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Long term behaviour of low and intermediate level waste packages under repository conditions

Results of a co-ordinated research project
1997–2002

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International Atomic Energy Agency

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FOREWORD

The development and application of approaches and technologies that provide long term safety is an essential issue in the disposal of radioactive waste. For low and intermediate level radioactive waste, engineered barriers play an important role in the overall safety and performance of near surface repositories. Thus, developing a strong technical basis for understanding the behaviour and performance of engineered barriers is an important consideration in the development and establishment of near surface repositories for radioactive waste.

In 1993, a Co-ordinated Research Project (CRP) on Performance of Engineered Barrier Materials in Near Surface Disposal Facilities for Radioactive Waste was initiated by the IAEA with the twin goals of addressing some of the gaps in the database on radionuclide isolation and long term performance of a wide variety of materials and components that constitute the engineered barriers system (IAEA-TECDOC-1255 (2001)). However, during the course of the CRP, it was realized that that the scope of the CRP did not include studies of the behaviour of waste packages over time. Given that a waste package represents an important component of the overall near surface disposal system and the fact that many Member States have active R&D programmes related to waste package testing and evaluation, a new CRP was launched, in 1997, on Long Term Behaviour of Low and Intermediate Level Waste Packages Under Repository Conditions. The CRP was intended to promote research activities on the subject area in Member States, share information on the topic among the participating countries, and contribute to advancing technologies for near surface disposal of radioactive waste. Thus, this CRP complements the afore mentioned CRP on studies of engineered barriers.

With the active participation and valuable contributions from twenty scientists and engineers from Argentina, Canada, Czech Republic, Egypt, Finland, India, Republic of Korea, Norway, Romania, Russian Federation, Spain, Thailand, United Kingdom, and the United States of America, this report provides an overview of scientific and technical issues related to the behaviour and performance of a wide range of low and intermediate level waste packages in the context of overall repository performance and safety. Specific approaches for the testing and assessment of waste package components, including modelling considerations in predicting waste package performance, are presented and discussed. In addition, the major findings of the research projects, carried out within the framework of the CRP, are presented, summarizing the variety of approaches and technologies used in waste package development, testing and evaluation.

The IAEA wishes to express its thanks to all of the participants in the CRP for their valuable contributions and to T. Sullivan for his assistance in finalizing the report. The IAEA staff members responsible for the completion of the CRP and publication of this report are R. Dayal and K.W. Han.

EDITORIAL NOTE

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Contributions by participants in the co-ordinated research project on long term behaviour of low and intermediate level waste packages under repository conditions

1. INTRODUCTION

1.1. BACKGROUND

Low and intermediate level radioactive waste (LILW) is being generated in increasing quantities in many countries as the demand for nuclear applications in medicine, research and industry, including nuclear power, is continually increasing. The potential hazards of radioactive waste to human health and the environment have been long recognized. Hence, national and international standards and guidelines dealing with radiation protection and radioactive waste management, including disposal, have been developed [1–11]. These are based on a substantial body of scientific and technical knowledge accumulated worldwide as a result of many years of experience in radioactive waste management and associated research and development [12–31]. The available disposal options for LILW involve a variety of repository components subjected to a range of environmental conditions. In order to assess and predict repository behaviour and performance over repository time-scales, the underlying scientific and technical issues, as well as a good knowledge and understanding of the behaviour of different materials, need to be clearly understood and appreciated. Thus, it is imperative that relevant information on the scientific and technical basis for establishing disposal facilities is available prior to undertaking such a project [32].

An important requirement for radioactive waste disposal involves the development of a safety case that provides reasonable assurance that the waste can be disposed of safely under the range of anticipated repository conditions. This requires a good understanding of the underlying processes affecting the behaviour and performance of a disposal system. This understanding, as well as other relevant information and data, is incorporated into models that predict the performance of a disposal system and its components over time [33–35]. As part of developing the safety case, the safety assessment relies on data pertaining to waste package performance. Although there are substantial amounts of data on waste package performance under laboratory conditions and over relatively short time frames, far less data are available under field conditions and over longer time frames.

Within the framework of the International Atomic Energy Agency's (IAEA) regular programme, Co-ordinated Research Projects (CRPs) provide an effective mechanism for Member States to participate in R&D projects of current interest. An important component of IAEA's programme on radioactive waste management is to facilitate the transfer and exchange of information and technologies among Member States. Several CRPs have been implemented that deal with different aspects of radioactive waste management.

Two recently completed CRPs have dealt with issues relating to the performance of engineered barriers in near surface disposal facilities [36] and extrapolation of laboratory data to time periods relevant to the isolation of long lived radionuclides [37]. This report deals specifically with a CRP on "Long Term Behaviour of Low and Intermediate Level Waste Packages under Disposal Conditions".

The CRP was launched by the IAEA in 1997 and completed in 2001. Fourteen Member States, comprising Argentina, Canada, Czech Republic, Egypt, Finland, India, Republic of Korea, Norway, Romania, Russian Federation, Spain, Thailand and the USA participated in the CRP. United Kingdom participated as an observer. Egypt and Thailand withdrew from the

CRP prematurely due to other commitments. The topics of the various research projects of the participating Member States are given in Table I.

TABLE I. TOPICS OF CRP RESEARCH PROJECTS OF PARTICIPATING COUNTRIES.

Country and institute	Chief scientific investigator	Title
ARGENTINA/ Comisión Nacional de Energia Atómica (CNEA)	T. R. Ramallo de Goldschmidt	Long term behaviour of waste package in repository conditions
CANADA/ Ontario Hydro Technologies	R. Dayal	(a) Waste package performance and gas generation under disposal conditions
Atomic Energy of Canada Ltd (AECL)	J. Rowat	(b) Solidification of low level radioactive waste at AECL's Chalk River Laboratories
CZECH REPUBLIC/ Nuclear Research Institute (REŽ)	A. Vokál	Long term behaviour of polyethylene high integrity containers under repository conditions
EGYPT/ Atomic Energy Authority – Hot Laboratory Center (AEA-HLA, LWMD)	M. Rashad El-Sourougy	Long term behaviour of low and intermediate level waste packages under repository conditions
FINLAND/ VTT Chemical Technology	H. Aalto	Behaviour of bituminized ion-exchangers under repository conditions
INDIA/ Bhabha Atomic Research Centre (BARC)	N.K. Bansal	Performance assessment of radioactive waste packages for disposal in near surface facilities
Republic of KOREA/ Nuclear Environment Technology Institute (KHNP)	C. Lak Kim J.W. Park	A study on the compliance of waste packages generated at nuclear power plants in Republic of Korea
NORWAY/ Institute for Energy Technology	P. Varskog	Release of radionuclides from nuclear waste barrels in a 27 year old LLW/ILW near surface repository
ROMANIA/ IFIN-HH	F. Dragolici	Durability of cemented waste under simulated conditions
RUSSIAN FEDERATION/ Scientific and Industrial Association "Radon" (SIA RADON)	I. Sobolev M.I. Ozhovan	Long term tests of low and intermediate level waste packages under experimental and field repository conditions
SPAIN/ Empresa Nacional de Residuos Radioactivos S.A. (ENRESA)	M. Navarro	Behaviour of concrete container (CE-2a type) in disposal condition
THAILAND/ Office of Atomic Energy for Peace	P. Yamkate	Behaviour of low and intermediate level waste in the environment of shallow land disposal
UNITED KINGDOM/ BNFL	H. Godfrey G. Jonsson	Status of intermediate level waste encapsulation at Sellafield/BNFL
UNITED STATES OF AMERICA/ Brookhaven National Laboratory	T. Sullivan	Modelling long term behaviour of low and intermediate level waste packages under repository conditions

In all, three Research Coordination Meetings (RCMs) were convened during the course of the CRP: the first one in Moscow, Russian Federation in 1997; the second one in Cordoba, Spain in 1999; and the third and final RCM in Prague, Czech Republic, in 2001. Given that the disposal programmes of the various participating countries are in varying stages of maturity and development, the Moscow RCM, in particular, provided a good opportunity for the participants not only to learn about each other's R&D activities, but also to develop a comprehensive understanding of waste package behaviour and performance and an appreciation of the key issues that are important in the performance of LILW packages. By early 1999, significant progress had been made in the various research projects of the participating countries. The Cordoba RCM afforded an opportunity to review the progress made in the research projects in the context of the objectives of the CRP and prepare a preliminary draft of the report. At the Prague RCM in June 2001, the results of the research projects were summarized. Common links in the various investigations, serving as a basis for consolidating and integrating the results of the CRP, were identified. In addition, the draft report on the topic was reviewed and revised.

1.2. OBJECTIVES

The overall objectives of the CRP were to promote R&D activities relevant to waste package performance, exchange and discuss information available on the topic in the various participating countries, and to review the research completed during the course of the CRP.

1.3. SCOPE

The report addresses the behaviour and performance testing of LILW package components in a near surface repository environment as presented and discussed in the research projects of the CRP. The focus of the report is on test methods and approaches applied to the assessment of waste package behaviour and performance. A secondary focus is on defining the link between data collection and safety assessment. The report summarizes the various test methods and approaches, experimental designs and conditions, and the modelling aspects considered in the country projects. Some aspects of waste package testing and performance discussed in the report include:

- Characteristics of waste package components
- Considerations in waste package testing
- Durability of waste forms and containers
- Containment properties of waste packages
- Potential for gas release from waste packages
- Modelling considerations in predicting waste package performance.

The major findings of each country project are also presented.

1.4. STRUCTURE

The report is divided into two main parts: (a) background information on near surface disposal concepts, waste package performance requirements, and approaches and methods to evaluate waste package performance, and (b) an Annex containing the individual country projects.

Section 2 provides an overview of the types of LILW that are considered suitable for disposal in near surface facilities. Section 3 presents some important concepts in near surface disposal that impact on data requirements for waste package performance and assessment. Section 4 presents a review and description of LILW packages and their functional requirements in a near surface disposal facility. Section 5 discusses waste package behaviour, taking into consideration the various factors, conditions and processes, which may affect performance. Section 6 presents various approaches to waste package testing and evaluation, along with a discussion on the application of the data to safety assessment.

The individual contributions of the CRP participants are presented in the Annex. Specifically, detailed information is presented on long term testing under disposal conditions (India, Norway, Russian Federation, Spain), waste container testing and behaviour (Czech Republic, India, Republic of Korea, Russian Federation, Spain), waste form development and testing and behaviour (Argentina, Canada, Republic of Korea, Finland, India, Romania, Russian Federation, United Kingdom, USA) and modelling waste package performance, including gas generation issues (Canada, Republic of Korea, Russian Federation, USA).

2. TYPES OF RADIOACTIVE WASTE

This Section summarizes the types of LILW that are suitable for disposal in near surface facilities. The wastes that need to be managed in a particular country depends on the national regulations and the extent of the use of nuclear energy and radioactive isotopes. Low and intermediate level waste results from a variety of sources, including the medical industry, hospitals, university research, government, industrial applications, nuclear power plants, and decommissioning of nuclear facilities. The variety of waste generators results in a wide range of physical, chemical and radiological properties of the wastes.

The IAEA Radioactive Waste Safety Standards (RADWASS) classification system [31] was developed to provide a generic approach to radioactive waste management, which identifies potential disposal options for various waste categories based on their specific characteristics, with the total activities and half-lives of the waste being the key distinguishing features and determining factors. Thus, geological disposal is required for the most active high level waste (HLW), spent fuel and long-lived LILW, which may take tens of thousands to hundreds of thousands of years to decay to acceptably low levels. Near surface disposal is an option suitable for short-lived LILW, containing mainly radionuclides, which decay to radiologically insignificant levels within a few decades or centuries [4, 31–35]. Limited concentrations of long-lived radionuclides may be present in LILW suitable for near surface disposal [33–35]. For example, institutional and decommissioning waste and much of the large volume of operational trash from nuclear power plants (paper, gloves, clothes, etc.) are contaminated with low levels of long lived radionuclides. Safety assessments can be used to derive both generic and site specific waste acceptance criteria [35] that limit concentrations or the total radionuclide-specific inventories being disposed. In particular, limits are often set for long-lived radionuclides.

Medical and research applications of radioisotopes are common worldwide. These generate solid radioactive wastes, including animal carcasses used for research purposes. The following radioisotopes may be present in these wastes: ^{3}H, ^{14}C, ^{18}F, ^{22}Na, ^{24}Na, ^{32}P, ^{33}P, ^{35}S, ^{36}Cl, ^{41}Ca, ^{45}Ca, ^{47}Ca, ^{46}Sc, ^{51}Cr, ^{57}Co, ^{58}Co, ^{59}Fe, ^{85}Sr, ^{89}Sr, and ^{99m}Tc. Liquid wastes, including organic solvents and liquid scintillators, are also produced, but these wastes have to be conditioned before they are suitable for near surface disposal [8].

Disused sealed radioactive sources can be considered as a special type of waste derived from medical, research or industrial users. A number of different radionuclides are used in disused radioactive sources, including ^{60}Co, ^{90}Sr, ^{137}Cs, ^{226}Ra, ^{241}Am and ^{252}Cf [26].

Large volumes of LILW, containing a wide range of radionuclides, are produced in the nuclear industry from research, uranium enrichment and fuel fabrication, reactor operations and fuel reprocessing. In countries with reactor operations, waste volumes arising from these sources are generally greater than from institutional producers. Decommissioning of nuclear facilities is another potential source of large volumes of LILW. Generally, about 95% of the total volume of radioactive waste produced in reactor decommissioning can be categorized as LILW. Countries with high rates of radioactive waste production need a well developed radioactive waste management infrastructure with treatment and conditioning facilities.

In countries with nuclear power production, LILW containing a variety of radionuclides are generated routinely. The vast majority of these radionuclides do not significantly contribute to potential human health impacts. Almost all of the disposed activity is found in relatively short lived (e.g., half-life less than approximately 30 years) radionuclides, including ^{137}Cs, ^{60}Co, ^{90}Sr, ^{3}H, and ^{55}Fe. For engineered disposal facilities, the short half-life of these radionuclides, the travel time to the accessible environment, and the waste container and waste form performance generally precludes them from being a serious concern in terms of projected dose through the groundwater pathway, although the gaseous pathway could be important for ^{3}H. However, their large inventories may potentially cause large doses to inadvertent intruders. The major contributors to projected dose in the ground water pathway tend to be the long lived, soluble and mobile radionuclides. These include ^{129}I, ^{99}Tc, ^{14}C, ^{36}Cl, and, under certain chemical conditions, uranium isotopes and their progeny species.

3. NEAR SURFACE DISPOSAL CONCEPTS

This Section provides an overview of the different types of disposal concepts that are currently in use for near surface repositories in many Member States. In addition, disposal concepts that impact on waste package performance requirements are discussed. These include the concepts of institutional control, protection of inadvertent intruders, and monitoring and surveillance.

3.1. DISPOSAL CONCEPTS

A range of technical solutions is possible for the emplacement of radioactive waste in the near surface environment. The selection of a disposal option depends on many factors, such as the source; characteristics and volume of the waste; climatic conditions, site characteristics, national legislative and regulatory requirements; radioactive waste management policies, etc. Near surface disposal options include two main types (basic concepts) of disposal systems: a) shallow facilities consisting of disposal units located either above (mounds, etc.) or below (trenches, vaults, pits, etc.) the original ground surface; and b) facilities where the waste is emplaced at greater depths in rock cavities or boreholes. In the first case, the thickness of the cover over the waste is typically a few metres, while in the second case, the layer of rock above the waste can be some tens of metres thick. These depths can be contrasted with geological disposal for long lived wastes, where the wastes are emplaced at depths of hundreds of metres. Borehole repositories are being considered and assessed for the disposal of disused radioactive sources [38].

The selection of a disposal concept has an important influence on waste package testing requirements. For example, selection of above-grade disposal (e.g. mound) may require different tests for waste package integrity under extreme temperature variations as compared to a below-grade facility.

3.1.1. Near surface disposal

In the past 50 years, concepts for radioactive waste disposal have developed and evolved. Most experience has been gained for near surface disposal facilities. During this period, there have been many examples of successful repository development, but also of failures in repository performance. Examples of such failures include the rapid leaching of radionuclides from some wastes and radionuclide releases due to the flooding of disposal trenches by rainwater or a rising water table (bathtubbing). The reasons for some of these past failures include inadequate characterization of the site, unsatisfactory performance of engineered barriers and inadequate control of the nature and inventory of long-lived radionuclides and other toxic waste emplaced in the repository. The lessons learned from these experiences have led to the adoption of improved concepts and technologies, such as IRUS in Canada, Centre de l'Aube in France, Rokkasho-mura in Japan, El Cabril in Spain, Drigg in the UK, and Barnwell and Richland in the USA. Many smaller repositories, constructed in various countries, are also in operation.

In near surface facilities, the basic disposal units, typically trenches or vaults, are often located in the vadose zone, the region that is above the groundwater table. However, in some countries, the local conditions require the disposal units to be constructed in the saturated zone, the region below the water table. In both cases, the disposal units need to be designed and constructed to limit the contact of water with the waste. To this end, near surface repository designs may include engineered components such as impervious covers, drainage systems, leachate collection systems and cut-off walls. A network of ditches may be used to facilitate the drainage of rainwater and minimize accumulation of water near the disposal units. Underground drains may be used to keep the disposal units dry, if the wastes are placed above the groundwater table. A leachate collection system may be used to collect any water that has infiltrated into the disposal units. Cut-off walls may be constructed to limit the horizontal groundwater flows or to provide structural integrity to a disposal facility.

Rock cavity repositories can be either natural or excavated by man in various geological formations. A rock cavity repository, SFR, was constructed at Forsmark in Sweden in crystalline rock, about 60 metres below the sea. It consists of different types of mined chambers adapted to the disposal of LILW. Two rock cavity repositories, similar to Forsmark with respect to both design and type of host rock, are in operation in Finland at Olkiluoto and Loviisa. These repositories are at a depth of approximately 50 m and are located below the groundwater table. An example of a rock cavity repository in the vadose zone is the Richard II disposal facility, located in an abandoned limestone mine near Litomerice in the Czech Republic. This repository, in operation since 1964, has the disposal rooms in the vadose zone about 50 m above the water table.

3.2. THE MULTIPLE BARRIER CONCEPT

In developing near surface disposal system concepts, reliance is placed on a multibarrier systems approach in which the site characteristics, the waste form and packaging and design all contribute to the isolation of the waste from the environment for time periods sufficiently long for radionuclides to decay to acceptable low levels. This is a general defence-in-depth approach used in other parts of the nuclear fuel cycle. The systems approach has been developed and adopted for both near surface and geological disposal. For near surface repositories, attention has focused on the development of robust designs of engineered barrier systems in which a combination of physical barrier and chemical controls provides a high level of radionuclide containment. The use of multiple barriers provides reasonable assurance of adequate performance of a repository.

3.3. INSTITUTIONAL CONTROL

For near surface repositories where the disposal units are close to the surface (within a few metres), institutional controls are needed to provide assurance of the adequate performance of the waste isolation barriers during the initial period when the activity of short lived radionuclides is still high. The anticipated duration of institutional control is an important strategic decision with significant implications for various aspects of the development of the disposal system, including the definition of waste acceptance criteria. If disposal takes place at greater depths, of tens of metres, such as in rock cavity repositories or moderately deep boreholes, which are also considered types of near surface disposal systems, less reliance is placed on institutional controls.

The duration of post-closure institutional controls can be reasonably expected to last up to a few hundred years. A period of 300 years, for example, would correspond to around ten half-lives of radionuclides such as ^{137}Cs and ^{90}Sr, which are often important radionuclides in short lived LILW. This has an important bearing on the testing and assessment of waste package performance in the context of repository design life.

3.4. MONITORING AND SURVEILLANCE

The near surface disposal concept usually envisages continued monitoring and surveillance of the site as a part of active controls after repository closure for a period of several decades to a few hundred years [21]. During this period, monitoring and surveillance represent an additional safety measure and contribute to confidence in the satisfactory performance of the facility. The acquisition of data from monitoring also contributes to general scientific and technical knowledge that can be used in the development and improvement of mathematical models for radionuclide transport and for assessing waste package performance and repository impacts.

3.5. HUMAN INTRUSION

Most human activities that could lead to wastes being disturbed (for example, home construction, farming and road building) do not penetrate more than a few metres below the surface. Exceptions are activities such as mining and drilling of wells. The greater depth (tens of metres) of rock cavity and borehole facilities means that these concepts are more intrusion-resistant than shallow facilities, and are, therefore, less dependent on institutional controls to ensure safety. For shallow land or above-grade disposal, concentrations of long lived radionuclides may be limited to protect inadvertent intruders.

4. DESCRIPTION AND FUNCTION OF WASTE PACKAGES

4.1. INTRODUCTION

A LILW package represents an engineered component of the repository, consisting essentially of a waste form and container. A liner and/or overpack, if used, are also considered to be an integral part of the waste package. Low and intermediate level waste packages can exhibit a large degree of variability in their design and composition because of the highly diverse nature of the different types of wastes and containers, as well as repository-specific conditions and waste acceptance criteria. Waste packages can range from a simple system, consisting of compacted waste in a carbon-steel container, to conditioned waste solidified in cement, placed in a high-density polyethylene (HDPE) container with a concrete overpack.

Solidification or immobilization and packaging of wastes are normally carried out to enhance the safety of the disposal system. In most cases, packaging is required to provide safety during transportation of the waste to the disposal site and during its emplacement in the disposal facility. With regard to the functional requirements during the post-closure phase, the waste package provides both physical and chemical containment of waste contaminants. In fact, the waste package serves as the first barrier in the series of barriers that contribute to radionuclide isolation from the biosphere. In the context of repository performance, waste packages generally serve the following functions:

- Limit the rate of radionuclide and contaminant release
- Provide mechanical support for other repository components

It is important to note that the waste package functional requirements can vary from one Member State to another or from one programme to another in a given Member State.

Depending on the nature of the waste, different types of conditioning materials can be used to stabilize waste, with cement being the most commonly used material. Bitumen, paraffin, and polymers are some of the other materials that have been used to condition the various types of wastes. Some wastes are not stabilized, so the waste form consists of originally contaminated material (paper, rubber, wood, metal, carcasses, etc.) in a compacted or super-compacted form. For waste containers, concrete and carbon steel are commonly used materials. Stainless steel and HDPE are other candidate materials that may be used for container fabrication. Examples of waste forms (and conditioning agents) and container materials currently in use in the participating Member States are provided in Table II.

4.2. WASTE PACKAGE PERFORMANCE

Waste package performance refers to the combined performance of the waste form, container, and liner or overpack, if present. From a safety assessment point of view, the essential features of waste package performance are structural integrity and radionuclide containment. Waste package performance determines the source term of the repository, i.e. the radionuclide flux leaving the disposal units. Releases of radionuclides from a disposal unit are a result of a number of physical and chemical processes occurring primarily in the presence of water. Generally, infiltrating water initiates container degradation and leaching of the waste form, giving rise to releases of radionuclides from the disposal facility. Microbially-mediated or corrosion-induced gases, such as $^{14}CH_4$, $^{14}CO_2$, $^3H_2$, H_2, etc., may also be generated as a result of waste form and container degradation in the presence of water. Generation and build-up of gases can affect both waste package and repository performance. However, the gaseous pathway is generally much less important than the aqueous pathway in terms of projected dose.

TABLE II. WASTE PACKAGE COMPONENTS BEING CONSIDERED IN THE PARTICIPATING MEMBER STATES OF THE CRP

Country	Waste Conditioning Materials	Container	Waste Type
Argentina	Cement	Steel	Operational waste from nuclear power plant (NPP); institutional waste
Canada	Cement Bitumen	Carbon steel Stainless steel	Operational waste from NPP; decommissioning waste from NPP; institutional waste; isotope production facilities
Czech Republic	Bitumen Cement	HDPE Carbon steel	Spent ion-exchange resin/sludge from NPP
Finland	Bitumen		Ion-exchange resin from NPP
India	Cement Polymers Bitumen	Carbon steel Concrete Stainless steel	Waste from NPP and fuel cycle facilities
Republic of Korea	Cement Paraffin	Carbon steel Stainless steel Concrete	Waste from NPP
Norway	Cement	Carbon steel with concrete lining	Institutional waste and fuel cycle facility waste
Romania	Cement	Carbon steel	Institutional waste
Russian Federation	Cement Bitumen Glass Metals	Carbon steel Stainless steel	Operational and institutional waste
Spain	Cement	Concrete	Operational and institutional waste
United Kingdom	Cement	Steel	Waste from NPP and fuel cycle facilities
United States of America	Cement Bitumen Polymers Glass	Carbon steel Stainless steel HDPE	Operational and institutional waste

Both the behaviour and performance of a waste package will depend on the nature of the waste package and repository site-specific conditions. LILW packages can be expected to exhibit a large degree of variability in their behaviour and performance due to the diversity in the types of wastes, waste forms, containers (Table II), site-specific conditions and the complex chemical, physical, and microbiological processes and interactions that are likely to take place in the disposal units.

Cement-based materials placed around waste containers for structural stability may be found in the form of backfill between waste containers or walls, ceiling, and floors that form a vault around the wastes packages [39]. The cement based materials may also be engineered to condition the near field chemical environment, thereby providing appropriate geochemical constraints that limit the dissolved concentrations, and hence release, of several safety-relevant radionuclides (^{14}C, the actinides, etc.) to low levels. Given the availability of relevant geochemical codes and associated thermodynamic databases, a geochemically conditioned system can be modelled to establish the source term which, in turn, is needed to assess repository performance. Another potentially important process likely to control radionuclide concentrations in the near field is sorption from the solution on to components of the disposal system, such as cementitious materials or other engineered backfill material. Sorption may be particularly important for ensuring disposal safety for radionuclides that have a high solubility and long half-life.

The waste form in itself often provides some degree of radionuclide containment. The physico-chemical properties of the waste form, including the nature of the contaminant, and environmental conditions, will determine the rate of radionuclide release. Once the container degrades, giving rise to access of water to the waste, releases of radionuclides are determined primarily by the waste form. Depending on the type of waste form, radionuclide release mechanisms can vary significantly. For example, cementitious waste forms exhibit diffusion-controlled release for many radionuclides although, for some radionuclides, the release mechanism is solubility-limited. In the case of activated metals in reactor decommissioning waste, the release is likely to be controlled primarily by the corrosion rate of the metal matrix, assuming the activation products are distributed uniformly in the metal matrix. In contrast, simple surface contamination on metal or other surfaces (e.g. lab trash, etc.) will be released instantaneously by solubilization.

In addition to contributing to waste containment, waste form stability is also important for the overall integrity of the disposal facility. For example, the waste form, together with the container, must have sufficient mechanical strength to withstand the load due to stacking of containers and backfill. Loss of waste package integrity can contribute to instability of the disposal vault and cover, which may lead to increased water flow to the waste. Impact resistance and compressive strength are important properties that are normally tested and assessed to ensure waste forms possess sufficient physical strength to maintain structural integrity under anticipated repository conditions.

Waste containers contribute to waste package and repository performance by delaying the release of radionuclides, thereby allowing the short-lived radionuclides to decay prior to mobilization. Estimation of container lifetime is necessary to establish how much credit should be assigned to the waste package for radionuclide containment.

Container performance and its lifetime are a function of the container material and design, degradation mechanism and rate, environmental conditions and groundwater chemistry. For metallic containers, the corrosion performance is an important indicator of container integrity and lifetime. Therefore, it is important to establish the underlying corrosion mechanisms that contribute to container failure for the various container materials. Corrosion-induced gas generation is another important consideration in repository safety assessment. For concrete containers, degradation of concrete needs to be considered to estimate container life. Polymer container materials (HDPE), on the other hand, are not susceptible to corrosion. However, creep, embrittlement, and irradiation induced degradation can affect the durability of HDPE containers.

5. APPROACHES TO WASTE PACKAGE TESTING AND EVALUATION

5.1. GENERAL CONSIDERATIONS

Waste packages are comprised of a waste form to stabilize and immobilize contaminants, and a container to provide shielding, containment and facilitate handling and transportation. If present, backfill, liners, and overpacks are also considered a part of the waste package. Common waste forms comprise liquid and solid waste stabilized in a matrix such as bitumen, or compacted wastes encapsulated in cement. Waste containers are manufactured in a variety of shapes, wall thicknesses and volumes, and are made from materials such as galvanized carbon steel or stainless steel, reinforced concrete or HDPE. All of the countries participating in this programme examined waste package performance. The details can be found in the Annex, which contains the reports from each country. For ease of reference for the reader, if a country report discusses results from a particular test, the country is listed following the discussion in this section of the report.

Waste package components are generally selected to provide a leach resistant matrix for contaminant immobilization and to provide mechanical stability to prevent subsidence and void formation in the repository. This is important during the post-closure repository phase. Waste package leach resistance, durability and compatibility are a function of a number of factors:

- Leach resistance: Factors that depend on repository conditions, such as leachate composition, temperature, formation of radiocolloids, and backfill moisture content, can appreciably affect radionuclide release from a waste package (Argentina, Russian Federation, Annex 1). Laboratory leach tests were carried out with a cement-simulated leachant to approximate the chemical conditions imparted by cementitious backfill (Canada, Czech Republic and Republic of Korea. See annex).

  In some cases, ancillary tests may be required to define the repository conditions. For example, the report from Spain discussed insertion of probes into the cement overpack to measure essential parameters that affect waste form leaching.

- Durability: Over the performance life of the disposal facility, a variety of chemical and physical environments that affect waste container and waste form durability may develop (Argentina, Czech Republic, India, Korea, Norway, Romania, Russian Federation, and Spain). The repository environment can affect waste package performance by providing redox conditions that inhibit corrosion (e.g. Norway).

- Compatibility: Interactions between different engineered materials in the disposal facility under the range of anticipated environments need to be evaluated. For example, waste package degradation products can influence the performance of engineered barriers.

5.2. TESTING APPROACHES

An important objective of this CRP was to determine which waste package testing procedures and approaches are in use to determine the behaviour of waste packages under repository conditions. There are three basic testing approaches:

- Laboratory tests;
- Field tests;
- Archaeological and natural analogues.

Laboratory tests have the advantage that tight control over the important parameters can be maintained. Further, the experiments can be designed to determine the mechanisms and processes that impact on performance, as well as the rate parameters. This information is often needed for long term predictive models. A limitation of laboratory tests is that often the test conditions do not match those encountered during disposal. Field tests have the advantage that the condition under which the performance variables are measured closely mimics those anticipated during disposal. Therefore, the data can provide a more representative depiction of performance. Field tests are limited due to expense and the duration (minimum of a few years). In addition, field tests have many uncontrolled variables (e.g. precipitation, temperature, etc.) that make data interpretation more complicated. Archaeological and natural analogues have the advantage of providing information on long term durability and stability of the materials under natural conditions. The major limitation of analogue studies is that detailed information on the initial characteristics and inventory, as well as the environmental conditions that the materials have been exposed to, are not well established. The parameters, which are measured in these tests, are given in Table III.

Laboratory tests on waste package performance are carried out practically in all Member States (annex). These tests are performed under controlled conditions according to internationally approved methods and standards. This is true for all parameters described above in Table III. For example, leach rate parameters that characterize the release of radionuclides are specified in International Standards Organisation (ISO) and IAEA standards. Member States have, in some cases, developed or customized tests to suit individual needs (e.g. American Nuclear Society Standard 16.1 (ANS 16.1, ISO 6961), etc.). One of the main advantages of standardized laboratory tests is that variability between tests conducted at different institutions is controlled and, therefore, experimental uncertainties are small. This allows the intercomparison of results. However, laboratory testing is limited to well-defined, controlled conditions (small sample sizes, ambient lab conditions, prescribed leachate replacement schedules, etc.) that do not represent actual repository conditions. Laboratory tests are also carried out over short periods of time, whereas the disposal period could be 300 years or longer. Laboratory tests are generally designed to provide conservative estimates of contaminant release.

Field or in-situ tests are being carried out by a number of participating Member States as a complement to the laboratory tests. Field tests generally provide data that represents more closely the actual or anticipated repository conditions, including interaction with the host media. Field testing can also be used to validate assumptions concerning the degree of conservatism in laboratory tests and provide data for more realistic estimates of contaminant release.

TABLE III. TESTS COMMONLY USED FOR ASSESSMENT OF WASTE PACKAGE PERFORMANCE

Types of tests	Properties	Characteristics and Parameters
(1) Laboratory tests	Durability	• Free water content • Compressive strength • Tensile strength • Radiation stability • Thermal stability • Porosity • Permeability • Corrosion rate • Biodegradation rate
	Radionuclide release – Liquid phase	• Release rate parameters – Leaching rate – Diffusion coefficient – Dissolution rate • Chemical parameters – Sorption coefficient – Solubility – Solution chemistry (pH, Eh, major ions, etc).
	Radionuclide release - Gas phase	• Release rate mechanisms – Radiolysis – Biodegradation – Corrosion
(2) Field tests	Durability	• Corrosion rate • Biodegradation rate
	Radionuclide release and transport	• Leaching rate • Diffusion coefficient • Sorption coefficient
(3) Archaeological and natural analogues	Durability	• Corrosion rate • Thermal stability
	Radionuclide release and transport	• Leaching rate • Diffusion coefficient • Sorption coefficient • Colloidal formation • Solubility

Field tests are generally tests conducted with samples that have waste package dimensions (or actual waste forms) and under field conditions selected to simulate actual repository conditions. The time frame for field tests is on the order of a few years, or even a few tens of years. Among the participating countries, field tests for the assessment of waste package performance under repository conditions are carried out in Argentina, India, Norway, the Russian Federation, and Spain (Annex). Parameters measured in these tests are expected to provide data that are more realistic for source-term model validation. Valuable information on the behaviour of waste package materials and behaviour is being obtained from field experiments currently underway in some countries (Norway, the Russian Federation, UK, etc.) on degraded waste packages retrieved from existing waste repositories. For example, clay-backfilled waste drums retrieved from a Norwegian burial site after 27 years exhibit little corrosion of the carbon steel drum. A potential shortcoming of the field tests is that there are no standard procedures because, by definition, they are site specific. The need for some guidance in field testing of waste packages has been expressed many times at international meetings.

Field tests also have limitations, perhaps the most serious being the duration of the testing period and the high costs, which limit the number of tests. Therefore, they cannot provide an absolute level of confidence. Archaeological and natural analogues can be used to enhance the level of confidence in field and laboratory data, by providing some long-term validation for important processes affecting waste package behaviour.

Natural and archaeological analogue studies provide information on long-term stability and durability. Analogue studies often prove useful in improving understanding of the impact of chemical processes (sorption, solubility, pH, Eh, etc.) on contaminant transport. Due to the limited knowledge of conditions, data from natural analogue studies are often difficult to use in mathematical models of performance. However, the data often provide confirmatory evidence and provide an independent method of demonstrating long-term performance.

5.3. REPOSITORY CONDITIONS

The repository environment is site and design specific, and hence unique for each facility. Waste package performance is affected by repository conditions; therefore, both waste form and container tests need to be selected to represent the actual or anticipated repository environment. Thus, a good understanding of repository conditions plays an important role in proper design of experiments for waste package performance assessment. However, in some countries, test conditions are prescribed by the regulatory authority. When test conditions that are not representative of the repository are prescribed, the conditions are meant to be more aggressive than anticipated conditions in order to provide conservative estimates of performance.

For defining repository conditions, it is convenient to further categorize repositories as either humid (the Russian Federation, India, Finland, Romania) or arid (Spain). Humid repositories are located in wet climate zones where precipitation is sufficient to promote infiltration of water into the subsurface; arid repositories are located in dry regions where minimal infiltration into the subsurface occurs. Properties that characterize repository performance include:

- temperature fluctuation,
- water permeability,
- resistance against chemical attack,
- mechanical durability,
- leach resistance of waste forms, and
- compatibility between materials in the disposal facility.

The relative importance of each of these properties is site and design specific. For example, the ability to withstand wide fluctuations in temperature is more important for an above-grade facility as compared to a rock cavern facility.

In addition, the relative importance of the various performance properties may reflect the need to address more than one degradation process. For example, the temperature durability of a waste package in an above-grade repository may be required to ensure mechanical resistance to temperature variations (e.g. freeze thaw cycles), and also to provide protection against loss of containment in the event of a fire scenario (e.g. forest fire). In a rock cavern repository, for example, mechanical strength may be required for a waste package to provide resistance against rock pressure. Depending on site specific situations, both field and laboratory test data may be required.

5.4. LINK BETWEEN DATA COLLECTION AND PERFORMANCE MODELLING

Waste package testing can have many objectives, including:

- screen candidate waste forms under a range of conditions,
- provide data for performance assessment studies, as well as for research investigations to determine fundamental mechanisms that control performance,
- demonstrate compliance with waste acceptance criteria (WAC), and
- verify solidification process control.

The type, quality, and quantity of the data will be different for each of the above objectives. From a safety assessment perspective, the main purpose of waste package testing is to demonstrate post-closure safety, hence, waste package data and testing should be focused on safety assessment needs (in particular, source term evaluation). In contrast, tests to demonstrate process control or compliance with WAC are generally not focused on safety assessment data needs. Research investigations are used to evaluate the fundamental mechanisms for contaminant release. To assist safety assessment, it is essential that the waste package testing programmes and safety assessment needs are communicated and co-ordinated. The link between experimental data and long term performance is achieved through modelling. Data based on short-term laboratory and field tests are extrapolated to longer time scales. Experiments should be designed to permit the appropriate scaling for extrapolation to repository time frames and scales.

5.5. MODELLING WASTE PACKAGE PERFORMANCE

Prior to the disposal of LILW, an assurance that disposal of the waste can be accomplished while protecting the health and safety of the general population is required. The long time frames over which public safety must be assured necessitates that the safety case relies, in part, on computer simulations of events and processes occurring well into the future. Safety assessment requires, in part, an understanding of the performance of the waste containers, waste forms, and engineered backfill. Other important roles for modelling include identification of data, design, and model development needs for defensible decisions about regulatory compliance, and development of WAC related to the quantities of radionuclides permitted for disposal. In this CRP, the focus of the work has been on identification of data and models necessary to evaluate waste package performance.

The long time frames, the lack of complete understanding of all of the processes that affect performance, and the natural variability inherent in waste package materials and their performance characteristics require that uncertainty analysis be performed. Although short-term measurements may provide the best available data for performance assessment, these data may not reflect processes that govern radionuclide release over repository time-scales. As materials age, their properties change, however, data collection usually does not take into consideration the degradation-induced changes over time. In some cases, e.g. compressive strength of cementitious materials, the performance may improve over time. In other cases, the performance may degrade over time. In order to consider the variability that may occur, uncertainty analysis is performed. Uncertainty analysis allows an examination of potential changes in system behaviour as a function of changes in model parameters. Single parameter uncertainty analysis can be performed in which one model parameter is changed and the impact on performance assessed. The process is repeated several times to examine the impact of changes in important variables on performance. Alternatively, Monte Carlo type analysis, in which multiple variables are changed during a single simulation and the process is repeated a large number of times to obtain a distribution of potential outcomes. In either case, the modelling is performed with the intent of showing that performance is acceptable under a wide range of conditions.

Another important modelling approach that can be used to address model development and data collection needs is sensitivity analysis. In sensitivity analysis, an evaluation similar in approach to an uncertainty analysis is performed with the objective of determining if a change in a parameter impacts on decisions pertaining to waste disposal. For example, two parameters often measured in backfill performance studies are bulk density and radionuclide distribution coefficient. After analysis, it may be found that changes in distribution coefficient have a major impact on performance, while changes in bulk density indicate only a minor impact. Thus, in this example, it is more important to accurately measure the distribution coefficient.

The following general approach is an example that might be used for developing defensible, long term waste package performance evaluations:

- Identify the chemical/physical conditions of the repository environment and waste characteristics (inventory, physical and chemical form, etc).

- Perform sensitivity studies, based on the available data and simple models.

- Identify important radionuclides and waste form, container, and backfill parameters that have the largest impact on performance.

- Perform durability and leach tests on waste package components to assess the various processes that may affect their behaviour and performance. Initially, these tests should be on a laboratory scale to gain experience on test methods. As the project evolves, field scale tests may be necessary to obtain the appropriate supporting data.

- Develop more complex models of the waste package behaviour to evaluate its performance over time. Mechanistic models are generally preferred. However, empirical models may be used if data are insufficient to support mechanistic models.

- Validate models by comparison with experimental results (e.g. lysimeter studies and leach tests) and/or with natural and archaeological analogues.

- Determine whether performance goals are met based on existing models and data. If not, return to the sensitivity analysis step and repeat the process with the more complex models and enhanced data. Repeat the steps until performance goals are met.

The above approach is iterative, starting with simple models and adding complexity as required to demonstrate that performance objectives are met.

5.5.1. Typical performance models

Waste disposal entails a wide range of waste containers and waste forms. Some of which may require unique models. For waste package performance models, three categories arise: container failure, waste form release, and container performance in inhibiting migration of radionuclides after release from the waste form. The following section discusses some of the models typically used in waste package performance assessment. The list is not complete nor is it meant to imply that other models can not be used. Detailed discussions of the models can be found in the individual country reports (Korea, Russian Federation, and USA).

5.5.2. Container failure model

The container provides a barrier to prevent water from contacting the waste form. An important consideration in modelling the release rate from the waste package is the time over which the container remains intact and isolates the waste from water. In general, the different sizes, shapes, and materials of the containers and the locally different environmental conditions would require a separate analysis of each container. However, this task would be overwhelming, as there may be tens of thousands of containers in a disposal facility. To simplify the task, assumptions are made which permit containers to be grouped into a few different categories. This homogenization process typically divides container types into half a dozen groups or less. Major categories are concrete, carbon steel drums, carbon steel liners, stainless steel drums and High Integrity Containers (HIC). Within each category of container, the performance of each individual container is assumed to be identical. An extension of the catastrophic failure model for each type of container is to consider a distribution of failures over time. In theory, the distribution can be any function. In most cases, the distribution of failure time approximates known statistical distribution functions such as the uniform, normal, lognormal, or exponential distribution functions. For example, one could assume that all carbon steel containers fail between 20 and 70 years with a constant failure rate (e.g., 2%/year, meaning 2 out of 100 containers per year). An example of the effects of distributed failure on waste package performance can be found in the USA country report.

There are two major categories of container failure mechanisms. Catastrophic failure in which the container is assumed to fail completely at the end of its service life and no longer provides a barrier to water contacting the waste form. The second failure mechanism is localized failure in which it is assumed that only a portion of the container fails at any time and it requires several years or longer for the entire container to totally fail. The country report from the Russian Federation discusses both general and local corrosion models and estimates container lifetime. In modelling container performance, the catastrophic container failure model is usually used.

5.5.3. Waste form release models

The waste form release models used in the safety assessment can be categorized into aqueous and gaseous phase. The aqueous release of radionuclides from the waste form is frequently conceptually modelled as occurring through one of the following four physico-chemical processes:

- Surface rinse with partitioning. In the absence of partitioning, the radionuclides are released instantly upon contact with water (i.e. after container failure). In this case, data are not needed for the waste form other than the inventory. If partitioning is modelled, the distribution coefficient of the radionuclide in the waste form is needed.

- Diffusion. This model requires the diffusion coefficient and geometry of the waste form.

- Dissolution. This model requires the waste form geometry and dissolution rate.

- Solubility limited release. This model requires the solubility limit for the radionuclide under the geochemical conditions expected in the repository.

The different aqueous phase waste form release models are provided in Table IV. Examples of the types of models commonly used for different waste form types are also provided in Table IV. In any case, supporting data must be generated prior to using any particular model. Examples of the application of diffusion and dissolution models can be found in the country reports from Canada, India, Korea, and the Russian Federation. The USA country report provides examples of applications of diffusion models to waste form performance.

TABLE IV. WASTE FORM AQUEOUS PHASE RELEASE MODELS

Release Mechanism	Applicability	Comments
Instantaneous (rinse)	Surface contaminated wastes, waste forms without release rate data	Highest release rate.
Surface Rinse with Partitioning	Surface contaminated wastes that sorb radionuclides (e.g. soils, sludges, ion-exchange resins).	Release rate controlled by transport of contaminants away from the waste form.
Diffusion	Solidified wastes (e.g. cements, polyethylene, bitumen).	Release rate decreases over time. Bitumen may swell due to uptake of water. Diffusion model is inappropriate when this occurs.
Dissolution or Corrosion (Uniform)	Release controlled by surface dissolution or corrosion (e.g. waste glasses, activated metals).	Constant release rate corrected for radioactive decay
Solubility Limited	Radionuclides with low-solubility in the expected chemical environment.	Release rate controlled by transport of the species away from the waste form.

For gaseous release of radionuclides, the mechanisms and processes that generate gas need to be evaluated. Helium, ^{3}H, ^{14}C, ^{85}Kr, ^{129}I, and ^{222}Rn can all exist in the gas phase and can be released from a variety of waste forms by different mechanisms. Gas may be produced in a disposal facility due to production of hydrogen from anaerobic corrosion of metals (Canada). Metals may arise from decommissioning wastes, or reprocessing of fuel such as Magnox (Canada, United Kingdom). Other sources for gas phase release include (Canada, Korea): (a) methane and carbon dioxide from microbial degradation of organic waste materials; (b) failure or rupture of sealed sources to produce ^{85}Kr, ^{222}Rn, ^{4}He and ^{3}H; (c) radiolysis to produce gaseous ^{3}H, ^{129}I, hydrogen and oxygen; (d) radioactive decay of ^{226}Ra to ^{222}Rn and (e) volatilization of liquid ^{3}H. The formation of radioactive gases may lead to release to the environment through gas-phase diffusion and advective transport mechanisms.

Release of ^{14}C in carbon dioxide or methane (^{3}H could also be released in methane) due to biodegradation requires a detailed analysis of the amount and types of organic material present in the facility and the rate of production of these gases (Republic of Korea, Canada). Modelling release of gas from sealed sources is typically achieved through assuming a time-to-failure of the seal followed by total release of the inventory at that time. Radiolysis has been found to produce limited amounts of gas and can often be shown to be unimportant as a mechanism for gas release even at the maximum cumulative radiation dose expected in low level waste forms, which are less than 10^{6} Gy (Korea). At levels above 10^{6} Gy, gas generation may become significant and estimates of its importance would depend on the dose rate as well as total dose. Release of ^{222}Rn can be calculated from the decay rate of the parent and knowledge of the distribution of the parent in the waste form. For surface contaminated wastes, release would occur upon decay. For solidified wastes, the gaseous ^{222}Rn would have to diffuse through the waste form. Diffusion of gases through solidified waste forms is likely to be much more rapid than diffusion of liquids. Build-up of ^{222}Rn gas pressure is not likely to occur because it will be in secular equilibrium with the parent ^{226}Ra (Table V). However, ^{4}He pressurization can occur in radium sources as a result of the generation of helium in the ^{226}Ra decay series. Examples of modelling gas generation and associated release of radioactivity, and its impact on repository integrity, are found in the Canadian and Korean country reports.

5.5.4. Waste container models for controlled release

Even after the containers have failed to provide isolation of the waste from the environment, the degraded containers may provide a source of sorption sites that may retard the movement of released radionuclides and thereby increase waste package performance. For example, metallic waste forms or steel containers may generate iron corrosion products that will sorb certain radionuclides. However, due to the uncertainties associated with corrosion product formation, credit for sorption on container materials is generally neglected in performance assessment for the waste package. If model evaluations were performed, data on the degree of sorption as a function of the amount of corrosion would be needed. Similarly, degraded concrete containers may provide sorption sites for released radionuclides. However, modelling of this phenomenon is not usually performed.

TABLE V. WASTE FORM GAS PHASE RELEASE MODELS

Release Mechanism	Applicability	Comments
Anaerobic corrosion of metals	Tritium containing wastes	Corrosion release of H_2 gas Metallic containers may also be a source of gases from corrosion.
Biodegradation	Organic wastes containing ^{14}C or tritium	Can produce $^{14}CO_2$, $^{14}CH_4$, or C^3H_3H
Radiolysis	High activity wastes, spent sealed sources	Not expected to produce substantial quantities of gases in most LLW. It may be a problem for spent sealed sources.
Time to failure	Sealed sources: ^{85}Kr, ^{4}He, ^{3}H	
Radioactive decay	^{226}Ra wastes	Produces ^{222}Rn, ^{4}He
Volatilization, equilibrium partitioning between liquid and gas.	Tritium containing wastes	Majority of tritium will remain in the liquid phase

5.6. DURABILITY DATA AND TESTING

Durability is one of the principal characteristics of the waste package. Waste package durability is needed for a period of time to reduce the risks to members of the public from disposed LILW to acceptable levels. The confinement of the radionuclides and structural integrity of the waste package are the most important properties that need to be understood with respect to waste package durability. Factors affecting the waste package durability during the disposal period need to be studied in the context of the waste package and the repository environment and its design life, and the following aspects need to be addressed:

- mechanical stability
- chemical durability
- microbiological durability
- radiation stability
- thermal stability

5.6.1. Functional requirements for the waste package in a repository

5.6.1.1 Radionuclide confinement

Confinement of the radionuclides within the waste package is important to keep the radionuclides out of the accessible environment. Continued confinement will allow time for the radionuclides to decay within the waste package. For example, a functional requirement of a concrete container may be to prevent the access of water to the waste form for a specified time.

5.6.1.2 Structural integrity

The continued integrity of the waste package is important with respect to the leaching of radionuclides and maintaining the structural integrity of the repository. Loss of integrity of the waste package will increase its susceptibility to leaching by creating pathways for the groundwater to penetrate the waste package and remove radionuclides. The waste package may also need to have sufficient strength to support overlying waste packages and the repository cover. Structural integrity may be supplied by the backfill, container, waste form or a combination of these waste package components. Understanding the deterioration of the waste package structure may be required to show that the repository is still protective of human health under degraded conditions.

5.6.1.3 Time

The period during which the performance characteristics of the waste package should be maintained must be in accordance with that determined by the safety assessment of the repository. Experiments to understand the deterioration of waste packages should take into account this time requirement.

5.6.2. Durability tests and approaches

The tests employed to assess the durability of the waste package depend on the characteristics of the waste and matrix, and the type of container for the waste.

The tests performed most often for cementitious materials are for mechanical resistance, thermal stability, chemical resistance, and microbiological degradation. Examples of durability tests on cementitious materials can be found in the country reports of Argentina, India, Republic of Korea, Romania and the Russian Federation.

Bitumenized waste forms are usually tested for mechanical resistance, microbial degradation, and radiation stability. Examples of these tests can be found in the country reports from Finland and the Russian Federation.

Mechanical and chemical resistance tests, as well as radiation stability tests, were carried out for glass waste forms (Russian Federation). For polymeric matrices, tests for compressive strength, thermal stability and homogeneity were employed and details can be found in the country reports from Korea and India.

For assessing the container material durability, tests for mechanical and chemical resistance, microbial degradation, radiation stability and thermal stability were employed. Details on container material durability testing can be found in the Argentina, Czech Republic, Spain and the Russian Federation country reports.

Examples of the types of tests, which could be used to determine the different aspects of waste package durability are shown in Table VI. For example, to determine the mechanical durability of the waste package, tests on compressive strength, tensile strength, porosity, Young's modulus, etc., could be carried out. The tests listed in the table are not exhaustive nor are they mandatory. The type of tests selected will depend on the requirements of the waste packages and repository. Testing should be carried out in accordance with national regulations and programme needs.

TABLE VI. EXAMPLES OF TESTS FOR WASTE PACKAGE DURABILITY

		Encapsulation matrix				Container material		
Durability parameter	Tests	cement	bitumen	glass	polymers	steel	concrete	polymers
Mechanical resistance	compressive strength	x		x	x	x	x	x
	tensile strength	x					x	x
	porosity	x	x				x	
	permeability	x					x	
	micro fracturing	x		x		x	x	x
	homogeneity	x	x	x	x			x
	Young's modulus	x					x	
	Creep		x		x			x
Chemical resistance	corrosion	x				x	x	
	calcium leaching	x					x	
	silica leaching			x				
	waste/matrix chemical interactions	x	x	x	x			
Microbial effects	gas generation	x	x				x	x
	chemical interactions	x	x				x	x
Radiation stability	gas generation	x	x					
	crosslinking		x		x			x
Thermal stability	thermal cycling	x			x	x	x	x

5.7. RADIONUCLIDE CONFINEMENT DATA AND TESTING

Radionuclide isolation is one of the essential features of repository performance. Waste package confinement plays an important role in the control of release of radionuclides to the other barrier components of the repository and eventually to the environment.

5.7.1. Measures of release

To evaluate radionuclide release rates and mechanisms, described in the previous section, the following parameters may need to be experimentally determined. Various types of experiments, ranging from laboratory to field scale, can be employed. Data obtained during retrieval of waste packages from repositories or from natural analogue studies are also useful for understanding release mechanisms.

(a) Leaching rate (g m^{-2} d^{-1})

The release of radionuclides from the waste package is often expressed in the form of the Incremental Fractional Release (IFR) or Cumulative Fractional Release (CFR). The IFR is the amount of contaminant released between experimental measurements normalized to the initial inventory of the contaminant in the waste form. The fractional leaching rate is the IFR divided by the time between measurements. The leaching rate is measured by standard leaching tests, such as ANS 16.1 or ISO 6961. The cumulative fractional release (CFR) is the ratio of the amount released divided by the initial inventory in the waste form. The CFR is the sum of all IFR_i and is a measure of the capability of the waste form to retain radionuclides. Fractional release rates can be translated into mass release rates using the radionuclide-specific inventory and surface area of the waste form..

(b) Diffusion coefficient (D, m^2/s)

The migration of radionuclides from many waste forms is controlled by the diffusion process. Diffusion coefficients can be determined experimentally by means of steady state movement through samples, or by measuring diffusion into or out of a sample. For example, in the Finnish project, radionuclide diffusion experiments were carried out on bitumen in diffusion cells. In this work, the diffusion experiments with tritiated water provided a conservative estimate for diffusion coefficients of other radionuclides.

The procedure for performing leaching experiments and obtaining the results in the form of diffusion coefficients is described in the 90-day ANS 16.1 test. This type of leaching experiment was performed in the Korean project. The ISO 6961 leaching test, which is similar to ANS 16.1, was carried out in Argentina project. ISO 6961 prescribes a longer experimental leaching time than ANS 16.1.

In developing an understanding of leach tests results, it is important to take into account the scale factor. The surface area to volume of the waste form has been found to be the appropriate scale factor for diffusion controlled processes. The larger this ratio, the larger the IFR, if all other parameters are the same.

Field experiments often, as was shown in the Argentina project, provide results that do not correspond directly to those obtained in the laboratory. This may be related to scale issues as the field tests often use full-size waste forms. However, it is more likely to be due to the different environmental conditions in the field as compared to those prescribed in standardized tests. In the study in Argentina, the field leaching results were lower than the predicted releases, based on laboratory experiments. Field experiments were also performed in the Russian Federation, Norway and India where the performance of various waste matrices was compared to laboratory data. In the Norwegian study, the results showed that almost all of the activity released from the waste packages was confined to 2 cm of clay surrounding the drum surface.

(c) Distribution coefficient (K_d, $m^3\ kg^{-1}$)

Surface contaminated waste may release all of their activity upon contact with water. This represents an upper bound on release rate, and experimental data are not needed. Some radionuclides, however, are sorbed on the waste matrix, which delays the instantaneous release of radionuclides. The distribution coefficient is a measure of the sorption capacity of the material for a given radionuclide. It is often experimentally determined from a mass balance of the amount of contaminant on the waste material divided by the concentration in water at steady state.

The distribution coefficient, K_d, is typically measured using steady-state, batch sorption methodology. More reactive (sorptive) radionuclides have higher distribution coefficients. Tritium exhibits negligible sorption as measured K_d values are close to zero. The sorption of various radionuclides on vermiculite or bentonite was studied in the India report.

(d) Dissolution rate ($kg\ m^{-2}\ s^{-1}$)

The dissolution rate is an experimentally determined measure of the rate of reactions that dissolve the surface of the waste form. Dissolution is often an important process for activated metals and glass. For these materials, characterization work must be conducted to determine the fraction of activity that is in the matrix of the waste form and the fraction that is sorbed on the surface. Simple surface contamination on metal or other surfaces will be released instantaneously and, therefore, should be modelled using an instantaneous release (e.g. surface rinse) model.

(e) Solubility limit (mol/l)

The release rate of some radionuclides is controlled by their solubility limit in the given environment. For example, the actinides species and some other radionuclides have low solubility in a cementitious environment. The solubility constraints on ^{14}C release in a cementitious environment have been investigated in Canada (Canada country report). The determination of radionuclide solubility must take into account the sorption of the radionuclides in waste package components, such as waste matrix, container corrosion products or other engineered barriers and the repository conditions (pH, Eh, water composition). Solubility can be determined experimentally or by geochemical speciation codes.

Determining a solubility limit is difficult. When using a model, uncertainty exists as to whether the proper geochemical conditions are modelled. When determining solubility limits experimentally, this is often analytically challenging due to low concentration levels and the possibility of sorption. Also, there is uncertainty over the representativeness of the experimental conditions for the range of expected environmental conditions. This is an important issue because solubility can change by orders of magnitude depending on chemical conditions.

5.7.2. Confinement function of containers

Waste containers can contribute to overall waste package and repository performance by delaying the ingress of water, thereby allowing the short lived radionuclides to decay to insignificant levels. Estimation of container lifetime is necessary to establish how much credit should be assigned to the waste container for radionuclide containment. For impermeable containers (metallic or HDPE), container lifetime is determined as a function of the container material and design, degradation mechanism and rate, environmental conditions and groundwater chemistry. These systems are generally modelled to be completely effective in isolating the wastes from contact with water for the duration of their lifetime. After this period, the containers are assumed to be completely ineffective at protecting the waste form. Tests for durability were described in section 3.3.

For concrete containers, water may percolate through the container, and the failure mechanism differs from impermeable barriers. Therefore, testing the confinement function of concrete containers differs from impermeable barriers and requires determination of concrete permeability, hydraulic conductivity and radionuclide diffusion coefficient, which includes the effect of sorption. It is important to consider how these properties may change over time as cracks form and propagate in the concrete. The Indian study investigated the service life of reinforced concrete, based on degraded concrete samples retrieved from disposal facilities (India).

5.7.3. Engineered backfill

Backfill materials can also significantly contribute to the confinement of radionuclides within the repository by decreasing the amount of water contacting waste packages and lowering the mobility of radionuclides by sorption and precipitation.

The primary parameters concerning the backfill confinement function are hydraulic conductivity, sorption, buffering capacity and redox capacity. Hydraulic conductivity is measured using standard tests, for example, the project in Romania (Romania country report). Sorption is measured using methods described in section 5.7.2. Sorption on backfill materials was studied in the project conducted in India by determining the K_d values. For certain radionuclides, determination of the buffering capacity and redox capacity of the backfill is important. These parameters are measured using standard analytical methods.

For example, cement-based backfill materials placed around waste containers for structural stability have a very high pH buffer capacity. The cement backfill can maintain the pH above 10 for hundreds of years, providing a favourable environment for solubility control on the release of radionuclides, such as the actinides, ^{14}C, etc. The effect of high pH, imparted by cementitious backfill, on ^{14}C release has been studied in Canada (Canada).

6. SUMMARIES OF THE CRP RESEARCH PROJECTS

6.1. CRP PARTICIPANTS’ RESEARCH PROJECTS

The research projects of the CRP deal with different aspects of LILW package component testing and performance assessment. Specific areas of research include testing and evaluation of waste forms (cementitious, bituminous, polymeric, metallic, glass- and paraffin-based), containers (carbon steel, stainless steel, concrete, high-density polyethylene) and, in some cases, whole waste packages. A range of processes has been selected to assess waste package performance. Some of these include leaching, diffusion, waste-form swelling, durability, microbial and corrosion-induced gas generation, irradiation-induced material degradation, source-term behaviour, and canister corrosion. A variety of test methods and approaches are being employed to assess waste package performance. These include testing in the laboratory and field, retrieval of old waste packages for evaluation, and predictive modelling. In some projects, experiments are designed to generate mechanistic data that allow extrapolation and prediction of waste package behaviour and performance over time. A summary of each country's research project is given below.

Argentina

The Argentina project focused on studies relating to waste form performance in terms of ^{137}Cs, ^{60}Co, and ^{3}H releases, microbially-mediated gas generation from stabilized waste, and corrosion-induced degradation of carbon steel and concrete containers. Tests to evaluate clay-based backfill are also underway. Results indicate that the clay used as backfill has a high retention capacity for ^{137}Cs. Tests on carbon steel container materials indicate a corrosion rate of 0.1 mm/yr. Tests on the various waste package components are continuing. More data need to be generated before meaningful extrapolation can be made to predict waste package performance over time.

Canada

Several broad areas of research that impinge on issues relating to the long-term performance of LILW packages under anticipated disposal conditions are being investigated as part of the Ontario Hydro Technologies project in Canada. Work has focused on assessment of waste form performance, definition of vault chemical conditions in the presence of cementitious materials, and establishment of source terms for safety-relevant radionuclides present in both reactor operational and decommissioning waste. The potential for gas generation from both corrosion and microbial degradation of waste package components was evaluated. Calculations were performed to estimate the type and magnitude of gases likely to be generated under disposal conditions and their impact on repository performance and integrity was assessed.

Studies at AECL Chalk River are focusing specifically on the development of performance criteria for waste forms that arise from the treatment of liquid LILW. A cementitious binder has been selected for solidification of the liquid wastes. Both physical and chemical properties are being evaluated to assess the durability and leaching requirements for waste forms.

Czech Republic

The Czech project is evaluating the performance of HDPE HIC for the disposal of spent ion exchange resins and sludge derived from a nuclear power plant. Specifically, laboratory tests are being carried out to assess irradiation-induced oxidation of the surface layer, following exposure to ^{60}Co irradiation at doses ranging from 0.035 to 8.55 kGy/h. Preliminary results indicate that irradiation dose rate has a significant effect on the oxidation stability of HDPE, thus affecting container lifetime.

Finland

Evaluation of bituminized ion exchange waste forms is the focus of the Finnish project, with particular emphasis on the water uptake and swelling processes. In addition, cementitious engineered barrier materials are being studied to assess their retardation properties for ^{137}Cs and ^{90}Sr, both representing major radionuclide constituents of the bituminized waste.

India

The Indian project is addressing several areas of R&D relating to LILW package performance under actual disposal conditions: (a) full-scale field testing of waste forms and waste packages; (b) stabilization of heat-generating spent sealed sources and evaluation of the resultant waste form; (c) service life of reinforced concrete, based on degraded concrete samples retrieved from disposal facilities; and (d) retention of ^{239}Pu and ^{241}Am in vermiculite- and bentonite-based backfill materials.

Republic of Korea

In the Korean project, studies are underway to demonstrate compliance of waste packages with the waste acceptance criteria established by the national regulatory body. Various types of waste packages, including carbon steel drums, high integrity containers, and concrete-lined drums, are currently in use at the Korean Nuclear Power Plants (NPPs). In addition, paraffin based waste forms are being generated at the NPPs. Most of the work completed to date has focused on potential gas generation in the waste packages. The principal gas-generating mechanisms being considered include metal corrosion, microbial activity in organic materials, and radiolysis in paraffin-based waste forms. Leaching studies on both simulated and actual paraffin- and cement-based waste forms are also underway.

Romania

In the Romanian project, experiments are underway to assess the durability of cement-based waste forms prepared with admixtures of bentonite and volcanic tuff. The effect of the presence of various complexing agents on the mechanical strength of the waste form is also being studied. Tests are underway to evaluate the effect of mineral additives on waste form permeability.

The Russian Federation

The Russian Federation project involves field testing of pilot- and full-scale waste packages subjected to repository conditions for a period of up to 12 years. The waste packages consist of cemented, bituminized and vitrified waste forms placed in carbon steel containers. The field testing is focusing on evaluation of the leaching behaviour of the waste forms and corrosion degradation of steel containers. The experimental results, based on 12 years of field testing, have been used to develop a model that represents the leaching behaviour of the waste forms studied. The model can be used to extrapolate long-term waste form behaviour in order to predict radionuclide releases over repository time-scales.

Spain

The Spanish project involves an assessment of the long-term behaviour of concrete containers, with particular emphasis on methodologies to estimate container lifetime. The concrete containers, instrumented with a series of sensors, are being studied under repository conditions, and monitored over time. The main parameters being monitored to assess concrete durability include temperature, deformation, electrical resistivity, corrosion potential, corrosion rate, and the availability of oxygen at the reinforcement.

United States of America

The USA project deals with modelling waste package performance as it relates to safety assessment of LILW disposal. The objective of the study was to demonstrate the link between data collection for waste containers and waste forms and model development needs in support of a defensible safety assessment. This was accomplished by reviewing the fundamental concepts behind safety assessment and demonstrating how waste package models can be used to support safety assessment. As illustrative examples of the role of waste container and waste package performance, three sample test cases were provided. The test cases examined the impact of distributed container failure times on projected release, the effects of diffusion coefficients on waste form release, and the influence of formation of a thin diffusive barrier on the surface of the waste form.

7. CONCLUSIONS

The development and demonstration of approaches and technologies that provide long term safety is an essential issue in implementing the safe disposal of radioactive waste. For LILW, waste packages can play an important role in the overall safety and performance of near surface repositories. Thus, obtaining a defensible technical basis for understanding waste package behaviour and performance is an important consideration in the development and establishment of near surface repositories.

In the context of near surface disposal, the two major functions of the waste package are its durability and leach resistance. An important part of the technical basis for understanding waste package performance is a robust testing programme. This programme may involve laboratory tests, field tests and analogue studies. It is important for the tests to provide data that helps understand long term behaviour under the anticipated environmental conditions. The report presents results of the CRP on long term behaviour of LILW waste packages under repository conditions, focusing on test methods and approaches that may be applied for the assessment of waste package behaviour and performance. Factors and conditions, as well as underlying processes, which may affect waste package performance are described. Data requirements, in particular mechanistic data that is amenable to extrapolation and modelling, are discussed.

The country research projects of the CRP are generating new information that is contributing directly, not only to their national programmes, but also to a better understanding of the behaviour and performance of LILW package components and packages under disposal conditions.

An important aspect of waste package testing and performance assessment that emerged from this CRP is the recognition by all participants that, for the purposes of predicting the future behaviour of waste packages on a time scale of ~300 years, a good understanding of the underlying processes controlling the performance of the various package components is needed.

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LOW AND INTERMEDIATE LEVEL WASTE PACKAGE ASSESSMENT UNDER INTERIM STORAGE AND FINAL DISPOSAL CONDITIONS

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Abstract

At present, in Argentina, only the low level waste are disposed off. With the purpose to demonstrate that the safety requirements will be achieved, a project has been launched that involves the characterization of the waste packages and studies of waste package behaviour under conditions that could affect its integrity and long term durability. At this time, two types of waste packages are being studied. One of them is a steel drum with evaporator concentrate immobilized in a cementitious matrix, derived from a Nuclear Power Plant. The other one is radioactive solid waste compacted into a steel drum, arising from medical practices. Also, a concrete container is being studied with the purpose of determining its long-term durability and the effects of different aggressive conditions on its integrity. Full-scale leaching and corrosion tests, simulating repository conditions, have also been initiated to assess the performance and behaviour of waste packages. In addition, tests on microbiological attack, acid rain, reinforcement corrosion and chemical agents effects are been implemented. In order to study the corrosion processes, tests on chloride and sulphate ions diffusion, concrete carbonation rate and carbonated layer thickness have been started.

1. INTRODUCTION

1.1. Technical background

Safety analysis is conducted to identify the potential risks to the public, resulting from the existence of a waste disposal facility and accident scenarios must be taken into account in order to determine the measures to be applied to mitigate risks during its operation and institutional control periods.

LLW are generally disposed off in near surface disposal facilities. The disposal concepts of this type of facility are based on the limitation of the specific and cumulative activity levels in the waste accepted for disposal, the waste isolation by the use of multiple and redundant barriers and the use of release detection methods and quality controls.

The first barrier used in this type of facility is the waste package, defined as the waste form and its container. The second barrier is the design of the disposal facility, with an adequate drainage and waterproof disposal cap, contributing to the chemical and mechanical stability of the waste package, protecting the waste package from water and preventing radionuclides release to the environment. The last barrier is the site where the facility is located, that means favorable hydrogeological characteristics and radionuclide retention capability of the surface layer.

Final disposal facility

A low Level Waste final disposal facility is located on the Ezeiza Radioactive Waste Management Area (ERWMA), consisting of two trenches. The first trench is 140 m long, 10 m wide and 1 m deep, with their capacity completed with 3400 waste packages. At present this installation is closed and covered. The second one, in operation, is 120 m long, 20 m wide and 1 m deep with a total capacity for 5600 conditioned drums.

The engineering design of the trenches consist of a excavation with engineering improvements, that is, a floor prepared with compacted loamy soil and crash stone, surrounded with a reinforced concrete wall and a pipe system that allow to drain the rain water during the operational period.

After their capacities were completed, the trenches are backfilled with fine dry sand, clay and native earth and covered with waterproof layer.

In order to demonstrate that the safety requirements will be achieved, it is necessary to understand the behavior of all components of the disposal facility.

The waste package, one of these components, requires to be studied in depth with the purpose to know and to understand several and complex processes, that affect as much the waste form as the container and consequently could affect the rest of the disposal components, regarding the surrounding near field conditions.

With this purpose, the Waste Management Unit of the CNEA has developed a program of R&D for the characterization of the waste package and its behavior facing different factors that could affect its integrity and long term durability.

Studies at lab scale were carried out as first stage of this program. These studies involved waste form characterization and its behavior regarding the radionuclide leaching and the mechanical resistance.

At present and as part of this CRP, studies at full scale about the behavior of the waste package under repository conditions are carrying out.

1.2 Objectives

The purpose of this work is to study the waste package behavior under repository conditions, considering extreme conditions during the institutional control.

The Low Level Waste Package was tested taking into account the waste form capability for radionuclides retention, the gas release from conditioned wastes, and the container durability, a carbon steel drum, related to the corrosion aspects.

On the other hand, a high performance concrete container was designed and constructed with the purpose to evaluate their durability as engineering barrier, in order to be used as container for interim storage, transport and final disposal for Intermediate Level Wastes.

1.3. Relevance for the national program

Waste management organization must demonstrate the safety of waste disposal during the operational and institutional control phases of the disposal facility. For this reason it is necessary to know the parameters that allow the modeling of the long-term behavior of the waste package in the repository.

In order to accomplish this performance demonstration and to obtain data to be used in the modeling of the waste behavior and the characterization of the source term, the Waste Management Unit of CNEA has considered relevant to participate in this CRP.

1.4. Scope of work

At present, two sorts of waste packages have being studied. One of them is a steel drum of 200 L of capacity with evaporator concentrate immobilized in a cementitious matrix, coming from a Nuclear Power Plant. The other one, is a radioactive solid wastes compacted into a steel drum of 200 L of capacity, coming from a medical practices.

Based on the characteristics of the present CRP, involving long-term tests, this program was planned to carry out in two phases.

The first phase consists of the implementation and development of a full scale leaching test to determine the release parameters for each nuclides and a container corrosion test in order to evaluate the container degradation factors.

The second phase, already implemented with results in progress, consist of two other studies: one of them is about the chemical and mechanical resistance of a multipurpose reinforced concrete container specially designed and the other about the gas release from compacted wastes at interim storage.

2. DESCRIPTION OF THE TASKS

The CRP started on 1998 June and was developed in four stages as follow:

- The first stage was devoted to plan and to implement the leaching test at full scale and corrosion test.

  With this purpose, a stainless steel tank of 3000 L of capacity was used as test holder; it was appropriately prepared in order to support all the filler materials, the total ground water required and the waste package to be studied.

  The materials employed to simulate the conditions of the trenches, crash stone, fine dry sand and loamy soil (35% humus, 65% clay) were poured in layers, inside the test holder.

  A net of pipes and valves used to transfer the ground water to and from the tank and a temperature control system, complete the device.

FIG.1. Assay holder.

FIG. 2. Waste package inside the assay holder.

- The second stage was to simulate the disposal conditions considering a hypothetical scenario.

  Although the engineering design and the normal operation conditions of the final disposal facilities are appropriates, with respect to limit the radionuclides release, in the present work extreme conditions have been supposed. The considered hypothetical situation involves the flooding of the trench, due to the increasing of the groundwater level.

  Another extreme supposition was that the waste package had suffered serious corrosive processes, before the flooding, such as total destruction of their lid and a partial lost of their lateral surface and base. With this purpose, the lid of the drum was extracted and several perforations on the lateral and bottom surface of the drum were made.

- The third stage was to select and to characterize the waste package to be studied.

  With this purpose a 200 L carbon steel drum, filled up to 98% of their volume, containing evaporator concentrated from nuclear power plant CNAI, immobilized in cementitious matrix, was selected and characterized.

- The fourth stage consisted on the full scale leaching test and the corrosion test.

  This stage began by middle of November 1998. Full-scale leaching test are conducted considering as specimen, a cementitious homogeneous waste form, and ground water as leachant.

  Partial volumes of leachate were collected and homogenized in an auxiliary container, and sampled to be analyzed chemically and radiochemically.

In connection with corrosion studies, a test was devised that permits the on-line monitoring of the corrosion of the metallic drum.

Samples cut from the same drum tested, immersed in the same test holder were tested. The different variables related with the corrosion processes were recorded.

Tests cells were buried nearby the drum, each one composed of three different electrodes. The working electrode -test coupon- is the metallic piece cut from a drum studied; the counter electrode is a piece of stainless steel and the reference electrode (a calomel saturated one) is mounted on a plastic tube that acts as a saline bridge when filled with ground water. The whole assembly is tightened with stainless steel bolts and nuts and completed with electric contacts, insulators, etc., as seen in the photo.

Only the central portion is exposed to corrosion, by means of a cross-scratched through the paint. Any other place, where a metallic part could be exposed was covered with several layers of bituminous epoxy paint to insure localization of the attack.

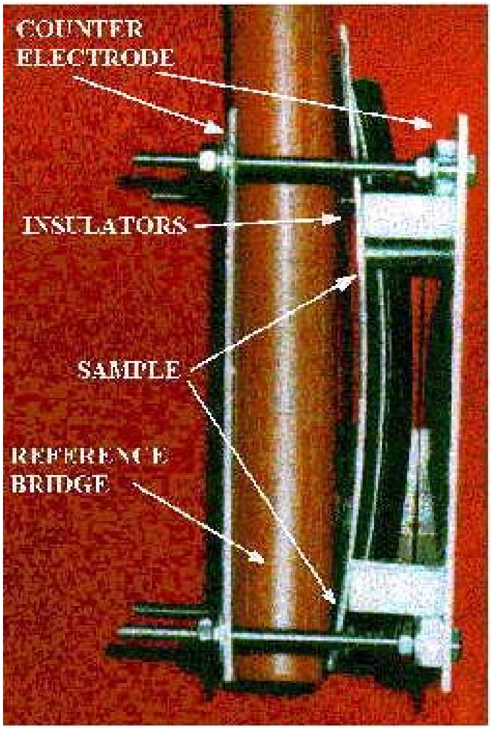

FIG. 3. Corrosion probe.

FIG. 4. Corrosion test electrodes array.

Fifteen cells were placed around the drum, at three different heights: lower, medium and upper zone, axially distributed in four sites; moreover, three cells more where buried in the central region of the upper cap, inside the "plenum", where a higher concentration of lixiviated products could be generated.

The investigations are being carried on using a 10 channels digital potentiostat-intensiostat. Two kinds of measurements are conducted at regular intervals: corrosion potential determinations and polarization scans of 20 to 40 mV of extension around this rest value to obtain information on the corrosion velocity. These results will give a general trend, to be compared with the real degree of the damage occasioned in each sample at the end of the test. Meanwhile, periodical chemical analysis of the waters will help to determine the pH, conductivity and concentration of aggressive ions.

At this moment and continuing with the present CRP, we have started other two different studies.

The first of them, has the objective to study the behavior of the waste package concerning to gas release under storage conditions. For this purpose, we have developed a system that allows measuring the gases released by the decomposition of radioactive solid compacted wastes, when those are under interim storage conditions.

With the aim to achieve favorable conditions for the gas generation, originated by microbial attack on the wastes, such as temperature and humid adequate, an assay device was developed consisting of a sealed drum, provided with a thermostat to assure a constant temperature during the whole period of the test, a gas sampling port and a manometer to verify the inner drum pressure.

The design of the system is showing in the following photo:

FIG. 5. Gas assay device.

FIG. 6. Gas sampling.

Periodically, samples of inner air of the drum were taken in order to determine, by Gas Chromatography, the concentration of the gaseous species present, such as methane, carbon dioxide and sulphidric acid.

The second study consisted in the development and construction of a high performance concrete container, in order to evaluate their behavior as engineering barrier in an intermediate level waste repository.

At present, the container was already built. Its design characteristics and the in-situ test results of the concrete quality used for its production, it allows to hope an excellent behavior like engineering barrier.

To demonstrate this last, different nondestructive test are developing, such as microbiological attack, acid rain effects, reinforcement corrosion and chemical agents' effects.

FIG. 7. High performance concrete container.

FIG. 8. Reinforcement corrosion.

Four sensors to determine the corrosion of the reinforcement bars were installed in the container. According to their location in the container (see Figure 9) the sensors were identified as:

LE: Lateral on the external reinforcement
LI: Lateral on the internal reinforcement
FS: Bottom on the superior reinforcement
FI: Bottom on the inferior reinforcement

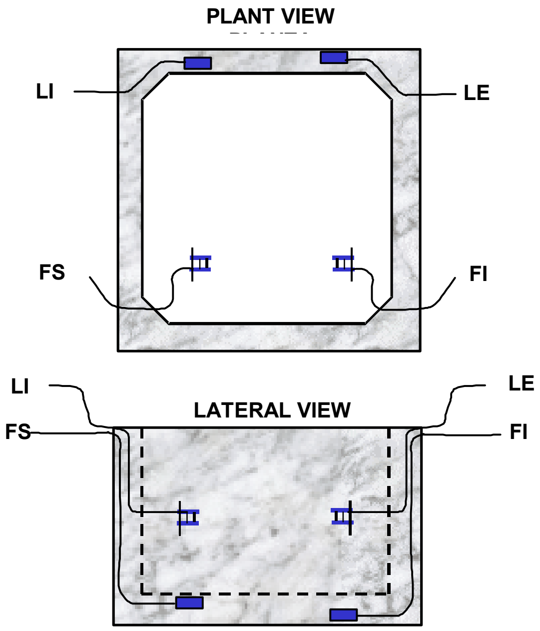

FIG. 9. Plan and lateral view of a test container, showing the position of the sensors for corrosion measurements.

At present, evolution of the corrosion potentials of the reinforcement bars are being monitored and methods about corrosion rate measurements “in-situ”, are in progress.

3. RESULTS

3.1 Waste stream characterization

Type of waste: Evaporator concentrated

TABLE I.1. WASTE STREAM CHARACTERIZATION

	Units	Results
Density	g/ml	1.057
PH		7.1 ± 0.1
Total Solids	wt.%	15.0 ± 0.25
Dissolved Solids	wt.%	12.5 ± 0.16
Suspended Solids	wt.%	2.5 ± 0.07
Organic material	g/ml	40
Chemical composition		
Silicon	g/l	0.60 ± 0.06
Chloride	g/l	10.4 ± 0.34
Iron	g/l	1.7 ± 0.09
Sodium	g/l	22.7 ± 1.19
Sulphate	g/l	1.3 ± 0.20
Boron	g/l	0.4 ± 0.15
Radiochemical Composition		
Co-60	kBq/ml	28 ± 1
Cs-137	kBq/ml	0,34 ± 0.07
H-3	kBq/ml	158 ± 7.4
Sr-90	kBq/ml	9.8 E-03 ± 3.0 E-03
Total Alpha	kBq/ml	5.3 E-04 ± 1.3 E-04

3.2 Cementitious matrix

Type of cement: ARS cement (sulfate resistant cement)

TABLE I.2. ARS CEMENT PHYSICAL CHARACTERISTICS

Retention on 75 microns sieve	4%
Specific surface Blaine	358 m^2/ kg
Normal paste (W/C)	0.22
Initial setting time	2 h 45 min.
Final setting time	4 h 30 min

TABLE I.3. ARS CEMENT MECHANICAL CHARACTERISTICS

	AGE 7 days	AGE 28 days
Flexural module (MPa)	5.6 ± 0.2	7.4 ± 0.2
Compressive strength (MPa)	32.7 ± 0.5	43.3 ± 1.4

3.3 Waste form formulation

TABLE I.4. PROBES EXTRACTED FROM THE REAL IMMOBILIZATION PROCESSES

Waste / Cement matrix: 0.45
Water/ Cement: 0.38
Bleeding: not detected
Setting time: Initial set: 4 h. Final set: 14 h

3.4 Lab scale results

Several specimens have been extracted during immobilization process in order to determine mechanical resistance (IRAM 1622 Standard) and leaching test (ISO 6961 Standard).

The cumulative fraction releases was plotted in function of t½ and the values of the diffusion coefficient for ^{137}Cs and ^{60}Co were determined from their slope. The results are presented in the following table and graphics.

TABLE I.5. TEST RESULTS AT LAB SCALE

Probes	Compressive strength IRAM 1622 (kg/cm^2)	Leaching test ISO 6961 (D: cm^2/día)	
		^{137}Cs	^{60}Co
P6228-11	175 ± 2	6.300E-05	1.300E-08
P6273-12	321 ± 21	3.200E-05	1.600E-08
P6300-13	285 ± 24	2.100E-05	1.500E-08
P6324-14	231 ± 9	1.300E-04	9.000E-09
P6449-15	216 ± 13	9.000E-05	2.100E-08
P6527-16	141 ± 29	6.000E-05	1.800E-08
P6611-17	139 ± 13	1.000E-04	3.700E-08

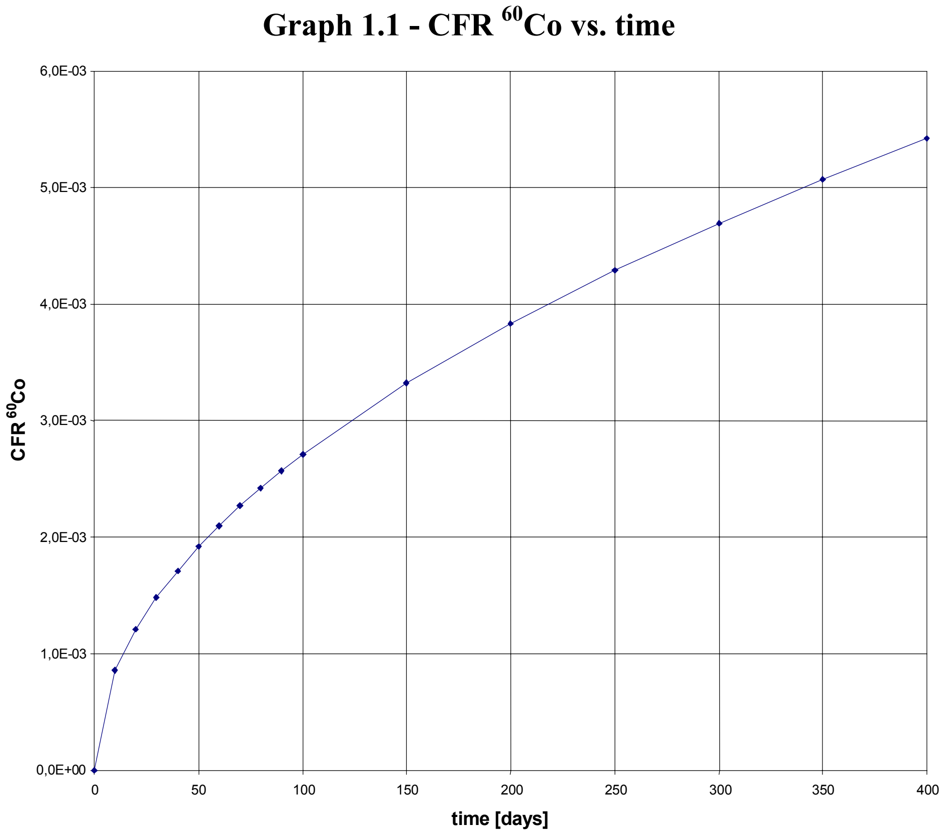

FIG. 10. Cumulative fractional release of ^{60}*C as a function of time.*

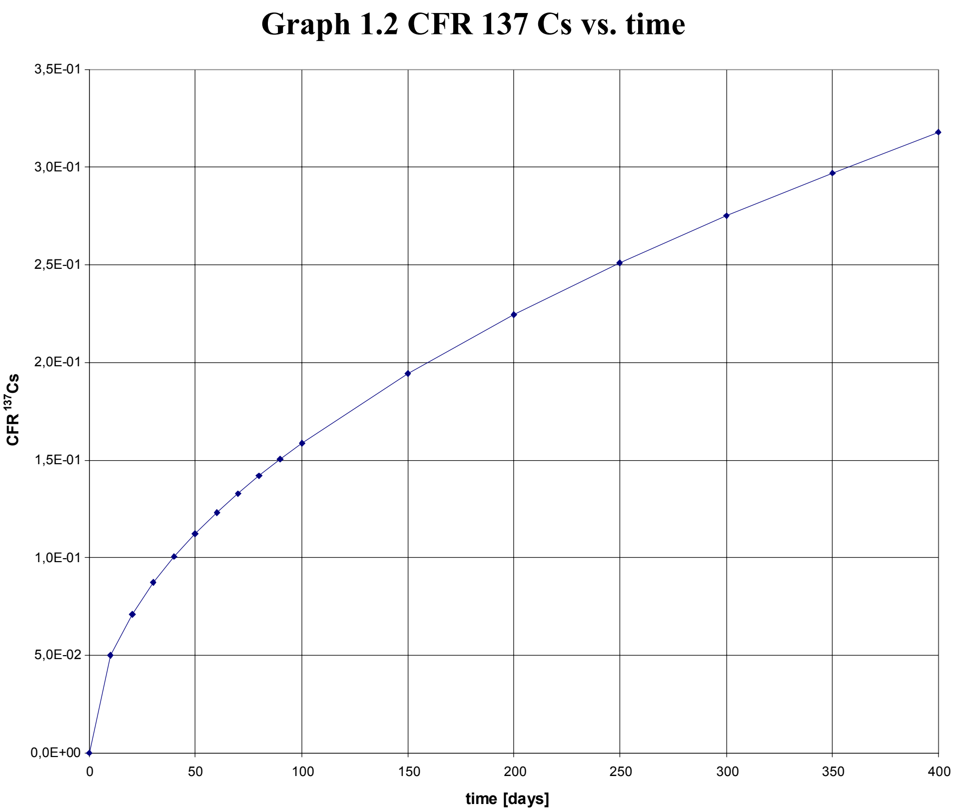

FIG. 11. Cumulative fractional release of ^{137}*Cs as a function of time.*

3.5 Full scale results

TABLE II.1. BLEND OF SOIL CHEMICAL ANALYSIS

	Units	Results
PH	---	8.3
Sulphide (S^{-2})	mg/dm^3	10
Acidic exchanged	------	2
Chlorides (Cl^-)	mg/kg	30
Wet	g/100g	7.14
Carbonates (CO_3Ca)	g/100g	0.98
Magnesium (MgO)	mg/kg	4200
Sulphates (SO_4^{-2})	mg/kg	165

TABLE II.2. GROUND WATER CHEMICAL ANALYSIS

	Units	Results
PH	---	6.9
Bicarbonates	mg/l	575
Carbonates	mg/l	7
Chlorides	mg/l	68
Sulphates	mg/l	34
Nitrates	mg/l	60
Calcium	mg/l	72
Magnesium	mg/l	36
Total iron	mg/l	0.6
Fluorine	mg/l	0.6
Total hardness (CO_3Ca)	mg/l	324
Fixed residual at 105°C	mg/l	927

3.6 Waste form characterization

TABLE II.3. WASTEFORM FORMULATION

Type of Cement Matrix: ARS
Type of Waste: Evaporator concentrated
Waste/cement matrix: 0.45
Mixed Time: 8 minutes
Bleeding: not detected
Exothermic peak: middle 110ºC – periphery 91ºC ± 8%
Setting time: initial set: 4 Hs. final set: 14 Hs.

TABLE II.4. RADIOLOGICAL CHARACTERIZATION OF THE WASTEFORM

Radionuclides	Total Bq
Co-60:	2.95 E09
Cs-137:	3.45 E07
H-3:	1.80 E010
Sr-90:	1.47 E06
Total Alpha	6.12 E04

TABLE II.5. CONTAINER CHARACTERISTICS
(CARBON STEEL DRUM OF 200 L CAPACITY)

TESTS		RESULTS
Drop Test	Horizontal	Not loss
	Inclined	Not loss
Air tightness test		Not loss
Hydraulic pressure		Not loss
Load resistance		Not dimensional changes

3.7 Leaching test at full scale

TABLE II.6. CUMULATIVE FRACTIONAL RELEASE VERSUS TIME

CUMULATIVE FRACTION RELEASE					
		^{60}Co	**^{137}Cs**	**^{90}Sr**	**^{3}H**
PERIOD	**TIME [days]**				
1	7	3,79E-05	3,19E-05	ND	6,11E-07
2	20	2,73E-05	6,81E-03	ND	1,54E-03
3	57	1,46E-05	1,78E-03	ND	3,94E-04
4	106	2,18E-05	1,79E-03	ND	4,22E-03
5	143	3,65E-05	1,93E-03	ND	1,13E-02
6	233	5,54E-05	3,94E-03	ND	1,36E-02
7	301	5,58E-05	4,50E-03	ND	2,45E-02
8	352	6,89E-05	4,58E-03	ND	2,52E-02
9	413	7,87E-05	4,89E-03	ND	2,55E-02
10	477	8,69E-05	5,23E-03	ND	2,66E-02
11	539	9,39E-05	5,55E-03	ND	2,74E-02
12	606	9,78E-05	5,79E-03	ND	2,86E-02
13	673	1,02E-04	5,93E-03	ND	2,98E-02
14	740	1,05E-04	6,42E-03	ND	3,73E-02
15	808	1,13E-04	7,13E-03	ND	4,83E-02
ND: Values below detection limits					

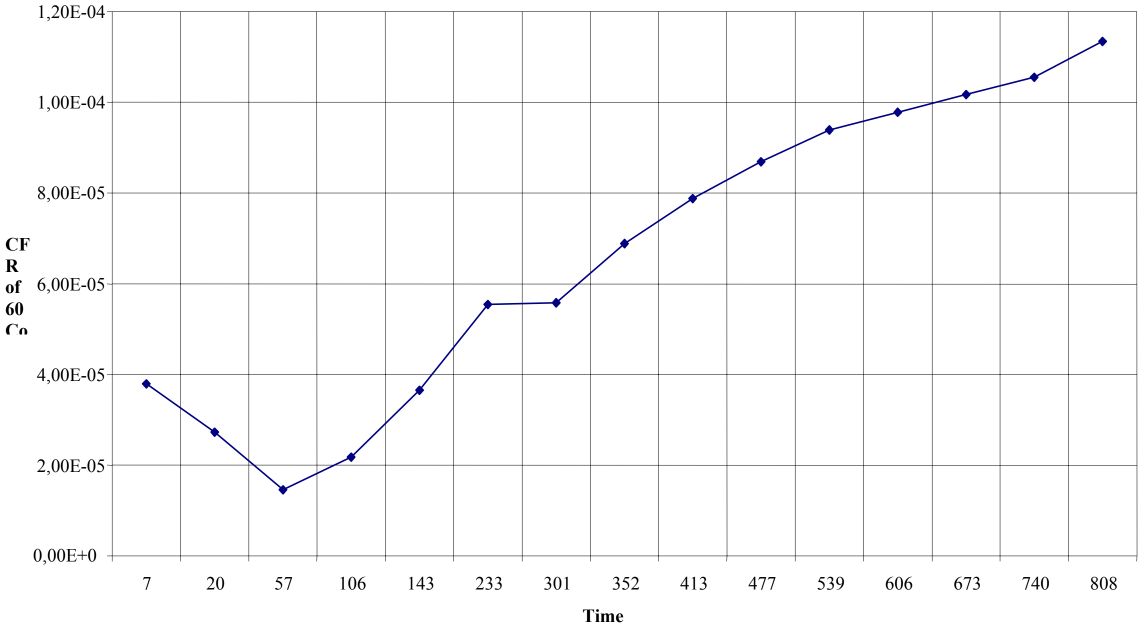

FIG. 12. Cumulative fractional release of ^{60}C as a function of time.

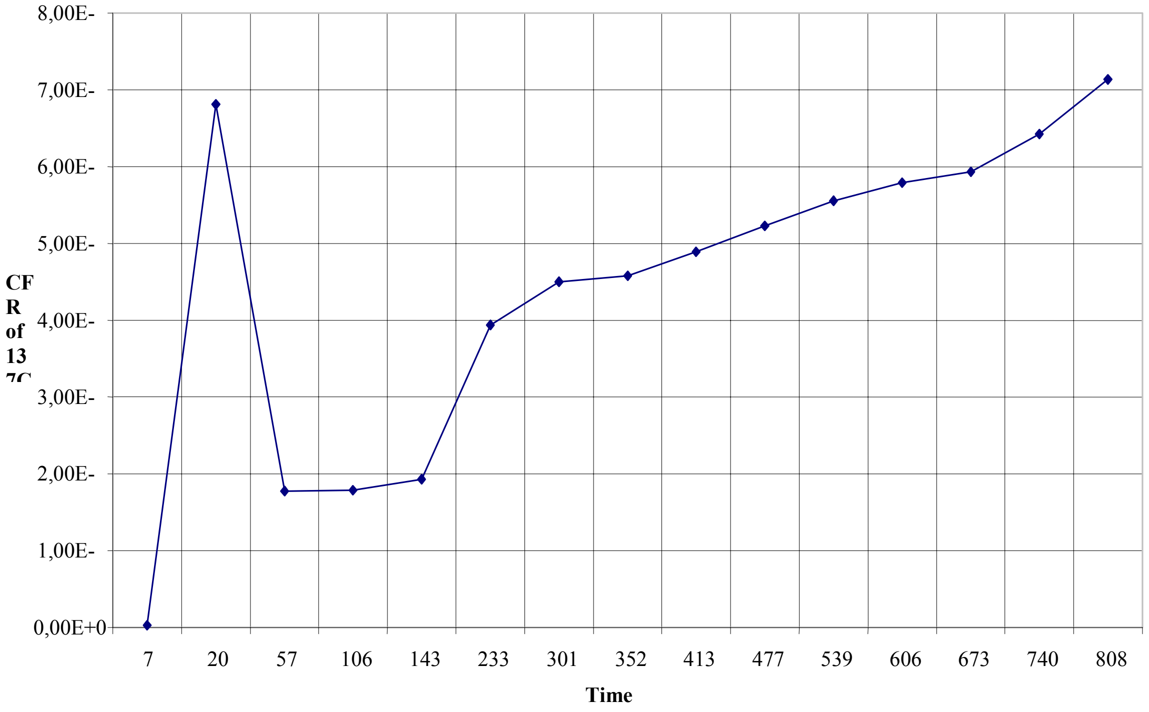

FIG. 13. Cumulative fractional release of ^{137}Cs as a function of time.

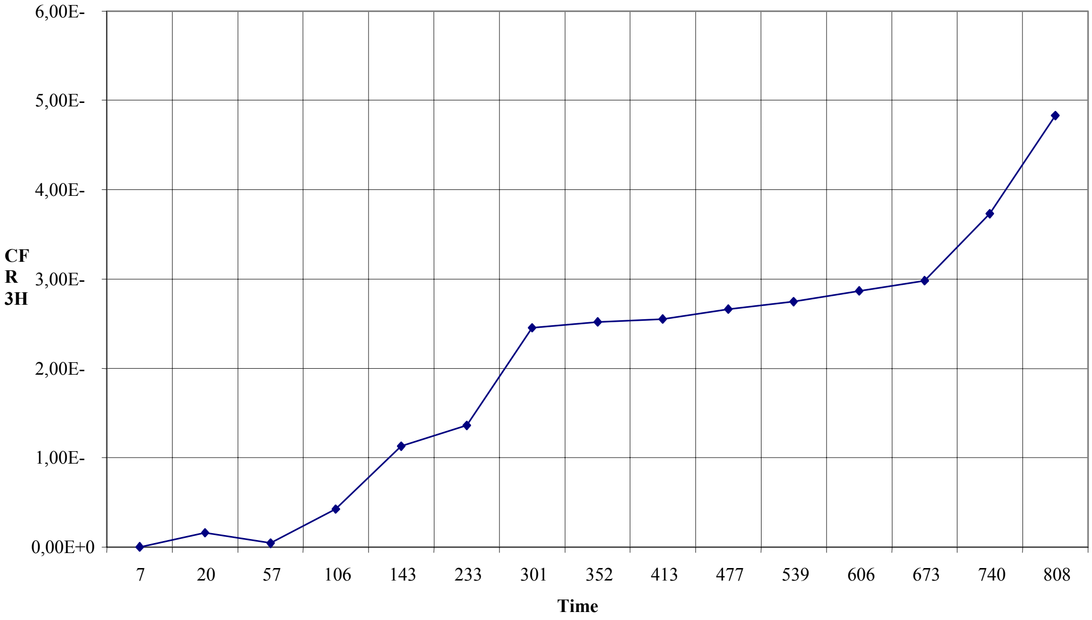

FIG. 14. Cumulative fractional release of ^3H as a function of time.

3.8 Diffusion coefficients

TABLE. 11.7. Calculated diffusion coefficients for ^{60}Co, ^{137}Cs, ^{90}Sr and ^{3}H.

Radionuclides	Slope (m)	Correlation Factors	Diffusion Coefficients [cm2/ day]
^{60}Co	7.00E-06	0.932387	4.21 E-09
^{137}Cs	3.00E-04	0.90849	7.74 E-06
^{90}Sr	ND	ND	ND
^{3}H	3.10E-03	0.991	8.26 E-04
ND: Values below detection limits			

3.9 Corrosion test at full scale

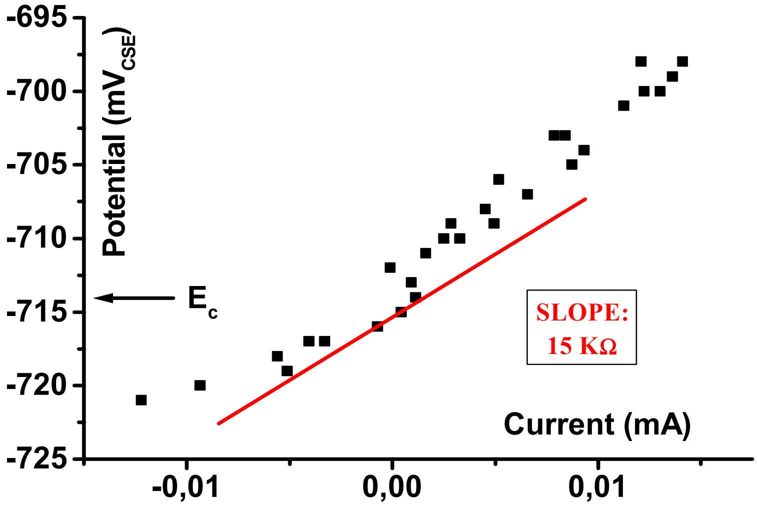

FIG. 15. Polarization slope obtained in one cell at the corrosion potential.

Polarization slope obtained in one cell at the corrosion potential.

3.10 Test results on concrete container

Laboratory Measurements Results

- Compressive strength
  28 days = 53 Mpa
  180 days = 57 Mpa

- Adiabatic temperature rise $\Delta T = 40$ °C (192 hours)

- Average water penetration = 15 mm

- Oxygen permeability
  kO 28 days = 0.30×10^{-16} m^2
  kO 180 days = 0.04×10^{-16} m^2

- Air permeability
  kT 28 days = 0.13×10^{-16} m^2
  kT 180 days = 0.02×10^{-16} m^2

- Average Ultrasonic Pulse Velocity = 4870 m/s

- Thermal cycle

  At 10 cycles Loss of Strength = 14%
  At 10 cycles Ultrasonic Pulse Velocity = 4800 m/s

In Situ Measurements Results

- Compressive strength
  at 28 days = 58 MPa
  at 180 days = 62 Mpa

- Oxygen permeability
  kO 180 days = 0.056×10^{-16} m^2

- Air permeability
  kT 56 days = 0.31×10^{-16} m^2

- Capillary suction 28 days
  $a_{3h} = 8.1\ g.m^2/s^{1/2}$
  $a_{24h} = 8.1\ g.m^2/s^{1/2}$

- Average ultrasonic pulse velocity = 4000 m/s

- Average covercrete thickness = 22 ± 3 mm

4. CONCLUSIONS

Although the elapsed time is not enough and the data obtained are not conclusive, it was possible to observe some trend about the behavior related to leaching. That is:

- The ^{60}Co was the less leached than the other ones studied. On the other hand, ^{137}Cs and specially ^{3}H were the radionuclides with the higher leaching rate. With respect to ^{90}Sr, the values fell under the detection limits.

- The Diffusion Coefficient obtained at full scale, (D_{60Co}=4.21E-09 cm^2/day; D_{137Cs}= 7.74 E-06 cm^2/ day; D_{3H}=8.26 E-04 cm^2/ day) were smaller than those obtained at lab scale with same waste form.

- A great dispersion in the leaching measurements it has been observed due to involuntary inclusion of colloidal particles in the leached, that adsorb radionuclides. Filtered samples showed the main proportion of the activity present in the colloid fraction.

- Soil samples, at different distances from the drum, will be taken in order to determine the radionuclides concentration profile.

Although the results obtained at the moment don't allow carrying out projections for the future, they could indicate that the clay used as backfill has a high Cs retention factor. A reason of this would be the montmorilonite present in clays, with high Cs retention characteristics.

With respect to carbon steel drum corrosion test, the results obtained indicate a moderate to low degree of degradation. The polarization slope indicates the apparent polarization resistance. When this value is computed with the normal corrosion parameters for the studied system, the corrosion current is calculated on 10^{-6} to 10^{-5} Amp/cm^2, which represents a dissolution rate less than 0.1 mm/year.

In spite of the tendency of the behavior that we could see at present, we were considering to extend the testing time, correcting some aspects of the procedures used, in order to obtain a set of values that allow us more precision and accuracy to be applying on the deep understanding of the waste package behavior.

Regarding to gas release, periodically samples of inner air of the drum were taken in order to determine by Gas Chromatography, different gaseous species such as methane, carbon dioxide and sulphidric acid. Up to now the gases were not detected due to the short lapsed testing time.

The concrete container was already built. Its design characteristics and the in-situ test results, it allows assuming an excellent behavior like engineering barrier.

Although the test results have shown an excellent performance of the concrete container, different nondestructive test to deal with the concrete behavior were planned and are in progress.

Tests on microbiological attack, acid rain, reinforcement corrosion and chemical agents' effects are been implemented.

In order to study the concrete corrosion processes, tests on chloride and sulphate ions diffusion, concrete carbonation rate and carbonated layer thickness were started and the first results are in progress.

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WASTE PACKAGE PERFORMANCE AND GAS GENERATION UNDER DISPOSAL CONDITIONS

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Abstracts

As part of Ontario Power Generation's (OPG) low an intermediate level waste management programme, research was undertaken to provide relevant information on the long term performance of waste forms and packages for both operational and decommissioning wastes, focussing on isssues that are important in repository design and safety assessment. Specific areas of research relevant to waste package performance included waste form evaluation, decommissioning waste characteristics, and potential gas generation issues. Waste form evaluation studies indicate that a cementitious matrix can be extremely effective in the retention of C-14 for extended time periods, especially in a high pH near-field environment. Estimated inventories and characteristics of potential low and intermediate level waste arisings from the decommissioning of OPG's 20 nuclear reactors indicate that are there some significant differences between the decommissioning waste and operational waste, which are likely to have an impact on the design and safety assessment of the planned disposal facility. Scoping calculations to estimate corrosion-induced and microbially-mediated gas generation in OPG's low level waste indicate that potentially significant amounts of hydrogen, carbon dioxide and methane could be produced from the organic and metallic constituents present in the waste. However, this gas production would not have any adverse impact on repository performance and safety.

1. INTRODUCTION AND BACKGROUND

The reference strategy for the management of radioactive waste at Ontario Power Generation (OPG) provides a broad framework for the long-term management of Used Fuel, and low and intermediate level waste (LILW) of which disposal is a major component (1). All low level waste (LLW), generated to date at OPG’s nuclear power stations, is currently in storage at the Bruce Waste Management Facility until a disposal facility becomes available. It is estimated that about 100,000 m^3 of operational LLW will have been generated by the end of OPG’s nuclear generation programme. Conceptual designs and cost estimates have been developed for a LLW disposal facility (2). The current reference plan calls for a LLW disposal facility to be in service in 2015.

As part of the overall reference plan for the disposal of LLW, work is continuing on the repository siting process, development of waste acceptance criteria, safety assessments of the disposal concepts, and other related issues, including the establishment of the characteristics and inventories of projected LILW arisings from the operation and planned decommissioning of nuclear power reactors.

2. OBJECTIVES

The main objective of this study is to provide relevant information on the long term performance of waste forms and packages for both operational and decommissioning wastes, focusing on issues that are important in repository design and safety assessment.

3. SCOPE OF WORK

Specific areas of research relevant to waste package performance included: Task 1 — Waste Form Performance; Task 2 — Decommissioning Waste Characteristics; and Task 3 — Gas Generation Issues.

4. RESULTS AND DISCUSSION

4.1. Task 1 — waste form performance

The laboratory investigations related to waste form assessment dealt specifically with ^{14}C waste. Substantial quantities of ^{14}C are produced during operation of CANDU reactors. Carbon-14 is present as dissolved carbonate/bicarbonate in the moderator heavy water and removed by moderator purification systems consisting of organic mixed-bed resin. The highest ^{14}C activities reported for the moderator resin range from 200-600 Ci/m^3. Other sources of ^{14}C waste include spent resins from the heat transport system, irradiated fuel storage bay, and decontamination operations. At the present time, the entire inventory of ^{14}C waste, primarily associated with spent ion exchange resin, is in interim storage at the Bruce Waste Management Facility.

Due to its relatively long half-life and its conservative migration behaviour in the geosphere, ^{14}C has been identified as one of the major fuel cycle nuclides that is radiologically significant over long time scales and will contribute to the exposure of large populations. For this reason, a great deal of laboratory work has been carried out at Ontario Power Technologies to assess the effectiveness of cement-based materials for ^{14}C retention. The main thrust of the study was, therefore, to evaluate the performance of cement based waste forms with regard to ^{14}C containment. Of particular importance are the geochemical processes controlling ^{14}C solubility and release under anticipated cement-dominated repository conditions. Specific details of the laboratory investigations are provided in a series of reports published on this topic (3-8). The main conclusions of the investigations with regard to the disposal of ^{14}C waste are summarized below:

i. Immobilization of ^{14}C spent resin waste in a cementitious matrix results in a cemented waste form with ^{14}C incorporated in the calcite crystals embedded in the matrix.

ii. Leaching studies of the ^{14}C cemented waste form under varying leachant flow rates indicate that the ^{14}C release behaviour can be attributed to the dissolution characteristics of calcite in the cemented waste form. The groundwater flow regime can exert a pronounced effect both on the chemical environment and ^{14}C release.

iii. For a cement-based repository, at relatively low flow or stagnant groundwater conditions, the near field would be dominated by alkaline chemical conditions, thereby inhibiting the release of ^{14}C from the waste form. Under high groundwater flow conditions, however, the near field is likely to be characterized by relatively neutral pH conditions, which, in turn, would promote calcite dissolution and hence the release of ^{14}C from the waste form.

iv. These findings have important implications with respect to ^{14}C isolation in a waste repository in the sense that the chemical buffering of the near field environment by cementitious materials will ensure extremely low solubility of calcite, thereby contributing to the retention of ^{14}C in the cemented waste form for an extended time period, irrespective of the physical integrity of the waste form.

4.2 Task 2 — decommissioning waste characteristics

An important aspect of decommissioning nuclear generating stations is the radioactive waste management issue. Although OPG has reference disposal plans for operational LLW and ILW, as well as for Used Fuel, there is no well-defined strategy for the disposal of decommissioning waste. It is generally recognized though that the management of reactor decommissioning waste is directly linked to the current planning assumptions for the disposal of operational low and intermediate level waste. Thus, information on the characteristics and inventory of projected decommissioning LILW is needed for establishing waste packaging and transportation requirements, identifying potential disposal options, and for estimating costs for the various disposal options. This information, in turn, is expected to contribute directly towards the development of a reference disposal plan for OPG's reactor decommissioning waste.

The specific objectives of Task 2 are to:

- Develop a reference inventory for OPG's decommissioning waste
- Establish a database on the characteristics and inventory of the decommissioning waste from OPG's five nuclear stations
- Compare the characteristics and inventory of OPG's decommissioning LILW with operational LILW
- Assess the potential implications and related safety-relevant issues in the context of disposal

Current status of work:

The information summarized in this paper on Task 2 is based on the following reports completed to date:

a) Bruce A&B Decommissioning Waste Arisings: Characteristics, Inventory and Relevant Disposal Issues (9)

b) Pickering A&B Decommissioning Waste Arisings: Inventory, Characteristics and Disposal Issues (10)

c) OPG's Reactor Decommissioning Waste Arisings. Paper presented at the Symposium on Decommissioning Planning, Radison Plaza Hotel, 23 September 1999, Toronto, Canada (11).

4.2.1 Decommissioning waste arisings

Based on the current planning assumptions (1), the twenty reactor units at OPG's five nuclear stations, following completion of their planned 40-year operating lives, would be decommissioned and then dismantled in order of their in-service dates. The planned shutdown dates for the start of decommissioning the stations are given below:

- Pickering — 2011
- Pickering — 2023
- Bruce — 2017
- Bruce — 2024
- Darlington — 2030

Key assumptions considered in the study for estimating reactor decommissioning waste inventories include the following:

- Reactor operating life is ~40 years, prior to station decommissioning
- Station decommissioning is based on a multistage process, lasting over a period of 40 years
  - Stage 1: Preparation for safe-storage (~1 year)
  - Stage 2: Safe-storage (~30 years)
  - Stage 3: Dismantling (~7 years)

Waste volume reduction options are not considered; thus, projected waste inventories represent conservative estimates of waste arisings. Waste inventories are presented as gross, packaged waste volumes, i.e. burial volume. Table 1 summarizes the chronology of waste arisings and projected inventories of LILW expected to arise from the decommissioning of OPG's nuclear power stations.

TABLE I. DECOMMISSIONING WASTE ARISINGS & INVENTORY

	Chronology	LILW Inventory (m^3)
Pickering A	2041–2046	22,213
Bruce A	2047–2052	18,222
Pickering B	2053–2059	16,312
Bruce B	2054–2059	19,290
Darlington	2061–2066	34,000
TOTAL	**2041–2066**	**110,037**

4.2.2 Waste types

Decommissioning LILW comprises three main types of waste:

- Non-processible Waste
  - Metallic components, structural steel, concrete rubble
- Compacted Waste
  - Dry active waste
  - Cellulosic materials, plastics, etc
- Processed Waste
  - Operating inventories
  - Decontaminating liquids
  - Ion exchange resins and filter cartridges

As an example, the relative volumes of the three principal types of waste generated from the decommissioning of Pickering nuclear stations A&B are shown in Figure 1. Non-processible waste represents about 2/3 of the total Pickering decommissioning waste inventory.

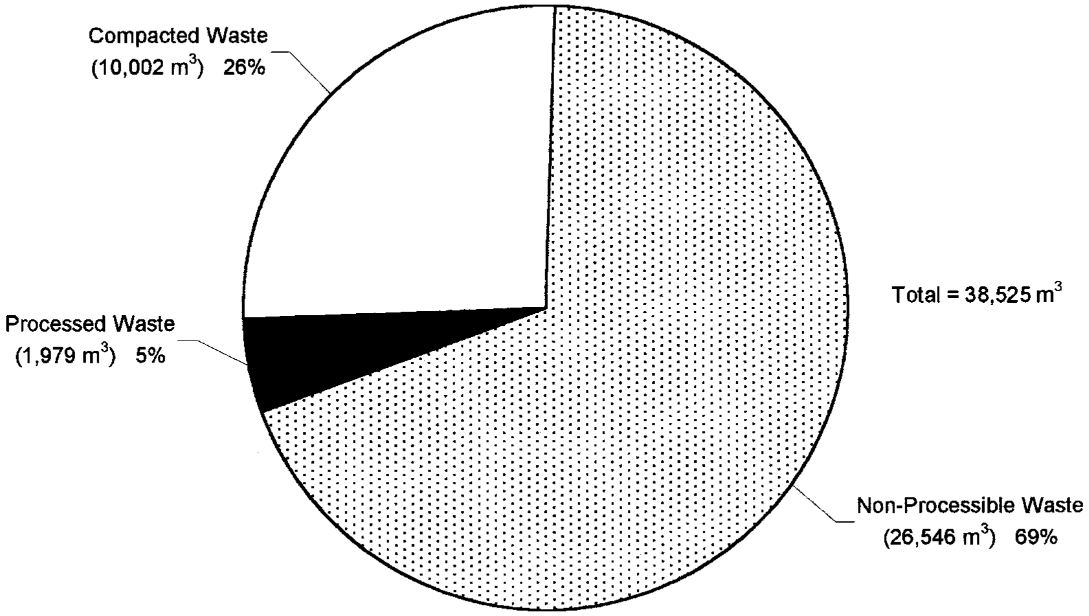

FIG. 1. Relative volumes of principal waste types in pickering decommissioning waste.

4.2.3 Large-size waste components

In addition to the types of waste described above, which can be packaged using conventional packaging technologies, there is another important type of waste comprising large waste components such as steam generators, pressurizers, moderator heat exchangers and pumps, and primary heat transport system (PHT) pumps and motors. These components are removed intact, in one piece, and assumed to serve as their own containers for disposal, with proper closure of all openings, access ways, penetrations, etc. It is assumed that light-density grout will be used to stabilize the internal contamination and plug the openings of the steam generators. An inventory of large-size waste components expected to arise from the decommissioning of Pickering A&B is presented in Table 2.

TABLE II. LARGE-SIZE COMPONENTS FROM PICKERING A+B DECOMMISSIONING

Component	Pickering A Number of items	Pickering A Volume[1) (m³)]	Pickering B Number of items	Pickering B Volume[1)] (m³)	Pickering A+B Number of items	Pickering A+B Combined Volume (m³)[1)]
Steam Generators	48	2,032	48	2,032	96	4,064
PHT Pumps	64	268	64	268	128	537
PHT Motors	64	216	64	216	128	431
Dump Tanks	4	220	0	0	4	220
Moderator System Pumps	20	20	20	20	40	40
Moderator Heat Exchangers	8	120	8	120	16	241
Cooling System Pumps	19	372	19	372	38	744
Cooling System Motors	19	271	19	271	38	542
Heat Exchangers	27	128	51	241	78	369
Fuel Storage Frames	150	4,426	61	1,459	211	5,885
TOTAL	**423**	**8,073**	**354**	**4,999**	**277**	**13,072**

[1)] Represents displaced volume.

4.2.4 Radionuclide inventory

The bulk of the radioactivity produced in an operating nuclear reactor is basically of two types:

a) Induced radioactivity resulting from the activation of materials directly exposed to the neutron flux

b) Contamination of material surfaces by radioactivity arising from the fission process in the fuel

Most of the induced radioactivity generated during reactor operation resides in the activated waste component of the decommissioning waste inventory. Fission-product contamination of the surfaces of reactor components and systems during reactor operation gives rise to the generation of contaminated waste.

Based on a 30-year deferred dismantling scenario, the total radioactivity estimated for OPG's decommissioning waste is approximately 7.9 x10^{17} Bq. Prompt dismantling would result in a larger radionuclide inventory. The principal contributors to the radionuclide inventory include the activation products, such as ^{59}Ni, ^{63}Ni, ^{94}Nb, ^{14}C, ^{36}Cl, ^{93}Zr, ^{93}Mo, and ^{60}Co, produced in reactor core components by neutron irradiation (Table 3). It is the activated component of the waste that is the prime contributor to the total radionuclide inventory. Other contributors include the fission products and actinides, such as ^{137}Cs, ^{90}Sr, ^{99}Tc, ^{129}I, $^{239+240}$Pu, ^{241}Am, ^{237}Np, derived from fuel defect releases and deposited on PHT system metal surfaces. Estimates of total induced radioactivity in Pickering A&B decommissioning waste are provided in Table 4.

TABLE III. ACTIVATION PRODUCTS FROM NEUTRON ACTIVATION OF REACTOR CORE COMPONENTS[1)]

^{93}Zr ($t_{1/2}$ = 1.5x10^6 yr)	Produced in Zr alloys
^{36}Cl ($t_{1/2}$ = 3.0x10^5 yr)	Produced in Zr alloy pressure tubes and calandria tubes; also produced in high-density, concrete shields used at PN1-4
^{59}Ni ($t_{1/2}$ = 76,000 yr)	Produced in both mild and stainless steels and nickel alloys
^{94}Nb ($t_{1/2}$ = 20,000 yr)	Product of ^{93}Nb which is found mainly in the Zr-2.5%Nb alloy pressure tubes; also a fission product
^{14}C ($t_{1/2}$ = 5,730 yr)	Produced in steel and body of pressure tube from nitrogen impurity; can also form in the heat transport and moderator systems and in the annulus gas system between the pressure tubes and calandria tubes of CANDU reactors
^{93}Mo ($t_{1/2}$ = 3,500 yr)	Produced from ^{92}Mo in alloy steels
^{63}Ni ($t_{1/2}$ = 92 yr)	Produced in nickel-bearing alloys used in the heat transport and moderator systems
^{121m}Sn ($t_{1/2}$ = 50 yr)	Formed from tin, the major alloying element in the Zircaloy-2 calandria tubes
^{3}H ($t_{1/2}$ = 12.3 yr)	Produced from deuterium and from heavy water as DTO; may occur in both aqueous and vapour phases; can be absorbed in porous materials such as concrete; also produced by (n, a) reaction on lithium added to heat transport system for pH control
^{60}Co ($t_{1/2}$ = 5.3 yr)	Major contributor to radiation dose during Stage 1 and Stage 3 decommissioning
^{55}Fe ($t_{1/2}$ = 2.7 yr)	Produced in mild and stainless steel, especially in end shields, and primary heat transport and moderator systems and in the corrosion products formed in these systems.

[1)] Listed in order of decreasing half-lives.

TABLE IV. ESTIMATES OF TOTAL INDUCED RADIOACTIVITY IN PICKERING DECOMMISSIONING WASTE[1, 2, 3)]

Radionuclide	Half Life (yr)	Radioactivity (Bq)	Percent of the Total
^{14}C	5,730	1.40 x 10^{15}	2.64
^{36}Cl	3.0x10^5	2.95 x 10^{13}	0.06
^{55}Fe	2.7	7.60 x 10^{14}	1.45
^{59}Ni	80,000	2.92 x 10^{15}	5.55
^{60}Co	5.3	2.38 x 10^{16}	45.0
^{63}Ni	100	2.18 x 10^{16}	41.3
^{93}Zr	95,000	1.28 x 10^{14}	0.24
^{94}Nb	20,000	2.00 x 10^{15}	3.78
Total		**5.28 x 10^{16}**	**100.0**

[1)] ^{14}C and ^{36}Cl inventories include activity associated with vault concrete in Pickering A.

[2)] It is assumed that the units have operated for a full, 40-year period at a lifetime operating capacity factor of 80%, followed by a 30-year period of safe storage.

[3)] Because of the very high levels of ^{55}Fe and ^{60}Co present initially at the time of reactor shutdown, significant levels of both radionuclides are still expected to be present at the end of the safe-storage period.

4.2.5 Waste forms

The waste forms that are expected to result from the decommissioning of CANDU reactors and are important from a safety assessment point of view are summarized in Table 5.

Related information on the underlying processes governing waste form dissolution and radionuclide release is also presented.

TABLE V. IMPORTANT DECOMMISSIONING WASTE FORMS

Radionuclide	Waste Form	Release Mechanisms	Remarks
^{14}C	Zircaloy	Corrosion rate controlled, congruent release with net dissolution of matrix	Zr alloy reactor core components, pressure and calandria tubes
^{14}C	Reactor vault concrete (calcite is the host phase)	Solubility-controlled, congruent release determined by calcite dissolution	Bioshield concrete at Pickering A only
^{36}C	Reactor vault concrete (a chloroaluminosilicate is the host phase)	Congruent release controlled by dissolution of chloroaluminosilicate	Bioshield concrete at Pickering A only
^{36}C ^{93}Zr ^{94}Nb	Zircaloy	Corrosion rate controlled congruent release with net dissolution of matrix	Zr alloy reactor core components, pressure and calandria tubes
^{59}Ni	Stainless steel	Corrosion rate controlled, congruent release with net dissolution of matrix	End fittings, shield plugs, space liners, etc.
^{137}Cs $^{239+240}$Pu ^{241}Am	Surface deposits on pressure tubes, PHT system, out-core components, etc.	Instantaneous release - no credit given to dissolution properties of deposit materials	Fission products and actinides

4.2.6 Implications for the disposal of decommissioning waste

There are some important differences between the decommissioning waste and operational waste that are likely to have an impact on the design and safety assessment of a disposal facility.

(a) Design issues

Total waste inventories: Assuming co-disposal of decommissioning waste with operational waste, it is evident that the final disposal volumes will increase significantly. This has a direct impact on facility design in that the volume capacity will have to be increased significantly to accommodate both operational and decommissioning waste inventories.

Large-size Waste Packages: It is estimated that approximately 930 large-component, waste packages will be generated as a result of decommissioning all OPG nuclear stations. The disposal of these large-size, waste packages will require some modification of the current reference repository concept developed for the operational waste, in particular the design of the access ramps and tunnels, and disposal vaults.

Gas Generation: A key characteristic of the decommissioning waste, relative to the operational waste, is the predominantly large inventory of metallic constituents. The potential for the hydrogen gas generation from the corrosion of the metallic waste and subsequent gas build up needs to be taken into account in the repository design process to minimize the possibility of gas over-pressurization in the disposal vaults.

(b) Safety assessment issues

Gas Generation: As discussed above, the potential for hydrogen gas generation and subsequent pressure build up is an important consideration in assessing the performance of a repository, given that the metallic constituents in the decommissioning waste comprise a large fraction of the total waste inventory. In this regard, safety assessment calculations need to be carried out to address the impact of potential gas generation on repository safety, including radiological and flammability hazard.

Radionuclide Inventory: An important aspect of co-disposing decommissioning waste with operational waste is the significant increase in the total radionuclide inventory. It is estimated that the reference radionuclide inventory for operational LILW would increase by about two orders of magnitude, as a result of decommissioning waste. Thus, for OPG's planned LLW repository, the radionuclide inventory would be dominated by the decommissioning waste component of the total waste inventory. This raises an important issue with regard to the safety assessment for the disposal of decommissioning waste.

The other important consideration is that the inventories of long-lived, neutron activation products, such as ^{36}Cl, ^{63}Ni, ^{93}Zr, ^{94}Nb, etc, are significantly larger for decommissioning waste as compared to operational waste. In addition, the decommissioning waste would increase the reference inventories of ^{14}C and the actinides, based on operational waste, by ~100%. Thus, the much larger inventories of these critical radionuclides associated with the decommissioning waste would have a direct impact on repository safety over a long period.

The decommissioning waste forms that are important from a safety point of view consist primarily of activated metallic components. Thus, the waste form behaviour is likely to be governed by the corrosion of the metal matrix, hosting the activation products. Radionuclide release would be expected to be congruent, determined by the dissolution of the metal matrix.

4.3 Task 3 — gas generation

The importance of gas generation and its impact has been identified as a potential safety issue in several low and intermediate level radioactive waste programmes (12,13,14). Because of potential impacts on repository safety, a number of disposal programmes have established waste acceptance criteria, specific to the gas-generating metallic and organic waste constituents for their disposal facilities.

The objective of this study was to (a) identify the potential gas-generating constituents in OPG's low level waste and waste packages; (b) conduct scoping and bounding calculations to estimate inventory-specific production rates and cumulative volumes of the gases likely to be formed; and (c) assess the potential consequences of gas generation on repository performance and transport of radioactivity to the biosphere for the conceptual designs under consideration.

A summary of the results and discussion, based on two reports completed on the topic of gas generation in OPG's LLW (15,16), is presented below. Because of the many conservative assumptions made in the scoping calculations, the results should be considered preliminary in nature. The results provide a basis for identifying refinements that would improve understanding of the conceptual repository design, processes that operate within the repository, and either reduce the uncertainty or the degree of conservatism in the assumptions and analyses.

4.3.1 Corrosion-induced gas generation

The potential metal-based materials (iron, zinc, aluminium, alloys) that can undergo corrosion reactions in OPG's LLW and waste packages include metallic waste constituents (including incinerator ash), containers, and rebar in concrete. The basic corrosion reactions for iron considered in the study are as follows:

$4Fe + 3O_2$ ---------------------------> $2Fe_2O_3$ (1)

$3Fe + 4H_2O$ --------------------------> $Fe_3O_4 + 4H_2$ (2)

Based on Eq (2), under anaerobic conditions, iron corrosion yields H_2 gas. Using conservative estimates, Eq (2) was used to estimate hydrogen gas production in OPG's LLW and waste packages. Release of ^{3}H associated with hydrogen gas production was also assessed to establish the radiological consequences of gas generation.

4.3.2 Microbial gas generation

Cellulosic materials, such as paper, cloth, cotton, and wood, in LLW are the most susceptible to microbial attack. In contrast, non-cellulosic waste components, such as synthetic plastics and rubbers, exhibit generally high resistance to decomposition by microorganisms. In developing models for microbial gas production, most studies have focused on cellulose degradation under anaerobic conditions based on the following reaction:

$C_6H_{12}O_6$ -----------------------------> $3CO_2 + 3CH_4$ (3)

The above reaction, representing microbial degradation of organic waste materials, is considered realistic and representative of repository conditions because anaerobic conditions are likely to dominate in the repository during most of the post-closure period. Using conservative assumptions, Eq (3) was used to estimate the production of CH_4 and CO_2, taking into account the inventory of the organic waste constituents in OPG's LLW and assuming total consumption of the waste materials.

The results indicate that potentially significant amounts of hydrogen, carbon dioxide and methane could be produced from the organic and metallic components of OPG's LLW during the anaerobic, post-closure phase. Table 6 provides an estimate of the total volume of hydrogen gas that could be generated from the corrosion of steel associated with OPG's LLW and disposal containers. Based on conservative assumptions, the calculations indicate a potential for as much as $\sim 8.3 \times 10^6$ m^3 of hydrogen production from a total metal inventory of 15.53×10^6 kg in OPG's LLW (and disposal containers). Likewise, Table 7 shows estimates of CO_2 and CH_4 generation from the microbial degradation of organic constituents in OPG's LLW. A total volume of 2.3×10^7 m^3 of gas could be generated in OPG's LLW during the anaerobic, post-closure phase of the repository, with H_2 representing about 1/3 and CO_2+CH_4 about 2/3 of the total gas volume. Corrosion of metallic constituents is likely to be the dominant gas production process because it persists over much longer time periods.

4.3.3 Consequences of gas generation

Scoping and bounding calculations were performed to assess potential consequences of gas production and migration on repository performance, such as radiological hazard, fire hazard and pressure build-up in the repository that can have an adverse impact on repository performance. Potential release of radioactivity, specifically ^{14}C and ^{3}H, associated with the bulk gases CH_4, CO_2 and H_2 as $^{14}CH_4$, $^{14}CO_2$ and $^{3}H_2$, were estimated (Table 8). The results are summarized below:

Scoping calculations indicate that, for both hydrogen and methane, the maximum gas generation rates are below the critical inflow rates necessary to cause fire or explosion. If minimum gas generation rates were to be considered, which are about three orders of magnitude smaller than the conservative rates given above, then the critical inflow rates would be significantly lower than the corresponding gas generation rates. Given the highly conservative assumptions considered in calculating both the gas inflow rates and gas generation rates, it is unlikely that significant flammable concentrations of methane and/or hydrogen will be produced at the surface. Thus, methane and hydrogen gas production in OPG's LLW inventory is unlikely to pose a significant fire or explosion hazard in the biosphere.

Using conservative assumptions, the radiological consequences of prompt transfer of bulk gases containing ^{14}C and ^{3}H have been estimated in terms of the maximum annual doses associated with these volatile radionuclides.

The maximum and minimum annual doses to an individual, occupying the small, poorly-ventilated house, associated with waste containing ^{14}C and ^{3}H are predicted to be:

$^{14}CH_4$: max = $9.5x10^{-6}$ Sv/yr
min = $6.7x10^{-7}$ Sv/yr

^{3}HH: max = $5.7x10^{-6}$ Sv/yr
min = $1.6x10^{-8}$ Sv/yr

Comparison of the calculated annual dose to an individual with the AECB risk limit of 10^{-6} per year, corresponding to an annual dose of $2x10^{-5}$ Sv/yr, indicates that the radiological consequences are not significant. These calculations, especially the maximum annual dose estimates for maximum gas generation rates, are based on extremely conservative assumptions. For example, if one were to consider more realistic conditions for gas generation, transport and dispersion, then the radiological consequences arising from the disposal of ^{14}C and ^{3}H containing waste would be extremely small. Further work is needed to establish the degree of conservatism in these calculations and to estimate the maximum annual dose to an individual based on a more realistic scenario.

TABLE VI. TOTAL VOLUME OF HYDROGEN GENERATED FROM CORROSION OF STEEL IN WASTE AND CONTAINERS[1)]

Waste	Containers	Metal Inventory ($x10^6$kg)	Hydrogen Produced[2)] ($x10^6m^3$)	% of Total H_2 Generated
Compacted+ Non-Processible		5.44	2.90	34.98
	Ash	0.17	0.09	1.09
	Compacted	4.32	2.31	27.86
	Non-Processible	5.60	2.99	36.07
Total		**15.53**	**8.29**	**100.0**

[1)] A conversion factor of 0.5338 m^3 H_2/kg was used to estimate the volume of hydrogen generated from the corrosion of steel in the waste and containers; see reference for detailed circulations.

[2)] At STP.

TABLE VII. TOTAL VOLUMES OF CARBON DIOXIDE AND METHANE GENERATED FROM ORGANIC WASTES[1)]

Organic Waste	Mass ($x10^6$kg)	CO_2[2)] ($x10^6m^3$)	CH_4[2)] ($x10^6m^3$)	Combined Volume[2)] ($x10^6m^3$)
Cellulose[3)]	8.57	3.00	3.00	6.00
Plastics[4)]	12.65	4.43	4.43	8.86
Total	**21.22**	**7.43**	**7.43**	**14.86**

[1)] Estimates are based on an organic waste to gas conversion factor of 0.35 m^3/kg for both cellulosic materials and plastics (including rubber) at STP; detailed calculations are presented in an earlier report [15].

[2)] At STP

[3)] Includes paper, wood and cotton.

[4)] Includes rubber.

TABLE VIII. SUMMARY OF THE PRODUCTION AND DISTRIBUTION OF RADIOACTIVE GASES[1, 2)]

Radionuclide	CH_4	CO_2	H_2	Total
^{3}H (Bq)	-	-	$3.92x10^{14}$	$3.92x10^{14}$
^{14}C (Bq)	$4.33x10^{10}$	$4.33x10^{10}$	-	$8.66x10^{10}$

[1)] For organic wastes, ^{14}C is assumed to be distributed equally between methane and carbon dioxide; the tritium inventory is assumed to be associated only with the metallic component of the compacted and non-processible waste category; hence, all tritium is associated with corrosion-induced hydrogen gas and none is released as tritiated methane.

[2)] Tritium inventory is decay-corrected only to 2034, the time of repository closure.

CONCLUSIONS

- Immobilization of ^{14}C spent resin waste in a cementitious matrix results in a cemented waste form with ^{14}C incorporated in the calcite crystals embedded in the matrix. Leaching studies indicate that the release of ^{14}C can be attributed to the dissolution of calcite and that the groundwater flow regime can exert a pronounced effect both on the chemical environment and ^{14}C release.

- These findings have important implications in respect of ^{14}C isolation in a waste repository in the sense that the chemical buffering of the near field by cementitious materials will ensure extremely low solubility of calcite, thereby contributing to the retention of ^{14}C in the waste form for an extended period of time, irrespective of the physical integrity of the waste form.

- Estimated inventories and characteristics of potential LILW arisings from the decommissioning of OPG's 20 nuclear reactors indicates that there are some important differences between the decommissioning waste and operational waste that are likely to have an impact on the design and safety assessment of a disposal facility. The implication is that data on decommissioning waste needs to be taken into consideration in the initial design of a new repository.

- Scoping calculations to estimate corrosion-induced and microbially-mediated gas generation in OPG's LLW indicate that potentially significant amounts of hydrogen, carbon dioxide and methane could be produced from the organic and metallic constituents present in the waste during the anaerobic, post-closure phase. However, further calculations show that potential gas production would not have any adverse effect on repository performance in respect of pressure build up, an explosion or fire hazard, or any radiological consequences as a result of ^{14}C or H_3 gaseous release from the waste.

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SOLIDIFICATION OF LOW LEVEL RADIOACTIVE WASTE AT AECL'S CHALK RIVER LABORATORIES

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Abstract

AECL is planning to upgrade the system for solidification of liquid waste generated by operations at its Chalk River site. Diverse operations at the site, which include research reactor operations, isotope processing and hotcell facilities, give rise to a variety of aqueous liquid wastes. This paper describes the considerations that went into the development of design specifications for wasteform performance (waste matrix and container) for the upgraded system. A discussion of the key performance parameters for wasteforms, specific to operations waste at Chalk River, is given.

1. INTRODUCTION AND OBJECTIVES

AECL is planning to upgrade the liquid waste solidification system in the Waste Treatment Centre (WTC) at the Chalk River Laboratories (CRL). One of the first steps in 8 the upgrade project was to develop performance criteria for the solidification and packaging of waste solids that arise from the treatment of liquid wastes from the WTC.

The study (now completed) was primarily concerned with performance criteria that affect the long-term management of these wastes, namely long-term storage and disposal considerations. The present note provides a summary of this study and the likely path forward for the WTC upgrade project.

2. THE CURRENT WTC WASTE PRODUCT

The present system at the WTC produces a waste form that is a blend of liquid waste solids and distilled bitumen (about 35 wt% waste solids). Bituminized waste from the WTC is packaged in 200 litre galvanized steel drums and stored in concrete bunkers. A number of factors led to the decision to upgrade the WTC's solidification system. The distilled bitumen waste form has poor immersion resistance and is generally less leach resistant than oxidized bitumen and other solidification matrices. There are few standardized performance tests for bitumen-solidified wastes (Davis et al. 1992). Fire safety is also regarded as a concern for bitumen solidification systems (IAEA 1997, Nedderman 1997).

2.1 Waste package performance: Long-term management issues

Recent IAEA safety requirements (IAEA 2000a) state that the main purpose of processing radioactive waste is to produce a waste is to fulfill the acceptance requirements for disposal. The requirements for handling, transport and storage of waste packages should also be fulfilled. The companion lAEA Safety Guide (IAEA 2000b) recommends that if the acceptance requirements for disposal of LIL W do not exist, the operator should give thorough consideration to waste package compatibility with anticipated repository acceptance requirements, to provide reasonable assurance that conditioned LIL W can be accepted for disposal (IAEA 2000b).

Canada does not have any LLRW disposal facilities. Most of the wastes emplaced in storage at CRL will eventually have to be retrieved and moved to a disposal facility or containment facilities designed for very long-term storage.

Waste form and container performance specifications are generally derived from site-specific risk assessments of disposal facilities (i.e., site-specific waste acceptance criteria (WAC)) or are prescribed by the regulatory authority. Neither option can be implemented for the WTC wastes because there are no LLRW disposal facilities in Canada and the Canadian regulator (Canadian Nuclear Safety Commission or CNSC) does not prescribe waste form performance specifications.

In the absence of regulatory and site-specific guidance, waste form and container performance specifications are derived from the following considerations:

- A review of international classification systems for radioactive waste to provide guidance on likely disposal pathways for solidified WTC radioactive waste.

- The compositional envelope of WTC liquid waste solids derived from best available data.

- Physical and leach performance specifications for radionuclides obtained from the widely-used criteria developed in other states.

- Leach targets for non-radiological contaminants taken from US Environmental Protection Agency (EPA) limits for land disposal of hazardous waste.

- Selection of a container that has a service life commensurate with the anticipated waste storage period at CRL (factoring in *future* handling and off-site transportation of the wastes).

- Consideration of the benefits of solids loading versus volume reduction.

- Assessment of the potential impact of complexing agents and gas generation.

4.2 Composition of WTG wastes

The chemical composition of the waste stream is an important factor for selecting solidification and container technology. The main issues associated with waste composition are:

- Concentrations of toxic non-radiological contaminants, which can potentially pose a long-term hazard to humans and the environment.
- Constituents that will impact on the leaching performance of the waste form (complexing agents and soluble solids).
- Constituents that are potentially corrosive to containers and constituents that might chemically interfere with curing, strength and long-term durability of waste forms.

The WTC presently receives liquid LLR W arisings from reactor operations, R&D labs and isotope production facilities on the CRL site. In addition to these arisings, future arisings are expected to come from the processing of stored liquid wastes (i.e., historic tank wastes), processing of tank and rod bay sludges and secondary streams from the processing of liquid high-level wastes.

The solidified LLRW from the WTC, which generally average less than 400 Bq/g of long-lived alpha emitters, fall within the IAEA's short-lived LIL W class (IAEA 1994). Common inorganic cations and anions (e.g., Na+, N03-, S042-) are, on a mass fraction basis, the main non-radiological constituents in WTC liquid waste arisings. Organic complexing agents typically comprise 5 to 10 wt% of waste solids; the hazardous metal content of waste solids is on the order of 1 wt% or less.

From process knowledge, it is expected that the complexing agents in routine arisings are those that are readily biodegradable (oxalic acid, citric acid and nitrilotriacetic acid or NT A) because there have been systematic efforts at CRL to eliminate widespread use of EDT A, which is not readily biodegradable. The complexing agents in stored liquid wastes are almost entirely comprised of oxalate and citrate, both of which are readily biodegradable.

4.3 Waste form performance specifications

Waste form performance specifications can generally be categorized as physical or chemical properties. Physical properties include strength, permeability, durability and physical form; chemical properties most often measure the resistance of the wasteform to leaching. The two are linked because the chemical composition of the waste solids can greatly influence the physical properties of the solidified waste. Many of the physical properties important for waste acceptance at storage and disposal facilities are common to practically all storage and disposal facilities.

In the absence WAC or prescriptive Canadian standards for waste form performance, the waste form performance specifications put forward in the US Nuclear Regulatory Commission's *Technical Position on Waste Form, Revision* 1, *January* 1991 (hereafter referred to as TP) were chosen. The main waste form performance specifications in the TP are:

1. Solidified waste specimens should have compressive strengths of at least 60 psi.
2. The radionuclide leachability index of waste specimens, as calculated in accordance with ANS 16.1, should be greater than 6.0.
3. Waste specimens should maintain compressive strengths following immersion for a minimum period *of 90* days.
4. Waste samples from full-scale specimens should be destructively analyzed to ensure that the product produced is homogeneous.
5. No more than 0.5 percent *of* the waste volume should be free liquid.
6. Waste specimens should be resistant to thermal degradation (-40°C to +60°C).
7. Waste specimens should remain stable after being exposed in a radiation field equivalent to the maximum level *of* exposure expected.

8. Waste form specimens should be tested for resistance to biodegradation.

To address the long-term health and environmental impacts that are associated with the hazardous metals in WTC solidified LLRW, it was recommended that WTC solidified waste should meet the US EP A treatment standards for land disposal *of* hazardous wastes. In particular, the TCLP leach performance limits for hazardous metals listed in the EP A's Universal Treatment Standards (EPA 1994).

There is no general rule for acceptance *of* wastes containing complexing agents-concentration limits for complexing agents in LLRW found in WAC are very much site-specific. Cement is probably the preferred waste form for LLRW containing complexing agents (Vjmelka et al. 1991, Hummel 1993, Dicke and Smith 1993). The reason is that is that radionuclides complexed with chelating agents are displaced by calcium in the cement pore water; the displaced metals generally form insoluble metals hydroxides which are therefore immobile.

4.4 Waste solidification matrices

Publications dealing with the properties *of* solidified wastes number in the thousands (see, for example, Gilliam and Wiles 1996; Conner and Hoeffner 1998a,b; EP A 1999). The most widely used matrices for waste solidification are: cementitious matrices, thermoplastic polymers (bitumen, sulphur-polymer cement, polyethylene) and thermosetting polymers (vinyl ester styrene, polyester resins, epoxy resins). The qualitative advantages and disadvantages *of* common waste solidification matrices have been summarized in several reviews (IAEA 1989, Cowgill 1991).

Cementitious materials are by far the most common solidification matrix for aqueous wastes. Some *of* the reasons for this are:

1. The technology for cement solidification is not complex and materials are relatively inexpensive.
2. Ease of mixing lends itself to production of a homogeneous waste form.
3. The matrix is compatible with a wide range of aqueous wastes and inorganic sludges.
4. Many waste disposal facilities have concrete backfills, making cement waste forms very compatible with the backfill material.
5. The high pH chemical environment in cement is ideal for immobilizing heavy metals and many radionuclides because metal hydroxides are in general very insoluble (e.g., the transuranics).
6. There is more performance data available for cementitious waste forms than for any other type of waste form
7. There are standardized tests for product evaluation (i.e., strength tests, leaching tests, immersion tests, etc.).

This is unlikely to change anytime soon; a recent comprehensive study that examined alternatives to cement and glass for the solidification of radioactive and mixed wastes concluded that no individual matrix was sufficiently developed to qualify as an alternative to cement and glass matrices (Bleier 1997).

Considering the extensive development work and body of knowledge for cementitious binders, it was recommended that WTC solids will be solidified in a cementitious matrix. Many substances can potentially interfere with the setting and curing of solidified wastes (Trussell and Spence 1994). However, cements capable of solidifying wastes containing high concentrations of soluble salts such as sodium nitrate and sodium sulphate have been developed in recent years. These cements typically utilize materials such as blast furnace slag and silica fume to improve waste compatibility (IAEA 1993). Experience with cementitious binders for solidification of low-level mixed wastes indicates that for a wide range of waste solids, a waste loading of between 0.5 and 2.0 kg of waste solids per kg of dry binder generally produces an acceptable waste form (Gering and Schwendiman 1997). As mentioned previously, cementitious matrices are the preferred matrix when complexing agents are present.

To reduce the possibility of interferences, it was recommended that the waste solids loading should be well below maximum waste solids loading (i.e., waste loading should not compromise performance criteria such as compressive strength and leachability).

4.5 Container for WTC solidified wastes

As mentioned previously, it is anticipated that WTC solidified wastes will have a relatively long period of storage at CRL before emplacement in a disposal facility. Hence, the waste container should meet the following requirements:

1. Be sufficiently corrosion-resistant to guarantee waste containment during the storage period (internal corrosion is usually the critical factor). Loss of containment due to corrosion would require repackaging of wastes and unnecessary radiation exposure of workers (contrary to ALARA), and would increase the volume of waste.

2. Have the mechanical strength to permit stacking -for efficient use of storage and disposal space.

3. Satisfy Canadian regulations for off-site transport of radioactive materials (essentially lAEA Safety Series No.6, see Grant and McLellan (1998).

4. Be sufficiently durable to remain intact during future retrieval and transport from interim storage to disposal.

According to transport regulations, WTC solidified wastes would be classified as Low Specific Activity III (LSA-III) materials. The type of transportation container appropriate for LSA-III wastes is an Industrial Package Type 2 (1P-2) or Industrial Package Type 3 (1P-3) container. The IP-2 container is adequate if the waste shipment involves exclusively LSA-III solidified wastes, otherwise an 1P-3 container is required.

1P-2 and IP-3 containers are not generally designed for long-term corrosion resistance. Hence, to obtain the required long-term corrosion resistance, it was recommended that WTC wastes be packaged in High Integrity Containers (HICs). HICs are designed to provide 300 years of waste containment and to satisfy the transport requirements of a Type A container. They also provide for passive ventilation of any radio lytic gases that are generated.

3. SUMMARY AND CONCLUSIONS

It was recommended that the solidified waste (i.e., the waste form) should meet at least the strength and leachability requirements in the US NRC's Technical Position on Waste Form. For hazardous metals, the WTC solidified waste should meet UTS leach performance standards.

A cementitious binder was recommended for solidification ofWTC waste solids for resons described previously (cementitious binders are also effective for contaminant immobilization when the waste solids contain complexing agents).

No decision has yet been made whether liquid wastes should be pretreated to remove organic complexing agents, or whether there should just be a limit imposed on complexing agent loading (the organic complexing agents present the liquid wastes are readily biodegradable).

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LONG TERM BEHAVIOUR OF POLYETHYLENE HIGH INTEGRITY CONTAINERS UNDER REPOSITORY CONDITIONS

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Abstract

Polyethylene High Integrity Containers (HICs) were proposed in 1996 for disposal of spent ion-exchange resins and sludge from Nuclear Power Plant Dukovany. Although these containers have been utilized in the USA for low-level radioactive waste storage and disposal since 1983 and have provided a cost effective alternative to waste solidification, they are not licensed in the Czech Republic. The main aim of this project was therefore to prove the suitability of these containers for conditioning of radioactive ion-exchangers and sludge from NPP Dukovany. The unclear issue concerning the polyethylene HIC is its long-term stability under the effect of low dose rates of ionising radiation. The objectives of the project focused therefore mainly on acquiring a deeper knowledge of the long-term behaviour of polyethylene under the low dose rates of ionising radiation of repository conditions. The Differential Scanning Calorimetry (DSC) was chosen as the basic methodology for the evaluation of polyethylene samples properties irradiated by Co-60 at various dose rates, ranging from 8.5 to 8855 Gy/h up to 100 kGy. This method makes possible to quickly evaluate the change of polymers thermo-oxidation stability after irradiation. The gel fraction was determined according to ASTM standard D 2765. The diffusion coefficient was determined in a special static-diffusion cell consisting of two parts divided by the polyethylene foil. The density of polyethylene samples was measured using double weighing method in air and ethanol. It was found that the gel fraction of originally cross-linked high-density polyethylene significantly decreases both with increasing absorbed doses and decreasing dose rates of irradiation. It suggests that the scission of polymer chains is pronounced at low dose rates. The most interesting are the results from the measurements of thermo-oxidation stability of irradiated polyethylene that strongly suggest that even very low absorbed doses of ionising radiation up to 10 kGy can have a significant effect on polymers properties when irradiated at very low dose rates. A correlation of the results obtained in this study with the measurements of mechanical properties of irradiated polyethylene could further deepen our knowledge and further specify the possible lifetime of polymer materials used as the part of radioactive waste packages in the storage or repository conditions. Without this correlation it is not easy to specify with any degree of certainty the time of embrittlement of polyethylene containers in radioactive waste storage or disposal facilities and to confirm or deny the suitability of polyethylene containers for medium level radioactive waste disposal, but the results suggest that polyethylene high integrity containers are not suitable for disposal of wastes giving the total absorbed dose higher than 50 kGy.

1. INTRODUCTION

In the Czech Republic there are two Nuclear Power Plants. The Dukovany NPP is under operation since 1985 and NPP Temelin is in the state of commissioning. It is estimated that during the operation of both NPPs about 2500 m^3 of spent ion-exchangers and 1000 m^3 of sludge, now stored in tanks of volume 460 m^3, will be accumulated. Most of ion-exchangers used in NPP Dukovany for the purification of water from various streams are synthetic organic resins typically consisting of polystyrene crosslinked by divinylbenzene. Only about 1/10 of high activity ion-exchangers are coming from primary circuit, the other part of low activity ion-exchangers 9/10 is coming from secondary circuit of NPP. Sludge is a very heterogeneous material of non-standard composition.

The high integrity containers (HICs) for low and intermediate level radioactive wastes may be defined as any vessel, drum or box, made from metal, concrete, polymers or composite materials that provide containment not only during handling and transport but practically for the whole lifetime of repository, namely, until the radioactivity has not been decreased by decay to the acceptable level. Leaching of radionuclides from the HIC would be negligible as long as the HIC retained its integrity [1].

The NUHIC product line of polyethylene High Integrity Containers of TFC Nuclear (now of NUKEM Nuclear Technologies) was proposed in 1996 for disposal of radioactive spent ion-exchange resins and sludge from Nuclear Power Plant Dukovany as a cost effective alternative to waste solidification [2]. The containers with dewatered spent ion-exchangers or sludge were to be placed into the concrete vaults of Dukovany surface repository.

The suitability of polyethylene high integrity containers for storage and disposal of radioactive wastes was studied mainly at Brookhaven National Laboratory in USA [3 – 6]. It has been shown that adequate integrity will prevail for a period of at least 300 years, especially if a concrete overpack will be provided so as to limit axial loading and associated creep/buckling of the containers due to the dead weight of the overlying soil. Nevertheless, the strong dose rate effect on the change of polyethylene mechanical properties was observed. The dose rate effect has been also observed in the case of other polymer materials used for radioactive wastes conditioning. For example, French scientists observed recently a significant dose rate effect on the thermo-oxidation of bitumen [9]. A significant increase of radionuclides leaching was observed in the case of vinyl ester resin solidified radioactive waste with the decreasing dose rate [10].

Polyethylene is also widely used for solidification of low level and mixed wastes [7]. Its advantage is a very low porosity that results in excellent leaching characteristics in a comparison to concrete matrix. Another advantage of polyethylene over another polymer matrix — bitumen — is better mechanical properties under the same waste loading and no fire danger during the waste processing. In general, polymers, and polyethylene in particular, have an excellent resistance to chemical corrosion. Polyethylene resists practically to all common constituents of mixed radioactive wastes [8]. Its great disadvantage is, however, a high susceptibility to ionising radiation under certain conditions

The principal reactions of the effect of ionising radiation on polymers can be described as follows [9]:

$RH \rightarrow R^{\cdot} + H^{\cdot}$ (1)
$R\text{-}R \rightarrow 2\,R^{\cdot}$ (2)
$R^{\cdot} + {\sim}R^{\cdot} \rightarrow R\text{-}R$ (3)
$2R^{\cdot} \rightarrow R{=}R$ (4)
$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$ (5)
$RO_2^{\cdot} + {\sim}RH \rightarrow RO_2H + R^{\cdot}$ (6)
$ROOH \rightarrow {\sim}RO^{\cdot} + HO^{\cdot}$ (7)
$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$ (8)
$HO^{\cdot} + RH \rightarrow HOH + R^{\cdot}$ (9)
$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow R\text{-}CO\text{-}R + ROH + O_2$ (10)
$R\text{-}CO\text{-}R \rightarrow RCO^{\cdot} + R^{\cdot}$ (11)

During the irradiation of polymers free radicals are formed as intermediate species (Eq. 1 and 2). This leads to the formation of crosslinks (Eq. 3), formation of unsaturation (Eq 4) and the uptake of oxygen (Eq 5), and consequently the formation of hydroperoxides (Eq 6).

The hydroperoxides are not stable and decay under the formation of not stable oxygen bonds (Eq. 10) and to the scission of polymer chains (Eq.11) that results in a decrease of polyethylene molecular weight and a deterioration of mechanical properties, manifested mainly by polyethylene embrittlement.

Although the polyethylene high integrity containers have been used in the USA for low-level radioactive waste storage and disposal since 1983, they are not licensed in the Czech Republic. The main aim of this project was therefore to prove the suitability of these containers for conditioning of radioactive ion-exchangers and sludge from NPP Dukovany and to support the Czech Power Company (CEZ) in licensing these containers in the Czech Republic for disposal of radioactive waste at the surface disposal facility in Dukovany. Now, however, the cementation for Dukovany NPP and bitumenization for Temelin NPP are preferred technologies for conditioning ion-exchangers and sludge. With the change of priorities of CEZ, the objectives of the project slightly changed more towards acquiring a deeper knowledge on the long-term behaviour of polymer containers and polymer waste forms under the irradiation by low dose rates from radioactive wastes.

The knowledge of the long-term stability of polymer waste packages components in low-dose rates of ionising radiation is important for an estimate of waste packages lifetime in repository conditions, and consequently for performance assessments of those repositories.

2. EXPERIMENTAL

Polyethylene studied was material used for production of NUHIC Polyethylene HIC containers polyethylene Marlex CL-200. It is crosslinked high-density polyethylene, manufactured by the Phillips 66 Company, and prepared by rotational moulding. The polyethylene is crosslinked using peroxide to the gel fraction of 66 %.

The Differential Scanning Calorimetry (DSC) was chosen as the basic methodology for the evaluation of polyethylene samples properties irradiated by Co-60. This method makes possible to measure thermal properties of materials (melting and fusion points, crystallinity). and it can also quickly evaluate the change of polymers thermo-oxidation stability after irradiation. The principle of this ASTM method [11] is based on the fact that oxidation is highly exothermic reaction and the onset of oxidation is clearly visible on a DSC trace. The time to the extrapolated onset of the exothermic reaction, under isothermal conditions, is called the Oxidation Induction Period (OIT).

Samples of dimension 15 x 8 x 1 mm were cut from Marlex CL 200 and irradiated by ^{60}Co-gamma source in PE capsules at various dose rates ranging from 8,5 to 8855 Gy/h and various absorbed doses up to 100 kGy. After irradiation the samples were kept at 4 ^{o}C at darkness. Absorbed doses of gamma radiation were measured by alanin by means of EPR (ElectroParamagnetic Resonance) method.

The irradiated samples were then both nonisothermaly in the nitrogen atmosphere and isothermally in oxygen or air tested at different temperatures in DSC equipment (DSC 7 - Perkin Elmer and DSC 910/2100TA - DuPont and TA Instruments). The calibration of DSC were made by the measurements of melting points of In and Zn.

The nonisothermal measurements were made in the range from 10 ^{O}C to 160^{o}C. The oxidation induction period (OIT) were measured isothermally at 145 ^{O}C.

The scheme of irradiation arrangement and sample preparation for the determination of depth profile of oxidation is given in Figure 1.

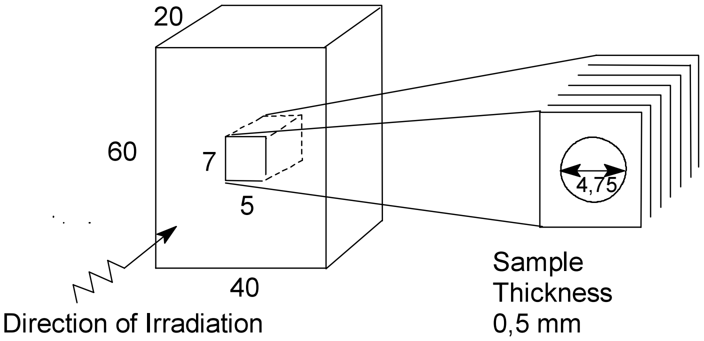

FIG. 1. Scheme of samples preparation. Before DSC measurements, the foils of 0,5 mm thickness were cut from the middle part of irradiated samples and from them the discs of 4,75. All dimensions on the picture are in mm.

Activation energy measurement — the determination of activation energy followed ASTM standard E 698. The samples were measured at DSC in nonisothermal regime at various scanning rates: 1,25; 2,5; 5; 10 a 20 °C/min. The oxygen flow was 50 ml/min.

Gel content measurement — the gel, i.e. insoluble, crosslinked part of polyethylene, was determined according to ASTM standard D 2765 after extraction with 15 ml of xylen with addition of antioxidant Irganox 1010. After extraction the samples were dried at vacuum oven at 110°C for 8 hours.

Diffusion coefficient measurement — the diffusion coefficient was determined on the foils of thickness 380 m in a special static-diffusion cell consisting of two parts divided by the polyethylene foil. Before the measurement the cell was evacuated and to the one part was injected oxygen under the pressure (p_i) of 125 kPa. The oxygen then diffuses to the second part of diffusion cell of the volume V_p. From the pressure increase $\Delta p_p/\Delta t$ with time, it was calculated permeability (P) according to the following equation:

$$P = \frac{\Delta p_p}{\Delta t} \cdot \frac{V_p l}{S p_i} \cdot \frac{1}{RT} \tag{11}$$

where l is thickness of PE foil, S area, T temperature of measurement (25 °C) a R is universal gas constant. From the time lag the diffusion coefficient was calculated according to the following equation:

$$D = {l^2}/{6 \cdot \tau} \tag{12}$$

***Density measurement** — the density of polyethylene samples was measured using double weighing method in air and ethanol using the following equation:*

$$\rho = (m_1 / m_1 - m_2) \times \rho_o \tag{13}$$

where m_1 is the weight in air, m_2 weight in ethanol and ρ_o is the density of ethanol.

3. RESULTS AND DISCUSSION

Estimates of cumulative doses to containers from ion-exchangers

The following assumptions were accepted to estimate the range of ionising radiation doses and dose rates from spent ion-exchange resins on polyethylene container walls:

The activity of ion-exchangers in HIC containers will reach the maximum values about 4 x 10^8 Bq/kg (80 % ^{137}Cs and 10 % ^{60}Co). The majority of short-term radionuclides such as ^{54}Mn, ^{134}Cs or ^{110m}Ag will decay in storage tanks. (The average ion-exchangers and sludge from NPP Dukovany, the composition of which is given in Table 1, does not reach the referenced activity.)

The height of HIC containers is 105 cm, radius 39 cm, and thickness 1–5 cm.

TABLE I. THE RADIOCHEMICAL COMPOSITION OF AVERAGE ION-EXCHANGERS AND SLUDGE FROM NPP DUKOVANY.

Isotope	sludge [Bq/kg]	ion-exchangers
Mn-54	3,18E+06	8,20E+06
Co-58	6,70E+04	4,72E+05
Co-60	1,83E+07	6,55E+06
Sb-124	3,00E+03	1,00E+04
Sb-125	8,00E+03	2,00E+04
Cs-134	3,11E+06	2,06E+07
Cs-137	1,24E+07	3,40E+07
Eu-152	8,00E+03	5,00E+03
Eu-154	3,00E+03	3,00E+03
Ag-110m	3,76E+05	2,20E+06
Ce-144		1,34E+05
Suma γ	3,76E+07	7,21E+07

The absorbed doses accumulated in polyethylene after given time of disposal for reference waste of activity 10^8 Bq/l are given in the Table 2.

TABLE II. THE ABSORBED DOSE AND DOSE RATE FOR REFERENCE WASTE OF γ ACTIVITY 4 X 10^8 BQ/KG.

Time [years]	Absorbed Dose [kGy]
10	14
30	21
60	24
100	26
300	27

The maximum absorbed dose should be about 27 kGy after 300 years. The dose rate is constantly decreasing. After 100 years the average dose rate is about 0,03 Gy/hr.

It is evident that it is not possible even to approach such low dose rates in experiments due to project time restrictions. The approach of polyethylene lifetime prediction was therefore based on an extrapolation from higher dose rates and higher total absorbed doses. For the first experiments we selected the total absorbed doses 10, 40, 50, 65, 70, 75 and 100 kGy and dose rates: 35, 150 and 1005 Gy/hr. The final experiment was then conducted at dose rate 8.5 Gy/hr.

The polyethylene changes after irradiation
a) Gel fraction

The polyethylene used for containers was crosslinked by peroxides, with the gel fraction, i.e. the crosslinked part of polyethylene, of unirradiated samples being about 66 %. The change of the gel fraction after irradiation in the form of relative values to unirradiated samples is shown in Fig. 2. It emerges that the gel fraction significantly decreases both with decreasing absorbed doses and dose rates. The less is the dose rate, the higher is the decrease of the gel fraction. It suggests that a decrease of gel content is the higher the lower is the dose rate. Almost no change of gel fraction was observed for the highest dose rate of 1050 Gy/hour.

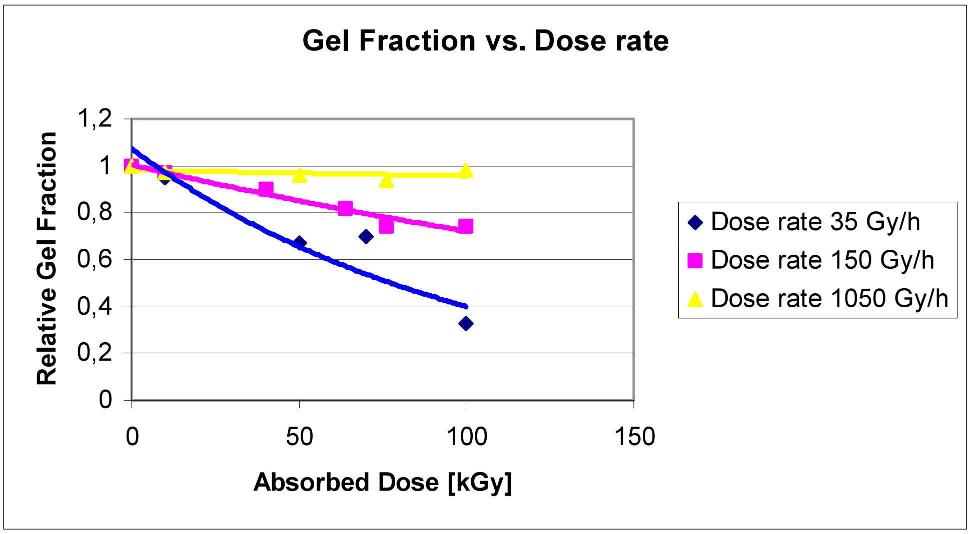

FIG 2. The gel fraction data *of irradiated samples.*

b) Melting points and heats of fusion

The samples after irradiation were melted, crystallised and again melted in DSC equipment. The results of the change of melting points and heats of fusion after the first and second DSC scan are given in the Table 3 and the change of heats of fusion in Figure 3.

TABLE III. THE CHANGE OF MELTING POINT OF HIC HDPE AFTER IRRADIATION (T_M AND H OF UNIRRADIATED SAMPLE 128.4 ^{O}C, 165 J/G)

	The melting points and heat of fusion of irradiated HDPE (°C)					
	Dose rate (kGy/h)					
	T_m (°C) 1st/2nd scan	H (J/g) 1st/2nd scan	T_m (°C) 1st/2nd scan	H (J/g) 1st/2nd scan	T_m (°C) 1st/2nd scan	H (J/g) 1st/2nd scan
The absorbed dose (kGy)	**1005 Gy/h**		150 Gy/h		3,5 Gy/h	
10	128.6/127.2	168.9/163	128.7/127.9	170.0/163.3	129.3/127.9	171.4/165.5
40			129.4/127.7	/170.9		
50	127.2/127	164.8/156,9			130.0/127.8	182.1/177.3
64			128.2/128.2	/163.5		
70					128.4/127.1	173.2/173
75	127.7/127.2	173.8/163,9	129.1/127.4	179.8/175.7		
100	128.5/127	171.9/160.7	128.4/127.2	179.0/172.8	129.4/127,1	183.2/177.1

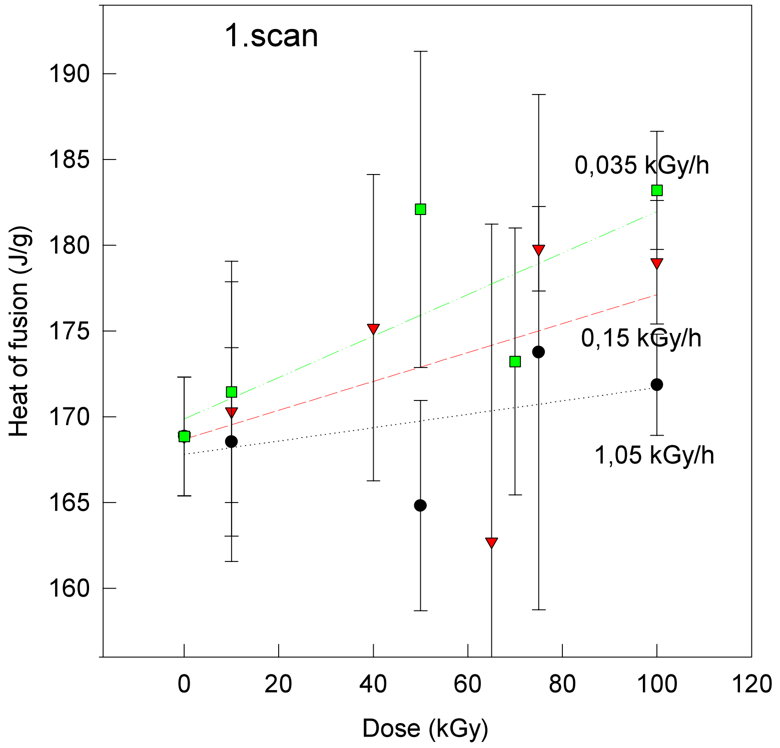

FIG. 3. The change of heat of fusion of irradiated polyethylene samples.

A slight increase of both melting points and heats of fusion with decreasing the dose rate and increasing the absorbed dose can be attributed to a slight increase of crystallinity resulted probably from the crystallization of chains scissioned during irradiation.

The DSC evaluation of thermo-oxidation stability of polyethylene irradiated by low dose rates

Irradiated samples were isothermally heated in the flowing air at DSC equipment in the way described above. Since oxidation is a highly exothermic reaction, onset of oxidation is clearly visible on a DSC trace. The time to the extrapolated onset of the exothermic reaction, under isothermal conditions, is called the induction period (OIT). Useful information can give also the time needed to achieve the maximum value of exothermic peak This ASTM method [12] enables to determine the oxidation stability of polyethylene and the possible lifetime of polymers.

The results from measurements of OIT at 145 ^{O}C are given in the following Table 4 and Figures 4 and 5.

TABLE IV. THE OXIDATION INDUCTION TIME OF IRRADIATED SAMPLES

	Oxidation induction time (min)		
	Dose rate (Gy/h)		
The absorbed dose (kGy)	1050	150	35
0	171.8		
10	139.1 ± 28,7	103.5 ± 7.7	104.0 ± 4.6
40	-	78.0 ± 15.4	-
50	101.1 ± 16.1	-	55.0 ± 7.7
65	-	60.3 ± 4.9	-
70			44.3 ± 1.9
75	115.8 ± 21.7	63.8 ± 7.5	-
100	86.5 ± 17.1	57.9 ± 6.6	43.8 ± 3.6

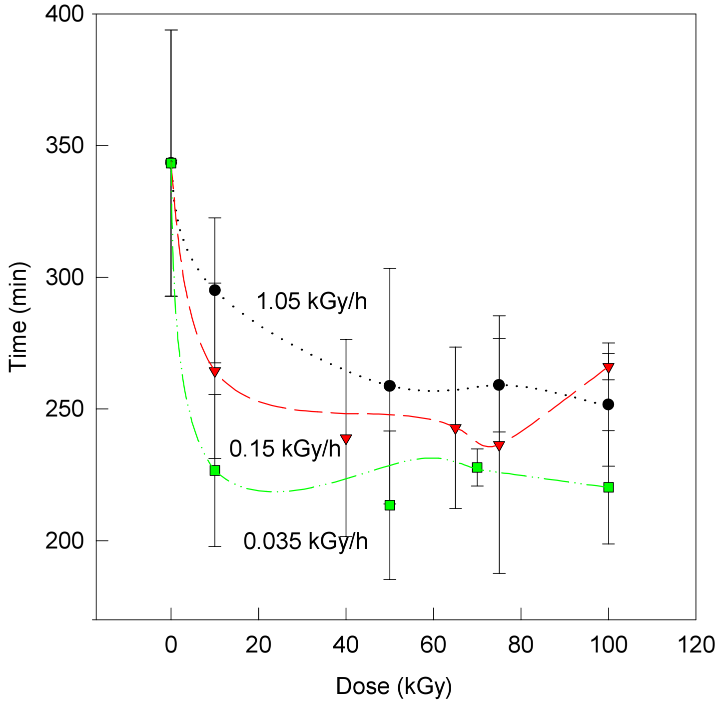

FIG. 4. The change of OIT with absorbed dose.

It is evident that the irradiation has an apparent effect on the start of polyethylene oxidation for all samples. This can be explained by the consumption of antioxidants, usually added to polyethylene, during heating in the treatment process (here rotational moulding). Oxidation rate increases both with the total absorbed dose and with decreasing dose rate of gamma radiation.

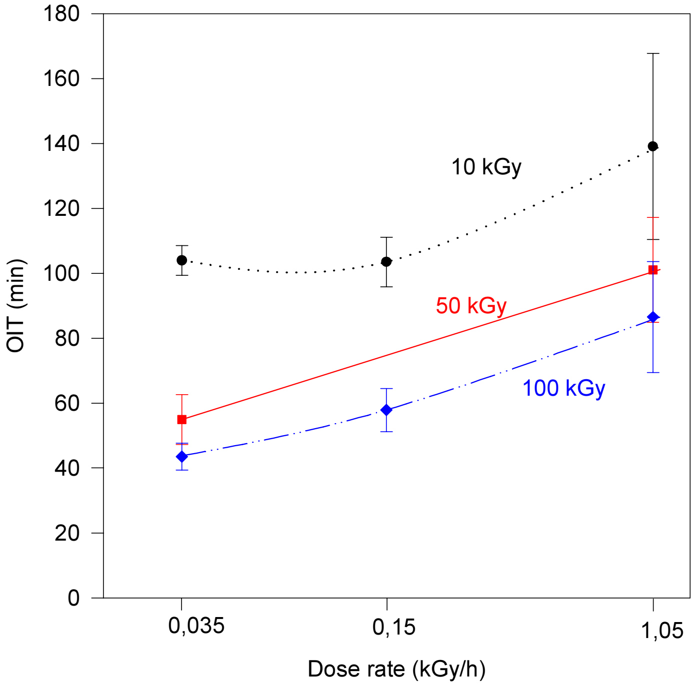

FIG. 5. The dependence of OIT on dose rate.

It is obvious that the reaction of free radicals formed during irradiation with oxygen (Eq.5) causes the change of polyethylene properties during irradiation. The rate of this reaction depends on the availability of oxygen and the availability of free radicals to react with oxygen. The rate of the consumption of oxygen is determined by the concentration of free radicals present in the reaction zone and the concentration of oxygen in this reaction zone. It is known that the concentration of oxygen in the surface layers (amorphous) is given by the value of oxygen solubility in polyethylene (7 x 10^{-7} mol cm^{-3}) [12]. The real concentration of oxygen in deeper layers of polyethylene depends therefore on the rate of oxygen diffusion and the rate of free radicals diffusion. The diffusion of oxygen was measured using method described above in experimental part. It was found that the diffusion coefficient of studied polyethylene has a value of about 8.8 x 10^{-11} m^2/s corresponding to the permeability 9.7 x 10^{-16} mol/(m.s.Pa).

The results of Oxidation Induction Time (OIT) in various layers of polyethylene samples of thickness 20 mm (depth profile), irradiated at dose rates of 38,2; 93,9 and 8550 Gy/h in the way described in Figure 1, are given in Figures 6 and 7. It is clear, despite the significant dispersion of data, caused by unhomogeneity of supplied material, that the dose rate has a great effect on the thermo-oxidation stability of irradiated samples. It can be seen that both for unirradiated and irradiated samples the thermo-oxidation stability is lower at the surface layers (till about 2 to 5 mm) than in bulk material. This is the probably the result of the surface degradation of the material during container manufacture. In the other part of samples the thermo-oxidation stability is not changing significantly with the distance from the surface. This suggests that the diffusion of oxygen does not play an important role in this process even at the highest used dose rate of 8550 Gy/h in the oxygen environment. Probably it is the question of availability of free radicals that must also diffuse to the reaction zone to react with oxygen. Since at high dose rates the free radicals do not have time to react with the oxygen, they react with other free radicals under the formation of cross-links or unsaturation.

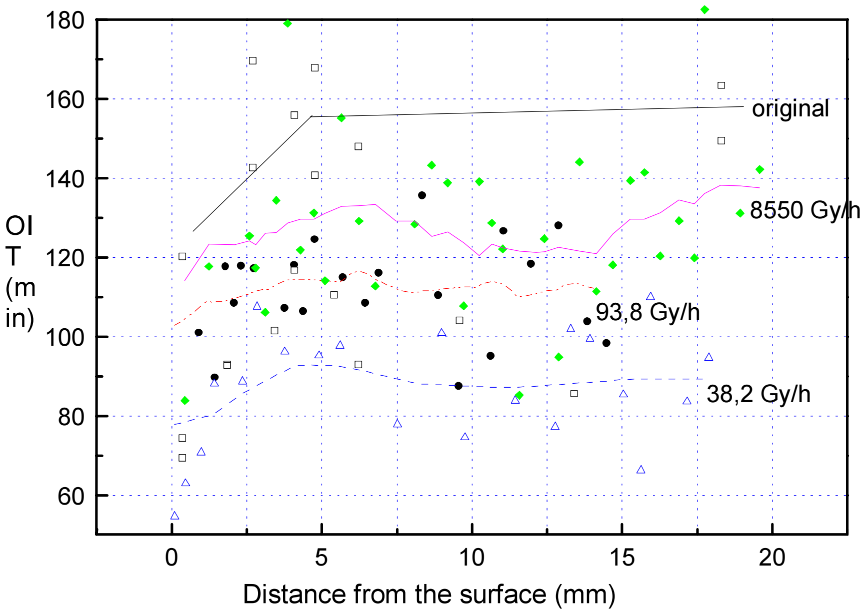

FIG. 6. The OIT data as a function of the distance from the sample surface
- unirradiated, ♦ - 8550 Gy/h, • - 93,8 Gy/h, Δ - 38,2 Gy/h.

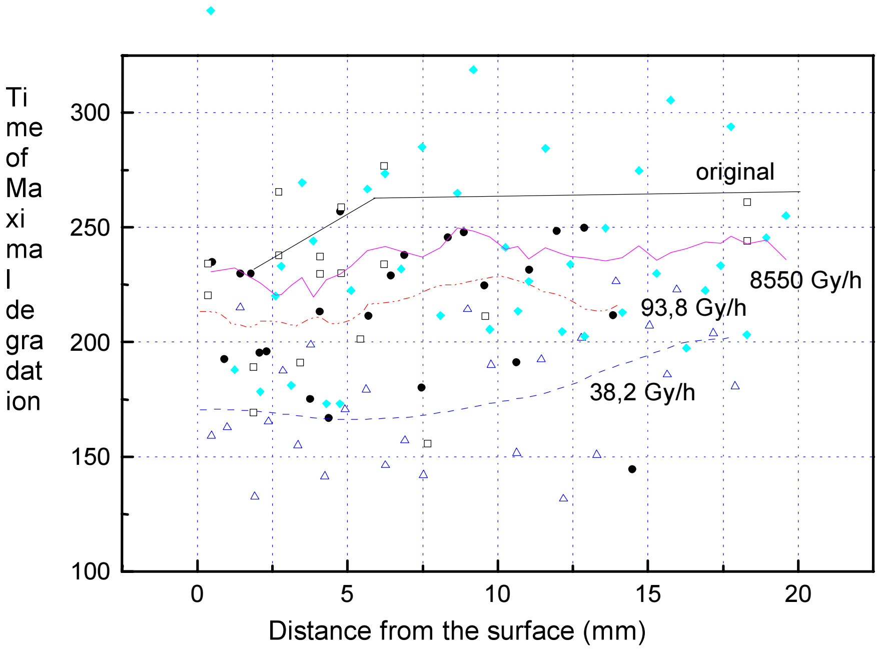

FIG. 7. The time to the maximal value of DSC peak as a function of the distance from the sample surface.

Δ 38,2 Gy/h, - unirradiated, ♦ - 8550 Gy/h, ● - 93,8 Gy/h

Irradiation at very low dose rates

To resolve the uncertainty of previous experiments, we irradiated polyethylene samples at the very low dose rate of 8.5 kGy both in air and nitrogen atmosphere. The irradiation to the absorbed dose of 26 kGy took up 3180 hours. The samples were in this experiment cut from the inside of the original 2 cm thick sample to avoid the surface layers damaged by heating during polyethylene manufacture. The DSC and density measurements were performed. Unfortunately, all DSC measurements were performed instead of 145 °C as previous samples at the temperature of 152 °C. The results of OIT at 145°C and the time to reach the maximum value of DSC peak of irradiated samples are given in the following Table 5 and Fig. 8.

TABLE 5: THE RESULTS OF THERMO-OXIDATION STABILITY OF POLYETHYLENE IRRADIATED AT LOW DOSE RATE IN AIR AND NITROGEN

Atmosphere during irradiation		Absorbed dose [kGy]			
		0	8.4	18.0	26
Air	OIT [min]	77.5 ±15.6	40.0 ± 9,8	30.7±14.5	22.7±6.8
	Max. peak [min]	171.7±28	112.9±32.9	132±31.8	81.3±9.8
Nitrogen	OIT [min]	77.5±15.6	40±8.4	31.8±5.9	35.1±4.8
	Max. peak [min]	171.7±28	126.7±27.7	130.0±31.8	121.0±12

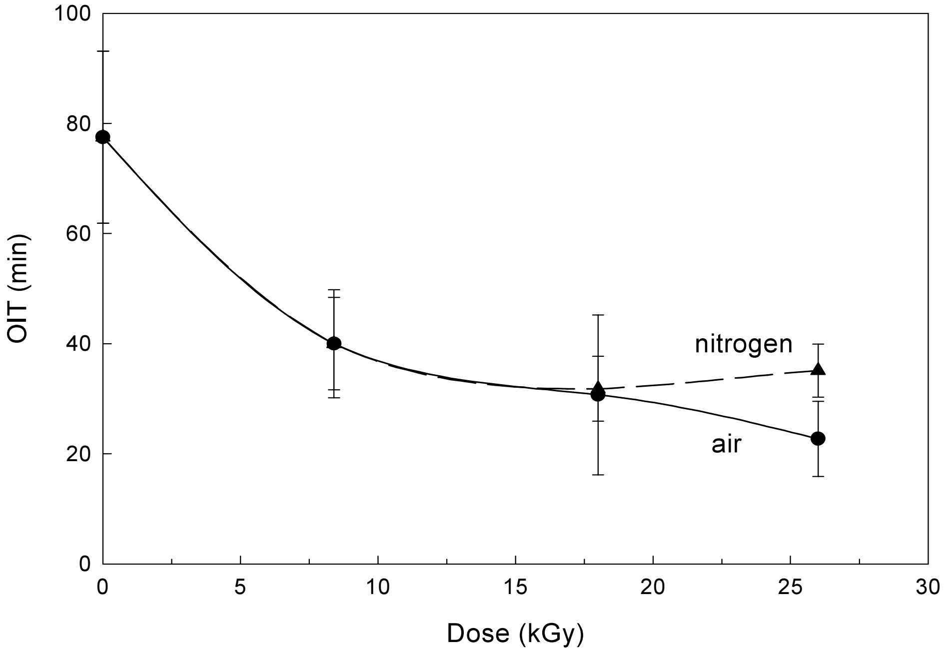

FIG. 8. A comparison of the change of oit of polyethylene after irradiation in air and nitrogen.

A comparison of the change of density of samples irradiated in air and nitrogen is then given in Figure 9.

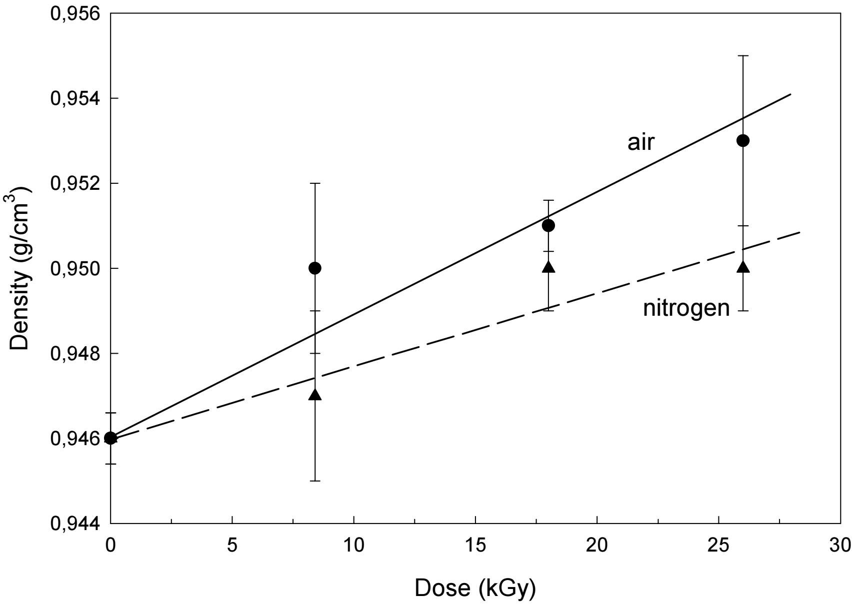

FIG. 9. The change of density after irradiation of polyethylene at dose rate of 8.5 Gy/hr.

It is evident that the atmosphere of irradiation has an effect on the change of polyethylene properties after irradiation. It can be seen more from the change of density than from the change of thermo-oxidation stability. The density is increasing due to uptake of oxygen in the polyethylene structure. As regards the difference between thermo-oxidation stability of samples irradiated in nitrogen and air, it is surprisingly lower than we expected. Until the dose of 18 kGy it is not evident any difference. This may be caused by the fact that before irradiation the samples were not evacuated to remove the oxygen trapped in the samples. Probably even small amount of oxygen can cause a dramatic decrease of polyethylene stability. This result also confirms our hypothesis given above that it is not diffusion of oxygen in polyethylene but the diffusion of free radicals from crystalline parts of polyethylene to the amorphous reaction zone that contributes to the effect of a decrease of polyethylene thermo-oxidation stability with the dose rate.

Activation Energy Determination and Polyethylene Lifetime Prediction

The rate of oxidation k is related to the temperature according to the well-known Arrhenius equation:

$$k = Ae^{-E/RT} \qquad (14)$$

The activation energy E was calculated using DSC according to the method described in the experimental part of this paper. The results are given in the following Table 6.

TABLE VI. THE DSC DATA FOR VARIOUS SCANNING RATES

Scanning rate (K/min)	**The temperature of the start of thermo-oxidation (°C)**	**Temperature of maximal peak (°C)**
20	214.52; 215.63; 220.62; 215.61; 218.38	238.40; 237.50; 245.48 238.54; 238.85;
10	207.77; 208.12; 211.37; 211.40; 209.90; 207.15;	219.20; 226.19; 225.94 224.53; 225.08;
5	196.12; 199.99; 195.53; 201.29; 195.58;	214.44; 214.13; 210.63; 213.95
2,5	191.70; 192.78; 185.96; 191.32; 185.75;	203; 202; 207; 206.1
1,25	180.96; 182.47; 183.61; 174.39; 181.18	196.50; 194.40; 193.50; 200.89; 201.74;
Activation Energy (eV)	1.29 ± 0,13	**1.23 ± 0,13**

The value of 1.23 eV corresponds to the value of 118.4 kJ/mol. The value of the rate of polyethylene oxidation k_{20} at normal temperature is in inverse relation to OIT (k_{20}/k_{145} = OIT_{145}/ OIT_{2O}). Using this relation it is possible to estimate the lifetime of polyethylene, i.e. the time to the induction of rapid oxidation, of an irradiated polyethylene at repository temperatures.

The results of the OIT values, recalculated to the temperature of 20 ^{o}C from all experiments, are given in Fig. 10. It is evident that the thermo-oxidation stability of polyethylene is greatly affected by a dose rate decrease. The absorbed dose of 10 kGy at dose rate of 8.5 Gy/hr is equivalent to the doses higher than 100 kGy when irradiated at dose rates about 1000 Gy/hr.

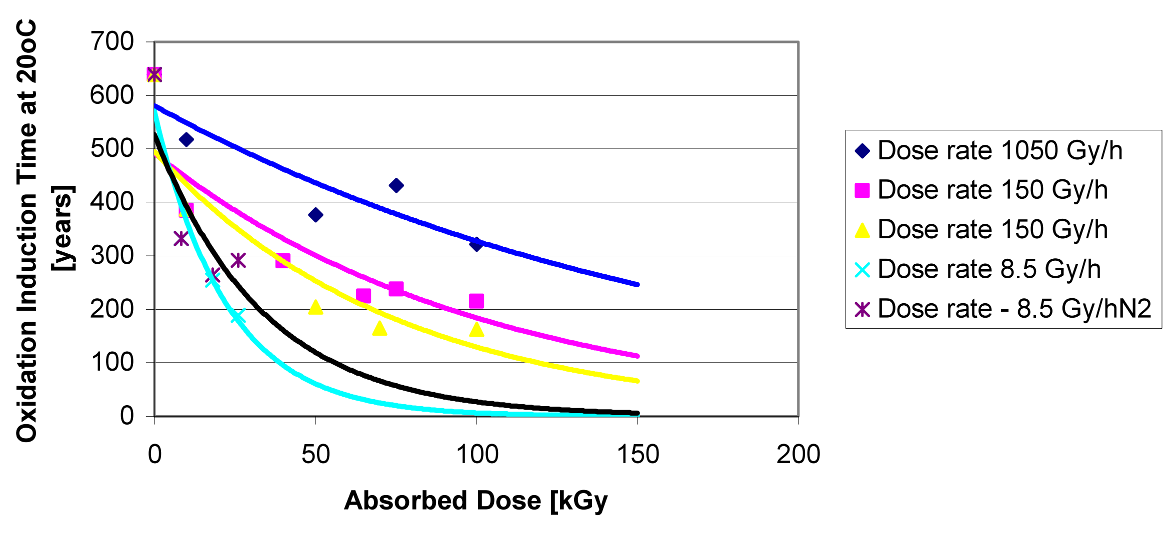

FIG. 10. Predicted effects of the dose rate on the decrease of oxidation induction time at 20 °C.

Despite the rather large scatter of data caused mainly by the significant heterogeneity of samples taken from the part of commercially prepared product, the results are convincing enough to say that the thermo-oxidation stability of polyethylene will be strongly decreased during the first years of irradiation from the radioactive waste giving the total absorbed doses in the range of tens of kGy. The temperatures about 20 °C can fully then finish the degradation of polyethylene after irradiation.

Due to large uncertainty, only very rough prediction of polyethylene under repository conditions can be made. We can assume that the total value of 27 kGy (Table 2) from ion-exchange resins will be accumulated just in the first years after disposal by the slowest dose rate of radiation (Tab.1). The time to the beginning of rapid oxidation is then in the range of 100 to 200 years. It is clear that thick polyethylene walls will not be destruct immediately, so that the ion-exchange resins of average activity 4 x 10^8 Bq/kg, giving the total absorbed dose about 27 kGy, can meet the requirements of 300 hundred years integrity after repository closure. We cannot, however, recommend the use of polyethylene containers of higher activity. The dose slightly exceeding 50 kGy absorbed by slow dose rate can fully destroy thermo-oxidation stability of polyethylene leading to the loss of containers integrity before usual 300 hundreds years limit.

4. CONCLUSIONS

This work helped to understand polymers behaviour under low dose rates of irradiation. The results obtained in this study strongly suggest that even very low absorbed doses of ionising radiation up to 10 kGy can have a significant effect on polymers properties when irradiated at very low dose rates. It was found that the thermo-oxidation stability of polyethylene was greatly decreased by doses below 10 kGy during irradiation at the dose rate 8.5 Gy/hr. This dose is equivalent to doses higher than 100 kGy when irradiated at dose rates about 1000 Gy/hr.

The absorbed doses leading to the destruction of polyethylene chains irradiated at low dose rates are in the range of the absorbed doses that can be accumulated in polyethylene containers from radioactive spent ion-exchange resins and sludge.

A correlation of the results obtained in this study with the measurements of mechanical properties of irradiated polyethylene could further deepen our knowledge and further specify the possible lifetime of polyethylene HICs under the low dose rate radiation of radioactive wastes. Also the use of specially prepared homogeneous polyethylene samples for experiments would greatly help to decrease the uncertainty related to the results. The necessity of a very long time to irradiate samples at a very low dose rate; however, prevent us to repeat these experiments with such samples. Without this it is not easy to specify with any degree of certainty the time of embrittlement of polyethylene containers in radioactive waste storage or disposal facilities and to confirm or deny the suitability of polyethylene containers for medium level radioactive waste disposal, but the results suggest that polyethylene high integrity containers are not suitable for disposal of wastes giving the total absorbed dose higher than 50 kGy.

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BEHAVIOUR OF BITUMINIZED ION-EXCHANGERS UNDER REPOSITORY CONDITIONS

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Abstract

This is a final report containing all the research activities and results from the period 13 July 1997–28 February 2001. The purpose of the research was to study the ageing behaviour of bituminized ion-exchanger product under simulated repository conditions. The chosen temperature in this study was 5–8°C and the equilibration solution used was artificial concrete water to simulate the conditions in the final disposal. The aim was to study the properties of wetted product as a release barrier for such important waste nuclides as Sr-90 and Cs-137, which are normal constituents of the bituminized ion-exchangers. All the nine exchanged waters were analysed by ion chromatography (IC) including the follow-up of the water absorption of the samples. All the samples, which were picked up for microscopic examination, have also been analysed. A saturation-elution test was performed with one diffusion sample using tritium (H-3) as a tracer. The results have been presented and further modelling will be performed later. Further two diffusion samples were tested using H-3, Na-22 and Cl-36 as radioactive tracers. The equilibration solution was artificial concrete ground water spiked with H-3 and Na-22 and in the other case with H-3 and Cl-36. Tritium was an internal reference when comparing the results of the equilibration behaviour of Na-22 and Cl-36. From the radioactive input cells samples were taken as a function of time to monitor the equilibration process. Elution of the samples and modelling of the results will be performed later. Na-22 and Cl-36 were chosen to demonstrate the behaviour of a simple anion and cation. Diffusion tests with important waste nuclides Sr-90 and Cs-137 have been scheduled to years 2001-2002. The aim of the performed research project was to study the barrier properties of the bituminized product. The measured parameters and modelling of the results will reflect the behaviour of the wetted product as a part of the multibarrier system providing input data for safety analysis.

1. INTRODUCTION

Approach of the studies has all along been experimental. Both real and simulated bituminized products have been studied. The main emphases have been put on long term leach testing, water absorption and swelling. The rewetting of the resin will increase the volume by 30 %, which is already taken into account in the void volume of the concrete container. Other topics have been the segregation of the granular ion-exchange particles due to density differences during the cooling period, corrosion of the steel drums, fire and impact testing of whole drums and radiolytic swelling. Long-term tests on the interaction of water and bituminized ion-exchange resin products [1,2,3,4] have been underway for about 19 years and are still continuing. In these long-term studies, the laboratory-size product samples made of granular ion-exchange resin have taken up amounts of water, which exceed the absorption capacity of the rewetting ion exchangers. The samples still continue to swell without levelling-off, which indicates void structure formation. Rewetting of bitumen ion-exchanger mixture is a diffusion-like process in the case of properly mixed products without voids.

However, in real bituminized ion-exchange resin product, all resin particles are not completely isolated by intact layers of bitumen, but are in contact with each other. The possible voids in the product thus form a complicated labyrinth for radionuclide migration.

The purpose of the research was to study the ageing behaviour of bituminized ion-exchanger product under simulated repository conditions. Normal leach tests are not adequate for assessment of long-term barrier properties of the product. Most leach test and water absorption tests have been performed at room temperature. However, the rate of water uptake and swelling has been found to be much faster at low temperatures [5]. The chosen temperature in this study was 5–8°C and the equilibration solution used was artificial concrete water to simulate the conditions in the final disposal. One of the aims was to study the wetting process of the product in microscale. By microscopic examination it was possible to gain more information about the behaviour of bituminized ion-exchange product as a function of time. This method offered a possibility to determine visually the velocity of the wetting front, the structural changes due to the wetting process and to find out the possible reaction mechanism. Simultaneously with the wetting of microscopic samples there were also in the same artificial concrete water identical samples for diffusion experiments. The aim of this work is to study the properties of wetted product as a release barrier for such important waste nuclides as Sr-90 and Cs-137, which are normal constituents of the bituminized ion-exchangers. Because the half-lives of these nuclides are about 30 years it would be beneficial for the safety analysis if a retardation effect could be counted on the wetted bituminization product.

According to the safety analysis of the repository for low and intermediate level wastes at Olikiluoto, following radionuclides in bituminized ion-exchange resin products were important: Sr-90, I-129, C-14, Ni-59, Tc-99, Cs-135, Pu-239 and Pu-240. The aim of this work is to study the properties of wetted product as a release barrier for such important waste nuclides as Sr-90 and Cs-137. Because the half-lives of these nuclides are about 30 years it would be beneficial for the safety analysis if a retardation effect could be counted on the wetted bituminization product. In the current safety analysis the age of a drum is supposed to be about 500 years and after that all the activities of the bituminized ion-exchangers will be released into the concrete container. Results of the diffusion tests will reflect the behaviour of the wetted product as a part of multibarrier system providing input data for safety analysis.

2. EXPERIMENTAL

2.1. Preparation of specimens

In the preparation of the test specimens for the diffusion experiment, a mixture of ratio 1:1 bitumen and dried ion-exchangers was used. The casting temperature was about 140°C. The mixture was cast in a specimen holder (od. 52 mm, id. 40 mm and height 40 mm). At the bottom of the holder a Teflon plug ensured the centred positioning of the cast sample. The thickness of the specimen was about 20 mm when a portion of 30 g of mixture was used. The specimen holder was planned such that the sample was in the centre and there was a space of 10 mm in both ends of the sleeve for swelling. The chosen wall thickness of the sleeve was 6 mm, so that after the wetting period the sample holder could be directly connected to end plates made of PVC. For the tightening of the junctions o-rings were used. These end plates were used when constructing diffusion cells for the diffusion tests. A cross-section of the specimen holder is presented in Figure 1.

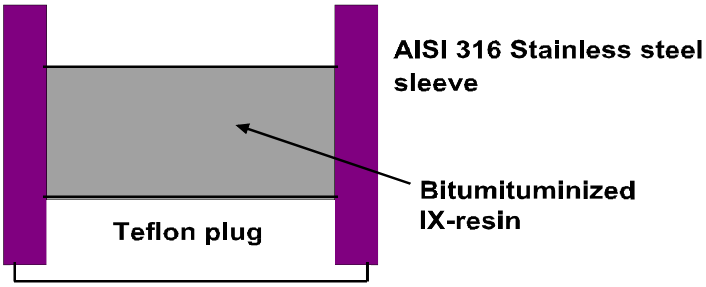

FIG. 1. A cross-section of the sample holder.

For the diffusion experiments, 20 specimens have been prepared by this method. In the preparation of microscopic specimens sample holders were identical except the wall thickness. Because the sample holders must be opened after certain period of wetting, the wall thickness is only 1 mm. The sleeve material is the same as for the diffusion sample holders and the bituminized ion-exchanger mixture used for casting had the identical composition as mentioned above. By this method 30 specimens have been prepared for microscopic examination.

2.2. Equilibration conditions

The equilibration temperature was 5–8°C and the equilibration solution used was an artificial concrete ground water to simulate the conditions in the silo. The composition of the simulated ground water is presented in Table 1. In Table 2 there are presented calculated ion concentrations and pH value in the artificial concrete groundwater.

TABLE I. CHEMICAL COMPOSITION OF THE ARTIFICIAL GROUNDWATER

Chemical	mg/L
Na_2SO_4	73.94
NaCl	264.07
$Ca(OH)_2$	739.47
KCl	62.68
KOH	24.58

TABLE II. CALCULATED ION CONCENTRATIONS AND THE PH VALUE IN THE ARTIFICIAL GROUNDWATER.

Ion	mg/L
Na^+	127.82
K^+	50.00
Ca^{++}	400.00
Cl^-	190.00
OH^-	346.92
SO_4^{--}	50.00
pH	12.31

Artificial concrete groundwater was prepared by adding the chemicals to CO_2 free distilled water in a small plastic barrel. To prevent the interaction between the equilibration solution and atmospheric CO_2, two valves were installed on the lid and thus it was possible to arrange nitrogen flow through the solution over night. Following morning all the specimens were piled to the bottom of the barrel. The lid was closed tightly and the nitrogen flow was connected on again. After four hours the nitrogen flow was disconnected and the small barrel was placed into a larger barrel. Between these barrel walls NaOH solution (1%) was poured. The lid of the larger plastic barrel was closed and through the two valves on the lid the space between barrels could be purged with nitrogen. After that the tight, closed, nitrogen purged barrel system was placed to an icebox where the temperature in this test was 5–8^{o}C. The barrel system is presented schematically as a cross-section in Figure 2.

FIG. 2. Wetting barrel system for the bituminized ion-exchange resin specimens to isolate atmospheric CO_2 from the artificial groundwater.

The rate of water uptake and swelling has been found to be much faster at low temperatures than at room temperature [5]. A plausible explanation is cracking of the matrix due to the brittleness of bitumen at low temperatures. Water absorption of the specimen was followed-up regularly during the wetting period. Simultaneously with the wetting of diffusion samples, there are in the same barrel identical samples for microscopic examination. Their water absorption was also followed-up regularly, simultaneously with the diffusion samples. From these samples three were picked up at a time for microscopic examination.

2.3. Microscopic examination

Using a stereo microscope of type Wild M8 microscopic examination of the bituminized ion-exchange samples has been performed. The magnification required ranges from 10 to 100. The equipment was provided with a camera adapter for documentation. A cold light source (150W) was used for illumination of the samples. By this way it was possible to avoid extra heating of the samples. Preparation of a sample for microscopic examination was done by cutting open the sleeve axially. Before cutting the test specimen was kept in an icebox over night. The broken surface of the sample was suitable for microscopic examination. Cylindrical specimens were split into two parts through the central axis. In a case of a series of samples as a function of time, it is possible to determine the velocity of the wetting front, changes in the structure, and to obtain more information about the reaction mechanisms involved.

3. RESULTS AND DISCUSSION

3.1. Water absorption

Nine water exchanges has been performed and the water samples have been analysed. The water absorption of some samples is presented as an example in Figures 3 and 4 in percentage units.

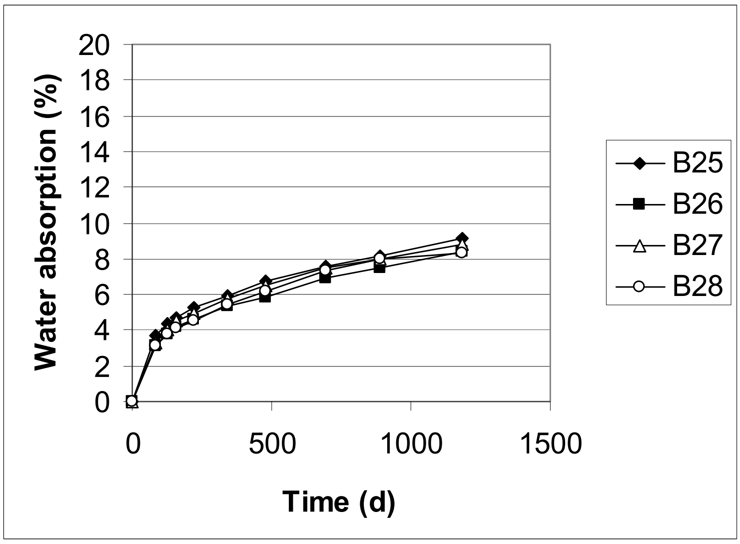

FIG. 3. Water absorption of some samples for microscopic examination as a function of time.

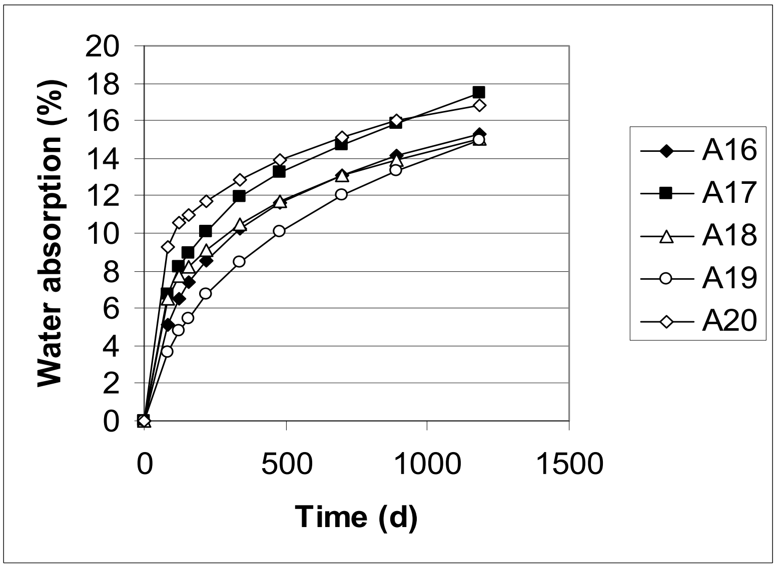

FIG. 4. Water absorption of some diffusion samples as a function of time.

The difference between these two sample series can be explained by intake of atmospheric humidity during the storage period prior to start of the equilibration. The diffusion samples were prepared 6 months before the start of the equilibration, whereas the samples for microscopic examination were prepared only a couple of days before. This means that the diffusion samples have absorbed water from air about 5 % during the storage.

3.2. Chemical analysis

Old and new equilibration solutions were analysed by ion chromatography (IC). Following ions were analysed: Na^+, K^+, and Ca^{++}, from cations and Cl^- and SO_4^{--} from anions. In connection of water exchanges pH values of all solutions were measured. All the determined ion concentrations are presented in Figure 5.

When comparing the determined values with calculated ones we can see that in the first water exchange concentrations of cations are decreased. The reason is that just in the beginning of equilibration, the cation exchange resin has still free capacity and it binds plenty of cations and donates equivalent amount protons to the solution. This means that the pH of the old solution will decrease. Also in some cases the sulphate concentrations were higher than expected. It seems that the sulphonic acid group, which is a functional group in the used cation exchanger, will partly be destroyed at the temperature of sample preparation. Thus it means that the thermal heating causes a partial degradation of the cation exchanger, and sulphate comes into the solution as a degradation product.

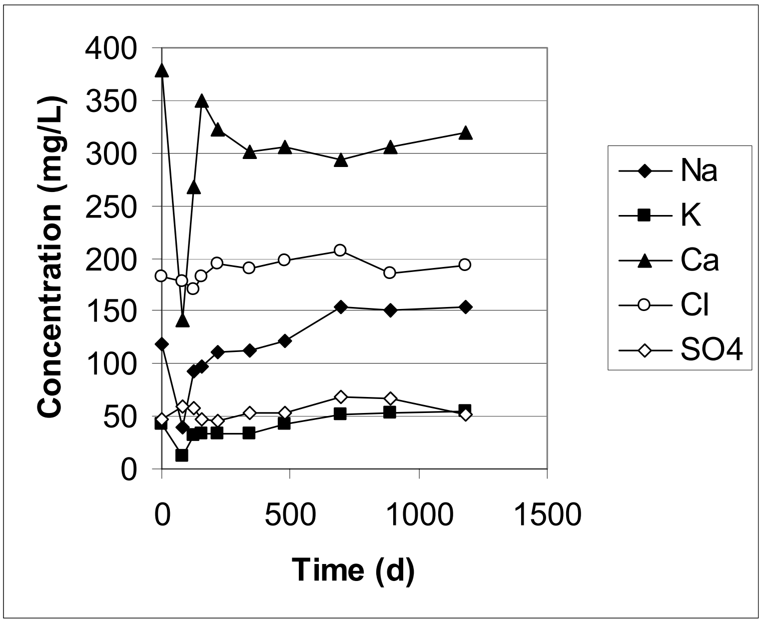

FIG. 5. Analysed ion concentrations as a function of time in old solutions.

3.3. Microscopic examination

Microscopic examination of the samples proved that in sample preparation during the cooling process segregation of ion-exchangers have occurred. This means that the density of granular resins at the bottom of the sample was higher than at the top. Actually the top surfaces of the samples were pure bitumen. From this reason the wetting front was advancing axially from the bottom to the top. The range of the wetting front as a function of square root of time is presented in Figure 6.

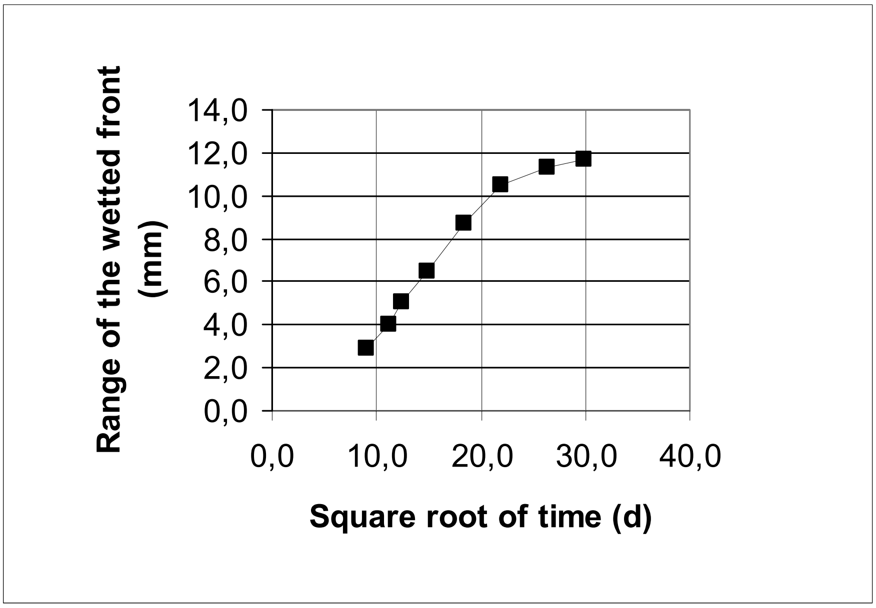

FIG. 6. Range of the wetting front as a function of square root of time.

The calculated points in Fig. 6 are each as an average of about 20 independent measurements. After three water exchanges the first signs of wetting process were visible at the top surfaces of the axially split samples. In connection of the ninth (9.) solution exchange, two diffusion samples have been picked up for an examination. The microscopic examination revealed that the range of the wetted front in diffusion samples was on average 10.7 mm (1184 d).

3.4. Diffusion tests

A diffusion test was carried out using tritium (H-3) as a tracer. The ends of the diffusion sample cylinder were plugged with PVC end plates. The equilibration solution used in this test was artificial groundwater spiked with tritium activity. The radioactive concentration of the solution was 10×10^6 DPM/mL. The input cell was filled with equilibration solution (4.35g) through the hole in the sleeve. After that the filling hole was closed with a plastic tape to prevent possible water evaporation. Through the output cell (volume 2.80 mL) a continuous flow of inactive artificial groundwater was running through small silicone tubes into a sample bottle by hydrostatic pressure. The construction of the diffusion cell has been presented in Figure 7.

FIG. 7. Construction of the diffusion cell.

The duration of the equilibration period was 18 days. Samples taken from the output bottles were analysed by a liquid scintillation counting (Wallac 1415) using OptiPhase Hisafe 3 as a scintillation liquid. Analysed samples were 4 mL and the amount of scintillation liquid used was 8 mL. The obtained results pointed out that the output samples did not contain any tritium. This means that the range of the wetting front has not yet reached the top of the bituminized ion-exchanger sample.

After the equilibration period of 18 days, the diffusion cell was dismantled and the sample sleeve was three times rinsed with inactive artificial groundwater to be sure that all the excess activity on the surfaces of the sample and sleeve has been removed. After that the sample sleeve was placed into elution vial containing 170 mL inactive artificial groundwater. The sample sleeve was periodically transferred to the next elution vial containing the same amount of inactive groundwater as earlier mentioned. All the samples were analysed by liquid scintillation counting as described above. The obtained results have been presented in Figure 8 in cumulative form as a function of time. Modelling of the results will be performed later.

Further two diffusion samples were used for saturation tests. These tests were performed using H-3, Na-22 and Cl-36 as radioactive tracers. The equilibration solution was artificial concrete ground water spiked with H-3 and Na-22 and in the other case with H-3 and Cl-36. From the radioactive input cells samples were taken as a function of time to follow-up the equilibration process. The results have been presented in Figure 9 and Figure 10.

Inactive artificial ground water was flowing through the output cells into the sample bottles by hydrostatic pressure as described above. The elution solutions were analysed for possible leaching of the radiotracers. The diffusion sample containing Na-22 activity was scanned by NaJ detector using a collimator with a slit of 1 mm to get an image of the activity distribution inside the bitumen sample as a function of time. The scanning was based on the high energetic gammapeak (1.2745 MeV) of Na-22.

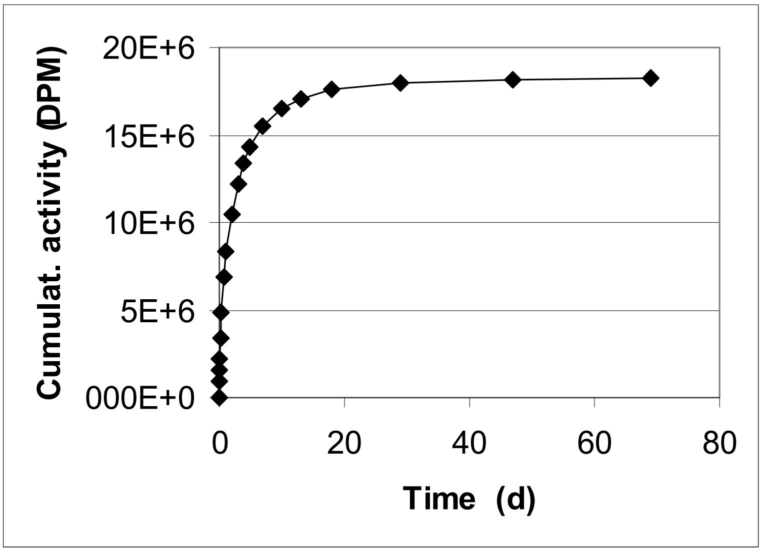

FIG. 8 Results of the saturation elution test presented in cumulative form as a function of time.

The diffusion tests concerning nuclides Sr-90 and Cs-137 are just going on and will be reported later according to the research programme financed by Posiva Oy.

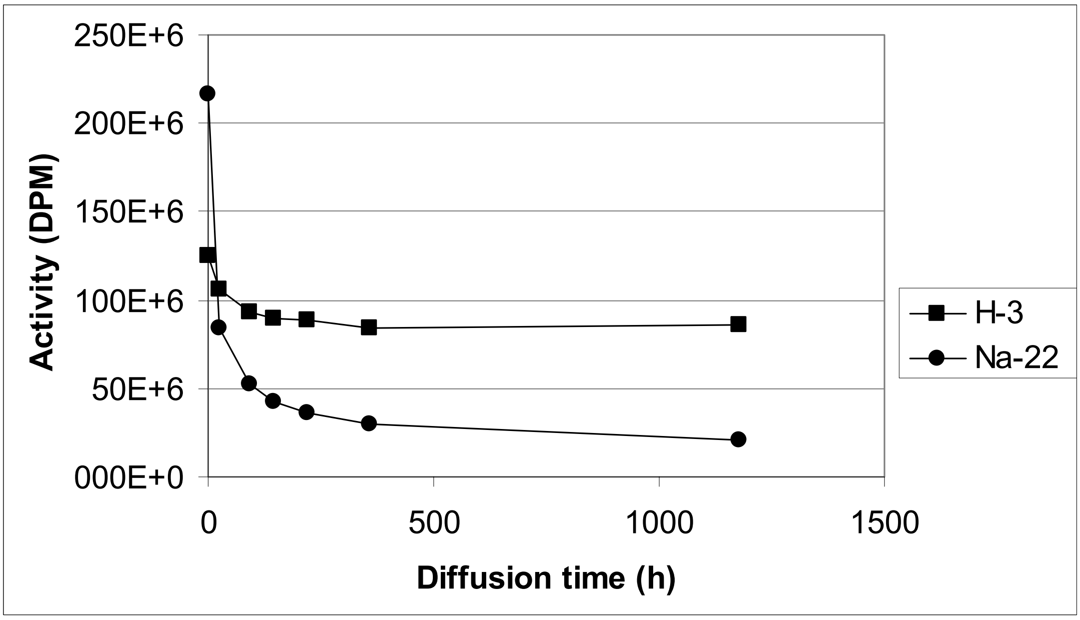

FIG. 9. Radioactive concentrations of H-3 and Na-22 as a function of time in the input cell of the sample A1.

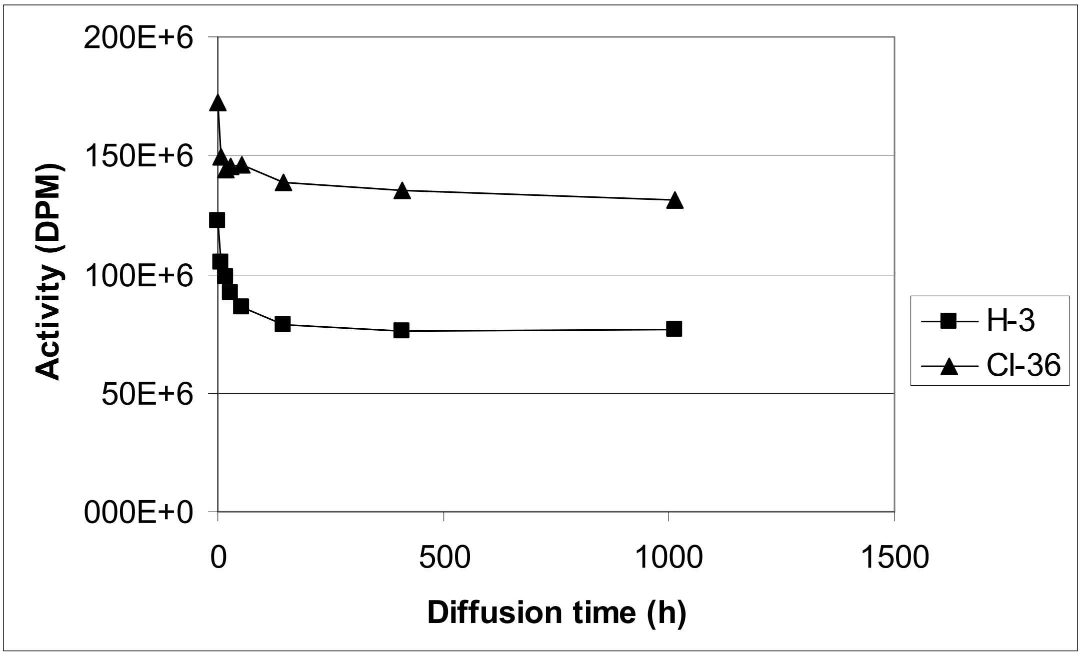

FIG. 10. Radioactive concentrations of H-3 and Cl-36 as a function of time in the input cell of the sample A3.

4. CONCLUSIONS

This is a final report containing all the research activities and results from the period 13 July 1997–28 February 2001. All the nine exchanged waters have been analysed by ion chromatography (IC) including the follow-up of the water absorption of the samples. All the samples, which were picked up for microscopic examination, have also been analysed. The microscopic examination revealed that the range of the wetted front seemed to be after six water exchanges (481 d) a linear function of the square root of time. But the following exchanges at 697 d and 890 d already pointed out that new chemical reactions have come into the picture. In connection with the ninth water exchange at 1184 d microscopic examination was not performed. The wetting process of the bituminized ion-exchanger product was slower than earlier expected. The main reason was the segregation of the ion-exchanger under the cooling process of sample preparation. Due to this through-elution diffusion test could not be applied but instead the saturation-elution test was chosen.

A saturation-elution test was performed with one diffusion sample using tritium (H-3) as a tracer. The results have been presented and further modelling will be performed later. Further two diffusion samples were tested using H-3, Na-22 and Cl-36 as radioactive tracers. The equilibration solution was artificial concrete ground water spiked with H-3 and Na-22 and in the other case with H-3 and Cl-36. Tritium was an internal reference when comparing the results of the equilibration behaviour of Na-22 and Cl-36. From the radioactive input cells samples were taken as a function of time to monitor the equilibration process. Elution of the samples and modelling of the results will be performed later. Diffusion tests with important waste nuclides Sr-90 and Cs-137 have been scheduled to years 2001-2002. The aim of the performed research project was to study the barrier properties of the bituminized product. The measured parameters and modelling of the results will reflect the behaviour of the wetted product as a part of the multibarrier system providing input data for safety analysis.

ACKNOWLEDGEMENT

This work is part of the research program of Posiva Oy belonging also to IAEA co-ordinated CRP-program entitled “Long Term Behaviour of Low and Intermediate Level Waste Packages Under Repository Conditions”.

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SAFETY ASSESSMENT OF RADIOACTIVE WASTE PACKAGES FOR DISPOSAL IN NEAR SURFACE DISPOSAL FACILITIES

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Abstract

Indian nuclear programme covers fuel production, power generation, research reactor, nuclear science, fuel reprocessing and isotope production for various applications. The radioactive waste generated is characterized systematically with respect to chemical and radiochemical properties. Waste management facilities are co-located with nuclear installations to avoid transportation through public domain. Coastal and inland sites have been characterized for geology, hydrology and metrological conditions.

The cement matrix used for the immobilization of radioactive chemical sludge and the polymer matrix for spent resin has been studied extensively. Plant scale experience has been gained in solidification of sludge/resin in appropriate matrix. A wide variety of waste packages are in use depending on the characteristics of waste / waste form, handling procedures and the need for providing isolation for long periods of time in a repository.

Safety of the disposal facility is ensured for a long period of time and a methodology for safety assessment has been evolved. Surveillance programmes have established the safe disposal of waste in India. A study to predict the service life of the concrete trench, concludes the long term safety of disposal systems.

This report describes characterization of waste, waste form, packages and disposal systems employed for management of low and intermediate level waste. The report also contains details of an experimental facility set up at Trombay to study long term behaviour of waste forms/packages under actual repository conditions.

1. BACKGROUND

International Atomic Energy Agency (IAEA) started the Coordinated Research Programme (CRP) on “Long Term Behaviour of Low and Intermediate Level Waste Packages under Repository Conditions” in September 1997. India participated in the CRP programme under project (9740) “Performance Assessment of Radioactive Waste Packages for Disposal in Near Surface Disposal Facilities.”

During the first research coordination meeting (RCM) held in Moscow, 24-28 November 1997, the present status of the near surface disposal facilities with respect to design, operation and safety assessment was presented. It was proposed to cover studies on waste, waste form container, backfill material, geology and hydrology of a coastal and inland disposal facility. Development of modeling methodology for safety assessment of disposal facilities, field experiments for durability of waste packages under repository conditions were also proposed. During the second RCM held in Cordoba 19-23 April 1999, the base line data on waste characteristics, waste form, and backfill material was presented. The coastal and inland sites have since been identified and characterised for their geohydrology, meteorology etc. An experimental facility to study the long term durability of waste form / packages under actual repository conditions has been set up at Trombay and the base line data has been generated. Efforts were also made to formulate a modeling methodology for safety assessment of disposal facilities. The input data base has been generated for the identified sites.

2. INTRODUCTION

The Indian Nuclear Programme covers power generation, research in nuclear science, isotope production for use in education, industry, hospital, agriculture etc. India has adopted closed nuclear fuel cycle and has established facilities for extraction of uranium, fuel fabrication, reactor operation and fuel reprocessing. In addition there are centers for carrying out research in nuclear science and facilities for isotope production. The waste management facilities are located along with nuclear establishments to avoid transport of radioactive waste to long distance through public domain. The low and intermediate level radioactive liquid waste is monitored and treated and bulk of the radioactivity is retained as process sludge / concentrate. The solid waste generated at the site is disposed in suitable engineering disposal facilities depending on the nature, activity content and surface dose. The periodic surveillance of sites has established isolation of waste from the environment.

3. CHARACTERIZATION OF WASTE

Characterization of waste helps in selection of suitable treatment, waste form, packaging and the engineered barrier. In order to make the waste management process technologically feasible and economically viable radioactive solid and liquid waste generated at different stages in various nuclear operating plant has been categorised depending on the activity level for liquids and surface dose for solids.

Keeping in view of the specific requirement of radioactive waste management of individual nuclear center, it was decided to provide adequate waste treatment / disposal facility at each nuclear center in place of having a single common disposal facility. Number of treatment / waste disposal facilities currently operating in India are presented in Table I.

TABLE I. WASTE MANAGEMENT FACILITIES IN INDIA

	Site	**Year of Commissioning**	**Nuclear Facility**
COASTAL	Trombay	1956	Research Reactors Fuel Fabrication Fuel Reprocessing Research Laboratories Isotope Production WIP
	Tarapur	1969	BWR (2 x 160MWe) Fuel Reprocessing Plant Fuel Fabrication Plant WIP
	Kalpakkam	1984	PHWR (2 x 170 MWe) Fuel Reprocessing Plant Research Laboratories Research Reactor (FBTR) WIP under construction
INLAND	Rajasthan	1972	PHWR,(1x100;1x200; 2x220MWe) Isotope Facility
	Narora	1989	PHWR, (2x220MWe)
	Kakrapar	1993	PHWR, (2x220MWe)
	Kaiga	2000	PHWR, (2x220MWe)

Trombay being the oldest and having multiple nuclear installation was selected as coastal site for systematic characterization and reconfirmation of the available data for the research coordinated programme. The facility at Kakrapar having PHWR (2 x 220 MWe) was identified as inland site for discussion in the CRP.

3.1 Characterization of waste, Trombay-coastal site

Low level radioactive liquid waste generation is around 1 x 10^5 m^3/year at Trombay. The gross activity of the waste is in the range of 1–30 Bq/ml having ^{137}Cs and ^{90}Sr as principal radioisotopes. Characteristics of liquid waste generated at Trombay site is presented in Table II. The waste is suitably decontaminated and the effluent is discharge to sea well below the limits prescribed by regulatory authorities.

TABLE II. RADIOCHEMICAL ANALYSIS OF LIQUID WASTE

Sr. No.	Characteristics	Reactor	Reprocessing	Laboratories	Decontamination Center
1	pH	7.6 – 9.6	8.0 – 8.8	7.2 – 8.6	7.6 – 8.8
2	Total Solids (ppm)	100 – 900	50 – 500	50 – 500	100 – 600
3	Gross β, γ (Bq/ml)	1 – 12	2 – 22	0.5 – 2	0.5 – 5
4	Gross α (Bq/ml)	< 0.03	< 0.06	< 0.02	< 0.03
5	Principal Isotopes	^{137}Cs, ^{90}Sr, ^{106}Ru, ^{125}Sb	^{137}Cs, ^{90}Sr	^{137}Cs, ^{90}Sr, ^{60}Co	^{137}Cs, ^{90}Sr

Radioactive solid waste of different nature, activity and surface dose is also generated at the site. Major waste components constitute spent resin, spent sources, process sludge, HEPA filters and combustible/non combustible assorted waste. Characteristic of the solid waste is presented in Table III and Table IV.

TABLE III. RADIOCHEMICAL ANALYSIS OF SOLID WASTES

Nature	Characteristics	Reactor	Reprocessing
Spent Resin	Volume (m^3/yr)	2-4	0.2-0.3
	Activity (MBq / g)	2-6	5-10
	Principal Isotopes	^{137}Cs, ^{90}Sr, ^{60}Co	^{137}Cs, ^{90}Sr
Sludge	pH	8.5 – 9.0	8.5 – 9.0
	Volume (m^3/yr)	10 - 40	5 – 10
	Activity (KBq / g)	2 – 8	0.5 – 2.0
	Principal Isotopes	^{137}Cs, ^{134}Cs, ^{90}Sr, ^{60}Co	^{137}Cs, ^{90}Sr, ^{60}Co
HEPA Filters	Volume (m^3/yr)	15-20	15-25
	Activity (KBq / g)	0.5-2.0	3-5
	Principal Isotopes	^{137}Cs, ^{90}Sr	^{137}Cs, ^{90}Sr, ^{239}Pu

TABLE IV. CHARACTERISTICS OF TYPICAL SPENT RADIATION SOURCE

Radiation Source	^{60}Co
Activity	1.3 x 10^6 GBq (36,000 Ci)
Size of source	38 mm ϕ, 700 mm (l)
No. of sources	95 (in two tile holes)

3.2 Characterization of waste, Kakrapar-inland site

Low level waste generated during operation/maintenance of PHWR reactor (2x200Mwe) is about 20,100 m^3/year. Most of the activity is from tritium and is discharged to the environment after providing necessary dilution. The liquid waste has been characterized for various parameters and the results are given in Table V.

TABLE V. RADIOCHEMICAL ANALYSIS OF LIQUID WASTE

Volume (m^3/year)	20,100
pH	7 – 8
Total dissolved solids (ppm)	50
Specific activity :	
^{3}H (kBq / ml)	4 – 5
β, γ (Bq / ml)	0.05 – 0.10
Principal Radionuclides	^{3}H, ^{137}Cs, ^{134}Cs

Solid waste consists of compressible waste, contaminated equipment, process sludge and spent resin. The volume disposed is about 70 m^3/year and its details are presented in Table VI.

TABLE VI. CHARACTERIZATION OF SOLID WASTE

Category	**Dose Rate mGy/hr**	**Principal Radio-nuclides**	**Vol. per year m^3**	**Remarks**
I	≤ 2	^{137}Cs, ^{134}Cs, ^{90}Sr	60	Compressible waste: cotton, plastic, mops, HEPA filter etc.
II	$> 2 \leq 20$	^{137}Cs, ^{134}Cs, ^{90}Sr	5.5	Contaminated equipment, process sludge etc
III	> 20	^{137}Cs, ^{134}Cs, ^{90}Sr	4.0	Spent resin

4. CHARACTERIZATION OF WASTE FORM

Radioactive waste is immobilised in an inert solid matrix to isolate the radionuclides from environment. Cement and polymer matrices have been employed for incorporating the waste. Cement waste is the most common waste form and is employed for immobilization of process sludge, liquid concentrates etc.. Polymerised waste form is adopted for spent resin waste. The waste form so obtained has been characterised for various properties like compatibility, density, compressive strength, porosity, leach rate, radiation stability etc. Typical characteristics of cement and polymer matrices are presented in Table VII.

TABLE VII. CHARACTERIZATION OF WASTE FORMS

Properties	**Cementised Waste Product**	**Polymerised Waste Product**
Waste loading (%)	60 – 70	55 - 60
Compatibility	With alkaline waste	With alkaline waste
Density (g/cc)	1.8 – 2.0	1.2
Compressive strength (kg/cm^2)	100 – 150	320
Porosity (cc/g), (total pore volume)	0.18 – 0.27	Non-continuous pores
Setting time (minutes)	100 – 300	NA
Leach rate (g/cm^2/day)	10^{-4} – 10^{-5}	10^{-5}
Radiation stability	upto 10^8 rads	upto 10^8 rads
Homogeneity	Good	Very good
Thermal Stability	Very good upto 100°C	Good upto 100°C

4.1 Matrix for heat generating spent radiation source:

Besides work on power reactor, fuel reprocessing etc, studies on waste form for spent radiation source is being pursued in India. It is a practice to store/dispose the spent radiation source after its use in industry, hospital, educational institutions etc. in a concrete lined steel pipes called tile holes. A programme was undertaken at Trombay to develop a suitable matrix for encapsulation of such sources. The matrix should provide better heat dissipation, thermal stability, monolithic mass and shielding. To simulate the field conditions, a metallic heater (25mm,ϕ x 40mm l) was embedded in the matrix. Various matrices such as cement: sand; cement: sand : iron filling ; cement : iron powder were evaluated for heat dissipation and strength. A center line temperature of 95°C was maintained for a month. The temperature at center and inner surface (3.0cm away) was measured by embedding thermometers. The study indicated that addition of iron filling as an ingredient in the cement matrix helps in better heat dissipation and improvement in compressive strength of conditioned product. The matrices were evaluated for their compressive strength and the results are given in Table VIII.

TABLE VIII. STUDIES ON IMPROVEMENT OF CEMENT MATRIX FOR SPENT RADIATION SOURCES

Curing temperature : 95°C; Curing time : One month; Block volume : 1 litre

Composition of Matrix	**Temp. at center °C**	**Temp. at surface °C**	**Compressive Strength kg / cm^2**	**Remarks**
Cement : Sand W/O Heater (400g:1200g)	-	-	232	Reference Block w/o heater
Cement : Sand with Heater(RT) (400g:1200g)	-	-	142	Reference Block with heater
Cement : Sand with Heater (400g:1200g)	95	65	148	--
Cement : Sand : Iron Filling (400g:960g:240g)	95	69	190	Addition of iron filling improves strength and heat dissipation
Cement : Sand: Iron powder (400g:960g:240g)	95	69	121	Addition of iron powder reduces the strength in comparison with iron filling.

Based on the laboratory experiments, cement : sand : iron filling as a matrix composition was selected for 200 l scale experiments. Two set up of experiments were conducted on the selected composition. In one set a center line temperature of 90°C was maintained and a temperature of 31.5°C was observed at surface. In second set a constant wattage of 400 w (equivalent to 25000 Ci of ^{60}Co) was maintained giving rise to a center line temperature of 205°C and surface temperature of 46°C. The metallic heater of 38mmϕ x 700mm(l) was used during the experiments to simulate the source dimensions as shown in Figure 1. The temperature at various locations was measured using thermocouples at various points.

Experiments are continued and it is planned to take core drill samples from various locations to evaluate their compressive strength and other properties. Characterization of the waste form provides important input for development of a model for safety assessment of near surface disposal facilities.

5. WASTE PACKAGES/CONTAINERS

Different types of containers/packages are used for handling and disposal, depending upon the type of waste, the radioactivity content and handling/retrievability requirements. Some of the containers/packages are shown in Figure 2 and Figure 3 [1]. Different types of packaging and their use for radioactive solid waste are presented in brief in the following paragraphs.

Soft package

In case waste materials are only suspect contaminated like tissue paper, rubber and plastic materials, cotton etc., they are packed in polyethylene bags, paper cartons or polyethene lined jute bags. Alpha contaminated low active liquid waste is immobilised in cement in 5 litre polythene carboys in glove box for ease of handling. Such packages are normally handled in reusable steel container.

Carbon steel drum

Mostly 200 litre capacity drums are being used for packing the solid / solidified waste. Some drums are specially made with concrete shielding inside for waste having higher activity content and / or not amenable for conditioning in suitable matrix. In applications such as packages for hulls, modified drums are used with provision for top closing with remote gadgets. Depending upon the nature of waste, drums are provided protective coatings of polyamide epoxy paint or fibre reinforced plastics.

Custom built container

Suitable custom built containers are provided for those wastes which are not amenable for packing in standard drum either due to size or specific process requirement. Generally these are constructed from carbon steel in thickness ranging from 3mm to 12 mm, Spent resins from power stations are transported in carbon steel hoppers after dewatering. At certain location, high integrity container (HIC) has been designed. It can accommodate a standard drum and has 250mm thick concrete shielding and weighs about 10 tons. HIC can serve the purpose of stand-alone type of disposal unit and can be transported to an off site location if required.

Stainless steel container

Stainless steel containers are used for packing alpha contaminated waste coming out of glove boxes. Such packages provide long term storage prior to disposal. Hulls wastes having alpha as well as beta-gamma contamination are proposed to be stored in stainless steel containers with remote handling provisions. Spent sources like ^{60}Co, ^{137}Cs, ^{192}Ir etc., sealed in stainless steel capsules are handled in secondary container with sufficient provision for shielding / cooling and other transport requirements. Such sources are decasked, embedded in cement-sand grout in another steel container prior to disposal.

6. CHARACTERIZATION OF BACK-FILL MATERIAL

Naturally available clay mineral such as vermiculite and bentonite are used as backfill material at various disposal sites in India. In order to test the suitability of these materials in terms of their retention potential with respect to various radionuclides, vermiculite and bentonite samples were taken up for detailed characterization. Properties evaluated cover cation exchange capacity (CEC), density, chemical composition, distribution coefficient with respect to various radionuclides like Cs, Sr, Am and Pu [2]. Details of the property evaluated for the above two clay minerals are presented in Table IX.

TABLE IX. CHARACTERISTIC PROPERTIES OF VERMICULITE & BENTONITE

Item	Vermiculite	Bentonite
Size (ASTM)	-30+70	- 200
True Density (g /cc)	2.6 to 2.7	2.4 to 2.6
CEC (meq/100 g)	40-50	50-65
Porosity (%)	50 – 60	40 – 60
Chemical Comp. (%)		
SiO_2	35 – 40	45 – 55
Al_2O_3	10 – 12	15 – 20
Fe_2O_3	6 – 8	3 – 6
MgO	20 – 25	3 – 4
Na_2O	--	1 – 2
H_2O	10 – 15	10 – 15
Distribution Coefficient (ml / g)		
^{137}Cs	2550	7000
^{90}Sr	1560	200
^{239}Pu	413	4000
^{241}Am	69	40

The backfill material is an important component of multibarrier concept being followed in radioactive waste management. The study will help in proper selection of backfill material while managing waste containing these radionuclides.

7. DISPOSAL FACILITY CONCEPT

For low and intermediate level waste (L & ILW), the disposal facility at any nuclear center is collocated with the waste generating facility / plant / laboratory in a controlled area within the fencing of the nuclear center. The disposal is carried out in near surface disposal structures laid out in the disposal facility in a manner which allows modular construction and surveillance through network of boreholes [3].

Three different type of disposal structures namely earth / stone lined trench, reinforced cement concrete trench and tile hole are used depending upon the radioactivity content of the package and site characteristics [4].

8. FIELD EXPERIMENTS ON WASTE FORMS/PACKAGES

An experimental facility has been set up at Trombay to study long term behaviour of waste forms/packages under actual repository conditions. The waste forms of different characteristics and compositions have been prepared using inactive as well as radioactive chemical sludge. The composition of various waste forms under study is given in Table X. Radiochemical analysis of the process sludge (active and inactive) is given in Table XI.

The blocks of 20 l and 200ml have been prepared in different types of containers. For comparison some blocks have been prepared without container also. The properties of the container used are presented in Table XII. The waste packages of different composition have been placed perpendicular to the flow of water in an earth trench. The blocks have been characterised for their dimensions, compressive strength and surface dose to generate base line data and the details of the same are described in Table XIII. The experimental repository details are presented in Table XIV.

TABLE X. COMPOSITIONAL DETAILS OF VARIOUS WASTE FORMS

Code No.	Block Details
100	Cement Block in MS Container (a)
200	Cement Block with inactive waste in MS Container (b)
300	Cement Block with inactive waste without container (b)
400	Cement Block with active waste in MS container (b)
500	Cement Block with active waste without container (b)
600	Cement Block with active waste + Vermiculite in MS container (c)
700	Cement Block with active waste + vermiculite without container (c)
800	Cement Block with active waste with backfill material (b)
900	Cement Block with inactive waste in Plastic container (b)

a) Cement : Water = 2 : 1, b) Cement : Waste = 2 : 1,
c) Cement : Waste : Vermiculite = 2 : 1: 0.1

TABLE XI. RADIOCHEMICAL ANALYSIS OF PROCESS SLUDGE (INACTIVE & ACTIVE)

Properties	Process Sludge	Inactive Sludge
pH	8.3	8.5
Total Solids (%)	1.90	2.4
Suspended Solids (%)	1.85	2.3
TDS (ppm)	650	920
Gross β γ KBq/ml	3.0	--
Radionuclides	^{137}Cs, ^{134}Cs, ^{90}Sr	--

TABLE XII. PROPERTIES OF THE CONTAINER

Container	Carbon Steel
Carbon	0.069 %
Sulphur	0.026 %
Phosphorus	0.024 %
Manganese	0.42 %
Silicone	0.045%
Average Thickness	2.0 mm
Paint	Epoxy
Plastic Container	High Density Polythene
Thickness	2.0 mm

TABLE XIII. CHARACTERIZATION OF WASTE PACKAGES

Identification Code	**Wt. of Block (kg)**	**Compressive Strength (kg/cm^2)**	**Surface Dose (mGy/hr)**
100	39.5	182	Inactive
200	34.5	175	Inactive
300	41.8	169	Inactive
400	37.8	180	0.15
500	43.5	172	0.09
600	41.0	160	0.09
700	47.2	158	0.07
800	36.0	170	0.22
900	42.0	173	Inactive

TABLE XIV. EXPERIMENTAL REPOSITORY DETAILS

Location	Trombay, BARC, Mumbai
Disposal module	Earth trench
Dimensions	20 m(l) x 2.5 m(w) x 2.5 m (d)
Soil	Clayey
Water table	1.0 - 3.0 m

Photographs of typical 20 l and 200 ml blocks, cage and complete experimental set are given in Figures 4–6. All the nine sets under study have been placed in the experimental repository as shown in Figure 7.

The blocks have been placed in a row about 2.5 m below the ground. Bore well pipes have been installed in the earth trench for monitoring the inlet as well as outlet streams. The blocks are placed perpendicular to the flow of ground water. Vermiculite, has been used as backfill material in one set of experiments to investigate the retention of radionuclides. The blocks will be retrieved periodically and will be evaluated for various parameters like compressive strength, leach rate, porosity/permeability, corrosion of container and biodegradation.

9. SERVICE LIFE OF CONCRETE TRENCH

In India, low and intermediate level radioactive solid waste is disposed in stone lined earth trench, reinforced concrete trench and tile hole. The analysis of water from nearby bore well and the radiation field monitored over the years has provided confidence in safe management of waste. A programme has been started to study the condition of old concrete trenches and to develop a reliable mathematical model to predict the service life of the same [5-7]. These trenches are receiving waste packages over the last four decades at Trombay, Tarapur and Rajasthan sites. The monitoring techniques employed are rebound hammer test and ultrasonic velocity test for predicting the strength and half – cell potential method for determining the probability of corrosion in reinforced bars. The physical and geo-chemical properties of soil and ground water of different disposal sites have been extensively determined. To study the durability of the trench against chloride and carbonate attack, weathering test experiments on concrete blocks are in progress. The experimental data will be used as input for development of a mathematical model for service life prediction of trenches. This work enhances the confidence level that during service life of trenches, the design of waste package is adequate to confine the radioactivity. Also it will provide very useful insight for remediation measures at future point of time.

10. GEO-ENVIRONMENT OF SITE

Geological environment of a site has an important bearing on the isolation of conditioned waste product housed in near surface disposal facility. Various elements of study influence the design of waste package and its performance in actual repository condition. In view of this geological environment of Trombay and Kakrapar site has been studied.

The Trombay island is situated in the north-western part of the Deccan Volcanic Province. At Trombay, basalt is the dominant rock occurring as horizontal lava flows forming the Trombay hills. The other rock types include granophyre, basic tuffs, oceanite and ankaramite and dolerite dykes, occupying intermediate positions. The Deccan basalt of Trombay area is a fine grained dark coloured amygdaloidal basalt. The amygdales are generally of secondary zeolite minerals. The area is covered by clayey soil, which is underlain by weathered basalt and followed by fresh basalt. Ground water table rises considerably during rainy season almost upto 0.5 m below surface and recedes down to 10 m depth during dry months. The ground water movement studies carried out at the site showed a velocity of 0.1 – 0.5 m/day. The average annual rain fall for the last 40 years is 2344mm. The distribution coefficient (Kd) values of soil samples obtained from site were analysed. The Kd value of 600 – 1000 ml/gm for Cs and 140 – 300 ml/gm for Sr indicated that soil has very good uptake capacity.

Solid waste management facility, Kakrapar is lying in basaltic formation of deccan trap of India. The top soil is silty loam of black cotton soil followed by highly weathered rocks. The lower strata are having fresh and hard gray coloured basalt. The site is about 2 km south of a river. The site receives about 1250 mm of rainfall annually. Being located in the proximity of a perennial river and water reservoir, the whole of the area gets recharged throughout the year. The water table is high in monsoon period. Geo-chemical and hydrological parameters of Trombay and Kakrapar site are presented in Table XV & XVI [8].

TABLE XV. PHYSICAL AND GEO-CHEMICAL PROPERTIES OF THE TROMBAY & KAKRAPAR SOIL

Parameters	Trombay	Kakrapar
Bulk Density (gm/cc)	1.7	1.2 – 1.4
Porosity (%)	30.0	36 – 50
pH	6.4 – 7.4	7.5 – 8.0
CEC meq/ 100 gm	38 – 76	38
Kd, ml/gm , ^{90}Sr	140 – 300	860-1700
Kd, ml/gm, ^{137}Cs	600 – 1000	480-2000

TABLE XVI. HYDROLOGICAL PARAMETERS OF TROMBAY & KAKRAPAR SITE

Parameters	Trombay	Kakrapar
Annual rain, (mm)	2344	1250
Ground water table, (m)	0.5 – 10.0	1.5 – 3.0
Ground water velocity, (m/d)	1.7 – 8.7	11.6 – 19.1

11. SAFETY ASSESSMENT

The safety of the disposal facility is to be ensured over a period of time for which a methodology has been evolved. Main components of the methodology are (i) release of radionuclides from the waste form (ii) transport of radionuclides from backfill material, vadose zone and then transport through the far field (iii) calculation of radiological dose to the critical group for different exposure pathways. This methodology is under constant review for refinement and is being applied for various waste disposal sites in India.

12. CONCLUSIONS

The radioactive waste has been characterised systematically at coastal site, Trombay and the inland site, Kakrapar to generate the base line data. The sites have also been characterised for geology, hydrology and the meteorological conditions. The cement matrix used for the immobilization of radioactive chemical sludge and the polymer matrix for spent resin have been studied extensively. Plant scale experience has been gained in solidification of sludge/resin in appropriate matrix. A wide variety of waste packages are in use depending on the characteristics of waste / waste form, handling procedures and the need for providing isolation for long periods of time in a repository. Surveillance data collected over the years has established isolation of radioactivity from the environment by engineered barriers like reinforced concrete trench/tile hole etc. The experimental facility set up in Trombay will provide data on waste form and waste packages under actual repository conditions over the years. Study is in progress to predict the service life of the concrete trench.

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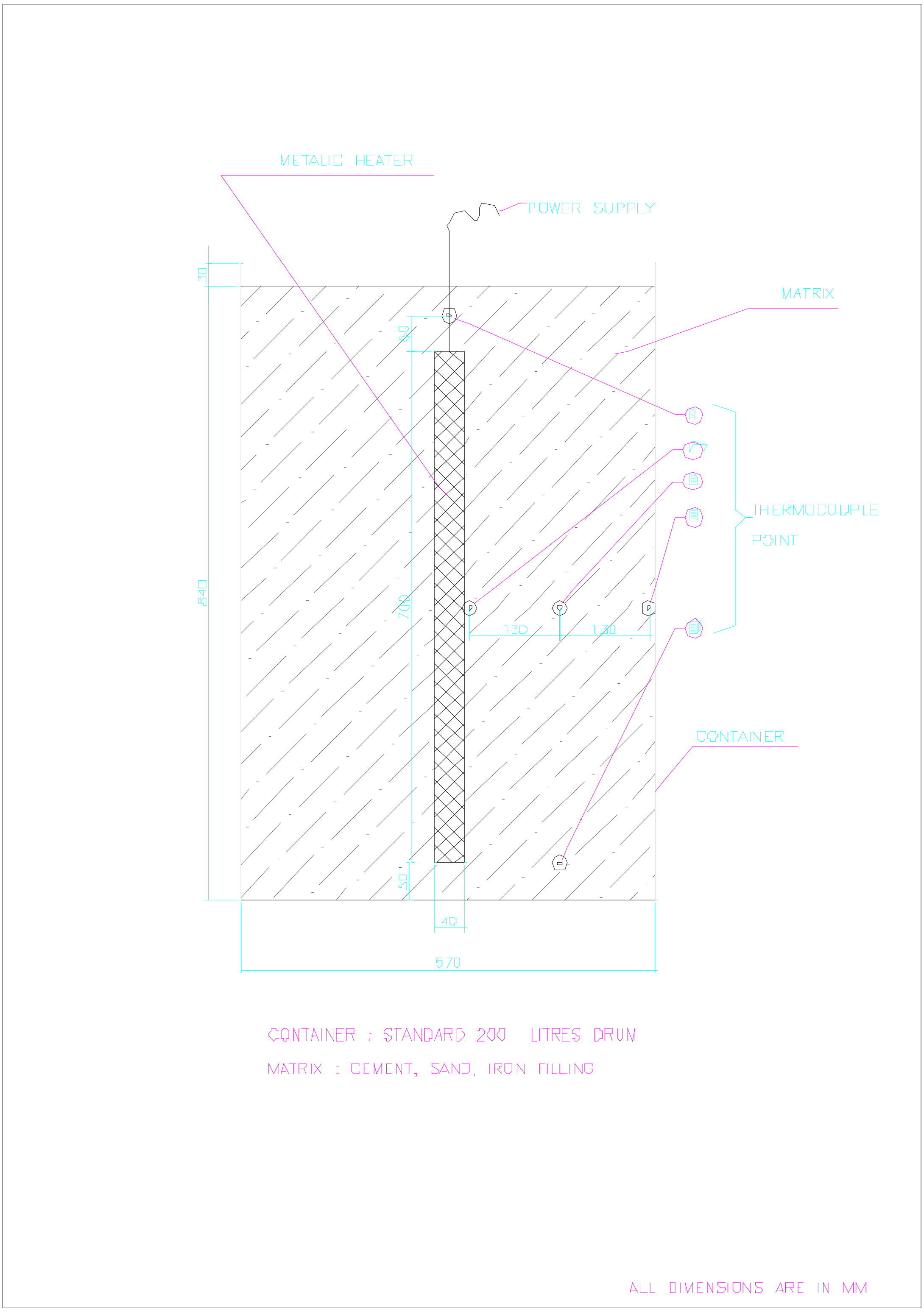

FIG. 1. Experimental setup for studying cement matrix at elevated temperatures.

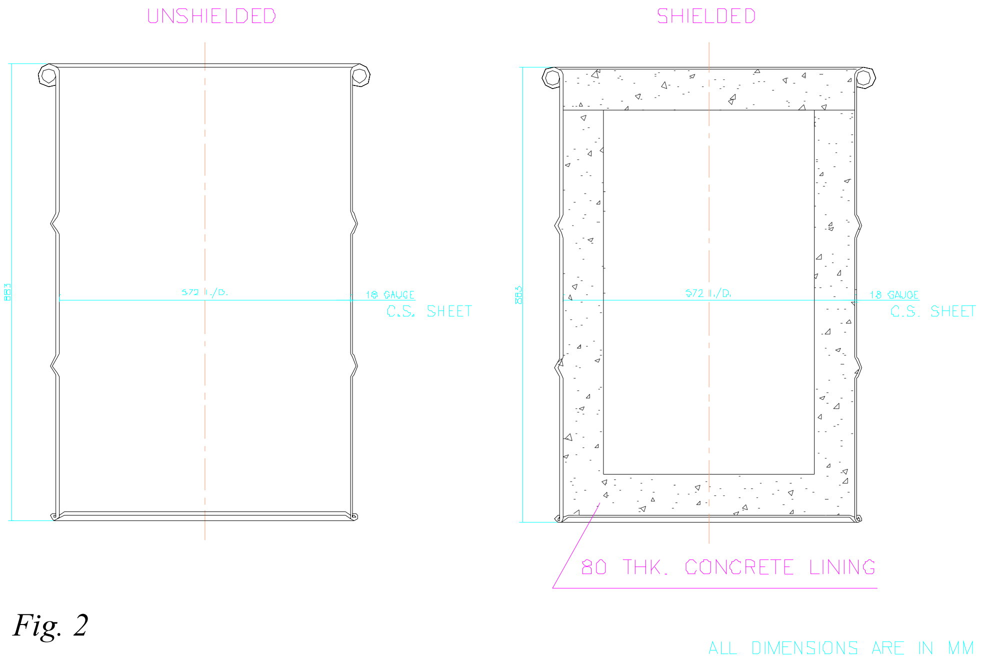

Fig. 2

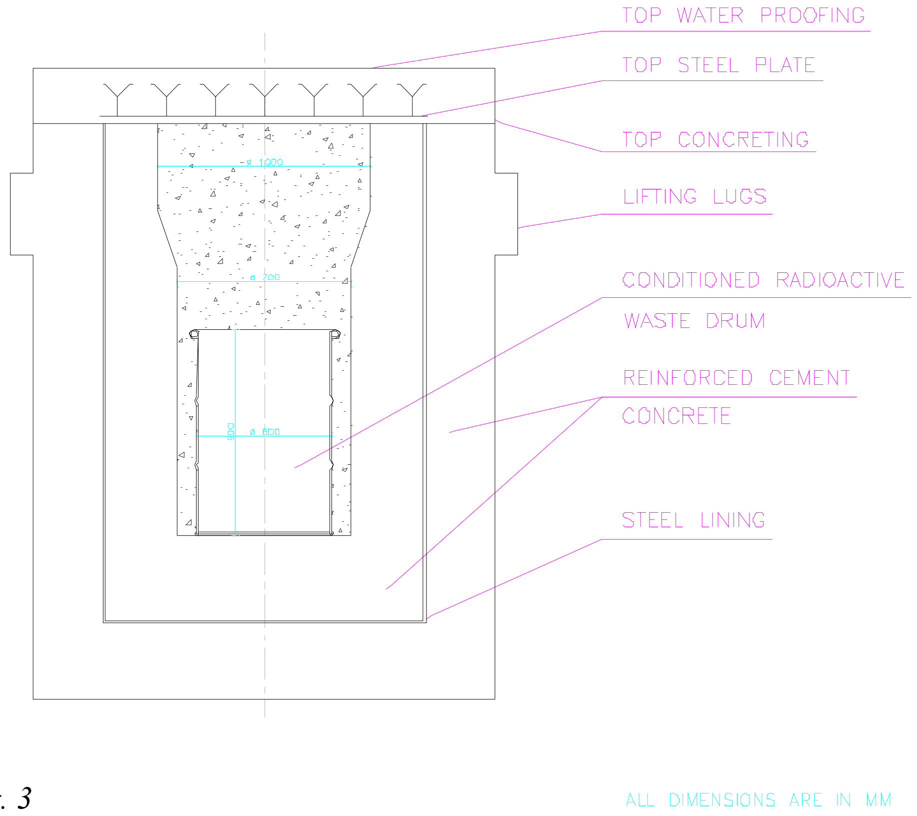

Fig. 3

FIG 2. A view of the carbon steel drum.

FIG 3. A view of the high integrity container.

FIG. 4. A view of experimental blocks.

FIG. 5. A view of cage for block retrieval.

FIG. 6. Typical set of blocks for field experiment.

1 - Clay formation

2 - Highly weathered basalt

3 - Fresh and hard basalt

4 - 20 liters waste blocks with cage

5 - 200 ml waste blocks

FIG. 7: Experimental repository at Trombay.

A STUDY ON THE COMPLIANCE OF WASTE PACKAGES GENERATED FROM NUCLEAR POWER PLANTS UNDER REPOSITORY CONDITIONS IN KOREA

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Abstract

In the Korean project, studies are to demonstrate compliance of waste packages with the waste acceptance criteria established by the national regulatory body. Various types of waste packages, including carbon-steel drums, high integrity containers, and concrete-lined drums, are currently in use at the Korean NPPs. In addition, paraffin based waste forms are being generated at the NPPs. Potential gas generation in the waste packages as well as the integrity of the engineered disposal vault under the pressure increase caused by gas generation was assessed. The principal gas-generating mechanisms being considered include: metal corrosion, microbial activity in organic materials, and radiolysis in paraffin-based waste forms. Leaching studies on both simulated and actual paraffin- and cement-based waste forms are carried out. The leaching tests were conducted according to ANSI/ANS-16.1 test procedure and the cumulative fractions leached (CFLs) of cobalt and cesium were obtained. The compressive strength before and after the leaching test was also measured. Leaching mechanisms from each waste form were identified and compared with the test results. Characterization data obtained and collected on solidified waste forms and waste packages were compiled into a package database search program (PACKDB) for later-use as the input data of source-term evaluation model in repository performance assessment.

1. TECHNICAL BACKGROUND

Various types of waste packages including carbon steel drums, high integrity containers (HIC), and concrete-lined drums are currently used in the nuclear power plants (NPPs) in Korea. According to waste acceptance criteria (WAC) for waste forms and packages promulgated by Korean regulatory body, regulation requires to confirm the compliance of waste packages to acceptance criteria on non-explosive and non-inflammable conditions of the package, waste forms conditioned by solidification, limitation of leach rates, etc. The compliance of these packages has not yet been investigated in view of the safety of disposal of the waste packages.

2. OBJECTIVES

In order to confirm the compliance of waste packages to WAC, the performance of waste packages including the integrity of the packages under the pressure increase caused by gas generation, leaching characteristics of actual waste forms from the

NPPs, and the compliance of waste packaging under repository condition were investigated.

3. RELEVANCE TO NATIONAL PROGRAMME :

As of the end of 2000, 16 nuclear power plants are being commercially operated, and application of radioisotopes in the industry is increased year by year in Korea. Based on the new plan of radioactive waste management approved by Korean Atomic Energy Committee in 1998, KEPCO, on behalf of government, is seeking the Low- and Intermediate-level radioactive waste(LILW) repository site through a voluntary participation of local government to operate the repository from 2008.

The generic waste acceptance criteria of disposal facility are prescribed in Korean Atomic Energy Act and MOST(Ministry of Science and Technology)-Notice No. 96-10.

4. SCOPE OF WORK

- Characterization of the waste packages currently used in Korea
- Assessment of gas generation from waste packages
- Investigation of leaching behavior of waste forms
- Evaluation of compliance of waste forms/packages under the repository condition

5. RESEARCH WORK DONE AND RESULTS

The summary of the work we have conducted is as follows:

- **Gas generation from radioactive waste packages under disposal conditions**

  For the assessment of the expected gas production in the waste packages, corrosion of metals, microbial activity of organic materials, and radiolysis are considered as the principal gas generation mechanisms. A comprehensive literature review was performed to understand each mechanisms and assessment methodologies. Based on the comprehensive data and information on radioactive packages and plant-specific process control programs, an estimate of the likely cumulative amounts and generation rates of gases within the waste packages has been performed.

- **Calculation of radiolytic gas production from waste packages, especially from paraffin waste form**

  A computer program, which is based on USDOE model, for calculating rates and total volumes of radiolytic hydrogen gas generated in radwaste packages was developed. Interactions among adjacent waste packages are included in the program by considering the contribution to the absorbed gamma dose rate when a large number of waste packages are emplaced together. The supporting analysis to compare the accumulated gamma energy between single drum and multiple-tied drums (arranged in 4*4*3 and 4*3*3 hexahedral geometry) are conducted using MCNP4B (Figures 1, 2). The resulting cumulative hydrogen gas generation from cement-solidified drum, HIC, and paraffin-encapsulated liquid concentrate drum shows an increase in the same order, although it is not likely to be significant amount.

- **Calculation of gas generation from Dry active waste(DAW) packages by metal corrosion and microbial degradation**

Calculations were made for gas concentrations and generation rates from Dry active waste(DAW) packages; a 200-L drum and an approximately 300-L over-pack drum, over an assessment period of one thousand years in a waste vault. The prediction was performed using GAMMON program developed by AEA Technology of the UK. To find out the effects of input parameters on the results, a sensitivity analysis was conducted. The main result is that total volume of gas generated depends on the pH and initial concentrations of oxygen in a waste vault. In the calculations, the repository was assumed to be completely anaerobic, resaturated at the time of closure, and buffered at pH 12. The results show that total accumulated amounts of gas generated from DAW package are in the ranges of 500~650 mol per package (Table 1).

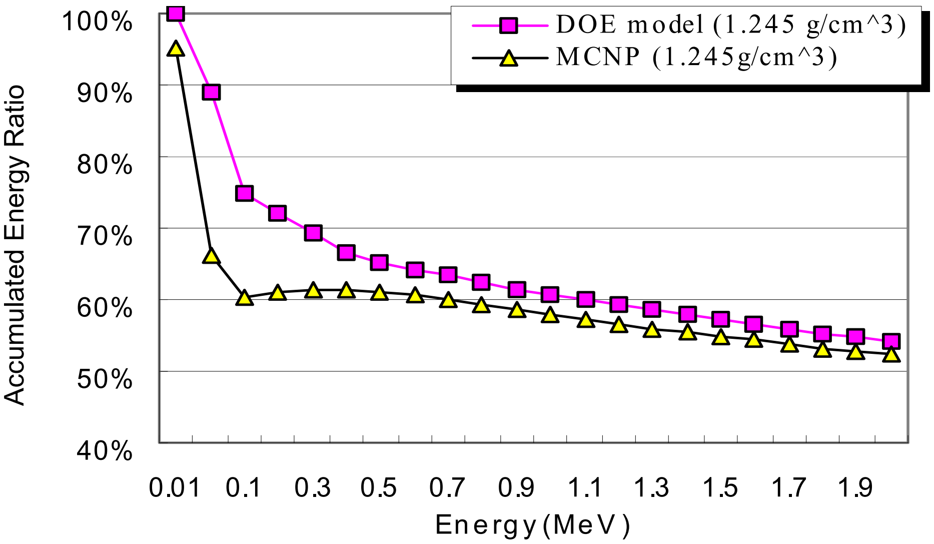


FIG. 1. Comparison of Differences on Accumulated Energy Ratio Between the Model Prediction and MCNP Calculation for the Single Drum Case

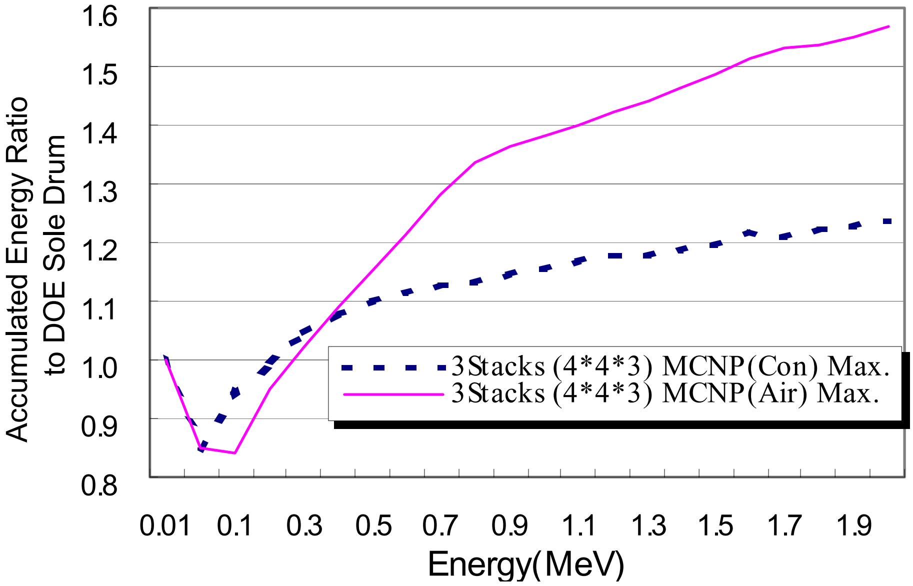


*FIG. 2. Comparison of Differences on Accumulated Energy Ratio Between the Single Drum Case and MCNP 4*4*3 Configuration According To Air and Concrete Backfill Conditions*

TABLE I. CUMULATIVE AMOUNTS OF MAJOR BULK GAS GENERATION

Waste Packages	**Cumulative amount generated (mol m^{-3})**			
	H2	**CO2**	**CH4**	**Total**
DAW(200L steel drum)	3.14E-4	1.06E+3	1.46E+4	2,520 (504 mol/drum)
DAW(350L repackaged steel drum)	3.17E-4	1.30E+3	2.06E+3	3,360 (672 mol/drum)
Cemented Spent Filter(200L steel drum)	7.25E+2	1.00E-9	1.55E+2	880 (176 mol/drum)
DAW(Concrete-shielded steel drum)	3.17E-4	3.58E+2	9.00E+2	1,258 (252 mol/drum)
Compressed Vinyl Waste(200L steel drum)	3.13E-4	1.66E+3	2.01E+3	3,670 (734 mol/drum)

– **Calculation of gas generation from other waste packages**

Calculation of gas generation from other waste packages such as spent filter drum, concrete-lined miscellaneous waste drum was made. In addition, the prediction of radioactive gases generation within waste packages was conducted.

– **Assessment of compliance of waste packages in aspect of gas generation**

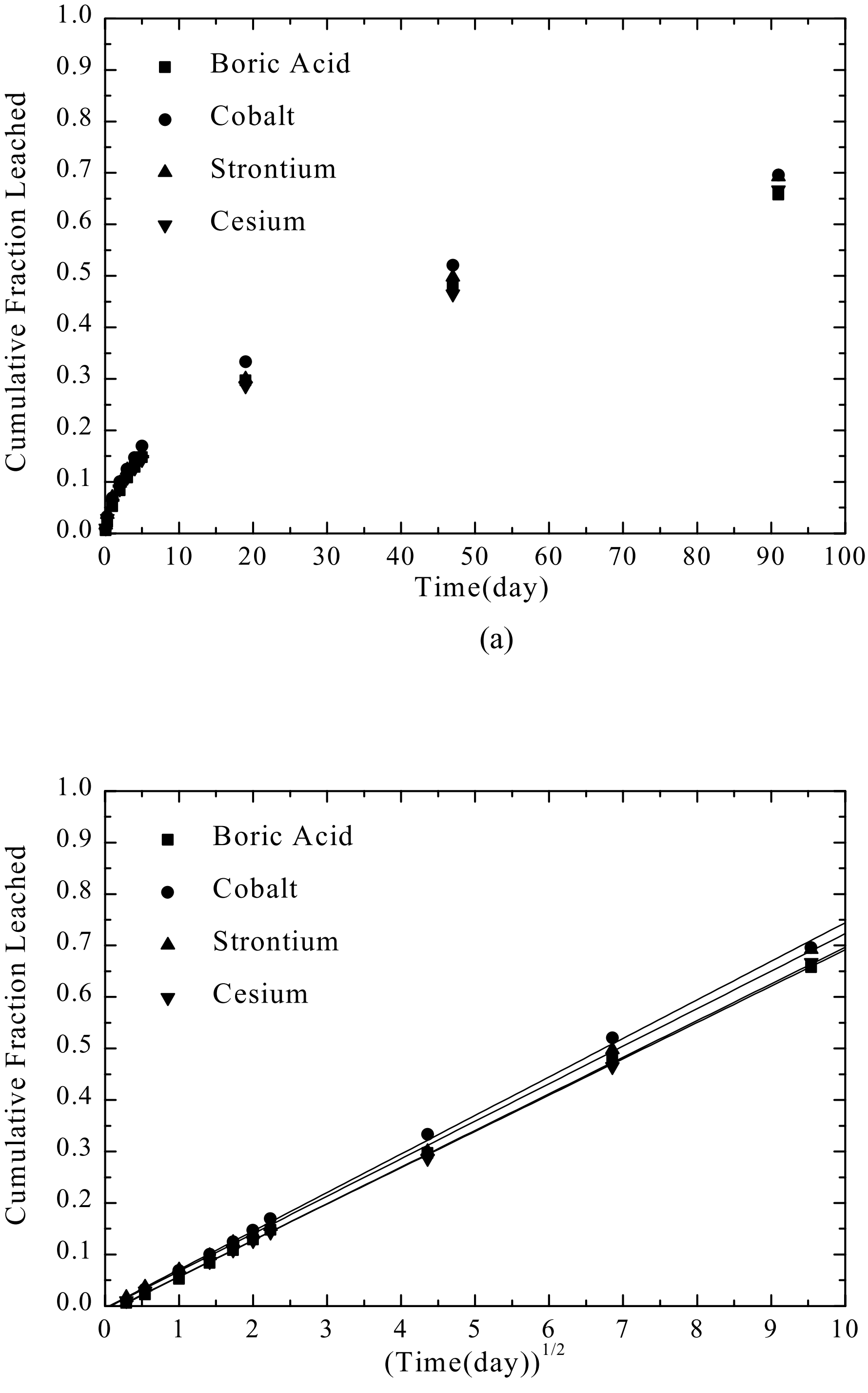
Because the potential for accumulation of potentially dangerous gas mixtures in a given waste package arises from imbalance between generation and removal processes, an existing gas diffusion model to consider loss mechanisms by which hydrogen can escape from the packages was implemented in a new computer program. In order to calculate pressure build-up and flammability hazard inside a sealed waste package, a hybrid approach was used to reflect both hydrogen generation in waste packages and hydrogen diffusion from these packages. Overpressurization inside the engineered barrier structure under repository condition was preliminarily assessed based on a simple analytical approach.

Predictions of the hydrogen concentrations within the paraffin-encapsulated drum head space showed that it will not exceed the lower flammability limit of 4% by volume. It is therefore concluded that flammability hazard caused by radiolytic hydrogen formation inside a paraffin-encapsulated drum will not exist. Overpressurization within the concrete vault caused by these gas productions will also not be occurred provided that the vault design is assumed to adopt porous concrete layer in its lower part of the structure.

- **Investigation of leaching characteristics of paraffin waste forms**

Low-level liquid borate wastes have been immobilized with paraffin wax using concentrate waste drying system(CWDS) in Korean nuclear power plants. Leaching tests of paraffin waste forms including boric acid, cobalt, strontium and cesium were performed to investigate the leaching characteristics of paraffin waste forms which had been generated in Korean nuclear power plants. The leaching tests were conducted according to ANSI/ANS-16.1 test procedure and the cumulative fractions leached(CFLs) of boric acid, cobalt, strontium and cesium were obtained(Figure 3).

The compressive strength before and after the leaching test was measured for various waste forms with different mixing ratios of boric acid to paraffin. It was observed that boric acid and other nuclides immobilized within paraffin waste forms were congruently released and the leaching rates were influenced by reacted layer depth as the dissolution reaction progressed. A shrinking core model based on the diffusion-controlled dissolution kinetics was developed in order to simulate the test results. The CFLs and the leaching rates were well expressed by the shrinking core model and the cross-sectional view of specimen after the test demonstrated the applicability of this model with the shrinking dissolution front to the leaching analysis of paraffin waste forms(Figures 4, 5).



(a)

(b)

FIG. 3. CFLs of Boric Acid, Cobalt, Strontium and Cesium Plotted as a Function of Time(a) and Square Root of Time(b)

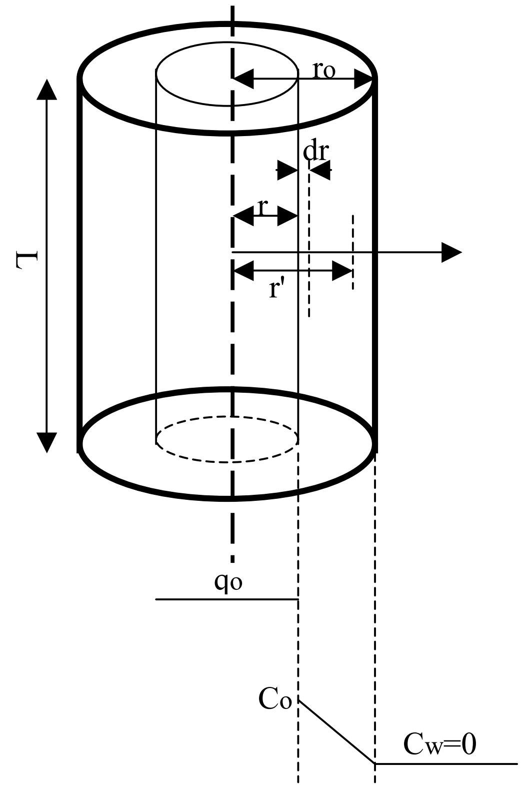


FIG. 4. Conceptual Diagram of Shrinking Core Model in Long Circular Cylinder Coordinates

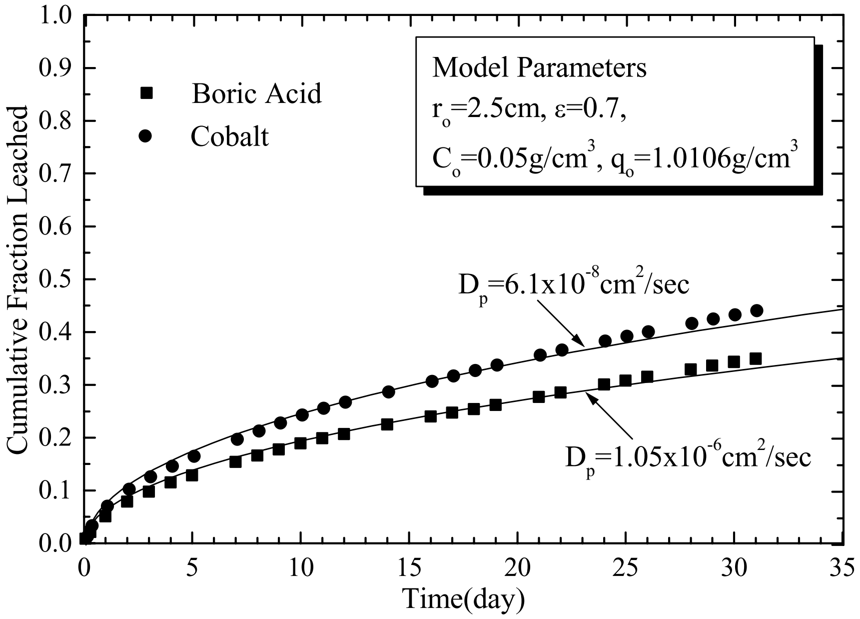


FIG. 5. Comparison between Model Predictions and Leaching Test Results in Long Circular Cylinder Coordinates

- **Experiment and analysis on leaching characteristics of actual cement waste form generated from nuclear power plant**

The leachability indexes of radionuclides contained in cement-solidified waste from an operating nuclear power plant in Kori were determined. Compressive strength of waste form after leach test was also measured. Samples of cement-solidified waste form were collected from Kori NPP unit 1. Samples were cored out from a full-scale waste form (200-liter drum size). Evaluation of leach data was performed using ANS 16.1 leach test procedure. The leachability indexes for cesium and cobalt isotopes were determined. Averaged leachability indexes were 8.6 for cesium and 11.4 for cobalt. Compressive strength after leach/immersion test was 7.34 MPa for the sample immersed in simulated sea-water and 8.34 MPa for the sample immersed in deionized water.

Cumulative release fractions for cobalt and cesium isotopes are shown in Figures 6 and 7 as function as square root of time. Release data for cobalt show two linear regions. This behavior shows a change of release mechanism. The predominant release mechanism of first period is called ‘surface effect’. The predominant release mechanism of first period may continue during the second period but may have little effect on second release. This effect may be negligible on second release. For Cesium, the surface effect release did not be shown as having one linear region. It is caused by high effective diffusivity and high solubility for cesium. These high values may mask any surface effects. The effective diffusivities are all the same for 90 days.

Semi-infinite diffusion model was used for analyzing the release mechanism of cement. It was found that the diffusion is the release control mechanism of cobalt, but surface effect must be considered, especially short-term leach test. The release control mechanism of cesium is diffusion. The depletion effect did not occur during the 90-day, leach test period. Semi-infinite model shows good agreement in comparison with the measured data(Figure 8).

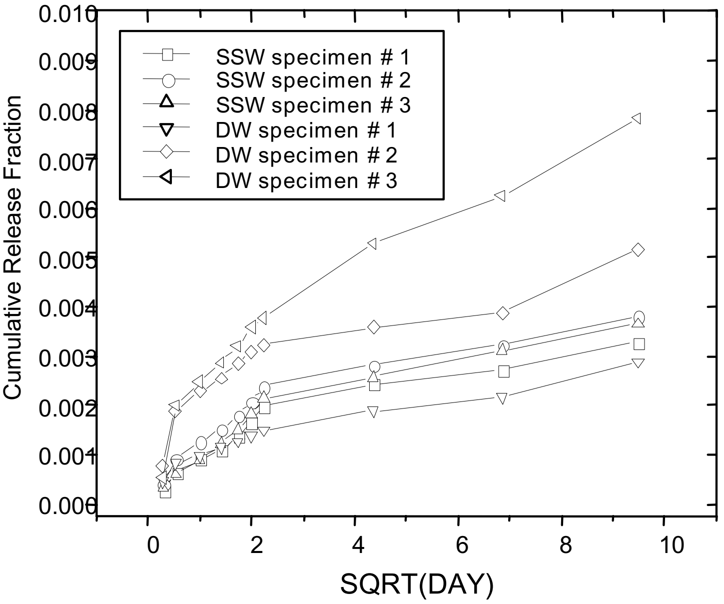


FIG. 6. Cobalt-60 Release from Cement Waste Forms as Functions of the Square Root of Time

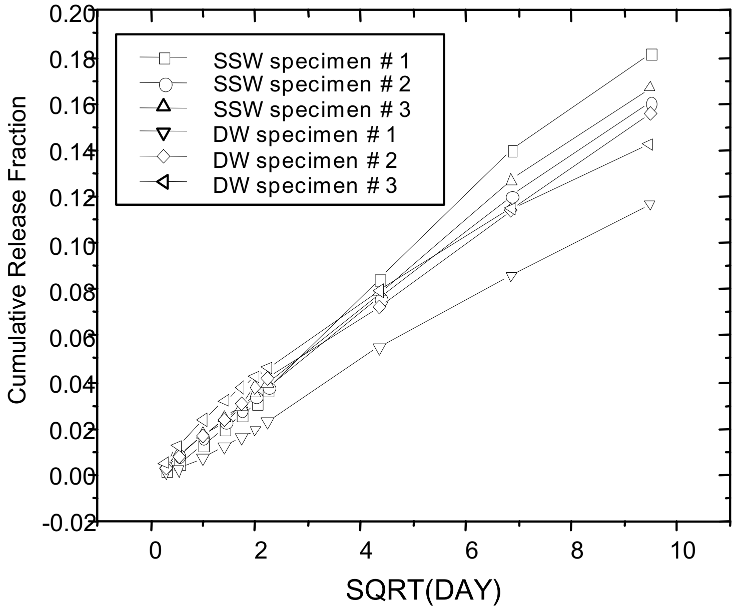
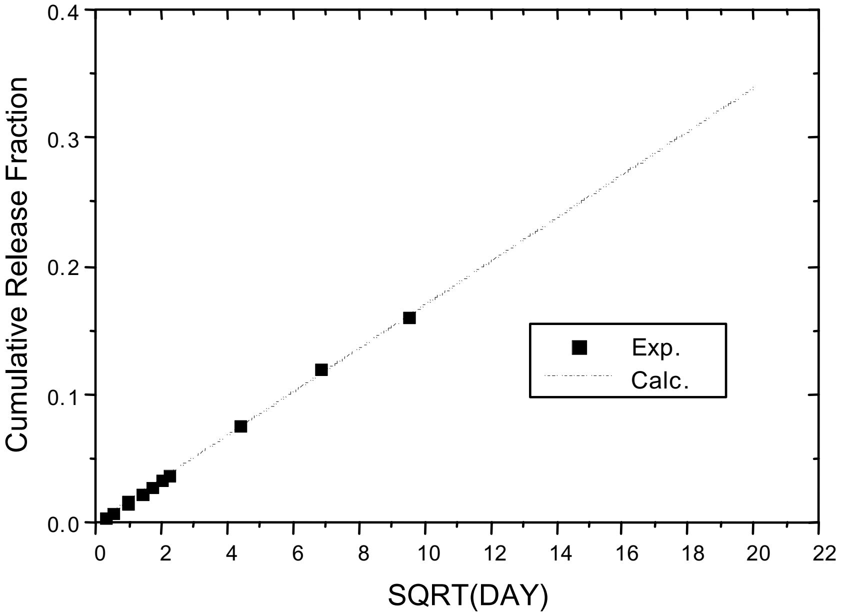
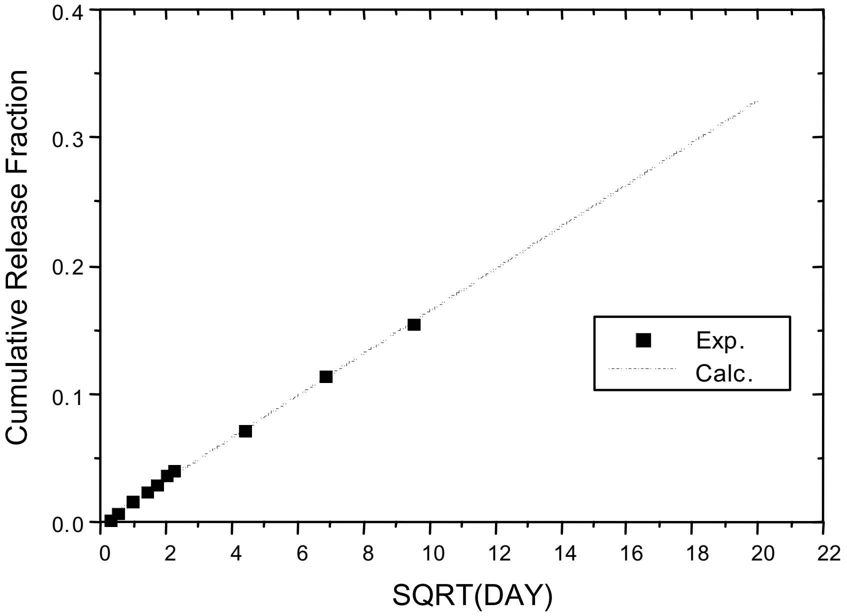


FIG. 7. Cesium-137 Release from Cement Waste Forms as Functions of the Square Root of Time



SSW- Cs

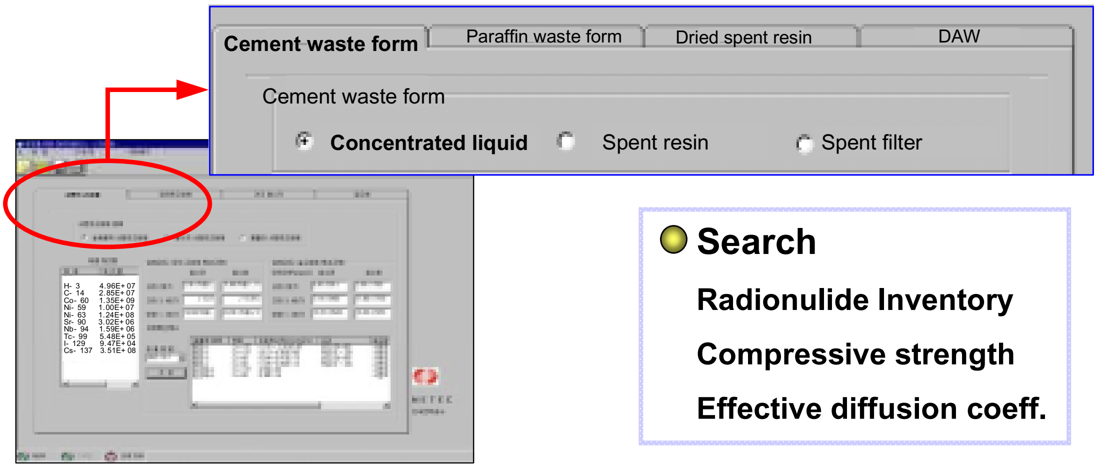


DW- Cs

FIG. 8. Comparison between Seim-infinite Diffusion Model Prediction and Leaching Test Results for Cesium-137

– **Data compilation of radioactive waste form and packages characteristics**

DOT drums, high integrity containers(HICs), and concrete packages are currently used at the nuclear power plants in Korea. Data and information on radioactive waste packages and plant-specific process control programs(PCPs) from domestic nuclear power plants have been collected and reviewed. Package database search program(PACKDB) are developed by using Visual Basic language. The purpose of this program is to regulate the collected data of waste package and waste form for later-use as the input data of source-term evaluation model in repository performance assessment. Database was composed of menus on file management, solidified waste form and waste package(Figure 9).



● Concentrated liquid ○ Spent resin ○ Spent filter

```
H-  3     4.96E+07
C-  14    2.85E+07
Co- 60    1.35E+09
Ni- 59    1.00E+07
Ni- 63    1.24E+08
Sr- 90    3.02E+06
Nb- 94    1.59E+06
Tc- 99    5.48E+05
I-  129   9.47E+04
Cs- 137   3.51E+08
```

FIG. 9. Illustrative View of Package Database Search Program(PACKDB)

– **Modification and revision of the REPS source-term code for the safety assessment of low- and intermediate-level waste disposal**

The existing REPS (Repository Source-term) code, which was developed by NETEC, includes the following submodels on surface water penetration into the repository, concrete degradation, corrosion of container drums, leaching of radionuclides from waste forms and migration of radionuclides from engineered disposal vault. The state-of-the-art on the concrete degradation and its effect on radionuclide transport and durability of disposal vault in view of service life were extensively reviewed. Improvement of data input on diffusion coefficient was made in the code. It can internally calculate the diffusion coefficient for each nuclide, not using default value in the previous version. And in order to facilitate the code usage enhancement of graphic user interface(GUI) was made. Simple data preprocessor and postprocessor were developed to run the code on PC Windows environment.

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LONG TERM BEHAVIOUR OF LOW AND INTERMEDIATE LEVEL WASTE PACKAGES UNDER REPOSITORY CONDITIONS

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Abstract

This work comprises the results of investigations conducted in connection with the cessation of a near surface LILW repository at Kjeller, Norway. The nearly 1000 drums in the repository was retrieved in the autumn of 2001 after 31 years of storage within the clay barrier. The repository contained 80 GBq plutoinum, 2.5 Gbq uranium and more than 1 TBg each of 90Sr and 137Cs. Studies of the integrity of the clay barrier showed that with two minor exeptions no contamination were present outside of the repository. Typically the radioactive species that had leaked from the few damaged drums were contained in the 2 cm of clay closest to the drum surface. Investigations of the physical condition of one waste drum subjected to 23 years of repository storage showed that little or no degradation had taken place either in the concrete shielding or in the inner steel container material. Except from 20 drums set aside for further studies, the whole inventory of the near surface repository have now been tranferred to the KLDRA-Himdalen repository and storage site.

1. INTRODUCTION

In 1970 a total of nearly 1000 drums and 19 other units containing radioactive waste were buried in clay at IFE-Kjeller. After a safety assessment he drums were disposed with approval from the Norwegian Radiation Protection Authority. The drums were stacked in two layers. The field had an area of 276 m^2.

The drums were buried in clay. The reason for choosing clay was that it provides a good barrier against leakage of radioactivity from the field. The water flow through clay is indeed low.

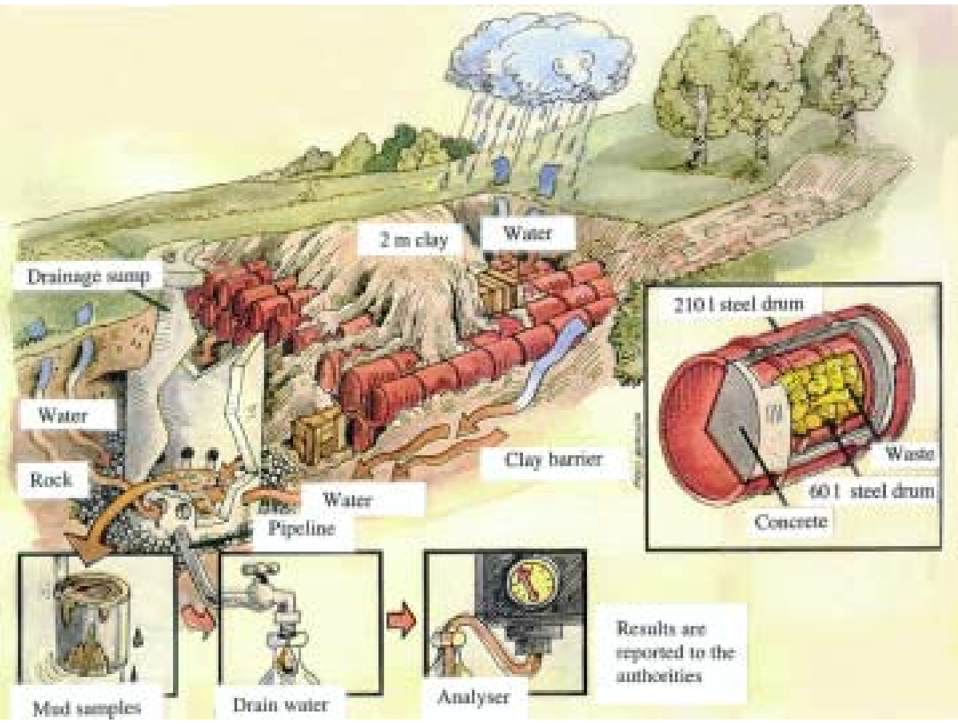

FIG. 1.1 Artistic view of the near surface repository at IFE-Kjeller.

Water running through the field is collected in a drain sump. The water is controlled before it is released. The annual release of radionuclides from the repository is estimated to less than 0.1% of the permitted release limit.

When the drums were buried in 1970, this method was recommended by the IAEA and in accordance with current international practise. Radiation protection policy has however changed since then. When the Norwegian parliament in 1994 decided to build a combined storage and repository for low- and intermediate level radioactive waste in Himdalen (KLDRA), it was also stated that the drums should be retrieved and transferred to this new repository.

It should also be mentioned that in 1993, representatives from the environmental foundation 'Bellona' committed a forced entry to the premises and uncovered some drums, one of which were damaged by the mechanical digger. IFE took advantage of the incident and dug up 5 drums for inspection. In addition, 10 drums were retrieved in 1994.

1.1 Inventory

The radioactive waste consists of laboratory waste, organic liquid absorbed in vermiculite and dried ion exchange mass. Metallic waste is embedded in concrete. For high dose rate waste, the drum is equipped with a lead inner container. The total activity in the repository is calculated to be 2 900 GBq (1.7.1997). The activities for the most important nuclides are shown in Table 1.1.

TABLE 1.1. INVENTORY OF THE NEAR SURFACE REPOSITORY AT IFE KJELLER

Nuclide	**Half-life [years]**	**Activity [1] [GBq]**
^{60}Co	5.3	60
^{90}Sr	28	1340
^{137}Cs	30	1360
^{239}Pu	24 000	85
U(nat)	$4.5 \cdot 10^9$	2.6
Other [2]	-	<100

[1] Activity as per 1. July 1997

2) Other nuclides includes ^{3}H, ^{14}C, ^{55}Fe and ^{204}Tl

The repository contains 80 GBq plutonium (35 g) in 166 drums and 2.5 GBq uranium (100 kg) from the former reprocessing pilot plant.

1.2 Contamination in the surroundings of the repository

With two exceptions, no contamination has been detected in the surroundings of the buried drums. One borehole close to the drain sump showed activity concentrations of ^{137}Cs of 10-600 Bq/kg. A trace of ^{137}Cs was also found in another borehole.

1.3 Contamination of clay and water in the repository

The activity levels on rust and clay from the drums range from 1.5 MBq/kg and down. Samples of water taken after retrieval of the drums had a content of ^{137}Cs in the range 1–50 Bq/l and for ^{90}Sr from 1–10 Bq/l. Clay and sludge profiles from the bottom of the repository had activity levels up to 100 kBq/kg in the first 2 cm. Samples from profiles showed that the activity was concentrated in the 2 cm of clay closest to the drum surface.

2. RETRIEVAL OF THE WASTE

Retrieval of the buried drums was carried out during the autumn of 2001. A major part of the drums were in remarkably good condition. Some drums had suffered from surface corrosion but no evidence of rupture of the inner container was observed.

The picture shows a drum that is lifted out from the repository. Clay on the drum surface is mechanically removed before the drum is lifted into a new drum. The new drum has a volume of 300 litres. The space between the old and the new drum is filled with concrete prior to transport to the KLDRA repository. The 166 drums containing plutonium (identified by having two bungs) shall be transferred to the storage tunnel at KLDRA.

FIG. 2.1 Retrieval of the waste drums.

An extensive program was set up to monitor activity in the surrounding clay. The Norwegian Radiation Protection Authority has provided free classification limits. None of the samples taken revealed activity concentrations above this level.

The area surrounding the repository and the repacking area was defined as a controlled area. Personnel doses were registered on a daily basis using electronic dosimeters in addition to the standard TL dosimeters. Monitoring of airborne radioactive particles was accomplished by the use of personal air samplers and a stationary air-monitoring unit. Whole body measurements of the staff involved were performed after end of the operation. The resulting personnel doses were low and no intake of radioactivity was found.

3. STUDY OF THE WASTE DRUMS

3.1 Identification and documentation

All drums were initially marked by drum numbers painted on the surface. For each drum number, there exists a drum journal with information on the waste and the type of container. The information content of the journal is, however, of variable value. Some of the drum journals do not contain information on radionuclides present or activity of the waste. After 21 years in the ground, the numbers on many drums were impossible to read. In conclusion, little is known about the activity and isotope contents of each drum. Drums containing plutonium were however easy to identify as the have two bungs.

All drums were given new identification numbers and were photographed before reconditioning.

3.2 Pilot study

One of the drums retrieved in 1993/1994 was selected for a pilot investigation. This drum was selected on the criteria that the outer surface was among the most heavily corroded and that information of the composition of the waste was available. The aim of the investigation was to:

- Determine if leakage of radionuclides through the barriers had taken place.
- Inspect the barriers, especially the concrete shielding, for visible degradation.
- Check the information in the journals on drum construction (shielding, inner container).

The method used was to drill out cores from the concrete shielding using a commercially available core drilling device generating cores with a diameter of 7 cm. The length of the cores corresponded to the thickness of the concrete shielding, typically 10–15 cm. Three cores were taken from the drum.

FIG. 3.1 Drilling cores from drums no. 6.

Visual inspection of the cores revealed that the concrete shielding was in remarkably good condition. No visible degradation or cracks were observed. The inner steel container was also found to be in good condition with no visible corrosion.

The cores have been analysed using high-resolution γ-spectrometry. The plan was to make a measurement of the inner and the outer core end and compare the spectra from the two sides. If there is a difference in activity, the cores will be sliced into appropriate samples for a quantitative analysis.

The measurements showed that the samples contained ^{137}Cs. It was, however, no difference in the activity on the two sides. It should also be noted that loose corrosion sampled from the outer surface of the drum had a much higher ^{137}Cs activity.

The conclusion was that the investigated drum was in good condition and that leakage of radioactive material from this drum had not taken place. It is necessary to investigate more drums to establish if this drum is representative for the majority of drums in the repository. The presence of ^{137}Cs on the outer surface does indeed indicate that some of the drums must have been leaking.

Measures have been taken to ensure that radiation protection is attended to during the investigation. All treatment of waste drums must be performed in an "active area", that is an area that only can be entered using protective clothing and wearing a personal dosimeter. Effort was made to find a suitable area with acceptable working conditions and where possible contamination from core drilling can be handled safely.

The external dose rate from the selected drum was rather low, typically 20 μSv/h. The main risk was thus connected to contamination. The core drill is cooled using running water, so the risk for generating airborne contamination was low. The spill water may however be contaminated. Care was taken to collect the water in a drip-tray. The amount of water used was kept as low as possible to reduce the amount of liquid waste generated. The idea was to let the water evaporate naturally from the drip-tray.

Protective clothing as rubber gloves and a disposable suit are to be used during core drilling. A full-protection breathing mask is required as some cooling water tends to spurt from the drill.

3.3 Further studies

Most of the nearly 1000 drums retrieved have already been reconditioned and are being transferred to the KLDRA repository and storage site.

Some few drums have however been put away to have the possibility to perform studies on degradation of barriers. Totally 20 drums are available, 10 of these are identified as "plutonium drums". These drums are temporarily stored at a cold storage at the IFE-Kjeller site. Investigation of these drums will depend on the interest and possibility for funding of this project.

DURABILITY OF CEMENTED WASTE IN REPOSITORY AND UNDER SIMULATED CONDITIONS

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Abstract

The research activities performed by the Department of Radioactive Waste Management are focused on the aqueous low level waste (LLAW) treatment products obtained by chemical precipitation and on the conditioning of these products by cementation. The individual mechanisms involved in the chemical precipitation process are directly dependent on the precipitate properties and structure, which are connected with the initial system composition and the precipitation procedure, i.e. reagent concentration, rate and orders of chemical addition, mixing rate and time and ageing conditions. In the case of conditioning by cementation, the chemical nature and proportion of the sludge or concentrates affect both the hydrolysis of the initial cement components and the reactions of metastable hydration constituents, as well as the mechanical strength and chemical resistance of the hardened cemented matrix. Generally, the study of the precipitation products and their behaviour during cementation and the long-term disposal is extremely difficult because of the system complexity (phase composition and structure) and the lack of non-destructive analytical methods.

1. BACKGROUND

The management of the non-fuel cycle radioactive wastes from all over Romania is centralized at IFIN — HH in the Radioactive Waste Treatment Plant (STDR). Final disposal is carried out at the National Repository of Radioactive Wastes (DNDR) at Baita Bihor. Wastes containing short-lived radionuclides, which do not require any special treatment, except the temporary retention at the producer for decay period, may then, be transferred as a normal non-radioactive waste. Wastes containing long-lived radionuclides are collected, treated and conditioned at IFIN — HH before final disposal.

TABLE I. TREATMENT AND CONDITIONING CAPABILITY OF STDR AT MAGURELE

SOLID WASTE	TREATMENT METHODS
LLW	Segregation, Incineration, Shredding, Compacting (220 Kg/cm^2) Conditioning in 100 l and 220 l drums by cementation (final: 220 l drums) Reconditioning of 220 l drums in 420 l drums
ILW, Spent Sources	Direct conditioning by cementation in 220 l drums
AQUEOUS WASTE	**TREATMENT METHODS**
LLW	Chemical treatment by precipitation (first step), using iron chloride, sodium phosphate, potassium ferrocyanide; DF = 30 (approx.) evaporation (second step), DF = 1000 (approx.) Total DF = 10000 (approx.) Release level after dilution in the river 1850 Bq/m^3 (5 x 10^{-8}Ci/m^3)
ILW, ^{3}H, ^{14}C	Direct conditioning by cementation

At present the containers used at STDR for packaging radioactive wastes are stainless steel and painted carbon steel drums of 100, 220 and 420 liter capacity. The annual production of final packages after liquid treatment is 150-200 standard 220 liter drums with a surface dose rate up 2 mSv/h, an activity up 3.7 x 10^{13} Bq/m^3 and surficial contamination for γ and β emitters up to 3.7 Bq/cm^2.

TABLE II. PRESENT STATUS OF STDR-IFIN-HH

Type Of Waste	**Storage Capacity (total)**	**Present Storage Status**	**Maximum Activity**	**Maximum Annual Arising**
Low Level Aqueous	2 x 300 m^3	~40%	37 MBq/m^3 (10^{-3} Ci/m^3)	10^3 m^3
Low Level Solid	20 m^3	3 m^3	37 MBq/m^3 (10^{-3} Ci/m^3)	10^3 m^3
Intermediate Level	200 m^3 (shielded drums)	12	Equivalent to surface dose rate of 2 mSv/h (200 mrem/h)	70 shielded drums
Spent Sources	3,000	40	370 TBq (10^4 Ci)	400
Fire Detectors	~10^5	16,908	1.85 x 10^7 Bq (0.5 mCi)	10^4
Neutron Sources	~100	18	Non established	20
Conditioned Package	3,000	800 (corroded drums)	Conforming with operation license	400

From November 1974, when the STDR became operational, to November 2000, the plant has treated nearly 26000m^3 of LLAW, 2100m^3 of solid low level waste LLSW and 4000 spent radiation sources, resulting in over 5500 conditioned drums. The transfer of conditioned wastes from the STDR to the DNDR for final disposal started in 1987 with an annual rate of nearly 500 drums up to 1993 and then 150-200 drums yearly.

National Repository for Low Level and Intermediate Wastes of Baita Bihor is operated under the responsibility of the IFIN — HH, organized within the Ministry of Research and Technology. Responsibilities after disposal are not yet defined. The repository was originally an exploration drift with several galleries at an open pit mine for uranium, which was exhausted in 1985.

Mining was carried out by conventional techniques to ensure access and ventilation in the disposal galleries. Operation at the repository started in 1985. Legal acceptance is provide by the National Commission for Nuclear Activities Control (CNCAN), the Bihor Country Authorities and Municipality of the local town, Nucet, and some upgrading activities are considered necessary.

The site is 840 m above Black Sea level in the North-West Carpathian Mountains, about 8 Km from the nearest community, the Baita village, and about 10 Km from a little town of Nucet within Cris river basin.

Originally there were exploration galleries and from one of them, Gallery 50, there were excavated 18 transversal galleries, 13 on the right and 5 on the left, used as depositing cells. Another one, Gallery 53, is used as an air intake.The repository is excavated in the Permian sandstones and phyllitic rocks with diabasic and granitic intrusions.

The present capacity in the galleries is 21 000 standard container (220 litter drums) with 800-m galleries and cross section of 10 m^2 available. This would ensure a period of 40 years storage capacity for radioactive wastes originating from the scientific research and industry. In the absence of an up dated Safety Analysis Report, The maximum radioactive content permitted by the Regulatory Body in the operation license is below the values reported for other mine galleries engineered repositories. The facility is 20% full. The capacity of repository could be extended up to 150 000–200 000 containers to be able to accept the Low and Intermediate Level Wastes arising from other sources.

2. OBJECTIVES; RELEVANCE TO THE NATIONAL PROGRAM

Disposal of the conditioned radioactive wastes is the final step of the radioactive management and its objective is the protection of population and environment.

The medium and long term safety assessment of every repository implies:

- The evaluation of normal and predictable phenomena, most of them depending on the technological aspects of the management steps (collection, segregation, treatment, conditioning, packaging, transport, disposal).
- The evaluation of the phenomena, which are not all certain in the disposed package or in the disposal environment over an established period.

For the first part of evaluation, it must be established that a laboratory and experimental field determination data are available for waste package characterization, at least:

- Leach rate correlated with medium/long term stability of the waste form;
- Corrosion resistance of the packaging material in the repository environment;
- Physical and chemical behavior of the back-filling material at the contact with waste matrix and packaging material.

The study based on this data will give the prime indication of the period of time during the leaching is absent and the rate of radionuclide release after advanced damage of the waste packages.

The purpose of this experimental program is to obtain a part of the data basis necessary for the approach of medium and long term assessment of the safety and performance of Baita — Bihor Repository.

The safety of the radioactive waste disposal is a priority issue concerning the protection of the environment and population. In this sense, the engineering multi-barrier system needs to be improved, especially, the waste conditioning matrix.

The research activities performed by Department of Radioactive Waste Management is focused on the LLAW treatment products obtained by chemical precipitation and on the conditioning of these products by cementation.

The individual mechanisms involved in the chemical precipitation process are directly dependent on the precipitate properties and structure, which are connected to the initial system composition and the precipitation procedure, i.e. reagent concentration, rate and orders of chemical addition, mixing rate and time and ageing conditions.

In the case of conditioning by cementation, the chemical nature and proportion of the sludges or concentrates affect both the hydrolysis of the initial cement components and the reactions of metastable hydration constituents, as well as the mechanical strength and chemical resistance of the hardened cemented matrix.

Generally, the study of the precipitation products and their behavior during cementation and the long-term disposal is extremely difficult because of the system complexity (phase composition and structure) and the lack of the non-destructive analytical methods. By chance, iron is commonly present in all systems and following the naturally ^{57}Fe isotope by Mossbauer Spectroscopy is possible to have valuable information about the composition structure and coordination of the iron containing species. For a more detailed characterization, a complementary analytical method was XRD, performed for precipitates and cemented matrices.

The following systems are considered for a detailed understanding of the species and mechanisms, the structure, properties and performances of the processes and behavior of the products:

- Study of iron precipitates obtained during LLAW treatment;
- Structural modifications in the iron hydrated oxides induced by foreign cautions;
- Precipitation processes with alternative and / or simultaneous presence of bivalent and trivalent iron ions;
- Influence of precipitation procedure on the decontamination factors;
- Dry and hydrated cement systems;
- Cementation of sludge chemical components;
- Influence of organic complexants on the cemented matrix performances and structure;
- Influence of mineral additives on the concrete;
- Thermal damage of simulated conditioned waste;
- Durability of cemented waste in repository and under simulated conditions.

Cement hydration is a process of cement and concrete transformation, which consist of chemical reactions between anhydrous cement particles and water producing hydrates. There is no simple relationship between hydration and setting. The setting process can be described as following two fundamental steps: the coagulation of grains and setting of the coagulated structure, which arises, simultaneously with the acceleration of the hydrate formation. The final stage of the setting process is a connected and strengthened system of particles. This system is used in the management of the radioactive waste for immobilization of radionuclides contained in the precipitation sludge, evaporation concentrate, incineration ash and spent ion exchangers.

To update the safety assessment, a large experimental database concerning the short and medium term cement matrix behavior is necessary, and based on these data to predict the long term behavior of the waste package and radionuclide dispersion in environment.

The selected matrices proposed for the study are normal cement and concrete compositions with and without mineral additives (bentonite and volcanic tuff) as reference samples, the conditioned matrices prepared with radioactive sludge non-active components (iron hydroxides and phosphate, calcium phosphate and copper ferrocyanide) and non-active matrices prepared with organic acids and salts (oxalic, citric, tartaric, EDTA). Similar samples were prepared with real radioactive sludge, concentrate and ash.

All samples were positioned in five points of Baita-Bihor repository and kept 1,2,5 and 10 years before mechanical and structural characterization. These results will be compared with results obtained for the same type of samples kept in laboratory conditions.

The presumed alteration of mechanical and physic-chemical properties will be correlated with a non-destructive analysis of the matrix performed by XRD, with thermal resistance tests and leaching experiments.

3. SCOPE OF WORK

3.1 Preparation and characterization of normal reference matrices based on different cement formulations

i. After one year were characterized the reference samples: cement-water (cement paste) and cement-sand-water (mortars), kept in Baita repository and under simulated conditions in distilled water and in bentonite in the Radioactive Waste Treatment Plant laboratory.

Samples of reference:

- cement — water with a cement/water ratio 2:1
- cement — sand - water with a cement/sand/water ratio 1:2:0.5

For the mechanical tests, the sizes of the samples were 40 x 40 x 160 mm (tested at bend and compression) and 20 x 20 x 20 mm (tested at compression). After the preparation, the samples were kept 24 hours in pattern, then in tight plastic bag for 7, 14 and 28 days for reinforcement.

The bend and compression tests were done in a construction material laboratory, using an electric press machine.

After 28 days the samples of reference were introduced in the National Repository. Some of these samples are kept in simulated conditions of laboratory.

ii. Sample kept in real repository conditions, at Baita-Bihor:

In the repository were placed different cement matrices prepared with bentonite and/or volcanic tuff, and with acids used in the decontamination processes.

iii. Samples kept in laboratory conditions.

Same samples were kept in laboratory conditions for comparison.

3.2. Influence of mineral additives on the mechanical performances of the conditioning matrix

The experience accumulated by the countries who developed nuclear programs in military and socio-economic fields and which produced important volumes of radioactive wastes, lead us to study some of mineral additives to be used in the conditioning and disposal technology. Is well known that mineral additives are diminishing the leaching rate of the radionuclides in the disposal environment.

The studies have the purpose to obtain the most propitious mixture of cement-bentonite and cement-volcanic tuff, which have the mechanical properties similar to the cement paste used for the conditioning of radioactive waste.

Taking into consideration the characteristics of these mineral binders: very good plasticity and capacity of adsorption, which lead at the decrease of porosity, in the future, the mixture is wished to be used at the Radioactive Waste Treatment Plant — NIPNE-HH-Bucharest, Magurele for the conditioning of the radioactive waste.

Bentonite is a clay already used in the technology of disposal as a filling material to diminish the radioactivity spreading because of degradation in time of the metallic package or the intrusion of casual waters.

Taking into consideration the property of mineral additives to fill in the presence of water, fact that drive to the apparition of the internal tensions in the matrix structure which guide at the apparition of the microfissure, the mixtures examinated by mechanical tests have in their composition max. 10% mineral binders.

It is of importance to choose some optimal indigene sorts of natural ion changers that can be used as effective barriers against the migration of radionuclides deposited in natural geological formations. In this respect, the volcanic tuff and bentonites existing in a series of ore deposits from Romania were studied and have been used. On the basis of this studies for confinement of nuclear wastes were chosen the volcanic tuff with 65% zeolites from Salaj region and bentonite from Valea Chioarului.

To study the mechanical behavior of the cement-mineral additive matrix, were prepared a series of samples containing cement and bentonite or volcanic tuff in different ratios. For the cement-bentonite-water system were used the following ratios: 1-0,05-0,5; 1-0,5-1,25; 1-0,05-0,5; 1-0,05-0,45; 1-0,1-0,5; 1-1-2,2; 1-0,2-0,7; and for cement-volcanic tuff-water: 1-0,5-0,5; 1-0,2-0,5; 1-0,1-0,5; 1-0,1-1.

The sizes of the samples were: 40 x 40 x 160 mm (tested at bend and compression) and 20 x 20 x 20 mm (tested at compression).

After the preparation, the samples were kept 24 hours in pattern, then in tight plastic purse for 7, 14 and 28 days, for reinforcement.

3.3. Influence of complexing agents on the mechanical performance of the conditioning matrix

Taking into consideration the fact that the conditioning technology of radioactive wastes foresce to include the sludge resulted from the chemical treatment of radioactive liquid effluents into cement matrix, is possible, during a long period of disposal because of the interaction between the complexing agents used and the matter, the cement matrix to be degraded, fact that can allow the radionuclide migration from the disposed container.

Radioactive effluents containing complexing agents as oxalic and citric acids are generated during the radioactive decontamination operation using chemical methods. The conditioning of these wastes by cementing process imposed the experimental determination of the mechanical performances of the matrix and the upper permissible level of complexing agent concentration.

The studies performed until now have as object to establish the upper level concentration of some decontamination solutions as citric acid, tartaric acid, oxalic acid, ammonium oxalate and sodium citrate which can be contained in the cement conditioning matrix, and do not affect its mechanical performances.

To determine the influence of complexing agents on the mechanical performances of cement conditioning matrix were prepared cubic samples (20 x 20 x 20 mm) using commercial Portland cement and solution of organic complexing acids or salts (citric acid, oxalic acid, tartaric acid, sodium citrate and ammonium oxalate).

The complexant concentration varied between 0,25% and 1%, in distilled and drinking water. The selected cement / water ratio was 0,5.

The experiments focused on:

- Establishing the firmness of the Pa 35 cement pastes and mortars in dependence on the water / cement ratio, so by classical methods (Tetmeyer probe for pastes and standard cone for mortars) and by trickling time through a funnel with a 15 mm aperture;
- Studying the influence of the tartaric acid, oxalic acid, citric acid, ammonium oxalate and sodium citrate solutions concentrations on water quantities used to obtain pastes with normal firmness and on Pa 35 cement setting;
- The oxalic acid, tartaric acid and ammonium oxalate solutions concentration influence above the strength of compression of the pastes with normal firmness ; for tests was used standard test bar cubes with 20 mm sides, and the strength of compression was tested at 28 days;
- Establishing the behavior in time of the mechanical strength, checking the strength of compression at 90 days and the adequate seemingly density in comparison with the standard tests characteristics prepared with drinking water and distilled water. The strength of compression was done using hydraulic presses.
- The citric acid, sodium citrate and ammonium oxalate solution concentration influence on the strength of compression at the age of 60 and 90 days ;
- For all the mixtures used in this research, were established the setting times (by using the Vicat device), outlining the specific time of set curves, characterized by setting beginning, setting interval and setting ending.

The standard test bar cubes were prepared by manual mixing, and the mixtures that were used do not raise problems about the workability of the paste, which was considered to be in standard limits.

3.4. X-rays diffraction investigations

The study contains X-rays diffraction measurements performed on Portland cement samples: hydrated, non-hydrated and thermal treated at: 100, 200, 400, 600 and 800^{o}C. The purpose of this microstructure analysis by X-rays diffraction was the identification of the compounds which appear at cement hydration, in order to obtain useful information to explain the structural modifications inducted both by some Fe compounds and by the radioactive precipitate on the cement matrix.

The following systems were prepared and investigated:

- Dry and hydrated cement;
- Mechanical mixtures of hydrated cement with iron hydroxides and iron phosphates, the main components of the radioactive sludge resulted in the chemical precipitation of the radioactive waste.

The aim of this work was to use the X-rays diffraction methodology for the characterization of the compounds, which appear at cement hydration and the iron components in the cement matrix obtained by the radioactive waste conditioning.

Much useful information can be obtained by using Mossbauer methodology as an associated method at X-rays diffraction.

These methods for "in situ" analysis estimate the modifications, which appear in a first approximation in the systems:

- cement-water (for reference);
- cement-water-iron compounds.

Portland type cement is commonly used as binder reagent and is composed mainly by trioxides: SiO_2, CaO and Al_2O_3 with small amounts of MgO, Fe_2O_3 and SO_3. The four basic compounds of the cement Portland are: $3CaO.Al_2O_3$ (tricalcium aluminate), $3CaO.SiO_2$ (tricalcium silicate), $2CaO.SiO_2$ (dicalcium silicate) and $4CaO.Al_2O_3.Fe_2O_3$ (tetracalcium aluminoferrite)

Cement hydration is a process of cement and concrete transformation, which consist of chemical reactions between anhydrous cement particles and water producing hydrates. There is a simple direct relation of cause - effect between hydration and setting. The setting process can be described as following two fundamental steps: the coagulation of grains and rigidification of the coagulated structure, which arises, simultaneously with the acceleration of the hydrate formation. The final stage of the setting process is a connected and strengthened system of particles. This system is used in the management of the radioactive waste for immobilization of radioelements contained in the precipitation sludge, evaporation concentrate, incineration ash and spent ion exchangers.

A number of workers have investigated hydration of the individual cement compounds in Portland cement paste used in radioactive waste conditioning. Work by Copeland et all suggests that hydration of the pure cement compounds is slower than that of the same compounds in cement paste. Also, water / cement ratio (w/c) influences the rate of hydration, the tendency being that the greater the w/c ratio, the greater the hydration rate. Alite and belite hydrate at very different rates, belites being much slower hydrate than alit.

For the X-rays diffraction and the Mossbauer study of dry, hydrated Portland cements, iron species and their chemical transformation during the cement hydration and hardening, a series of samples were prepared starting from two Portland cement batches N and V (N was fresh and V six months stored).

Samples with a cement / water ratios varying from 10:1 to 2:1 were prepared as follows:

NH(or VH) 101-10 g cement+1ml distilled water
52 – 5 g cement+2ml distilled water
21 – 2 g cement+1ml distilled water

The hardening of the N batch hydrated samples was faster than the V batch samples of hydrated cement with a cement/water ratio =2:1 was termically treated at 100, 200,400, 600, 800°C for 1 hour.

The samples of iron hydroxides were prepared as follows:

- Fe1:20ml $FeCl_3$ (40%) in 1l water were neutralized with 52,5ml NaOH(20%),final pH was 6,2
- Fe2:20ml $FeCl_3$ were neutralized adding 55ml NaOH diluted in 1l water,final pH:7,4
- Fe3:50ml NaOH+20ml $FeCl_3$ diluted in 1l water,final pH:7,1
- Fe4:20ml $FeCl_3$/1l water+32 g Na_3PO_4,final pH:6,0

Conditioned samples of precipitates were prepared as follows:

- FeN (V):525-5 g cement+2,5 g wet precipitate
- FeN (V):55-5 gcement+5 g wet precipitate.

These samples were investigated by X-rays diffraction an appropriate method for investigation of the cement hydration-hydrolysis mechanism and the influence of iron compounds on the cement mixture.

3.5. Studies of dynamics of water in hydrating cement pastes by inelastic slow neutron scattering (samples with $CaO•SiO_2$, $Fe_2(PO_4)_3$ and NaCl)

In the inelastic neutron scattering experiments taken on DIN-2PI high intensity time of flight spectrometer at the fast pulsed reactor IBR-2 of the Frank Laboratory of Neutron Physics at JINR Dubna, the microdynamics of cement mixtures is studied. The samples of $CaO•SiO_2$ mixed both with H_2O and D_2O were prepared in Institute of Physics and Nuclear Engineering IFIN HH Bucharest. The data are analyzed in terms of the generalized vibration density spectra (GVDS) derived from double differential cross section. The hydrated cement matrix in presence of fresh precipitate of ferric hydroxide (Fe $(OH)_3$), phosphate ($Fe_2(PO_4)_3$) and NaCl are also investigated.

Chemically, cement produces a reacting matrix with a porous microstructure. Therefore knowledge of the dynamics and developing microstructure is important to assess the compatibility of radioactive waste streams with cement to be able to predict the performance of the waste form during storage and disposal. To improve the safety of disposal, it would be necessary to immobilize these wastes to produce a long-term stable solid waste form. Cement hydration is a process of cement and a concrete transformation, which consists of chemical reactions between anhydrous cement particles and water producing hydrates. Generally, the study of the precipitation products, their behavior during cementation is difficult because the system complexity (phase composition and structure). Hydrating cement pastes, as a complex disordered system, have been studied up to now by small angle neutron scattering (SANS) neutron diffraction and Mossbauer Spectroscopy. Here we report first experiments performed on such as samples using inelastic slow neutron scattering technique. A special attention in this paper is paid to the behavior of water and heavy water in such as matrix with a porous microstructure. It seems that the hydrating cement pastes are forming fractal structures with a size of fractals of the nanometers order. The (GVDS) for all investigated samples support such as conclusion.

The experimental information obtained from a neutron scattering process on a hydrogenated system is essentially determinate by the very large incoherent scattering cross section of proton, ($\sigma_{inc} >> \sigma_{coh}$ and about 10-20 times larger than that of other elements) and the small H mass. The incoherent cross section by supposing H atoms forming a simple cubic Bravais lattice can be written:

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc} = \left(\frac{\sigma}{4\pi}\right)\left(\frac{k}{k_0}\right)S_{inc}(Q,\omega) \tag{1}$$

where $S_{inc}(Q,\omega)$ is the incoherent scattering function. The conservation of momentum and energy during the scattering yield:

$$Q = \left|k_0 - k\right|;\ \omega = \varepsilon = E_0 - E \tag{2}$$

where E$_0$, E, k_0 and k are neutron energy and wave vector before and after scattering and Q is the scattering vector. The generalized vibration density of states (GVDS) can be obtained in the harmonic one-phonon approximation by:

$$S_{inc}(Q,\omega) = \left(\frac{F(\ \omega / k_B T)}{2M|\omega|}\right)Q^2 g(\omega)\exp(-2W) \tag{3}$$

with g(T) the GVDS, F(x) the thermal population factor given by $F(x)=(e^x-1)^{-1} + 1/2\ (1\pm1)$ with the upper and lower sign corresponding to phonon creation and phonon annihilation, respectively and exp(-2W) is the Debye-Waller factor usually defined by $\exp(-Q^2\rangle u^2\langle)$ where $\rangle u^2\langle$ is the mean-square amplitude of the proton.

On the other hand in a scattering process on deuterated systems coherent scattering dominates and GVDS can be derived from the experimental data by a method assuming the average of the coherent effective cross-section due to the variation of the final wave-vectors orientation of neutrons:

$$\sigma(E_0 \to E)_{\theta_1,\theta_2} = \int_{\theta_1}^{\theta_2} \sin\theta \frac{d^2\sigma}{d\Omega dE} d\theta \cong \frac{b_{coh}^2 \exp(-2W)\left(Q_2^4 - Q_1^4\right)}{8k_0^2 M} \frac{g(\omega)}{\omega\left(\exp(\ \omega / K_B T) - 1\right)} \tag{4}$$

with b$_{coh}$ the coherent scattering length and Q$_1$ and Q$_2$ the minimum and the maximum values of the wave vector transfer Q of neutrons scattered between angles θ_1 and θ_2.

3.6. Permeability studies on different cement matrices in addition with bentonite and/or volcanic tuff

From the nuclear security point of view, the behavior of the conditioned waste package, which is the most important barrier, must be studied the permeability of the cement conditioning matrix. The studies performed for several years have as object to obtain a cement matrix with high mechanical resistance and low permeability.

In laboratory were done determination of the fresh cement characteristics and on the strengthen cement paste, resulting:

- L2 usability;
- Content of rally air – 6,5%
- Apparent density – 2.225 kg/m^3.
- Low-plastic firmness – 2,5 cm.

The samples (cubic samples — 20 cm size) were liable to a water jet at 12 atm, and was measured the water height in the sample.

The composition of the samples used for the permeability test is presented below:

Pa 35 cement	**Bentonite/Volcanic tuff (additive)**	**Water**	**Ratio**	
			W/A*	**W/C**
Kg/m^3	Kg/m^3	L/ m^3		
C - 667	-	333	-	0,5
B - 625	62,5	312,5	0,454	0,5
VT - 625	62,5	312,5	0,454	0,5
B+VT - 625	31,75 + 31,75	312,5	0,454	0,5

* A = additives (bentonite or/and volcanic tuff)

3.7 Studies of dynamics of water in hydrating cement pastes by inelastic slow neutron scattering (cement + bentonite samples with different rates)

The neutron spectrometry techniques provide a powerful tool for non-destructive evaluation and of the structure and dynamics studies of the condensed matter of particularity importance on the materials, which present high interest both of fundamental and applied point of views. In the last time the neutron scattering methods (small angle neutron scattering SANS), neutron diffraction (ND), qvasielastic neutron scattering QENS and inelastic neutron scattering, INS) have been oriented to investigate the structure and the dynamics of hydrated cement pastes [1-10]. As it is known, when ordinary Portland cement (OPC) is mixed with water, a period of rapid reaction lasting only a few minutes is followed by an induction period during which the hydration reactions proceed at a much slower rate. After a period of a few hours, the rate of reaction increases again and the cement begins to harden. Cement also produces a reaction matrix with a porous microstructure. The evolution of the inner structure of the hardened cement paste as well as the hydration kinetics is of great interest. Many investigators have studied the process of cement hydration with a variety of tools, because understanding of and control over the cement hardening process is obviously of great economic importance [11, 12]. Nevertheless many aspects of the cement hydration process remain unexplained OPC is a heterogeneous material composed of four major and several minor crystalline compounds, the phase composition is highly variable. The structure and reactivity of the individual compounds are strongly influenced by the condition under which they are formed and started, the type and concentration of impurities, the nature and concentration of their structural disorder and their particle size distribution. In order to simplify the investigation of the cement hydration problem, one can study the individual cement compounds instead of OPC. The rate of hydration of cement compounds is normally measured by thermal calorimetric, which gives the overall kinetics at early times but not measure the rate of product formation directly. Quantitative x-ray diffraction analysis (QXDA) can be used to measure the rate at which the starting compound is consumed and ignition techniques can used to measure the amount chemically water but neither of these techniques can be used. To monitor the early kinetics. These difficulties encouraged the development of new analytical tools such as: real time measurements of the progress of cement hydration using neutron diffraction [13], Ramon scattering [14], synchrotron x-ray diffraction [15], quasielastic neutron scattering [16-18]. The quasielastic neutron scattering can be used to probe the chemical state of water in the cement system, the rate of reaction product formation can be measured by determining the rate at which freely diffusing pare water is converted into bound water within the reaction product. Neutrons are scattered by a hydrating cement paste, both elastically and inelastically. The scattered intensity is dominated by the scattering dorm hydrogen because of its large incoherent cross section compared to other elements present in a cement paste [19]. The elastically scattered component of the spectrum has a Gaussian distribution in energy of a width determined by the energy resolution of the spectrometrum. The integrated intensity of this component is directly proportional to the number of hydrogen nuclei that are, chemically bound to the cement gel and henceimmobile. The inelastically scattered neutrons exhibit a Lorentzian energy distribution with a width that is related to the state of diffusion (translational and rotational) of the hydrogen atoms over time of scale given by:

$$\Delta t \cong \frac{}{\Delta E} \qquad Q = (4\pi/\lambda)\sin\theta/2 \tag{5}$$

And a distance scale:

$$\Delta L \cong \frac{2\pi}{Q} \tag{6}$$

Here h is Plank's constant, λ is the neutron wavelength, ΔE is the energy resolution of the instrument, θ the neutron scattering angle [20]. Because the cement paste, pore water and hydration products contain hydrogen atoms, these characters make quasielastic neutron scattering ideal for the study of the rate of reaction in hydrating cements. QENS measurements of a hydrating cement paste can directly quantify the fraction of water in the sample that is chemically bound. If the stoichiometry of the reactions is sufficiently well understood, the bound water index (ratio of chemically bound water to total water) can be converted to the degree of reaction and the measurements used for detailed studies of the reaction kinetics. The problem becomes more complicated if various chemical components added in order to improve the quality of cement used for radioactive waste conditioning. To improve the safety of disposal, it would be necessary to immobilize these wastes to produce a long term stable solid waste form.There is a limited knowledge of the chemical reactions and the products formed during the mixture of the cement with solid or liquid waste and water. The study of the precipitation products and their behavior during cementation and the long-term dispersal is an extremely difficult task. More information related to the prance of various precipitations can be obtained by means of the inelastic neutron scattering. The latter technique can give the same information live QENS and more than that if provides now data about the vibration states of the system in presence of these precipitates. The investigation of cementing conditioning system involving nonhydrated and hydrated cement and matrices prepared from anhydrous cement and fresh precipitate of ferric hydroxide, phosphate, calcium hydroxide, bentonita in the presence of both H_2O and D_2O is the main aim of the present investigation. Among most other methods, neutron scattering allows a detailed understanding of the static and dynamic properties on an atomic scale of materials that occur in our environment. Combined with x-ray scattering a very large range of momentum and energy transfers can be covered thanks to the high complementarily of both techniques. The most relevant, unique character of neutrons that cannot be matched by any other techniques, can be summarized as follows:

- The neutron interacts with the atomic nucleus and not with the electrons as x-rays does. This has important consequences:
  - The response of neutrons from light atoms like hydrogen or oxygen is much higher than for x-rays;
  - Neutrons can easily distinguish atoms of comparable atomic number;
  - Neutrons distinguishes isotopes; for example, deuteration of macromolecules allows focusing on specific aspects of their atomic arrangement on their motion.

- For the same wavelength as hard x-rays the neutron energy is much lower and comparable to the energy of elementary excitations in matter. Therefore, neutrons do not only allow the determination of the "static average" chemical structure, but also the investigation of the dynamic properties of the atomic arrangements that are directly related to the physical properties of materials.

- By virtue of its neutrality, the neutrons is rather weakly interacting with matter, which means that there is almost no radiation damage to living objects under study. Also, the rather weak interaction with matter results in a large penetration depth and therefore the bulk properties of matter can be studied. This is also important for the investigation of materials under extreme conditions such as very low and high temperatures high pressure, high magnetic and electric field etc.

- The neutron a carries a magnetic moment that makes it an excellent probe for the determination of magnetic structures and magnetic excitations.

The monoenergetic neutrons with the energy E0 = 10.476 meV and an experimental resolution of DE = 0,5 meV, measured by means of a vanadium sample has been used to investigate the following samples:

Here C denotes Portland Cement; B - bentonite and D_2O is heavy water.

$C + Ca(OH)_2O + D_2O$
$C + D_2O(100\%)$
$C + B + D_2O$
$C + Ca(OH)_2 + D_2O$
$C + Al(OH)_3 + D_2O$
$C + Al(OH)_3 + D_2O$
$C + NaSiO_2 + D_2O$
$C + H_2O$
$C + B + H_2O$
$C + Ca(OH)_2 + H_2O$

The measurements have been performed by means of the time of flight spectrometer DIN-2PI, set up at 2-nd channel of the reactor IBR-2. Time of flight spectra taken within an angular range of $6–134^0$ by using He^3 counters.

4. RESULTS

4.1 Preparation and characterization of normal reference matrices based on different cement formulations

In Table 3 are presented initial and after one year disposal values obtained for the cement: water and in Table 4 for the cement: sand: water mixture.

TABLE III. CEMENT, WATER

Sample (prisms/ cubes)	**F_{bend} (daN)**	**R_{bend} (daN/cm^2)**	**F_{comp} (daN)**	**R_{comp} (daN/cm^2)**
I. cement: water after 28 days	294	69	4553 / 1340	285 / 335
II. cement: water after 1 year disposal under distilled water (laboratory conditions)	353	83	6813 / 1133	426 / 283
III. cement: water after 1 year disposal under bentonite and distilled water (laboratory conditions)	362	84	7031 / 1139	439 / 284
IV. cement: water after 1 year disposal in real conditions: samples placed in 5 positions	296 to 465	71 to 108	4956 to 6356/ 1505 to 1740	369 to 400/ 376 to 435

TABLE IV. CEMENT, SAND, WATER

Sample (prisms/cubes)	**F_{bend}(daN)**	**R_{bend} (daN/cm^2)**	**F_{comp} (daN)**	**R $_{comp}$ (daN/cm^2)**
V. cement: sand: water after 28 days			/ 1288	/ 322
VI. cement: sand: water after 1 year disposal under distilled water (laboratory conditions)	318 / -	58 / -	5506 / 1285	344 / 321
VII. cement: sand: water after 1 year disposal under bentonite and distilled water (laboratory conditions)	422 / -	98 / -	4310 / 1325	330 / 661
VIII. cement: sand: water after 1 year disposal in real conditions a. 1 position b. 2 position c. 3 position d. 4 position e. 5 position	410 / - 490 / - 503 / - 436 / - 345 / -	95 / - 114 / - 117 / - 101 / - 80 / -	5015 / 1305 5644 / 2592 5100 / 1287 5832 / 1317 5969 / 1175	313 / 325 352 / 377 318 / 321 364 / 329 373 / 293

For both cases we can observe, as was expected, the increasing of all resistance values after one year disposal for all examined samples. Comparing the obtained results for the samples kept in real and simulated conditions, we can see that the mechanical resistances are similar. There are slow increases of the resistance values for the samples kept in bentonite with distilled water than those kept in distilled water. The mechanical resistances obtained for all the samples are included in the accepted limits for the matrix durability. Thus, disposal conditions haven’t influenced the mechanical properties of the cement matrix after one year disposal. The results show us that bentonite seems to have a positive influence on the examined matrix quality.

4.2 Influence of mineral additives on the mechanical performance of the conditioning matrix

The combination of the cement with bentonite establish an evolution of the reologic characteristics, in which course are noticed more stages.

The results shows that with the growth of the content of bentonite, are growing the viscosity and the fluently threshold, but the permeability and the mechanical resistance are diminished. This behavior can be explained by the retaining of a part of the water volume by the cement, and also by the manifestation of a false setting phenomena generated by the partial flocculation of the bentonite in the presence of cement.

The second stage corresponds to the mixing up of the compound and its specific feature is the diminishing of viscosity. From now on, in the time interval before the starting of the cement setting, the viscosity doesn’t record significantly variations. In the last stage, the viscosity growth, behavior explained by the starting of the cement setting.

In the presence of water, the bentonite influence the cement: bentonite exert on cement a “buffer” action of delaying or, even more, of braking the reactions between cement and water, which can explain the late set of the paste and the smaller mechanic resistance, that those obtained for the cement-water paste.

From other point of view, after the cement-bentonite reactions appear secondary compounds of cementation.

The reinforced mixture is defined by slow permeability: at 28 days the permeability index is about 10^{-6} cm/s; in time the permeability recede up to 10^{-7} cm/s.

One of the conditions that are necessary to take in consideration, is the size of the bentonite and volcanic tuff particles. Using bentonite with big size particles, the mechanic resistance, the drying contraction, the swollen at moisture and the material length (durability) are negatively influenced.

The samples which contain volcanic tuff have smallest values of mechanical resistance, but by the technically point of view, they are situated in the limits forecasted in standards.

In the following Table are presented the most significant mixtures obtained, which have the best mechanical properties in comparison with the cement paste, used now at the conditioning of radioactive wastes.

TABLE V. STRENGTH AT BEND AND COMPRESSION. INITIAL VALUES FOR CEMENT-MINERAL ADDITIVES SAMPLES

Sample	**F_{bend} (daN)**	**R_{bend} (daN/cm^2)**	**F_{comp} (daN)**	**R_{comp} (daN/cm^2)**
Cement-water (prisms) (reference system) – 2 samples	261 to 308	61 to 72	4500 to 5120	281 to 320
Cement-water (cubes) (reference system) – 4 samples			680 to 1040	170 to 260
Cement-volcanic tuff-water 1: 0,1: 0,5 (prisms) – 3 samples	165 to 263	38 to 61	2750 to 3170	171 to 198
Cement-volcanic tuff-water 1: 0,1: 0,5 (cubes) –12 samples			470 to 710	117 to 177
Cement-bentonite-water 1:0,01:0,5 (prisms) – 3 samples	208 to 297	48 to 69	3050 to 4530	190 to 283
Cement-bentonite-water 1: 0,1: 0,5 (prisms) – 3 samples	202 to 258	47 to 60	4630 to 5850	289 to 365
Cement-bentonite-water 1: 0,1: 0,5 (cubes) - 10 samples			1000 to 1650	250 to 412

The samples which contain volcanic tuff have smallest values of mechanical resistance, but by the technically point of view, they are situated in the limits forecasted in standards.

4.3 Influence of complexing agents on the mechanical performance of the conditioning matrix

In generally, the recorded influences are reduced at low concentrations of solutions. Once with the growth of the concentration, is ascertain that the acids and their salts interfere in the cement paste chemistry and had setting delay effects (over 0,6% - 0,7%), and at 1% concentrations, the mixtures present over 20 hours interval until setting end. This fact drives at the conclusion that concentration higher than 1% delay too much the cement reinforcement phenomena, and must be avoided.

In Table 6 are presented the compression tests results for the mentioned solutions, in comparison with standard tests: standard test bar cubes made with drinking water and with distilled water.

TABLE VI. STRENGTH AT COMPRESSION. INITIAL VALUES FOR CEMENT — COMPLEXING AGENTS SAMPLES

Composition Standard test bar with-	**Concen tration (%)**	**Period (days)**	**F_c (daN)**	**S_c (daN/ cm^2)**	**Period (days)**	**m (g)**	**ρ_s (g/cm^3)**	**F_c (daN)**	**S_c (daN/ cm^2)**
Distillate water	-	28	1720 2090	430 522,5	90	17,4 17,2	2,18 2,15	2160 2890	540 722,5
Drinking water	-	28	1600 1930	400 482,5	90	14,4 15,2	1,80 1,90	1450 1600	362,5 400
Oxalic acid	0,25	28	1810 2100	452,5 525	90	14,9 15,2	1,86 1,90	1660 1830	415 457,7
Oxalic acid	0,5	28	1800 1960	450 490	90	17,3 16,5	2,16 2,06	1740 2310	435 577,7
Oxalic acid	1	28	1850 2100	462,5 525	90	14,7 15,2	1,84 1,90	1270 1470	317,5 367,5
Tartaric acid	0,25	28	1410 1860	352,5 465	90	16,2 17,0	2,03 2,13	1380 2120	345 530
Tartaric acid	0,5	28	1130 1560	282,5 390	90	15,9 16,5	1,99 2,06	980 1000	245 250
Tartaric acid	1	28	120 200	30 50	90	14,7 13,3	1,84 1,66	40	80 20
Citric acid and distilled water	0,25	60	1820 2090	455 522,5	240			1570 1720	392,5 430
Citric acid and distilled water	0,5	60	1920 2800	480 700	240			1880 1930	470 482,5
Citric acid and distilled water	1	60	800 1175	200 294	240			1090 2030	272,5 507,5
Citric acid and drinking water	0,5	60	1500 1625	375 406	240			1430 1580	395 357,5
Citric acid and drinking water	1	60	1540 2000	385 500	240			1550 1700	387,5 425
Ammonium oxalate	0,25	28	1670 2280	417,5 570	90	17,2 17,0	2,15 2,13	1640 1700	410 425
Ammonium oxalate	0,35	28	1790 1830	447,5 457,5	90	15,8 17,1	1,98 2,14	1750 2090	437,5 522,5
Ammonium oxalate	0,5				90	16,5 16,8	2,06 2,10	1450 1730	362,5 432,5
Ammonium oxalate	1				90	14,5 16,1	1,81 2,01	1870 2130	467,5 532,5
Sodium citrate	0,25				90	16,2 17,5	2,03 2,19	2620 2660	645 655
Sodium citrate	0,5				90	16,8 16,3	2,10 2,04	1990 2530	497,5 632,5
Sodium citrate	1				90	16,5 16,8	2,06 2,10	1360 2280	340 570

For each composition was moulded 6 standard test bar cubes, and the values presented in the table reflect the minimum and maximum strength at compression values obtained.

The tables contain the results obtained for 0,25%, 0,5% and 1% concentrations, considered to be representative for the research.

Comparing the results obtained after 28, 60, 90 and 240 days, is ascertain that for concentrations of solution used at decontamination, comprised between 0,25% and 0,5%, the mechanical performances are similarly with the results obtained for reference cement matrix samples (exception doing the tartaric acid).

With the growth of concentration over 0,5% values, the mechanical strength became smaller and smaller, the recorded values are situated much under the necessary limits needed for the radioactive waste conditioning matrix.

4.4. X-rays diffraction investigations

The X-rays investigations was performed with a diffraction system using Cu-kα radiation. The computer was associated for data computerized analysis. Calculating "d" parameters for all diffraction maxims which appears in the polycrystalline mixture spectrum and comparing with "d" values from ASTM (American Society for Testing Materials) cards can be obtained an qualitative analysis for crystalline phases.

Generally, the study of the precipitation products resulted in the radioactive waste processing and their behavior during the cementation and long term disposal is extremely difficult because of their complexity (phase composition and structure) and the lack of the non-destructive analytical methods.

As a result of X-rays diffraction analysis on the samples: dry and hydrated cement, thermally treated hydrated cement at different temperatures (100, 200, 400, 600 and 800°C) and iron precipitates conditioned by cementation, was obtained diffraction spectra.

Besides the XRD method, the necessity of other structural correlated measurements (Mossbauer spectroscopy) was revealed.

Because the iron is commonly present in nearly all systems and following the naturally ^{57}Fe isotope by Mossbauer spectroscopy is possible to have valuable information about the composition, structure and coordination of the iron containing species.

The Mossbauer measurements were performed with a constant acceleration spectrometer using ^{57}Co(Rh) radioactive source. The experimental spectra were mostly recorded at room temperature (RT) and 80K,but for some samples the 4 K spectra were obtained in order to have a better knowledge of the samples.

By this micro-structural analysis, X-rays diffraction was identified the new formations, which appear at cement hydration and structural transformation, which appears at thermal treatment of the hydrated cement. The aim of this analysis is to obtain useful information about structural modification induced by some iron compounds, which are the main components of the radioactive sludge.

The results obtained in this work give us more information about physic-chemical processes, which are the basic processes for the cement hardening and the formation of concrete resistance structures.

XRD spectrums of the dry cement show us the significant presence of the calcium silicates which lines are overlapped.

Besides the calcium silicates were identified the others mineralogical compounds: tricalcium aluminize and tetracalcium aluminoferrite. The intensities of the characteristically peaks of these compounds are very small in comparison with those of the calcium silicates. So it appears that from the quantitative point of view the calcium silicates have a high proportion than the tricalcium aluminize and tetracalcium aluminoferrite.

Besides the specific peaks of mineralogical compounds of the cement, we also notice the presence of Portland cement clinker.

XRD spectrums of the hydrated cement emphasize crystalline hydrated newformations such as: tricalcium hydrosulfataluminate similar to the natural ettringite, $Ca(OH)_2$ well crystallised from the intergranular solution, the hexagonal calcium hydroaluminate $C_4AH_{13.}$ Compounds like calcium hydrosilicates and calcium hydroferrites are difficult to emphasize because of the higher spectrum background. There are also identified tricalcium silicates , dicalcium silicate and tricalcium aluminize which remain unreacted.

Thermal treatment of the hardened hydrated cement alters the hydrating product composition and structure. Are noticed a significant growth of the $Ca(OH)_2$ characteristically lines, which presents a higher grade of crystalinity. The hexagonal calcium hydroaluminate are transformed in cubic calcium hydroaluminate. The trisulfatate calcium hydroaluminate is thermally discomposed. At 100°C thermal treatment determine densification and structuration of the tobermorite gel.

When the temperature rise from 400 to 600°C and after 1 hour heating at 600°C two effects are noticed:decreasing of the specifically lines of the $Ca(OH)_2$ that is discomposed at 500°C and increasing of the specifically tobermorite lines, which gives a strain structure to the hardened cement.When temperature is raising the transformation of the calcium hydrosilicate CSH (I) in CSH (II) is noticed.

At 800°C after 1 hour of thermal treatment free CaO as well β-C_2S appears. The CaO appearing determine the volume inconstancy and has a negative effect on the hardened cement.

Mossbauer spectroscopy and XRD investigated the conditioned samples of precipitates. The Mossbauer spectra obtained for 1FeV, 2FeV, 3FeV, 4FeV reflected the best-embedded precipitate is one prepared with diluted $FeCl_3$ added on concentrated NaOH (3FeV), the cementation process implying one part cement and one part wet precipitate. The worst embedded precipitate is 4FeV because the iron phosphate avoids the embedding process.

4.5 Studies of dynamics of water in hydrating cement pastes by inelastic slow neutron scattering (samples with $CaO \bullet SiO_2$, $Fe_2(PO_4)_3$ and NaCl)

An incident neutron energy of 4.439 meV on the sample allowed to take the time of flight inelastic scattering spectra within of kinematics space (energy and wave vector transfer), $(Q,h\omega)$ with $0.15A^{-1} < Q < 2.7A^{-1}$ and $0 < h\omega < 200$ meV. After that the well known corrections for a time of flight neutron scattering experiment have been applied to the spectra; the final results are analyzed in terms of the generalized vibration density of states. The latter physical quantity for the cement hydrating pastes with H_20 is derived according to the formula (3) and it is shown in Fig.1. For the sake of the completeness we also present the frequency spectra of the liquid water measured by INS. In this case $g(h\omega)$ is obtained from the monophononic approximation for incoherent scatteres. The data shown for two scattering angles $\theta = 33^0$ and $\theta = 85^0$,clearly demonstrate that the coherent effects can be neglected and no angular dependence of the frequency spectra is detected. Another observation concerns the comparison of the frequency spectra of the water and that for various cement pastes. From earlier experiments it is known that the frequency distribution of light and heavy water do look similarly and the hindered rotation peak is shifted towards lower energies as the temperature is increased. It is also found that the ratio $(E_{max})H_2O/(E_{max})D_2O = 1.34$, is not far from $[2]^{1/2}$, if the H and D nuclei were the scattering centers and the motion was simple harmonic vibration. From Figure 1 is clearly observed that the the low lying energy region of frequency spectra for H_2O and D_2O (Fig.2) is present in the (GVDS) derived for various cement hydrating pastes. It could be interesting for a further experiment to study the role of the small energy vibrations of the water molecules on the physical properties of the cement as the temperature is lowered or increased. This question is open for new investigation. Unfortunately at this stage of the experiments one cannot formulate a final conclusion on the role played by the hindered rotation of the water ($h\omega \sim 60$ meV) on the dynamics of the cement pastes. While the high frequency limit of the frequency spectra in liquid water is cut at about 90 meV, this limit for various cement pastes is much higher and is extended up to 175 - 200 meV. This large limit is in agreement with the GVDS measured on SiO_2 [6]. The previous investigations shown that the hydrating cement pastes are forming fractal structures with the volume/mass fractals of nanometers order. As it is known, the nanocrystalline materials are defined as materials composed of crystallites smaller than 100 nm. The (INS) experiments performed on various nanocrystalline materials demonstrate that in comparison to material with large crystallites the nanocryslalline one shows two distinct differences in its (GVDS). In the low lying energy range ($h\omega \sim 15$ meV), (GVDS) is more than twice and increases to the density of grain boundaries. A second effect is the broadening of the (GVDS) similar to the effect observed in the case of the hydrating cement pastes as complex disordered systems. This becomes clearer from the comparison of (GVDS) for SiO_2 [6] to our results. This conclusion has to be proved by new investigation over different relaxation times of the investigated samples. A slow dependence of the (GVDS) broadening is also observed for various precipitation products both for the features in the energy range $h\omega = 75$ -100 meV and for $h\omega = 150$ - 175 meV. In order to get new information about the microdynamics of the precipitation products in the hydrated cement pastes during cementation, new experiments at various temperatures and relaxation times are planned. This could enlighten also the temperature dependence of the low lying energy vibration of the water molecule and its influence on the bulk properties of the concrete.

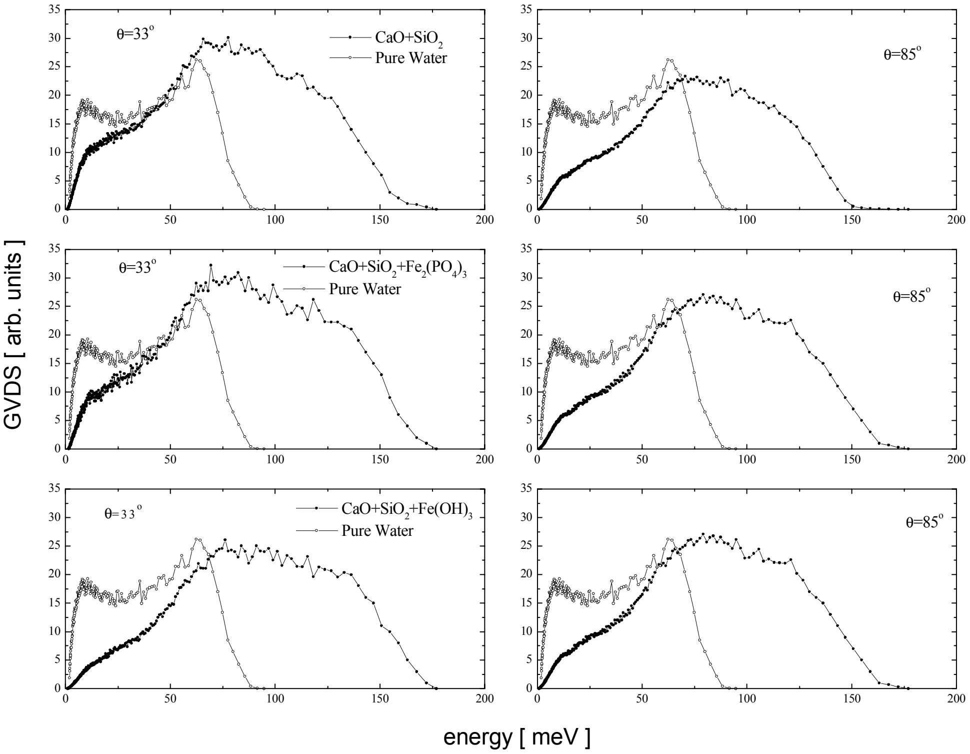

FIG. 1. Generalized vibration density of states for various cement components light-water hydrated.

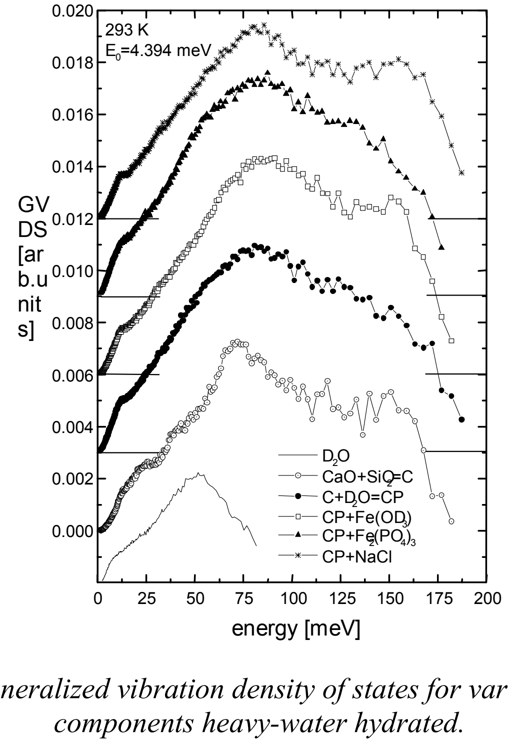

FIG. 2. Generalized vibration density of states for various cement components heavy-water hydrated.

4.6 Permeability studies on different cement matrices in addition with bentonite and/or volcanic tuff

The permeability study was based on the compositions obtained after the mechanical characterization. The results are presented in Table 7.

TABLE VII. INFLUENCE OF THE MINERAL ADDITIVES ON THE CEMENT MATRIX PERMEABILITY

Cement sample	**Cement measure**	**Mineral additive content**		**Total (c-a) content**	**Water**	**Water/ ligand ratio**	**Water penetration height**
	Kg/m^3	Kg/m^3	%	Kg/m^3	L/ m^3		cm
C 1	667	-	-	667	333	0.5	7.2
C 2	667	-	-	667	333	0.5	5.0
C 3	667	-	-	667	333	0.5	4.6
B 1	625	62.5	10	687.5	312.5	0.454	3.2
B 2	625	62.5	10	687.5	312.5	0.454	4.0
B 3	625	62.5	10	687.5	312.5	0.454	3.7
T 1	625	62.5	10	687.5	312.5	0.454	5.0
T 2	625	62.5	10	687.5	312.5	0.454	5.3
T 3	625	62.5	10	687.5	312.5	0.454	4.8
BT 1	625	62.5	10	687.5	312.5	0.454	5.7
BT 2	625	62.5	10	687.5	312.5	0.454	4.9
BT 3	625	62.5	10	687.5	312.5	0.454	5.1

Results obtained at the permeability test leads to the conclusion that the bentonite retains the water and so the matrix has a lower permeability. This can be explained by the formation of a supplementary gelic mass which collimate the cement pores increasing the compactity and by modification of the dimensional spectra of the pores with diminishing the pores easy accessible to water.

4.7 Studies of dynamics of water in hydrating cement pastes by inelastic slow neutron scattering (cement + bentonite samples with different rates, etc.);

The time of flight spectra taken from the sample above-mentioned are presented in Figures 3–4. In this figures the abscissa and the ordinate axes represent respectively: intensities measured at various scattering angles as a function of time of flight. The intensity (counts) is proportional to the double differential time of flight cross section:

$$d^2\sigma / d\Omega dt \tag{7}$$

Where dΩ is the solid angle under which the sample is seen by detector, t is time of flight of the scattered neutrons from the sample to the detector. For each sample, 20 spectra corresponding to the following angular range have been measured:

$$\phi_s = 6^0 \div 134^0 \tag{8}$$

and a transfer energy range in the scattering process of:

$$\omega = 0 - 200 meV \tag{9}$$

The time of flight channel width was taken at 8 sec. The analysis of the dynamic processes, which have place in the investigated samples, can be done in terms of the neutron scattering spectra shown in Figures 3–4. On the figures are also indicated the quantities of each component used in the sample preparation. The two spectra shown in each figure is an average over first ten angles (small) and over the last ten angles (large) in the interval 6^0 – 134^0. Two main parts of the inelastic scattering spectra have to be distinguished namely: the elastic component ranged within time of flight channel number: 670–800 and inelastic ranged within channels 300–670.

Roughly speaking the dynamics processes of these samples are dominated by the dynamics of water and heavy water. How these dynamics are influenced by the presence of various added precipitates we shall see further. The energies corresponding to various dynamic processes are indicated on the figures. The general analysis of the all obtained spectra in Figures 3–4 having as a reference point the spectra measured on C + H_2O and C + D_2O leads to the following conclusions:

- The dynamics of the cement hydrated with H_2O and D_2O is dominated by the latter ones the energy of 10 meV corresponds to the molecule vibration of the water molecule taken as a whole entity. While the peaks observed at 60 meV respectively 68 meV are assigned to be hydrogen rotation around to the center of mass of the water molecule which approximately coincide with the position of the oxygen atom. A small observed difference is due to deviation from an isotropy harmonic oscillation behavior of the H and D.

- The difference observed from the spectra at small and large scattering angles demonstrate a highly anisotropy of the static structure of these samples.

- The samples prepared by means of light water reveal more structural spectra and a more active dynamics 22 meV and 42 meV stands for the vibrations of the cement matrix. This dynamics is more attenuated by D_2O

- From the observation summarized items 1–3 one can arrive to the conclusion that the cement prepared with D_2O is better than one based on H_2O. The D_2O molecule is more bounded than H_2O.

- The presence of bentonite at large quantities as 10 g has an influence on the dynamics of deuterium while the vibrations of the D_2O molecule remains unchanged. A small amount of bentonite as 20 g has favorable role on the dynamics of D. Consequently, we can estimate that bentonite in large quantities has a positive role in the cement dynamics and its macroscopic properties.

- A very interesting dynamic structure picture is given by the presence of the Ca(OH) precipitate. The dynamics of D_2O molecule remain about unchanged while the presence of H in $Ca(OH)_2$ shows that the dynamic spectrum is very reach in details and the peaks are very well located. This dynamics is influenced by the quantity of $Ca(OH)_2$. A smaller quantity of the latter one consists of an attenuation of the vibration dynamics of the sample. Therefore we can appreciate that the smaller optimized quantity of $Ca(OH)_2$ precipitate has a better consequence on the quality of cement.

- The dynamics derived from the spectra show that the $Al(OH)_3$ precipitate compared to the $Ca(OH)_2$ has a much less influence on the dynamical properties of the C + D_2O and do not depends in a obviously way like in the case of bentonite or $Ca(OH)_2$.

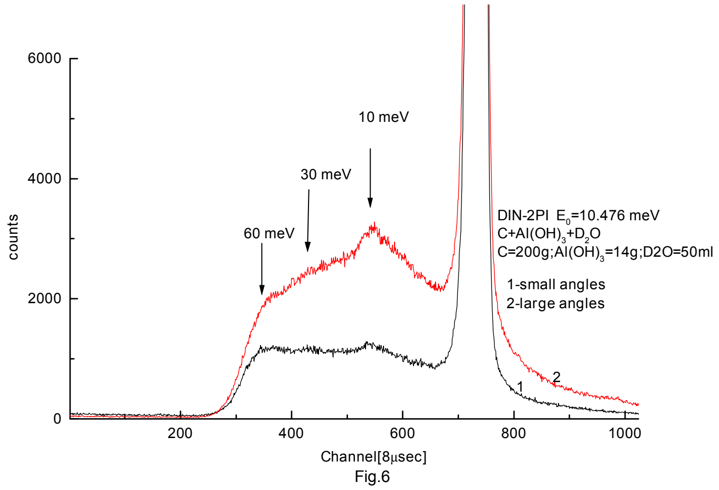

FIG. 3. Time of flight spectrum for cement + bentonite samples.

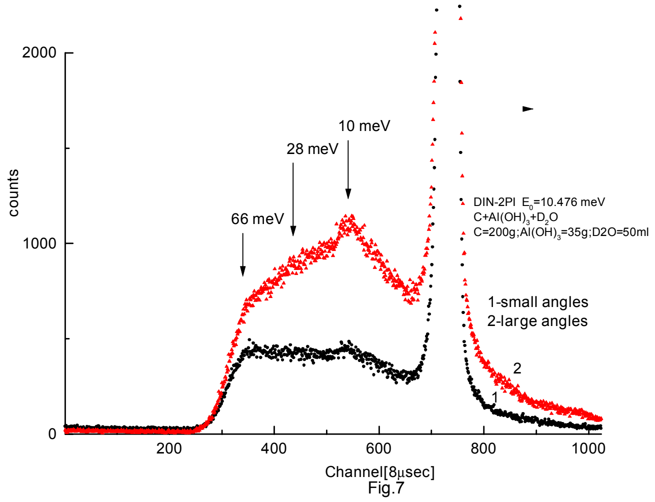

FIG. 4. Time of flight spectrum for cement + bentonite samples

4.8 Mechanical characterization of samples kept in Baita repository and in laboratory after three years

No.	Sample (prisms/cubes)	R_{bend} (daN/cm^2)	R_{comp} (daN/cm^2)
1.	cement - bentonite - water (1:0,1:0,5)	54,8	285 /
2.	cement - volcanic tuff - water (1:0,1;0,5)	65,2	334 /
3.	cement - bentonite - volcanic tuff – water (1:0,05:0,05:0,5)	66,1	301 /
4.	cement - sand - water (1:2:0,5) after 3 years disposal under distilled water (lab. conditions)	87,2	501 / 380
5.	cement - sand - water (1:2:0,5) after 3 years disposal under bentonite and distilled water (lab. conditions)	78,1	441 / 455
6.	cement - water (1:0,5) after 3 years disposal under distilled water (lab. conditions)	89,6	513 / 642
7.	cement - water (1:0,5) after 3 years disposal under bentonite and distilled water (lab. conditions)	102,1	545 / 409
8.	cement - oxalic acid (1%) (1:0,5)	30,9	352 / 410
9.	cement - tartric acid (0,25%) (1:0,5)	57,7	453 / 472
10.	cement - citric acid (0,25%) (1:0,25)	38,8	405 / 457
11.	cement - oxalic acid (1%) (1:0,5) after 3 years disposal under drainage water	81,3	578 / 562
12.	cement - tartaric acid (0,25%) (1:0,5) after 3 years disposal under dreaned water	107,1	460 / 747
13.	cement - citric acid (0,25%) (1:0,25) after 3 years disposal under dreaned water	83,7	731 / 573
14.	cement - oxalic acid (1%) (1:0,5) after 3 years disposal under distilled water	119,2	584 / 573
15.	cement - tartaric acid (0,25%) (1:0,5) after 3 years disposal under distilled water	113	608 / 352
16.	cement - citric acid (0,25%) (1:0,25) after 3 years disposal under distilled water	113,5	628 / 830
17.	cement - iron hydroxide (wet) (1:0,5)	55,6	376 / 291
18.	cement - iron hydroxide (dry) (1:0,5)	107,8	502 / 470
19.	cement - iron hydroxide (wet – washed) (1:0,5)	69	357 / 270
20.	cement - iron hydroxide (wet-boiled) (1:0,5)	-	/ 269
21.	cement - iron phosphate (wet) (1:0,5)	64,4	430 / 380
22.	cement - iron phosphate (wet-washed) (1:0,5)	27,6	178 / 144
23.	cement - iron phosphate (wet-boiled) (1:0,5)	64,1	415 / 391
24.	cement - iron phosphate (dry) (1:0,5)	77,5	361 / 380
25.	cement - iron hydroxide (wet) (1:0,5) after 3 years disposal under dreaned water	-	/ 441
26.	cement - iron hydroxide (wet–washed) (1:0,5) after 3 years disposal under dreaned water	-	/ 355
27.	cement - iron hydroxide (wet-boiled) (1:0,5) after 3 years disposal under dreaned water	-	/ 430
28.	cement - iron phosphate (wet) (1:0,5) after 3 years disposal under dreaned water	-	/ 395
29.	cement - iron phosphate (wet-washed) (1:0,5) after 3 years disposal under dreaned water	-	/ 355
30.	cement - iron phosphate (wet-boiled) (1:0,5) cement - iron phosphate (wet-boiled) (1:0,5)	-	/ 404

4.9 Small angle neutron scattering studies

Portland cement is the most popular material used in Nuclear Waste Treatment Plants around the world, to include nuclear waste inside a sealing concrete matrix and after that to store it in special repositories.

Knowing the behavior in time of such a material and finding the possibility to improve the technology the risk of environmental contamination due to accidental leakage will be minimized.

Depending of technology there are two major chemical substances accompanying the waste, $Fe(OH)_3$ and $FePO_4$ precipitates.

Mechanical tests shown that some proprieties like strength, durability and stress resistance of cement are affected from these ingredients, also the permeability of water is increasing.

Portland cement paste consists of many crystalline and non-crystalline phases in various ranges of sizes. The crystalline phases are embedded in amorphous phases of hydration products. The kernel of the hydrating grain is unreacted Portland cement [1].

SANS-experiments have shown the correspondence of the development of the radii of gyration with the increasing volume of the hydration products. Therefore the radius of gyration is a useful scattering parameter for the characterization of the hydration progress [2]. The scattering curves point to the appearance of fractal components in the microstructure [3]. From inelastic neutron scattering experiment performed at DIN-2PI instrument on samples containing Portland cement + D_2O + $Fe(OH)_3$ and $FePO_4$ precipitates, I. Padureanu et al. [4–5] have drawn the conclusion that there exists unbounded water molecules in the structure of that mixture. This might be caused due to the influence of the precipitates mentioned above to the hydration process. Seems that water dynamics on nanometer scale modify the fractal structure of cement.

The heterogeneous nature and chemical complexity of cement pastes makes the characterization of this system difficult. The most important component of a hardened cement paste, calcium silicate hydrate (C-S-H), is poorly crystalline or amorphous. A hardened cement paste is a live system: fluids in the cement paste pores continue to react, albeit slowly, with the remaining unhydrated cement and the cement hydration products that form and are imbedded in the paste.

In response to environmental influences, some of the hydration compounds can become unstable and others precipitate from the pore liquid with beneficial or deleterious effects.

Contrary to the general opinion that cement and concrete are durable materials, it is surprising to find out that the cement paste is, instead, fragile. Dehydration, such as that which occurs in an electron microscope sample stage, can alter irreversibly the morphology of the paste, making microscopic examinations difficult and sometimes inconclusive [6].

The aim of the reported study is to investigate by means of SANS method structural changes in cement paste due to the influence of the concentration of embedded substances $Fe(OH)_3$, $FePO_4$, $Ca(OH)_2$ and bentonite.

5. RESULTS

We have made our investigation on cement samples with a specific concentration of $Fe(OH)_3$, $FePO_4$, $Ca(OH)_2$ and bentonite mixed with known ratios of ordinary water and D_2O. The samples were prepared at the Nuclear Waste Treatment Plant from the IFIN-HH, Bucharest, Romania. There are eleven types of samples with the following content:

1. Cement1 = H_2O+cement 10g cement+4ml H_2O; w/c = 0,40
2. Cement2 = D_2O+cement+$Ca(OH)_2$ (1) 20g cement+1g $Ca(OH)_2$+7ml D_2O
3. Cement3 = D_2O+cement+bentonite (2) 20g cement+2g bentonite+10ml D_2O
4. Cement4 = D_2O+cement+bentonite (1) 20g cement+0.2g bentonite+6.2ml D_2O
5. Cement5 = D_2O+cement+$Fe(OH)_3$+FePO 10g cement+3g $Fe(OH)_3$+3g $FePO_4$+3ml D_2O
6. Cement6 = D_2O+cement+$FePO_4$ 20g cement+1.4g $FePO_4$+6ml D_2O
7. Cement7 = D_2O+cement+$Fe(OH)_3$ 30g cement+0.9g $Fe(OH)_3$+12ml D_2O
8. Cement8 = 50%D_2O+50%H_2O+cement 10g cement+3ml H_2O+3ml D_2O; w/c = 0,60
9. Cement9 = 50%D_2O+50%H_2O+cement 10g cement+2.5ml H_2O+2.5ml D_2O; w/c = 0,50
10. Cement10 = 50%D_2O+50%H_2O+cement 10g cement+2ml H_2O+2ml D_2O; w/c = 0,40
11. Cement11 = D_2O + cement+ $Ca(OH)_2$ (2) 20g cement+5g $Ca(OH)_2$+10ml D_2O

Scanning Electronic Microscopy (SEM) carried out (Fig. 5 and 6) on the same samples shown aspects of the microstructure on micrometer scale, different from that of normal cement paste.

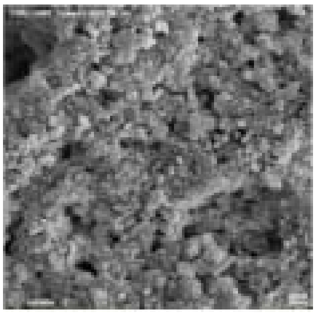

FIG. 5. Cement paste with H_2O.

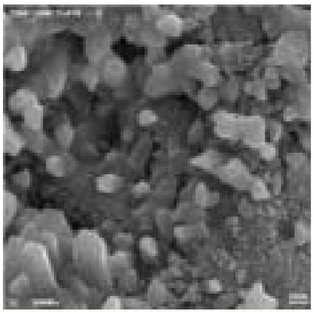

FIG. 6. Cement paste with H_2O+$FePO_4$.

The scattering patterns from all the samples, obtained at small-angle neutron scattering spectrometer at Frank Laboratory of Neutron Physics from Joint Institute for Nuclear Research in Dubna, Russia are shown in Figure 7.

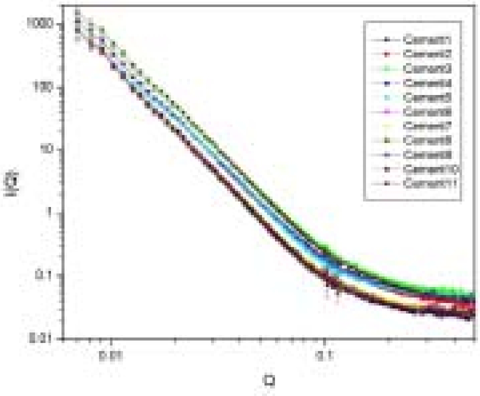

FIG. 7. Scattering curves from cement samples.

Preliminary results emphasize that we can use a function type like the following equation to describe the data:

$$I(Q)=AQ^{-c}+B \quad (10)$$

A good fit for the curves shown above is obtained when C<4 around the value 3.5.

For Q values higher then 0.1 we observe a fractal behavior. The cement microstructure has the characteristics of surface and volume fractals. Combined techniques SEM and SANS reveal that the development of nucleation and agglomeration for the growth of cement hydrating grain are some how different when foreigner substances interfere in the hydration process.

The fractal geometry can be discussed in many ways but in the simplest terms, fractal objects are “self-similar” over a wide length range.

6. FUTURE PROSPECTS

We intend to study how various concentrations of this substances induce micro structural changes in the normal cement paste, how the size of fractals is influenced from these factors and of course to obtain information about the hydration mechanism.

Main conclusions and recommendations

1. The mechanical performances of the cement-mineral additive matrix are influenced only at more than 10% addition of bentonite or volcanic tuff. The very good mechanical behavior of the samples, drives at the conclusion that the mixture could be used in the disposal process, with good results, if the future structure characterization would prove the role as engineered barriers.

2 Complexing reagents reduce drastically the mechanical performances. The chemical nature of the complexant play an important role, the damaging effect is more pregnant for tartaric and citric acid as far as oxalic acid. In any case is a maximum limit of concentration, which is acceptable for mechanical performance.

3 The mechanical resistances obtained for all the samples, after one year disposal, are included in the accepted limits for the matrix durability. Thus, disposal conditions has not influence the mechanical properties of the cement matrix after one year disposal. The presented results, show us that bentonite seems to have a positive influence on the examined matrix quality. These results are preliminaries, following to be completed these data with the obtained data after three years disposal.

4. XRD initial investigation of a part of waste form samples shows complex changes in the structure and components. The analyses of the dry and hydrated cement Portland and the simulated radioactive waste processing products by XRD and Mossbauer spectroscopy proved that despite of the investigated systems complexity, the main chemical species can be identified. By XRD method was obtained informations concerning products and transformations that are the basis of the cement Portland hardening. From the X-rays difractogrames was observed a direct crystallisation of the hexagonal calcium hydroaluminates the others hydration products. These products, because of their instability have the tendency of transformation in the cubic calcium hydroaluminate that is responsible for the mechanical resistance. The gypsum presence

in the cement composition is favorable because they determine the tricalcium monosulfatat hydroaluminate formation, which gives to the hardened cement better mechanical properties. Using the Mossbauer spectroscopy at various temperatures, a sensitive characterization of various cement samples could be performed. The cement/water ratio directly influenced the distribution of iron in various phases, the new hydrated species being evidenced from the increase of the central part of the Mossbauer spectra, both at 80K and 295K. The mechanism of hydration/hydrolysis process was confirmed by the low temperature measurements. The new results obtained concerning the iron in cements are more spectacular than those on pure precipitates and offered large possibilities for a detailed characteristic of the mechanism during the cementation process.

5. The results of inelastic slow neutron scattering on various hydrated cement pastes with light and heavy water in the presence of several precipitating products are presented. The data are analyzed in terms of generalized vibration density spectra; The presence of the small energy vibrations spectrum of the water molecules in the (GVDS) for all measured samples has to be noted; The large energy range of the (GVDS), hT ~ 0 – 200 meV, as well as its structure features shows that the hydrating cement pastes are forming fractal structures of nanometer order; A rather significant influence of the precipitating products on the broadening of the (GVDS) in the intermediate and a high-energy range is observed.

6. Results obtained at the permeability test leads to the conclusion that the bentonite retains the water and so the matrix has a lower permeability. This can be explained by the formation of a supplementary gelic mass which collimate the cement pores increasing the compactity and by modification of the dimensional spectra of the pores with diminishing the pores easy accessible to water.

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LONG TERM TESTS OF LOW AND INTERMEDIATE LEVEL WASTE PACKAGES UNDER FIELD AND EXPERIMENTAL REPOSITORY CONDITIONS

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Abstract

Borosilicate waste glass, cement and bitumen waste forms containing actual intermediate-level radioactive waste from the Kursk RBMK reactor were manufactured and placed for testing at an open testing site and in shallow-ground repositories. Leaching behaviour of the waste forms was evaluated by monitoring the contamination of contacting water. Estimated radioactivity leach rates of the three waste forms were in a narrow range in the repositories (below accepted in RF leach rate limits for solidified waste forms), but varied in a wide range at the open site owing to weathering of bitumen and cement waste forms. The repositories were opened after 12-year testing for visual examination, sampling and analysis. All retrieved waste forms were in good physical condition. The study has revealed some ageing processes in cement and bitumen waste forms, which can significantly affect their physical and containment properties.

1. INTRODUCTION

MosSIA ‘Radon’ is the radwaste management agency of the Moscow Government. Its main task is to monitor the radiological situation in Moscow and near-by districts and to organise the centralised collection, transportation, treatment, conditioning and storage of institutional radioactive waste. Liquid wastes and sludges make up a significant proportion of the waste stream.

Application of near surface storage and disposal options at the SIA ‘Radon’ repository site requires the implementation of measures that will provide protection of human health and the environment. Well-founded choice of waste form for radionuclide encapsulation and immobilisation is among these measures. The waste matrix is considered the most important barrier to radionuclide release in the accepted multi-barrier waste disposal concept. Knowledge concerning the long-term behaviour of waste forms/packages under various conditions, representing a reasonable future evolution scenarios for the disposal system and its surroundings, is of great importance for an overall disposal safety.

For over two decades, the SIA ‘Radon’ has been investigating three main types of matrices for conditioning short lived low and intermediate level wastes (LILW). Cement, bitumen and vitrified waste blocks, produced by pilot scale and industrial facilities, were placed for long term testing at the open testing site and into experimental shallow-ground repositories. Conditions of the long-term field tests may be considered as simulating the most rigorous (among usual) near-surface storage/disposal conditions when denudation of the waste forms occurs (open site tests) or when backfill or soil surrounding the waste units become saturated with groundwater (tests in shallow ground repositories). Results from 12yr tests with intermediate level cement, bitumen and borosilicate glass waste forms are presented in the report.

2. EXPERIMENT

2.1. Experimental conditions

Nature tests of waste forms (cement, bitumen, glass) and waste containers have been carried out since 1987 under fluctuating ambient conditions of the open testing site and moisture saturated conditions of shallow ground repositories. Repository conditions are characterised by a free access of groundwater (infiltrated precipitation) to waste forms through a covering of host loamy soil and a backfill of coarse sand. In the report, we summarise the results obtained from 12-yr experiments with cemented, bituminised and vitrified waste samples in the repositories and at the open site.

Waste forms were placed on stainless steel trays; each supplied with a water collection system to accumulate the water that comes into contact with the waste form. Deep trays (40 cm in depth) were used in the repositories. The bottom depth was about 2 metres below the land surface. Pure coarse sand was used to fill the remaining free space in the deep trays to prevent waste forms from direct contact with soil and to facilitate water infiltration and accumulation in a water trap. Description of test condition for the open testing site and experimental repositories is given in more detail elsewhere [1,2].

2.2. Manufacture of waste forms and packages

Waste forms were manufactured in industrial-scale bituminisation and cementation facilities and in a pilot vitrification plant using operational waste from the Kursk nuclear power plant. Technical grade and naturally occurring materials such as quartz sand, loam and datholite concentrate were used for waste glass preparation. The molten glass was produced in a pilot plant «Epos» with a single-stage slurry-fed Joule-heated ceramic glass melter (process temperature below 1150°C) and poured into containers of carbon steel. Annealing was not applied. Bitumen blocks were prepared using a thin-film rotor mixer-evaporator URB-8 and hard bitumen BN-IV. Ordinary portland cement was used for liquid waste cementation.

Cement K-28 and PZ-87, bitumen K-27 and PR-11, and glass samples K -26 and BS-10 were analogues prepared from the same batch in each case.

2.3. Radioactive waste description

Real intermediate-level operational waste from the Kursk reactor RBMK was used. The waste represented sludge with a salt content ~340 g/l. The main radionuclides in the waste were ^{137}Cs (82%), ^{134}Cs, and ^{60}Co (Table I). $NaNO_3$ was the main non radioactive component of the waste (86 wt.% of dry weight) (Table II).

TABLE I. RADIOACTIVITY OF KEY ISOTOPES IN THE LIQUID WASTE, Bq/L

^{137}Cs	^{134}Cs	^{60}Co	^{90}Sr	^{239}Pu	β_{tot} (^{137}Cs)	β_{tot} (^{90}Sr+^{90}Y)	α_{tot} (^{239}Pu)
$4.1\cdot10^6$	$8.5\cdot10^5$	$5.3\cdot 10^4$	$1.5\cdot10^2$	$5.0\cdot10^3$	$6.7\cdot10^6$	$4.0\ 10^6$	$3.0\cdot10^3$

TABLE II. COMPOSITION OF THE WASTE DRY MATTER, wt. %

Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{3+}	Al^{3+}	SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}	CO_3^{2-}	Others
26.4	0.7	0.3	0.1	0.3	0.01	2.7	59.6	3.4	0.2	2.0	4.29

2.4. Waste form description

Radiometric and other parameters of waste forms used in the experiments are given in Table III. The data on β_{tot} and α_{tot}, average for the batch of solidified waste in each case, were obtained from technology operators and need to be re-counted using direct measurements. Initial specific radioactivity of waste form samples from the repositories corrected for decay are given in Table III as β_{tot}(^{90}Sr+^{90}Y).

TABLE III. CHARACTERISATION OF SAMPLES USED FOR LONG-TERM TESTING

Matrix	Sample/Test condition	Weight kg	Waste loading wt.%	Density g/cm^3	β_{tot},	α_{tot}(^{239}Pu)	β_{tot}(^{90}Sr+^{90}Y)/ β_{tot} ^{137}Cs
					Bq/kg		
Cement	PZ-87/Op.s.	16.3	37.5	1.5	$2.10\cdot10^6$	-	-
	K-28 / Rep.	44.0[1]	37.5		$2.10\cdot10^6$	-	$1.0\cdot10^6/2.4\cdot10^6$
Bitumen	PR-11/Op.s.	21[2]	30.7	1.1	$3.29\cdot10^6$	$3.89\cdot10^2$	-
	K-27/ Rep.	310.2	30.7		$3.29\cdot10^6$	$3.89\cdot10^2$	$2.4\cdot10^6/3.5\cdot10^6$
Glass	BS-10/ Op.s.	37.8	35.0	2.46	$3.89\cdot10^6$	$1.40\cdot10^4$	-
	K-26 / Rep.	190[3]	35.0		$3.74\cdot10^6$	$1.30\cdot10^4$	$3.7\cdot10^6/6.1\cdot10^6$

[1] Total weight of two orthocylindrical samples (∅=h=24 cm); [2] sample in the form of obelisk (h=30, 25x25, 35x35) in container; [3] net weight of six blocks in six carbon steel containers of rectangular form (20x25x42cm).

Initial specific radioactivity of β-emitting nuclides in all waste forms was of the same order of magnitude. Data on contact area in Table III refer to a geometrical surface area of samples or the top open surface area of samples tested in containers (PR-11, BS-10, and K-26).

Table IV illustrates the chemical composition of cement, bitumen and glass-forming mixture used as encapsulation materials for the waste. Besides, some important thermo-physical parameters of bitumen are given. Chemical composition of the waste glass in Table V was calculated for the whole glass batch.

TABLE IV. MATRIX MATERIAL CHARACTERISATION

Sample	Matrix material	Composition of the matrix, wt.%	Physical parameters of the bitumen
RZ-87, K-28	Portland-cement	CaO, 62-67; SiO_2, 20-24; Al_2O_3, 4-7; Fe_2O_3, 2-5; MgO, 0.35-4.5; SO_2, 0.1-1.5	
PR-11, K-27	Bitumen, BN-IV	Oils (aliphatic hydrocarbons) 50.0 Resins 11.0 Asphaltenes 39.0	Depth of penetration (25°C): 21-40 mm Softening temperature: 70°C Flash temperature (open crucible): 230°C
BS-10, K-26	Borosilicate glass	Sand, 27.7; loam, 23.1; datholite concentrate*, 49.2 (* CaO, 28.6, SiO_2, 30.7; B_2O_3, 17.8; Fe_2O_3, 2.6; H_2O, 7)	

TABLE V. WASTE GLASS CHEMICAL COMPOSITION, WT. %

Na_2O	K_2O	CaO	Al_2O_3	B_2O_3	Fe_2O_3	SiO_2	NaCl	Na_2SO_4	Others
16.1	0.5	15.5	2.5	7.5	1.7	48.2	1.2	1.1	5.7

2.5. Experimental procedures

The way used to quantify the amount of leached radioactivity was to measure the volume and radioactivity concentration of contacting rainfall and groundwater. Water sampling was performed periodically, usually twice a month, except for winter months. Aliquots were analysed using radiometric, γ-spectrometric, radiochemical, and chemical methods and techniques. The same methods, XRD and autoradiography were applied to samples of waste forms, container material, repository backfill and soil/host rock [2]. The samples of soil/rock were also characterised using grain-size and ion exchange capacity analyses. Solid samples from the repositories were collected when the repositories were opened in summer 1999, after 12yr testing. Altogether 250 samples of waste forms, sandy backfill, soil, excavation-damaged and intact host rock were collected for study. Photographs of the opened repositories and waste forms are shown in Fig. 1.

3. RESULTS AND DISCUSSION

3.1 Waste form leaching behaviour: results and interpretation

Long-term field tests of solidified radioactive waste forms show the alteration of monitoring parameters of contacting waters with time. Figures 2 and 3 illustrate the alteration dynamics of contacting water contamination for the open site tests and repository tests. Peaks of radioactivity release were the most intensive in the first year for glass and cement waste forms. The process was more protracted for the bitumen waste forms (2-3 years). Detected peak radioactivity values and time of their detection (days from the start of the experiment) are given in Table VI. For comparison, ratios of β_{tot} radioactivity mean in contacting water to background mean and coefficients of radioactivity leach rate decrease are also presented.

Average annual radioactivity concentrations in water that contacted with the waste forms are given in Table VII. Information on the total volume of water (leachate) that had been pumped out of each repository or collected into pails at the open site is also provided. Calculated leach parameters for the waste forms are provided in Table VIII.

TABLE VI. SOME RADIOMETRIC AND LEACH RATE PARAMETERS OF LEACHATE WATERS

	Peak β_{tot} in contact water	Ratio of β_{tot} mean to background β_{tot} mean		Coefficients of leach rate decrease (ratio of 12yr mean to 1st year mean)	
Sample	Bq/L (day)	First year	12 years	β_{tot}	^{137}Cs
PZ-87	3444 (251,280)*	1573	-	1.6	
K-28	329 (192)	23.3	11.7	2.8	1.2
PR-11	2109 (210) 6300 (648)	535	457	1.7	2
K-27	115 (247) 170 (944)	11.5	4.7	6	1.5
BS-10	133 (15)	16	9.5	3	7
K-26	66 (245)	7.2	4.6	2	2.5

*Maximum of 4300 Bq/L was registered at the 2180th day of experiment in a period of enhanced block degradation

TABLE VII. RADIONUCLIDE CONTAMINATION OF LEACHATE WATERS

Waste matrix	Sample	Average annual specific radioactivity, Bq/L (for n^{th} year of exposure)					Total water volume, L
		1	2	6	10	12	
Cement	PZ-87	2328	1676	1551	-	-	444
	K-28	65.8	43.1	26.7	25.3	25.5	1747
Bitumen	PR-11	1310	1190	833	696	677	735
	K-27	32.4	21.9	15.7	11.7	10.2	1439
Glass	Bs-10	40.3	27.3	16.9	15.2	14.0	800
	K-26	20.4	18.5	13.0	10.9	10.0	937

Experimental burial K-28 (cemented RW)

A view of the opened pan containing two cement blocks

Cement block

Experimental burial K-27 (bitumen RW)

Opened burial (deep tray contains bitumen block and sandy backfill)

A view of the bitumen block after sampling

Experimental burial K-26 (vitrified RW)

Opened burial

Vitrified waste block in the carbon steel container

FIG.1. Opened experimental repositories and waste form samples.

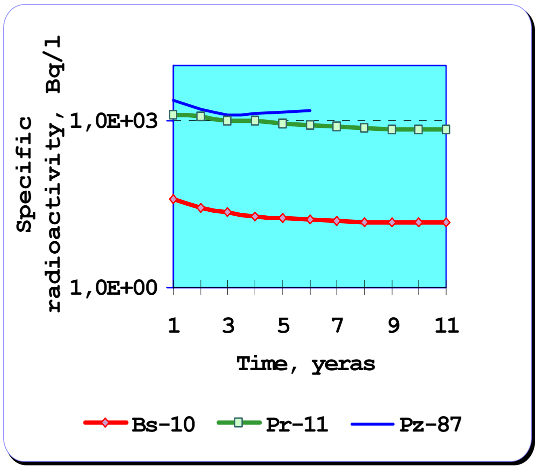

FIG. 2. Specific radioactivity of rainfall in groundwater contact with glass (BS-10), bitumen (K-27) & cement (PZ-87) waste blocks
Average annual values vs. time.

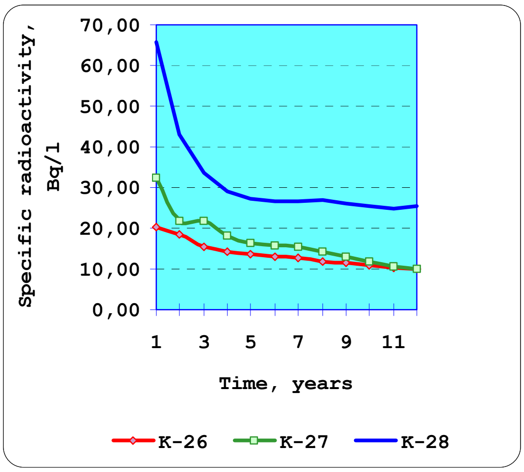

FIG. 3. Specific radioactivity of bitumen (PR-11) in contact with glass (K-26), & cement (K-28) waste blocks.
Average annual values vs. time.

As expected, waste glass was the most leach-resistant in the open-site tests. Visually the bitumen block PR-11 showed no defects (e.g. formation and propagation of cracks) at any stage of the 12yr experiment, but the surface has lost its lustre. Weathering of the bitumen material caused the leach rate to increase dramatically (more then two orders of magnitude) as compared with the bitumen sample K-27 in the repository. Leach rates were up-to 44 times higher then those for the glass block BS-10. Enhanced degradation of cemented waste form (PZ-87) was observed in the 6th year of the experiment at the open site. That process led to increase in radionuclide leaching and block failure.

TABLE VIII. LEACHING PROPERTIES OF THE TESTED WASTE FORMS

Matrix	**Sample**	**Leach rate, g/cm^2day (for nth year of exposition)**					**Leached radioactivity fraction, %**	
		1	2	6	10	12	1-st yr.	Total
Cement	PZ-87	$1.8\bullet10^{-4}$	$1.2\bullet10^{-4}$	$1.1\bullet10^{-4}$	-	-	0.43	2.02
	K-28	$4.8\bullet10^{-6}$	$3.1\bullet10^{-6}$	$1.9\bullet10^{-6}$	$1.8\bullet10^{-6}$	$1.7\bullet10^{-6}$	0.01	0.04
Bitumen	PR-11	$7.3\bullet10^{-5}$	$6.3\bullet10^{-5}$	$5.7\bullet10^{-5}$	$4.4\bullet10^{-5}$	$4.4\bullet10^{-5}$	0.11	0.65
	K-27	$7.1\bullet10^{-7}$	$4.6\bullet10^{-7}$	$2.2\bullet10^{-7}$	$1.5\bullet10^{-7}$	$1.2\bullet10^{-7}$	0.001	0.002
Glass	BS-10	$3.0\bullet10^{-6}$	$1.9\bullet10^{-6}$	$1.3\bullet10^{-6}$	$1.1\bullet10^{-6}$	$1.0\bullet10^{-6}$	0.002	0.007
	K-26	$1.3\bullet10^{-6}$	$1.2\bullet10^{-6}$	$8.5\bullet10^{-7}$	$6.9\bullet10^{-7}$	$6.4\bullet10^{-7}$	0.0004	0.001

A drop in radioactivity of groundwater in the repository K-27 to levels only slightly higher than those for the K-26 was observed during the experiment (Table VII). Taking into consideration that the surface area available for leaching was much greater in the case of bitumen block compared with the waste glass[1], calculated radioactivity leach rates were at the lowest level for the bitumen waste form. Radioactivity leach rates calculated for the cemented waste form (K-28) were only 2-3 times higher then those for the waste glass. For all three tested waste forms, radioactivity leach rates appeared to approach a steady-state value after about a decade of testing under the repository conditions. In the repository tests, the following leach rate means for the whole 12yr testing period were obtained, in g/cm^{2}day: 6.4• 10^{-7} (total β) and 2.3•10^{-7} (^{137}Cs) for the vitrified waste forms; 1.2• 10^{-7} (total β) and 5.9•10^{-8} (^{137}Cs) for the bitumen waste form; 1.7• 10^{-6} (total β) and 1.4•10^{-6} (^{137}Cs) for the cemented waste forms. All measured leach parameters were below leach rate limits accepted in Russia for solidified radioactive waste products. Figure 4 shows the time dependencies of radionuclide inventory fractions leached from the glass (K-26), bitumen (K-27) and cement (K-28) waste forms in the repositories.

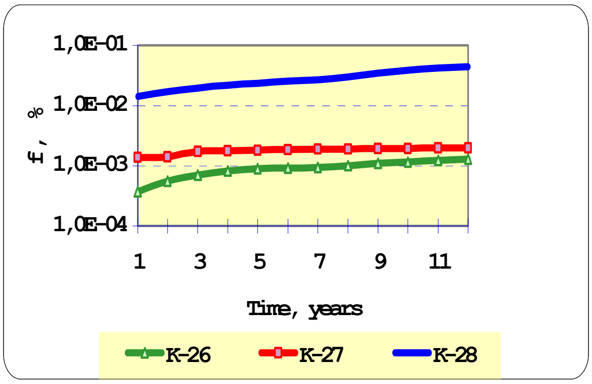

FIG. 4. Radionuclide inventory fraction leached from the glass (K-26), bitumen (K-27) and cement (K-28) waste blocks as a function of time.

According to experimental results, estimated leach rates were in a narrow range for all waste forms when tested in the repositories, and in a wide range when tested at the open site. However, estimated leach rates fulfil the reasonable demands on safe disposal of LILW[2].

For better understanding of the waste form leaching behaviour, concentrations of non radioactive components were measured in the leachate groundwaters. Data in Table IX are concentration means for the first year of the experiment and for the whole 12yr testing period. Ratios of concentration means to background means for various ion species in the leachate groundwaters were calculated for the 1st year of the experiment and for the total 12yr testing period. Increase in concentrations of NO_3^-, Na^+ and K^+ was very significant in leachate groundwaters extracted from the repositories K-27 and, especially, K-28 in the first year. Changes in groundwater chemistry were rather insignificant in the waste glass repository.

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[1] Only the top open surface area of the six glass blocks in the repository K-26 was taken into account in the leach rate calculations.

[2] According to waste acceptance criteria in Russia, limits for leach rate are: for cement and bitumen waste forms, <10^{-3} g/cm^{2}day (^{137}Cs, ^{90}Sr); for HLW phosphate glass, 10^{-5}-10^{-6} g/cm^{2}day (^{137}Cs).

TABLE IX. CONCENTRATION MEANS OF ION SPECIES IN THE REPOSITORY GROUNDWATER

Parameters and ion species	Exposure duration, years	Concentration (mg/L) or parameter means and background (Bg) means		
		K-26/Bg	K-27/Bg	K-28/Bg
pH	1	7,53/7,4	8,03/7,4	9,53/7,4
	12	7,93/7,5	8,08/7,5	8,40/7,5
TDS*	1	518/339	845/339	1474/304
	12	404/282	646/282	717/272
Na^+	1	34,64/13,75	186/13,8	491/13,4
	12	63,40/12,82	167/12,8	202/12,7
K^+	1	3,70/0,73	5,53/0,73	30,66/0,69
	12	3,72/1,33	4,62/1,33	22,65/1,35
Ca^{2+}	1	78,99/54,99	54,12/54,99	8,51/53,28
	12	46,30/50,01	39,05/50,01	27,76/49,71
Mg^{2+}	1	32,3/21,00	27,91/21,00	7,92/21,71
	12	27,75/21,24	26,32/21,24	17,55/21,71
$Fe_{tot.}$	1	9,33/2,24	0,52/2,24	0,49/1,81
	12	2,02/1,16	0,56/1,16	0,53/1,08
Cl^-	1	33,11/18,36	30,31/18,36	39,87/16,86
	12	24,08/11,14	19,89/11,14	12,74/10,55
NO_3^-	1	2,22/2,05	174/2,05	568/1,99
	12	4,23/2,39	36,5/2,39	161/2,40
HCO_3^-	1	435/295	505/295	465/283
	12	373/265	542/265	453/261
SO_4^{2-}	1	13,93/10,59	21,12/10,59	36,88/9,40
	12	10,62/9,16	18,83/9,16	23,50/9,16
Mineralisation**	1	500/350	920/350	2290/350
	12	780/640	1080/640	1273/640

*Total dissolved salt content.

**Dry residue after water evaporation.

Groundwater chemistry changed from the initial (HCO_3^- -Ca^{2+}) -type to (HCO_3^- Na^+-K^+)-type for the waste glass repository, to (HCO_3^- NO_3^--Na^+)- type for the repository with the bitumen waste form, and to (HCO_3^- NO_3^--Na^+-K^+)- type for the cemented waste repository.

3.2. Characterisation of waste forms retrieved from the burial site

Experimental repositories containing cement, bitumen and vitrified waste forms were opened in July 1999 after 12yr testing. General impression from physical state of the samples could be formulated as «very good». Visual examination showed no evidence for the formation of cracks and degradation. Waste form samples for analysis were broken mainly off the upper corner parts of the waste forms.

3.2.1. Cement waste form

Both of the two cemented waste blocks were visually in remarkably good condition (Fig.1). No cracks could be seen in any part of the samples. Sampling was performed with only one of the two blocks; two samples were split off from top and bottom surfaces of the orthocylindrical block. Considerable effort was required to break off the samples, especially the bottom one. However, surprisingly low compression strength was measured on three prepared specimens (~1 MPa). The samples could be characterised as fragile. When broken for grinding, the cement material represented very hard granules and pieces.

` Cement samples were analysed using X-ray diffraction analysis, chemical, radiochemical, radiometric and γ-spectrometric methods and techniques. Humidity was measured in the same day when sampling was performed. The average humidity was about 4%. Radiometric, γ-spectrometric and chemical analyses are presented in Tables X and XI. γ-spectra were identical for the top and bottom samples.

TABLE X. RADIOMETRIC AND γ-SPECTROMETRIC ANALYSES OF THE K-28, Bq/kg.

β_{tot} (^{137}Cs)	β_{tot} (^{90}Sr+^{90}Y)	α_{tot} (^{239}Pu)	^{137}Cs	^{134}Cs	^{60}Co
$1.2\bullet10^6$	$7.5\bullet10^5$	$3.6\bullet10^3$	$1.1\bullet10^6$	$3.6\bullet10^3$	$3.6\bullet10^3$

*Measurement error 10%.

TABLE XI. CHEMICAL COMPOSITION OF THE K-28 SAMPLE AFTER 12YR TESTING, wt.%

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cl^-	SO_4^{2-}	PO_4^{2-}	Others
23.95	3.84	2	32.84	3.09	1.28	0.43	0.11	1.77	0.11	30.58

X-ray diffraction pattern for the bottom cement sample is shown in Figure 5. The following crystalline phases were detected: calcite, vaterite, portlandite, natrium ferrite monohydrate, natrium chlorate monohydrate and. Ettringite phase was not found in our cement samples. Only insignificant differences were detected in the XRD spectra of the top sample: α - quartz peaks were less marked in the top sample.

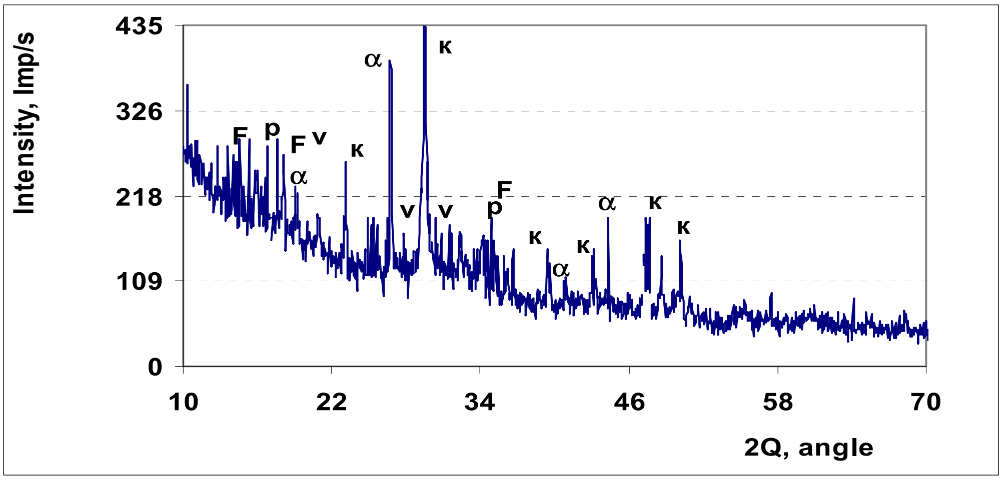

FIG. 5. X-ray diffraction patterns for the bottom cemented waste sample
K—- calcite, V — vaterite, P — portlandite, F- $NaFeO_2 \bullet H_2O$, Cl - $NaClO_4 \bullet H_2O$, α - α-SiO_2.

3.2.2. Bitumen waste form

Bitumen block retrieved from the repository K-27 was in good physical condition. Visually, no cracks or fractures could be detected. Four samples of the bitumen material were split off from the corner and upper middle parts of the bitumen block during the repository opening (Fig. 1). Thermo-physical, physical, and radiometric characteristics were determined for the bitumen samples (Tables XII, XIII). Fractionation into salt and bitumen phases and into bitumen fractions was performed to study the radioactivity distribution among phases and fractions.

TABLE XII. PHYSICAL AND THERMO-PHYSICAL PARAMETERS OF THE BITUMEN WASTE MATERIAL

Parameters	Density, g/cm^3	Humidity, %	Softening temperature, °C	Flash point, °C (closed crucible)
Initial	1.10	1.30	not determined	not determined
Final	1.25	1.96	95.5	257.5

Penetration depth (final) could not be measured, it was essentially nil for standard test conditions (standard test needle, 100g load, 25°C). For lack of some initial thermo-physical parameters, we cannot conclude on their alteration. Nevertheless, it was evident that bitumen material became harder and more thermostable.

Radiometric and γ-spectrometric analyses of bitumen samples taken from corner and upper middle parts of the bitumen block are given in Table XIII. Data on α-radioactivity are contradictory and are not reported here.

TABLE XIII. AVERAGE RADIOMETRIC AND γ-SPECTROMETRIC DATA FOR THE BITUMEN SAMPLES, Bq/kg.

β_{tot}* (^{90}Sr+^{90}Y)	^{137}Cs	^{134}Cs	^{60}Co
$1.2 \cdot 10^6$	$2.0 \cdot 10^6$	$5.5 \cdot 10^3$	$4.2 \cdot 10^3$

*Measurement error 10%.

Average volumetric radioactivity of bitumen samples was found to be about 2 times less than the initial one. Since the samples for analysis were split off from the upper part of the bulky bitumen block, it was supposed that the lower results are most likely due to waste salt settling during block manufacture.

To estimate vertical distribution of radionuclides and salts in the bitumen matrix, a sample 15-cm in height was analysed. One vertical and three horizontal (upper, middle and lower) 2-3 mm thick sections were cut off from the sample. From Table XIV it is seen that salt content diminished with distance from top to lower part of the sample. The next stages were to separate and analyse bitumen and salt phases of these sections and to further separate extracted bitumen into fractions of oils, resins and asphaltenes[3]. Results are given in Tables XV and XVI. Concentrations of some ion species in the extracted salt samples are listed in Table XVII.

TABLE XIV. RADIOMETRIC AND γ-SPECTROMETRIC ANALYSES FOR HORIZONTAL AND VERTICAL SECTIONS OF THE BITUMEN SAMPLE, Bq/kg

Section	β_{tot} (^{90}Sr+^{90}Y)	^{137}Cs	^{134}Cs	^{60}Co	Salts, wt.%
Vertical	$1.00 \cdot 10^6$	$1.70 \cdot 10^6$	$6.20 \cdot 10^3$	$4.00 \cdot 10^3$	7.75
Upper, horizontal	$1.50 \cdot 10^6$	$2.20 \cdot 10^6$	-	-	7.25
Middle, horizontal	$1.70 \cdot 10^6$	$2.60 \cdot 10^6$	-	-	13.50
Lower, horizontal	$0.93 \cdot 10^6$	$1.37 \cdot 10^6$	$5.30 \cdot 10^3$	$4.50 \cdot 10^3$	14.30

TABLE XV. RADIOMETRIC AND γ-SPECTROMETRIC ANALYSES OF SALT SAMPLES EXTRACTED FROM VARIOUS SECTIONS OF THE BITUMEN SAMPLE, Bq/kg.

Section	β_{tot} (^{90}Sr+^{90}Y)	α_{tot} (^{239}Pu)	^{137}Cs	^{134}Cs	^{60}Co
Vertical	$2.45 \cdot 10^6$	2.00	$4.20 \cdot 10^6$	$2.05 \cdot 10^4$	$1.28 \cdot 10^4$
Upper, horizontal	$0.87 \cdot 10^6$	$2.6 \cdot 10^3$	$1.25 \cdot 10^6$	-	$6.75 \cdot 10^3$
Middle, horizontal	$0.50 \cdot 10^6$	1.50	$0.65 \cdot 10^6$	-	$7.90 \cdot 10^3$
Lower, horizontal	$0.63 \cdot 10^6$	$1.5 \cdot 10^3$	$0.93 \cdot 10^6$	-	$6.90 \cdot 10^3$

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[3] Salts were separated from bitumen using a sohxlet extractor and CCl_4 as an extractant.

TABLE XVI. RADIOMETRIC AND γ-SPECTROMETRIC ANALYSES OF BITUMEN AFTER EXTRACTION OF SALTS FROM VARIOUS SECTIONS OF THE BITUMEN SAMPLE, Bq/kg.

Section	β_{tot} ($^{90}Sr+^{90}Y$)	^{137}Cs	^{134}Cs	^{60}Co
Vertical	$0.64\cdot10^6$	$0.94\cdot10^6$	$3.80\cdot10^3$	$4.10\cdot10^3$
Upper, horizontal	$0.57\cdot10^6$	$1.00\cdot10^6$	$3.75\cdot10^3$	$2.90\cdot10^3$
Middle, horizontal	$1.10\cdot10^6$	$2.20\cdot10^6$	$5.45\cdot10^3$	$5.70\cdot10^3$
Lower, horizontal	$0.71\cdot10^6$	$1.60\cdot10^6$	$6.,80\cdot10^3$	$6.25\cdot10^3$

TABLE XVII. CONCENTRATIONS OF SOME ION SPECIES IN THE EXTRACTED SALT SAMPLES, wt.%

Section of the bitumen sample	Na^+	Cl^-	SO_4^{-2}
Vertical*	32,08	2,85	2,66
Upper, horizontal	30,00	0,17	1,06
Middle, horizontal	35,50	0,71	1,27
Lower, horizontal	36.40	0,62	1,44
Initial data	*26,4*	*3,4*	*2,7*

* Measured in the acid extract

A solvent fractionation method of Helton and Trecksler was used to further separate the extracted bitumen samples into fractions of asphaltenes, saturated and aromatic hydrocarbons, and to analyse the radioactivity distribution among these fractions. Quantitative isolation of asphaltenes from other bitumen fractions was performed twice and included dissolution of bitumen phase in benzene, asphaltene precipitation with pentane, filtration and filter washing with pentane, dissolution of asphaltene fraction (on a filter) in hot bensene, after that the procedure of precipitation and washing was repeated. Analytical results are given in Tables XVIII and XIX.

TABLE XVIII. FRACTIONAL COMPOSITION OF THE EXTRACTED BITUMEN SAMPLES, WT.%.

Section	Asphaltenes	Saturated hydrocarbons	Aromatic hydrocarbons
Vertical	43,2	30	25
Upper, horizontal	51,2	26	19
Middle, horizontal	44,3	32	21
Lower, horizontal	45,4	30	22

TABLE XIX. RADIOMETRIC AND γ-SPECTROMETRIC ANALYSES OF BITUMEN FRACTIONS ISOLATED FROM THE BITUMEN PHASE AFTER SALT EXTRACTION, Bq/kg (n.d.— not detected).

Section	$\beta_{tot}(^{90}Sr+^{90}Y)$	^{137}Cs	^{134}Cs	^{60}Co
Vertical	$0.6\bullet10^{6}$	$0.9\bullet10^{6}$	$3.8\bullet10^{3}$	$4.1\bullet10^{3}$
Asphaltenes	$1.6\bullet10^{6}$	$1.5\bullet10^{6}$	$6.8\bullet10^{3}$	$5.5\bullet10^{3}$
Saturated hydrocarbons	$2,0\bullet10^{4}$	$2.2\bullet10^{4}$	n.d.*	n.d.
Aromatic hydrocarbons	$6.4\bullet10^{3}$	$8.3\bullet10^{3}$	n.d.	n.d.
Upper	$0.6\bullet10^{6}$	$1.0\bullet10^{6}$	$3.8\bullet10^{3}$	$2.9\bullet10^{3}$
Asphaltenes	$0.84\bullet10^{6}$	$1.42\bullet10^{6}$	$4.7\bullet10^{3}$	$5.5\bullet10^{3}$
Saturated hydrocarbons	trace	n.d.	n.d.	n.d.
Aromatic hydrocarbons	n.d.	n.d.	n.d.	n.d.
Middle	$1.1\bullet10^{6}$	$2.2\bullet10^{6}$	$5.5\bullet10^{3}$	$5.7\bullet10^{3}$
Asphaltenes	$0.84\bullet10^{6}$	$1.40\bullet10^{6}$	$4.5\bullet10^{3}$	$7.7\bullet10^{3}$
Saturated hydrocarbons	trace	n.d.	n.d.	n.d.
Aromatic hydrocarbons	$6.5\bullet10^{3}$	$1.2\bullet10^{4}$	n.d.	n.d.
Lower	$0.7\bullet10^{6}$	$1.6\bullet10^{6}$	$6.8\bullet10^{3}$	$6.3\bullet10^{3}$
Asphaltenes	$0.76\bullet10^{6}$	$1.50\bullet10^{6}$	$4.3\bullet10^{3}$	$5.0\bullet10^{3}$
Saturated hydrocarbons	trace	n.d.	n.d.	n.d.
Aromatic hydrocarbons	$5.9\bullet10^{3}$	$1.7\bullet10^{4}$	n.d.	n.d.

The noticeable fractional increase in asphaltenes (from initial 39 wt.% to 43-51 wt.%) had occurred to the end of 12yr testing period. From Table XIX it can be seen that a significant proportion of radioactivity associated with the bitumen originates from the asphaltene fraction. Saturated hydrocarbons retain only trace amounts of the radioactivity.

3.2.3. Vitrified waste form

One of six containers containing waste glass K-26 was extracted from the repository for visual examination and glass sampling. A big representative sample of vitrified material was taken from the open upper part of the glass block. Cracks could be seen in the glass surface, but they had possibly originated from the molten glass cooling mode (annealing was not applied).

Glass sample was analysed using compression strength measurements, X-ray diffraction analysis, chemical, radiochemical, radiometric and γ-spectrometric methods and techniques. Compression strength was in the range of 30 to 80 Mpa. Radiometric and γ-spectrometric analyses are presented in Table XX γ- and α-spectra were identical for glass samples from different sampling points.

TABLE XX. RADIOMETRIC AND γ-SPECTROMETRIC ANALYSES OF THE WASTE GLASS SAMPLE, Bq/kg.

β_{tot} (^{137}Cs)	β_{tot} ($^{90}Sr+^{90}Y$)	α_{tot} (^{239}Pu)	^{137}Cs	^{134}Cs	^{60}Co
$3.8\bullet10^6$	$2.2\bullet10^6$	$1.5\bullet10^4$	$4.1\bullet10^6$	$2.9\bullet10^4$	$1.7\bullet10^4$

*Measurement error 10%.

Chemical analysis of the waste glass after 12yr testing is given in Table XXI. Measured concentrations of the most soluble components such as Na and K oxides were somewhat higher than initial data calculated for the whole waste glass batch (Table V).

TABLE XXI. CHEMICAL COMPOSITION OF THE WASTE GLASS MATERIAL, wt.%

SiO_2	Al_2O_3	B_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cl^-	SO_4^{2-}	PO_4^{2-}	Others
37.29	3.29	4.5	1.93	14.5	0.49	21.72	1.1	4.87	0.74	0.19	9.38

A broad band due to scattering by the glassy matrix could be seen on diffraction patterns of the glass sample. The uniformity of diffraction patterns of samples taken from different sampling points suggests a fairly uniform glass structure.

3.3. Radioactive contamination of the repository environment

Samples of soil/host rock were taken at 4 depth levels, 0-0.3, 1.2-1.45, 1.70-2.15, and 2.65 meters below the land surface at three distances from the tray. Drill cores of the intact host rock were sampled at the depths of 1.90 to 2.90 meters below the land surface. Altogether 222 samples 0.3 to 1 kg in weight were collected from the repositories: 77, 90 and 55 samples for K-26, K-27, and K-28, respectively.

Table XXII illustrates average and minimum - maximum contamination levels in the soil/host rock environment. Average levels for total β and total α were of the same level as background.

TABLE XXII. AVERAGE AND MINIMUM - MAXIMUM RADIOACTIVITIES* IN THE HOST ROCK SURROUNDING THE REPOSITORIES, kBq/kg.

	β_{tot}	α_{tot}
K-26 (glass)	0.98 0.65-1.21	1.20 0.62-1.60
K-27 (bitumen)	0.94 0.88-1.03	0.93 0.66-1.25
K-28 (cement)	1.10 0.81-1.10	0.77 0.40-1.10
Background	1.1	0.97

*Radioactivity analyses of the fill-up soil samples to the depth of 1.2-1.3 meters were not used in the calculations because radionuclide transport from the repositories to the land surface was considered as insignificant.

3.4. Predictive modelling of the waste form behaviour

A mathematical approach has been developed to predict radionuclide release from radioactive waste forms. To calculate some model parameters, we used experimental data from 12yr field tests described in the previous sections and in [3–12].

The radionuclide release from the waste glass is assumed to be controlled by the processes of diffusion limited ion exchange and glass network dissolution. For mathematical modelling the long-term behaviour of the nuclear waste glass, we used the glass dissolution model described in. [3]. This model is phenomenological and requires the knowledge of experimentally derived parameters. The total radioactivity that will be released from the waste glass into the contacting water Q_{tr} is expressed by the equation representing the integral over time of the radionuclide flux per unit surface area:

$$\mathbf{Q_{tr}} = \mathbf{a}(\pi/\lambda)^{1/2}\Phi(\sqrt{\lambda\mathbf{t}}) + \mathbf{b}[1-\exp(-\lambda\mathbf{t})]/\lambda + \mathbf{nk}\big[1-\exp[-(\mathbf{k}+\lambda)\mathbf{t}]\big]/(\mathbf{k}+\lambda) \qquad (1)$$

where λ_i = decay constant, t = exposure time, k = initial surface radionuclide dissolution rate in water; n = initial concentration of the radionuclides at the glass surface; a and b = constants depending on glass composition and experimental conditions, determined experimentally; and $\Phi(\sqrt{\lambda}t)$ = error function integral expressed as

$$\Phi\,(x) = 2/\sqrt{\pi}\int_0^{\mathbf{x}}\exp(-\mathbf{t}^2)\mathbf{dt} \qquad (2)$$

The constant a depends on the effective diffusion coefficient D_{eff} of the radionuclide in the glass matrix as follows

$$a = 2Sq_0\left(D_{eff}/\;\pi\right)^{1/2} \qquad (3)$$

where S is the glass surface area, and q_0 is the initial radioactivity of a volume unit. The constant b is related to the glass dissolution rate R through the relationship

$$b = 2Sq_0R \qquad (4)$$

The constants a and b are defined from processing experimental data. Both efficient diffusion coefficient and dissolution rate can be found out from formulae (3) and (4).

For a very long exposure period when $\lambda t >> 1$, the amount of radioactivity released from a unit glass surface area Q_{tr}, approaches a constant (maximum) value:

$$\mathbf{Q_{tr}} \rightarrow \mathbf{a}(\pi/\lambda)^{1/2} + \mathbf{b}/\lambda + \mathbf{nk}/(\mathbf{k}+\lambda) \qquad (5)$$

Parameters were calculated that describe waste glass leaching and dissolution - glass dissolution rate, R (experimental results), effective diffusion coefficient (^{137}Cs), D_{eff}, and the accumulative leached inventory fraction for a period of 300 years, f_{300}. The parameter values obtained through data processing are given in Table XXIII.

TABLE XXIII. PARAMETERS CHARACTERISING GLASS DISSOLUTION, RADIONUCLIDE DIFFUSION AND RADIONUCLIDE RELEASE FROM THE BOROSILICATE WASTE GLASS

Parameter	K-26 (repository)	BS-10 (open site)
Glass dissolution rate, R, µm/year	≥0.002	0.42
D_{eff}, cm^2/d	$2.96{\cdot}10^{-12}$	$1.57{\cdot}10^{-11}$
F_{300}, %	$2.3{\cdot}10^{-3}$	$2.1{\cdot}10^{-2}$

The radionuclide release from the bitumen and cement waste forms was supposed to be controlled by radionuclide diffusion through the bitumen or cement matrix. The same formula as in the diffusion model for waste glass was used to calculate leach radioactivity fractions vs. time (i.e. assuming coefficient *b* in equation (1) is nil).

Radionuclide release curves were plotted for experimentally derived and calculation results. The curves for the waste glass K-26, bitumen K-27, and cement K-28 (near-surface repository) are displayed in Figure 6.

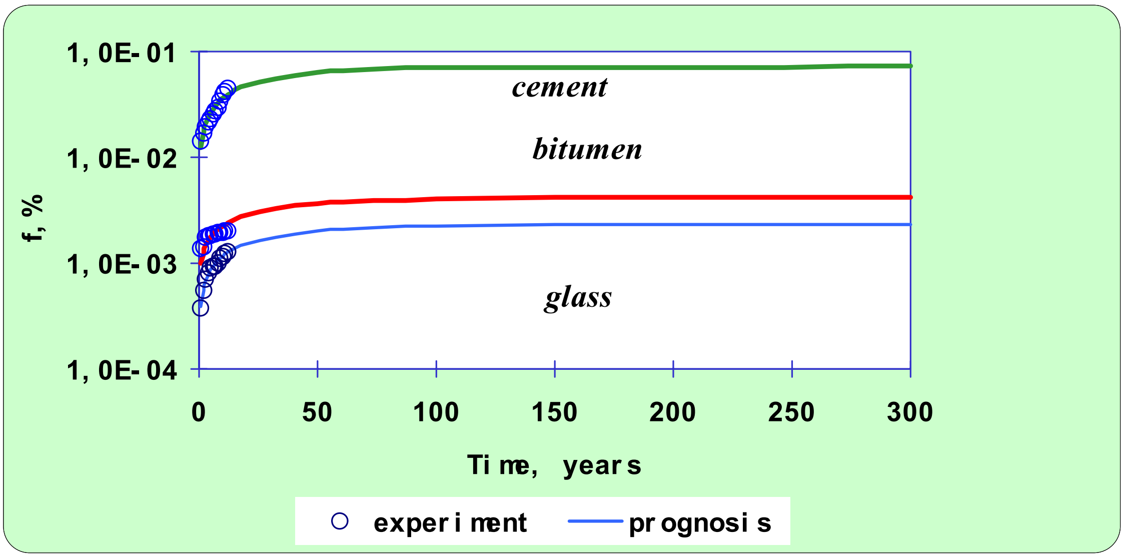

FIG. 6. Curves of radionuclide release from borosilicate waste glass K-26, bitumen K-27 and cement K-28 in a humid repository site plotted for experimental and simulation data.

According to the calculation results, $f_{max} = 2.3 \bullet 10^{-3}$% of the initial radioactivity will be released from waste glass K-26 into the environment within a proposed institutional control period of 300 years under conditions of a near-surface repository and in the absence of additional engineered barriers. Calculated maximum leached radioactivity fractions for the bitumen (K-27) and cement (K-28) waste forms were

$4.2 \bullet 10^{-3}$% and $7.2 \bullet 10^{-2}$%, respectively.

Thus, knowledge of the waste glass leaching behaviour during first decades of disposal allows the extrapolation of the glass behaviour over periods of a few hundred years. To perform this extrapolation, two experimentally derived parameters are needed: effective diffusion coefficient (D_{eff}) and glass dissolution rate (R). We determined these two parameters using experimental data derived from 12-year test. In fact, we suppose that the effective diffusion coefficient as well as glass dissolution rate will remain the same over the entire period of storage. This means that we do not expect significant changes to occur in the bulk glass structure (and in groundwater chemistry) during 300-year storage. In assessing whether this hypothesis is reliable or not, we can refer only to available knowledge about glasses. Lifetime of glasses concerning their possible devitrification is much longer than hundreds of years and can approach millions of years. The assumption that the geological environment will remain similar to current one is also quite acceptable for a few hundred years. Therefore, in our case of the relatively short time of a few hundred years, the applied two-parameter model could be rather trustworthy. Field tests with the waste forms are being continued. That will help validate the accuracy of our estimations and, if necessary, correct the model.

3.5. Corrosion of carbon steel containers

Longevity of construction materials for waste containers is of great importance for shallow land repositories. Radionuclides can escape from sealed containers into the environment only after the container walls are breached.

Data on corrosion rate of carbon steel were obtained from open field tests of containers containing vitrified and bituminised waste of intermediate-level activity. Experiment description and results were provided in [12,13]. The work performed to date has produced the data on lifetime of carbon steel containers under humid ambient conditions. The models of general and pitting corrosion proposed by J.H. Lee, J.E. Atkins and R.W. Andrews [14] were used. The authors developed the models for corrosion of carbon steel in water and humid air on base of numerous results generated during 16- year experiments. The principal parameters considered were the following: test duration, average annual temperature, average relative air humidity and concentration of sulphur dioxide in air.

To estimate carbon steel lifetime, the real depth of corrosion penetration must be determined. For this aim, the samples of carbon steel, 50x50 mm in size, were cut from the containers containing solidified waste (waste packages are under testing at the open testing site). The wall thickness of containers was 1.5, 2, and 2.5 mm. The samples were treated mechanically and chemically for removal of corrosion products [2,3]. For the selection of etching solution, reference samples of carbon steel were used.

Data processing led to the following results. For 2 mm-thick carbon steel used as a container material for vitrified waste with the initial radioactivity $1 \cdot 10^7$ Bq, corrosion rate for 18-year exposure time was about 101 g/m^2 yr. and penetration rate was 13 μm/yr. For the 1.5 mm-thick carbon steel used as a container material for vitrified waste of the total radioactivity $7.0 \cdot 10^7$ Bq, corrosion rate for 9-year exposure in the same conditions was 191 g/m^{2}yr., and penetration rate was 24 μm/yr. 2.5 mm-thick carbon steel was used to manufacture container for bituminised waste (total radioactivity $1.0 \cdot 10^8$ Bq). Average corrosion rate for 10-year test period was 186 g/m^{2}yr. and penetration rate was 24 μm/yr. According to the model of general corrosion of the carbon steel barrier in a humid air, container lifetime t is given by

$$t = \left(\frac{D}{D_o} \right)^{1.64} , \tag{6}$$

where D_o represents corrosion penetration depth in μm and is determined empirically; D = barrier wall thickness.

The model of carbon steel pitting corrosion in a humid air (equation 6) has been applied. The following container lifetimes were obtained: 25 years for 1.5 mm-thick steel and vitrified waste, 30-60 years for 2 mm-thick steel and vitrified waste, 50 years for 2.5 mm-thick steel and bituminised waste.

4. CONCLUSIONS

Waste forms, full size waste packages and blocks containing intermediate-level radioactive waste have been tested at the open testing site and in the shallow-ground experimental repositories of the SIA «Radon» testing site.

- Leaching behaviour of cement, bitumen and borosilicate glass waste forms was characterised through measuring the contacting water contamination by radioactive and non-radioactive components of the waste. Vitrified waste forms were the most resistant to weathering and leaching. Weathering of the bitumen waste form at the open site resulted in significant leach rate increase as compared with the leach rate of bitumen material under repository conditions. Rapid weathering of the cement waste block had led to its complete destruction after six-year exposure at the open site.
- In the repository tests, the following leach rate means for the whole 12yr testing period were obtained, g/cm^{2}day: 6.4• 10^{-7} (total β) and 2.3•10^{-7} (^{137}Cs) for vitrified waste forms; 1.2• 10^{-7} (total β) and
- 5.9•10^{-8} (^{137}Cs) for bitumen waste form; and 1.7• 10^{-6} (total β) and 1.4•10^{-6} (^{137}Cs) for cement waste form. All leach parameters were below leach rate limits accepted in Russia for solidified radioactive waste products.
- Experimental results from field tests were used to calculate some parameters of the model applied for predicting the waste form behaviour over extended time periods. Leached radioactivity fractions calculated for institutional control period of 300 years were as follows: 2.3•10^{-3} for vitrified waste forms, 4.2•10^{-3} for the bitumen waste form, and 7.2•10^{-2}% for the cement waste form.
- Physical condition of the waste forms was estimated after repository opening. Waste form samples were characterised using various methods and techniques. Noticeable ageing of the bitumen and cemented waste forms was detected. The ageing revealed itself in increased cement sample brittleness and in changes in fractional composition of bitumen. After 12yr storage, a significant proportion of radioactivity became associated with the asphaltene fraction of the bitumen matrix.
- Corrosion behaviour of carbon steel container material under humid conditions of the open site was examined. A model was applied to estimate the lifetimes of containers containing intermediate level vitrified and bitumen waste forms.
- The nature, extent and distribution of radionuclide contamination in the repository near field were studied.

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BEHAVIOR OF CONCRETE CONTAINER CE-2 A UNDER DISPOSAL CONDITIONS

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Abstract

The disposal system of El Cabril consists of waste emplaced inside concrete containers CE-2a type. These containers are stored in disposal cells, each of which has a capacity for 320 containers.

Both the containers and the disposal cells are designed to withstand extreme loads, including the site safety earthquake (SSE). The concrete used for the cells and containers was defined following a research programme, the objective being to optimize the durability of the concrete barriers. For this reason performance criteria are required regarding the long-term behaviour for the objective of concrete durability of 300 years. These criteria are divided in three categories: (a) Optimization of design; (b) Estimation of concrete container lifetime; and (c) Demonstration of the long-term behaviour of concrete container disposal conditions.

Regarding the demonstration of the long term behaviour there is a research program of an instrumented container type CE-2a under repository conditions, there is a 1:1 scale concrete container manufactured in accordance with the procedures in force at El Cabril but with a series of sensors incorporated prior to concreting and to mortar injection, located both on the inner surface of the structural walls of the container and embedded in the mortar of the block. This container is located inside a test concrete cell.

The first step in performance of this study was to identify the parameters of greatest interest recordable using the currently available resources, by means of sensors embedded in the concrete. The parameters selected were as follows: Temperature, Deformation, Electrical resistivity, Corrosion potential, Corrosion rate, Availability of oxygen at the reinforcement.

Two particular aspects were analyzed: a) the behaviour and suitability of the sensors, and b) their indications as parameters indicating the behaviour of the concrete and its reinforcement.

1. INTRODUCTION

Since 1988, ENRESA is developing the R&D programme about the optimization of the durability of the reinforcement concrete structures involved in safety barrier of the repository of El Cabril, with the cooperation of Spanish Institute Eduardo Torroja.

1.1 Background

The criteria taken into account in designing the CE-2a type concrete container used for the storage of low and intermediate level radioactive wastes at the El Cabril facility are as follows: Structural (resistance, transportability, shielding), and Durability. The R&D programme of optimization of durability of concrete structures (included the CE-2a type container) has been divided in tree phases:

1.1. Phase one: Optimization of the design

- Identification of the aggressive agents affecting the concrete container: on the one hand the external agents (water, temperature variations and the land), and on the other the internal agents which are the wastes with their different characteristics, the main agents being sulphates, borates and chlorides.

- Identification of the attacks process that might affect the concrete and reinforcing elements, and which might impact their durability.

The attacks, which might affect the concrete may be classified in different ways, among which are those applied by the RILEM32-RCA commission, the ASTM 632 standard and the ACI-2R 11 committee.

In our case the following classification might be established:

Nature of the phenomenon	Type of attack	
Physical-Chemical	Formation of expansive compounds	- sulphates - arid-alkali
	Leaching-hydrolysis	
	Ion exchange	- acid attack - seawater - ammonium salts
Mechanical	Fissuration	- retraction - deformation
Physical	Freezing-defreezing	
	Erosion-abrasion	
	Recrystalization of salts	
Biological	Action of sulphate-reducing bacteria	

The durability of the reinforced concrete structures is the result of a dual protective action exercised by the concrete on the steel:

- The concrete covering constitutes a physical barrier.
- The high alkalinity of the concrete develops on the steel a passivating layer that maintains it unaltered for an indefinite period of time.

There are, however, aggressive environments or added substances in the mix that may cause corrosion of the reinforcement. Essentially there are two reasons for the destruction of the passivating layer on the steel:

- The presence of a sufficient amount of de-passivating ions (chlorides)
- Reduction of the alkalinity of the concrete due to reaction with the acid substances in the medium (the CO2 in the atmosphere produces carbonates, as a result of which the process is known as carbonation).

In the first case the corrosion is local, while in the second it is generalized.

In the specific case of the El Cabril facility, the selected location is considered to be particularly compatible with long-term concrete performance:

- The site is a considerable distance from any marine environment.
- The water table does not contain sulphates or any potentially aggressive substance.
- The site is located in a rural area with no abnormal atmospheric contents of CO2 or other contaminants.
- The climate is favourable and no important phenomena of freezing-thawing are expected.
- The possibility for degradation due to expansive aggregate-alkali reactions has been avoided by suitable material selection.

With above-mentioned considerations a technical specification of raw materials and concrete container manufacturing was elaborated.

Degradation due to biological action is significant only in environments suitable for the development of biological cultures, as a result of which it may be considered negligible in the area of El Cabril.

1.1.2. Phase two: Estimation of concrete container lifetime

On the basis of different analyses carried out in the laboratory, the only foreseeable causes of degradation have been determined to be the following:

For concrete: leaching of the concrete by water.

For the reinforcement: carbonation of the outer layer during the period in which the containers are kept in contact with the air.

It is not foreseen that any other possible causes of degradation could occur at El Cabril, if suitable controls are maintained during container manufacturing and handling.

Given that the objective of this phase is to confirm the conservatism of the hypotheses adopted in calculating radiological impact, and that in this respect the engineered barriers are assumed to undergo complete degradation after 300 years, modelling has been limited to a 300-year period.

With respect to carbonation several tasks have been undertaken, these briefly being as follows:

a) Study of carbonation rate in raw specimens stored under similar atmospheric conditions, using the square root law.

b) Periodic measurement of the air permeability of the real containers to account for variability throughout the structure and evolution with time.

The carbonation rate measured in the specimens is of the order of 1.5 mm/year, this meaning that after 50 years the carbonation depth might be approximately 10 mm, and after 300 years some 26 mm, far below the current thickness of the reinforcement cover (40 mm).

Leaching occurs as a result of the flow of water with low salt contents, or acid. For the measured water permeabilities of concrete of 10 x 10-11 to 10 x 10-12 m/s, the advance of the water over 300 years would be at most between 10 and 100 mm, this being less than the thickness of the container wall (150 mm), as a result of which it may be concluded that the leaching phenomenon is highly improbable and of insignificant effect.

There may be a phenomenon of capillary water absorption, however. The coefficient of capillarity for concrete is 13.22; with this value the penetration of water in 300 years due to capillary effects would be 229 mm, but there would be no flow of water, which might give rise to leaching.

The air permeabilities of concrete rank mainly between good and very good.

Finally and as regards chloride leaching a study is now under way to characterize the corrosion resistance of the metallic container, as well as the diffusion coefficient of the chlorides in the surrounding cementitious materials. The results will make it possible to calculate the hypothetical period taken by the chlorides to reach the reinforcement.

1.1.3. Phase three: Demonstration of the long-term behaviour of container concrete under disposal conditions

Two parallel courses of work are currently being applied with a view to checking the behaviour of the concrete containers under disposal conditions.

On the one hand there is a programme for tracking of the characteristics of the concrete used in manufacturing the containers, as regards durability, and on the other, a programme consisting of the construction of a concrete container which is placed under conditions identical to those used for waste disposal, with a set of internal instruments allowing insight to be gained into its long-term behaviour.

1.2. Objectives

With the general objective of to verify the behaviour of concrete container CE-2a under disposal conditions, the following three main objectives was planed in this project:

1. Verify the behaviour of the concrete container in its main characteristic (confinement and durability) in the repository conditions.

2. Predict the behaviour of concrete container CE-2a for the period of the design of the repository of 300 years (period of time that is consider in the safety analysis).

3. Develop a technique that permit to analyse the parameter of behaviour of the concrete container CE-2a, with non destructive methods.

1.3. Relevance to Spanish radioactive waste programme and to Agency´s CRP

The facilities at El Cabril are designed as a near-surface disposal facility for low and intermediate level radioactive wastes, and must meet two basic objectives:

- To ensure the immediate and deferred protection of the public and the environment.
- To allow free use to be made of the site after a maximum 300 years, without any radiological limitations.

Two needs may be deduced from the aforementioned objectives:

- Isolation of the waste packages from water
- Limitation of radioactivity levels

Together with man, water is the possible vehicle for dispersion of the stored radioactivity. The disposal facility must, therefore, be isolated from the groundwater (by placing the waste packages above the water table) and from surface waters (by avoiding flood areas and watercourses and protecting it from rainfall).

Moreover, by adopting pessimistic hypotheses regarding human intrusion at the end of the surveillance period, of a maximum 300 years, the total activity and maximum mass activity must be limited such that the impact involved be acceptable.

The Spanish disposal facility for low and intermediate level radioactive wastes is designed as a near surface repository.

The waste packages most of which are 0.22 m3 steel drums, are placed inside concrete disposal containers. The drums (or pellets from the supercompaction process) are then immobilized inside the concrete container, forming a block weighing some 25 tons and having external dimensions of 2.25 x 2.25 x 2.20 metres.

These containers are stored in disposal cells, each of which has a capacity for 320 containers and approximate external dimensions of 24 x 19 x 10 metres.

Both the concrete containers and the disposal cells are designed to withstand extreme loads, including the site safety earthquake (SSE). The concrete used for the cells and containers was defined following a research programme conducted by the Spanish Institute Eduardo Torroja, the objective being to optimize the durability of the concrete barriers. The concrete used is of high characteristics resistance and compactness and is sulphate and seawater resistant (despite the low concentrations of sulphates and chlorides in the site water).

The conceptual design of the disposal facility is constituted by a multiple barrier system.

This system is made up of three barriers:

- Firstly, the concrete containers with inmobilized wastes inside.

- A second barrier formed by the concrete disposal cells, the cap and the infiltration control network, which limits the access of water to the waste packages and allows any water that may have come into contact with them to be controlled and treated where necessary.
- The third, or geological, barrier is the surrounding land. This would limit the impact of a possible release in the event of an accident or in the hypothetical case of total degradation of the first two barriers.

The main elements involved in the first two barriers is the concrete; for this reason performance criteria are required regarding the long-term objective of concrete durability, 300 years, for all the concrete structures.

This is the reason for the relevance of R&D programme about durability of concrete barrier, and the use of the results in the safety analysis of the repository. The conclusions would be used in the design of new repositories and the definition of technical prescriptions for regulatory bodies.

1.4. Scope of work

In order to cover the objectives of the project, the R & D program was divided in two parts: verification of the characteristic of concrete used to manufacture the container CE-2a (for verifying the objectives 1 and 2), and verification and analysis of the measurements of the Instrumented Container (for verifying the objective 2 and 3).

- Verification program of the characteristics of concrete used to manufacture the containers

As regards tracking of the characteristics of the concrete used to manufacture the containers, the following tests are periodically performed at the Eduardo Torroja Research Centre, with specimens placed into laboratory and in disposal conditions:

- Porosimetry by mercury intrusion
- Capillary absorption
- Mechanical compression strength
- Water permeability under pressure
- Determination of crystalline phases by X-ray diffraction
- Penetration of carbonation

Research program of the Instrumented Container type CE-2 a.

There is a 1:1 scale concrete container manufactured in accordance with the procedures in force at El Cabril but with a series of sensors incorporated prior to concreting and to mortar injection, located both on the inner surface of the structural walls of the container and embedded in the mortar of the block.

This container is located inside a concrete cell. Following backfilling of the existing space with gravel, an upper concrete slab was constructed and the assembly was waterproofed, such that the conditions of thermal insulation and waterproofing be similar to those of a disposal cell. This test cell has a lower drainage outlet connecting it to the outside, similar to those connecting the real cells to the ICN.

All the sensors are placed in one half of the container, the other half remaining intact, such that if necessary it would be possible to carry out destructive studies of its evolution without there being any influence from the positioning of the sensors and the inevitable penetrations.

For the performance of this study was necessary to identify the parameters of greatest interest recordable using the currently available resources, by means of sensors embedded in the concrete. The parameters selected were as follows:

- Temperature
- Deformation
- Electrical resistivity
- Corrosion potential
- Corrosion rate
- Availability of oxygen at the reinforcement

2. EXPERIMENTAL APPROACH

2.1. Preliminary tests and sensor types

It should be pointed out that although there are various types of sensors on the market for embedding in concrete, only those for the measurement of deformations, temperature and corrosion potential are habitually used.

The other sensors used have been developed specifically for this test. The resistivity and corrosion rate sensors have been the first allowing measurements to be taken by means of embedded sensors.

The most important problems encountered have been manufacturing sensors sufficiently robust to withstand the concrete pouring, compaction and steam curing stages and the prolonged contact with an alkaline medium such as concrete.

The sensors finally used were as follows:

- Temperature (To)	- Cu/Constantan
- Deformation (□)	- Vibrating cord.
- Corrosion potential (Ecorr)	- Mn/Omn and Ti wire
- Resistivity (□)	- stainless disc and Ti wire - stainless disc and Mn/Omn - two stainless rods in parallel.
- Availability of O2 (O2)	- as for resistivity
- Corrosion rate (Icorr)	- stainless disc and Ti wire. - stainless disc and Mn/Omn

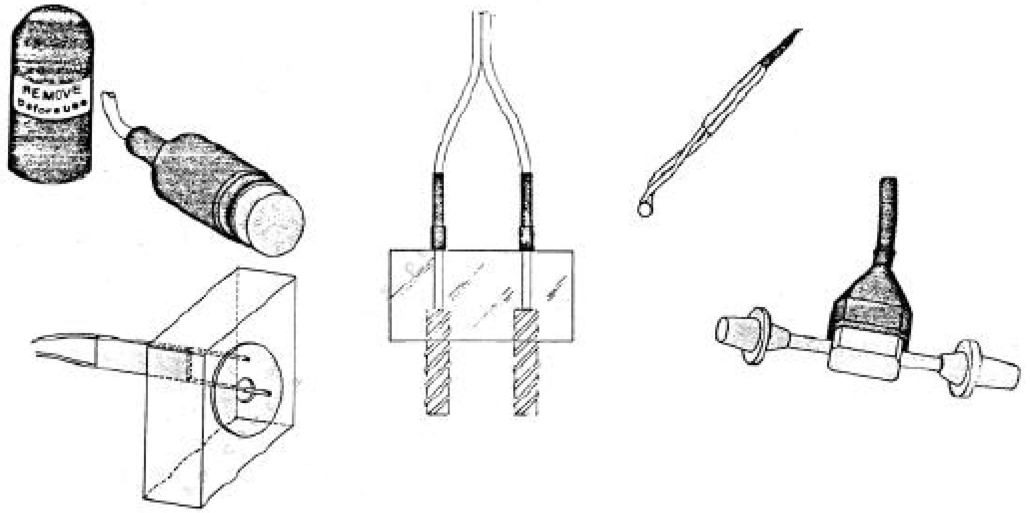

FIG. 1. Different types of sensors embedded in a test sample.

All these sensors were embedded during the testing phase in a sample with a long bar that acted as the reinforcement, as shown in Figure 1. All the tests for setting up of the measurement and continuous recording methods were performed on this sample using GEO-LOGGER.

2.2. Description of measurement methods and instrumentation (Geo-logger)

The Geo-logger is essentially a potentiostat/galvanostat that allows continuous measurement and recording to be accomplished on up to 50 channels. The software makes it possible to programme the sequence of measurements and generates a system of alarms when the recorded values exceed a previously determined range. The system has been developed by Geocisa specifically for the present test.

As regards the measurement methods used, those relating to To, * and Ecorr are simple recordings of the responses generated by the sensors. For the measurement of D, Icorr and O2, on the other hand, it is first necessary to generate a signal disturbing the sensor (auxiliary and reference electrodes) and the reinforcement (working electrode), the response to this induced disturbance being recorded.

Resistivity, D, is measured by means of the “current interruption” method, which records the instantaneous voltage drop that occurs when an electrical signal is generated and then cut. The instantaneous voltage drop that occurs at the moment of this cut is known as the “ohmic drop” and allows electrical resistivity to be calculated if the geometric parameters are known. In the present case, the “disc-infinite bar” approach is used, and D is given by the expression D = 2R f, where R is the ohmic drop and f the diameter of the disc (2 cm).

Corrosion rate, Icorr, is obtained by means of the “culostatic” method, which allows Icorr to be calculated through Polarization Resistance:

$$RP = \left(\frac{?_E}{?_I}\right) E < 50mV$$

The value of $?_E$ is obtained from the discharge curve (following the current cut-off) and $?_I$ is the current applied (galvanostatic test).

The value of Icorr is obtained by means of the Stern formula:

$$Icorr = B/R$$

where B is a constant, which in the present case has been given a value of 26 mV.

Oxygen availability is obtained by recording the intensity measured on polarization of an electrode of defined surface area (disc or rod) at -75 mV (ECS).

This intensity allows the flow of oxygen being reduced on the metal to be calculated by Faraday's Law:

$$\frac{mol\ of\ O_2}{m^2 . s} = \frac{I}{4F}$$

I = current density (A/m^2)
F = Faraday constant

2.3. Container manufacturing and positioning of sensors

Once the methodology has been set up and correct operation of the Geo-logger has been verified, the entire device was transferred to El Cabril for positioning in the pilot container.

The first step in this respect consisted of positioning the groups of sensors as indicated. It may be appreciated that 21 groups of O^2, D, Ecorr and Icorr sensors were positioned, along with 9 T^o and * groups, on the walls of the container at different heights and with different orientations.

Details of the positioning of these sensors and their contacts with the container reinforcement are shown in Figure 2.

A further 6 groups were positioned on the drums located inside the container . In order to ensure correct electrical contact with the drum, an area measuring 20x20 cm was cleaned of external paint, the contact then being accomplished by means of welding . These drums were filled with sand.

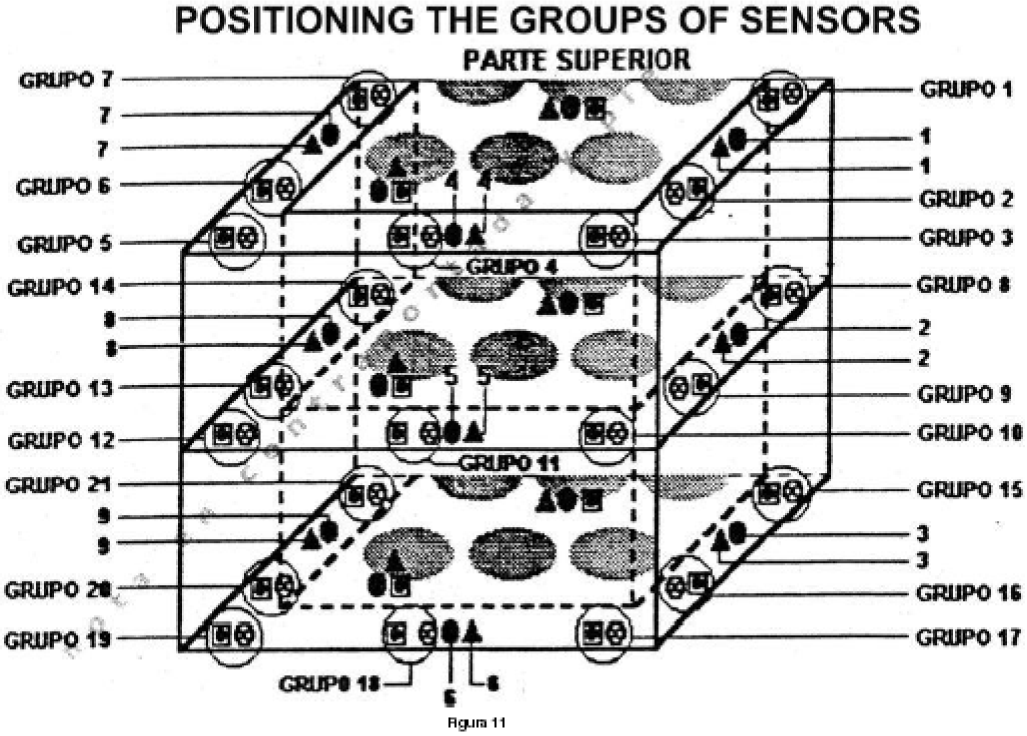

FIG. 2. Positioning of the sensors in the container reinforcement.

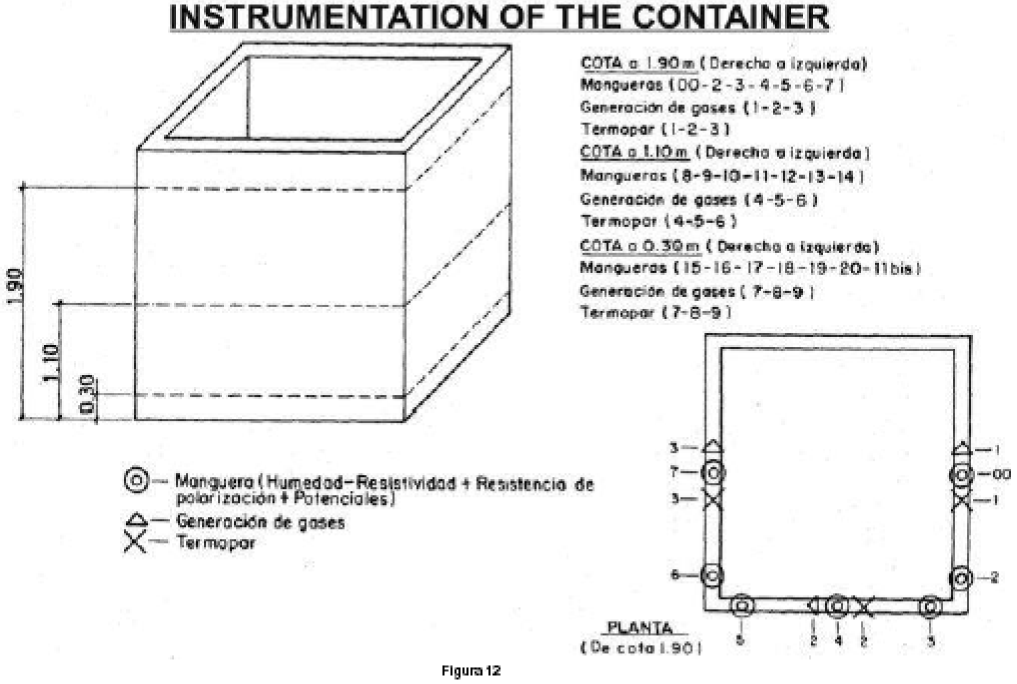

FIG. 3. Instrumentation of the container.

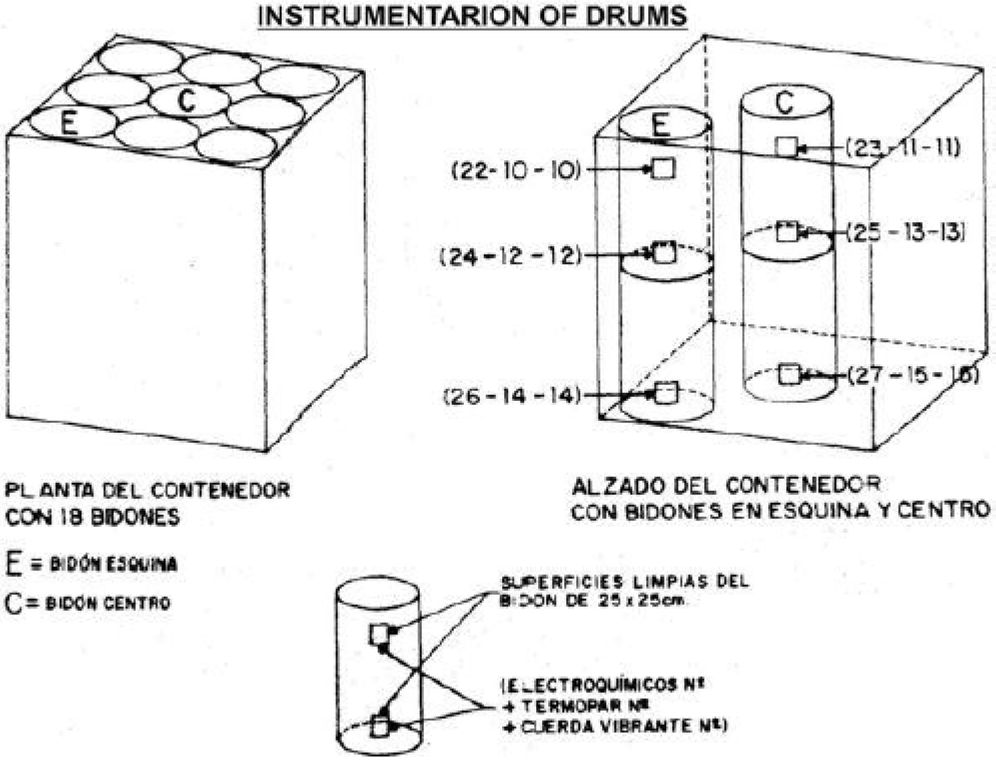

FIG. 4. Instrumentation of drums.

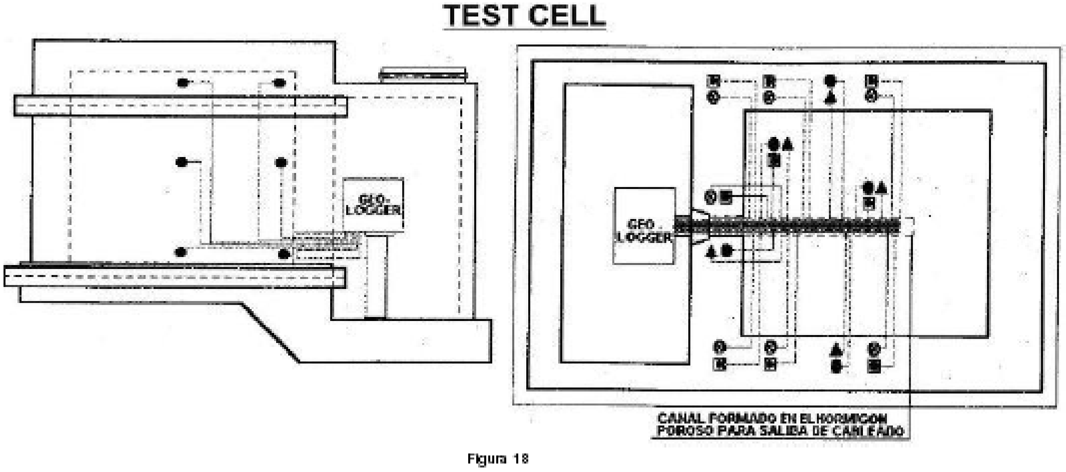

FIG. 5. A schematic of the test cell.

The entire assembly of drums + container was finally manufactured using the normal procedure.

Data recording commenced about one month after manufacturing of the container.

The instrumentation consisted overall of the following: 26 groups of electrochemical sensors, 15 deformation sensors and 15 temperature sensors. A further group of sensors is set aside in the specimen used for the preliminary tests as channel 0.

Placing of the pilot container in an enclosure simulating a disposal cell.

Following the initial period of curing of the container, the latter was transferred to what was to be its burial enclosure, which purports to reproduce the conditions of a disposal cell once covered by the layer of mould.

The enclosure in which the container was located is made up of two parts: a) one housing the container which is isolated by 50 cm-thick concrete walls simulating the cell and b) a second housing the Geo-logger and the specimen used for all the preliminary tests, with the embedded sensors and serving as a reference. More recently the humidity and temperature of this measurement enclosure have also been recorded.

Continuous recording of data and data analysis.

Since the pilot container was positioned in the cell, different measuring sequences have been adjusted with a view to optimize recording, such that sufficient data be obtained without saturating the system with an excessive and unnecessary flow of information.

Channel zero corresponds to the register of the reference specimen located in the measuring enclosure adjacent to the container.

Only a relatively small percentage (10%) of the sensors have failed, the majority having operated correctly since the beginning of the recording process.

Since start-up of the system, the following three main events have occurred:

Data recording was interrupted soon after start-up due to abnormalities being detected in the main feed line for the network to which the Geo-logger is connected. Appropriate current stabilizers had to be installed.

The following sequence and measurement sensors were finally adopted:

hour	type of measurement
2	T^o, *, D
4	Ecorr
5	O_2
8	T^o, *, D
13	O_2
14	T^o, *, D
17	Icorr
20	T^o, *, D
21	O_2
23	Icorr

The system may currently be said to be in a normal recording situation.

3. RESULTS AND DISCUSSION

The summary of the results obtained from the beginning of the project will be divided in two parts: the verification program of the characteristic of the concrete used to manufacture the containers and the verification of the instrumented container under repository conditions.

3.1. From the verification programme of the characteristic of concrete used to manufacture the containers CE-2a

TABLE I. CHARACTERISTICS OF CONTAINER CE-2A CONCRETE

TEST	ARITHMETIC MEAN	STANDARD DEVIATION	RELATIVE DEVIATION
Total porosity (% weigh)	3.55	± 0.27	± 7.5%
Apparent density (g/ml)	2.5	± 0.00	± 0.00%
Total pore area (m2/g)	6.3	± 0.70	± 11%
Avg. Pore diameter (□m)	0.025	± 0.007	± 28%
Coef. Resistance to water penetration (x E+07) (m)	81	± 15	± 18%
Coef. Capillary absorption(x E-04)	10	± 3	± 30%
Effective porosity (x E-02)	2.8	± 0.8	± 28%
Breaking strain (Kp/cm2)	575	± 35	± 6.4%

Those data indicate that the concrete used for manufacture container has an appropiate characteristic and good quality in a long term.

3.2 From the instrumented container CE-2a

Two aspects of the results obtained may be analyzed: the behaviour and suitability of the sensors, and their indications as parameters indicating the behaviour of the concrete and its reinforcement.

Behaviour and suitability of the sensors

TABLE II. SENSORS IN OPERATION

Measurement	Sensor
Availability of oxygen	Mn- elect A – elect O
Resistivity	Stainless disc- Ti wire
Corrosion potential	Mn- wire and Ti- wire
Corrosion rate	Stainless disc- Mn wire
Extensometry (Deformation)	Vibrating cord
Temperature	Cu

The following sensors have not produced better results or they have not been properly measured:

Did not produce better results	Stainless disc- Mn wire/ Resistivity Stainless disc- Ti wire/ Oxygen Availability
Did not measure properly	Mn- stainless wire/ Corrosion Rate Mn- stainless- elec A / Oxygen Availability

More than 90% of the sensors placed in the instrumented container are in operation, with properly measured and results.

3.3. Behaviour of the concrete and reinforcement

The results obtained by the sensors for the last 6 years are indicated in the following figure. In this figures have been a grouped the sensors into four categories depending of the sensors have placed in the instrumented container.

The reference group of sensors measure the behaviour of a specimen test placed outside the instrumented container cell, and is used to follow the operation of the sensors.

The figures named “upper group of sensors” represent the average of measures (T^a, deformation, etc.) of each type of sensors that are placed in the upper part of the instrumented container.

The figures named “middle group of sensors” represent the average of measures (T^a, deformation, etc.) of each type of sensors that are placed in the middle part of the instrumented container.

The figures named “lower group of sensors” represent the average of measures (T^a, deformation, etc.) of each type of sensors that are placed in the lower part of the instrumented container.

4. CONCLUSIONS

4.1 The following conclusions may be deduced from the results obtained in the develop of the project

1. The average of operating sensors is about 90%, which is considered satisfactory.
2. The sensors permit to follow properly the concrete hydro-thermal conditions, and the parameters related with the steel corrosion.
3. The reinforcement of the container and the steel of the drums is perfectly passive.
4. The concrete of the container is in process of drying and densification.
5. Inside the container the oxygen content is quite clearly high.
6. The temperature has a great influence in all of the parameters as a consequence of seasonal cycles, resistivity (it decreases with increasing T^a), deformation (the concrete expands when T^a increases), oxygen availability (this increases with T^a). The changes are minimal in Ecorr and zero in the case of Icorr.

7. The availability of oxygen is the most difficult parameter to interpret. In general the amounts of oxygen detected are high, that indicate there are not anaerobic conditions.

4.2. Major accomplishments reached in the project

At present, the durability of concrete structures is one of the most important issues in the design of the low and intermediate disposal facilities, due to the necessity that these structures withstand the external and internal conditions, for 300 years.

Some approximations exclusively consider certain requirements for concrete composition, properties and composition of concrete constituents, curing and most of the time concrete compressive strength.

Later has been included other parameters in order to control the quality of the concrete, like permeability coefficient, carbonation rate and diffusion coefficient. And laboratory test methods have been developed to measure these parameters, and to follow its evolution in time.

After that, the next step was to develop and to set up on-site methods that permit the designer and operator to monitor the evolution of the concrete structures and to predict its behaviour in the long term (the aim of the project).

These are the main accomplishments reached in the project:

(1) The definition of the measured relevant parameters for analysis of the behaviour of concrete container under disposal conditions:
Carbonation (passive reinforcement)
Permeability
Strength resistance/thermal cycle
Anaerobic conditions
Corrosion rate/Corrosion potential.
Resistivity.
Deformation
Oxygen availability

(2) The selection of the suitable on-site sensors for the relevant parameters for concrete long-term behaviour .Availability of oxygen(Mn-electA-elect O); Resistivity (stainless disc-Ti wire); Corrosion potential (Mn-wire and Ti- wire); Corrosion rate (stainless disc- Mn wire); Deformation (vibrating cord); Temperature (Cu)

(3) The development a Data-logger that permit to collect the measurement of each sensor.

(4) To manufacture an instrumented concrete container with more than 130 sensors (26 groups of electrochemical sensors, 15 deformation sensors and 15 temperature sensors).

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STATUS OF INTERMEDIATE LEVEL WASTE ENCAPSULATION AT SELLAFIELD/BNFL

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Abstract

BNFL has been successfully carrying out the encapsulation in cement of intermediate level waste generated from reprocessing at Sellafield for over 11 years. Currently four plants are in operation encapsulating wastes generated at the Sellafield site. Two further plants are being developed for the encapsulation of wastes arising from historic operations. The wastes encapsulated range from chemically inert to fairy chemically reactive solid and slurry wastes. In this report an overview is given of the wastes processed, the processes employed and the development work which has been carried out to understand how these wastes perform and evolve with time is discussed.

1. INTRODUCTION

Whilst no specific work was carried out for this co-ordinated research programme by the UK, BNFL have participated in the programme as an observer. This report has been written to give an overview of the current intermediate level waste encapsulation operations and developments at Sellafield.

The intermediate level wastes generated at Sellafield are derived from the reprocessing operations carried out at the site. These wastes include solids waste such as Magnox or oxide fuel element cladding, supercompacted wastes, and slurry wastes such as iron hydroxide flocs from effluent treatment and centrifuge cake from reprocessing operations. In addition, there are similar wastes which have been stored for several decades at Sellafield in tanks, silos and stores for example historic arisings of Magnox fuel element cladding.

All current arisings generated at Sellafield are encapsulated in cement in one of the four presently operating encapsulation plants using vibrogrouting, in drum mixing or super-compaction followed by grouting. The grouted products are then stored at Sellafield.

For the historic arisings, development work is currently underway to determine how to retrieve the waste and produce products suitable for disposal. Methods currently proposed include drying followed by super-compaction for wet material and direct grouting for dry material.

For each of the encapsulation processes employed at Sellafield development work has been carried out to:

- Gain a detailed understanding of cement hydration processes and hydration products.
- Gain a detailed knowledge of how the waste and cement interact in both the short term during the encapsulation process, grout setting and during longer term storage.
- Gain an understanding the effect of scale up on the cementation processes from laboratory to full-scale operations.

- Show that the physical and chemical properties of the product are satisfactory and to understand how these evolve with time: e.g.
    - Radiation Stability
    - Thermal conductivity
    - Permeability and porosity
    - Chemical reactions between the waste and the cement such as corrosion
    - Mechanical properties, dimensional stability, homogeneity and density
- Understand of the performance of the plant during operation and demonstration that this is consistent with producing products of the required quality.
- Demonstrate satisfactory performance of the product under accident conditions, e.g. fire and impact testing.

2. RESULTS AND DISCUSSION

Magnox Encapsulation Plant

The Magnox Encapsulation Plant was opened in 1990 and since then has encapsulated over 6300m^3 of Magnox fuel element cladding from reprocessing operations. The waste is generated when the fuel is removed from the element by stripping away the Magnox cladding which is an alloy consisting largely of magnesium. This creates pieces of Magnox fuel element swarf of varying lengths as illustrated in Figure 1**Error! Reference source not found.**.

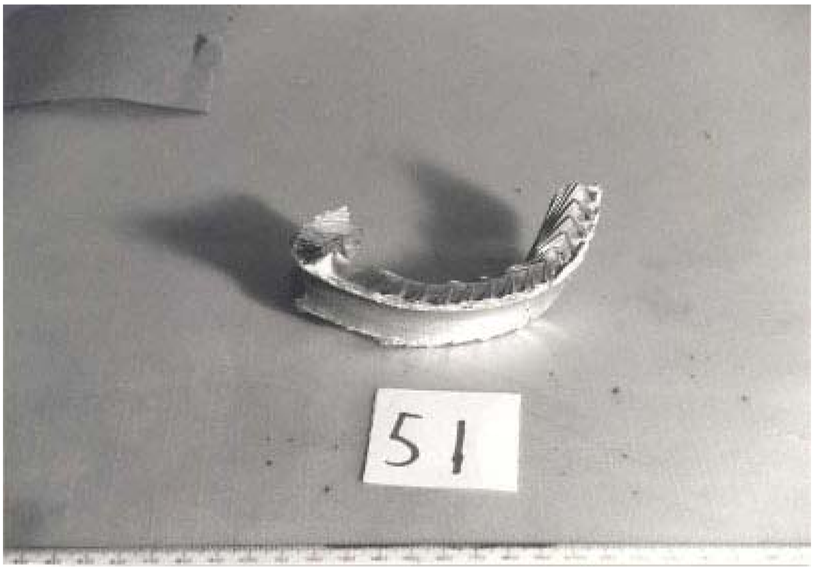

FIG. 1. Example of a piece of Magnox fuel element swarf.

To remove the risk of fire, and reduce the risks associated with hydrogen generation from corrosion, the Magnox fuel element swarf is stored and transported under water in a container dosed with sodium hydroxide to the Magnox Encapsulation Plant. Here the contents of the container are tipped into a 500 litre stainless steel encapsulation drum, and the water removed. The waste is then encapsulated in a blast furnace slag and ordinary Portland cement grout using a vibrogrouting process to increase the fluidity of the grout through shearing and achieve satisfactory infilling of the waste. Once the grout has set and any bleed water has evaporated a pulverised fuel ash and ordinary Portland cement grout cap is applied to the top of the drum. This fills any ullage remaining in the drum and seals any loose activity remaining on the surface of the product. The cap is then allowed to set, the drum lidded, decontaminated if necessary, and sent to a store for storage. An example of an encapsulated Magnox fuel element swarf product is shown in Figure 2.

The major issue associated with the encapsulation of Magnox fuel element swarf waste has been the corrosion of the Magnox metal in the encapsulated product. The corrosion of Magnox metal mostly generates hydrogen and magnesium hydroxide. The magnesium hydroxide formed occupies a larger volume than the original Magnox metal and hence has the potential to expand, causing stresses in the grout matrix to develop which may eventually lead to cracking and failure of the waste form.

A large amount of work has been carried out to understand the corrosion behaviour of Magnox metal encapsulated in blast furnace slag and ordinary Portland cement grouts. This work has investigated:

- The total amount of corrosion required before the product fails including understanding the effects of the expansive corrosion product on the grout and wasteform as a whole.
- The rate at which Magnox corrodes with time and changing conditions within the encapsulated waste.
- The effects the degree of corrosion seen by the Magnox before encapsulation may have on the quality of the product. This has allowed some older Magnox arisings which have been stored underwater for some years to be encapsulated using this process.

From the information generated a range of times before product failure has been determined and these timescales shown to be consistent with those required for interim storage before ultimate disposal.

Other issues associated with developing the encapsulation process are discussed in the next section on the encapsulation of solid waste from the reprocessing of oxide fuel in the Waste Encapsulation Plant.

FIG. 2 Encapsulated magnox fuel element swarf

Waste Encapsulation Plant

The Waste Encapsulation Plant was built to encapsulate both solid wastes and slurries arising from the reprocessing of oxide fuels in THORP. It has been operating since 1994 since when approximately 1700m^3 of waste have been processed. The solid waste consists of cropped lengths of the stainless steel or zircalloy fuel elements (hulls) with their end assemblies. The encapsulated slurries are spent pond filter precoat, spent ion exchanger resin, barium carbonate from the treatment of carbon dioxide off gas containing C^{14} and insoluble particulates passing through the fuel dissolution process known as centrifuge cake. Examples of hulls and barium carbonate slurry are shown in Figures 3 and 4.

FIG. 3. Oxide fuel element hulls.

FIG. 4. Barium carbonate slurry from THORP and iron floc from the Enhanced Actinide Removal Plant.

The hulls are encapsulated in a similar manner to the Magnox swarf in the Magnox Encapsulation Plant. A container of hulls is transported from THORP to the Waste Encapsulation Plant in a suitably engineered flask. At the Waste Encapsulation Plant the container is removed and the hulls are tipped with their covering water into a 500 litre stainless steel encapsulation drum. Before encapsulation the cover water is removed to leave a minimal volume of water associated with the hulls. The rest of the process is the same as for encapsulating Magnox swarf in the Magnox Encapsulation Plant; the hulls are then encapsulated in a blast furnace slag and ordinary Portland cement grout using a vibrogrouting process to increase the fluidity of the grout through shearing and achieve satisfactory infilling of the waste. Once the grout has set and any bleed water has evaporated, a pulverised fuel ash and ordinary Portland cement grout cap is applied to the top of the drum. This fills any ullage remaining in the drum and seals any loose activity remaining on the surface of the product. The drum is then lidded and the cap allowed to set. The drum is then lidded, monitored for contamination and decontaminated if necessary, and sent to a store for storage. An example of an encapsulated hulls product is shown in Figure 5.

FIG. 5. Encapsulated oxide fuel element hulls.

As the hulls are made from zircalloy and stainless steel which are relatively stable in cement the major issues in developing the encapsulation process were associated with developing the grout and grouting process, for example:

- Developing a grout formulation which stays fluid for long enough for a drum to be processed satisfactory.
- Ensuring the grout sets in a suitable length of time for plant throughput, without an excessive exotherm or bleed being present.
- Ensuring that the grout is dimensionally stable and has sufficient strength.
- Developing a system for cleaning the grout from the transfer pipework.

Encapsulation of the slurries follows an in drum mixing process where the cement powders are added to a 500-litre encapsulation drum containing the waste. Again, the waste is transferred from THORP to the Waste Encapsulation Plant in a container in a flask. At the Waste Encapsulation Plant the contents of the container are tipped into a holding tank and the contents kept agitated to prevent settlement and keep the contents homogenised. There are separate tanks for acidic and alkaline waste streams and several alkaline wastes can be mixed in the same tank. Before encapsulation the contents of the tank are sampled and the solids content measured. The contents are then metered into a 500 litre encapsulation drum containing a mixing paddle and the acidic waste pre-treated to prevent adverse reaction with the alkaline cement powders. Once in the drum the slurry is then mixed with the paddle to ensure that the solids are resuspended and blast furnace slag and ordinary Portland cement powders are fed to the drum whilst the paddle rotates to mix the powders. The results of the solids content measurement define the grout formulation required and hence the total amount of powders that need to be added. After mixing, the paddle is left in the grout and the product allowed to cure. Once the product has set and there is no bleed present it is capped with a pulverised fuel ash and ordinary Portland cement grout. The drum is then lidded and the capping grout allowed to set. The drums are then checked for contamination and if necessary decontaminated before being dispatched to a product store for storage.

All the slurry wastes encapsulated in the Waste Encapsulation Plant are relatively inert when encapsulated in cement so the major issues in the development of the encapsulation process were associated with defining in suitable formulation envelopes, which could:

- Accommodate a range of slurries having different solids contents and made up from a mix of several materials with a range of densities in varying proportions.
- The formulation envelopes generated had to have suitable setting properties, dimensional stability and strength without an excessive curing exotherm or bleed.

Waste Packaging and Encapsulation Plant

In 1994 BNFL started operating the Enhanced Actinide Removal Plant and its associated encapsulation plant the Waste Packaging and Encapsulation Plant. The Enhanced Actinide Removal Plant is designed to treat acidic active waste streams, bearing iron, generated from reprocessing on site before their discharge and since starting operations approximately 2600m^3 of waste has been encapsulated in the Waste Packaging and Encapsulation Plant. The process involves adding sodium hydroxide to the iron bearing acidic streams; this neutralisation results in the formation of a ferric hydroxide floc. The majority of the alpha activity co-precipitates with the floc leaving purified aqueous liquor whilst the inclusion of relatively small volumes of specific chemicals at the precipitation stage improves the beta activity removal. Then the precipitated floc is dewatered using an ultrafilter to increase the solids loading. Once a batch of floc has been prepared it is pumped to a storage tank in the waste packaging and encapsulation plant and kept agitated. Batches of this floc, as shown in [..], are metered into a 500-litre stainless steel drum containing a paddle where it is mixed with a conditioning agent. The conditioning agent overcomes some of the problems associated with encapsulation of these flocs which are discussed later. Once the conditioning agent has had time to act the waste is rehomogenised using the paddle and pulverised fuel ash and ordinary Portland cement powders mixed into waste. The product is then allowed to set and for any bleed evaporate or be reabsorbed. A pulverised fuel ash and ordinary Portland cement grout is then added to fill the remaining voidage in the drum and seal loose activity on the surface of the product. The drums are then checked for contamination and if necessary decontaminated before being dispatched to a product store for storage.

A typical product produced in the Waste Packaging and Encapsulation Plant is shown in Figure 6.

FIG. 6. Example of a Waste Packaging and Encapsulation Plant product.

During the development of the encapsulation process the major issues associated with encapsulating the flocs produced by the Enhanced Actinide Removal Plant were:

- The dimensional stability of the flocs in a cement matrix.
- The effects of chemical species present in the flocs on the cement hydration.

During the early stages of the development work it was found that the iron floc was dimensionally unstable due to a reaction between the cement and the floc which caused the product to shrink and crack. Experimental studies have identified the reactions which were occurring and from this understanding a suitable conditioning stage was identified which enabled satisfactory product to be produced. This conditioning stage worked by ensuring that these reactions had taken place before the waste was encapsulated.

The flocs produced by the Enhanced Actinide Removal Plant come from several sources with each source adding differing amounts of additional chemical species to the standard iron floc. Examples of the species present are chromium, aluminium, and nickel hydroxides and some inorganic and organic phosphates. These species can significantly effect the properties of the grout through accelerating or retarding the various cement hydration reactions resulting in grouts which can thicken up too quickly and become unmixable, or grouts which are very weak, take a long time to set and gain insufficient strength. These issues have been overcome by:

- Pre-treatment of the floc before encapsulation with a suitable conditioning agent.
- Careful selection of the blend of powders used and the amount of powders added to the waste.
- An understanding of the effects of the different chemical species on cement hydration reactions, followed by the definition of suitable of concentration limits for these species in the floc, and control of the composition of the encapsulated floc to be within these limits.

Waste Treatment Complex

The Waste Treatment Complex processes Plutonium Contaminated Material generated at Sellafield as a result of fuel cycle operations and the decommissioning of obsolete plants. It has been operating since 1998 and has processed about 800m^3 of waste. Most of the waste processed consists of 200 litre steel drums containing items from plutonium handling operations, wrapped in PVC. Initially these drums are assayed to determine the amount of plutonium and other radionuclides present in the drum. A remote inspection is also carried out using x-rays to determine the nature of the waste being processed. The 200 litre drums of waste are then supercompacted to produce a puck. This compaction reduces the amount of waste produced by a factor of about 5.

The compacted waste pucks are loaded into 500 litre stainless steel product drums and the internal volume of the 500 litre drum is filled with a pulverised fuel ash and ordinary Portland cement grout. The drums are then checked for contamination and if necessary decontaminated before being dispatched to a product store for storage. An example of encapsulated supercompacted pucks produced in the Waste Treatment Complex is shown in Figure 7.

FIG. 7. Example of supercompacted plutonium contaminated waste encapsulated in the Waste Treatment Complex.

The major areas of work carried out to support the encapsulation of supercompacted plutonium contaminated waste drums in the Waste Treatment Complex were:

- The development of a suitable grout formulation which was fluid enough to infill all the voids associated with the supercompacted pucks, had a sufficient working time and set in a suitable period.
- Understanding the evolution of the waste in the package. For example, the corrosion of the steel drum, the degradation of the organic waste in the puck, and the effects of radiation on the waste and grout.

Historic wastes

At Sellafield there is a large volume of historic intermediate level waste which was generated before the encapsulation processes were developed. This waste was stored dry or under water in silos depending on its source. Work is now underway to retrieve these wastes and process them with a view to eventual disposal in the UK's deep underground repository.

There are two major sources of historic waste arisings with disposal routes under development. These consist of Magnox metal, steel, graphite, aluminium, uranium, spent ion exchanger, organics and large pieces of redundant equipment stored either dry or underwater. The wastes stored under water also include a large amount of sludge formed from the corrosion of the Magnox and other metallic wastes present. The current envisaged processes for treating the wet wastes is to dry and supercompact the waste to minimise the volume of the waste and then grout the pucks produced in a pulverised Fuel ash and ordinary Portland cement grout in 500 litre stainless steel drums. The waste which has been dry stored is currently planned to be encapsulated in a 3m^3 stainless steel box using a blast furnace slag and ordinary Portland cement grout.

There are several challenging issues associated with the retrieval and encapsulation of these wastes. Examples of these are:

– Chemical reactivity of the waste for example aluminium and Magnox.
Variability and inhomogeneity of the waste and the range of physical properties of the waste from one source, e.g. particle size.

Figures 8 and 9 show examples of type of material typical of historic waste which has been stored under water.

FIG. 8. Example of simulated corroded Magnox fuel element cladding waste, which has been stored underwater.

FIG. 9. Example of simulated corroded Magnox fuel element cladding waste, which has been stored underwater — containing large pieces.

Aluminium can create problems when encapsulated in cement due to its rapid reaction with the highly alkaline water present in the cement grout to form aluminium hydroxide and hydrogen gas. There are two aspects to this reaction which have had to be overcome to allow the encapsulation of aluminium:

- The high volumes of hydrogen generated whilst the grout is curing and plenty of water is available for reaction.

- The effects of continued but slower corrosion on the encapsulated product in the long term.

The high volumes of hydrogen generated during curing can be overcome by designing the process in a manner which will safely dissipate the hydrogen generated and by controlling the amount of hydrogen which could be generated from the waste. The long-term corrosion is a similar issue to that for the encapsulation of Magnox fuel cladding where the formation of the corrosion product is an expansive process. Continued corrosion and expansion can eventually cause failure of the product. A large amount of work has been carried out to understand the corrosion reactions of aluminium in cement, and also the effects of the continued hydration and evolution of the cement matrix on aluminium corrosion.

Another difficulty in developing a process for the treatment of these historically generated wastes is the large amount of variability present in the physical properties and composition of the wastes. These can vary widely within a single source, for example a wet sludge of corrosion products can be present with medium sized pieces of the original material, e.g. relatively uncorroded Magnox fuel element cladding and large pieces of material, e.g. scaffolding poles. Additionally there is potential for one type of material in the waste to affect the performance of another for example the corrosion rates can be effected through galvanic coupling. The processes developed for processing these wastes need to be sufficiently robust to cope with the wide range of materials which could be received. Good characterisation of the waste is essential to understand the waste compositions which could occur. One way in which it is proposed to reduce the effects of this variability is to segregate some of the material before treatment. For example the waste which has been stored under water will have the larger items separated and size reduced before compaction to allow compatibility with the compaction process.

3. SUPPORT WORK TO EXISTING AND FUTURE PLANTS

A large amount of data has been generated in support of the existing plants and processes, and those currently under development. However, modifications and optimisation of these processes is requiring continued development work. This is building on the knowledge gained so far and expanding it so that the operation of the plants is continuously improving. Work is also being carried out to increase the understanding of the evolution of the waste packages in the product stores to ensure their suitability for disposal when the UK deep underground repository becomes available.

In addition, BNFL has recently set up a Centre for Waste Immobilisation Technology at Sheffield University in the UK. This has the aims of

- Increasing the fundamental understanding of the relationships governing the processing of waste streams and the subsequent performance of the resulting waste forms.
- Providing additional knowledge required to satisfy national and international regulators, customers and stakeholders.
- Gathering and critically appraising information on the use of novel and alternative immobilisation technologies developed internationally and to examine their potential application to existing and future waste streams.
- Acting as the central point for BNFL in establishing a world-wide network of organisations performing research in immobilisation.
- Increasing international awareness of BNFL's commitment to performing fundamental research in immobilisation science and its application.
- Providing a core of researchers in the immobilisation area performing industrially applicable fundamental research, but who are removed from the immediate pressures of plant support operations.

4. CONCLUSIONS

BNFL have generated an extensive scientific, engineering and operating knowledge base in relation to the encapsulation of wastes in cement. This knowledge base has enabled these wastes to be encapsulated and an understanding to be gained of how the products will evolve with time.

BNFL has been successfully encapsulating Intermediate Level Wastes from its reprocessing operations at Sellafield for 11 years and has encapsulated about 11,500m^3 of waste to date. A wide variety of materials are routinely encapsulated ranging from fairly inert slurries and metals, through supercompacted plutonium contaminated material to more problematic materials such as iron hydroxide flocs and Magnox fuel element cladding.

The next phase for the processing of waste at Sellafield is the treatment of historical arisings of intermediate level waste and work is currently underway to develop these processes.

WASTE CONTAINER AND WASTE PACKAGE PERFORMANCE MODELING TO SUPPORT SAFETY ASSESSMENT OF LOW AND INTERMEDIATE-LEVEL RADIOACTIVE WASTE DISPOSAL

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Abstract

Prior to subsurface burial of low- and intermediate-level radioactive wastes, a demonstration that disposal of the wastes can be accomplished while protecting the health and safety of the general population is required. The long-time frames over which public safety must be insured necessitates that this demonstration relies, in part, on computer simulations of events and processes that will occur in the future. This demonstration, known as a Safety Assessment, requires understanding the performance of the disposal facility, waste containers, waste forms, and contaminant transport to locations accessible to humans. The objective of this study is to demonstrate the link between waste container and waste form data collection and model development needs to support a defensible safety assessment. This is accomplished by reviewing the fundamental concepts behind safety assessment and demonstrating how waste package models can be used to support safety assessment. Waste container and waste form performance are often central to the case for making a safety assessment. As illustrative examples of the role of waste container and waste package performance, three sample test cases are provided. An example of the impacts of distributed container failure times on cumulative release and peak concentration is provided to illustrate some of the complexities in safety assessment and how modeling can be used to support the conceptual approach in safety assessment and define data requirements. Two examples of the role of the waste form in controlling release are presented to illustrate the importance of waste form performance to safety assessment. These examples highlight the difficulties in changing the conceptual model from something that is conservative and defensible (such as instant release of all the activity) to more representative conceptual models that account for known physical and chemical processes (such as diffusion), The second waste form example accounts for the experimental observation that often a thin film with low diffusion properties forms on the waste form surface.

1. INTRODUCTION

Prior to subsurface burial of low- and intermediate-level radioactive wastes, a demonstration that disposal of the wastes can be accomplished while protecting the health and safety of the general population is required. The long-time frames over which public safety must be insured necessitates that this demonstration relies, in part, on computer simulations of events and processes that will occur in the future. This demonstration, known as a Safety Assessment, requires understanding the performance of the disposal facility, waste containers, waste forms, and contaminant transport to locations accessible to humans. The objective of the co-ordinated research programme is to examine the state-of-the-art in testing and evaluation short-lived low- and intermediate-level waste packages (container and waste form) in near surface repository conditions.

The link between testing and evaluation of waste package performance and safety assessment is modeling. The objective of this study is to demonstrate the link between data collection and model development needs to support a defensible safety assessment. This is accomplished by reviewing the fundamental concepts behind safety assessment and demonstrating how waste package models can be used to support safety assessment. Safety assessment for low- and intermediate-level wastes is a complicated process involving assumptions about the appropriate conceptual model to use and the data required to support these models. Typically due to the lack of long-term data and the uncertainties from lack of understanding and natural variability, the models used in safety assessment are simplistic. However, even though the models are simplistic, waste container and waste form performance are often central to the case for making a safety assessment.

As illustrative examples of the role of waste container and waste package performance, three sample test cases are provided. An example of the impacts of distributed container failure times on cumulative release and peak concentration is provided to illustrate some of the complexities in safety assessment and how modeling can be used to support the conceptual approach in safety assessment and define data requirements. Two examples of the role of the waste form in controlling release are presented to illustrate the importance of waste form performance to safety assessment. These examples highlight the difficulties in changing the conceptual model from something that is conservative and defensible (such as instant release of all the activity) to more representative conceptual models that account for known physical and chemical processes (such as diffusion), The second waste form example accounts for the experimental observation that often a thin film with low diffusion properties forms on the waste form surface. The implications of formation of such a layer on release are investigated and the implications of attempting to account for this phenomena in a safety assessment are addressed.

2. SAFETY ASSESSMENT

A number of important concepts distinguish safety assessment for radioactive waste disposal from typical engineering analyses. These concepts lead to a definition that emphasize safety assessment as a multi-disciplinary, iterative process focused on regulatory compliance rather than an analysis of a disposal system for the purpose of predicting actual outcomes. Safety assessment is defined as: *the iterative process involving site-specific, prospective evaluations of the post-closure phase of the system with three primary objectives: 1) to determine whether reasonable assurance of compliance with quantitative regulatory performance objectives can be demonstrated, 2) to identify data, design, and model development needs for reaching defensible decisions about regulatory compliance, and 3) to identify waste acceptance criteria related to quantities of wastes for disposal*. This paper deals primarily with the second aspect in the definition, namely, the identification of data design and model development needs for waste package components.

Critical to the definition and objectives are the phrases *prospective modeling* and *reasonable assurance*. These phrases infer that the results are not intended to be interpreted as "predictions" of actual behavior. The goal of safety assessment is to determine the conditions for which reasonable assurance of compliance with performance objectives can be provided; the goal is not to predict the actual outcome. Rather, the modeling is directed toward developing a sufficient understanding of the system behavior to support *decisions* about design and closure conditions. Because of the inherent uncertainties in the long-term processes and events, judgment will be a necessary part of the process of assessing the defensibility of the conceptual models It is important to understand that the uncertainty discussed with regard to safety assessment is really the uncertainty with respect to the decision (i.e., regulatory compliance), not the uncertainty associated with the numerical results of the assessment. The safety assessment results are largely a function of the data, design, and assumptions considered in the analysis. Changes to any one of these can result in changes in the conclusions resulting from the assessment. To develop reasonable assurance, it is necessary to obtain an improved understanding of those aspects of system performance that are important to the decision; it will not require a perfect representation of all processes. This need for professional judgment requires that careful attention must be paid to documenting, justifying, and defending the conceptual models, data selections, and results.

Safety assessments require an analysis of the health impacts resulting form disposal of radioactive wastes. This is a complex problem involving many scientific disciplines. To make the problem tractable, the safety assessments are usually conducted by dividing the analysis into components. The major components are: (1) infiltration and cover performance, (2) waste container performance, (3) waste form performance, (4) transport through the vadose zone, (5) groundwater transport, (6) biotic transport, (7) atmospheric transport, and (8) exposure and health effects to man. The results from one component are used to provide input to the other components until potential exposure to radioactivity is assessed and compared to dose or risk-based regulatory standards.

Waste container and waste form performance can be crucial components in conducting a defensible safety assessment. Due to the potential for the waste container and waste form to control release over long periods of time, modeling of waste package and waste form performance is required. Examples of the role of modeling to determine of container performance and waste form performance on release are provided in the next sections. The results of the model exercises are discussed in the context of how the modeling can help define data, design, and modeling needs to perform a defensible safety assessment.

3. EXAMPLE OF THE ROLE OF WASTE CONTAINER PERFORMANCE ON SAFETY ASSESSMENT

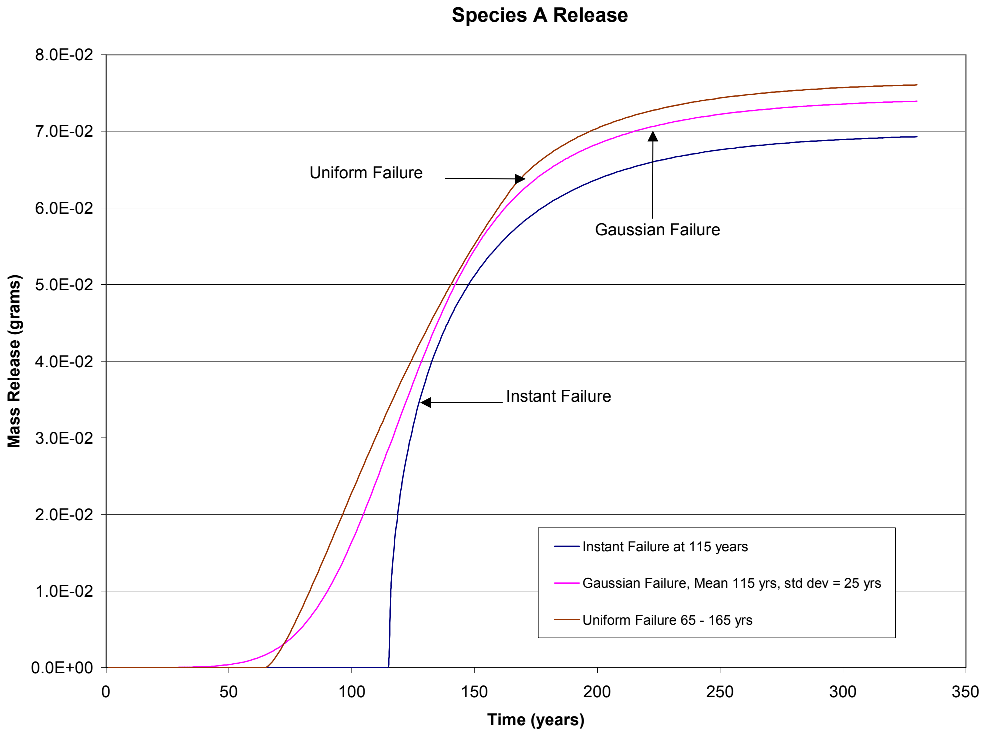
To demonstrate how modeling can be sued to defend decisions on data collection needs and conceptual approach to making a safety assessment an example of the effects of distributed container failure is presented. The example was calculated with the DUST-MS computer code (Sullivan, 2001) and considered diffusion controlled release from a cylindrical waste form. In this problem, the first species, Species A, has a 44.7 year half-life, while the second species, Species B, has a 7.7 10^4 year half-life. Three container failure modes are modeled, instant failure of all containers at 100 years after emplacement, Gaussian distribution failure rate with a mean life of 100 years and a standard deviation of 25 years, and uniform failure rate starting at 50 years and ending 150 years after emplacement. The disposal facility was started in 1950, however, this group of containers was not buried until 1965. Thus, the instant failure time is at 115 years from the problem start time, 1950. The waste form originally contains 1 gm of Species A and species B is absent. Species B is produced from the radioactive decay of Species A. The waste form has a radius of 25 cm and both species have a diffusion coefficient of 10^{-8} cm^2/s. These values cause release to occur over hundreds of years (much longer than the range in container failure times).

Figure 1 presents the total release of Species A and B as a function of time and container failure rate. For species A, the instant failure model begins release 115 years after the problem start time and has the lowest total release. This is due to the releases starting later and the effects of radioactive decay. The total release is less than 0.07 grams from an initial inventory of 1.0 grams. The release for the Gaussian failure model begins at the earliest of the three models due to the tails of this distribution. The uniform failure model releases the most of species A, approximately 0.075 grams. All of species A that decays prior to release is converted to Species B. The release of Species B is displayed in Figure 1. In this case, the instant failure model has the highest total release of Species B, releasing 0.54 grams. The cumulative release at the end of the problem simulation time is within 1% for all three container failure models. Thus, in terms of total mass release, the result is insensitive to container failure rate.

Figure 2 displays the concentration in the solution contacting the waste form as a function of time. As material is released from the waste form, the concentration increases. It decreases in time due to radioactive decay and advection moving the radionuclides away from the waste form. In both cases, Figure 2, the instantaneous failure model has the highest solution concentration. This is expected because in this model, all containers fail at a single time. For Species A, the peak concentration is $2\ 10^{-9}$ g/cm^3 when instantaneous failure occurs. For the Gaussian failure distribution and uniform failure rates, the peak concentration is less than $3\ 10^{-10}$ g/cm^3, almost an order of magnitude lower than the instantaneous case. For species B, similar results occur. For the instantaneous failure model, the peak concentration is $7.1\ 10^{-9}$ g/cm^3. For the Gaussian and uniform failure rates, the peak concentration is less than $1.3\ 10^{-9}$ g/cm^3. For the uniform failure rate, the peak in Species A concentration occurs approximately between 90 and 100 years. Radioactive decay causes the concentration to decrease after this time even though additional containers fail until 165 years. For species B and a uniform container failure rate, the concentration increases until 165 years when all containers have failed. After this time, the concentration decreases due to transport away from the waste form. For the Gaussian failure rates, the concentration follows a smoother distribution reflecting the container failure rate.

The difference in predicted concentration as a function of the failure model is a function of many parameters including radioactive decay, container failure rate, waste form release rate, and the parameters that define transport away from the waste form. However, as shown in this example, it may be substantial. Considering that most performance objectives for a waste disposal facility are concentration or dose (which is linearly proportional to concentration) based, the use of distributed failure models can have a significant impact when assessing performance.

At this point, the analyst can make technically defensible decisions about data needs and conceptual approach to modeling the release of radioactivity from the waste package. In the preceding example, it is clear that if the criteria for demonstrating safety is the cumulative amount released, there is little justification for using a distributed failure model and for collecting the data necessary to support such a model. However, if the criteria is the peak concentration, and an order of magnitude reduction is meaningful in terms of meeting regulatory limits, the analyst can make a case for using a distributed container failure model and collecting the data to support the failure distribution to be used in the safety assessment.



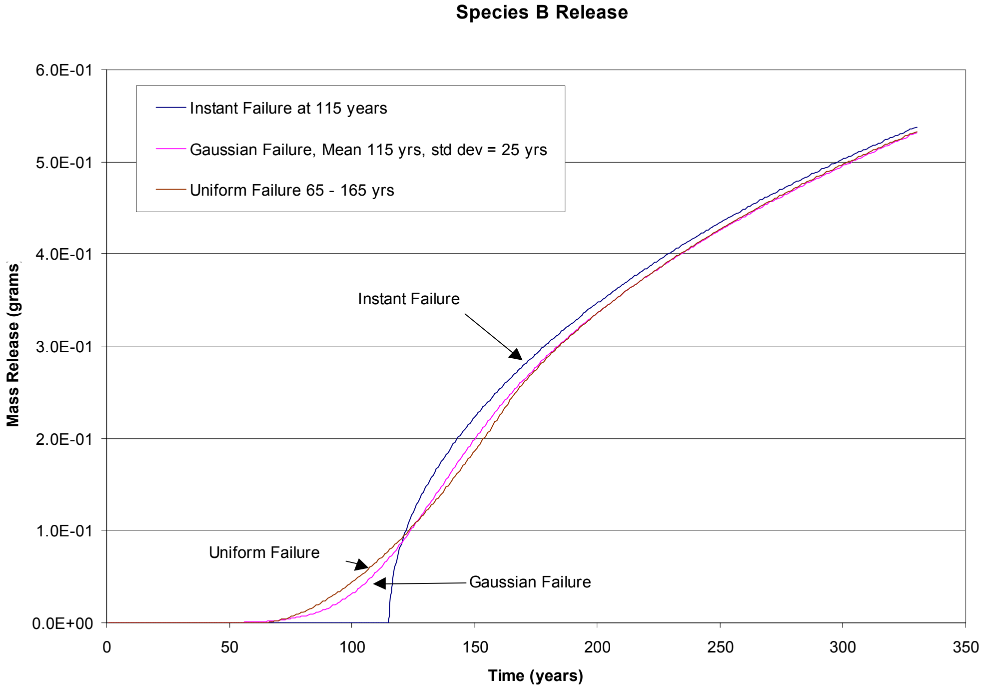
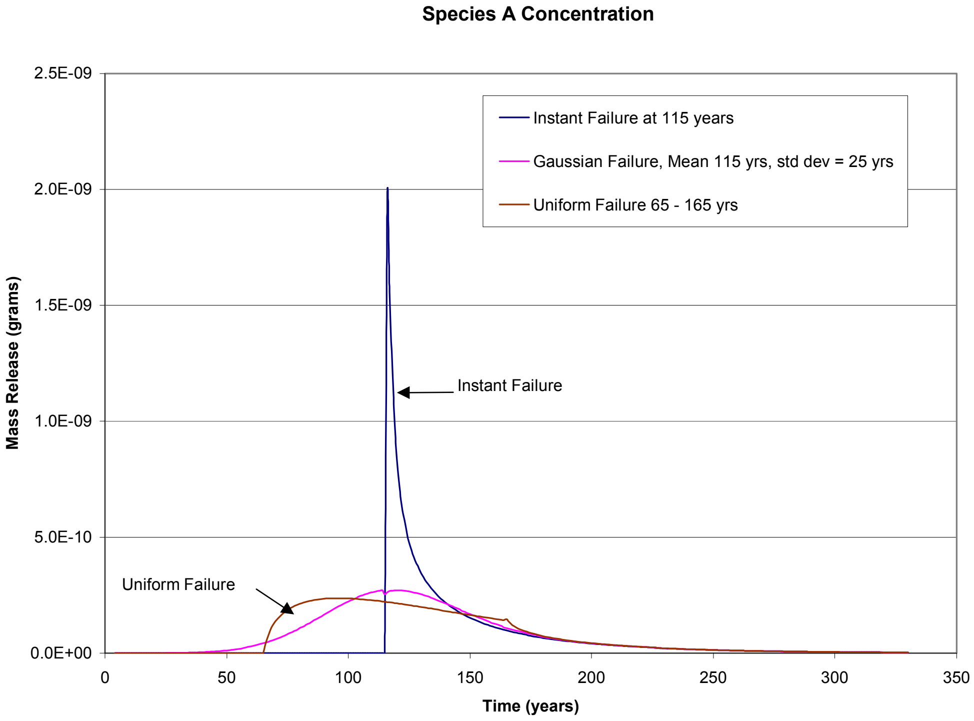


FIG. 1 Cumulative Release of Species A and B for three failure rates.



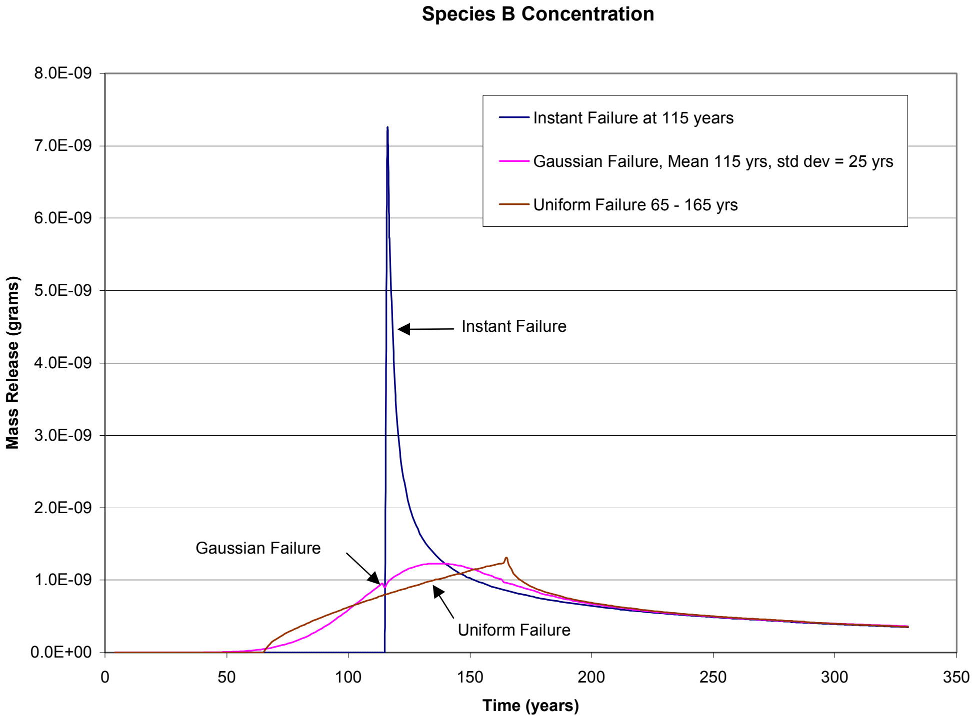


FIG. 2. Concentration of Species A and B over time for three different container failure rates.

4. EXAMPLE OF THE ROLE OF WASTE FORM PERFORMANCE ON SAFETY ASSESSMENT

It is clear that waste form performance can have a pronounced effect on release. In the most conservative calculations, the waste form is assumed to instantly release the entire inventory. This approach is often used whenever data are unavailable to support more detailed release calculations or in cases when this assumption does not change the demonstration that regulatory risk or dose based limits are not exceeded. Assuming instant release is the easiest to justify, (it can not be worse than that, although when ingrowth is an issue even this may not be true) and requires the least data (only the total inventory is required). However, in most cases, credit will have to be claimed for controlled release performance for the waste forms that contain the bulk of the activity.

For cement waste forms data often support use of a diffusion controlled release model. To examine the effects of waste form performance on release two examples will be provided. In the first, example the cumulative fractional release from a 200 liter drum is presented as a function of waste form diffusion coefficient, Figure 3. Three diffusion values were used, 10^{-10}, 10^{-12}, and 10^{-14} m^2/s. The 10^{-10} m^2/s value represent the maximum acceptable value for a waste form in the United States. Measured values for cement waste forms are generally between 10^{-12} and 10^{-16} m^2/s depending on the radionuclide as well as the cement composition.

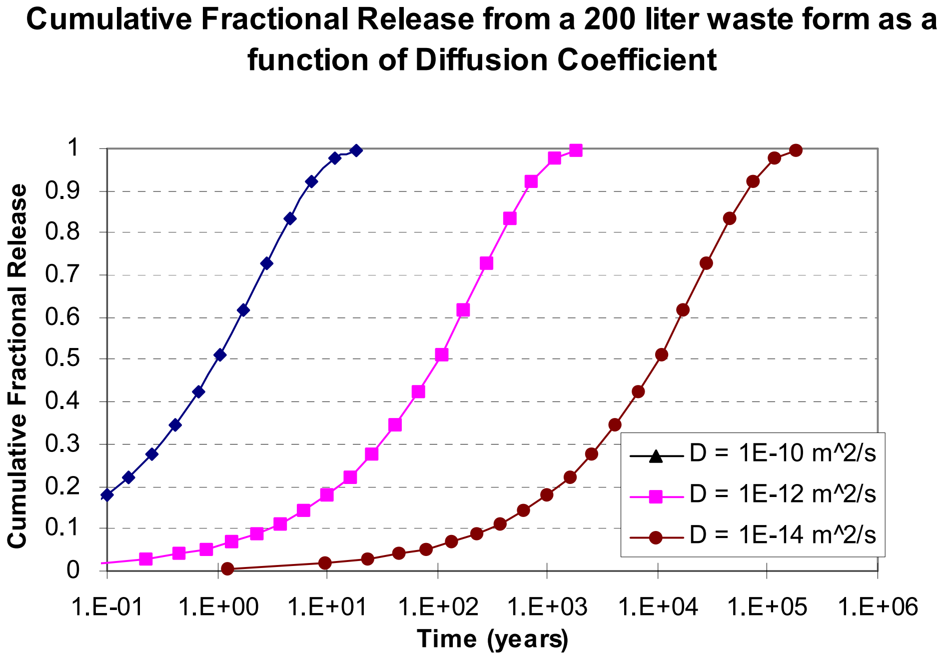


FIG. 3 Cumulative fractional release from a 200 liter waste form

From the semilog plot presented Figure 3 it is seen that the diffusion coefficient has a pronounced effect on release. Having a diffusion coefficient of 10^{-10} m^2/s releases approximately 50% of the mass in the first year. Thus, it may be only a factor of two better than the instant release model in terms of peak concentration. The release rate for the diffusion controlled model decreases monotonically with time. Therefore, the first year has the highest release rate. For a diffusion coefficient of 10^{-12} m^2/s the total released is just under 6%, and for a diffusion coefficient of 10^{-14} m^2/s, less than 0.6% is released in the first year.

Often leaching experiments for cement waste forms have led to formation of a thin carbonate layer at the edge of the waste form. Once this layer is formed, the release rates are often substantially reduced. In the next example, a comparison is made between the release rate for a 200 liter waste form with a diffusion coefficient of 10^{-12} m^2/s and a second waste form that has a thin, 0.001 m, surface layer that acts as a diffusion barrier. Two different values of the reduced value of the diffusion coefficient were used in the example, 10^{-14} m^2/s and 10^{-16} m^2/s while in both cases the bulk of the waste form has a 10^{-12} m^2/s diffusion coefficient.

Figure 4 presents the cumulative fractional release over 10 years for the three cases on a semilog plot. Formation of a thin film leads to a substantial reduction in the release rate. In this example, if the outer 1 mm of the waste form had a diffusion coefficient of 10^{-14} m^2/s, (2 orders of magnitude less than the bulk diffusion coefficient) the release rate was decreased by an order of magnitude. For a surface film diffusion coefficient of 10^{-16} m^2/s, the release is three orders of magnitude less than without the diffusion barrier.

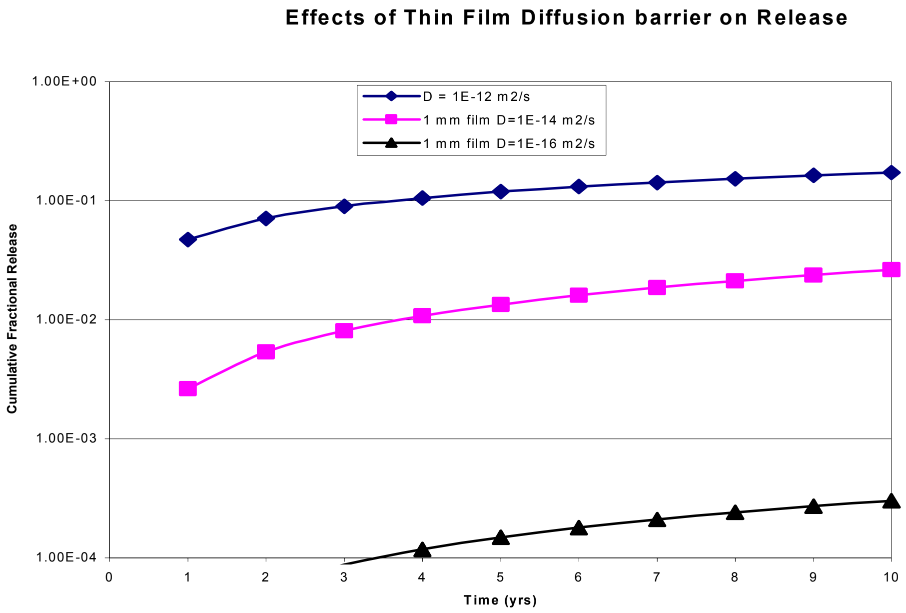


FIG. 4 Effects of 1 mm Diffusion Barrier on Cumulative Fractional Release

The analyst can use the type of information in these two examples to determine if it is necessary to collect data on diffusion coefficients from waste forms or on the formation of thin diffusion barrier on waste forms. As more information is required, the level of uncertainty increases and the amount of supporting information needed to defend the data increases. For example, at the most conservative level, assuming total release from the waste form, data on diffusion coefficients are not needed. If the analysis assumes diffusion is the rate controlling release mechanism, data must be collected on the waste form geometry and diffusion coefficients must be measured for the anticipated range of environmental and waste form compositions that may occur. This will lead to a collection of diffusion coefficient values and evidence will have to be supplied to support selecting values for the assessment. If the conceptual model selected for the safety assessment goes one step further and relies on the formation of a thin film on the surface of the waste form that acts as a diffusion barrier, the amount of data required to support this model increases again. In this case, questions pertaining to the time it takes to form the film (if it takes more than one year, it may be too slow to impact on peak dose), the geochemical conditions leading to film formation, and the thickness and stability of the film over time all need to be addressed. Thus the analyst must judge if the added time and expense to collect the data and the added risk in obtaining regulatory acceptance of the data and conceptual model justify the benefit the data will provide in terms of leading to lower predicted release rates and ultimately to lower dose or risk to man. If it can be shown that a simple conceptual model is defensible and helps to meet safety assessment dose limits, more complex models are not warranted .

5. CONCLUSIONS

Modeling performs the link between the theoretical underpinnings of waste form performance, data collection and interpretation, and use of this knowledge to perform a safety assessment. Safety assessment for low and intermediate level wastes is a complicated process involving assumptions about the appropriate conceptual model to use and the data required to support these models. Typically due to the lack of long-term data and the uncertainties from lack of understanding and natural variability, the models used in safety assessment are simplistic. However, even though the models are simplistic, waste container and waste form performance are often central to the case for making a safety assessment. This paper provided examples of the role of modeling in defining data and model development needs to perform a defensible safety assessment. An example of the impacts of distributed container failure times on cumulative release and peak concentration was provided to illustrate some of the complexities in safety assessment and how modeling could be used to support the conceptual approach in safety assessment and define data requirements. The key point of the example is that modeling work can be used prior to extensive data collection to define the conceptual approach to safety assessment and data needs. Two examples of the role of the waste form in controlling release were presented to illustrate the importance of waste form performance to safety assessment. These examples highlight the difficulties in changing the conceptual model from something that is conservative and defensible (such as instant release of all the activity) to more representative conceptual models that account for known physical and chemical processes (such as diffusion) Adding model complexity adds to data requirements and adds to the risk that the data will not be acceptable to regulatory agencies. These added costs must be balanced against the benefits obtained for the entire safety assessment. In general, modeling of waste package performance is a critical step in supporting a safety assessment and should be used to support the selection of conceptual models and define data requirements.

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