects on package performance can be avoided by judicious modifications of the package design, such as increasing the thickness of the sorptive barriers, or by use of sorptive materials that are not as susceptible to damage as other candidates.

• Sorption tests must be performed without radiation exposure (data from recommendation 7.4.1 can be used), with radiation exposure, and the results compared. Dose rate effects may play a significant role (see Section six) in test simulations so that testing should also be performed concurrently with radiation exposure. These three experiments can then be compared to determine if radiation effects are significant, and if they can be simulated, or if sorption testing must be done in an applied radiation field. During these tests, the effect of radiation on radionuclide specification (Section 6.6.2) should also be considered.

7.5 Radiation Effects

In Section six, we have identified certain areas where additional research would be useful in establishing how radiation effects should be accounted for in waste package testing. Here we present our specific recommendations along these lines. The recommendations here pertain directly to test development; additional research of a more general nature is proposed in the Task 1 draft report issued under the present contract in May 1980.

7.5 1 Comparison of Radiation Effects Produced by Internal and by External Sources

• Without exception, those measurements of which we are aware indicate that the leach rates of waste glasses are only slightly modified by the buildup of internal alpha-decays. Nevertheless, it is also an established fact that selective etching occurs along charged particle tracks in glasses (and, apparently, in minerals), and that surfaces may be rendered susceptible to chemical attack on heavy-ion implantation. At this point, we have no reason to question *a priori* the validity of experiments on samples doped with alpha-emitters; we have pointed out earlier that experiments with implanted particles at surfaces may fail to simulate the radiation damage resulting from alpha particles and recoil nuclei in internal alpha-decay. However, we feel that it is essential that the difference between results obtained with ion-implanted and with internally doped samples be thoroughly understood. This will require a detailed characterization and comparison of the radiation damage produced by each technique, under standard test conditions (which, so far, have been lacking). We also recommend that such a comparison also be carried out for samples damaged by neutron irradiation or internal fission (a good start here has been made in Europe). This work may lead to the establishment of a reliable screening procedure, which could precede or even preclude tedious testing with doped waste forms (Section 6.4.1).

What we propose here is not a trivial undertaking. It is not yet obvious how best to characterize the radiation damage formed by the different techniques. Both bulk and surface sensitive measurements will probably be required. We envision the various samples subjected to a common test of chemical durability, which may differ in some respects for standard leach tests. Alpha particle effects and helium buildup may be studied by alpha bombardment either prior or subsequent to neturon or heavy particle bombardment. If this program is undertaken, we feel it might best be carried out at a dedicated laboratory possessing both the irradiation facilities and the analytical capability to conduct standardized comparisons.

7.5.2 Radiolysis Studies

It is important to identify as quickly as possible those tests which must carried out during irradiation. Radiolysis tests are a case in point. Radiolysis of leachants or corrosive agents must be considered when evaluating the long-term durability of containers or waste forms. This may be done in several ways:

a) By carrying out all tests under irradiation.

b) By carrrying out certain generic measurements to establish worst case conditions, and subsequently testing the material under these conditions.

c) By rigorously demonstrating on an anayltical basis that radiolysis is entirely negligible in a given situation.

We feel that option b) is generally preferable. Option a) may be unnecessarily involved, and option c) may be useful in only a few cases (the Swedish containers, for example).

- We recommend generic measurements which include an assessment of radiolysis products which would be anticipated in typical repository ground waters. The extent to which these depend upon temperature and radiation dose rates should be established. (It may also be necessary to take account of the composition of anticipated test specimens.) Subsequently, testing should be carried out during gamma irradiation under worst case conditions. Both containers and waste form materials should be so tested.

While we do not anticipate extensive degradation of the bulk properties of heavy metal containers due to gamma irradiation alone, confirmatory examination should also be carried out during these tests. In fact, we recommend that a preliminary screening be implemented promptly in this area. Metal samples could be heavily gamma-irradiated in various atmospheres and then mechanically tested. These measurements would settle the question of bulk irradiation effects and, in addition, would be useful in investigating "radiochemical" effects which are said by Russian workers to occur at exposed surfaces during in-air storage of radioactive wastes.

7.5.3 Radiation Dose Rate Studies

- We have recommended that at some point all waste package materials should be exposed to total radiation doses typical of those anticipated in the repository configuration. This will be necessarily involve administering the radiation does at does rates which are at least hundreds, if not thousands, of times greater than those encountered in the repository. We recommend that research be conducted to determine, as well as possible, whether the production of radiation damage at high dose rates does in fact represent worst case conditions.

The most straightforward way to do this is to compare the radiation damage formed at the same total dose for different dose rates. In practice, it is often difficult or impossible to vary the dose rate over a sufficiently wide range. This is probably the case for internal alpha decay. Under these conditions, about the best one can do is to try to establish the dose rate scaling from a mechanistic viewpoint. For example, if the apparent saturation of stored energy buildup on swelling in glasses is simply due to statistical limitations on the number of available sites for displaced atoms, dose rate effects may be negligible. On the other hand if over long periods of time processes can occur whereby the number of sites for displaced atoms is increased (through formation of aggregates by diffusion of point defects, for example), experiments at high dose rates may underestimate the radiation damage formed in the repository. Alternately, this could be counterbalanced by slow thermal annealing. Research should address these mechanistic considerations, specifically considering the effect of temperature. The central thrust should be to establish worst case conditions for testing.

7.5.4 Study of Ionizing Radiation Effects

- We recommend that research be carried out to investigate the effects of ionizing radiation on the formation of radiation damage due to internal alpha decay in waste forms. Tests might be carried out on generic materials by subjecting doped samples to heavy gamma or electron irradiation before substantial alpha-decay has accumulated. The radiation damage could then be compared to that in similarly doped samples which have not been exposed to ionizing radiation. The sequence might then be reversed to determine if ionizing radiation anneals or supresses the alpha-decay damage. A few such measurements should be sufficient to determine if extensive testing of waste forms under the combined effects of alpha-decay and ionizing radiaiton is required. If such testing is not critical, the test program may be considerably simplified.

- We recommend that experiments be carried out to determine whether the charge or mobility of atomic species in the waste form will be significantly modified during ionizing radiation. These measurements can be carried out on prototype waste form materials during either electron or gamma irradiation. Techniques such as spectroscopy, electron spin resonance, or electrical conductivity all may be useful. Measurements could, in fact, be carried out on waste form/container material "sandwiches" to investigate the possibility of charge layers at surfaces etc. A few scoping experiments here would be very useful in determining if extensive critical testing during ionizing radiation is necessary.

7.5.5 Simulation of Transmutations

o We recommend that work begin immediately to arrive at a suitable method for simulating beta transmutations in waste forms. Emphasis should be placed on crystalline materials and the effects of ionizing radiation on compensating the changes in valence which accompany transmutations must be considered. Some idea of the stability under transmutations could be obtained by comparing the structures of waste forms doped with transmutation products with those containing simulated parent radionuclides.

7.6 Test Recommendations

In this section, we summarize our present recommendations relative to a testing strategy for waste package evaluation.

7.6.1 General Considerations

- Waste package evaluation should begin with single component testing.

- The most important (key) tests are those which directly evaluate radionuclide release. These are leach tests on waste forms, corrosion tests on containers, and sorption tests on backfill materials.

- Ancillary tests and measurements are necessary to ensure that leach, corrosion, and sorption tests rigorously assess worst case conditions. We feel that the most important ancillary test involve radiation effects. Mechanical tests will also be important.

- Tests should be selected with a view toward how accurately the results can be interpreted. Critical evaluation cannot be based on generic materials alone.

- In key tests, both static and dynamic conditions should be investigated, under simulated repository environments:

  Liquid phases should duplicate expected ground waters and solid phase should match actual materials in form and composition.

  Temperatures should span the range anticipated in repositories.

  Contact time is the most difficult parameter to estimate under repository conditions. Existing data do not provide a basis for accurate estimates.

- Scaling and extrapolation are among the most formidable and difficult steps involved in waste package evaluation. Generally:

  Steady state conditions must be achieved for extrapolation in all key tests.

  Long term predictions can be either empirical or mechanistic. The latter are inherently preferable, but difficult to establish in practice.

We anticipate that it may be necessary in certain cases to resort to a worst case evaluation strategy, rather than attempt a precise (and time-consuming) predictive evaluation of long term behavior.

- Once the behavior of single components is established in key tests, the parts must be "summed" to arrive at a performance evalaution for the entire waste package.

- Synergistic effects may be of critical importance in evaluating the overall performance of a waste package by "summing the parts". Synergistic effects should be considered both in key tests on individual components, and in specific experiments with model waste packages.

- There are three ways in regulatory criteria which can be applied to "sum the parts" of a waste package: (1) by requiring that <u>all</u> components satisfy release criteria, (2) by requiring that a "strong link" component meet release criteria, or lastly, (3) by requiring that the integrated package meet release criteria. The first strategy is themost conservative and difficult to achieve. In the second strategy, one is not really faced with the problem of accurately summing the parts; however, only a relatively limited number of packages may qualify. On the other hand, the third strategy may qualify mc waste packages, but involves a rigorous assessment of overall performance. The probability that a waste package can be delivered to meet 10CFR60 criteria depends sensitively on whether methods can be derived to confidently assess the <u>overall</u> package performance. Reliance on a single "strong link" decreases the number of possible candidates.

- We feel that, if a retrievability scenario is ultimately adopted, waste package "testing" might continue after the waste packages are emplaced. This envisions something more than remote monitoring. Possibly small "surveillance" waste packages could be periodically retrieved and examined.

7.6.2 <u>Leach Testing</u>

- Single pass continuous flow leaching is the recommended dynamic test. Leachants used for key testing should be actual ground waters, equilibrated with backfill/overpack material.

- Leaching of multibarrier waste forms should be carried out both on pristine samples and, more importantly, on samples where the barrier has been penetrated.

- It is not permissible to use "steady state" laboratory leach rates for radionuclides to predict long term release behavior unless either of two conditions are met:

The relative "steady state" release rates are sensibly identical for all radionuclides and host elements (i.e., incongruent dissolution is not occurring).

or

The durability of the altered structure which results from extensive incongruent dissolution of the waste form has been adequately determined.

- If the above conditions cannot be satisfied for a particular waste form, all long term release predictions must be based upon the release rates referred to the most volatile element. We are entirely aware that these may be greater than the "steady state" release values for certain radionuclides measured in the lab time frame.

- It is not permissible to estimate fractional release rates in a waste form from laboratory leach rate data unless it is explicitly established that the laboratory leach rate is in fact independent of the parameter used to scale lab data to the actual waste form. A typical scaling parameter is the "surface-to-volume ratio." There is no reason to expect that leach rates in general will be independent of this scaling parameter.

- We anticipate that in many waste packages, the container will be primarily called on to satisfy the 10CFR60 criterion of near-zero release for the first 1000 years. Consequently, it is the ability of the waste form to retain long-lived radionuclides which may be of primary importance. This should be reflected in leach testing.

- Initial breaching of a waste container or other traumatic events in the repository may result in leach rates which are, for a short time, several orders of magnitude greater than the steady-state values. In many cases, such a short duration "pulse" will probably represent no real hazard in terms of total radionuclide release. We recommend that the release rate criteria in 10CFR60 be so structured that such acceptable pulses do not violate the criteria.

7.6.3 Corrosion Testing

- Initial screening of candidate materials should be carried out in laboratory tests to determine the relative susceptibility to pitting, crevice, intergranular, or stress corrosion.

- The test environment should simulate repository conditions.

- As in leach testing, accelerated testing and/or extrapolation will be required in corrosion studies. Tests may be accelerated by increasing temperatures or corrosiveness of solutions. The usefulness of this latter method for extrapolation purposes is questionable.

- Conservative estimates may obtained if "worst case" experiments can be carried out under conditions which lead to well defined steady-state corrosion.

- Corrosion rates are most easily determined and extrapolation simplified for candidate materials which exhibit uniform corrosion, as opposed to pitting, crevice, intergranular, or stress corrosions. For applications such as waste containers, it would be best to select materials which are unlikely to suffer localized corrosive attack under repository conditions or to pursue a multi-barrier approach.

- Key testing of container materials should be carried out under site-specific conditions. These conditions should have the material under the anticipated maximum temperature and stress expected in the selected repository, and in contact with the backfill material. The sampling plan should determine both the nature of corrosive attack and the steady state corrosion rates.

- In situ testing could be continued by placing retrievable coupons of the container materials in the repository next to emplaced containers. These coupons would then be periodically retrieved to monitor the performance of the container.

7.6.4 Sorption Testing

- A combination of column and batch tests is recommended for sorption testing. Multiple testing of the candidate materials under different initial conditions will be required.

- Desorption as well as sorption tests will be required.

- Both sorption capacity and selectivity of the barrier components must be determined.

- Sorption tests cannot be accelerated. However, steady-state conditions can be achieved in laboratory experiments in practical time frames.

- Dynamic sorption tests should be carried out using either fractured or unfractured columns of the candidate host rock. Columns made from ground repacked material may be used only to test overpack-backfill material.

- Chromatographic column tests are not appropriate for either host rock or overpack-backfill testing, unless difficulties arise with other techniques.

- Radionuclide breakthrough in the column should be measured as a function of chemical variables, such as Eh and pH. The distribution of radionuclides in the column should also be determined following sorption or desorption testing.

7.6.5 Radiation Effects

- Realistic estimates of the radiation environment will be an absolute necessity in establishing test conditions for waste package components. Once these are assembled, detailed simulation of radiation effects may prove unnecessary in many cases.

- At some point in the waste package evaluation, it will be necessary to test waste forms or waste package materials which have received radiation doses at least as large as those anticipated in the repository.

- No waste package should be considered in which realistic radiation doses cannot be administered for test purposes without using highly atypical test specimens.

- There is no standard method for simulating alpha recoil damage in waste forms. In certain waste forms, such as multiphase ceramics, there is reason to believe that the spatial distribution of radiation damage may have an effect on waste form durability.

- Neutron irradiation should not be considered as an acceptable simulation of internal alpha decay damage for key testing in systems where the alpha emitters are inhomogeneously distributed, unless it is first established either that uniform irradiation can represent worst case conditions or that the distribution of radionuclides within the host is not critical in radiation damage formation.

- Steps must be taken to ensure that the spatial distribution of radionuclides and radiation damage in test specimens corresponds to that anticipated in the actual waste form. Leach testing should be carried out on samples obtained from both the internal and surface regions of prototype waste forms.

- Screening tests must be carried out to determine the effect of radiolysis of liquid media in leaching, corrosion, and sorption tests. The measurements should be carried out during ionizing radiation and be aimed at establishing worst case conditions.

- We recommend that efforts be directed toward developing acceptable simulations of transmutation effects in waste form materials. At some point in the test program, all waste form candidate materials must demonstrate adequate resistance to transmutation effects.

7.6.6 Future Work

The results and discussion presented above summarize our initial review of test development relevant to waste package evaluation. In this review, we have largely been concerned with general questions of testing philosophy and methodology, rather than specific recommendations for a given test procedure. The intent thus far has been to identify the critical tests, and to raise those issues which must be satisfactorily addressed in order to arrive at a valid test program. This phase has, for the most part, been completed.

In the next phase of this task, the object is to address the issues previously raised (for example, to determine as far as possible what will constitute worst case conditions for testing "generic" waste packages in the tests identified previously) in order to arrive at detailed test recommendations. Time can be saved if the screening tests carried out in DOE laboratories on candidate waste package components can be made as compatible as possible with those ultimately required for licensing. To this end, it is our intent to submit, in the near future, a hypothetical test program aimed at evaluating a "generic" waste package. While such a program may be incomplete, we feel that it will form a useful focal point for the detailed considerations which must precede development of a final test program.

7.7 References

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[1]Available in public technical libraries.