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INFORMAL REPORT

TECHNICAL FACTORS AFFECTING LOW LEVEL WASTE FOR ACCEPTANCE REQUIREMENTS

DRAFT REPORT

D. R. MacKenzie, F. Vaslow, D. Dougherty, and S. Chan

August 1982

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Manuscript Completed: August 1982

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ABSTRACT

This report provides technical support to NRC in connection with the proposed rule 10 CFR Part 61 and NRC's draft Branch Technical Position (BTP) on waste form. Six specific areas are addressed, namely: the technical basis for limiting containers of radioactive gases to atmospheric pressure and 100 curies; the requirements to demonstrate that a stable waste would be recognizable for 300 or 500 years; the feasibility of achieving less than 5% deformation in buried wastes; the adequacy of ASTM tests G21 and G22 for testing for biodegradability; the adequacy of ASTM test B553 for testing for thermal degradation; and the basis for determining if a waste is explosive or pyrophoric. The principal conclusions of the report follow. A maximum pressure of 1.5 atmospheres for radioactive gases is acceptable, but the radioactivity limit should depend on the isotope, the quality of the container and the properties of the site. Site and package qualities and a wet/dry cycling test are suggested that appreciably increase the probability of indicating whether a waste would have long-term recognizability. Achieving deformation of buried waste of <5% would not be feasible using current solidification methods with either metal or polyethylene containers. ASTM tests G21 and G22, with modifications, are suitable for biodegradability testing. A modified form of ASTM B553 is adequate for thermal testing. Required information on pyrophoric and explosive materials is provided by tests given in Department of Transportation regulation 49 CFR Parts 172 and 173.

CONTENTS

CONTENTS, Continued

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TECHNICAL FACTORS AFFECTING LOW-LEVEL WASTE FORM ACCEPTANCE REQUIREMENTS

1. INTRODUCTION

The proposed 10 CFR 61(1) contains a section (61.56) on the requirements to be met by low-level waste (LLW) for shipment to a burial site and for burial at the site. Such requirements are necessary since the burial site alone cannot be expected to provide the necessary degree of isolation of the waste. In general, the requirements can be considered as applying to the waste form, since it is recognized that the metal containers normally used will be breached within a relatively few years. For the less hazardous Class A wastes, waste form can be quite diverse and stability requirements are minimal. The more hazardous Class B and C wastes have stricter performance requirements, which are intended to provide stability for at least 150 yrs.

The structural and other aspects of that stability will depend largely on the properties of the waste form. Thus NRC has prepared a draft Branch Technical Position (BTP) on waste form(2) to provide guidance to waste generators on test methods and criteria for waste forms acceptable to NRC in terms of the proposed 10 CFR 61 regulations. This technical position applies to all waste generators who solidify wastes or use high integrity containers in order to meet the Class B and C stability requirements.

NRC has requested BNL for technical support in connection with the proposed 10 CFR 61 regulations and the draft BTP on waste form. In particular, NRC has stipulated that work be concentrated on specific areas relevant to the requirements of the proposed 10 CFR 61. The six specific questions raised by NRC, each addressed in a separate section of this report, are the following:

1. What is the technical basis for limiting the pressure (1 atm) and activity (100 curies) of radioactive gases? Should limit(s) different from those set out in proposed 10 CFR 61.56 be established?

2. What would be required to demonstrate that a proposed stable waste will be recognizable for 300 or 500 years?

3. What is the feasibility of achieving less than 5 percent deformation in wastes considering current methods and practices of solidification using cement, asphalt and vinyl ester-styrene systems which may not result in completely filling the container with solidified waste? Can modified (but practicable) procedures help to achieve this or should the 5% limit be changed to reflect current practice?

4. Are the testing techniques to demonstrate resistance to biodegradation specified in ASTM G21 and ASTM G22 adequate to test wastes typically solidified using cement, asphalt or vinyl ester-styrene processes? If these tests are inadequate, identify alternative testing required to demonstrate stability from biodegradation.

5. Is the testing specified in accordance with ASTM B553 (to assure that wastes can be shown to be resistant to thermal degradation) adequate for solidified wastes? If this testing is not adequate, identify what alternative testing is required to show resistance to thermal degradation.

6. What basis should be used to determine if a waste should be considered as explosive or pyrophoric?

2. TECHNICAL BASIS FOR LIMITING THE PRESSURE AND ACTIVITY OF RADIOACTIVE GASES

2.1 Present Situation in Terms of Regulatory Needs

In discussing the minimum requirements for all classes of wastes to be disposed of in near surface burial, Section 56 of the draft regulation 10 CFR 61 sets out criteria for packages containing gaseous wastes. Two requirements are specified:

1. A total pressure not exceeding one atmosphere at 20°C
2. A total activity not exceeding 100 Ci per container.

No information on the technical bases for the individual package activity or pressure requirements is given in the draft Environmental Impact Statement(3) on 10 CFR Part 61, nor is further information provided in any part of the proposed 10 CFR 61. The second requirement reflects current practice at operating LLW burial sites, but a technical basis for it could not be found. Representatives of South Carolina and Washington (presently the only states permitting commercial burial of gaseous radioactive wastes) were contacted to determine their reasons for the limit.[*] Both respondents indicated that there was no quantitative basis for that limitation, but in view of the high mobility and difficulty of control of a released gas a relatively low and conservative limit was set. The first requirement, though apparently more restrictive than the current burial site practice (internal pressure of the container no greater than 1.5 atmospheres), is still reasonably in line with it. Again no definitive basis was available. NRC has requested that a technical rationale be provided either for retaining the present limits or for replacing them with more suitable values. Accordingly, the technical factors which affect the setting of limits for pressure and activity are examined in the following sections (pressure limit, Section 2.2; and activity limits, Section 2.3) and conclusions are drawn regarding appropriate limits.

2.2 Maximum Pressure for Gaseous Wastes

The rupture of containers holding gaseous radioactive wastes at pressures well above ambient would lead to a much more rapid release and spread of the hazardous material than for packages in which the gas is contained at ambient pressure. This is so since, for containers at ambient pressure, the release rate from a leaking container is controlled by diffusion of the gas while for pressurized containers release is controlled by the pressure difference across the leak. Hence, from the standpoint of limiting exposure due to a leaking

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[*] Telephone conversations with Michael Tkacik, South Carolina Bureau of Radiological Health, and Lee Gronemyer, Washington State Radiation Control Program, May 1982.

container, this pressure difference should be as close to zero as possible or slightly negative, since for the case of diffusion controlled release dilution of the gas would be maximized.

This argument, of course, does not of itself preclude the disposal of pressurized gaseous waste. However, as with the handling of any material packaged under pressure, such disposal would require extra care in both packaging and handling so as to compensate for the increased risks involved. The increased risks caused by pressurization are, to a certain extent, summarized by the regulations governing the transportation of gaseous waste.(4,5) For noble gases, shipments of pressurized gases are placed in a higher risk category by the Department of Transport (DOT) than those for unpressurized noble gases. (It must be noted, however, that this is not the case for shipments of ^3H gas.)

The intent of a regulation on container pressure should be to ensure relatively slow release of activity in the event of a sudden rupture and to avoid essentially immediate release which could take place if a container were under high internal pressure, as well as to minimize the risk of a container breaking due to its internal pressure. Requiring containers to be filled at close to ambient pressure will accomplish these objectives. The authors feel that the maximum of 1.5 atm currently permitted at burial sites is close enough to ambient to constitute a minimal extra risk over a required 1.0 atm maximum (at 20°C or any other ambient temperature). An internal pressure of 1.5 atm is not large enough to rupture a properly designed container, and in terms of release of the gas after accidental breakage, only one third of the contents would be immediately released, with release of the remainder being diffusion controlled.

2.3 Total Package Activity

Limits on the transporation of radioactive gases(4,5) vary greatly depending on the chemical nature, pressure and radioactive properties of the gas, but for the most common radioactive gases $^3H_2$ and ^{85}Kr, 1000 Ci per container for Type A shipments and 50,000 Ci per container in Type B shipments are permitted for the unpressurized gases. The limits are subtantially lower for other radioactive gases and pressurized gases other than $^3H_2$. There is no basis in the DOT transporation requirements for 100 Ci limitations on $^3H_2$ and ^{85}Kr.

In order to determine whether the limitation has technical justification, one must consider the consequences of release of the package contents both during and after burial of the waste. Any limitations on activity allowed in the package must be set not only with the guidelines for waste classification of Table 1 of the proposed 10 CFR 61 in mind, but also in such a way that existing regulations governing exposure to both workers and the general public are not exceeded. Taken at face value, this appears to imply that activity limits for gaseous wastes should be radionuclide specific. Given the range of conceivable gaseous radioactive wastes, however, it was felt that a detailed case-by-case analysis was outside the scope of this work. A generic methodology for such an assessment, however, is outlined. In addition, for two common gaseous wastes, ^{3}H and ^{85}Kr, this methodology is discussed in order to determine what the maximum activity limits for these gases should be.

2.3.1 General Methodology

For a waste package containing gaseous wastes, two credible breach scenarios are assumed. In the first, the package is breached during emplacement, and the entire content of the package is released. In this case, release is directly to the atmosphere and doses to workers on-site and to the general public off-site can be limited to inhalation and contact doses. In the second scenario, total release occurs after burial. For this case, the credible pathway for exposure consideration depends upon the particular gas or gases involved. In addition to the atmospheric release discussed above, certain gases, e.g. $^{3}H_2$, can be readily incorporated into the groundwater and, hence, for these gases exposure to the general public via contamination of the groundwater must be assessed.

With respect to the short term atmospheric release of radioactive gases, exposure must be calculated for two release conditions:

1. The release and mixing in a confined space, taken as 10 m^3, (occupational exposure),
2. The unrestricted area exposure caused by the movement of the above contaminated volume of air with the wind, from the inner edge of the buffer zone to the outer edge.

Radiation exposure is proportional to the product of the concentration of the radioactive substances in air and the duration of the exposure. The exposure may be expressed as a time integral over the concentration or as a length of time for a fixed concentration. The maximum concentrations allowed by 10 CFR Part 20(6) are for periods of 13-40 hour weeks (1 quarter year) for occupational exposure and one full year for non-occupational (unrestricted area) exposures. The maximum concentration is taken as an average over the quarter or year. Tolerances can thus be expressed in terms of the time necessary to reach the 10 CFR 20 maximum exposure. For the purpose of this report, the most restrictive limits of 10 CFR Part 20 for routine release of radioactivity are used. Under certain conditions, quarterly exposures can be 2.4 times those given in Table 2.1 and exposure under accidental conditions can be much larger even than these.

For tritium, two possible modes of exposure can occur, depending on whether the tritium is rapidly absorbed by the lungs and skin (as $^{3}H_2O$) or the body is immersed in, but does not absorb, tritium (as $^{3}H_2$). Since tritium gas is only slowly converted to tritiated water in air, it will be assumed that short-term exposures from accidental releases of $^{3}H_2$ are through the immersion mechanism only. Other tritium-containing gases may be treated in accordance with their similarity in chemical behavior (e.g., solubility in water) to $^{3}H_2$ or $^{3}H_2O$.

For exposure in unrestricted area, an atmosphere diffusion equation (Eq. 2.1)(7) can be used to calculate the exposure integral. For an instantaneous (puff release) at ground level from a point source, the exposure integral at a receiving point at ground level in the center of the puff trajectory may be expressed as(7)

$$\psi_p = \frac{Q}{\pi \sigma_{yI} \sigma_{zI} \overline{u}} \tag{2.1}$$

where

Q is the quantity of radioactivity in Ci,

σ_{yI} is the standard deviation of radioactivity in the vertical direction for an instantaneous release,

σ_{zI} is the standard deviation of radioactivity concentration in the lateral direction at distance for instantaneous release, and

$\overline{u}$ is the average wind velocity during the release period.

σ_{yI} and σ_{zI} are functions of the air turbulence class and distance of the receiver from the origin of the release. Values are available in tables in Reference 7. The application of this treatment to the release of two gases, $^3H_2$ and ^{85}Kr, is given in Section 2.3.2.2.

After burial, the release to the atmosphere of gases from the waste package will be slowed by diffusion of the gas through the soil as well as, in the case of $^3H_2$, by conversion of much of the gas to ^3H_2O which would largely remain in the soil. Thus, exposure due to this pathway will be less than accidental release prior to burial and can be neglected with respect to determining the maximum allowable activity for a single package of gaseous radioactive wastes. Hence, after burial, the pathway which must be considered for the purposes of setting this limit is groundwater migration. It should be recalled that for gases not readily incorporated in the groundwater, e.g., ^{85}Kr, this pathway need not be considered at all.

Modeling the transport of radionuclides via the groundwater is complex and, of necessity, site specific. Hence, it was felt that a definitive calculation for even a single isotope such as tritium was beyond the scope of this work. The Draft Environmental Impact Statement on 10 CFR 61(8) describes one such model which would be applicable if the tritium gas released were rapidly converted to ^3H_2O in the soil.

2.3.2 Activity Limits for ^{85}Kr and ^{3}H

2.3.2.1 Release in a Confined Space

From the maximum allowable concentration given by 10 CFR 20 and the duration of exposure, i.e., in an occupational quarter or a whole year, the maximum allowable exposures can be calculated. For each gas and each concentration of gas in the confined space, the time necessary to reach the quarterly maximum can be calculated. Two cases were selected for calculation: rupture of a 100 Ci container into a 10 m^3 volume (10 Ci/m^3), and rupture of 1000 Ci container into an approximately 10 m^3 volume (100 Ci/m^3). It was assumed for both cases that mixing occurred rapidly with respect to the exposure period. Table 2.1 gives the results of this calculation. It is evident from this Table that an accidental release of a 1000 Ci (or even a 10,000 Ci) container of ^{3}H would allow ample time for worker evacuation. For ^{85}Kr, however, a 1000 Ci container rupturing under these conditions would not allow a reasonable time for evacuation. Thus, in this case, a limit of 100 Ci per container appears reasonable for ^{85}Kr.

Table 2.1

Isotope	Maximum Allowable Exposure Ci/m^3·s	Time in Seconds to Reach Quarterly Maximum Dose	
		10 Ci/m^3	100 Ci/m^3
^{3}H	3740	374	37
^{85}Kr	19	2	0.2

2.3.2.2 Puff Release From the Inner Edge of the Buffer Zone

The exposure integral for an instantaneous release from a point source given by Equation 2.1 describes a scenario in which a container of radioactive gas releases its entire contents to the atmosphere in a very short period of time, but with little instantaneous expansion of the gas. Obviously, the value of this integral is a function of the distance from the source and this is reflected by a dependence of σ_{yI} and σ_{zI} at this distance. Slade(7) gives estimates of these parameters for unstable, neutral, and very stable turbulence conditions for distances ranging from 100 to 4000 meters. These are reproduced in Table 2.2. Since the buffer zone in a shallow land burial site need only be some 30 m, use of these estimates reflects conditions of release much more toward the interior of the disposal site than 30 m.

According to Safety Guide 24,(9) a wind velocity of 1 m/s and turbulence class F (moderately stable) should be assumed. Since data for the instantaneous release are not available for moderately stable conditions, calculations were made for neutral and very stable conditions.

For neutral conditions, the values of ψ_p for 100 and 1,000 Ci are 2.1 $Ci/m^3 \cdot s$ and 21 $Ci/m^3 \cdot s$, respectively. For very stable conditions, the respective values are 33 $Ci/m^3 \cdot s$ and 330 $Ci/m^3 \cdot s$. The concentration limits for non-occupational exposure given in 10 CFR Part 20 imply a maximum allowable value for this integral of 1260 $Ci/m^3 \cdot s$ for ^3H and 12.6 Ci/m^3 for ^{85}Kr. Thus, 1,000 Ci of ^3H would be acceptable under either turbulence condition; 100 Ci of ^{85}Kr is an acceptable limit only if the guideline assumed conditions more turbulent than very stable. Since the required meteorological condition(9) (moderately stable) is intermediate between neutral (F) and very stable (G), the authors believe 100 Ci of ^{85}Kr is acceptable but not 1000 Ci.

Table 2.2

Suggested Estimates for σ_{yI} σ_{zI}, and $\psi_p \bar{u}/Q$(7)

Parameter	Conditions	100 m	4000 m	Approximate Power Function [a,b]
σ_{yI}	Unstable	10.0	300	$0.14(x)^{0.92}$
	Neutral	4.0	120	$0.06(x)^{0.92}$
	Very stable	1.3	35.0	$0.02(x)^{0.89}$
σ_{zI}	Unstable	15.0	220	$0.53(x)^{0.73}$
	Neutral	3.8	50.0	$0.15(x)^{0.70}$
	Very stable	0.75	7.0	$0.05(x)^{0.61}$
$\psi_p \bar{u}/Q$	Unstable	2.12×10^{-3}	4.81×10^{-6}	$4.20(x)^{-1.65}$
	Neutral	2.08×10^{-2}	5.30×10^{-5}	$35.5(x)^{-1.62}$
	Very stable	3.26×10^{-1}	1.30×10^{-3}	$3.30(x)^{-1.50}$

[a] The power functions are only applicable in the range of distance given.

[b] x is the distance from the source in meters.

2.3.2.3 Release to Groundwater

As discussed in Section 2.3.1, the modeling of radioactivity movement in groundwater is beyond the scope of this work. For $^3H_2$ gas, published data(10) indicate rates of conversion in soil of $^3H_2$ gas to ^3H_2O or $^3H^1HO$ of 0.6 to 24 hours for half conversion. Hence, on the time scale of groundwater movements, the gas would be completely converted to tritiated water and the model for ^3H_2O transport used in the Environmental Impact Statement could be used. In the transit time from the release point of the gas to the nearest boundary of the disposal site, which would be at least 30 yrs, the tritium leaking from any gas container would be mixed with and indistinguishable from any other tritium release of the site. Hence, the release of gaseous $^3H_2$ to groundwater could not be modeled separately from the total tritium release of the site. Although no quantitative specifications can be placed on the maximum container size, the release rate from the gas container should not exceed that from other tritium wastes of equal activity and the total release rate must depend on total site inventory and site hydrology. 10 CFR 61 (proposed) requires that a maximum site specific inventory be established for tritium and other long lived and/or highly mobile nuclides, based on site hydrology and container release rates.

2.3.3 Influence of Container Properties

In view of the variability of site hydrologies and the necessity of considering total tritium inventories and release rates, no container limit can be set based on release to groundwater. Sinced the major concern in burying gaseous tritium wastes is the high mobility of the escaped gas, the major considerations must be the integrity, release rates and long-term stability of the tritium gas containers. The radiation level outside a container due to internal tritium is essentially zero so the handling and storage of sufficiently secure containers present no radiation safety problem. In essence the maximum limits for tritium gas must be set according to the properties of the container. With containers of assured integrity and long-term stability, it is possible that limits of 1000 Ci or larger could be acceptable.

2.4 Conclusions and Recommendations

Based on the above analysis, it is evident that the technical basis for a limitation on the maximum pressure should be based on the lowered risk associated with handling unpressurized containers. With regard to the limitation on the maximum activity allowed for gaseous waste packages, a general methodology is proposed which is based on the following credible release scenarios: release of the package contents to a confined area during handling, storage or burial of the waste (occupational hazard), and puff release of the package contents to an unrestricted area during burial of the waste. The general methodology is applied to packages containing one of the two isotopes ^{3}H and ^{85}Kr. For packages containing tritium gas, the upper limit per container will depend on the retention qualities and stability of the container. The recommendations are summarized as follows:

- Permitting a maximum of 1.5 atm total pressure in gaseous waste containers is considered acceptable.
- The limitation of the maximum activity for gaseous wastes to 100 Ci per package should be changed to a radionuclide specific limit.
- The limitation with respect to release to groundwater should be based on container integrity, release rate, and long-term stability, taking account of overall site inventory and site hydrology. The groundwater release scenario does not apply to ^{85}Kr or other noble gases.
- Based on the air transport scenarios considered, it would appear that a maximum activity limit for ^{85}Kr of 100 Ci/package would be consistent with regulations governing both occupational exposure and exposure to the general public. For ^{3}H, a corresponding limit could be as high as 1000 Ci/package.

3. REQUIREMENTS TO DEMONSTRATE THAT BURIED WASTE WILL BE RECOGNIZABLE FOR 300 OR 500 YEARS

In this section we discuss the problems involved in trying to demonstrate long-term recognizability of buried radioactive wastes, and attempt to develop a rationale for comparing stability and recognizability. An evaluation of currently used waste forms is given, in relation to the destructive forces which will be encountered after burial and which will affect the stability/recognizability of the waste. Factors are discussed which must be considered in devising a short-term test to demonstrate long-term stability. Development of a wet/dry cycling test based on extensively used standard tests is described. A test of this type is applicable to concrete waste forms and may prove acceptable for organic forms. If so, it could aid greatly in showing that a waste form has a reasonable probability of meeting the proposed 10 CFR 61 stability requirements.

3.1 Background and Limitations

In Subpart A of the proposed 10 CFR Part 61, Section 7(b)(5), Class C wastes are defined as containing a maximum concentration of radionuclides such that, at the end of 500 years, remaining radioactivity will be low enough that it poses no danger to public health and safety. Subpart A clearly indicates that Class C wastes must be recognizable, as provided by stability [Section 7(b)(5)], in the event of intrusion after the 100-year institutional control phase of the burial site. Subpart A does not mention recognizability in connection with Class B wastes, but Subpart D, Section 55(b) requires that Class B waste meet the stability requirements of Section 56, and Section 56(b) states: "...stability is a factor in limiting exposure to an inadvertent intruder, since it provides a recognizable and nondispersible waste." It is thus evident that Class B waste should be included with Class C waste for considerations of recognizability.

BNL has been asked to specify what would be required to demonstrate that a stable waste will be recognizable for 300 or 500 years. Except for the special case of high integrity containers (required by the draft BTP on waste form to have a minimum lifetime of 300 years), waste is taken to refer to the waste form, as indicated by Section 7(b)(5) of 10 CFR 61 and by the introduction to the draft BTP. The authors consider that waste forms could be defined as recognizable if they retained their original simple geometric shape and a reasonable degree of coherence so that they did not crumble on being struck with a light hand tool such as a shovel. The waste should otherwise be easily distinguishable in color and texture from the surrounding soils.

Although there are many instances of man-made or natural objects surviving for thousands of years, in most cases the survival has depended on a particularly favorable climate or microenvironment or some highly resistant property of the object. For nuclear wastes, it will not be possible to choose the most favorable environment, although site selection can eliminate many of the most destructive environmental conditions. Also the waste forms will not be made of the most resistant material available. After 100 years of burial (institutional control phase), the hazard levels of the nuclear wastes will not be especially high and for waste of low activity levels it will probably not be beneficial to society to use rare or very expensive high technology materials for either waste forms or containers.

Many ordinary materials such as Portland cement concretes, asphalts, and some plastics appear to be very stable when they are protected from the more severe environmental attacks. Unfortunately, except for asphalt, none of the materials including modern Portland cement has been available for 500 years so that their stability over this time period has not been tested. Even granting the stability of pure solidification materials, the wastes contained in the matrix of a waste form can greatly alter its properties so that the overall stability of the resulting waste form cannot be accurately predicted.

Both 10 CFR 61 (proposed) and the draft BTP on waste form link recognizability with stability, noting that stability provides a recognizable waste. Thus the problems involved in demonstrating recognizability for a long period are the same as those for demonstrating long-term stability. Since presently available tests are inadequate to predict such stability, since long-term experience concerning waste form performance does not exist, and since unforseen events or processes can occur over a period of several centuries, indisputable demonstration that a waste form will be stable for 500, or 300, or even 150, years is not possible. The best one can do is show a reasonable probability that, under conditions likely to prevail, a waste form will meet the stability requirements given in 10 CFR 61 for the designated length of time.

Appropriate and extensive long-term testing could indicate a reasonable probability of achieving the 150 year stability required by 10 CFR 61, Section 56(b). Such long-term testing is presumably not currently feasible, so that the short-term tests specified in the BTP are considered by NRC to give a useful indication of waste form suitability, and could in any event, identify forms which would not be suitable. The authors take the position that a waste form considered acceptable as regards long-term stability -- in particular stability for at least 150 years -- will have a reasonable probability of being recognized for several times that period. This is based on the argument that recognizability does not require the same degree of stability needed to satisfy the structural stability criteria of the regulation, and the small amount of degradation permitted by the stability tests, if continued for further periods comparable to the original 150 years, would not be sufficient to cause loss of recognizability.

On the basis of this reasoning, the uncertainty associated with "reasonable probability" is such that the difference between 300 and 500 years has little significance. Thus, if a waste form were judged to have a reasonable probability of being recognizable for 300 years, it would have a somewhat lower probability of being recognizable for 500 years, but that probability could still be considered reasonable within the uncertainties involved.

3.2 Assessment of Currently Used Waste Forms

This section describes the destructive forces which can degrade a waste form, and the properties of presently available waste forms as related to those forces.

3.2.1 Environmental Forces

The external destructive forces on a waste package are the normal physical, chemical and biological processes associated with the geology of any near surface layer of the earth. There seems to be no evidence that these basic forces will change significantly at any given location over the course of a few hundred years. The physical and chemical forces include:(11) disruption by freezing of water in cracks and pores, dissolution and decomposition by rain and groundwater, particularly by carbonic and other acids in the water, and cyclic changes of wetting and drying which can disrupt the solid by causing irreversible volume changes. Oxidation as a destructive force in rocks occurs mostly after initial disintegration of the rock by other forces. However, oxidation may be a primary factor in the disintegration of organic waste forms buried in soils with high oxygen levels. The disruptive force of mechanical shearing can occur in sloping zones or any other place where shear stresses are present. Materials on the surface exposed to sunlight may undergo photochemical reactions as well as large thermal fluctuations.

Biological effects (which are inherent parts of the geological process) include the generation of CO_2 which increases groundwater acidity, the generation of organic acids and complexants, and disruptive mechanical forces from plant roots and fungal hyphae. Organic materials near the earth's surface are directly consumed in generating the CO_2 and organic acids. In addition to the common carbon-consuming biodegrading organisms, there are others which can oxidize ferrous ion to ferric ion, and sulfide ion to sulfates or sulfuric acid. Under reducing (anoxic) conditions sulfates can be reduced to sulfides or sulfur, and nitrates to nitrogen or ammonia. Each of these special organisms also requires a carbon source and other nutrients. Each process could have a deleterious influence on a susceptible waste form.

The biological forces are highly dependent on the nature of the site. High relative humidities, high nutrient levels (e.g., phosphorous and soluble nitrogen) and moderate temperatures are required for rapid biological growth.(12) Although oxygen is not essential for the growth of organisms, biodegradation with oxygen is generally much faster than without. The presence of large quantities of easily biodegradable organic materials in the burial site can, as mentioned, lead to increased corrosion and elution of contaminants through the biogenic creation of organic and carbonic acid and complexants.(12)

In addition to the external forces on the waste form, the wastes may also contain internally destructive elements. Radiation can lead to embrittlement, gas production, the production of corrosive agents such as H_2SO_4 and HCl, and in extreme cases liquefaction. For Class B stable wastes containing isotopes with half-lives substantially longer than 5 years and maximum activities given by Table 1 of the proposed 10 CFR 61, calculated(13,14) maximum radiation doses will be of the order of 2 to 3 x 10^8 rad. For matrix materials such as cement, vinyl ester-styrene, urea-formaldehyde, polyethylene, and epoxy, embrittlement and gas formation may occur at these radiation levels, but little other damage(15,16) should occur and the materials should be acceptable for solidification. Asphalt, however, could be seriously damaged at these levels of radiation.(12)

Class C wastes containing the same isotopes will be subjected to considerably higher doses, and even Class B wastes containing Co-60 could potentially receive a maximum total dose of about 10^{10} rad. Cement, polystyrene, and epoxy resins cured with aromatic curing agents, probably could withstand such a dose without serious deterioration, however bitumen and most other plastics would be destroyed.(13,14)

Internal chemical effects could occur through slow reactions of the waste with the solidification agent. These could lead to eventual disintegration of the solid. Thus, sulfates and nitrates could slowly react with the cement matrix destroying its resistant properties.

The materials to be used for waste forms must withstand at least some of the above forces for up to 500 years. Since properly buried wastes will be below the frost line, they will not be subject to freeze-thaw cycles or photochemical effects, and temperature fluctuations will be small (Section 6.1). Shear forces may be large in the first few years after burial, however the filling in of voids and settling should probably reduce the mechanical forces to simple isotropic pressures in a few years. Wet/dry cycling and dissolution remain as probably the most active external physical destructive forces; consequently, wastes with the least penetration of water and the smallest internal surfaces (capillaries and cracks) can be expected to be the most stable.

3.2.2 Waste Form Materials

Solidified wastes are generally packaged in carbon steel drums or containers (liners). It is not expected that the steel containers will last 150 years, and pits, openings, and total disintegration will occur in much shorter times. Hence, such containers will not aid in the long-term recognizability of wastes. The recently introduced high density polyethylene drums, however, may well prove otherwise. Should their lifetimes turn out to be comparable to those expected of polyethylene high integrity containers, they will obviously contribute greatly to long-term recognizability. In essence, they might by themselves, provide the required period of recognizability, and would be expected to protect the waste form for a large fraction of that period.

The resistance to alteration of any of the solidified waste forms depends both on the matrix material and the type and relative quantities of waste contained. Although many studies of waste form properties have been and are continuing to be made,(17-20) information on the long-term stability of the forms remains limited and often conflicting. Much of the work has been directed towards obtaining shippable solids rather than long-term durable materials. The following is a very brief discussion of available information on some of the principal waste forms.

3.2.2.1 Portland Cement

Portland cements of various grades have been among the most common solidification agents used in the USA. Roman hydraulic cements similar in many respects to modern Portland cement have withstood weathering for thousands of years. Modern cement has been available for only about 150 years with the quality steadily improving since then. There is no long base of experience to evaluate the durability of presently available high quality concretes. However, over periods of 50-100 years, some well prepared Portland cement concretes under moderate conditions have shown little evidence of disintegration.(21,22) For the highest resistance, a concrete must contain a weather resistant, chemically inactive aggregate, and, most important, the minimum quantity of water that allows mixing and handling.(14,15) A concrete with the miminum water quantity will have both the highest strength and the minimum porosity and permeability consistent with the amount of Portland cement in the mixture. Environmental conditions that favor durability include minimum exposure to water flows, low levels of acid, sulfate, and chloride in any contacting water, and minimum exposure to cycles of wetting and drying.(23,24) Freeze-thaw cycles are destructive to permeable concretes, however it is not likely that low-level nuclear wastes will be buried above the frost line.

The requirements for a waste form are generally contradictory to those for a resistant Portland cement concrete. The wastes are often soluble or chemically reactive materials rather than inert aggregates. Since many wastes are liquids, a maximum volume of liquid is often used rather than the minimum required for good concretes. Ion exchange resins are particularly difficult to treat in that their volumes are very sensitive to the local vapor pressure of water and to the ionic content of water in contact with the resins. Since in addition, resins are solidified with large quantities of internal water, the obtaining of a stable concrete wasteform containing ion exchange resins is a very difficult matter.(17,25-28) By careful experiment and low waste-to-cement ratios, stable solids have been obtained for laboratory size samples, however, it is not clear that stable solid could be obtained in production samples. Additives such as sodium silicate, adsorbents, pH buffers, and proprietary materials have been used for waterproofing and stabilization of waste-cement solids. Also, claims have been made for proprietory processes, that a highly stable material is formed.(29) Insufficient information is presently available to determine whether these treatments do give long lasting stable materials.

3.2.2.2 Urea-Formaldehyde

Urea-Formaldehyde has been a convenient and frequently used solidification agent. A deterrent to its use has been the large quantity of highly acid water used as a catalyst in the polymerization reactions, which may be exuded after disposal. Claims have been made for proprietary processes that they have eliminated this problem, however there is no certainty. Little information is available on the long-term stability of urea-formaldehyde polymers. In some experiments, water appears to move rapidly through the matrix,(17) leading to questions of the long-term stability. Also, the material has the composition of a nitrogeneous fertilizer suggesting that a high level of biological activity might exist within or close to the waste form. The possibly high permeability and potential susceptibility to biological effects suggest a relatively low durability for the material.

3.2.2.3 Vinyl Ester-Styrene Polymer

Vinyl ester-styrene polymer is a proprietary material(30) that has been used on a limited basis in the USA and Europe. The material is water resistant, of low porosity, and resistant to mild acids and bases.(17,18,20) The manufacturer has stated that it is resistant to biological attack, which is in agreement with tests made for other aromatic ester polymers.(31) Tests have shown that the properties are little affected by a variety of nuclear waste materials and radiation doses to 10^9 rad.(18)

A possible drawback to vinyl ester-styrene is a sensitivity to organic solvent saturated water which apparently causes serious degradation.(32) The material should not be buried where contamination with organic materials is possible. As with other synthetic resins, the substance appears promising but no long-term experience is available.

3.2.2.4 Bitumens and Asphalts

Bitumens and asphalts, naturally occurring or as residues from petroleum refining, have been in common use in Europe for waste solidification.(33) Several grades are available; the most resistant appears to be a material that has been partially air oxidized at a high temperature.(17)

The asphalts are thermoplastics similar in many ways to the synthetic resins. They are water resistant, nonporous and resistant to mild chemical reactants. They appear to be compatible with most nuclear wastes, although a waste containing a high level of sodium sulfate was substantially degraded by water leaching(34) Bitumens are biodegradable, susceptible to photochemical damage and generally are not long lasting when exposed to the atmosphere and light.(35) Photochemical degradation is, of course, not a factor in buried wastes and atmospheric degradation will be limited. As mentioned earlier, bitumen and bitumen-salt samples showed appreciable deterioration on being irradiated to 5 x 10^8 rad.(15) This sensitivity would exclude the use of bitumen for wastes expected to receive doses of this magnitude. The existence of natural ancient bitumen deposits however, indicates that in massive form and under favorable conditions, i.e., low oxygen, low levels of biological nutrients, and absence of light, the bitumens are very stable.

3.2.2.5 Polyethylene and Expoxy Resins

Polyethylene(36) and epoxy resins(18) have had limited usage in Europe and Japan for waste solidification. In the U.S., high density polyethylene appears to be the material of choice for high integrity containers, and in that use constitutes the barrier to release of radioactivity normally provided by the waste form. Many properties of polyethylene and epoxy resins are similar to those of vinyl ester-styrene. Polyethylene is composed of hydrocarbons only, and if the fraction of low molecular weight fragments is small, may be more resistant to environmental changes than epoxy or vinylester resins. This applies particularly to interaction with water. A lower degree of brittleness for polyethylene may also improve the properties somewhat over those of the other resins. As with the other organic solidification agents, protection from light and weathering are necessary. The materials appear promising although little information is available on long-term durability.

3.3 Design of a Test for Long-Term Stability

We discuss here design of a test for waste form stability, rather than recognizability. This is partly because recognizability does not lend itself to unambiguous definition, but also because the proposed 10 CFR Part 61, Section 56(b), requires a definite 150 year minimum period over which Class B and C waste must be stable. In Section 3.1 we have linked recognizability with stability and taken the position that, if a waste were stable for 150 years, it would be recognizable for a considerably longer period such as 300 or 500 years. The tests given in the draft BTP can be considered as screening tests which show whether a waste form is unsuitable, but not whether it is suitable to the extent of being stable for 150 years. The type of short-term accelerated test which we propose, based on a series of wet/dry cycles, while still only a screening test, is felt to be capable of giving more of an indication of long-term stability than the present BTP tests, particularly under the adverse conditions encountered at burial sites where the wastes will periodically be in contact with water.

Currently, an insufficient technical data base is available to determine whether a test procedure applicable to concrete waste forms can be generalized to include organic matrices such as bitumen and vinyl ester-styrene polymer. There is a good technical basis to support the contention that a wet/dry cycling test could be used for qualifying organic waste forms, but the limited observations which have been reported preclude setting a pass/fail criterion at this time. Additional experience must be gained on the behavior of organic matrices under alternate wet and dry conditions before it will be feasible to write a standard procedure.

3.3.1 Desirability of Considering Wet/Dry Cycling

In Section 3.2.1, the destructive forces acting on buried waste are discussed. Most of them are currently addressed in the draft BTP, however, the destructive effect of wet/dry cycling is not addressed and, in view of its potential severity, the authors consider that it should be. Wet/dry tests are particularly applicable to concrete, which is currently used to solidify the bulk of the low-level waste in the U.S., and could prove to be applicable to organic forms as well. It is conceivable that if waste were buried in certain desert locations it could escape wetting for a period of several hundred years. However, it is apparent that a number of burial sites will have to be located in areas such as the eastern part of the country where there is appreciable rainfall. Realistically, then, due consideration must be given to the effect on waste stability of alternate wetting and drying. Thus, it is felt that a properly designed test based on a series of wet/dry cycles, in addition to short-term screening tests already specified in the BTP, could aid greatly in showing a reasonable probability of long-term stability and/or recognizability. Providing a good basis for such a test are two currently used durability tests, a Bureau of Reclamation test for resistance of concrete to sulfate attack,(21) and ASTM D559-57, entitled, "Standard Methods for Wetting and Drying Tests of Compacted Soil-Cement Mixtures."(37)

3.3.2 Presently Required Waste Form Tests

The draft BTP on waste form requires that the waste forms be tested for compressive strength, radiation stability, biodegradation, leaching (over a period of water immersion of at least 90 days), and thermal stability. The compressive strength test is repeated on the radiation, thermal, and leach test samples after the respective treatments. The major acceptance criterion for waste forms is that the compressive strength after treatment be at least 50 psi.

The question arises as to whether these tests are sufficient to predict the probability of a waste form being stable for at least 150 years, and if not, whether the tests can be modified to give better predictions, or whether better, more predictive tests are available. It is likely that a waste form that fails the draft BTP stability tests would not be recognizable after 150 years, however there is no evidence that a waste form passing these tests would be recognizable after 150 years. Of these screening tests, radiation stability tests involving a generally known and reproducible stress should give reasonably accurate predictions of stability. The thermal test is directed toward short-term effects in storage and shipping since, after burial, the waste will not be exposed to below freezing or high temperatures (Section 6.1). The biodegradation tests are important in determining stability and are discussed in a separate section (Section 5). Leaching test results in themselves are not directly related to stability since removal of trace radioactive components from a waste form could have a negligible effect on the dimensions and stability of the matrix. This leaves the compressive strength test (before and after various treatments) as the one most pertinent to this discussion.

In order to evaluate the compressive strength test and other possible short-term tests for predicting stability and recognizability, one must consider the major environmental stresses on the waste form (discussed in Section

3.2.1), as well as the nature and limitations of possible tests. The major environmental stresses, in addition to biodegradation, are considered to be waste dissolution in water contacting the wastes, and wet/dry cycling.

3.3.3 Considerations in Use of Short-Term Tests

3.3.3.1 Relation to Field Conditions

Ideally, any test should reproduce, as closely as possible, the time scale and physical and chemical conditions expected in the field. The time scale for 300-year prediction would be too long to be practical and accelerated tests become necessary.(38) In an accelerated test, the most important stresses expected in the field are applied to laboratory specimens in a highly amplified manner. Although the conditions may be very different from those in the field and interpretations of the tests may not be completely clear, if the tests are carefully designed, they nevertheless may give the best obtainable predictions of long-term behavior. Verification of an accelerated test can only be obtained by comparison with actual field results over the expected lifetime of the wastes.

3.3.3.2 Importance of Rate of Change of Properties

A most important point about tests, accelerated or not, for long-term behavior is that the rates of change of properties are as important as the intrinsic values of the properties. If a rate of change can be determined with confidence and the mechanism of the process causing the change is known, it will generally be possible to predict the property of a material at some future time. A static test can only determine the property at the time of testing which may or may not be related to future behavior. In measuring rates of change, it should be remembered that a waste form may change its properties (e.g., weight or dimension) relatively rapidly as it initially comes to equilibrium with new environmental stresses. However, if the waste is to be stable for a long time, the rate of change must become very small or undetectable in a measuring period short compared to the expected lifetime of the waste. It is always possible that drastic changes in mechanism and degradation rates might take place after the test is finished. Nevertheless, within limited time periods and with limited information on mechanisms, such tests provide the best available means of predicting long-term behavior.

A similar thought, particularly referring to plastic materials, is expressed in the ASTM test C 581-74,(39) "Chemical Resistance of Thermosetting Resins Used in Glass Fiber Reinforced Structures." In the section (9.1) on interpretation of results it is stated that, "Because of the chemical nature of certain types of plastic material, the rate of change with time is more significant than the actual value at any one time. A plot of the test results will indicate whether a particular specimen will approach constant flexural strength, flexural modulus or hardness with time or will continue to change as the test progresses."

3.3.4 Standard Tests for Durability

Standard tests for durability have been applied to materials with properties generally similar to those of solidified nuclear wastes which are exposed to conditions similar to those of shallow land burial. In ASTM test D559-57 Standard Methods for "Wetting-and-Drying Tests of Compacted Soil Cement Mixtures,"(37) hardened soil-cement specimens (generally mixtures of soil and Portland cement) are subjected to repeated wetting and drying cycles. Weight and volume (dimension) changes are recorded after each cycle and separate specimens are abraded with a wire brush in a standardized manner. Twelve cycles are recommended and the failure criteria are a breakdown of the specimen or excessive loss of weight. The temperature and cycling time of the test (5 hours in potable water at room temperature, 42 hours drying in an oven at 71°C) are specified in the test but are considered as largely arbitrary.*(40)

A similar test is used by the U.S. Bureau of Reclamation(21,41) for testing the durability of cement in high sulfate waters and soils. The major difference from the ASTM test is that different cycling times and temperatures (16 hours soaking in 2.1% Na_2SO_4 solution at 25°C, and 8 hours drying in an air stream at 54°C) are used along with a high sulfate immersant solution. The number of cycles is indefinite with dimensional (length) measurements being made at arbitrary time intervals--not after each cycle. The failure criterion is 0.5% expansion which can be directly related both to the chemistry of reaction of sulfate with the Portland cement matrix and to quantitative deterioration of structural properties.

For the Bureau of Reclamation test an acceleration factor (ratio of failure time in the field to failure time in the laboratory) is given as 8 but even so, test runs extended for up to 6 years. Unaccelerated tests of concrete durability have lasted 20 years or more.(42) No other information has been obtained on the existence of short-term tests for predicting the long-term properties of waste material.

The ASTM test has been applied to testing the durability of soil-cement highway foundations,(40) which are not normally exposed to direct weathering, and of solidified hazardous wastes(43) intended for shallow land burial. The hazardous solid wastes were solidified by proprietary processes and no published details are available, however the wastes were stated to be mostly inorganic materials--largely solidified with Portland cement.** Initial compressive strengths ranged from 7 to 4500 psi(43) and materials with

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*Information on the soil-cement test is based in part on telephone conversations with M. R. Palermo and J. L. Mahloch, U.S. Corps of Engineers, Vicksburg, MS; R. E. Landreth, U.S. EPA, Cincinnati, Ohio; M. C. Anday, Highway Research Board; and R. G. Packard, W. Binchak, and P. Nussbaum of the Portland Cement Institute.

**Telephone conversation with R. E. Landreth, U.S. EPA, Cincinnati, April 1982.

compressive strengths below 1000 psi generally failed the test. A representative of the U.S. Army Corps. of Engineers* attributed most of the failure to the abrasion required by the ASTM test. The abrasion is extremely agressive and is probably an unrealistic requirement for waste forms.

3.3.5 Properties on Which to Base a Test

As concerns a property to be evaluated (after exposure to stress) recognizability is not an attribute which can be measured quantitatively. What can be measured are various physical properties that can be related to the stability or durability of the waste form. Among physical properties that can be measured are compressive strength (as in the BTP test), impact strength,(44) external dimensions,(21,37) and mass.(37)

3.3.5.1 Compressive and Impact Strength

Compressive strength and impact strength tests are destructive, requiring separate samples for every measurement. If a long test sequence is to be run, a large number of samples of a high degree of reproducibility are required. Since for long-term predictions, small changes must be measured, reproducibility and accuracy of measurement in a test are necessary. Compressive strength measurements are generally not reproducible to $<\pm 10\%$,(17,45) so that the small changes with time which one would like to be able to observe would be very difficult to measure using such a test. Nevertheless, compressive strength is probably the most widely used test, and although no explicit relationship between compressive strength and durability is available, the test is useful and should be carried out using samples that have undergone the wet/dry sequence of tests. The impact strength test has not been widely used and will not be considered further.

3.3.5.2 Dimensions and Weight

Change in dimensions (volume) and weight as the basis for a durability test have been discussed in connection with the standard tests described in Section 3.3.4.

These measurements are nondestructive, and can be made very easily and accurately. With regard to soil-cements, it is stated that "...precise length changes are considered to be a very sensitive and direct measure of deterioration."(40) Also in Section 3.2.1 in discussing envirnomental stresses, it was pointed out that repeated wetting and drying could cause irreversible volume changes leading to the disintegration of native rocks. Consequently, length changes appear to be a valid criterion for use in determining the durability of cement-based waste forms. In tests of nuclear waste forms solidified with epoxy and with polyester resins,(18) 1% expansions were found after 45 and 90 days of soaking in water. If the expansion of these or

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*Telephone conversation with M. R. Palermo, U.S. Army Corps. of Engineers, Vicksburg, MS, April 1982.

other organic waste forms remained at this value, their stability need not be impaired, however any continuing change could indicate instability. Although a data base is not generally available relating the durability of resins to volume changes, the high sensitivity attainable and the probability that any continuing change signifies deterioration suggest that a method based on measurement of dimensions could be valid for organic solidification matrices.

Excessive weight changes should also be a valid criterion for rejection. Loss of weight would directly signify dissolution. A continued gain in weight would almost certainly indicate the deterioration of a waste form.

3.3.6 Development of a Specifdic Wet/Dry Cycling Test for Waste Forms

As pointed out in Section 3.3.1, the Bureau of Reclamation test for resistance of concrete to sulfate attack(21) and ASTM test D559-57(37) (described in Section 3.3.4), provide a good basis for a wet/dry cycling test for waste form stability. They were designed, however, only for concretes, so that modifications are required to make them generally applicable to organic materials as well as concretes. In particular, indications of failure have to be specified differently for the two classes of compounds.

In the following sections, the criteria for rejection are discussed and required modifications to the standard tests are outlined.

3.3.6 1 Criteria for Acceptance

With respect to pass-fail criteria for concrete waste forms, failure of the compressive strength test after wet/dry cycling would constitute failure. An unusually large decrease in compressive strength between "before" and "after" samples should also be considered a failure. In terms of dimensional changes, Packard and Chapman(40) state that expansions of about 0.1% indicate failure for soil-cement specimens. Initially, on being exposed to wet/dry cycling, soil-cement samples contracted; however, an increasing rate of expansion occurred as the sample began to deteriorate. The value of 0.1% change in length is the same as that used in concrete durability testing in sulfate solution,(46) and would be the value proposed in our test for concrete waste forms. It should be noted that this criterion for rejection of concrete waste forms conflicts with the definition of stability given in the proposed 10 CFR 61. Section 56(b)(1) of 10 CFR 61 describes a structurally stable waste form as one that will maintain its physical dimensions within 5%. In view of the extensive experience with concrete testing mentioned in previous sections, it seems that no concrete waste form could be considered stable if it showed even 1% change in dimensions.

For the organic matrices, bitumen and synthetic polymers, no specific failure or acceptance criteria are available. As with concrete waste forms, failure of the compressive strength test (where applicable) would be considered as a failure of the waste form. Changes of dimension and weight are used as measures of damage in ASTM test D543-67, "Resistance of Plastics to Chemical Reagents,"(47) but no definite failure criterion is given. As pointed out in Section 3.3.3.2, ASTM test for plastics, C581-74,(39) makes clear that it is the rate of change of a property that is important, not the actual value at any one time.

Significant dimensional changes may well occur as a result of the newly applied environmental stresses early in a test. There is, however, no data base from which to obtain values for setting a limit on the extent of expansion (or contraction) which should be permitted for different organic matrices. Indeed, as mentioned in the last paragraph, the rate of change rather than the absolute change of dimensions is more important, although the maximum absolute change must also be limited. Stability is associated with zero change, thus, regardless of what happens during the early stages of a test, towards the end of the test any changes should have essentially stopped.

3.3.6.2 Research Needed for Developing Acceptance Criteria for Testing Organic Waste Forms

A generally applicable wet/dry cycling test would appear to be a valuable addition to the tests presently required in the draft BTP. At present, lack of information on the effects of alternate wetting and drying of organic matrices prevents setting a pass/fail criterion for these materials. The authors believe that this situation should be corrected by building up the necessary data base in a timely manner. In particular, mass and dimensional changes should be determined for the matrix materials bitumen, vinyl ester-styrene polymer and high density polythelyene, exposed to a relatively long series of wet/dry cycles, preferably 100 or more. Polyethylene is included because, as a container material in high integrity containers, it will provide stability for the waste. The same types of measurements should also be made for simulated or actual waste forms made with bitumen and vinyl ester-styrene.

3.3.6.3 Required Modifications to Standard Tests

The duration of the testing (number of cycles) should attempt to reflect the estimated degree of acceleration of the test and the desired lifetime of the waste form. The acceleration factor of this test depends on the high rate of wet-dry cycling as compared with that expected in the field and generally more severe conditions of wetting, drying, and possibly aggressiveness of the wetting solution. As with any accelerated test, it is not possible to quantitatively assess these factors without field experience for comparison. For a very crude estimate of the acceleration factor, the following argument is offered. The nuclear waste forms will presumably be subjected to cycling during the burial period and the duration of the test should correspond to the number of natural cycles expected. At the depths the nuclear waste forms will be buried (2 meters or more) wetting and drying will probably be seasonal or annual (wet in spring during spring runoff, dry in autumm and winter) rather than following individual precipitation events. Thus, each laboratory cycle could correspond to one year in the field and 150 cycles would be required to test for 150 year stability. It is reemphasized that the estimate of this acceleration factor is questionable and that field experience alone can determine the extent of its validity.

Details of the sample size, cycle times, soaking solution, and drying procedures can be developed as appropriate modifications of the standard ASTM and Bureau of Reclamation tests.(21,37,40) In order to reduce the cycling time, the 24-hour cycle of the Bureau of Reclamation test rather than the 48-hour cycle of the ASTM test is recommended. To compensate for the reduced drying time (6 hours rather than 48 hours) forced air rather than oven drying should be used, but this modification would also bring the degree of drying closer to that expected in the field.(40) The drying temperature is selected as 50°C which is a compromise between a value of 23°C recommended in Reference 40 for frost-free areas, and the ASTM value of 71°C which would probably be too hot for asphalt-based solids.

3.4 Summary and Conclusions

- In both the proposed 10 CFR 61 and the draft BTP on waste form, recognizability is closely linked with stability. The authors consider that anything which contributes to stability of a waste form also contributes to recognizability. In order to demonstrate that a proposed stable waste would be recognizable for 300 or 500 years, the following steps would be necessary. Tests measuring properties associated with stability would have to be carried out in such a way that the measurements could be made for a sufficiently long time, and/or with sufficient accuracy as a function of time, that extrapolation to hundreds of years would be unquestioned. It would then have to be demonstrated that the values of the measured properties at the extrapolated time were still within the limits which would permit calling the waste stable and/or recognizable. For a realistic extrapolation, the mechanisms of degradation must either be known or known to be unchanged throughout the required period. Since such information is not available, it is concluded that indisputable demonstration of long-term waste form stability (at least 150 years) is not possible, and the best one can do is obtain indications of a reasonable probability that the waste form will remain stable for the designated time, given expected processes and events.

The potential of the currently used waste form materials to provide long-term stability has been examined on the basis of available information. The principal conclusions are given below.

- Portland cement concretes, without added waste, have a high potential for resisting for long periods the destructive geological, chemical, biological, and radiation forces which would be encountered in burial sites. Since, however, the requirements for a waste form are generally contradictory to those for a resistant concrete, it cannot be assumed automatically that durable waste forms will result from use of high quality cements and aggregates. This is particularly true when the waste consists of ion exchange resins. Insufficient evidence is presently available to draw definite conclusions.

- Of the organic matrices, asphalt or bitumen is the only one which has been in use for a long period, but, of course, not mixed with low-level nuclear waste. All the organic forms are subject to biodegradation, and there is some evidence that urea-formaldehyde could be more susceptible than the others. It appears also to have a high permeability to water. These two factors indicate a potential low durability. Polyethylene, epoxy resins, and vinyl ester-styrene polymer have reasonably good resistance to radiation. Radiation resistance of bitumen is much lower, so care would be required to limit the doses it was permitted to receive. Polyethylene, epoxy resins, vinyl ester-styrene polymer, and bitumen all appear promising, but again information is not available to permit extrapolation to long times.

Factors concerned with developing a test for durability of a waste form have been considered. Standard tests for concrete stability could be applied, with modification, to conrete waste forms, but not enough is known about the behavior of organic materials to determine whether this type of test could be applied to organic waste forms. Specific considerations and conclusions follow.

- Tests requiring only one measurement, such as compressive strength tests, can give only rough indication of a waste form's long-term stability. A single measurement provides information on the property measured at the time of measurement only, and is of limited value for predictive purposes. The compressive strength test is, however, a useful before/after check to indicate possible deterioration which may have occurred as a result of other tests such as thermal, radiation and biodegradation.

- The standard tests which could be used as the basis for a test for long-term waste form stability are wet/dry cycling tests extensively used to measure concrete durability. The tests are non-destructive, and the measurements can be made with good precision since the properties measured are weight and dimensions. Compressive strength testing could also be performed at the completion of the cycling tests.

- Applicability of this type of test to concrete waste forms is obvious, but insufficient information is available to write a test procedure suitable for organic waste forms. The main obstable is inability to set a pass/fail criterion for these organic waste forms. Only very small dimensional changes (0.1%) are allowed in the standard concrete durability test (ASTM D-559-57), but because of the completely different structure of bitumen and synthetic organic polymer matrices, such a small change limitation for organic forms is probably not justified.

- Absolute change in dimension, within reason, may not even be a valid pass/fail criterion for organic forms. A reasonable position can be taken that rate of change of dimensions is an appropriate basis for acceptance or rejection. Dimensional changes may occur early in a test period as a result of the newly applied environmental stresses. However, if the waste form is stable, the rate of change of dimensions should approach zero after a reasonable period. Thus, a test would put a limit not on the absolute amount of change, but rather on the rate of change permitted toward the end of the test period.

- The addition of a generally applicable wet/dry cycling test to the draft BTP would be advantageous in giving an improved indication that a waste form would be stable for a relatively long period. Since not enough information is presently available to apply such a test to organic waste forms, it is recommended that research be carried out in a timely manner to obtain the data to demonstrate general applicability. In particular, mass and dimensional changes should be determined for bitumen, vinyl ester-styrene polymer and high density polyethylene, exposed to a relatively long series of wet/dry cycles, preferably 100 or more. Polyethylene is included because, as a container material in high integrity containers, it will provide stability for the waste. The same types of measurements should also be made for simulated or actual waste forms made with bitumen and vinyl ester-styrene.

4. FEASIBILITY OF ACHIEVING LESS THAN 5% DEFORMATION IN WASTES

4.1 Background

The stability requirements for Class B and C wastes, as set out in Section 56(b) of the proposed 10 CFR 61, include maintenance of their physical dimensions within 5% over a period of at least 150 years. Deformation of the waste form or collapse of the container due to void space between waste form and container permits subsidence of the ground above it, which could lead to infiltration of water and possible unexpectedly rapid migration of radionuclides leached from the waste. It is therefore desirable to keep the deformation at a minimum. The 5% value for permitted deformation is based on allowing a 1 to 1.5-ft subsidence over the 8 m (26 ft) disposal depth of an assumed reference facility.(48) This subsidence can readily be taken care of by mounding over the trench.

In light of this requirement, BNL has reviewed current solidification and packaging methods to determine if this limit can be met by current practices or whether modification of these practices will be required. To obtain relevant information, discussions have been held with personnel from Hittman Nuclear and Development Corporation (HNDC) and Chem-Nuclear Systems, Incorporated (CNSI), who provide waste containers for the nuclear industry, particularly the electric utilities, and carry out the actual processing and preparation for disposal of wastes for a number of industrial clients. Since nuclear power plants as a class are the largest generators of Class B waste, discussions were also held with personnel of six plants--Dresden, Duane Arnold, James A. Fitzpatrick, Kewaunee, Trojan, and Vermont Yankee--regarding their radioactive waste disposal practices.

4.2 Processes Leading to Subsidence

Subsidence can result from deformation or collapse of the waste form after container failure, or collapse of the container into void space between waste form and container. These two general processes are discussed in separate section (4.2.1 and 4.2.2).

4.2.1 Waste Form Deformation

Porosity such as occurs in concrete, or other micro void spaces, will not lead to collapse of a waste form. Keeping the form reasonably free of macro void spaces, which could permit collapse, is not difficult. Current methods of solidifying wastes by mixing waste and binder in situ are well developed to yield sound monoliths, and forms with essentially no macro voids can be easily achieved.

Dissolution or any other leaching mechanism coupled with migration of the leached material out of the burial zone is not expected to lead to appreciable deformation of waste forms prepared from the materials BNL has been asked to consider--cement, asphalt, and vinyl ester-styrene polymer. The stability of these materials to destructive forces encountered during burial is discussed in Section 3.2. The waste forms must meet the requirements of 10 CFR 61, Section 56(b), and the draft BTP that they remain stable on exposure to moisture or water after disposal. In addition, burial site suitability requirements in 10 CFR 61 Section 50 should preclude licensing of a site where waste will be in frequent or prolonged contact with water. Biodegradation, which is discussed in Section 5, can be extensive and could potentially lead to considerable trench slumping from loss of material from an organic waste form. It is, therefore, necessary to ensure that waste forms are not susceptible to biodegradation by carrying out recommended testing as described in Section 5. Similarly, the BTP on waste form requires that testing be carried out to verify stability of waste forms to radiation, and if they are indeed stable no voids will result from radiation effects.

4.2.2 Deformation Due to Voids in Containers

There are two principal ways in which buried waste containers can deform to lead to subsidence.

1. The top of a metal container holding solidified waste can corrode to the point where it collapses under the weight of the trench backfill, unless the solid waste form completely fills the container.
2. The top of a plastic high integrity container (HIC) which is not completely filled with dewatered resin will deform (i.e., partially collapse) under the weight of the overburden.

These are discussed in Sections 4.2.2.1 and 4.2.2.2, respectively, in the light of information obtained from vendors and utilities.

4.2.2.1 Experience With Steel Drums and Liners

Utilities often use both drums and liners for shipping solidified waste. The current material of choice for these containers is carbon steel, however 55-gal drums fabricated from polyethylene are beginning to be used. Although they are not HICs, the comments in the next section (4.2.2.2) on deformation of polyethylene HICs apply also to these polyethylene drums. Utilities may use drums routinely, but contract with a vendor for special jobs, for which liners are used. Some plants contract to have all their waste disposed of by the vendor. At three of the six utilities surveyed, an on-site vendor representative supervised solidification of the waste or filling of containers with dewatered resins. Both vendors and all the power plants surveyed were in agreement that, for economic reasons, they would fill all types of containers to capacity if it were feasible. Most filled their containers with solid waste to within 10-15% of capacity. One of the vendors (CNSI) has two sizes of carbon steel liners which they fill only 1/2 to 3/4 full with cement because of weight limitations of the shipping casks. The other vendor (HNDC) has a similar problem, but is in the process of redesigning the shipping casks to permit use of "full" containers. Both vendors and the power plants surveyed routinely fill carbon steel drums, and liners not limited by weight restrictions, to within a few inches of the top. The current standard methods for solidifying power plant wastes involve mixing the waste and binder in situ. This precluded complete filling of containers, since spilling has to be avoided and allowance made for small inaccuracies in metering the waste and binder constituents. A freeboard of 4-5 inches in a 6-foot diameter liner was considered achievable. This corresponds to a void space of 6-7% in a 6-foot high liner, but the same freeboard in a 3-foot high liner, such as Hitmann's HN-600, and in 55-gal drums, corresponds to 12-14% void space.

4.2.2.2 Behavior of HICs

Power companies have not yet had much experience with HIC's, but those that ship dewatered resin have had broad experience in filling other containers. Two different methods are used. One method, used particularly with powdered resins, is to centrifuge the resins to remove water and dump the dewatered resins into a hopper from which containers are loaded. The other method involves sluicing resins from a spent resin holding tank, or directly from a bed, into the liner, letting the water drain and pumping it away. This method does not lend itself to filling containers as completely as does the first method, even if the process is repeated, since a container completely filled with resin slurry will no longer be filled once the resin has settled and the water removed. Also, even if a container could be completely filled from a hopper, there remains a problem with powdered resins. Two of the utilities contacted ship dewatered powdered resin, and both have observed that the resins, which are light and fluffy after dewatering, can be compacted to about 60-70 of their initial volume in a shipping container. It is not known whether this degree of compaction would occur during shipping and handling of powdered resins, but evidently considerable compaction can occur even with bead resins. In the few instances where liners containing dewatered resin have been opened at Barnwell,* compaction of bead resin of up to 20% had apparently occurred. Further compaction would occur due to deformation of resin particles to fill in the void spaces between them once the container top, under the pressure of the overburden, begins to press down on them. With the relatively uniform spherical particles which constitute bead resins, there is still over 30% void space in a close-packed bed. Thus it can be concluded that HIC's containing dewatered resin would have considerably more than 5% effective void space, and this situation would lead to subsidence by the second mechanism listed above, i.e., deformation or deflection of the container lid under the weight of the overburden.

High density polyethylene appears to be the vendors' choice as the material of construction for HICs, despite the fact that it evidently will not eliminate the problem of trench subsidence, one of the purposes of developing

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*Telephone call, D. R. MacKenzie to J. Ott, CNSI, April 2, 1982.

HICs. According to the publication describing Hittman's prototype HICs,(49) the containers will be domed and after burial the polyethylene dome, as would a dome of any other plastic, will undergo creep as a result of the stress imposed by the overburden. It is stated that "the container meets the overburden requirements not by supporting the overburden, but by deforming without rupture and then relieving the buildup stress."

In discussion* with the author of the Hittman report,(46) he stated that there was a mitigating factor in connection with the HIC deformation, namely that the process was rapid in relation to the operating period of a burial site. Thus, even if void spaces in HICs and consequent deformation of the containers led to an undesirably large extent of subsidence, this would occur in a relatively short time and the condition could be corrected by adding more backfill.

The argument for relatively rapid deformation under an expected overburden pressure of up to 50 psi appears to be valid. The general principles are corroborated by a recent article in "Modern Plastics Encyclopedia,"(50) which discusses deformation of plastics, particularly as regards creep. Creep under constant load involves a first-stage of large and rapid initial deformation, followed by a second stage where deformation continues at a relatively low constant rate. A third stage, ending in rupture, occurs if the load is maintained. This stage is expected by the vendor not to be reached with buried HICs since the deforming top would first come to rest and be supported on the waste resin. However, since the resin itself may deform and gradually fill in the void spaces between resin particles, it is not clear to BNL whether the container will be able to deform, without rupture, to the full extent demanded by these conditions. This, in any case, is a matter to be dealt with in licensing the HIC; our concern here is with the rate of creep deformation.

No exact calculations are possible without knowing the properties of the specific material to be used in the HIC, but what quantitative information could be found on polyethylene deformation under constant load indicates that a comparatively high rate would be expected for the large (6 ft diameter), relatively thin sheets comprising the tops of HICs. Thus, the contention that deformation after burial would be complete in a period of time shorter than the operational phase of the burial site seems warranted.

It should be noted that site maintenance, including correction of subsidence, is required during the active institutional control period,(51) which is presumed to last for 100 years after site closure. Subsidence due to collapse of HIC tops should therefore be taken care of regardless of the length of time taken for the collapse to occur, but it would obviously be advantageous if this task were completed during the operational phase.

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*Telephone call, D. R. MacKenzie to J. Williams, February 15, 1982.

4.3. Achievability of <5% Deformation of Waste

Current solidification procedures as practiced by the vendors and all the power plants questioned would not generally achieve <5% void space. In order to achieve a freeboard corresponding to <5% void space (e.g., 1.5 in for the HN600 liner) it appears that waste and binder would have to be mixed in a separate container and poured into the shipping liners. This would probably have to be done in batches to end up with exactly the correct volume of solidified waste, and would add to the exposure of workers because of the increased time involved. It undoubtedly is technically feasible for concrete and probably would be for the vinyl ester-styrene process, but would not be for fast setting cements such as Delaware Custom Material. Asphalt appears not to be currently used in the U.S., but it should be feasible to mix it with waste in a separate heated vessel and pour into a waste container.

In order to meet a requirement of <5% void space without changing present methods, an additional step can be added to the solidification process, e.g., filling the void space with an inert, nonradioactive, free-flowing material such as sand. All the utility and industry personnel interviewed agreed that such an approach was technically feasible, but several nontechnical objections were raised. One was that a waste package having sand on top of a solid would no longer contain a homogeneous waste form, and as such would not be accepted by the burial sites. Review of burial site requirements for Barnwell and Hanford failed to turn up any rules regarding homogeneity, except for distribution of transuranic isotopes. It is concluded that this objection is invalid, since it does not apply at all if transuranic isotopes are not involved, and if they are involved, the waste form homogeneity criterion need apply only to the solid, not to the inert nonradioactive topping.

The other objections were either directly or indirectly economic. Addition of another step to the waste disposal process adds to the utilities' costs. Filling could be accomplished either by an automatic system, which would have to be developed and installed at considerable expense, or by personnel manually dumping sand in the liner. The latter procedure involves not only the additional expense of the extra step, but causes higher exposure of workers to radiation, levels of which can be quite high around a loaded shipping container. These objections are certainly valid, but we feel that the fractional increase in the cost of waste disposal caused by the extra step would not be large.

4.4 Conclusions

Based on the information obtained from vendor representatives and nuclear power plant personnel, properties of standard waste forms, and the probable performance of HICs, the following conclusions are drawn:

- Section 56(b)(1) of the proposed 10 CFR 61 calls for a structurally stable waste form which will maintain its physical dimensions within 5%. The waste forms which BNL has been asked to consider--cement, asphalt, and vinyl ester-styrene--are capable of meeting this requirement as long as they are resistant to degradative mechanisms such as radiolysis, biodegradation, and alternate wet/dry cycles. Adequate testing must be carried out to demonstrate such resistance.

- Section 56(b)(3) requires that void spaces within the waste and between the waste and container be reduced to the extent practicable. Normal procedures do not cause formation of any macro void spaces in the waste form itself. For metal containers, it is concluded that current solidification methods will not normally allow achievement of <5% void space between the top of the container and the waste form. For tall containers, <10% would be achievable, but for commonly used 3-ft high containers such as the HN-600 and 55-gal drums, this would be difficult and a readily achievable limit would be <15%.

- In order to achieve <5% void space, methods would have to be changed, or a step added by requiring that the waste containers be topped off with an inert nonradioactive material such as sand. Both these alternatives are technically feasible but would result in increased cost to the utilities and, depending on the method used, increased radiation exposure to personnel.

- A possible alternative to a requirement of <5% void space would be to set a readily achievable limit of <15% and require higher mounding over the filled and compacted trench to allow for extra subsidence. Permitting the additional 10% void space could lead to approximately 2 ft of subsidence for the reference 8 m (26 ft) trench depth, so an extra 3 ft of earth in the trench cap would adequately allow for the maximum possible subsidence due to voids.

- It would probably not be feasible to achieve <5% deformation of polyethylene HICs routinely. However, there is a high probability that deformation of buried HICs would be complete well within the operating period of a burial site, so that any subsidence could be taken care of by addition of more backfill, and therefore, a minimum void or deformation requirement need not be applied to HICs. The same comments apply to other polyethylene containers, such as 55-gal drums.

5. ADEQUACY OF ASTM TESTS G-21 AND G-22 FOR TESTING RESISTANCE TO BIODEGRADATION OF SOLIDIFIED LOW LEVEL WASTE FORMS

5.1 Introduction

The proposed 10 CFR Part 61 requires that Class B and C radwaste be stable for at least 150 years. Resistance to biodegradation is part of the requirement for stability. Any substance subject to microbial attack will biodegrade under favorable environmental conditions of temperature, moisture, nutrient availability, pH, and others. The direct effects of biodegradation on a waste form include loss of mass and mechanical strength. Secondary effects may include chemical degradation caused by deleterious waste products from microbe metabolism and changes in trench chemistry. These secondary effects may exacerbate the loss of stability from direct effects.

All microbes require a source of carbon, nitrogen, and liquid water for metabolic activity.(49) Trace minerals and other chemicals are also required. Organic components in radwaste can provide the carbon substrate and possibly nitrogen and other chemicals. Carbon dioxide, other gases, and organic acids, aldelydes, alcohols, and amines are products of biodegradation,(52-55) along with increased microbe mass. Since CO_2 is readily determined titrimetrically, it has proven to be one of the most convenient methods of determining microbial activity in soil.(54)

Radwaste disposed of in shallow land burial may be solidified with cement, bitumen (asphalt) or plastic. Cement itself is not biodegradable by direct microbial attack, but it is subject to secondary degradation from CO_2 and organic acids. Concrete may be degraded(56) by water containing 140-400 ppm CO_2 as a mixture of bicarbonates and carbonic acid. Acetic acid, butyric acid and lactic acid, all of which are metabolic wastes, are also known to attack concrete.(56) A cement waste form incorporating organic matter may biodegrade directly. Cement used to solidify sulfate or nitrate salts can be attacked when the trench environment becomes anaerobic and these anions are used as oxidizers in place of oxygen (see below). Bitumen consists largely of a mixture of polynuclear aromatic hydrocarbons (PNAs) which are extremely persistent in the environment.(57) Laboratory studies(57) on PNAs attributed their very low rate of biodegradation in the biosphere to lack of solubility, the lack of microbe cell membrane permeability (cells must assimilate a molecule to degrade it), and to enzymatic specificity (most cells do not have enzymes able to oxidize PNAs). A short-term study(58) of bitumen biodegradation in nutrient culture under optimum conditions is available. The rate of biodegradation was monitored by CO_2 evolution. Solidification in plastic is exemplified by the DOW process(59) in which waste is solidified with a "modified" vinyl ester styrene resin. Synthetic polymers are generally resistant(60-62) to microbial attack, however, they often contain additives which are biodegradable. Sulfate, nitrate, and phosphate salts are metabolized by certain microbes and may render a waste form biodegradable provided the requisite carbon substrate is also available.

Shallow land burial environments start out aerobic so that biodegradation will produce principally CO_2 as waste gas. When the oxygen concentration drops below approximately 3×10^{-6} M(63,64) anaerobic respiration begins and nitrate is used as the oxidizer. Upon nitrate depletion the metal cations Mn(+4) and Fe(+3) are reduced to Mn(+2) and Fe(+2). Sulfate is the next oxidizer utilized in natural systems. Sulfate reduction is carried out by specialized obligate anaerobic bacteria, Desulfovibris, Desulfomonas and Desulfomaculum which reduce sulfate to sulfide (CO_2 is still being evolved as the metabolic waste gas at this point). Finally, when the sulfate has been exhausted, CO_2 may be used as an oxidizer. When this occurs, methane is evolved as the gaseous carbon waste. Methane(65) has been detected in shallow land burial trenches indicating that the trench environment may cover the full range from aerobic to strictly anaerobic. This simplified description of the changes occurring as microbiological conditions go from aerobic to anaerobic has been "linearized" for clarity. Generally, several of these processes would be operating simultaneously depending on the localized environment, which includes microbe numbers and types, as well as the chemical factors.

5.2 Long Time Projections

Quantitative temporal data have been reported(66-68) for the biodegradation of polyethylene. These experiments were based on scintillation counting $^{14}CO_2$ evolved from ^{14}C labelled polyethylene. Radioisotope analysis permitted much better sensitivity and accuracy than the classical and still viable titrimetric methods(54,69) of measuring biologically evolved CO_2. The results indicate that the biodegradation is very slow (only about 0.5% of the material had degraded in two years under both nutrient culture and actual soil conditions) and that the rate decreases with time. In the initial paper(66) of this series the authors noted that a plot of fractional decomposition vs log (time) produced a straight line. From this they presented a model equation for the biodegradation as a function of time:

$$\frac{\Delta W}{W} = K \log(t) \tag{5.1}$$

where W = sample weight, $(\Delta W/W)$ = fractional decomposition at time t. The function as presented(66) is flawed since, for $t < 1$ the function is negative, at $t = 1$ it is zero, and one should not be taking the logarithm of a dimensioned quantity. An acceptable function, mathematically speaking, is obtained by defining a reduced time function, $T = (t/t_o)$ where t_o = time at the start of biodegradation and which must be specified as a positive number (say, 1 day for convenience). This function now has an initial value of 0 (i.e., $\log(1) = 0$), increases with increasing T and has the correct qualitative "shape". Although it is doubtful that this function is of much quantitative value, since it was not repeated in the subsequent papers,(67-68) it is, in fact, the only attempted quantification of biodegradation rate seen in the literature surveyed to date. In Reference 68 the shape of the biodegradative rate curve is described as "parabolic" but not quantified, for example as:

$$\frac{\Delta W}{W} = kt^{1/n} \qquad (5.2)$$

where n = 2. In Reference 68 the authors conclude that the lower molecular weight fraction (oligomers) in the polyethylene are the entities being biodegraded and the rate of biodegradation slows with time because of the limited supply of oligomers available on the surface and the low rate of release of these relatively large molecules from the bulk material to the surface.

An interesting result(61) supporting the utility of equation (5.2) is provided by data on the biodegradation of caprolactone polyester. This polymer is readily biodegraded in soil. Measurements of the weight loss of a small bar and a small pot of caprolactone polyester biodegrading in soil as a function of time indicated that the fraction degraded was linear with time, i.e., n = 1 in equation (5.2). The weight loss of the bar was 42% and that of the pot was 95% in one year. Biodegradation of both bar and pot was characterized by severe pitting and not a uniform thinning of the orginally smooth structures. The implication of the linear rate relationship is that the large molecules of the caprolactone polymer are not more resistant to biodegradation than are the oligomers in the material. The significance of n in the factor $t^{1/n}$, Equation (2), can thus be interpreted as follows: if n = 1 then there is no differentiation in biodegration due to differences in the size of the polymer molecules, whereas if n > 1 then some molecules, presumably the smaller oligomers, are biodegraded preferentially.

It should be emphasized that no definitive mechanistic model can be constructed on the basis of the results of the two experiments described above. Equation (5.2) is presented solely as a useful aid in interpreting the observation that the rate of biodegradation of a material known to be resistant to microbial attack (polyethylene) decreases with time while that of a material known to be readily biodegraded (caprolactone polyester) does not. It may or may not be more generally applicable.

Other observations(60-62) of the biodegradation of synthetic polymers indicate that additives (antioxidants, plasticizers, slip agents, etc.) often provide the biodegradable substance and that when it is gone the polymeric substrate remains. The polyethylene studies(66-68) were performed using material without additives. Results of biodegradability tests(61) on polymers containing additives have been compared to results of the same tests on material without additives. The additives were removed by solvent extraction. The solvent extracted material showed markedly less microbial activity than the as-received polymer when tested according to ASTM D-1924-63 (ASTM G-21(70) is the updated version of this test).

Biodegradative gas generation in bitumen(58) has been reported for both aerobic and (nominally) anaerobic conditions. Rates of gas generation (in units of moles/year/drum) presented in the format lower limit-(most probable range)-upper limit, were: for aerobic conditions, 0-(0.1-3.4)-8; for anaerobic conditions, 0-(0.6-4.8)-8. These results are relative to a drum of bitumen solidified waste that would be expected(71) to be capable of producing a producing a total of about 2000 moles of gas by biodegradative mechanisms. A suggestion which seems reasonable(72) is that these rates represent maximum values and will decrease with time, since bitumen consists of an assortment of hydrocarbons, largely PNAs, of which only a fraction are relatively easily biodegradable.

One may conclude from this review of the literature that stability based on resistance to biodegradation should be evaluated with respect to the substrate material in the solid waste form and not on small amounts of additives or impurities which allow a rapid surface attack by microbes but do not significantly degrade the long-term stability of the substrate. Further, the rate of biodegradation does not appear to be a unique function of time, which would permit long time extrapolation of the data to 150 years. This implies that any test for biodegradation based upon the currrent literature would only indicate relative differences in stability among waste forms and would identify any obviously deficient waste forms having only limited short-term stability.

5.3 Tests for Biodegradability: Comment and Evaluation

The draft BTP waste form stability requirement for resistance to biodegradation specifies that no indication of culture growth should be visible in ASTM tests G-21 (Determining Resistance of Synthetic Polymeric Materials to Fungi)(67) and G-22 (Determining Resistance of Plastics to Bacteria).(73) The test conditions of optimum temperature, humidity and nutrient salts assure culture growth if even a small fraction of the sample can be utilized as a carbon source for microbial metabolism. These ideal growth conditions are supposed to compensate for the short duration of the test as compared with the 150 years required of actual waste. The question is whether failing of G-21 or G-22 implies that the long-term stability requirement will not be met. The answer to this question is--not necessarily. Recognizing that the solidification medium isolates the waste from the environment, then biodegradation of the solidification medium is unacceptable. From this standpoint, biodegradation of some minor constituent and essentially limited to the surface of the waste form should not constitute failure of the test for resistance to biodegradation. The pass/fail criterion applied to G-21 and G-22 test results do not differentiate between biodegradation capable of consuming the waste form and surface biodegradation due to minor chemical constituents accessible on an otherwise resistant substrate. The solvent extraction test results(61) on polymers mentioned in Section 5.2 provide a relevant example of this.

Applicability of G-21 and G-22 must also be considered relative to the waste form. These tests are specified for polymeric materials, which makes them formally applicable only for evaluating the Dow process waste forms of those here considered. Application to bitumen and concrete waste forms is certainly possible, but the criteria for evaluation of test results may have to be modified at a later date based on experiments not yet available in the literature. Bitumen biodegrades,(58) but this is probably due to small amounts of the chemical components of the material which are readily attackable. No long-term biodegradative rate data are available on bitumen, but it is believed that the rate should decrease with time as in polyethylene.(66-68) Biodegradation results on bitumen should parallel those on polymeric materials in the sense that surface attack may occur, but surface degradation alone should not be the reason for failure of the waste form to meet long-term stability requirements. The G-21 and G-22 tests on cement waste forms should retain the pass/fail criterion as written in the BTP because cement is porous. Biodegradative attacks would probably not only proceed into the bulk of the cement waste form, but the metabolic waste products of such microbial attacks might accelerate the degradation. Secondary effects such as chemical attack by microbial waste products are not addressed in G-21 and G-22. Chemicals produced as waste by microbes are known to attack concrete(56) and would probably conribute to deterioration of a concrete waste form.

5.4 Recommendations for the use of ASTM G-21 and G-22 in Testing Resistance to Biodegradation: a Modified Procedure

It is our recommendation that the specimen waste form be tested in accord with the ASTM G-21 and G-22 procedures. If there is no indication of culture growth, the waste form meets the draft BTP waste form requirement for resistance to biodegradation. For a cement waste form that fails, this failure is final, for reasons pointed out in Section 5.3. For polymeric or bitumen failures, additional testing described below should be performed.

- If culture growth is observed upon completion of the test for polymeric or bitumen waste forms, remove the test specimen from the culture, wash it free of all culture and growth with water and only light scrubbing. Extract the specimen by immersing completely for five minutes in ethanol, five minutes in acetone and one minute in methanol. The specimen should be agitated or the liquid stirred to assure effectiveness. If any or all of the solvents mentioned are inappropriate due to incompatibility with the substrate or failure to extract the suspected minor chemical fraction, then an appropriate solvent should be substituted and/or delete one or two steps in the extraction process. Air dry the specimen at room temperature and repeat the test. If, in the repeated test, a growth rating at least one number lower on the 0-4 scale of G-21 is obtained and the observed culture growth is rated no greater than 1 on this second test, then the test will be considered as being passed.

- If a specimen solidified using bitumen or polymeric materials showed growth during testing by ASTM G-22, the test should be repeated following the extraction procedure described above. If any growth is observed after the second test, the waste form must be considered to have failed the test.

5.5 Conclusions and Recommendations

- The ASTM G-21 and G-22 tests can be used to measure waste form biodegradability. Since G-21 and G-22 do not differentiate between microbial attacks which can consume the waste form and surface growth which leaves the substrate intact, modifications to these tests have been suggested for plastic and bitumen waste forms; the test for cement waste forms is not modified (Section 5.4).

- The ASTM G-21 and G-22 tests are not ideal in that long-term behavior is not specifically measured. Ideally a test which measured the rate of biodegradation allowing direct extrapolation of short-term results to long-term performance should be performed. Data on the biodegradation of polyethylene and caprolactone polyester provide the only examples of attempts at such modelling found to date.

- Research should be performed on a variety of waste form binder materials to determine quantitative short-term rates of biodegradation by measuring CO_2 generation from microbe respiration. Such experiments have the potential to provide data which would permit the extrapolation required for long-term prediction. The results of these tests should then be compared with the results of G-21 and G-22 tests on these materials in order to determine if the tests for biodegradation recommended in the BTP should be changed.

6. TEST FOR DEMONSTRATING STABILITY TO THERMAL DEGRADATION

6.1 Requirements for a Test

NRC's draft Branch Technical Position (BTP) requires that wastes be resistant to thermal degradation, and specifically states that specimens should maintain a minimum compressive strength of 50 psi following thermal testing. After burial at a minimum depth of 2 m at a burial site anywhere in the continental U.S., a waste package will undergo only very small changes in temperature. The temperature will not fall to freezing (0°C) and will probably not rise above 20°C.(74) At a depth of 5 m and lower, the temperature range experienced will be even narrower, i.e., roughly 5°C on either side of a mean value between 10 and 15°C. Thus, once waste is buried, no thermal degradation will occur and the only period during which a waste form could be subjected to significant thermal stresses would be during interim storage and handling.

During above ground storage in the open, the surface of a solid monolithic waste form of 6 ft^3 (contained by a 55-gal drum) or larger could experience daily temperature fluctuations as great as 50°C. In the interior, temperature change would be much less, particularly for very large waste forms (e.g., those in 6-ft diameter by 6-ft high liners). In the summer, the surface temperature might reach 50°C or higher, depending on storage conditions and geographical location. In the winter, in the continental U.S., a temperature of -40°C is normal, but infrequent, and temperatures below this can be regarded as unusual occurrences in areas with the most severe climate, and as not occurring at all in most of the country. A test for thermal degradation should cover at least this temperature range, even though any given waste form is unlikely to be subjected to the full range. The low temperatures obviously will not cause any thermal decomposition of the waste form, but could lead to degradation due to the shock of cyclic expansion and contraction, particularly if contained water were subjected to freeze-thaw cycles.

6.2 Test for Thermal Degradation

In BNL-NUREG-29714, Davis and Gause(75) have considered the matter of testing for thermal degradation of low level waste forms and have reviewed various ASTM methods designed for non-waste form concrete and plastics. They conclude that ASTM-B553-79 (Standard Test Method for Thermal Cycling of Electroplated Plastics)(76) "with modifications can be used to test the effect of simulated temperature extremes to which solidified waste forms may be subjected." We agree with this statement and conclude that an adequate test to ensure that solidified wastes will be resistant to thermal degradation can be developed with ASTM-B553 as the basis. Since the test was designed for electroplated plastic parts, some modification of the procedure is required, as well as addition of observations to be made on completion of the test. These are discussed below, and the proposed test procedure is given in Appendix A.

6.2.1 Modifications Required

1. The nature of the samples to be tested must be specified. To be consistent with the requirements of the BTP, they should be cored samples from a simulated full-size waste form, or from an actual waste form if the generator wishes. The principal stipulation is that they be suitable for carrying out the same compressive strength test as required to qualify the waste form orginally.
2. A minimum of four samples should be used. They should be held in containers in such a way that the containers do not provide support. The containers must close tightly so there will be no loss by evaporation of any free liquid which may be formed.
3. In Section 5.4 of ASTM-B553, only one high and one low temperature need by specified, namely, 60°C and -40°C, respectively.
4. Section 5.4.5 does not specify the number of cycles to be performed. A series of 30 cycles is recommended, to correspond to temperature cycling during a month's storage. Thirty is considered a reasonable number in that, while storage times could be longer than a month, the overall requirements are probably conservative since the temperature extremes specified are greater than can occur in actual daily fluctuations.

6.2.2 Additional Observations Required

Section 6.15 of B553 specifies only recording the extent, nature, and location of any defects observed as a result of the test. In a test for waste forms, this is only a minimum requirement. As pointed out in BNL-NUREG-29714,(75) visual observation of changes, such as cracking spalling, and deformation (i.e., dimensional changes), should be recorded; and, more importantly, the compressive strength, any weight loss, and amount of any free liquid formed. These last properties must have values consistent with the acceptability criteria given for waste forms in 10 CFR 61, Section 56(b), and the BTP. If statistics are inconclusive for the measurements of four samples, cycling should be repeated with a larger number.

6.3 Conclusions

- After burial, solidified waste will not undergo temperature fluctuations which could cause thermal degradation. Thus, it is only during interim storage and handling that waste forms can be subjected to significant thermal stresses.
- A test method based on ASTM-B553-79 can provide the necessary thermal cycling to test adequately for any thermal degradation of a waste form which might occur during such storage and handling.

- The point which must be stressed in guidance to generators is that the importance of the test hinges on the measurements made after completion of the cycling (compressive strength, weight loss and amount of free liquid formed) which must demonstrate that the waste form satisfies the stability requirements of Section 56(b) of 10 CFR 61.

7. BASIS FOR CONSILERING THAT A WASTE IS EXPLOSIVE OR PYROPHORIC

In order to facilitate the handling of low level nuclear wastes at a disposal site and to provide protection of public health and safety, 10 CFR Part 61 provides that low level wastes must not be explosive or pyrophoric [Sections 56(a)(4) and (a)(6)]. Explosive or pryophoric wastes could endanger handling personnel and conceivably could result in the scattering of radioactive substances and exposure to persons in unrestricted areas.

These concerns are very similar to those of the Department of Transportation (DOT) for shipping hazardous wastes and DOT has already provided rules for determining whether wastes are explosive or pyrophoric.

In assessing whether a low level nuclear waste is explosive or pyrophoric, primary reliance should be placed on the list and definitions contained in the Department of Transportation regulations for the transport of hazardous materials, 49CFR Parts 172(77) and 173.(4) Most ordinary substances of an explosive or pyrophoric nature are listed, along with the type of hazard they present, in "The Table of Hazardous Substances," in Section 101 of 49 CFR 172, or will be clearly covered by one of the definitions of Part 173. An index of general requirements for the shipping of hazardous substances, which is essentially a short list of explosive and pyrophoric materials, is given in 49 CFR 173 and reproduced in Appendix B. For substances not listed or defined some tests can be made by the shipper, however, for many explosives and pyrophoric substances tests must usually be made by specially equipped laboratories. Definitions of explosive and pyrophoric materials, specifically banned substances, and available tests are described below.

7.1 Explosives

An explosive is defined in Subpart C of 49 CFR 173 as "any chemical compound, mixture or device, the primary or common purpose of which is to function by explosion, i.e., the substantially instantaneous release of gas and heat..." A large number of classes and specific explosive compounds are described differing in the speed and violence of the explosive reaction, the conditions that can initiate the explosive reaction and the size and use of the material.

The transport of substances (other than those classed as explosives) which can detonate (sudden and violent explosion) in a fire is forbidden [Section 173.21(d)]. Tests of the capability of a substance for detonation must be made under the direction or supervision of the U.S. Department of Energy (DOE) in accordance with the procedures contained in DOT TB 700-2 (May 19, 1967).

The transport of a material which is liable to decompose or polymerize at a temperature of 130°F (54°C) or less with the evolution of a dangerous quantity of heat or gas is forbidden [Section 173.21(b)] unless the material can be stabilized or inhibited in a manner that will preclude such reactions. The determination of the applicability of this provision to a particular substance can be made using ASTM procedure E 487-74.(78)

The transport of explosive compounds mixtures or devices which ignite spontaneously or undergo marked decomposition when subjected to a temperature of 167°F (75°C) is forbidden [Section 173.51(a)]. Although nuclear wastes nominally would not be classified as explosives, reactive materials being considered for disposal should be tested for decomposition or ignition at 167°F (75°C) for 24 hours. The test sample should be placed in a glass or metal tube inside a heated block or furnace. Adequate safety precautions should be provided should a violent reaction occur.

The transport of hazardous materials in the same package, the mixing of which would be liable to cause a dangerous evolution of heat or gas, is prohibited [Section 173.21(a)]. Thus, strong oxidizers such as nitrates, permanganates, perchlorates, etc., could not be shipped in the same package as reducible wastes such as organic compounds and reactive metals.

7.2 Pyrophoric Materials

Pyrophoric liquids are defined as any liquids that ignite spontaneously in dry or moist air at or below 150°C. The test for pyrophoric liquids used by the Bureau of Explosives, Association of American Railroads is given in Appendix D.

Pyrophoric solids are included under the classification of "Flammable Solids" (49 CFR 173 Subpart E). Flammable solids are any solid materials other than those classed as explosives which under conditions normally incident to transportation are liable to cause fire through friction, retained heat from manufacture or processing or which can be ignited readily and when ignited burn so vigorously and persistently as to cause a serious transportation hazard. Included in this category are spontaneously combustible and water-reactive materials such as powdered and scrap metals and highly reactive bulk metals.

7.3 Conclusions

In assessing whether a low level nuclear waste is explosive or pyrophoric, primary reliance should be placed on the list and definitions contained in the DOT regulations for the transport of hazardous materials, 49 CFR Parts 172 and 173. A test for pyrophoric liquids is given by the Bureau of Explosives, Association of American Railroads, and pyrophoric solids are described and classified in Subpart E of 49 CFR 173. An index of general requirements for the shipping of hazardous substances which is, in essence, a short list of hazardous (i.e., explosive and pyrophiric) materials is given in 49 CFR 173. The full list in Section 101 of 49 CFR 172 should be consulted for other materials and the type of hazard presented.

8. CONCLUSIONS AND RECOMMENDATIONS

In this section, the conclusions and recommendations for each of the task areas are presented under their separate headings.

8.1 Technical Basis for Limiting the Pressure and Activity of Radioactive Gases

- Permitting a maximum of 1.5 atm total pressure in gaseous waste containers is considered acceptable.

- The limitation of the maximum activity for gaseous wastes to 100 Ci per package should be changed to a radionuclide specific limit.

- The limitation should be based on dose calculations performed for the release scenarios described in Section 2.2.2. Although the airborne release scenarios are amenable to generic analysis, release to the groundwater after burial depends on both the particular isotope and the disposal site. Hence, site-specific groundwater migration modeling would have to be conducted before limits could be set.

- Based on the air transport scenarios considered alone, it would appear that a maximum activity limit for ^{85}Kr of 100 Ci/package would be consistent with regulations governing both occupationsl exposure and exposure to the general public. For ^{3}H, a corresponding limit could be as high as 1000 Ci/package.

8.2 Requirements to Demonstrate That Buried Waste Will be Recognizable for 300 or 500 Years

- In both the proposed 10 CFR 61 and the draft BTP on waste form, recognizability is closely linked with stability. The authors consider that anything which contributes to stability of a waste form also contributes to recognizability. In order to demonstrate that a proposed stable waste would be recognizable for 300 or 500 years, the following steps would be necessary. Tests measuring properties associated with stability would have to be carried out in such a way that the measurements could be made for a sufficiently long time, and/or with sufficient accuracy as a function of time, that extrapolation to hundreds of years would be unquestioned. It would then have to be demonstrated that the values of the measured properties at the extrapolated time were still within the limits which would permit calling the waste stable and/or recognizable. For a realistic extrapolation, the mechanisms of degradation must either be known or known to be unchanged throughout the required period. Since such information is not available, it is concluded that indisputable demonstration of long-term waste form stability (at least 150 years) is not possible, and the best one can do is obtain indications of a reasonable probability that the waste form will remain stable for the designated time, given expected processes and events.

The potential of the currently used waste form materials to provide long-term stability has been examined on the basis of available information. The principal conclusions are given below.

- Portland cement concretes, without added waste, have a high potential for resisting for long periods the destructive geological, chemical, biological, and radiation forces which would be encountered in burial sites. Since, however, the requirements for a waste form are generally contradictory to those for a resistant concrete, it cannot be assumed automatically that durable waste forms will result from use of high quality cements and aggregates. This is particularly true when the waste consists of ion exchange resins. Insufficient evidence is presently available to draw definite conclusions.

- Of the organic matrices, asphalt or bitumen is the only one which has been in use for a long period, but, of course, not mixed with low-level nuclear waste. All the organic forms are subject to biodegradation, and there is some evidence that urea-formaldehyde could be more susceptible than the others. It appears also to have a high permeability to water. These two factors indicate a potential low durability. Polyethylene, epoxy resins, and vinyl ester-styrene polymer have reasonably good resistance to radiation. Radiation resistance of bitumen is much lower, so care would be required to limit the doses it was permitted to receive. Polyethylene, epoxy resins, vinyl ester-styrene polymer, and bitumen all appear promising, but again information is not available to permit extrapolation to long times.

Factors concerned with developing a test for durability of a waste form have been considered. Standard tests for concrete stability could be applied, with modification, to concrete waste forms, but not enough is known about the behavior of organic materials to determine whether this type of test could be applied to organic waste forms. Specific considerations and conclusions follow.

- Tests requiring only one measurement, such as compressive strength tests, can give only rough indication of a waste form's long-term stability. A single measurement provides information on the property measured at the time of measurement only, and is of limited value for predictive purposes. The compressive strength test is, however, a useful before/after check to indicate possible deterioration which may have occurred as a result of other tests such as thermal, radiation and biodegradation.

- The standard tests which could be used as the basis for a test for long-term waste form stability are wet/dry cycling tests extensively used to measure concrete durability. The tests are non-destructive, and the measurements can be made with good precision since the properties measured are weight and dimensions. Compressive strength tests could also be performed at the completion of the cycling tests.

- Applicability of this type of test to concrete waste forms is obvious, but insufficient information is available to write a test procedure suitable for organic waste forms. The main obstable is inability to set a pass/fail criterion for these organic waste forms. Only very small dimensional changes (0.1%) are allowed in the standard concrete durability test (ASTM D-559-57), but because of the completely different structure of bitumen and synthetic organic polymer matrices, such a small change limitation for organic forms is probably not justified.

- Absolute change in dimension, within reason, may not even be a valid pass/fail criterion for organic forms. A reasonable position can be taken that rate of change of dimensions is an appropriate basis for acceptance or rejection. Dimensional changes may occur early in a test period as a result of the newly applied environmental stresses. However, if the waste form is stable, the rate of change of dimensions should approach zero after a reasonable period. Thus, a test would put a limit not on the absolute amount of change, but rather on the rate of change permitted toward the end of the test period.

- The addition of a generally applicable wet/dry cycling test to the draft BTP would be advantageous in giving an improved indication that a waste form would be stable for a relatively long period. Since not enough information is presently available to apply such a test to organic waste forms, it is recommended that research be carried out in a timely manner to obtain the data to demonstrate applicability. In particular, mass and dimensional changes should be determined for bitumen, vinyl ester-styrene polymer and high density polyethylene, exposed to a relatively long series of wet/dry cycles, preferably 100 or more. Polyethylene is included because, as a container material in high integrity containers, it will be relied upon to provide the required stability. The same types of measurements should also be made for simulated or actual waste forms made with bitumen and vinyl ester-styrene.

8.3 Feasibility of Achieving Less Than 5% Deformation in Wastes

- Section 56(b)(1) of 10 CFR 61 calls for a structurally stable waste form which will maintain its physical dimensions within 5%. Waste forms of the materials which BNL has been asked to consider--cement, asphalt, and vinyl ester-styrene--are considered capable of meeting this requirement as long as they are resistant to degradative mechanisms such as radiolysis, biodegradation, and alternate wet/dry cycles. Adequate testing must be carried out to demonstrate such resistance.

- Section 56(b)(3) of 10 CFR 61 requires that void spaces within the waste and between the waste and container be reduced to the extent practicable. Normal procedures do not cause formation of any macro void spaces in the waste form itself. For metal containers, it is concluded that current solidification methods will not normally allow waste form. For tall containers, <10% would be achievable, but for commonly used 3-ft high containers such as the HN-600 and 55-gal drums, this would be difficult and a readily achievable limit would be <15%.

- In order to achieve <5% void space, methods would have to be changed, or a step added by requiring that the waste containers be topped off with an inert nonradioactive material such as sand. Both these alternatives are technically feasible but would result in increased cost to the utilities and, depending on the method used, increased radiation exposure to personnel.

- A possible alternative to a requirement of <5% void space would be to set a readily achievable limit of <15% and require higher mounding over the filled and compacted trench to allow for extra subsidence. Permitting the additional 10% void space could lead to approximately 0.7 m (2 ft) of subsidence for the reference 8 m (26 ft) trench depth, so an extra 1.0 m (3 ft) of earth in the trench cap would adequately allow for the maximum possible subsidence due to voids.

- It would probably not be feasible to achieve <5% deformation of polyethylene HICs routinely. However, there is a high probability that deformation of buried HICs would be complete well within the operating period of a burial site, so that any subsidence could be taken care of by addition of more backfill, and therefore, a minimum void or deformation requirement need not be applied to HICs. The same comments apply to other polyethylene containers, such as 55-gal drums.

8.4 Adequacy of ASTM Tests G-21 and G-22 for Testing Resistance to Biodegradation of Solidified Low Level Waste Forms

- The ASTM G-21 and G-22 tests can be used to measure waste form biodegradability. Since G-21 and G-22 do not differentiate between microbial attacks which can consume the waste form and surface growth which leaves the substrate intact, modifications to these tests have been suggested for plastic and bitumen waste forms. The test for cement waste forms does not require modification.

- The ASTM G-21 and G-22 tests are not ideal in that long-term behavior is not specifically measured. Ideally, a test which measured the rate of biodegradation allowing direct extrapolation of short-term results to long-term performance should be performed. Data on the biodegradation of polyethylene and caprolactone polyester provide the only examples of attempts at such modelling found to date.

- Research should be performed on a variety of waste form binder materials to determine quantitative short-term rates of biodegradation by measuring CO_2 generation from microbe respiration. The results of these tests should then be compared with the results of G-21 and G-22 tests on these materials in order to determine if the tests for biodegradation recommended in the BTP should be changed.

8.5 Test for Demonstrating Stability to Thermal Degradation

- After burial, solidified waste will not undergo temperature fluctuations which could cause thermal degradation. Thus, it is only during interim storage and handling that waste forms can be subjected to significant thermal stresses.

- A test method based on ASTM-B553-79 can provide the necessary thermal cycling to test adequately for any thermal degradation of a waste form which might occur during such storage and handling. A proposed test procedure is given in Appendix A.

- The point which must be stressed in guidance to generators is that the importance of the test hinges on the measurements made after completion of the cycling (compressive strength, weight loss and amount of free liquid formed) which must demonstrate that the waste form satisfies the stability requirements of Section 56(b) of 10 CFR 61.

8.6 Basis for Considering That a Waste is Explosive or Pyrophoric

In assessing whether a low level nuclear waste is explosive or pyrophoric, primary reliance should be placed on the list and definitions contained in the DOT regulations for the transport of hazardous materials, 49 CFR Parts 172 and 173. A test for pyrophoric liquids is given by the Bureau of Explosives, Association of American Railroads, and pyrophoric solids are described and classified in Subpart E of 49 CFR 173. An index of general requirements for the shipping of hazardous substances which is, in essence, a short list of hazardous (i.e., explosive and pyrophoric) materials is given in 49 CFR 173. The full list in Section 101 of 49 CFR 172 should be consulted for other materials and the type of hazard presented.

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APPENDIX A

TEST FOR DEMONSTRATING STABILITY TO THERMAL DEGRADATION

1. The heating and cooling chambers used shall conform to the description given in ASTM-B553-79, Section 3.

2. A minimum of four samples are required. They must be cored samples from simulated full-size waste form (or actual waste form if desired), and must be suitable for use in compressive strength tests carried out according to ANSI/ASTM-C39-72.

3. Each sample is placed in a container which is large enough that it does not provide support to the sample. The container must close tightly so there will be no evaporative loss of any free liquid. Containers can be made of metal or any material unaffected by the test conditions.

4. Marked containers with samples are placed in the test chamber and a series of 30 thermal cycles is carried out following the directions given in Section 5.4.1 through 5.4.4 of ASTM B553. The high temperature limit of the cycles is 60°C and the low temperature limit -40°C. During the cycling, samples are to be rotated randomly or in a pre-determined manner to compensate for any thermal gradients in the temperature-controlled chambers.

5. At the conclusion of the 30 cycles, the samples are removed from their containers and visual changes (e.g. shrinkage, cracking, spalling, deformation) are noted. Weight loss, amount of free liquid and compressive strength are determined and recorded. If statistics are inconclusive for the four samples, the test must be repeated with a larger number.

6. To qualify the waste form, the tested samples must, as a minimum, show <5% change in dimensions (shrinkage), liberate <1% by volume free liquid, and have a compressive strength >50 psi.

APPENDIX B

INDEX OF GENERAL REQUIREMENTS FOR SHIPMENTS AND PACKAGING OF HAZARDOUS SUBSTANCES

PART 173—SHIPPERS—GENERAL REQUIREMENTS FOR SHIPMENTS AND PACKAGINGS

Subpart A—General

Subpart B—Preparation of Hazardous Materials for Transportation

Subpart C—Explosives and Blasting Agents; Definitions and Preparation

CLASS A EXPLOSIVES; DEFINITIONS

CLASS B EXPLOSIVES; DEFINITIONS

CLASS C EXPLOSIVES; DEFINITIONS

Sec.
173.102 Explosive cable cutters; explosive power devices, class C; explosive release devices, or starter cartridges, jet engine, class C explosives.
173.103 Detonators, Class C explosives, and detonating primers, Class C explosives.
173.104 Cordeau detonant fuse, mild detonating fuse, metal clad or flexible linear shaped charges, metal clad.
173.105 Percussion, tracer, combination, time fuzes and tracers.
173.106 Cartridge bags, empty, with black powder igniters, igniters, safety squibs, electric squibs, delay electric igniters, igniter fuse-metal clad, and fuse lighters or fuse igniters.
173.107 Primers, percussion caps, grenades, empty, primed, and cartridge cases, empty, primed.
173.108 Common fireworks, signal flares, hand signal devices, smoke signals, smoke candles, smoke grenades, smoke pots, and Very signal cartridges.
173.109 Toy caps.
173.110 Charged oil well jet perforating guns, total explosive content in guns not exceeding 20 pounds per motor vehicle.
173.111 Cigarette loads, explosive auto alarms, toy propellant devices, toy smoke devices, trick matches, and trick noise makers, explosive.
173.112 Oil well cartridges.
173.113 Detonating fuzes, class C explosives.
173.114 Actuating cartridges, explosive, fire extinguisher or valve.
173.114a Blasting agents.

Subpart D—Flammable, Combustible, and Pyrophoric Liquids; Definitions and Preparation

173.115 Flammable, combustible, and pyrophoric liquids; definitions.
173.116 Outage.
173.117 Closing and cushioning.
173.118 Limited quantities of flammable liquids.
173.118a Exceptions for combustible liquids.
173.119 Flammable liquids not specifically provided for.
173.120 Automobiles, motorcycles, tractors, or other self-propelled vehicles.
173.121 Carbon bisulfide (disulfide).
173.122 Acrolein, inhibited.
173.123 Ethyl chloride.
173.124 Ethylene oxide.
173.125 Alcohol, n.o.s. (flammable liquid).
173.126 Nickel carbonyl.
173.127 Nitrocellulose or collodion cotton, fibrous, or nitrostarch, wet; nitrocellulose flakes; colloided nitrocellulose, granular, flake, or block, and lacquer base or lacquer chips, wet.
173.128 Paints and related materials (flammable liquids).

Sec.
173.129 Polishes, (flammable liquids).
173.130 Refrigerating machines.
173.131 Road asphalt, or tar, liquid.
173.132 Cement liquid, n.o.s.; container cement; linoleum cement; pyroxylin cement; rubber cement; tile cement; wallboard cement; coating solution (flammable liquids).
173.133 Spirits of nitroglycerin.
173.134 Pyrophoric liquids, n.o.s.
173.135 Diethyl dichlorosilane, dimethyl dichlorosilane, ethyl dichlorosilane, ethyl trichlorosilane, methyl trichlorosilane, trimethyl chlorosilane, and vinyl trichlorosilane.
173.136 Methyl dichlorosilane and trichlorosilane.
173.137 Lithium aluminum hydride, ethereal.
173.138 Pentaborane.
173.139 Ethylene imine, inhibited, and propylene imine, inhibited.
173.140 Zirconium, metallic, solutions, or mixtures thereof, liquid.
173.141 Amyl mercaptan, butyl mercaptan, ethyl mercaptan, isopropyl mercaptan, propyl mercaptan, and aliphatic mercaptan mixtures.
173.143 Methylchloromethyl ether, anhydrous.
173.144 Ink (flammable liquid).
173.145 Dimethylhydrazine, unsymmetrical, and methylhydrazine.
173.146 Heaters for refrigerator cars, flammable liquid fuel type.
173.147 Methyl vinyl ketone, inhibited.
173.148 Monoethylamine.
173.149 Methyl magnesium bromide in ethyl ether in concentrations not over 40 percent.
173.149a Nitromethane.

Subpart E—Flammable Solids, Oxidizers, and Organic Peroxides; Definitions and Preparation

173.150 Flammable solid; definition.
173.151 Oxidizer; definition.
173.151a Organic peroxide; definition.
173.152 Packing.
173.153 Limited quantities of flammable solids, oxidizers and organic peroxides.
173.154 Flammable solids, organic peroxide solids and oxidizers not specifically provided for.
173.154a Fusees.
173.155 Bags, nitrate of soda, empty and unwashed.
173.156 Barium peroxide and calcium peroxide.
173.157 Benzoyl peroxide, chlorobenzoyl peroxide (para), cyclohexanone peroxide, dimethylhexane dihydroperoxide, lauroyl peroxide, or succinic acid peroxide, wet.

Sec.
173.158 Benzoyl peroxide, dry; chlorobenzoyl peroxide (para) dry; cyclohexanone peroxide, dry; lauroyl peroxide, dry; or succinic acid peroxide, dry.
173.159 Burnt cotton.
173.160 Calcium chlorite and sodium chlorite.
173.161 Calcium phosphide.
173.162 Charcoal.
173.163 Chlorate of soda, chlorate of potash, and other chlorates.
173.164 Chromic acid or chromic acid mixture, dry.
173.165 Coal, ground bituminous, sea coal, coal facings.
173.166 Cobalt resinate, precipitated, calcium resinate, and calcium resinate fused.
173.167 Cotton waste, oily.
173.168 Lithium amide, powdered.
173.169 Fiber, burnt.
173.170 Fibers or fabrics impregnated, saturated or coated.
173.171 Fish scrap or fish meal.
173.172 Hair, wet.
173.173 Aluminum dross or magnesium dross.
173.174 Iron sponge, spent oxide, spent iron mass, spent iron sponge.
173.175 Lacquer base, or lacquer chips, dry.
173.176 Matches.
173.177 Motion-picture film and X-ray film.
173.178 Calcium carbide.
173.179 N-methyl-N'-nitro-N-nitrosoguanidine.
173.180—173.181 [Reserved]
173.182 Nitrates.
173.183 Potassium nitrate mixed (fused) with sodium nitrite.
173.184 Nitrocellulose or collodion cotton, wet; or nitrocellulose, colloided, granular, or flake, wet, nitrostarch, wet, or nitroguanidine, wet.
173.185 Paper stock, wet.
173.186 Paper waste, wet.
173.187 Peroxide of sodium.
173.188 Phosphoric anhydride.
173.189 Phosphorus, amorphous, red.
173.190 Phosphorus, white or yellow.
173.191 Phosphorus pentachloride.
173.192 Ammonium picrate, picric acid, trinitrobenzoic acid, and urea nitrate, wet.
173.193 Picric acid, trinitrobenzoic acid, or urea nitrate, wet.
173.194 Potassium permanganate.
173.195 Pyroxylin plastic scrap.
173.196 [Reserved]
173.197 Pyroxylin plastics, in sheets, rolls, rods, or tubes.
173.197a Smokeless powder for small arms.
173.198 Sodium hydride.
173.199 Rags, oily.

Sec.
173.200 Rags, wet.
173.201 Rubber scrap, rubber buffings, reclaimed rubber, or regenerated rubber.
173.202 Sodium metal liquid alloy, potassium metal liquid alloy, and sodium potassium liquid alloy.
173.203 Tetranitromethane.
173.204 Sodium hydrosulfite.
173.205 Sodium picramate, wet.
173.206 Sodium or potassium, metallic; sodium amide; sodium potassium alloys; sodium aluminum hydride; lithium metal; lithium silicon; lithium ferro silicon; lithium hydride; lithium borohydride; lithium aluminum hydride; lithium acetylide-ethylene diamine complex; aluminum hydride; cesium metal; rubidium metal; zirconium hydride, powdered.
173.207 Sulfide of sodium or sulfide of potassium, fused or concentrated, when ground.
173.208 Titanium metal powder, wet or dry.
173.209 Tankage, garbage, and tankage fertilizers.
173.210 Tankages, rough ammoniate.
173.211 Textile waste, wet.
173.212 Trinitrobenzene and trinitrotoluene, wet.
173.213 Wool waste, wet.
173.214 Hafnium metal or zirconium metal, wet, minimum 25 percent water by weight, mechanically produced, finer than 270 mesh particle size; hafnium metal or zirconium metal, dry, in an atmosphere of inert gas, mechanically produced, finer than 270 mesh particle size; hafnium metal or zirconium metal, wet, minimum 25 percent water by weight, chemically produced (See Note 1), finer than 20 mesh particle size; hafnium metal or zirconium metal, dry, in an atmosphere of inert gas, chemically produced (See Note 1), finer than 20 mesh particle size.
173.216 Zirconium picramate, wet.
173.217 Calcium hypochlorite, hydrated, calcium hypochlorite mixture, dry; lithium hypochlorite mixture, dry; mono-(trichloro) tetra-(monopotassium dichloro)-penta-s-triazinetrione, dry; potassium dichloro-s-triazine-trione, dry; sodium dichloro-s-triazinetrione, dry; trichloro-s-triazinetrione, dry.
173.218 Isopropyl percarbonate, unstabilized.
173.219 Potassium perchlorate.
173.220 Magnesium or zirconium scrap consisting of borings, clippings, shavings, sheets, turnings, or scalpings, and magnesium metallic (other than scrap), powdered, pellets, turnings, or ribbon.

Sec.
173.221 Liquid organic peroxides, n.o.s., and liquid organic peroxide solutions, n.o.s.
173.222 Acetyl peroxide and acetyl benzoyl peroxide, solution.
173.223 Peracetic acid.
173.224 Cumene hydroperoxide, dicumyl peroxide, diisopropylbenzene hydroperoxide, paramenthane hydroperoxide, pinane hydroperoxide, and tertiary butylisopropyl benzene hydroperoxide.
173.225 Phosphorus trisulfide, phosphorus sesquisulfide, phosphorus heptasulfide, and phosphorus pentasulfide.
173.226 Thorium metal, powdered.
172.227 Urea peroxide.
173.228 Zinc ammonium nitrite.
173.229 Chlorate and borate mixtures or chlorate and magnesium chloride mixtures.
173.230 Sodium, metallic, dispersion in organic solvent.
173.231 Calcium, metallic, crystalline.
173.232 Aluminum, metallic powder.
173.233 Nickel catalyst, finely divided, activated or spent.
173.234 Sodium nitrite and sodium nitrite mixtures.
173.235 Ammonium bichromate (ammonium dichromate).
173.236 Decaborane.
173.237 Chlorine dioxide hydrate, frozen; chloric acid.
173.238 Aircraft rocket engines (commercial) and/or aircraft rocket engine igniters (commercial).
173.239 Barium azide—50 percent or more water wet.
173.239a Ammonium perchlorate.

Subpart F—Corrosive Materials: Definition and Preparation

173.240 Corrosive material; definition.
173.241 Outage.
173.242 Bottles containing corrosive liquids.
173.243 Closing and cushioning.
173.244 Limited quantities of corrosive materials.
173.245 Corrosive liquids not specifically provided for.
173.245a Corrosive liquids, n.o.s. shipped in bulk.
173.245b Corrosive solids not specifically provided for.
173.246 Antimony pentafluoride, bromide pentafluoride, iodine pentafluoride, bromine trifluoride, and chlorine trifluoride.

Sec.
173.247 Acetyl bromide; acetyl chloride; acetyl iodide; antimony pentachloride; benzoyl chloride; boron trifluoride-acetic acid complex; chromyl chloride; dichloroacetyl chloride; diphenylmethyl bromide solutions; pyrosulfuryl chloride; silicon chloride; sulfur chloride (mono and di); sulfuryl chloride; thionyl chloride; tin tetrachloride (anhydrous); titanium tetrachloride; and trimethyl acetyl chloride.
173.247a Vanadiam tetrachloride and vanadium oxytrichloride.
173.248 Acid sludge, sludge acid, spent sulfuric acid, or spent mixed acid.
173.249 Alkaline corrosive liquids, n.o.s.; Alkaline liquids, n.o.s.; Alkaline corrosive battery fluid; Potassium fluoride solution; Potassium hydrogen fluoride solution; Sodium aluminate, liquid; Sodium hydroxide solution; Potassium hydroxide solution; Boiler compound, liquid, solution.
173.249a Cleaning compound, liquid; Coal tar dye, liquid; Dye intermediate, liquid; Mining reagent, liquid; and Textile treating compound mixture, liquid.
173.250 Automobiles, other self-propelled vehicles, engines or other mechanical apparatus.
173.250a Benzene phosphorus dichloride and benzene phosphorus thiodichloride.
173.251 Boron trichloride and boron tribromide.
173.252 Bromine.
173.253 Chloracetyl chloride.
173.254 Chlorosulfonic acid and mixtures of chlorosulfonic acid-sulfur trioxide.
173.255 Dimethyl sulfate.
173.256 Compounds, cleaning, liquid.
173.257 Electrolyte (acid) and alkaline corrosive battery fluid.
173.258 Electrolyte, acid, or alkaline corrosive battery fluid, packed with storage batteries.
173.259 Electrolyte, acid, or alkaline corrosive battery fluid, packed with battery charger, radio current supply device, or electronic equipment and actuating devices.
173.260 Electric storage batteries, wet.
173.261 Fire-extinguisher charges.
173.262 Hydrobromic acid.
173.263 Hydrochloric (muriatic) acid, hydrochloric (muriatic) acid mixtures; hydrochloric (muriatic) acid solution, inhibited; sodium chlorite solution (not exceeding 42 percent sodium chlorite); and cleaning compounds, liquids, containing hydrochloric (muriatic) acid.
173.264 Hydrofluoric acid; White acid.
173.265 Hydrofluosilicic acid.
173.266 Hydrogen peroxide solution in water.

APPENDIX B, CONTINUED

Sec.
173.267 Mixed acid (nitric and sulfuric acid) (nitrating acid).
173.268 Nitric acid.
173.269 Perchloric acid.
173.270 Phosphorus tribromide.
173.271 Phosphorus oxybromide, phosphorus oxychloride, phosphorus trichloride, and thiophosphoryl chloride.
173.272 Sulfuric acid.
173.273 Sulfur trioxide.
173.274 Fluosulfonic acid.
173.275 Difluorophosphoric acid, anhydrous, monofluorophosphoric acid, anhydrous, hexafluorophosphoric acid, and mixtures thereof.
173.276 Anhydrous hydrazine and hydrazine solution.
173.277 Hypochlorite solutions.
173.278 Nitrohydrochloric acid.
173.279 Anisoyl chloride.
173.280 Trichlorosilanes.
173.281 Benzyl bromide (bromotoluene, alpha).
173.282 Isopropyl percarbonate, stabilized.
173.283 Fluoboric acid.
173.284 Tungsten hexafluoride.
173.285 [Reserved]
173.286 Chemical kits.
173.287 Chromic acid solution.
173.288 Chloroformates.
173.289 Formic acid and formic acid solutions.
173.290 Mixtures of hydrofluoric and sulfuric acid.
173.291 Flame retardant compound, liquid.
173.292 Hexamethylene diamine solution.
173.293 Iodine monochloride.
173.294 Monochloroacetic acid, liquid or solution.
173.295 Benzyl chloride.
173.296 Di iso octyl acid phosphate.
173.297 Titanium sulfate solution containing not more than 45 percent sulfuric acid.
173.298 Memtetrahydro phthalic anhydride.
173.299 Etching acid liquid, n.o.s.
173.299a Tris-(1-aziridinyl) phosphine oxide.

Subpart G—Compressed Gases; Definition and Preparation

173.300 Definitions.
173.300a Approval of independent inspection agency.
173.300b Approval of non-domestic chemical analyses and tests.
173.300c Termination of approval.
173.301 General requirements for shipment of compressed gases in cylinders.
173.302 Charging of cylinders with non-liquefied compressed gases.
173.303 Charging of cylinders with compressed gas in solution (acetylene).
173.304 Charging of cylinders with liquefied compressed gas.
173.305 Charging of cylinders with a mixture of compressed gas and other material.
173.306 Limited quantities of compressed gases.
173.307 Exceptions for compressed gases.
173.308 Cigarette lighter or other similar device charged with fuel.
173.314 Requirements for compressed gases in tank cars.
173.315 Compressed gases in cargo tanks and portable tank containers.
173.316 Liquefied hydrogen.

Subpart H—Poisonous Materials, Etiologic Agents, and Radioactive Materials; Definitions and Preparation

173.325 Classes of poisonous materials.
173.326 Poison A.
173.327 General packaging requirements for Poison A materials.
173.328 Poison A materials not specifically provided for.
173.329 Bromacetone; chlorpicrin and methyl chloride mixtures; chlorpicrin and nonflammable, nonliquefied compressed gas mixtures.
173.330 Chemical ammunition.
173.331 Gas identification sets.
173.332 Hydrocyanic acid, liquid (prussic acid) and hydrocyanic acid liquefied.
173.333 Phosgene or diphosgene.
173.334 Organic phosphates mixed with compressed gas.
173.335 [Reserved]
173.336 Nitrogen dioxide, liquid; nitrogen peroxide, liquid; and nitrogen tetroxide, liquid.
173.337 Nitric oxide.
173.338—173.342 [Reserved]
173.343 Poison B.
173.344 General packaging requirements for Poison B liquids.
173.345 Limited quantities of Poison B liquids.
173.346 Poison B liquids not specifically provided for.
173.347 Aniline oil.
173.348 Arsenic acid.
173.349 Carbolic acid (phenol) liquid.
173.350 Chemical ammunition.
173.351 Hydrocyanic acid solutions.
173.352 Sodium and potassium cyanide solutions, and cyanide solution, n.o.s.
173.353 Methyl bromide and methyl bromide mixtures.
173.353a Methyl bromide, liquid and nonflammable, nonliquefied compressed gas mixtures.
173.254 Motor fuel antiknock compound or tetraethyl lead.
173.355 Phenyldichlorarsine.
173.356 Thiophosgene.

Sec.

173.357 Chloropicrin and chloropicrin mixtures containing no compressed gas or Poison A liquid.

173.358 Hexaethyl tetraphosphate, methyl parathion, organic phosphate compound, organic phosphorus compound, parathion, tetraethyl dithio pyrophosphate, and tetraethyl pyrophosphate, liquid.

173.359 Hexaethyl tetraphosphate mixtures; methyl parathion mixtures; organic phosphorus compound mixtures; organic phosphate compound mixtures; parathion mixtures; tetraethyl dithio pyrophosphate mixtures; and tetraethyl pyrophosphate mixtures, liquid (includes solutions, emulsions, or emulsifiable liquids).

173.360 Perchloro-methyl-mercaptan.

173.361 Aldrin mixtures, liquid, with more than 60 percent aldrin.

173.362 4-Chloro-o-toluidine hydrochloride.

173.362a Dinitrophenol solutions.

173.363 General packaging requirements for Poison B solids.

173.364 Limited quantities of Poison B solids.

173.365 Poison B solids not specifically provided for.

173.366 Arsenic (arsenic trioxide) or arsenic acid (solid).

173.367 Arsenical compounds, n.o.s.; arsenate of lead; calcium arsenate; Paris green; and arsenical mixtures.

173.368 Arsenical dust, arsenical flue dust, and other poisonous noncombustible byproduct dusts; also arsenic trioxide, calcium arsenate, and sodium arsenate.

173.369 Carbolic acid (phenol), not liquid.

173.370 Cyanides and cyanide mixtures, dry.

173.371 Dinitrobenzol (dinitrobenzene).

173.372 Mercury bichloride (mercuric chloride).

173.373 Ortho-nitroaniline and para-nitroaniline.

173.374 Nitrochlorbenzene, meta or para.

173.375 Sodium azide.

173.376 Aldrin and aldrin mixtures, dry, with more than 65 percent aldrin.

173.377 Hexaethyl tetraphosphate mixtures; methyl parathion mixtures; organic phosphorus compound mixtures, organic phosphate compound mixtures; parathion mixtures; tetraethyl dithio pyrophosphate mixtures; and tetraethyl pyrophosphate mixtures, dry.

173.379 Cyanogen bromide.

173.381 Irritating materials; Definition and general packaging requirements.

173.382 Irritating materials, not specifically provided for.

173.383 Chemical ammunition.

173.384 Monochloracetone, stabilized.

Sec.

173.385 Tear gas grenades, tear gas candles, or similar devices.

173.386 Ethiologic agents; definition and scope.

173.387 Packaging requirements for etiologic agents.

173.388 Labeling of packages containing etiologic agents.

173.389 Radioactive materials; definitions.

173.390 Transport groups of radionuclides.

173.391 Limited quantities of radioactive materials and radioactive devices.

173.392 Low specific activity radioactive material.

173.393 General packaging and shipment requirements.

173.393a U.S. Atomic Energy Commission approved packages; standard requirements and conditions.

173.393b International shipments and foreign-made packages; standard requirements and conditions.

173.394 Radioactive material in special form.

173.395 Radioactive material in normal form.

173.396 Fissile radioactive material.

173.397 Contamination control.

173.398 Special tests.

Subpart I—Special Requirements for Certain Rail Shipments or Movements

173.426 Cars, truck bodies or trailers containing lading which has been fumigated or treated with flammable liquids, flammable gases, poisonous liquids or solids, or poisonous gases.

173.427-173.431 [Reserved]

173.432 Tank car shipments.

Subpart J—Other Regulated Material; Definition and Preparation

173.500 Definitions.

173.505 Exceptions for Other Regulated Material (ORM).

173.510 General packaging requirements.

Subpart K—Other Regulated Material; ORM-A

173.605 Ammonium hydrosulfide solution, ammonium polysulfide solution, bromochloromethane, dibromodifluoromethane, dichlorodifluoroethylene, dichloromethane, methyl chloroform, perfluoro-2-butene, tetrachloroethylene, and trichloroethylene.

173.610 Camphene.

173.615 Carbon dioxide, solid (dry ice).

173.620 Carbon tetrachloride, ethylene dibromide (1,2-dibromoethane), and tetrachloroethane.

173.630 Chloroform.

173.635 Ferrophosphorus.

173.645 Ferrosilicon.

Sec.

173.650 Hexachloroethane.

173.655 Naphthalene or naphthalin.

Subpart L—Other Regulated Material; ORM-B

173.800 Ammonium hydrogen sulfate, ammonium fluoride, barium oxide, chloroplatinic acid, copper chloride, ferric chloride, lead chloride, molybdenum pentachloride, potassium hydrogen sulfate, sodium aluminate, sodium hydrogen sulfate, and/or sodium hydrogen sulfite (each in solid form).

173.850 Lime, unslaked; quicklime; and calcium oxide.

173.860 Mercury, metallic.

173.861 Gallium metal, liquid.

173.862 Gallium metal, solid.

Subpart M—Other Regulated Material; ORM-C

173.906 Inflatable life-rafts, escape slides, and evacuation slides.

173.910 Ammonium sulfate nitrate.

173.915 Battery parts.

173.920 Bleaching powder.

173.925 Box toe board.

173.930 Burlap bags, used and unwashed or not cleaned.

173.931 Burlap cloth, burlap bags, new, used, and washed, or vacuum cleaned, wheel cleaned, or otherwise mechanically cleaned.

173.945 Calcium cyanamide, not hydrated.

173.952 Castor beans and castor pomace.

173.955 Coconut meal pellets.

173.960 Copra.

173.965 Cotton and other fibers.

173.970 Cotton batting, batting dross, wadding, seed hull fiber, shavings, pulp, and cut linters.

173.975 Cotton sweepings; and textile, cotton, felt, or wool waste.

173.980 Excelsior.

173.985 Exothermic ferrochrome, ferromanganese, and silicon-chrome.

173.990 Feed, wet, mixed.

173.995 Fish scrap and fish meal.

173.1000 Garbage tankage, rough ammoniate tankage, or tankage fertilizer.

173.1005 Hay or straw.

173.1010 Lead dross or scrap containing 3 percent or more free acid.

173.1020 Magnetized material.

173.1025 Ferrous metal borings, shavings, turnings, or cuttings (excluding stainless steel).

173.1030 Oakum or twisted jute packing.

173.1035 Oiled material.

173.1040 Pesticide, water-reactive.

173.1045 Petroleum coke, uncalcined.

173.1060 Rosin.

173.1065 Rubber curing compound, solid.

173.1070 Sawdust or wood shavings.

173.1075 Scrap paper or waste.

173.1080 Sulfur.

Sec.

173.1085 Yeast, active (in liquid or compressed form).

173.1090 Asbestos.

Subpart N—Other Regulated Material; ORM-D

173.1200 Consumer Commodity.

Subpart O—Other Regulated Material; ORM-E

173.1300 Hazardous waste, liquid or solid, n.o.s.; hazardous substance liquid or solid, n.o.s.

APPENDIX A—METHOD OF TESTING CORROSION TO SKIN

AUTHORITY: 49 U.S.C. 1803, 1804, 1808; 49 CFR 1.53(e), unless otherwise noted.

NOTE: Nomenclature changes to Part 173 appear at 43 FR 48643 (Amdt. 173-121, Oct. 19, 1978.)

NOTE: For a notice document notifying shippers of hazardous materials of the applicable regulations in this part see 40 FR 33066, Aug. 6, 1975.

Subpart A—General

§ 173.1 Purpose and scope.

(a) This part defines hazardous materials for transportation purposes and prescribes certain requirements to be observed in preparing them for shipment by air, highway, rail, or water, or any combination thereof.

(b) A shipment that is not prepared for shipment in accordance with this subchapter may not be offered for transportation by air, highway, rail, or water. It is the duty of each person who offers hazardous materials for transportation to instruct each of his officers, agents, and employees having any responsibility for preparing hazardous materials for shipment as to applicable regulations in this subchapter.

(c) When a person other than the person preparing a hazardous material for shipment performs a function required by this part, that person shall perform the function in accordance with this part.

[Amdt. 173-94, 41 FR 16062, Apr. 15, 1976, as amended by Amdt. 173-100, 41 FR 40476, Sept. 20, 1976]

APPENDIX C

TEST FOR PYROPHORIC LIQUIDS, BUREAU OF EXPOLSIVES, ASSOCIATION OF AMERICAN RAILROADS

ASSOCIATION OF
AMERICAN RAILROADS
OPERATIONS AND MAINTENANCE DEPARTMENT · BUREAU OF EXPLOSIVES
RARITAN CENTER · BUILDING 817 · EDISON, NEW JERSEY 08817 · 201/225-1618

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PYROFORIC APPARATUS DESCRIPTION AND PROCEDURE FOR USE

The Bureau of Explosives' pyroforic apparatus consists of a metal enclosure 4 feet by 4 feet x 12 feet. Both ends may be completely or partially closed by hinged metal covers 4 feet by 4 feet. There is a transverse metal partition four feet from one end of the large metal box.

In the smaller compartment (4' x 4' x 4') are placed an electric heater connected to a rehostate, a variable speed blower and an electric hotplate with an open container of water on it.

The output of the blower is connected to a 3 inch sheet metal pipe which passes through the metal partition into the larger chamber, makes a 90° turn downward and terminates in an inverted metal funnel having a maximum diameter of 24 inches. Thermocouples near the blower intake in the smaller compartment and near the center of the funnel in the larger compartment measure the temperatures at these points.

In use the heater is turned on (if necessary), the blower speed adjusted to give an air velocity of 5 miles per hour near the center of the funnel and the water on the hot plate brought to boiling. The apparatus is allowed to run and adjusted so that the air coming out of the funnel is 80°F plus or minus 1°. The unit is run this way for at least two hours to assure that a stable condition has been reached.

Four liters of dry soft-wood sawdust are arranged in a conical shape in a circular metal pan 24 inches in diameter and 3 inches deep. The top of the cone is flattened to a diameter of about 6 inches. The pan and sawdust are placed near the open end of the larger compartment and using protective clothing and remote handling equipment, 800 ml of the liquid under test are poured onto the pile of sawdust. The pan and contents are then pushed directly under the funnel. The mixture is left under the funnel until fire occurs or for a maximum time of two hours.

PAR

INTERIM REPORT

NRC Research and/or Technical Assistance Rept

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