DELIVERABLE REPORT

Thermal treatment for radioactive waste minimisation and hazard reduction

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THERAMIN Project Partners

Andra	Agence nationale pour la gestion des déchets radioactifs – France
CEA	Commissariat à l'énergie atomique et aux énergies alternatives – France
GSL	Galson Sciences Limited – UK
FZJ	Forschungszentrum Juelich GmbH – Germany
LEI	Lithuanian Energy Institute – Lithuania
NNL	National Nuclear Laboratory – UK
ONDRAF/NIRAS	Organisme National des Déchets RAdioactifs et des matières Fissiles enrichies – Belgium
ORANO	Orano - France
SCK•CEN	The Belgian Nuclear Research Centre – Belgium
USFD	University of Sheffield – UK
VTT	Teknologian Tutkimuskeskus VTT Oy (VTT Technical Research Centre of Finland Ltd)
VUJE	VUJE a.s. – Slovakia

THERAMIN End User Group

Andra	Agence nationale pour la gestion des déchets radioactifs – France
CEA	Commissariat à l'énergie atomique et aux énergies alternatives – France
EDF	Electricité de France – France
Fortum	Fortum Oyj – Findland
IGD-TP	Implementing Geological Disposal of Radioactive Waste Technology Platform
Nagra	Die Nationale Genossenschaft für die Lagerung Radioaktiver Abfälle – Switzerland
ONDRAF/NIRAS	Organisme National des Déchets RAdioactifs et des matières Fissiles enrichies – Belgium
RWM	Radioactive Waste Management Ltd – UK
Sellafield	Sellafied Ltd – UK
TVO	Teollisuuden Voima Oyj – Finland

List of acronyms

EC	European Commission
WMO	Waste Management Organisation
ILW	Intermediate Level Waste
LLW	Low Level Waste
TRL	Technology Readiness Level
WP	Work Package
WAC	Waste Acceptance Criteria
PCT	Product Consistency Test
ISG	International Simple Glass

1 Introduction

1.1 Background

The **The**rmal treatment for **ra**dioactive waste **min**imisation and hazard reduction (THERAMIN) project is a European Commission (EC) programme of work jointly funded by the Horizon 2020 Euratom research and innovation programme and European nuclear waste management organisations (WMOs). The THERAMIN project is running in the period June 2017 – May 2020. Twelve European WMOs and research and consultancy institutions from seven European countries are participating in THERAMIN.

The overall objective of THERAMIN is to provide improved safe long-term storage and disposal of intermediate-level wastes (ILW) and low-level wastes (LLW) suitable for thermal processing. The work programme provides a vehicle for coordinated EU-wide research and technology demonstration designed to provide improved understanding and optimisation of the application of thermal treatment in radioactive waste management programmes across Europe, and will move technologies higher up the Technology Readiness Level (TRL) scale. The THERAMIN project is being carried out in five work packages (WPs). WP1 includes project management and coordination and is being led by VTT. WP2 evaluates the potential for thermal treatment of particular waste streams across Europe; this WP is led by GSL. In WP3, the application of selected thermal treatment technologies to radioactive waste management is demonstrated and evaluated; this WP is led by Andra. In WP4, the disposability of the thermally treated radioactive waste products is assessed; this WP is also led by Andra. WP5 concerns synthesis of the project outcomes and their dissemination to other interested organisations.

WP4 aims to carry out an evaluation of the disposability of thermally treated waste products and of the manageability of the resulting secondary waste, depending on the waste stream/treatment process combinations and depending on the disposal concepts in each participating country. So as to achieve this goal, WP4 is structured in 3 main tasks:

- Task 4.1: Identification and review of criteria and requirements for the disposability of thermally treated waste products

  Under this task, Waste Acceptance Criteria (WAC) of interest and requirements in terms of behaviour and performance of waste products will be identified. Moreover, required characterisation tests will be determined.

- Task 4.2: Study of thermally treated waste products and secondary waste

  Under this task, characterisation tests will be carried out on thermally treated waste products and secondary waste. Some relevant existing data will be shared.

- Task 4.3: Downstream / Safety Case implication

  This task will be focused on the disposability of thermally treated waste based on the identified criteria and the experimental data from the 2 previous tasks.

This report focuses on subtask 4.2.1 which is dedicated to the definition and the adaptation of characterisation tests.

1.2 Objectives of this Report

The purpose of this report is:

1) To present the characterisation methods which were selected for the project THERAMIN.
2) To adapt these characterisation methods to the requirement of the project. The selected parameters are described.

These methods constitute the common basis of characterisation for the project and are accessible to all THERAMIN partner laboratories. However, even if not described in this report, it doesn't prevent partners from carrying out more specific tests in addition to these ones.

1.3 Scope of this Report

After a first step of identification (see report D4.1), the experimental methods were compared and contrasted to select a set of simple tests which can provide basic information on the samples studied in WP4. As previously mentioned these simple methods don't prevent partners from carrying out other tests (not described in this report).

The selected characterisation tests will be carried out on samples produced in WP3 but also on samples from treatment tests outside the project. Tests started mid-2018 and will end mid-2019. The results will be useful for the last task developed in WP4, i.e. the downstream/safety case implication.

1.4 Report Structure

The remainder of this report is set out as follows:

- Section 2 is a short reminder of the characterisation methods of interest which were identified for the project THERAMIN
- Section 3 presents the characterisation tests which were selected for the project and how they were adapted
- Section 4 sets out the conclusions of this report.
- Section 5 lists the references used in this report.

2 Short reminder of characterisation method of interest for thermally treated waste products

The first part of WP4 was dedicated to the identification of characterisation requirements to evaluate the disposability of thermally treated waste products. This work was achieved through the following methodology (see report D4.1 for more details):

- Identification of relevant WAC for thermally treated waste products,
- Review of WAC to select the ones requiring characterisation tests,
- Identification of physicochemical parameters which relate to the list of identified criteria,
- Identification of characterisation tools which can provide data on the identified criteria,
- Selection of tests which will be carried out in the project.

As a result, the following table was produced. It contains the list of WAC requiring characterisation and the potential tools which could be used. Because of the duration of the project and the financial limitation, it is not possible to carry out all these tests in WP4, and some of them have been selected. The result of this selection is detailed in part 3.1.

Table 1: WAC and associated characterisation tools

Waste Acceptance Criteria	Characterisation tools which can be used
No free liquid or gas	TGA, XRF, electron microscopy …
Permeability and/or diffusivity of the waste sufficient to evacuate gas or other products	XRF, electron microscopy …
No or limited content of hazardous materials (combustible, pyrophoric, reactive, etc.)	XRF, XRD, ICP after dissolution …
Immobilisation of radionuclides	α spectrometry, autoradiography, Raman spectroscopy …
Limited voids / limited porosity	WAXS, BET (open porosity) …
No hot spots	XRF, electron microscopy …
Leaching behaviour of the waste product	leaching tests, ICP, IC, UV-Vis spectroscopy, α spectrometry …
Mechanical resistance of the waste product (mechanical constraint in disposal, impacts, etc.)	hardness, Young's modulus, toughness …
No metal with a redox lower than 0.84 V HSE	XRF, electron microscopy …
Thermal conductivity of the waste product (especially for self-heating waste)	thermal conductivity measurement …

3 Definition and adaptation of characterization tests

The characterization panel was discussed and chosen during a consensus discussion held during the WP4 meeting at Marcoule, the 2nd of February 2018 (see Minutes of WP4 meeting, 2018).

3.1 Selected characterization techniques

A common basis for solid characterizations is chosen to test:

- the degree of homogeneity of the sample and to verify the absence of free liquid or gas,
- the overall chemical composition of a homogeneous sample or the local compositions of a heterogeneous sample,
- the amorphous or crystalline nature of a sample and the structure of the crystals present in a crystallized sample.

The analytical techniques that constitute the common basis of characterizations are listed below and are accessible to all THERAMIN partner laboratories.

- Scanning electron microscopy (a technique that produces high resolution images of a sample surface using electron–matter interactions. It can be associated with X-ray energy dispersive microanalysis to study the chemical composition of the sample by using the X-radiation caused by the electron beam).
- X-ray fluorescence spectrometry (a technique for the chemical analysis of the composition of the sample).
- *And/or* electron microprobe (non-destructive technique used to determine the chemical composition of small volumes of solid materials).
- *And/or* inductively coupled plasma analysis after dissolution of the solid (a physical method of chemical analysis that allows for the quantification of almost all dissolved elements simultaneously).
- X-ray diffraction (provides access to a variety of information contained in the arrangement of elements within a sample).

Depending on the nature of the samples and the national radioactive waste management context, partners may also be required to use other techniques, e.g.:

- total organic and inorganic carbon analyses,
- qas physisorption to determine the specific surface area of a powder sample,
- thermal conductivity,
- transmission electron microscopy.

Finally, the chemical durability of the samples against the hydrolysis process will be estimated by leaching tests based on the ASTM Standard Test Method C 1285 – 14 “Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)” (ASTM International 2014) and described in the following paragraph.

3.2 Leaching tests method

As a common basis for leaching tests, the PCT-B procedure described in the ASTM Standard Test Method C 1285 – 14 (ASTM International 2014) was chosen and adapted collaboratively (Table 2). This procedure is useful to obtain initial information about chemical durability and alteration mechanisms and will avoid the findings to be limited to a specific repository concept. This methodology will enable partners to take the obtained results into account in their national context. Nevertheless, this common basis represents the reference case and does not prevent partners from carrying out additional tests, in other conditions.

Table 2: Experimental conditions of leaching tests compared to those recommended by the standard ASTM Standard PCT-B Test Method (ASTM International 2014).

	ASTM PCT-B Test Method	**Selected conditions**
Type of waste form	Radioactive, mixed, simulated, hazardous	Sample to be tested in the framework of WP4
Usage	Scoping tests, crystallization studies, comparative waste form evaluation	Comparative waste form evaluation
Test vessel	Unsensitised Type 304L stainless steel or PFA TFE-fluorocarbon vessel related to >0.5 MPa	Unsensitised Type 304L stainless steel or PFA TFE-fluorocarbon vessel related to >0.5 MPa
Test duration	7 days ± 2% or varying times	≥ 28 days
Leachant	ASTM Type 1 water or other solutions	High quality pure water High pH solutions or groundwater as additional tests
Condition	Static	Static
Minimum sample mass	≥ 1g	Refer to “Leachant volume”
Particle size	U.S. Standard ASTM – 100 to + 200 mesh (0.149 to 0.274 mm) or other sizes which are <40 mesh (0.420 mm)	0.125 to 0.250 mm (a particle size more adapted for heterogeneous samples)
Leachant volume	10 ± 0.5 $cm^3 \cdot g^{-1}$ of sample mass or other volume/sample mass	A sample-surface-area to solution-volume ratio (*SA*/*V*) of 10 m^{-1}
Temperature	90 ± 2°C or other temperature provided that any changes in reaction mechanism are noted	90 ± 2°C
Atmosphere	Air or CO_2-free air	Air
Type of system	Open to transport in PFA TFE-fluorocarbon, closed to transport in stainless steel	Closed to transport

If obtaining a powdered sample is not possible because of the quality or nature of the sample, leaching test on monoliths are possible, based on ASTM Standard Test Method C 1220 – 17 “Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste” (ASTM International 2017). In this second test method suitable for radioactive waste form material specimens, a specimen of known geometric surface area is immersed in a known volume of leachant in a test vessel (PTFE, steel, titanium, fused silica; Figure 1) that is sealed and placed in an oven (± 1°C) set at a defined temperature for a defined time period without agitation. Aliquants of the leachate solution are removed and analyzed for pH and various components that were released from the specimen during the test. The concentrations of dissolved soluble components are used to determine the extent of reaction. A separate test is conducted to provide data for each test condition (duration, temperature, *S*/*V* ratio, leachant composition, etc.). The saw-cut specimens are polished using successively finer grit paper with water (or absolute alcohol) lubrication. Saw-cut specimens will have a surface finish similar to 200-grit. For typical glasses, the test specimen surface finish is 600-grit. The selected test conditions – test duration, leachant, *S*/*V* ratio, temperature and atmosphere – are identical to those described in the third column of Table 2.

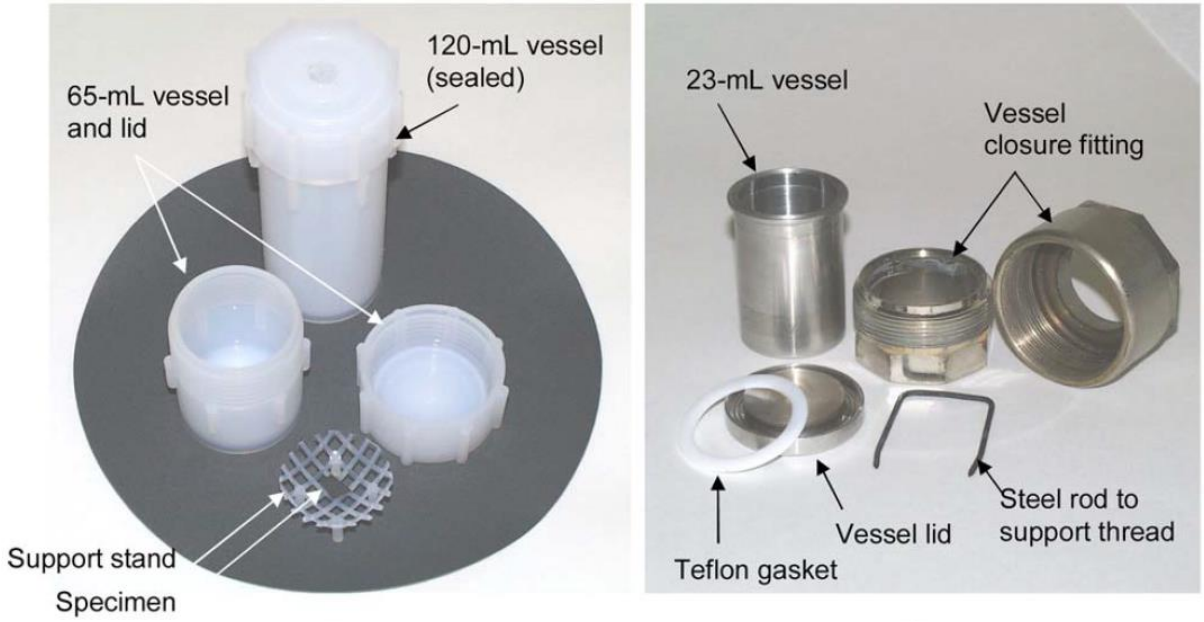

Figure 1: Examples of PFA TFE-fluorocarbon reactor and support (left) and Type 304-L steel test vessel, support and closure fitting (right) (ASTM International 2017).

In addition to the tests carried out on the samples to be tested in the framework of Work Package 4, an intercomparison of the results obtained by the different partner laboratories will be conducted. It will be based on a leaching test under the conditions defined in Table 1 on an international reference glass of nuclear interest, called ISG glass (Gin, Abdelouas et al. 2013). This glass was produced in 2012 by MoSci Corporation (Rolla, MO, USA). Three individual batches yielding approximately 25 kg of glass cullet each were produced by blending powdered raw materials in a V-blender. Each batch was melted in high purity fused silica crucibles in an electric furnace at 1300°C and water quenched to produce glass frit. After drying in an electric oven the three batches of frit were blended together to create a master lot. This frit was then re-melted in platinum–rhodium crucibles in an electric furnace at 1300°C for approximately four

hours, stirred once with a quartz rod, and cast into a graphite mold. The ingots were annealed at 569°C for 6 h in an electric oven and cooled to room temperature at a rate of 50°C per hour (Gin, Jollivet et al. 2015). A detailed analysis carried out by Savannah River National Laboratory (Marra, Crawford et al. 2012) showed that the composition was within the stated synthesis specifications (Table 3). A few grams of an ISG glass powder of 125-250 µm particle size (specific surface area measured by krypton adsorption and application of the BET model equal to 345 $cm \cdot g^{-1}$) washed by an iterative decanting process in acetone and absolute ethanol to remove fine particles were prepared by the CEA and shipped to partner laboratories.

Table 3: Nominal composition of ISG glass.

Oxide	**SiO_2**	**B_2O_3**	**Na_2O**	**Al_2O_3**	**CaO**	**ZrO_2**
Wt%	56.2 ± 1.5	17.3 ± 0.9	12.2 ± 0.7	6.1 ± 0.8	5.0 ± 0.6	3.3 ± 0.5
Mol%	60.1	16.0	12.7	3.8	5.7	1.7

Element	**Si**	**B**	**Na**	**Al**	**Ca**	**Zr**	**O**
Wt%	26.3	5.4	9.0	3.2	3.6	2.4	50.1
Mol%	18.0	9.6	7.6	2.3	1.7	0.5	60.3

4 Conclusions

The objectives of this document were (i) to present the characterisation tests which were selected for the project, and (ii) to present the parameters of these tests. These tests and associated parameters were especially discussed during the WP4 meeting held in Marcoule, the 2nd of February 2018. This report compiles the results of the discussions and the agreement which emerged.

5 References

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