IAEA-TECDOC-1563

Spent Fuel and High Level Waste: Chemical Durability and Performance under Simulated Repository Conditions

Results of a Coordinated Research Project
1998–2004

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FOREWORD

Spent fuel is an inevitable residue of the production of electricity by nuclear power. The main strategies of spent fuel management include the spent fuel direct disposal route and the reprocessing route. Today a new strategy of partitioning and transmutation is being pursued for the management of long lived actinides and fission products, that can in the future be separated. However, even if this route is successful, it will never be possible to burn all of them in advanced fuel cycles. In the reprocessing route, almost 100% of the fissile material is separated from the rest of the fission products and other actinides generated by nuclear transformations. Taken all together these constitute the high level wastes, which are to be conditioned in a glass matrix in view of their final disposal in deep geological formations. The concept of direct disposal of unprocessed spent fuel consists of final disposal, once encapsulated in proper disposal canisters, in the same geological formations as the vitrified wastes.

It is important that the conditioned spent fuel and other conditioned high level wastes have a certain stability and maintain it for a required period of time, that is several thousand years. The changes in the physical and chemical characteristics that may happen in contact with water at elevated temperatures, together with the roles played by the rock media and the different components of the barriers system need to be assessed. This assessment must also take into account the timing and paths that radionuclides would require to reach the biosphere and the consequences to the living organisms in the environment (the performance assessment). The practical objective of the ongoing research is to be able, ultimately, to model the rate of the radioactive release from the waste forms, and subsequently from the engineered barriers.

In spite of numerous data available on the release of radionuclides from various waste forms, the studies to model all processes involved is a much larger task than this coordinated research project (CRP). The local characteristics of the disposal site are the specific constrains of any characterisation process. Eventually the availability of field data, together with such a modeling capability can help to pave the way for approved disposal sites.

With this CRP, the IAEA has tried to have an interchange of experience among leading research groups on the R&D of the waste forms behaviour and give access to very valuable information on its evolution to many other countries. The task was started with R. Burcl, of the Nuclear Fuel Cycle and Waste Technology Division as scientific secretary. His participation was followed by that of J.L. González. Four RCMs have taken place, and a consultant meeting was held to extract the main results of the CRP, and give their conclusions. The results of the CRP were presented to the international research community at the 29th International Symposium on the Scientific Basis for Nuclear Waste Management, MRS 2005, in Ghent.

The CD which accompanies this TECDOC contains the full contributions by participants to this work, as well as a complete report of work carried out as a related CRP in the period 1991–1998, entitled, Performance of High Level Waste Forms and Packages under Repository Conditions. For this earlier work, the chief scientific investigators were from Argentina, Belgium, Canada, China, Czech Republic, Finland, France, Germany, India, Japan, Russian Federation, and the United States of America. They met in four Research Coordination Meetings in Karsruhe (1991), Bombay (1993), Tokai (1995) and in Avignon (1997) to present the scientific reports from participating laboratories, discuss results and provide recommendations for future work.

The IAEA officer responsible for this publication was P.J.C. Dinner of the Nuclear Fuel Cycle and Waste Technology Division.

EDITORIAL NOTE

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SUMMARY

This CRP, which began in 1998 and was completed in 2004, continued the work of an earlier CRP on Performance of High Level Waste (HLW) Forms and Packages under Repository Conditions.

The chief scientific investigators for the more recent CRP were from Argentina, Australia, Belgium, China, Croatia, Czech Republic, France, India, Japan, the Republic of Korea, the Russian Federation, Spain and the United Kingdom.

Experimental work carried out under the CRP focussed on the formulation and analysis of samples of real and simulated HLW and irradiated fuel, especially radionuclide leaching behaviour under conditions representative of a repository environment. Modelling studies pertinent to the development of repository assessment methodologies also formed part of the work program. Four research coordination meetings and one consultant's meeting were held.

The importance of this work can be seen in its stated objective of developing the scientific and technical basis for geological disposal to support safety and performance assessments.

Types of HLW matrices investigated included spent fuel, glasses, and ceramics. During the period spanned by the two CRPs, glass technology came to be regarded as relatively mature, and further development focussed on ceramic forms, such as synthetic rock (SYNROC). The range of materials, waste forms and anticipated repository conditions being considered in the programs of the participants made the comparison of results between investigators challenging. The CRP meetings provided an excellent forum for the discussion amongst the experts of the details of their processes, analytical approaches and results. These discussions gave rise to suggestion that future work should address:

- Standardized, collaborative experimental protocols for package-release studies.
- Structured development and calibration of predictive models linking the performance of packaged waste and the repository environment.
- Studies of the behaviour of the waste, including active waste samples, which can be extrapolated over long time periods.

This TECDOC, while focussing on the achievements of the second CRP, also contains a CD of the full-text of the first CRP. In this way, the overall history of the involvement of the IAEA in the development of high level waste forms for future repository application is captured in a manner likely to prove most useful to those who contributed to it.

1. INTRODUCTION

1.1. WASTE FORMS AND DURABILITY

At the beginning of the nuclear era, only the nitric residues arising from the reprocessing of spent fuel were considered as high level waste (HLW). Today most of the fuel extracted every year from nuclear reactors is considered as waste, with a relatively small quantity of spent fuel being reprocessed. When managed as a waste, spent fuel will need to be conditioned into an acceptable waste form for deep geological disposal.

In the 1970s, the significant HLW forms were calcines, amorphous products resulting of the dehydration and denitration of the waste solution, different kinds of glasses, (phosphate and borosilicate). Some ceramics were also investigated [1]. Included among those categories were synthetic ion-exchange materials of the formula A[M2OxH]y, where A could be a metal, and M could be Ti, Zr, Nb or Ta, characterised by a high affinity for polyvalent cations.

By the 1980s, well-defined waste forms other than glass matrices were introduced [2]. Glass ceramics were developed in an attempt to improve thermodynamic stability by inducing crystallization of desired phases. Results did not show any improvement in chemical durability and, consequently, little development was done. Within the ceramic forms, work on synthetic rock (SYNROC) was advancing. Of special interest were those from titanate, which in the first versions considered hollandite ($BaAL_2Ti_6O_{16}$), perovskite ($CaTiO_3$), and zirconolite ($CaZrTi_2O_7$). Monolithic SYNROC can also be fabricated by a number of techniques, such as hot uniaxial pressing, hot isostatic pressing, or cold pressing followed by sintering.

As of today, besides research and development on spent fuel, most of the research is done only on glass matrices and ceramic waste forms. Nevertheless, the only industrial process for high level waste immobilisation is vitrification with glass.

To check durability of the waste forms, several leaching methods have been defined but none of them can be considered as standard. The Soxhlet method was used to check on durability during the development of new waste form composition, to evaluate changes due to radiation damage or following devitrification of glasses. Tests may be either done under static or dynamic conditions, but irrespective of the test method, analytical work is required following leach tests. Multielement analysis of leachates is routinely performed using X ray diffraction, electron microscopy, etc.

Variables affecting the leaching rate during testing have to be agreed on as the most relevant to the expected hydrogeological conditions of the disposal site. Among the main variables to be considered are: the flow rate, the time of leaching, the temperature and the leachant composition.

Among the results to be measured, the most important is the solubility. Under low-flow or static leaching conditions, the concentration of dissolved species increases with time, until the solution concentration reaches its solubility limits. Surface alteration is the second result to be considered. Other effects on the waste forms, which have to be investigated over many years, are the effects of radiation (due to β and γ self irradiation or irradiation from nearby rods) on the matrix, with alteration of the active surface in relation to the volume of the waste form, and the effects of radiolysis due mainly to long term alpha radiation, which affects the chemical composition of the water immediately next to the waste.

The capacity to model all the effects involved in the dissolution of the waste form, in conditions similar to the disposal site, is the final goal of all the research undertaken by many research groups over many years. As we will see in this report, this kind of investigation is far from being finished.

1.2. OBJECTIVE

The overall objective of the CRP, and of this publication, is to contribute to the development and implementation of proper and sound technologies for the evaluation of high level wastes and spent fuel long term behaviour in deep disposal sites. The sharing of information and comparison of the results from many countries involving differing waste forms under simulated conditions should help to better understand the various processes involved. The data related to those processes analysed together by research groups both from those countries with advanced developments on the subject, and by small groups from countries with limited financial resources for large research investments, give consistent conclusions on the research that is missing. At a final stage (beyond the objective of this CRP), operators of final disposal sites in various countries will have to determine waste acceptance criteria for future deep disposal sites that can only be achieved if the waste forms, the host rock, and the engineered barrier system interactions are well characterised.

1.3. SCOPE OF THE CRP

The project has covered studies on dissolution of glasses and ceramic matrices and spent fuel. It has also made the link between the experimental models and performance assessment models. Fourteen research groups have participated. They were from Argentina, Australia, Belgium, China, Croatia, Czech Republic, France, India, Japan, Republic of Korea, Russian Federation (two different groups), Spain and United Kingdom: a wide range of countries with and without nuclear power plants, or reprocessing activities.

The orientation of the activities as it was indicated in the terms of reference of the CRP were foreseen to be:

- Methods of estimation of potential impact of predisposal activities on the state of the package and its behaviour during final disposal.
- Identification of potential storage/repository conditions.
- Evaluation and comparison of various methods for experimental work on waste packages in simulated repository conditions.
- Evaluation and comparison of various key factors affecting the performance and chemical durability of various waste forms in simulated repository conditions.
- Extrapolation of experimental models into performance assessment models.
- Identification of the most significant parameters which should be taken into account in waste package specification.

Achievement of the last two items presented too large a step for the research groups to properly address in the frame of the CRP. In particular, no conclusions can be made based on the research done with respect to the package specifications. However, the necesssary steps to permit this in future work were identified. The rest of the items listed were achieved.

1.4. STRUCTURE OF THE REPORT

The objectives and scope of the CRP are provided in the introduction. The role of the CRP in developing the safety case for deep geological disposal is outlined in Section 2. This is followed by summaries of the work performed by the CRP participants. A summary of the results achieved overall is contained in Section 4. Sections 5 and 6 contain the conclusions and recommendations respectively. Detailed contributions by the participants are included on a CD-ROM distributed with thispublication. Also on the CD-ROM are the main results and the complete contributions by the participants achieved in an earlier CRP (1991–1998), not yet published, but which addressed a similar topic.

2. THE CRP AND THE SAFETY OF THE DEEP GEOLOGICAL DISPOSAL

In the 2002 International Conference on Issues and Trends in Radioactive Waste Management [3] it was recognized that deep geological disposal programmes were at very different stages of their development amongst the participating countries, with planned dates for receiving wastes spanning 2010 to 2050. Nevertheless, there were clearly discernible commonalities and trends, which enabled the international community to focus its efforts in this long term management effort.

Disposal of spent nuclear fuel or of high level wastes in geological formations is presently considered their unique, realistic final destination. In the future, some new advanced fuel cycles and advanced fuel treatments such as partitioning for further transmutation might change the view of the quantities to be disposed of, but it is unlikely that deep disposal will not be needed.

The safety of the deep disposal site is to be assessed on the basis of a safety case developed from the scientific and technical basis for geological disposal [4]. The core of the safety case consists of safety and performance assessments. In a safety assessment, the estimated consequences of any releases from the repository are compared with the appropriate safety criteria, whereas in a performance assessment (PA), the evolution and performance of the isolation barriers is estimated. The performance assessment is a formal method of quantifying the behaviour of each component of the disposal system as it evolves with time and of translating this behaviour into estimates of its impact on the overall performance of the containment system. Safety assessment and PA share most data requirements and attempt to assess the quantitative impacts of the following factors characterizing the disposal system:

- The properties of the radioactive waste to be disposed of and their possible variabilities;
- The materials and structures planned to be used in the principal design alternative;
- The properties of the geological environment surrounding the repository and the knowledge of the processes taking place in the rock, as well as of their variability;
- The behaviour of the radionuclides in both geosphere and biosphere and their radiological impact on human health;
- The processes by which materials interact.

This knowledge is needed to evaluate the proposed disposal system and confirm that it can achieve the required performance. One of the purposes of the assessment tools is to estimate the consequences of one or more of the containment barriers not performing as designed and, consequently, of radionuclides being released from the repository in unexpected amounts.

The properties of the radioactive wastes will be modified by the effects of the ground water and thus its composition and flow are to be simulated at the laboratory level. That is why the two main variables used in the leaching tests for this CRP are:

- The rate at which water can enter the near-field and reach the wastes.
- The chemistry of the water reaching the wastes.

For many geological environments being considered for disposal, groundwater flow (advection) will be the most significant factor affecting near-field performance. In some extremely low permeability formations diffusion is the dominant mechanism affecting solute transport.

Deep groundwater is often characterized by high solute concentrations. It is to be expected that water in many potential disposal environments might be quite saline or even a dense brine. Water chemistry will be affected by contact with the engineered barrier system of the repository which may differ significantly from the host rock. For example:

- Concrete leachate with high pH value can initiate reactions, which may result in both positive (iron passivation) and negative (zinc dissolution) impacts.

- Introduction of heat generating wastes into the system results in increased saturation levels and, consequently, in a change of equilibrium values.

3. SUMMARIES OF THE CRP PARTICIPANTS' RESEARCH PROJECTS

The waste forms studied in this CRP cover glass and ceramic matrices, and spent fuel. Studies covered waste form composition and properties, thermal and radiation studies, effects of leaching composition and environmental conditions on leaching properties, with further work on scaling-up of experiments and the modelling of waste-form performance. The studies undertaken by the participants in the CRP to characterize the behaviour of the waste under repository conditions are given in this Section. Table I gives an overview for participating countries, of their potential repository environments and the high level waste forms under investigation.

TABLE I. OVERVIEW ON DIFFERENT HLW FORMS STUDIED BY PARTICIPANTS OF THE CRP

		Glass			*Ceramic*			*Spent fuel*	
Country	**Potential Repository Environment**	**Inactive**	**Doped**	**HLW Form**	**Inactive**	**Doped**	**HLW Form**	**U**	**Spent Fuel**
Argentina	-	BG, Ph	BG						
Australia	-					B			
Belgium	Clay	BG	BG	BG				U	
China	-				R, P, Py				
Croatia	-	Ph							
Czech Rep.	-				B, P, Z				
France	Clay, Granite	B	B	B	Z, GC	Z, GC			
India	Granite	BG		BG					
Japan	Granite	BG	BG						
R. Korea	Granite								SF
Russian. F.	Porphyrite	BG, Ph	BG, Ph					U	SF
Spain	Clay/Granite							U	
UK	-				O	O			

B: Brannerite; BG: Borosilicate glass; GC: Glass ceramic; O: Overview; Ph: Phosphate glass; P: Perovskite
Py: Pyrochlore; R: Rutile; SF: Spent fuel; U: UO_2; Z: Zirconium

3.1. ARGENTINA (D. RUSSO, CNEA, BARILOCHE)

Argentina has researched two different aspects of waste forms: the effects of alpha radiation on sintered glass and the iron based glasses for immobilisation of nuclear wastes containing high concentration of Uranium.

By studying the effects of alpha radiation, an analogy to the influence of self radiation of the glass in disposal conditions can be obtained. Two approaches to the irradiation were undertaken and analysed:

(a) doping the glass forms with an alpha source, and

(b) promoting alpha radiation through neutron bombardment on glass samples, using the nuclear reaction 10B(n,α)7Li where 10B is one of the natural glass component.

The interest in glass as a form of immobilisation with high concentration of Uranium is driven by the need to accommodate spent nuclear fuel from research reactors. In general, it is necessary to provide isotopic dilution of the uranium to an average of about 4% ^{235}U.

In the research undertaken, the thermal transformations that occur in iron phosphate glass forms were studied and analysed. This includes several compositions of Fe_2O_3, of P_2O_5 and of UO_2, including Al_2O_3 and Na_2O, added as glass modifier. In addition the Argentinean research has also begun tests of glass sintering with the addition of U_3O_8, with promising results. Glass transition, crystallisation and melting temperatures were identified. Studies on chemical durability conclude that Aluminum containing borosilicate are more durable than Sodium containing glass.

3.2. AUSTRALIA (Y. ZHANG, AUTRALIAN NUCLEAR SCIENCE & TECHNOLOGY ORGANISATION, MENAI)

The work being carried out at ANSTO covers the dissolution of synthetic brannerite in acidic and alkaline fluids, the effects of solution pH and U valence state on the dissolution of U-substituted thorutite, and kinetic modelling of the oxidative dissolution of brannerite. Brannerite (UTi_2O_6, monoclinic crystal system with space group C2/m, and both U and Ti occupying distorted octahedral coordination polyhedra), which exists naturally in many uranium ore bodies, has attracted recent attention as a minor phase in the pyrochlore-rich ceramic formulations designed to immobilise surplus plutonium.

The dissolution of synthetic brannerite in aqueous media under atmospheric redox conditions has been studied. Bicarbonate increases uranium release and enhances the dissolution of brannerite. Compared to UO_2, brannerite is more resistant to dissolution in bicarbonate solutions.

The dissolution of the thorium analogue of brannerite and U(IV)/U(V) doped Th-brannerite in aqueous media under atmospheric condition has been studied to elucidate the effects of pH and uranium valence state on the dissolution rate. The normalised U dissolution rates suggest brannerite is less durable with U(V) doping. Transmission electron microscopy examination of specimens after leaching, revealed few surface alteration products, which is consistent with the nearly stoichiometric dissolution of thorium brannerite. A conceptual model for uranium release from brannerite was developed. It consists of two reaction steps: oxidation of surface uranium(IV) atoms, and subsequent detachment of U(VI) atoms into solution, which is catalysed by surface coordination with protons (acidic media) or carbonate species (alkaline media in equilibrium with the atmosphere). A kinetic rate-law is derived for this simple reaction mechanism and fitted to experimental data. The resulting predictive equation for uranium releases gives an upper limit from brannerite over a range of conditions and experiment types.

3.3. BELGIUM (P. VAN ISEGHEM, SCK/CEN, MOL)

The Belgian programme is considering both the closed and open fuel cycle options. In the closed cycle, HLW glasses from the former Eurochemic reprocessing plant and from the French R7T7 plants are studied. R&D is focused on the interaction with the Boom Clay disposal host and potential near-field environments. Experimental studies on inactive and doped glasses, analytical and geochemical modelling studies and *in situ* "CORALUS" test are reported. In laboratory testing we developed new configurations to investigate various coupled processes:

(a) combined glass leaching/Si diffusion in clay,

(b) diffusion/sorption/precipitation of Si in clay,

(c) effect of the presaturation of clay with Si, and

(d) the mobile concentrations of e.g. Np, Tc, Se in clay slurries after leaching from glass.

The results are discussed in the final report. In the CORALUS *in situ* test, we installed all tubes in the underground laboratory (SCK•CEN site), and retrieved two of them after an interaction time of ~1 year.

The R&D on the geological disposal of spent fuel in Boom Clay is focused on two major issues: (1) studying the effect of α-activity and of Boom Clay on the dissolution of α-doped UO_2 (simulating spent fuel ages between 150 and 90000 years), and (2) studying the influence of potential backfill materials (apatite, cement, sand) on the α-doped UO_2 dissolution rate. Different experimental set-ups have been elaborated. Flow-through tests in clay water and static tests in clay slurries were carried out in reducing conditions. The UO_2 matrix is dissolving with a long term dissolution rate of ~30 $\mu g.m^{-2}.d^{-1}$ in a Boom Clay slurry. No relationship is observed between the α-activity of the UO_2 and the dissolution rate.

3.4. CHINA (S. LUO, CHINA INSTITUTE OF ATOMIC ENERGY, BEIJING)

The China Institute of Atomic Energy has conducted research into several aspects relevant to this CRP: durability of glass, different kinds of Synroc for immobilisation of Actinides (Perovskite, Zirconolite and Pyrochlore) and immobilisation of Technetium with Synroc. Immobilisation of Actinides (by using Uranium tailings) was investigated but the results obtained on the waste forms (loading up to 15%wt of waste) gave only "fair" results.

Regarding Synrocs, Neodymium and Uranium were used as analogues for trivalent and tetravalent actinides respectively. Physical properties, durability tests and radiation tests were undertaken. Radiation tests were done through heavy ion bombardment that provides a fast and simple method for the simulation of alpha recoil damage. The defects produced by irradiation were studied by using the positron annihilation technique.

3.5. CROATIA (A. MOJUS-MILANKOVIC, RUDER BOSKOVIC INSTITUTE, ZAGREB)

Iron phosphate glasses (IPG) are being investigated at the Ruder Boskovic Institute as an alternative to borosilicate glasses. The structures of IPG with varying content of Fe have been studied. IPG demonstrates very good chemical durability, attributed to the Fe-O-P bonds, which are more hydration resistant than P-O-P bonds usually present in other phosphate glasses. This glass can melt at temperatures where Cs is not volatile.

The research has dealt with some liquids from Hanford. Dissolution rate of IPG containing nuclear waste from tank B-110, is comparable to that for borosilicate glasses. Waste in this tank has a high chrome content. Chemical durability was determined from the dissolution rate, and product consistency. Vapor hydration tests gave an idea of the solubility limit for these high chrome waste forms. The X ray diffraction analysis did not determine any crystalline Cr2O3 phase. The Raman spectra give evidence of the structural evolution of glasses as a function of their waste content fraction.

The last part of the research was devoted to investigating the suitability of IPG for vitrifying sodium bearing waste with the aim to producing a waste form with high waste loading and acceptable durability. The Cold Crucible Induction Melting (CCIM) technique has also been explored, since it eliminates many materials and operating constrains (chemical corrosion of the melters and of the metal electrodes). The high waste loading, low melting temperature of IPG, rapid furnace throughput and potential for melting in cold cucible melters, offer a means to significantly reduce costs for vitrifying sodium bearing wastes.

3.6. CZECH REPUBLIC (V. BALEK, NUCLEAR RESEARCH INSTITUTE, REZ)

The Rez Institute has studied the effects of microstructure changes on the mobility of radionuclides in simulated high level waste ceramics. Under this, ceramic matrices were characterized from the viewpoint of the micro structure and transport property changes caused by leaching. The effect of leaching on the thermal stability of the ceramics was characterised. The behaviour of the matrices in simulated repository conditions was predicted by using the results of mathematical modelling. Using Radon as an example for mobility, it was deduced through calculation, that micro-structural changes strongly influence Radon mobility. Also, through diffusion structural analysis, Radon atoms were used as a micro-structure probe and a tracer to model the mobility of species similar in size to Radon atoms, i.e. water molecules.

3.7. FRANCE

French research has been conducted towards giving solutions to the ”third axis” of the 1991 French law on waste management, which requires investigation of waste conditioning and long term storage. Developments made in the area of waste treatment and conditioning were targeted at ensuring the availability of qualified processes that could be applied to historic waste to be recovered, or to improve a number of existing processes. The work done in recent years has provided a solid scientific basis for long term waste behaviour, with detailed modelling and experimental validation of the principal phenomena at work, considering all different types of packages. Important results are now available concerning both the possibility of significantly reducing the quantity and radiotoxicity of long lived waste, and for the modes of waste conditioning applicable to long term interim storage facilities.

3.8. INDIA (P.K. WATTAL, BHABHA ATOMIC RESEARCH INSTITUTE, MUMBAI)

India has studied glass-forming systems based on lead and barium silicate glasses for the immobilisation and retention of sulphate bearing wastes. After melting, while lead borosilicate at 25 %wt PbO did not result in a homogeneous liquid, as phase separation was observed, barium borosilicate at 19%wt BaO was homogeneous with a lower leaching rate. Barium was found to be more effective in retaining the sulphate within the glass matrix.

Homogeneity and micro-structural characterisation was done using scanning electron microscopy (SEM) and back-scattered electron microscopy (BSEM).

India has also made some tests at plant scale with lead borosilicate, having vitrified nearly 5000 litres of very high level wastes. Based on the difficulties encountered using lead borosilicate, it was concluded that a barium borosilicate glass system would be able to accommodate sulphate wastes without impairing the other properties of the product.

3.9. JAPAN (M. YUI, JAPAN NUCLEAR CYCLE DEVELOPMENT INSTITUTE, TOKAI-MURA)

The Japan Nuclear Cycle Development Institute has developed an in-house thermodynamic database of radioactive elements and has performed glass durability studies for the disposal of high level wastes under Japanese conditions. The applicability of that database has been checked to perform a realistic analysis of the solubility of radioisotopes. It was concluded that most aspects of the present database are applicable.

The main research issues concerning data-base applicability are:

- Improved stability of solid phases, in particular the solubility of amorphous phases in crystalline phases.

- Redox state of Pu. As the redox state of Pu (trivalent or tetravalent) can affect its migration parameters, it is important to have available, solubility measurements based on confirmation of Redox state. The results demonstrate that the database has to be revised.

- Applicability in cementitous conditions. The applicability of the database to a highly alkaline environment needed to be checked because the use of cement material is expected for tunnel mechanical support. Improvements are also needed to the data-base in this area.

Other studies pursued by the Japan Nuclear Cycle Research Institute include co-precipitation, glass alteration under high pH conditions and natural analogue studies. Important conclusions related to glass dissolution, e.g. the rate controlled by diffusion. Cs uptake in secondary phases is derived from the work done. Natural analogue studies involved observation of volcanic glasses from the Kanto region.

3.10. REPUBLIC OF KOREA (K.S. CHUN, KOREA ATOMIC ENERGY RESEARCH INSTITUTE, TAEJON)

The R&D for the disposal of spent fuel accumulated over the lifetime of NPPs in the Republic of Korea has been underway since early 1997, (i.e. since before this CRP began) in order to develop a reference repository system by 2006. KAERI joined the CRP under this global R&D programme, and especially in the context of its long term dissolution experiment that has been carried out since 1998. The purpose of the experiment is to get the information on corrosion behaviour of spent fuel, and to obtain the release rate of radionuclides from the fuel within domestic bentonite and synthetic granitic ground water. Specimens of fuel with burn-up up to 39 GWd/tU, with and without bentonite, have been subjected to leaching. The effects of bentonite on the dissolution rate, and of structural materials, copper and stainless steel on caesium release have been identified.

3.11. RUSSIAN FEDERATION

3.11.1. A.A. Bochvar All-Russian Scientific Research Institute of Inorganic Materials (P. Poluektov, Moscow)

The A.A. Bochvar All-Russian Scientific Research Institute of Inorganic Materials has investigated the structure of some physical and chemical properties of specimens able to be vitrified in cold crucible melters. They represent two mineral groups, pyroxenes and garnets. Pyroxene minerals are capable of isomorphous incorporation of Alkali, Alkaline-earths elements as well as Al^{+3} and Fe^{+3}. Pyroxene use is suggested for incorporation in HLW as well as fractions of calcium and strontium. In the work performed, a matrix composition that corresponds to natural occurring mineral was studied.

It is necessary to obtain sufficiently complete information on the main physical-chemical and thermal properties of the synthesised compositions. Investigations into these properties are aimed at determining and identifying the changes of their structures and properties. Properties of borophosphate glass were determined by X ray diffraction and scanning electron microscopy, on samples subject to heat treatment at the critical temperature for crystalization.

Experience with a one-stage solidification process using a direct-heating electric furnace to produce phosphate glass on an industrial-scale was shared with the participants. Also, the development of a new technology for immobilising liquid radioactive wastes into vitreous and mineral-like compositions employing a two-stage process described as a “cold crucible induction melter” was presented as a promising direction in the field of radioactive waste management. This is a compact process which avoids direct contact between melter-material and molten oxide and permits synthesis of compounds with a wide range of compositions involving different melting temperatures.

3.11.2. V.G. Khoplin Radium Institute (A. Aloy, St.Petersburg)

The V.G. Khoplin Radium Institute has undertaken the study of UO2 from RBMK-1000 fuel under storage conditions. It also has studied the barrier properties of the mountain rocks (such as the Nizhnekankiy Massif), which are potentially suitable for deep disposal.

The spent fuel was tested at several temperatures under humid conditions. It was observed that with high temperatures, UO_2 is transformed into hexagonal U_3O_8. Oxidation of U_3O_8 in Nitrogen/Oxygen (below 0,5% O_2) atmosphere has also been tested.

Another investigation related to fuel is the comparison of the solubility of UO_2 powder, UO_2 pellets and spent fuel particles. The best results were achieved with the latter.

Regarding the barrier properties of the mountain rocks, the research was aimed to investigate the sorption ability of typical rock samples of the Nizhnekankiy granitic Massif in reference to some actinide elements. Using simulated ground waters, the tests were performed under static conditions with bits of fractured rocks. Distribution coefficients for Americium, Plutonium and Neptunium were determined for different grains of rock. Obtaining of high distribution coefficients and retention factors provide a good basis for continuation of the study of the protective properties of the massif for future repository design.

3.12. SPAIN (A. MARTÍNEZ-ESPARZA, ENRESA, MADRID)

Work by ENRESA shows the utility of data provided from experiments with spent fuel analogues to test the mechanisms and the influence of relevant parameters in spent fuel alteration under repository conditions.

The occurrence of natural uraninites with several alteration degrees as a function of their location has supplied complementary information about the behaviour in natural systems of uranium dioxides, and some radionuclides included in it. In addition, dissolution experiments by using these minerals as solid samples have also given some new evidences on the processes taking place in such systems.

For the evolution of irradiated fuel under interim storage conditions and in deep geologic storage, the oxygen to metal ratio before the water access to the fuel is a factor with great influence on the enhancement of spent fuel leaching. This effect has been also studied by means of spent fuel analogues and by using artificially aged fuel. Studies on spent fuel research have been made in collaboration with other research institutes, including the Institute of TransUranide, of Karlsruhe.

A conceptual and mathematical model was developed with the aim of studying the stability of spent fuel under repository conditions. Both the alteration of the fuel matrix as well as the radionuclide release were considered. ENRESA has compared the different approaches used in performance assessment exercises to describe spent fuel alteration under repository conditions.

3.13. UNITED KINGDOM (S. KING, NIREX, DIDCOT)

Nirex has developed programmes of work on preliminary and generic performance assessment for geological environments found in the UK. Investigations of conditions for co-disposal of ILW/LLW and HLW/SF taking into account potential specific chemical thermo-mechanical interactions of high level waste matrices with the repository environment was also part of the work. This also included literature research to build confidence in chemical data and other parameters used in performance assessment, development of a source term model for HLW/SF, and investigation of the effect of chemical and other parameters on performance. The work performed in the last part of the CRP was dedicated to giving results for the national consultation on Managing Radioactive Waste Safely. A literature review of the range of immobilisation matrices for waste management options was undertaken, as well as preliminary calculations to investigate the key issues for disposal of radioactive materials not currently declared as waste.

4. SUMMARY OF THE RESULTS ACHIEVED

4.1. GLASS

4.1.1. Compositions

Nuclear waste glasses have complex compositions since they contain various elements such as fission products, transuranics, corrosion products and other salts from the high level waste. In addition, glass additives have to be incorporated to meet the specifications required in the final vitreous waste form. In general, among the glass compositions reported, borosilicate glasses are widely used. Phosphate based glasses that could be complementary to borosilicate glasses are also used.

Some of the developments and characterization results of the glasses reported in the CRP are as under:

Borosilicate glasses

In certain historic high level waste containing molybdenum and phosphorus (legacy solutions derived from early reprocessing programmes), limited loading capacity of molybdenum and phosphorus in conventional borosilicate glass is well recognized (max. up to 4 wt %). Borosilicate formulations were modified to immobilize up to 12 wt % of MoO_3 from these wastes and also higher contents of actinides and rare earth elements from wastes generated from high burn up fuels. Barium borosilicate formulations were developed to incorporate sulphate in the glass up to 2.5 wt %. Borosilicate glass formulations have also been developed for the immobilization of ~13 wt % of UO_2 or 6 wt % of PuO_2.

Some countries have developed the cold crucible technique. This enables higher waste loading, immobilisation of reprocessed high burn up fuels, and eliminates corrosion of the melter wall. It is recommended that technology information exchange continue, and the technology be demonstrated at a large scale.

Phosphate glasses

Phosphate based glasses are being proposed for the wastes rich in constituents such as Cr, Sr, Mo, SO_4, Cl, U and actinides. Iron phosphate glasses (IPG) were reported as promising matrices for the immobilization of chromium and high uranium wastes. The solubility limit of Cr_2O_3 in these iron phosphate melts was reported to be about 2.6 mass %, compared to < 1 mass % in common borosilicate glasses. Thus IPG could accommodate high Cr_2O_3 contents and the base glass composition is also flexible. Their chemical durability is excellent. UO_2 could be accommodated up to 10 wt % in iron phosphate glasses, however part of it was present in the form of segregates in the glass matrix. Borophosphate glasses are also developed for the conditioning of high level reprocessing waste.

It is recommended to study the long term thermal stability of phosphate glasses in more detail.

4.1.2. Characterization of the glasses

In general, the valence states of U and Pu in borosilicate glasses are U (IV) or U (VI) and Pu(IV). The maximum fraction of devitrification in the R7T7 reference borosilicate glass (developed by France) is about 4.2 vol. %. No important radionuclides with long term safety concerns were found in the devitrified crystalline phases.

Typical compositions of borosilicate and phosphate based glasses studied are summarised in Table II.

TABLE II. TYPICAL COMPOSITION OF BOROSILICATE AND PHOSPHATE BASED GLASSES STUDIED AND REPORTED.

Country	**Waste Type**	**Glass Type**	**Major Constituents**	**Melter Type**
FRANCE	(i) Normal reprocessing waste	Borosilicate (R7/T7) (waste oxide: 13%)	SiO_2, B_2O_3, Al_2O_3, Na_2O, CaO, MgO, Fe_2O_3, Li_2O, ZnO, P_2O_5, FP, CP, ZrO_2, NM &Actinides	Metallic Melter-(Industrial scale)
	ii) Mo-rich waste: (MoO_3 90 g/L, $P_2O_5$15g/L)	UMo-MoSnAl (MoO_3: 10-12%)	SiO_2, Na_2O, Al_2O_3, P_2O_5, B_2O_3, CaO, ZnO, ZrO_2, MoO_3	Cold Crucible Melter (Laboratory scale)
	ii) HLW from high burn-up fuels (60 000 MWd/t)	Lanthanide-alumino-borosilicate (Rare Earths: 16%)	SiO_2, B_2O, Na_2O Al_2O_3 CaO, ZrO_2, RE_2O_3	Cold Crucible Melter (Laboratory scale)
BELGIUM	High alumina waste	High-alumina borosilicate (Al_2O_3: 19.8%)	SiO_2, B_2O, Na_2O, CaO, Li_2O, Al_2O_3	Ceramic Melter (Industrial scale)
INDIA	High sulphate waste	Barium borosilicate (SO_4: 3%)	SiO_2, B_2O_3, BaO, UO_2, Na_2O, Fe_2O_3, Cs_2O, SrO, RuO, SO_4	Metallic Melter (Industrial scale)
CROATIA	High chrome Hanford waste	Iron Phosphate Glass (~4.5 mass %)	Fe-P Cs_2O, Na_2O, Al_2O_3, PbO, Bi_2O_3, MoO_3, SrO, CrO_3	Laboratory Scale
ARGENTINA	High uranium waste	Iron Phosphate Glass (UO_2: 7-10%)	Fe_2O_3, P_2O_5, Al_2O_3, Na_2O, UO_2	Laboratory scale
RUSSIAN FEDERATION	High alumina waste	Borophosphate System (Al_2O_3: 19%)	Na_2O, B_2O_3, P_2O_5, Fe_2O_3, CaO, MnO, Al_2O_3, CeO_2, La_2O_3, Nd_2O_3, Cr_2O_3	Laboratory scale

4.1.3. Methodologies

The commonly available chemical durability tests that have been employed include MCC-1 and Soxhlet Leaching (initial rate), MCC-3 (decreasing rate and steady-state), PCT-ASTM C-1285-97 (final rate) and VHT (secondary phase formation).

DTA/TG analysis has been carried out to determine the glass transition temperature, crystallization temperature and melting point. Dilatometric measurements have been used to confirm the data obtained in the DTA/TG experiments and also to get the softening point and thermal expansion coefficients.

Microstructural characterisation methods for homogeneity and surface alteration/ secondary phase included SEM as a general method for determining inhomogeneities, XRD for the identification of secondary phases, EPMA for depthwise/cross-sectional variation and FTIR and TEM for detailed analysis. Electrical conductivity measurements have been carried out using Impedance Spectroscopy. Structural studies of the glass using Raman Spectroscopy and NMR are also reported. Other investigations include, EPR, HREM, etc., depending on the specific waste compositions.

Radiation damage studies on glasses have been reported by doping the glasses with an alpha source or by promoting internal alpha radiation through neutron bombardment of the glass samples.

Laboratory studies have been carried out to address long term dissolution of HLW glasses in clay related media and specific information or parameters for modelling have been determined. An integrated in-situ test (CORALUS) was also elaborated as a demonstration test, and for comparison with laboratory experiments and modelling predictions.

In view of the fact that the crystalline tetravalent actinide oxides are in general about eight orders of magnitudes less soluble than the amorphous phases, solubility measurements at higher temperatures have been conducted to study the transformation of amorphous to crystalline phases (UO_2). These studies are conducted under rigidly controlled redox conditions.

Volcanic glasses having been in contact with the seabed or land clay formations were studied as natural analogues for the borosilicate glasses.

4.1.4. Results

Some of the important results of the long term behaviour and performance under simulated repository conditions reported are:

- China and India reported initial generic studies of the long term interaction between HLW glass and different groundwaters, occasionally loaded with host rock materials.
- Russia (Radium Institute) obtained very promising results for the sorption / migration of Pu (IV) on a candidate granitic rock. This could assist the future development of a disposal concept and orient future R & D work.

The database and understanding of the long term glass dissolution in pure water and of the enhanced dissolution when clay was added to the solution were significantly extended.

- Fully loaded radioactive glass exhibited the same basic dissolution behaviour in pure water as the inactive reference glass.
- A close link between the results of R&D and the performance assessment study in candidate disposal hosts was established by elaborating a thermodynamic database for the radionuclide solubility and speciation. The validity of the database was checked by

specific validation tests. In addition, co-precipitation / solid solution, glass dissolution at high pH and natural analogue studies were also performed.

- The initial dissolution rate for the glass in solid clay has been determined. The residual dissolution rate in clay was determined by presaturating the clay with silica. Residual dissolution rates are at least two orders of magnitude lower than the initial rates. The solubilities in clay medium of the long-lived radionuclides (Np, Tc, Se, Sn, Zr, Pd) released from the glass have been measured.
- Natural glass analogues having been in contact with clay deposits for 1.4 million years have shown an interaction film of only 1.2 mm thick, revealing only very limited glass dissolution.
- The CORALUS in-situ test has been operated for two years successfully, and the results will be compared with the data from laboratory experiments.

4.2. SPENT NUCLEAR FUEL

Four countries have participated in the spent fuel section in the present CRP: Belgium, Republic of Korea, Russian Federation and Spain. Belgium, Republic of Korea and Spain focused on LWR spent fuel behaviour after rupture of the canister under repository conditions and the Russian Federation focused on RMBK-1000 spent fuel thermo-oxidizing behaviour in dry storage conditions for pre-disposal long term storage.

The studies were carried out with real spent fuel, UO_2 matrix and chemical analogues. Different approaches based on modeling and experimental results have been applied. A summary of the different spent fuels studied and experimental results are given in Tables III and IV.

The main conclusions from these R&D studies are:

- The chemical durability of spent fuel is acceptable under the conditions studied. The predicted lifetime of the spent fuel as a waste form would be as long as 10^4-10^8 years, thereby indicating spent fuel is a good waste form and an effective barrier for radionuclide releases over very long times.
- The radionuclide inventories in different spent fuel materials — along with the impurities, half-lives, radiotoxicity and solubility of critical radionuclides, and container composition — strongly affect the durability of the spent fuel, and have a great influence on the radionuclide release.
- Under interim storage conditions, an oxidation of real spent fuel up to $U/O_{2.4}$ has been observed. This could be due to the low burnup or the low enrichment of the fuel
- Tests in the presence of different candidate clay-type near and far field materials were developed in Belgium and in the presence of container and bentonite in the Republic of Korea. In the presence of Boom Clay, the initial dissolution rate is one order of magnitude higher than without the presence of clay. This effect of enhanced dissolution due to the presence of clay is correlated with the presence of a much smaller dissolution rate which occurs as soon as the clay is saturated. A decreased radionuclide release is also observed if compacted bentonite is present (the case of tests in Korea). This may be due to a limiting of the inventory of radionuclides released into the solution phase.

- Studies on the effect of alpha irradiation on the dissolution behaviour of UO_2 doped pellets have shown low dissolution rates for higher alpha doses, which is opposite to the current hypotheses. Possible explanations may be the presence of complexes involving humic acids from the uranium pre-oxidized by the alpha irradiation, or secondary phase formation.
- Finally, experiments with the aim of developing a kinetic model for prediction of spent fuel behaviour under repository conditions have been developed for performance assessment exercises. A clear effect of the burn-up has been shown.

TABLE III. SPENT FUEL TYPES AND CHARACTERISTICS STUDIED IN THE CRP

Country	**Type of Fuel/ Storage/disposal**	**Container/ Backfill Material**	**Container Material and Fuels**	**Waste Matrix Durability**
Russian Federation (27.000tU)	RBMK-1000 20GWd/tU Interim Dry	N_2 gas cover	Unspecified "Cans"	In progress in different gases and environments
Belgium	UO_X Repository Boom Clay	Not yet defined	Carbon steel 2.000 y Lifetime	
R. Korea (32.000tU)	UO_X PWR Granite	Calcium bentonite	Copper	IRF of Cs : <3% IRF of Sr : 0.4%
Spain 19.680 Assemblies 99% Wastes (6.750 tU)	UO_X (30-47GWd/tU) PWR/BWR Repository Clay/Granite	Borosilicate glasses spheres. Not defined Bentonite	Carbon steel 4 PWR/ 8 BWR >1.000 y <10.000 y	10^6-10^8 y 10^{-4} Instant Release Fraction

TABLE IV. DISSOLUTION RATES OF SPENT FUEL AND CHEMICAL ANALOGUES (MG m^{-2} d^{-1})

Country	**Spent fuel**	**Alpha doped**	**Uraninite**
Belgium		0.03-0.40	2.0 – 3.3 x 10^{-5}
Korea (Republic of)	$6.4x10^{-7}$ for U $4x10^{-5}$ for Cs		
Spain	1.4-5.5 mg m^{-2} d^{-1} $6.8x10^{-11}$-$2.7x10^{-10}$ mol.m^{-2} s^{-1} 3 mg m^{-2} d^{-1} UOX 2 mg m^{-2} d^{-1} MOX		4.22x10-10 mol.m^{-2} s^{-1}

Some spent fuel issues for further study:

Future work should be focused on more realistic models with long term experiments more representative of the behaviour for prediction times of thousands of years and with standard test methods, reaction apparatus, and sample-reactivity ranges.

Pre-oxidation of the fuel accelerates the dissolution of the matrix and of the radionuclides included in it in gap and grain boundaries. More work needs to be done to quantify this effect.

The long term dissolution rate will govern the durability of the matrix and will be used for predictions of long term performance. The microstructure and radionuclide inventory distribution in the pellet will govern the dose-rate and water-layer irradiation close to the pellet. In the absence of other oxidants, this irradiation will be the dominant oxidant-generation mechanism for interaction with the matrix and dissolution of it. Further clarification of this mechanism is needed.

The potential formation of a secondary phase, and its influence on the rate of alteration of the matrix is another point to clarify. In particular, the influence of potentially beneficial mechanisms on the oxidation/dissolution rate, such as an H_2 effect on reduction/consumption of oxidants, precipitation and secondary phase formation needs to be clarified, and incorporated into the matrix alteration model in order to develop more realistic models of matrix dissolution.

Further integration of efforts between laboratories and comparisons of results between them will be useful to understanding the fundamental phenomena and development of quantitative models. This will require careful, detailed planning

4.3. CERAMIC WASTE FORMS

Titanate ceramics (an assemblage of crystalline titanate minerals) have been developed since the late 1970's to provide an alternative to glass for the immobilisation of HLW from spent fuel reprocessing and separated actinide-rich wastes. The obvious advantage of these is that titanate minerals can accommodate actinides and FPs in their crystal structures. This offers good resistance to chemical alteration even in hydrothermal conditions. Recent studies also confirmed that radiation damage in the crystalline lattices has no significant detrimental effect on the overall chemical durability of the ceramic waste forms.

The research work performed by the CRP participants covers a wide range of activities including: test-sample formulation, dissolution mechanisms, effects of actinide valence state and solution pH. Chemical durability was investigated for pyrochlore-rich formulations (of HLW), zirconolite glass-ceramics (for actinide-rich wastes) and near single phase titanate ceramics (rutile and perovskite for ^{99}Tc, brannerite and zirconolite for actinide-rich wastes), under laboratory or simulated repository conditions. For this chemical durability testing, standard methods, such as MCC, PCT and single pass flow through (SPFT) were generally applied to obtain leach rates.

The main results from this part of the CRP include:

- Perovskite and rutile were investigated for the feasibility of immobilizing ^{99}Tc. The XRD, SEM analysis confirmed that the major phases were perovskite and rutile. They can accommodate up to 35 % of Mn (Tc) in their crystal structures. The leaching results and XRD analysis of samples after leaching indicated that perovskite may be more suitable for immobilization of Mn (Tc).
- A pyrochlore-rich ceramic formulation was tested to determine its long term chemical durability under simulated repository conditions (in the presence of granite, cement, bentonite and simulated canister corrosion product, Fe_3O_4). The leaching tests were

performed at $90^{o}C$ for two years. Leach rates seemed to reach a relatively constant value after 182 days (~10^{-3} g m^{-2} d^{-1}).

- Leach tests with zirconolite and zirconolite glass-ceramics were performed at $90^{o}C$. It was found that the initial leach rates for zirconolite were much lower than those for zirconolite glass ceramics. In addition, leach rates over longer period (1 year) were found to be less than 10^{-6} g m^{-2} d^{-1}, at least two orders of magnitude lower than those for borosilicate glasses.

- The dissolution behaviour of brannerite has been studied. The presence of phthalate has little effect on uranium release from brannerite, however bicarbonate enhances the dissolution of brannerite. In general, brannerite is more resistant to dissolution than UO_2 in both acidic and alkaline solutions, under atmospheric conditions. In under-saturated conditions at $90^{o}C$, the dissolution of brannerite is incongruent (preferential release of uranium) at pH 2 and nearly congruent at pH 11. TEM examinations reveal a polymorph of TiO_2 (pH 2 specimen) and a fibrous Ti-rich material (pH 11 specimen) as secondary phases.

- The effects of uranium valence state and solution pH on the chemical durability of brannerite have been studied by using a Th analogue of brannerite (thorutite) doped with U(IV) or U(V). The presence of U(V) in the U(V) doped sample was confirmed by near infrared diffuse reflectance spectroscopy. The observed V-shape pH dependence of uranium release rate is believed to be related to the U(IV) oxidation reaction upon dissolution. Overall, brannerite is less durable with dilute U(V) doping than U(IV) doping and Th-brannerite is appreciably more durable than its U-counterpart.

- A conceptual model for uranium release from brannerite has been developed. It consists of two simple reaction steps: oxidation of surface U(IV) atoms, and subsequent detachment of U(VI) atoms into solution, which is catalysed by surface coordination with protons (acidic media) or carbonate species (alkaline media in equilibrium with the atmosphere). The resulting predictive equation for uranium release qualitatively describes the pH-dependent behaviour observed in experiment, and quantitatively gives an upper limit for uranium release from brannerite over a range of conditions and experiment types.

- A literature review has been performed to provide an overview of the immobilisation options for separated plutonium wastes. In comparison, ceramic waste forms perform better than glasses in terms of chemical durability. In general, it is difficult to make absolute comparison of plutonium release rates from different waste forms, because of the variability of waste streams, experimental methods and reporting.

- Diffusion structure analysis (DSA) and scanning electron microscopy (SEM) were successfully used to study the effect of leaching on the subsurface microstructure changes for ceramics (zircon, brannerite, perovskite and zirconolite).

Some for ceramic waste form issues for further study:

- It has been recognized that specific leaching protocols should be developed to collect comparable data on long term chemical durability of candidate waste forms.

- The effect of repository environment (in the presence of canister corrosion products, cement, bentonite, host rock, etc.) on the waste form durability should be addressed further in any future programmes.

- The relatively short term laboratory data should be linked with the results of natural analogue and modelling studies to allow a better description of long term chemical durability to be developed.

5. CONCLUSIONS

While the technology for vitrification of high level waste has matured and become state of the art, the technology for producing ceramic waste forms for high level radioactive waste has also progressed significantly.

Activities are on-going to develop new glass and ceramic compositions for specific wastes — e.g. historical waste, materials testing reactor waste, partitioned waste, etc.

There is a need to have a stronger focus in the joint programme on the long term behaviour of the HLW forms, taking into account boundary conditions of the disposal concept and the needs of the performance assessment.

6. RECOMMENDATIONS

Taking into account the progress achieved and reported in this CRP, and on the evolutions reported worldwide, we conclude that there is a need for a continuing effort on the long term durability of high level waste forms. This enhanced focus on the long term durability is, amongst others, based on the current state of the art on HLW durability, where a "final" and very small dissolution rate is the "final" stage in a sequence of different dissolution processes. This approach of identifying a long term ("final") dissolution rate might be adapted to different high level waste forms, such as spent fuel and ceramics. Such a coordinated programme should take into account the boundary conditions of the disposal concepts (i.e. the repository environment), and the needs of the performance assessment for a repository.

This new focus will lead to improved effectiveness in future R&D programmes.

In the absence of candidate disposal sites, generic studies should be conceived. The following parameters should be taken into account:

- Use of different reference groundwaters;
- Presence of solids (near-field or far-field materials);
- Careful control of the environmental conditions;
- Determination of the uncertainties of the results.

Reference test concepts or plans to be used by experimental investigators should be adapted from existing procedures whenever possible.

A quality assurance plan should be adopted, focussing in particular on the documentation of the results.

The output of such studies should aim to provide basic parameters to be used in modeling. The R & D would then allow the development of databases for the specific waste forms as an input for conceptualizing disposal scenarios and preliminary performance assessment studies.

If one (or more) reference disposal sites are available in the near future, it is recommended that future research in this area:

- Focus the R & D on the long term behaviour of the HLW waste forms and on the processes controlling it.
- Recognize the interaction between the waste form and the disposal concept (choice of the engineered barriers and compatibility issues, etc) and the performance assessment (input data to provide, scenarios to adopt, weight given to the different barriers, etc).
- Elaborate a rationale for experiments, modeling (geochemical, analytical), natural analogues, and demonstration tests. Radioactive samples should be included in such a programme.
- Assess the experimental methodology (choice of experimental parameters, environmental parameters, data collection uncertainty). The methodology to accelerate the long term dissolution at laboratory scale needs to be carefully considered in order to come up with a scientifically defensible regime.

- Identify the parameters likely to be considered in future repository performance assessments, and identify the uncertainties in the modeling calculations for the lifetime of the waste form.

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