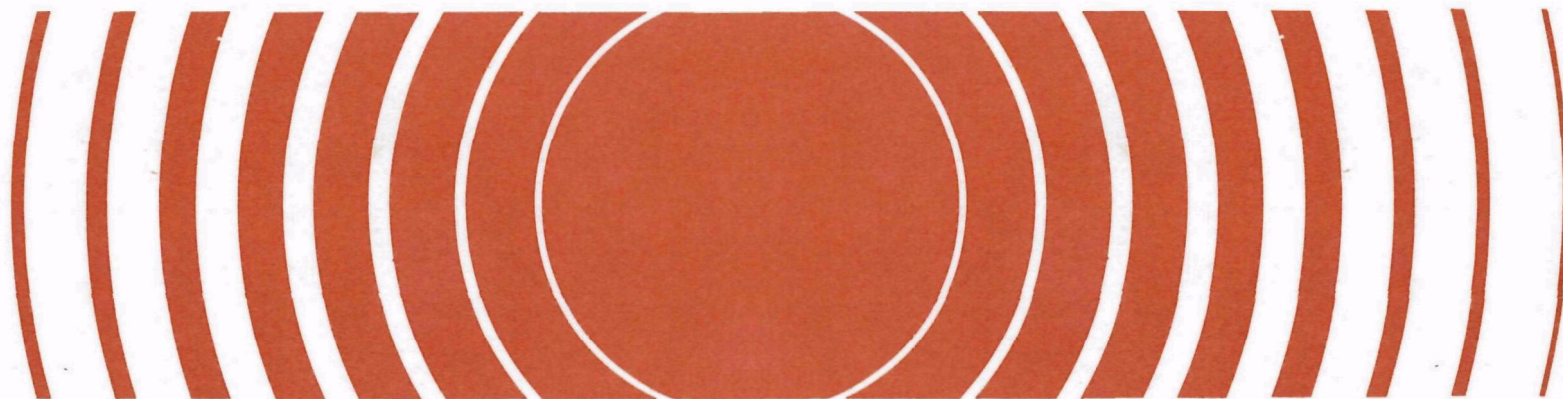

Radiation



Sediment Monitoring Parameters and Rationale for Characterizing Deep-Ocean Low-Level Radioactive Waste Disposal Sites



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for Characterizing
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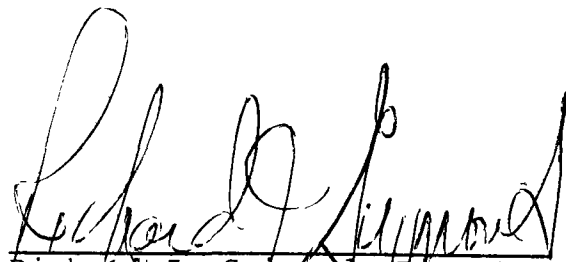
FOREWORD

The Environmental Protection Agency (EPA) was given a Congressional mandate to develop criteria, standards, and regulations governing the ocean disposal of all forms of wastes pursuant to Public Law 92-532, the Marine Protection, Research, and Sanctuaries Act of 1972. Within this Congressional mandate, EPA has initiated a specific program to develop regulations and criteria to control the ocean disposal of low-level radioactive wastes (LLW).

The EPA Office of Radiation Programs (ORP) has conducted feasibility studies to determine whether current technologies could be applied toward determining the fate of radioactive wastes dumped in the past. After successfully locating radioactive waste containers in three of the primary LLW disposal sites previously used by the United States, ORP initiated disposal site characterization studies to: (1) determine the biological, chemical, and physical parameters, (2) identify and ascertain the distribution of radionuclides within the sites, and (3) evaluate previous packaging techniques and materials.

The purpose of this document is to provide a rationale for the sediment measurements that will indicate radionuclide retention characteristics at potential LLW disposal sites in the deep-ocean environment. Prior to sediment sampling, the site selection shall have been directed to specific areas by site selection criteria supported by geophysical data to indicate site stability. Sediment sampling is conducted to meet the sediment monitoring and criteria needs for site characterization.

The Agency invites all readers of this report to send any comments or suggestions to Mr. David E. Janes, Director, Analysis and Support Division, Office of Radiation Programs (ANR-461), Washington, DC 20460.



Richard J. Guimond, Director
Office of Radiation Programs

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TABLE OF CONTENTS

	Page
Foreword	iii
Acknowledgments	v
1.0 Sediment Monitoring Parameters and Rationale	1
1.1 Introduction	1
1.2 Special Considerations for Low-Level Radioactive Wastes ..	2
1.3 Parameters Already in the Ocean Disposal Regulations	4
1.3.1 Organic Carbon	5
1.3.2 Sediment Texture Grain Size	5
1.3.3 Recommendations	7
1.3.4 Mineral Composition of Sediment	7
1.3.5 Recommendations	8
1.4 Consideration of Parameters Not In Existing Regulations ..	9
1.4.1 Sorption Distribution Coefficient (Kd)	9
1.4.2 Recommendations	10
1.4.3 Sediment Redox Considerations	11
1.4.4 Recommendations	14
1.4.5 Determination of pH	15
1.4.6 Recommendations	15
1.5 Geotechnical Parameters	15
1.5.1 Recommendations	16

TABLE OF CONTENTS (Continued)

	Page
1.6 X-radiographs	16
1.6.1 Recommendations	16
1.7 Correlation with Geological Stability	16
1.7.1 Recommendations	17
1.8 Sampling Density	17
1.9 Summary of Recommendations	18
1.10 Future Considerations:	
Implementation of Section 424, Public Law 97-424 ..	19
References	21

1.0 SEDIMENT MONITORING PARAMETERS AND RATIONALE

1.1 INTRODUCTION

The purpose of this document is to discuss the need and present the rationale for special sediment monitoring parameters and criteria to characterize LLW disposal sites meeting the International Atomic Energy Agency (IAEA) recommended minimum disposal depth of 4000m. The IAEA disposal depth limitation was developed pursuant to the London Dumping Convention, to which the United States is a signatory. Sediment monitoring requirements for ocean disposal of all wastes are contained in Part 228 of the current Ocean Disposal Regulations (42 FR 2462, January 11, 1977). Part 228 contains general requirements and does not specifically address sediment monitoring requirements for disposal of packaged LLW. Part 228 does acknowledge, however, that there may be special requirements for deep-sea monitoring. Paragraph 228.13(e)(3)(ii) states that "additional parameters may be selected based on the materials likely to be in the wastes dumped at the site." The sediment measurement parameters required for all wastes are: organic carbon, texture, particle size distribution, major mineral constituents, and settling rate. For LLW, all of these parameters, with the exception of settling rate, will be used. Some modifications of methods to characterize sediments are necessary because of the sediment conditions in the deep ocean and the nature of the wastes.

This document recommends additional baseline sediment monitoring parameters and criteria to address the special considerations applicable to ocean disposal of packaged LLW. The existing EPA waste package performance criteria require that LLW must radiodecay to environmentally acceptable levels within the expected immobilization period of the waste package and the surrounding sediment. Using a multibarrier approach for containment of the LLW at the site, the engineered waste package represents the primary barrier. The natural retention afforded by the physicochemical characteristics of deep ocean sediments constitutes an additional barrier. Some of these factors can be measured. Estimates of the ability of the physicochemical environment to increase radionuclide retention in the sediment, or to restrict radionuclide movement to the water column after release from a waste package, are considered as part of the sediment monitoring recommendations.

This document addresses geotechnical parameters which may be used to estimate the extent of penetration of a free-falling waste package into the sediment and to provide baseline data for evaluating the option of subseabed disposal of LLW. The correlative value of sediment monitoring criteria to (a) geologic stability of the disposal site and (b) interactions of the sediment and its environment with the waste package is presented. It also presents a discussion of specific sediment parameters applicable to a deep-ocean LLW disposal site. Numerical limits are proposed where applicable. A Methods Manual, with recommended testing procedures, will be provided as a separate document (EPA 520/1-87-011, June 1988).

The Methods Manual addresses the use of geophysical methods including bathymetric and side-scan sonar techniques to determine the geologic stability of a candidate site prior to sediment monitoring. It was developed to provide details of the recommended sediment testing techniques for the sediment monitoring parameters discussed in this report. It is an important ancillary supplement to the sediment monitoring parameters and criteria. It is intended to assure uniformity in analyses of sediment samples and in reporting data.

1.2 SPECIAL CONSIDERATIONS FOR LOW-LEVEL RADIOACTIVE WASTE

The present ocean disposal regulations look to the engineering of the waste package (the container and the solidification agent containing the waste) as the primary barrier to prevent direct dispersion of any LLW into ocean waters. In a multibarrier protection system, the sediment constitutes an additional natural barrier to the migration of radionuclides if the waste container has been breached by natural or accidental causes. The sediment can only be an effective barrier, however, if the waste container is in contact with the sediment. Release of radionuclides from any seawater-exposed area of the container could "short circuit" the sediment sorption mechanism by moving radionuclides directly into the water column. However, some scavenging of radionuclides by suspended particulates in the benthic boundary layer will probably occur. Biological activity of organisms living in or on the sediment (bioturbation) could also "short circuit" radionuclide retention by increasing the rate of dispersion; however, this activity can also carry radionuclides deeper into the sediment and thereby provide greater immobility. Any site selected for LLW should have comparatively low biological activity.

A waste container in contact with deepsea sediment creates an environment where information on the sediment composition and the oxidation-reduction (redox) state of the sediment may be used to predict both the time of release of waste from a container and the potential for immobilization of some of the radionuclides upon their release to the sediment environment. The redox environment immediately adjacent to and beneath a waste container, however, is altered by the weight of the container on the sediment. Therefore, knowledge of the geotechnical properties (e.g. compressive strength) of the sediment and sediment surface will facilitate assessment of this effect and will allow prediction of the depth of penetration of the waste package into the sediment upon impact at terminal velocity. This will establish the initial extent of sediment-container physicochemical interactions. Any additional burial of the drum by sedimentation at the site is considered desirable and will increase the amount of sediment retention afforded if a waste package were to release its contents.

To assess the impact of radionuclide release at a LLW site, it is important to know the radionuclides in the waste that are most likely to be detrimental to biota or man and the sediment retention potential of those radionuclides. The radionuclides of importance are those that are (a) primary constituents of LLW, (b) enduring or persistent (e.g. have a half-life of 5 years or more) and, (c) biologically toxic. According to Wild et al (1981), the radionuclides in LLW that meet one or more of these criteria include tritium, carbon-14, cobalt-60, nickel-59 and-63, strontium-90, niobium-94, technetium-99, iodine-129, cesium-137, uranium-235, and uranium-238. Those radionuclides that meet all three criteria include cesium, cobalt, and strontium. Therefore, focus will be on cesium, cobalt and strontium for assessment of the predicted retention by sediment. Other radionuclides may be considered during any further development or revisions to regulations and criteria; and site characterization will include analysis of parameters sensitive to prediction of retention for all the radionuclides of importance in a LLW package.

Since the physicochemical processes controlling sorption of radionuclides onto the sediment are complex and are not the same for all radionuclides of concern, the determination of the sorption distribution coefficient (K_d) on site-specific sediments gives the best state-of-the-art assessment of radionuclide retention. The test is performed under similar environmental conditions (both oxidizing and reducing) as exist in the prototype sediment. Tritium, carbon-14, and iodine-129, however, have little or no retention and little purpose is served in performing laboratory analyses on them. One of the radionuclides in which solubility changes enormously with slight changes in redox potential is technetium-99. Some of the other radionuclides; e.g., cobalt-60, and uranium isotopes, are also affected to some degree by redox state. The K_d of cesium isotopes, strontium-90, and other cations exhibiting a single oxidation state are most affected by the amount and type of sorptive minerals and surface area of the sediment. Some radionuclides form soluble complexes with organics that might occur in the waste form or sediment; e.g., cobalt-60 is known to be mobilized by organics such as EDTA. Some radionuclides also coprecipitate with iron and manganese oxyhydroxides.

It is feasible to predict, within limits, the potential retention of radionuclides of concern if adequate measurements for characterization of the sediment are performed at a prospective LLW site. Such an approach might eventually be extended to the heavy metal analogs in hazardous waste.

The sediment parameters relating to site selection and baseline monitoring of a LLW site will include: (a) those parameters already in place in paragraph 228.13(e)(3) of the Regulations, where applicable, and (b) recommended parameters that relate to measurement of radionuclide retention (e.g. K_d s) or which predict the retention of radionuclides in the sediment.

1.3 PARAMETERS ALREADY IN THE OCEAN DISPOSAL REGULATIONS

The parameters required by the current EPA Ocean Disposal Regulations are applicable to LLW disposal sites. Paragraph 228.13(e)(3) lists organic carbon, texture, particle size distribution, major mineral constituents, and settling rate as required measurements for sediment analyses. These sediment parameters, however, must be addressed by methods applicable to the special nature of low-level radioactive waste and the deep-ocean environment. Settling rate, listed in paragraph 228.13(e)(3), is not applicable to the disposal of LLW, however, because radioactive wastes are presumed to be packaged in containers as specified in paragraph 227.11(b)(1).

1.3.1 ORGANIC CARBON

The concentration of organic carbon (regardless of source) in sediments within the deep-ocean environment is an index to the total organic matter in sediments, and to the biomass of living organisms in the overlying water-column and adjacent areas. It is important in siting considerations since relatively higher levels of organic carbon in sediments at a prospective LLW disposal site would make the site less suitable for disposal of wastes due to a higher probability of having biological pathways to the surface waters. The presence of organic matter in sediment can also be detrimental for radionuclides that form complex chemical bonds, in that their retention by sediment is reduced. Radiocobalt, for example, is known to form organic complexes in shallower ocean areas, resulting in virtually no retention by geologic media. Information about the organic chemical complexes formed by radionuclides is incomplete, making prediction of radionuclide retention by the sediments more difficult. According to Emery and Uchupi (1972), the concentration of organic carbon in the deeper waters of the Western Atlantic Ocean is generally less than 0.5 percent. Typical results for organic carbon, measured in surficial sediment samples, in the vicinity of LLW disposal sites are as follows: NW Atlantic (2,800m site), 0.6 percent; NE Atlantic, 0.2-0.3 percent; Pacific (Farallon Islands), 0.6 percent.

Determination of organic carbon involves high temperature combustion using a carbon analyzer on samples from which the inorganic carbon (carbonate carbon) has been removed; the latter is accomplished by either wet or dry leach techniques.

1.3.2 SEDIMENT TEXTURE GRAIN SIZE

The sediment texture grain size is one of the most important and versatile of the sediment monitoring parameters at a prospective LLW site. This parameter (a) provides a basis for classification of the sediment by grain size (b) correlates with geotechnical parameters (Keller et al, 1979) and the sorptive properties of the sediment (Onishi et al, 1981), (c) allows for mathematical computation of overall mineral percentages in a sediment sample that was analyzed for mineral content in specific sand, silt and clay-size fractions (Neiheisel, 1983) and, (d) provides an indication of site stability.

The sediment texture classification is based on the percentage of sand, silt, and clay-size fractions in accordance with the nomenclature of Shepard (1954). A color description precedes the sediment size classification. The triangular textural diagram used for sediment classification is depicted in Figure 1 of the Methods Manual (EPA, 1988). Ten categories of sediment are classified based on the percentage of sand, silt and clay-size materials in the sediment. These are sand, clayey sand, sandy clay, clay, silt, silty sand, clayey silt, sand-silt-clay, silty clay, and sandy silt. In this classification, the sand-size material is sediment greater than 0.062 mm, silt-size material is sediment less than 0.062 mm but greater than 0.002 mm (2 micron size) and clay-size material is all sediment less than 2 micron size. The 62-micron size is recommended (Galehouse, 1971) for the boundary between silt and sand because (a) most investigators use Stokes' law up to this size-limit of sand and (b) the 62-micron stainless steel sieve is convenient for removing coarser size materials from the finer material to be analyzed by sedimentation (silt and clay) techniques. The 2-micron size is the preferred dividing-line between silt and clay-size materials as a mineral composition change usually occurs at this size-boundary. Using the above texture size classification, the typical sediment description for the Atlantic 2,800m LLW disposal site is clayey silt, with an olive grey color.

The process of determining the percentages of grains representative of particular sizes is known as grain-size analysis. The grain-size distribution of the sediment sample is determined by combining the analytical results from the sand, silt, and clay fractions. The grain-size distribution of the sand-size fraction is determined by sieve analysis or by using the rapid sediment analyzer, in which sediments of less than 0.062 mm size are analyzed by sedimentation techniques. The methods used depend on the type of sediment encountered. The technique to be used can normally be determined by visual inspection of the sediment cores. Some of the methods that are acceptable, widely used, and available, are described in detail in a Methods Manual (EPA, 1988).

1.3.3 RECOMMENDATIONS

Sediment analyzed for texture should be representative of the top 30 cm of sediment core from a LLW site. Based upon observations from the deep submersible ALVIN (Hanselman and Ryan, 1983) during an EPA Office of Radiation Programs survey at the Atlantic 3,800m LLW disposal site, and similar observations during EPA submersible surveys at the Atlantic 2,800m site and the Pacific Ocean Farallon Islands site, we do not expect waste drums to penetrate deeper than 30 cm into the sediments. This depth is also the sediment recovery depth obtained by conventional sediment box corers. Subcore samples obtained from the box core will thus provide relatively undisturbed sediment for the various tests to be made on the sediment.

The proposed disposal site should be free of exposed bedrock and display uniformity of sediment texture and relative geologic stability across the site. To ensure uniformity of sediment texture over a proposed site, we recommend that the average sediment texture to 30cm depth for each sample location should fall in a close pattern on the triangular diagram that constitutes the Shepard Texture Classification Chart; and the number of different types of sediment should not exceed 3 of the possible 10 textural descriptions displayed on the chart. Such uniformity of texture across the proposed site will reflect on uniform, stable, geologic processes in the area.

1.3.4 MINERAL COMPOSITION OF SEDIMENT

The current Regulations cite "major mineral constituents" as one of the sediment parameters. However, an important consideration in the assessment of a LLW site in a deep-ocean environment is a reasonably precise evaluation of the mineral composition of both major and minor mineral components (sorptive minerals may occur in the minor component). This parameter indicates (a) the potential retention of radionuclides by the sediment (b) the geologic stability of the site (c) presence of economic mineral deposits, and (d) dynamic factors and sediment source considerations.

An accurate assessment of mineral composition (± 10 percent) would reflect on the potential retention of radionuclides that are known to exhibit sorption primarily by cation exchange and sediment surface area phenomena. According to Onishi et al (1981), the radionuclides in LLW that are most strongly affected by cation exchange and surface area include cesium, strontium, uranium and radium. The minerals most capable of affecting cation exchange and having the greatest surface area are the clay minerals (generally less than 2-micron size in diameter) and zeolites. The sorptive minerals most responsive to cation exchange, in order of priority, are smectite (montmorillonite), zeolites, illite, kaolinite, and chlorite. The greater surface area occurs in smectite (montmorillonite) and zeolites which are generally confined to the clay-size (less than 2 microns). The general distribution of sediment composition in relation to grain-size distribution is given by Neihsel (1983) for ocean sediment at the Atlantic 3,800 m LLW disposal site. This study demonstrates the fact that a major portion of the highly sorptive minerals and those with greatest surface area occur in the less than 2-micron size (clay) fraction. Since a composition change commonly occurs between silt and clay-size materials and most of the sorptive materials occur in clay-size fraction, it is desirable to separate these size fractions for individual chemical and X-ray diffraction analysis. Average mineral composition (prior to separation) may be computed using the texture grain-size curve. An accuracy of ± 10 percent is considered desirable if the mineral data is to be of assistance in the assessment of radionuclide retention or geologic stability of site. The methods for recommended detailed mineral analyses are included in a Methods Manual (EPA, 1988).

1.3.5 RECOMMENDATIONS

Evaluation of the potential for radionuclide retention requires a detailed mineral analysis of the sediment that exceeds the "major minerals constituents" cited in paragraph 228.13(e)(3) of the current regulation. It is recommended that a method with at least ± 10 percent mineral accuracy be specified for the potential prediction of radionuclide retention such mineral precision would provide.

1.4 CONSIDERATION OF PARAMETERS NOT IN EXISTING REGULATIONS

The current regulations do not contain sediment monitoring criteria that address the parameters which (a) measure radionuclide retention and (b) provide prediction potential of radionuclide retention by the sediment. These considerations are addressed below with recommendations.

1.4.1 SORPTION DISTRIBUTION COEFFICIENT (K_d)

The sorption distribution coefficient (K_d) of a radionuclide is a measure of its retention potential determined by laboratory analysis of site-specific sediment. The K_d is used to determine the degree of partitioning between radionuclides in solution and the same radionuclides in the solid phase. The K_d , in effect, represents the relative length of time a radionuclide, released to the sediment environment in solution, is impeded from movement toward the water column by sorption onto solid surfaces. The factors that affect the K_d of a radionuclide vary with the sorptive minerals of a particular sediment, particle size, pH, Eh (redox), and chemical speciation of the radionuclide released from the waste container.

The process by which the radionuclides are removed from the dissolved phase by particulate matter or sediment is generally referred to as scavenging (IAEA, 1986). If the release of the dissolved phase is into the sediment surrounding the waste package, the scavenging is essentially the sorption distribution coefficient (K_d) that is measured from specific sediment at the site. Any release of the dissolved phase directly to the water column from the waste package, however, is more difficult to estimate for retention of the radionuclide(s) because of the dynamic nature of the particulate matter in the benthic nepheloid layer (BNL). Nyffeler and Godet (1986) describe the nature of the BNL for a basin in the NE Atlantic. Since the BNL particulate matter is recognizably higher in organic matter than the consolidated sediment at a candidate disposal site, the sorption distribution coefficient (K_d) of this material may differ from the consolidated sediment. While this probable difference is recognized, it is as yet not determined whether it is significant enough to warrant a separate test. If such testing were warranted, it would require enough sample to perform the test; the "fluff" or unconsolidated sediment layer from sediment cores might be the most practical representative sample of this material.

The laboratory batch tests for K_d are described in a Methods Manual (EPA, 1988) in terms of R_d which is the distribution ratio, instead of the distribution coefficient (K_d). The use of K_d implies sufficient knowledge of the chemical systems under investigation to ensure that a final reversible equilibrium is attained. In natural systems this is not always the case, so the value R_d is determined. This is calculated in the same manner as K_d but does not carry with it the thermodynamic requirements of a system at equilibrium. The distribution ratio (R_d) and the distribution coefficient (K_d) are defined identically, but, in actuality, R_d is only equal to K_d at equilibrium.

The K_d s of radionuclides are site specific, and laboratory measurements are only as accurate as the ability exists to duplicate deep-ocean conditions. Onishi et al (1981) cites K_d measurements from a wide range of environments, and data bases have been developed for various programs which indicate the range of values possible. Radionuclides with virtually no retention by any environment are the most predictable; these include tritium, carbon-14, and iodine-129. However, for other radionuclides of interest, such predictability is not possible, and few measurements are available to compare potential K_d s that exist in ocean environments. Since K_d measurements for radionuclide retention are expensive (approximately \$1,000 per radionuclide per sample), the number of tests performed should be limited to those radionuclides of most concern.

The methods commonly employed include the batch test and sediment column method. Since the redox state constitutes a primary factor for redox sensitive nuclides, this condition must also be considered in the laboratory testing. The redox conditions in the deep-ocean environment are addressed in Section 1.4.3.

1.4.2 RECOMMENDATIONS

It is recommended that at least one sediment core from each prospective LLW disposal site be measured for K_d 's of radionuclides of concern including, as a minimum, cobalt, cesium, and strontium. The measurements should be conducted on samples representative of the sediment to 30 cm depth.

1.4.3 SEDIMENT REDOX CONSIDERATIONS

The retention of some of the radionuclides in the LLW at a deepsea disposal site is sensitive to the oxidation-reduction (redox) state of the sediments. The redox state at most disposal sites will range from oxygenated (aerobic) conditions on the surface to reducing (anaerobic) conditions with depth. This decrease of oxygen with depth is indicative of oxygen consumption in the sediment below the sediment-water interface and reflects input of organic carbon (Murray and Grundmanis, 1980). In a qualitative sense this is related to distance from the continental margins where production occurs. Both the Atlantic and Pacific are similar in this respect. The depth to oxygen depletion in the sediments in the Atlantic Ocean has been reported by several investigators (Schmidt 1979, Carpenter et al 1983, Wilson et al 1983, and Van der Loeff and Lavaleye 1984), who indicate typical ranges from 10 to 30 cm depth to oxygen depletion.

At the NE Atlantic LLW disposal site Van der Loeff and Waijers (1985) report that average depths of oxygen penetration extend to 50 cm and as much as 100 cm. Wilson et al (1983) reports the greatest depth to oxygen depletion (10 m) in the Atlantic in the Cape Verde Abyssal Plain. In the Pacific Ocean investigations, Grundmanis and Murray (1982) report oxygen depletion as relatively rapid in the first 10 to 15 cm of sediment depth in the equatorial region, where the concentrations of surface organic carbon are also high. Elsewhere in the Pacific, investigations indicate the aerobic zone extends to several meters in depth in the sediment.

The range of the oxygenated sediment environment may vary in depth from less than the diameter of a 55-gallon waste drum to as much as several meters. The retention of several radionuclides, including technetium, uranium, cobalt, and nickel, is affected by the redox state. This parameter requires special attention in the assessment of radionuclide retention in the sediment of a deep ocean LLW site. Remobilization at lowered redox potentials below the depth where oxygen reaches zero also causes an upward diffusion transport of manganese.

Concentrations of sulfide sulfur, iron, and manganese observed in the sediment profile can be used for understanding variations in redox sensitive radionuclides. These parameters also provide a rough correlation with redox conditions obtained by the more precise measurement of NO_3 in sediment pore water for determination of oxygen depletion. Care must be exercised in the use of these parameters; e.g., if detrital pyrite or relict conditions occur in the sediment, interpretations might be misleading. However, the use of these parameters in a well-characterized sediment is considered of interpretative value in correlating with the redox condition of the sediment column. In order to be effective, measurements should be made at 5 cm intervals for the full 30 cm of sediment core. Thus the thickness of the aerobic layer to oxygen depletion could, in a thoroughly characterized site, be estimated to within approximately 5 cm if the redox boundary occurs within the sediment core.

Sulfur compounds in marine sediments range from 0.02 to 2.0 percent and reduction of sulfate to sulfide will not occur in the aerobic layer. In fact, sulfide formation in sediments occurs well below the sediment depth of measurable oxygen depletion. For example, Schmidt (1979) estimated the depth of sulfide formation would occur at 50 cm depth at a Gulf of Maine 2,500m depth location in the Western North Atlantic where pore water chemistry and Eh meter studies indicated the depth to oxygen depletion at 30 cm. For sulfides to form in the anaerobic layer, both iron and sulfate-reducing bacteria must be present. The presence of both sulfate-reducing bacteria and iron in the sediment will generate pyrite (FeS_2) in the anaerobic layer. The sulfide sulfur test is a relatively simple and inexpensive test that has limited application and in some cases may be used to correlate with the approximate boundary to the anaerobic layer.

The redox state and sulfide formation are also of interest in waste container corrosion. For example, a steel drum, well below the depth of oxygen depletion and in the presence of anaerobic, sulfate-reducing bacteria, would be corroded by a process called cathodic depolarization (Uhlig, 1971). As Dexter (1982) indicates, the bacteria utilize hydrogen in their metabolism to reduce sulfates to sulfides. The sulfides, in turn, form an iron-sulfide scale on the steel which is cathodic to a bare steel surface. Thus, this mechanism of corrosion occurs in anaerobic conditions where there is a source of sulfate.

The manganese and iron in sediments correlate with the redox state and radionuclide retention potential of sediments. Under oxidizing conditions, iron is highly insoluble. However, under mildly reducing conditions, Fe^{++} may be solubilized and precipitate in sulfide-bearing sediments. Technetium from a LLW waste drum, released to a reducing environment, has been reported to be immobilized in the presence of Fe^{++} (Van der Graff et al, 1984). Manganese is also controlled by the redox state, and the factors which cause remobilization and deposition of manganese influence the migration potential of cobalt and nickel.

The process of manganese reduction and mobilization in marine sediment is well documented. Froleich et al (1979) describe the accumulation of manganese at the surface of the anaerobic boundary layer in marine sediment. A manganese "spike" at this sediment depth essentially marks the point of oxygen depletion. This spike of manganese can be used to estimate the depth at which anaerobic conditions prevail in the sediment; however, because of the sharpness of the boundary, care must be exercised in the sample spacing requirements. The manganese profile is also a mirror image of the iron profile; manganese increases as iron decreases in the sediment core. The inflection points on a concentration-versus-depth plot of manganese and iron are thus also of value for correlation with the redox boundary which is determined by more precise methods. The interpretation of these parameters is difficult unless the point of precipitation lies well below the zone of bioturbation.

The inductively coupled plasma (ICP) spectrometer method and atomic adsorption spectrophotometry (AAS) methods are commonly used to determine manganese and iron in marine sediment. These should be conducted on sediment samples at 5 cm intervals to assist in determining redox trends with depth for the 30 cm of core length.

An electrometric method that reflects on the redox state of marine sediment is the Eh meter, using a combination of platinum and reference electrodes. Measurements are read in millivolts. The measurements, however, are rather qualitative because of the complex electrochemistry involved if more than one mineral system or valence state is present. According to Meyer (1982), the use of the Eh probe will not indicate whether oxidation or reduction will occur but will give an approximate indication of oxidizing or reducing conditions. Lindberg and Runnells (1984) also question the analysis of redox state by simple electrochemical means.

Any valid Eh measurement of sediment redox conditions must be performed as soon as the core sample is collected aboard ship. A plastic liner with holes drilled at 5 cm intervals is inserted into the box corer to prepare the sample for prompt Eh measurements. As an example, samples obtained in this manner at the Atlantic 2,800m LLW disposal site in the fall of 1984 indicated oxygenated conditions for the top 16.5 cm of sediment core. At 16.5 cm depth, a measurement of 229 mV was obtained, indicating that the redox boundary was probably being approached and could be expected perhaps within several more centimeters. Schmidt (1979) used both the Eh meter and pore water chemistry analysis for oxygen depletion in an investigation of sediment from a 2,500m depth in the NW Atlantic and found that the point of oxygen depletion coincided with an Eh reading of 225 mV.

The redox state of the sediment is best determined by analysis of the oxygen depletion in the pore water of the sediment with depth. The most quantitative measurement for the determination of oxygen depletion is the nitrate test of the sediment pore water. Sayles and Livingston (1984) discuss this method for marine sediment cores. The extraction of pore water from the sediment for nitrate analysis is relatively complex; however, this method of approach is the most reliable technique available for determination of redox conditions with depth in the sediment.

1.4.4 RECOMMENDATIONS

The redox state of the sediment at a prospective LLW site should be measured because of its requirement in (a) Kd measurement of sediment involving redox sensitive radionuclides and (b) providing data that has direct application to prediction of radionuclide retention. The measurement of redox as a sediment monitoring criteria parameter should include:

- (1) Measurement of oxygen depletion in pore water by nitrate analysis as a primary technique for determination of redox state of the sediment.
- (2) Measurement of (a) Eh (by Eh meter), (b) sulfide sulfur, and (c) manganese and iron in the sediment at 5 cm intervals to 30 cm depth for sediment characterization and interpretative values relative to sorption of redox sensitive radionuclides and correlation with the redox conditions measured in (1) above.

1.4.5 DETERMINATION OF pH

Measurement of pH is important to characterizing sediment in a LLW disposal site. According to Zobell (1946), the pH range of recent marine sediments is 6.4 to 9.5 and that of Eh is from +0.350 to -0.500 mV. In the deepsea environment, pH will be more constant whereas the Eh will vary widely in relation to changes in redox conditions. Typical pH values of sediment samples taken in the vicinity of LLW disposal sites in the Atlantic and Pacific Oceans are 7.2-7.8 (NW Atlantic), 7.9-8.1 (NE Atlantic), and 7.9 at the Farallon Islands (Pacific).

The most common method for pH measurement is the electrometric determination of the activity of the hydrogen ion by potentiometric measurement using a glass electrode and a reference electrode. Determinations of pH should be made aboard ship soon after receiving the sediment aboard and as soon as possible at the laboratory where it is sent for the other tests.

1.4.6 RECOMMENDATIONS

It is recommended that pH be included as a sediment monitoring requirement for any proposed low-level radioactive waste site. This inexpensive parameter has application in radionuclide retention prediction for most radionuclides of interest.

1.5 GEOTECHNICAL PARAMETERS

Analysis of sediment geotechnical properties provides insight into the penetration potential of waste packages into the bottom sediments and probable subsequent settlement of waste packages. The analysis may provide information on the past geological stability of a site and show if active erosion or rapid sediment loading is occurring. The engineering information will aid in evaluating the sites for waste package insertion and burial should subseabed disposal be considered a viable option in the future for LLW.

The parameters to be measured will focus on establishing the general engineering characteristics of the sediment and permit some prediction of behavior under various loading conditions (e.g., waste package emplacement or impact). These parameters may include those measured or determined from index properties (liquid limit, plastic limit, and water content), strength, and consolidation tests. The U.S. Geological Survey is currently investigating the geotechnical test parameters which are appropriate for deepsea disposal sites.

1.5.1 RECOMMENDATIONS

It is recommended that basic index properties (liquid limit, plastic limit and water content) be included in sediment monitoring criteria. This test can be used to (a) compare bottom penetration of the waste drum and (b) correlate with geologic stability of the site. This and other geotechnical tests are relatively simple and inexpensive, and provide fundamental engineering information.

Under consideration is the emplacement of LLW beneath the sediment surface. For this proposed option, additional geotechnical parameters attendant to deep-sea penetration and burial (e.g., consolidation, triaxial, and vane shear tests) are being evaluated.

1.6 X-RADIOGRAPHS

X-radiographs of sediment cores allow the nondestructive observation of certain textural and structural features of the sediment. The x-radiographs reveal biological activity (bioturbation) in the sediment.

X-radiographs are made of each core to 30 cm depth to determine the extent of bioturbation in the sediment. The bioturbation process could accelerate the transport of radionuclides from within the sediment to the sediment-water interface as well as acting as a means of transporting radionuclides sorbed at the surface to depth. The depth of bioturbation is correlative with redox conditions in that it relates to activity in the oxygenated layer of sediment. However, the depth to the base of bioturbation activity is not to be considered the point of oxygen depletion since other factors are involved.

1.6.1 RECOMMENDATIONS

It is recommended that x-radiographs be required in the evaluation of LLW disposal sites. Since bioturbation is considered an undesirable entity, the degree of bioturbation could be indexed in some manner, based on density of biological structures. The index number could be instrumental in picking the most acceptable site.

1.7 CORRELATION WITH GEOLOGICAL STABILITY

Some of the sediment monitoring parameters may be used to correlate with geologic stability of a site as well as provide predictive capabilities for radionuclide retention. These include (a) detailed mineral composition, (b) x-radiographs, (c) index properties, and (d) texture.

The detailed mineralogy of the sediment used to predict sorption capabilities of the sediment also reflects on the geologic stability of the site. As an example, Van der Loeff et al (1984), interprets the uninterrupted and constant composition of the clay fraction in the NE Atlantic LLW dumpsite as indicative of stable geologic conditions in the top layer of sediment. They also correlate turbidite (rapid deposition layers) and nonuniform conditions with changes in mineralogy laterally at deeper depth in cores.

The x-radiographs of sediment cores, in addition to indexing biological activity, reveal sediment structures and layers in the sediment. Any disruption of sediment pattern not related to biological activity would relate to geologic stability of the site. Uninterrupted sediment layers would correlate with geologic stability of the site.

The index properties also relate to the geologic stability of an area. As an example, Keller et al (1979), reporting on the geotechnical properties of the upper continental slope off the Atlantic coast, effectively correlates the physical properties with depositional stability of the region. In addition, any major variations of sediment texture reflect on the geologic stability of the site.

1.7.1 RECOMMENDATIONS

It is recommended that sediment monitoring criteria parameters that serve as predictors of radionuclide retention also serve as a monitor of geological stability at the site.

1.8. SAMPLING DENSITY

The size of a deep-ocean LLW disposal site will not exceed 100 square miles (360 km²). The density of sampling locations within a proposed LLW site will be in accordance with the specifications provided in the existing Regulations (par. 228.13(e)(1)(ii)). The maximum number of replicate samples at each station of a proposed site will coincide with the number indicated in paragraph 228.13(e)(1)(i). The actual number of samples to be tested to a minimum 30 cm depth will depend on the homogeneity of the sediment parameters at the site.

1.9 SUMMARY OF RECOMMENDATIONS

The existing Ocean Disposal Regulations contain provisions for measurement of sediment parameters in paragraph 228.13(e)(3), which support the sediment monitoring needs for LLW at deep ocean sites. These parameters include organic carbon, texture, particle size distribution, major mineral constituents, and settling rate. Because LLW will be containerized, as specified in paragraph 227.11(a)(1) of the Regulations, settling rate will not apply. The special requirement for predicting sorption potential of the sediment will require modification of existing parameters listed in paragraph 228.13(e)(3) to include (a) detailed mineral analyses (b) texture grain-size, (c) measurement of sorption distribution coefficient (Kd) of Cs, Co, and Sr and (d) site characterization parameters that include the following: redox measurements (nitrate analysis of pore water for oxygen depletion), pH, Eh, manganese, iron, and sulfide sulfur.

The cost of parameters specified for measurement would approximate the following:

<u>Measurement</u>	<u>Average Cost Per Analysis</u>
pH and Eh (shipboard) -----	\$ 15.00
Pore Water (nitrate analysis for oxygen depletion) -----	\$ 200.00
Kd of selected radionuclides -----	\$ 1,000.00
Detailed Mineral Analysis -----	\$ 400.00
Sulfide Sulfur, Mn, and Fe -----	\$ 75.00
Sieve & Pipet Analysis -----	\$ 120.00
Hydrometer Analysis -----	\$ 45.00
Coulter Counter Analysis -----	\$ 25.00
Organic Carbon -----	\$ 25.00
Index Properties -----	\$ 75.00
X-radiograph -----	\$ 300.00

These are the basic costs of a normal operating laboratory and do not include ship costs, collection apparatus, storage, or personnel costs.

Additional parameters that relate to physical response of the sediment to impact of the waste container are still being evaluated.

1.10 FUTURE CONSIDERATIONS: IMPLEMENTATION OF SECTION 424,
PL 97-424

The purpose of the proposed criteria is to determine acceptability of a specific site that meets the general site selection criteria by evaluating and quantifying its geochemical and geotechnical immobilization characteristics. The evaluation of specific wastes proposed for disposal at a specific site will require the preparation of a Radioactive Material Disposal Impact Assessment (RMDIA). When such an assessment is prepared, a critical determination will be whether the radionuclides will be immobilized at the site. If a satisfactory determination is made that immobilization of the specific wastes will occur, then an important consideration arises. If radioactive isotopes are released by a waste package and retained by the sediment at a site, rather than dispersed, the radionuclide concentrations in the sediment will increase. It will become important to establish sediment quality criteria or concentration limits linked to effects on indigenous marine organisms. The primary effects on marine organisms would occur through ingestion of materials. The availability of radionuclides to infauna and sessile epifauna is directly linked to the sediment dynamics (sediment-water interaction).

Although the proposed criteria are directed at the sediment dynamics, particularly physicochemical immobilization processes, the establishment of sediment criteria will also be necessary to determine the acceptable amount of radioactive material that can be disposed of at a site.

While it is beyond the scope of the proposed criteria to consider specific permit evaluation requirements, early consideration of some of the questions attendant to setting sediment quality criteria would be useful.

The need for sediment monitoring are different for ocean disposal of hazardous waste than for LLW. These differences are apparent if a comparison is made of the spectrum of approaches available for setting sediment quality criteria for hazardous waste versus LLW.

At a national perspective workshop on the scientific approaches for establishing sediment quality criteria, convened by EPA in November 1984, a review was made of the pros and cons of the various methodologies available. The status report on this effort, released by EPA in March 1985, identified four general approaches for development of sediment quality criteria. These were the (a) background concentration approach, (b) equilibrium partitioning approach, (c) water quality criteria approach, and (d) bioassay approach. Within each of these approaches, hazardous compounds included polar organics, nonpolar organics and heavy metals. Of these approaches, all but the background concentration approach and bioassay approach require the use of water quality criteria. Virtually no water quality criteria exist for radionuclides except for the Interim Drinking Water Standards. Therefore, the background approach seems most feasible since, unlike the other approaches, it does not rely on water quality criteria to set sediment quality criteria. The background approach relies on the establishment of a reference concentration against which increasing concentrations at a site can be compared in order to determine the extent and magnitude of effects from disposal operations. The reference concentration reflects the ambient concentrations existing at a site (e.g., from nuclear fallout prior to its use for any disposal operation). While it may be assumed that the reference concentration for radionuclides represents a "No-effects Level," setting sediment quality criteria requires (1) cytogenetic and other measurement and evaluation techniques (see Prepermit Testing Protocols to establish the "No-effects Level") and (2) assessment of the factors controlling radionuclide retention and bioavailability at deep ocean disposal sites. As a starting point, the radionuclides in the waste could be divided into groups that respond to similar predictive factors. One group might be iodine, carbon, and tritium, which have virtually no retention in any known sediment. Another waste group might contain cationic species affected by type and amount of sorptive minerals. Still another group that is sensitive to oxidation conditions would require assessment in both oxidizing and reducing environments. Radionuclide groups responsive to chelating agents, ligands, or other chemical factors (coprecipitation, etc) would require further consideration. Although seemingly complex, this approach is feasible because the deep ocean environments have more stable conditions (constant pH, salinity, etc) than other more variable environments such as fresh water or shallower marine water disposal sites.

With the above information, sediment quality criteria could be established for radionuclides, and applicable requirements of an EMDA could be evaluated.

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