Deliverable 9.7: ROUTES – Review of radioanalytical characterisation of selected radioactive wastes and wastes with complex chemical and toxic properties

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Deliverable 9.7: ROUTES – Review of radioanalytical characterisation of selected radioactive wastes and wastes with complex chemical and toxic properties

Work Package 9 "ROUTES"

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Executive Summary

Radioanalytical characterisation is a vital part of the waste management route for radioactive wastes. It ensures the compliance with waste acceptance criteria for interim storage, long-term storage and final disposal and therefore contributes to the safe handling of radioactive waste. The objective of this deliverable is a comprehensive description of radioanalytical characterisation, including

- the identification of characterisation techniques,
- the comparison of characterisation methods applied for the same waste in different countries,
- the analysis of existing approaches and identification of knowledge gaps, as well as
- to give recommendations both for future research and development (R&D) tackling the identified knowledge gaps and for characterisation approaches for countries with non-developed waste management concepts.

The first part of this deliverable describes the motivation and criteria for radioanalytical characterisation of waste by analysing the countries regulations, the distribution of responsibilities, as well as the motivation and techniques for characterisation. This section shows, that the majority of the participating member states (MS) of this deliverable have individual national regulations in place or have regulations based on Council Directive 2011/70/Euratom. In approx. 2/3 of the countries the respective waste owner is responsible for the characterisation of waste, while approx. 1/3 of the countries have assigned this task to national organisations. In general, the motivation for characterisation cited by the participating MS with implemented regulations is the verification of compliance with legal regulations or waste acceptance criteria (WAC), utilising a combination of non-destructive and destructive methods, as well as numerical models and scaling factors.

The second part of this deliverable presents identified radioanalytical characterisation approaches for six selected waste types: graphite, sludge, organic waste, spent ion exchange resins (SIERs), U/Ra/Th bearing waste and decommissioning waste. The radionuclide inventory of waste is highly dependent on waste type, such as graphite or spent ion exchange resins (SIERs), but also on the waste history or generation. Relevant for the selection of radioanalytical characterisation methods is moreover the physical and chemical form of the waste, such as liquid or solid, untreated or treated, or, non-conditioned or conditioned. This part identifies applied characterisation techniques specific for the selected waste types. Additionally, for the selected waste types, different characterisation approaches currently applied in different countries contributing to this deliverable are outlined.

In the third part, the different radioanalytical characterisation approaches and common issues are analysed waste type specific. Amalgamated, common issues for all addressed waste types are representative sampling and legislative challenges, such as missing WAC. For graphite, additional challenges in identifying disposal options arise from the ^{36}Cl content. For sludge, additional challenges arise from chemical properties such as reactivity, inflammability or gas generation, as well as big volumes of this waste type from oil- and gas-industries. A SIERs specific challenge is the gas generation due to radiolysis, as well as the determination of ^{226}Ra and ^{232}Th inventory of non-conditioned mixed waste containing SIERs. For U/Ra/Th bearing wastes, the variety of waste types containing is one of the challenges associated with it. Another issue is the large volume of U/Ra/Th bearing wastes, especially from non-nuclear facilities and the monitoring of ^{222}Rn release, especially for open pit storage of uranium mining tailings. As waste from decommissioning is a broad category, only general issues have been mentioned by participating countries. One specific challenge for decommissioning waste is the reduction of waste volume classified as low-level waste (LLW) and very low-level waste (VLLW) and increase the volume classified as exempted waste.

From the analysed issues, still existing knowledge gaps are derived and recommendations for future R&D to close identified knowledge gaps given. The origin of most identified characterisation issues are of financial or legislative nature, but also characterisation issues based on missing input from research and development have been identified. Regarding the recommendations for future R&D activities, a

common similarity of most waste addressed types is the representative sampling and improvement as well as validation of scaling factors.

In the last part, means of providing an efficient transfer of knowledge and experience to countries without mature waste disposal concepts and recommendations for the selection of applicable radioanalytical characterisation methods, e.g., for small inventory member states (SIMS) are given. For these countries, recommended non-destructive methods are the dosimetry and the gamma spectrometry. As destructive method, only liquid scintillation counters are recommended by task participants. Stated reasons for not recommending a specific technology are based on the costs of equipment, maintenance, specific know-how needed to operate the equipment, as well as limited applicability of the technology. The obstacles for SIMS on radioanalytical characterisation can be condensed to two main reasons: Availability of know-how and availability of equipment. Therefore, three actions will be recommended:

- Development of a guide on radioanalytical characterisation dedicated to SIMS
- Knowledge transfer program on technology application
- Research project on the development of a mobile facility for characterisation

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Glossary

AMS – Accelerator Mass Spectrometry

DA – Destructive Analysis

DGR – Deep Geological Repository

DTM – Difficult-to-measure

ETM – Easy-to-measure

EW – Exempt Waste

HLW – High Level Waste

HPGe – High Purity Germanium

HPLC – High Performance Liquid Chromatography

IAEA – International Atomic Energy Agency

IBM – Intermediate Bulk Container

ICP-MS – Inductively Coupled Plasma - Mass Spectrometry

ILW – Intermediate Level Waste

ISOCS – In Situ Object Counting System

LEGe – Low Energy Germanium

LL – Long-lived

LSC – Liquid Scintillation Counter

LLW – Low Level Waste

MCNP – Monte Carlo N-particle Radiation Transport Code

MLW – Medium Low Level Waste

MS – Member State

NDA – Non-destructive Analysis

NORM – Naturally Occurring Radioactive Material

NPP – Nuclear Power Plant

OBM – Oil-based muds

PG - Phosphogypsum

R&D – Research and Development

RAW – Radioactive Waste

RN – Radionuclide

SF – Scaling Factor

SFM – Spent Filter Material

SIER – Spent Ion Exchange Resin

SIMS – Small Inventory Member States

SL – Short-lived

TOS – Theory of Sampling

TSO – Technical Support Organisation

UNGG – Natural Uranium Graphite Gas Reactor

WAC – Waste Acceptance Criteria

VLLW – Very Low Level Waste

WAC – Waste Acceptance Criteria

WMO – Waste Management Organization

1. Introduction

Waste management routes in Europe from cradle to grave (ROUTES) - WP9 - is a strategic study in the European Joint Programme on Radioactive Waste Management (EURAD).

ROUTES Task 3 aims at describing and comparing characterisation approaches of radioactive wastes. Its main objectives are to:

- Identify characterisation techniques,
- Compare characterisation methods applied for the same waste in different countries,
- Analyse existing approaches,
- Identify knowledge gaps and
- Give recommendations for future R&D, as well as characterisation approaches for countries with non-developed waste management concepts.

In order to achieve its objectives, Task 3 consists of two subtasks, each disseminating its results in a dedicated deliverable. The subtasks of Task 3 are entitled as follows:

- Subtask 3.1 – Radioanalytical characterisation of radioactive waste and waste with complex/toxic properties.
- Subtask 3.2 – Characterisation and segregation of legacy waste.

This deliverable summarises the results of subtask 3.1. The work done within this subtask was aimed to collect, analyse and compare existing knowledge about techniques and practices for radioanalytical characterisation of radioactive waste. It is linked to Task 2 and Task 4 of the ROUTES WP, identifying challenging wastes and WAC, respectively.

Chapter 3 of this deliverable summarises the identified motivations and criteria for radioanalytical characterisation of radioactive wastes for each participating country. These criteria are, e.g., treatment, reprocessing or WAC for existing repositories.

In Chapter 4, the contributors have provided experiences on characterisation of radioactive waste in their respective country and collected radioanalytical techniques are analysed for each selected waste type. This chapter is initiated by an introduction on representative sampling for solid and liquid wastes, which is vital for reliable characterisation results.

In Chapter 5, the applied characterisation approaches discussed in the previous chapter for each selected waste type, including radioactive wastes with complex chemical properties and toxic radioactive wastes, are analysed. Based on the analysed knowledge and experience, issues and underlying knowledge gaps have been identified in order to give recommendations for further R&D to eliminate them.

In the last chapter of this deliverable, Chapter 6, means are considered of providing an efficient transfer of knowledge and experience to countries with less developed waste management concepts, e.g., to SIMS.

2. Methodology

This subtask has first focused on answering the questions related to the characterisation of challenging radioactive wastes. These challenging wastes were elaborated in the frame of ROUTES Task 2, which aims at identifying challenging wastes to be collaboratively tackled within EURAD. Within this report, the information of and provided by the participating countries in the subtask 3.1 of the ROUTES work package are presented and analysed. A questionnaire facilitated to collect, and then to analyse and compare existing knowledge on radioanalytical characterisation techniques and practices for challenging wastes in these participating countries. However, due to various reasons, the usual characterisation approaches cannot be directly applied on some of these wastes. To this end, knowledge, and experience in the characterisation of such wastes have also been collected and analysed in order to identify the main problems and gaps in knowledge and to formulate recommendations for further R&D to eliminate them.

For this purpose, additional country-specific data and information on motivation and criteria for characterisation of radioactive waste have been prepared and shared by the participating countries of this task within the ROUTES work package. These have been prepared by the respective countries under the guideline of predefined and distributed questions in order to provide comparable data:

1) What is the legislation regarding radioanalytical characterisation in your country? Is it mandatory, e.g. because of treatment/reprocessing/WAC?
2) Is there an underlying concept for radioanalytical characterisation of radioactive waste (RAW) and the selected characterisation methods? If yes, what is this concept? If no, is this a problem/challenge?
3) Are there different strategies/concepts or legislative boundaries for radioanalytical characterisation of different waste types? (E.g., sludges, organic wastes, SIERs, U/Ra/Th bearing wastes, decommissioning waste (concrete))
4) Who is responsible for characterisation?

Moreover, a pre-designed table, with the 12 challenging waste types identified in ROUTES Task 2, was distributed to all participating countries for completion in order to gather currently applied radioanalytical characterisation methods. Based on the result of this table, this work focused on six families of wastes common to the different participating countries. These are the following wastes: Graphite, sludge, organic waste, spent ion exchange resins (SIERs), U/Ra/Th bearing waste and decommissioning waste. The results are presented in Chapter 4. Additionally, successes and difficulties in radioanalytical characterisation have been described by selected countries for each of the discussed waste types and are presented in this section.

The analysis of existing approaches, issues and knowledge gaps, as well as R&D recommendations in Chapter 5 have been evaluated by volunteering participants of this task. The foundation for these sections were given by the country-specific information provided by the participating countries and a workshop in May 2022 (Month 36 of EURAD), where all gaps and needs have been discussed in plenum. The recommendations for radioanalytical characterisation in countries with non-developed waste management concepts in Chapter 6 are based on a questionnaire sent to all task participants, asking to indicate which characterisation technologies for unconditioned waste they would recommend for SIMS, considering the restrictions SIMS might face.

3. Motivation and criteria for characterisation

One of the task objectives is the analysis of existing approaches for radioanalytical characterisation. Therefore, within the work of this task, the motivation for characterisation of radioactive waste and the criteria on how to characterise radioactive waste have been requested from the involved member states (MS). This section provides a global analysis of the common motivation and criteria for characterisation and highlights differences. The underlying information provided by the participating MS can be found in Appendix A.

To evaluate the motivation and criteria for waste characterisation, four topics have been addressed by the participating member states concerning the countries regulations, the distribution of responsibilities, as well as the motivation and techniques for characterisation.

Regulatory framework:

Regarding the regulatory framework in the different countries two backgrounds exist: First, six out of ten participating MS have individual national regulations in place, which in part directly refer to waste acceptance criteria (WAC) for disposal facilities. Second, three out of ten participating member states have regulations based on Council Directive 2011/70/Euratom. Additionally, Portugal has national regulations for clearance and exemption of waste in place based on Council Directive 2013/59/Euratom. Only one participating MS, Cyprus, has no legislation on radioactive waste management yet.

Responsibilities:

In six out of ten participating MS, the waste owners or producers are solely responsible for waste characterisation. In general, in these countries the methodology for characterisation has to be approved by the waste management organisation (WMO) or the regulatory body and the results are regularly reviewed. In three countries (Bulgaria, Cyprus and Portugal), national organisations (e.g., WMO or TSO) are responsible for the characterisation of radioactive waste. Spain has chosen a middle course, where the waste producers are responsible for the determination of easy-to-measure (ETM) radionuclides, while a national organisation is responsible for the determination of difficult-to-measure (DTM) radionuclides.

Motivation for characterisation:

The motivation for characterisation cited by the participating MS with implemented regulations is the verification of compliance with legal regulations or WAC. This compliance should ensure a verified waste inventory, operational safety as well as long-term safety of the disposal facility.

Techniques for characterisation:

In general, the characterisation of radioactive waste relies on a combination of non-destructive (e.g., gamma spectroscopy) and destructive (e.g., liquid scintillation counter) methods, as well as numerical models and scaling factors. Most countries have implemented a universal characterisation strategy for the different wastes types, but conduct additional specific approaches for selected waste types.

4. Radioanalytical characterisation methods

Within this chapter, existing knowledge about techniques and practices for radioanalytical characterisation will be analysed and compared. These techniques were collected from the task participants, who were asked to fill in a table compiling, for each waste type defined in Task 2, the respective characterisation needs, methods/technologies and possible R&D gaps and needs.

4.1 Introduction

4.1.1 Waste type selection

In a first step, information was gathered from task participants on all challenging waste types defined in Task 2 of ROUTES, as well as the overall category of general RAW. The selection of challenging waste types includes: sludge, organic waste, SIER, bitumized waste, graphite, U/Ra/Th bearing waste, decommissioning waste, spent fuel, disused sealed radioactive sources, reactive metal or waste containing reactives, as well as chemotoxic waste. Additionally, participants were able to add waste types of high importance for their country.

To enable comparison of radioanalytical characterisation methods, only the waste types for which significant feedback has been provided by participating countries have been analysed and compared in following sections 4.2 to 4.7. The collection of radioanalytical characterisation methods has been completed by examples from different countries at the beginning of each section. Additionally, as the collection of representative samples is crucial for the successful and reliable characterisation of radioactive waste, an introduction to common liquid and solid wastes sampling techniques is given in Sections 4.1.2 and 4.1.3, respectively.

4.1.2 Sampling techniques for radioanalytical characterisation of liquid wastes

The ultimate aim of sampling is to analyse a representative sample of the whole. This requires sampling by taking a portion of the material, analysing the sample and reporting the results. An important step in this process is the handling of the sample, which ensure that the sample integrity is not compromised.

The type of material to be sampled may be homogeneous or heterogeneous liquid wastes. Homogeneous material resulting from known situations (e.g., process wastes) may not require an extensive sampling protocol if the material remains homogeneous. Heterogeneous and unknown liquid wastes require further sampling and analysis to ensure that the different components are represented. The process of sampling liquid waste raises the following challenges reported by participating countries. Some feedback or experience to solve these challenges are also reported when relevant.

Challenge 1 - The most important aspect of heterogeneous liquid samples is the retrieval of a representative sample.

> → To solve this, an attempt must be made to maintain sample integrity by preserving both its physical form and chemical composition. The specification of sampling according to standard protocols and the proper use of appropriate sampling equipment leads to the accomplishment of these goals.

Challenge 2 - In the case of organic wastes (e.g., oils, scintillation liquids, solvent extraction liquids, miscellaneous solvents) sampling of high active organic waste can be problematic due to radiolysis and subsequent gas production.

Challenge 3 – For organic waste, sampling two-phase sample, either liquid and organic or liquid and solid (e.g., sludge, which is a mixture of denser solids suspended in liquid, usually water) is also an issue.

Challenge 4 - As the sludge stored in the tanks and ponds tends to precipitate, the implementation of sampling for a better knowledge of radiological and chemical inventory is very

complicated. This results in different stratifications that prevent from obtaining representative samples. [1]

→ With regard to the conditioned sludge, some of the drums in **Spain** are corroding, which makes necessary to repackage them and transfer them to new containers. Therefore, a sampling and analysis regime is needed for this part of conditioned sludge.

→ In **Spain**, radiological characterisation and basic chemical analysis are performed every year in each NPP. This helps to maintain the scaling factors for the different waste streams.

→ In **France**, and in the **UK** difficulties arise, due to sludge presenting a high variability, whether by the different production processes implemented over time, or by the heterogeneity of precipitated sludge in tanks. Nevertheless, the chemical and radiological composition of the stored sludge is tried to be determined both by historical records and characterisation campaigns carried out multiple times with sampling at different depths. This enables a preliminary approach to the radiochemical content. However, additional specific characterisations during operations to retrieve waste may be required to choose and operate the most suitable conditioning method.

→ **Greece** also raised the fact that major difficulties related to the characterisation of sludge are related to homogeneity aspects.

→ For its side, **Belgium** announced that chemical analysis techniques are not reliable for sludge, inducing few information and the chemical composition of those wastes.

Challenge 5 - Where materials in the gas or vapour phase are present in relatively high concentrations, the possibility of a flammability hazard should be recognized.

→ The vapour phase is unlikely to contain high levels of radioactivity unless the species incorporates ^{14}C and ^{3}H, which may be the case for radioactively labelled compounds. Other inert radioactive gases, such as Kr, Xe and Rn, do not normally form organic compounds.

4.1.3 Sampling techniques for radioanalytical characterisation of solid wastes

The radiological characterisation of solid waste includes establishing the listing of radionuclides and their specific activity. Performing a reliable categorisation of the waste per treated unit (drum, container, etc.) on the basis of the relevant WAC and taking into account long-term safety criteria, is a complex task. It is a fact that some of the most safety-critical radionuclides in the long-term are DTM radionuclides, which means that non-destructive analysis is unsuitable for a correct characterisation. Moreover, the activity of the DTM radionuclides can be determined by a radionuclide vector, where the associated scaling factors are defined based on measurements and/or calculations/models. In terms of scaling factor determination, IAEA documentation [2] advices the following: *"Ideally there should be a sufficient number of samples collected in order to limit the uncertainty to within an acceptable range, although either for operational or historical reasons this may not always be possible. The acceptable range will vary according to the needs of the waste characterisation program, national regulations, WAC, etc. A factor of 10 is typically used as the bounds for the 'acceptable range'."*

In carrying out the data analysis to define the scaling factors, the following factors determine the uncertainty or level of conservatism:

- The number of radiochemical analysis data points:
  - The number of data points is sufficient when investment in additional sampling and measurement produces no appreciable improvement in the statistical uncertainty.
  - At some point additional samples will not reduce uncertainty and some decision will be required to set an appropriate course of action to meet the characterisation objectives.
- The dispersion or variance of data (regression is based on normal distribution); and

- The determination method (geometrical mean, linear regression of logarithm, etc.).

Before implementing a sampling program, its objectives should be established, as they are the main determining factor in establishing the sampling strategy and protocol. In many cases, the sampling strategy consists of a mix of in-lab and in-situ measurements to achieve the predefined objective(s) effectively and efficiently.

In the context of initial nuclear site characterisation in constraint environments, the INSIDER project (2017-2021, [3]) developed and validated a new and improved integrated characterisation methodology and strategy during nuclear decommissioning and dismantling operations of nuclear power plants, post-accidental land remediation or nuclear facilities under constrained environments. One of the important outcomes of this project is a statistical approach guideline, that is transformed into a web tool, which serves as a more user-friendly interactive interface. The web tool, named STRATEGIST [4] (Sampling Toolbox for Radiological Assessment To Enable Geostatistical and statistical Implementation with a Smart Tactic), intends to guide the expert in handling the problem definition and applying a strategy based on proper data analysis and sampling design for initial nuclear state characterisation in view of decommissioning. It provides general recommendations for the sampling design approach, making a distinction between probabilistic and non-probabilistic approaches, and designs with equal or non-equal probability of selection. It is not meant to provide the non-specialist with a comprehensive mode of operation for the complete process of initial nuclear state characterisation in view of decommissioning. Nor is the proposed approach pursuing to be a stepping-stone towards international standardisation. The web tool is quite general in providing information on methods for data analysis and sampling design, and can also be used for characterisation of radioactive waste.

One of today's most challenging projects, besides characterisation of conditioned legacy waste, is the characterisation of untreated legacy wastes with respect to the recently finalized set of WAC of the project cAt of near surface disposal site in Dessel. This untreated legacy waste is stored in 200-l drums and the contents of the drums can be linked to a variety of origins over both Belgoprocess sites. In the paper of Tuerlinckx [5], the focus is on concrete waste, abrasive blasting residues and contaminated soil. A clear challenge lies in obtaining a sufficiently reliable characterisation taking into account the radionuclides which are of great concern for long-term safety (e.g. ^{241}Am, ^{129}I and plutonium isotopes) based on a theoretical safety case. A robust representative sampling process was developed based on the Theory of Sampling (TOS). A so-called Replication Experiment was conducted to survey and quantify the intrinsic heterogeneity of selected typical materials for a range of critical parameters. The approach used by Belgoprocess takes its point of departure on the solid basis of the TOS as the necessary-and-sufficient guide for design, development and implementation of a reliable, representative sampling methodology. The TOS is a universal, scale-invariant framework for understanding sampling and all potential associated errors. One of TOS' primary principles states that representative sampling of a heterogeneous material (lot) must be in the form of a composite sampling process, involving enough increments extracted (Q) in such a way that the entire lot has even odds for being sampled. Another aspect rule of TOS is that all (composite) sampling procedures are multi-stage procedures, which is necessary to counteract the various effects stemming from the specifics of the lot heterogeneity. Based on the analysis of suitably representative samples, the classic drawbacks of commonly used techniques like drum-level non-destructive analysis (NDA) gamma spectrometry can be countered. This will be a great asset in case of legacy waste characterisation or in case of very heterogeneously distributed parameters which need to be analysed at very low levels.

In summary terms there is a need to ensure that the measurements (and samples) will be representative of the materials or waste being characterised and provide characterisation results that are statistically valid.

4.2 Identification of radioanalytical techniques: Graphite

Graphite waste originates mainly from NPPs and research reactors. Irradiated graphite is a long-lived, low-activity waste. Radioanalytical characterisation procedures are necessary for safety assessment of the disposal concepts and to comply with the waste acceptance criteria.

For treatment of graphite, Framatome (France) studied, in the 1990s, the feasibility of an incineration concept [6]. The objective was to destroy the irradiated graphite and make it completely inorganic at a sufficiently high temperature. The advantage of this method was that the initial volume of graphite could be greatly reduced. The exhaust gases could only be released after the immobilisation of $^{14}CO_2$ and ^{14}CO in the carbonate by the reaction with $Ca(OH)_2$ or $Ba(OH)_2$, otherwise an organised incineration has to be carried out to ensure an acceptable concentration of ^{14}C in the exhaust gas. However, following additional investigations conducted by EDF and the CEA within the framework of the PNGMDR 2016-2018 (French National plan for the management of radioactive materials and waste), the thermal treatment of graphite was considered irrelevant; the decontamination performance obtained were far from the objectives set, and the margins for progress in this area appeared to be limited [7]. Moreover, the discharges generated by the process were significant in relation to the benefit gained in terms of residual activity in ^{14}C and ^{36}Cl in the treated graphite.

According to the ROUTES survey, only French graphite sleeves from the dismantling operational phase of the Bugey 1 nuclear reactor are already conditioned and stored in a final repository. The wastes from Bugey-1 NPP were ranked into dedicated packages before to be blocked with cement [8]. Two different types of matrixes were studied for graphite waste in France: graphite/glass mix or cement. In order to satisfy the requirements for incorporation of the graphite into a cement matrix, it was necessary to determine the ^{36}Cl content.

4.2.1 Approaches & Experience on characterisation of graphite

France

In France, graphite waste comes from the first generation of nuclear power plants, the natural uranium graphite gas reactors (UNGG). These wastes are:

- Graphite bricks stacks that make up the stack of UNGG reactors;
- Graphite liners sleeves, which housed the fuel cartridges. The graphite liners sleeves from the dismantling of the Bugey 1 nuclear reactor were conditioned and disposed of in the Aube surface disposal (CSA) due to their very low content in ^{36}Cl. The liners sleeves from the other reactors are currently in other intermediate storage facilities.

Notably due to their content in ^{14}C and ^{36}Cl, these wastes are long-lived low-level wastes (LL-LLW), for which the disposal facility is under study. Consequently, the waste acceptance criteria (WAC) are not yet known. In any case, the determination of ^{36}Cl content might help identifying disposal options.

Thus, the producers of graphite waste are seeking to characterise the radionuclides linked to the activation of graphite. Indeed, many radionuclides present in graphite could be produced by neutron activation of impurities, surface contamination terms from nuclear fission or other structures in the reactor after decades of operation. The radioelements are mainly: ^{14}C, ^{3}H, ^{36}Cl, ^{41}Ca, ^{59}Ni, ^{60}Co, ^{55}Fe, ^{110m}Ag, ^{109}Cd, ^{90}Sr, ^{93}Zr, ^{129}I, ^{134}Cs and ^{137}Cs.

For this purpose, France characterises these wastes in the same way as their current practices by several destructive and non-destructive analysis are used, such as:

- dose rate measurement (radiation meter);
- measurement by gamma spectrometry;
- direct measurement with COMO 170 (contaminameter);

- direct measurement by sampling and analysis (scaling factor);
- verification of the radiological cleanliness of the package: swipe test.

Netherless, the easiest way to assess the radionuclide inventory of the irradiated graphite should be proceeded, e.g., by interpreting radiochemical measurements on irradiated graphite sampled. But in the case of irradiated high purity graphite for nuclear applications, high discrepancies have been observed on radionuclide measurements, particularly for radionuclides which precursors are present in traces. Indeed, the assessment of a radionuclide inventory based only on a low number of radiochemical measurements leads in most cases to a gross over- or underestimation, which can be detrimental to graphite waste management. Besides, the concentration of impurities in graphite is not well characterized, or possibly unknown, and remains below the chemical detection limit. EDF has therefore studied a mathematical methodology that combines calculation tools and radiochemical analysis results, and the first results obtained have been interpreted by IRSN, with the goal of linking the results provided by the mathematical analysis to the physical properties and processes that occur during the irradiation of the graphite components. This strategy is called the reverse method and aims to assess the radionuclide inventory as precisely as possible [7].

Germany

The German AVR research reactor in Juelich, a graphite moderated high temperature pebble-bed reactor, was shut down in 1988. It contained two types of graphite: a high-purity graphite, which was used as moderator in the core structure and carbon bricks as outer layer, which served as heat protection for the metallic structure of the reactor. In a campaign around the year 2000, samples of both graphite types were radio-chemically analysed at the research centre in Juelich [8].

In a first step, the dose rate of the respective sample was analysed. Subsequently, gamma-spectrometry was used to determine the dominant beta and gamma emitters ^{60}Co, ^{134}Cs and ^{137}Cs. To eliminate the graphite matrix, the sample was then incinerated at 800°C under continuous O_2 gas flow.

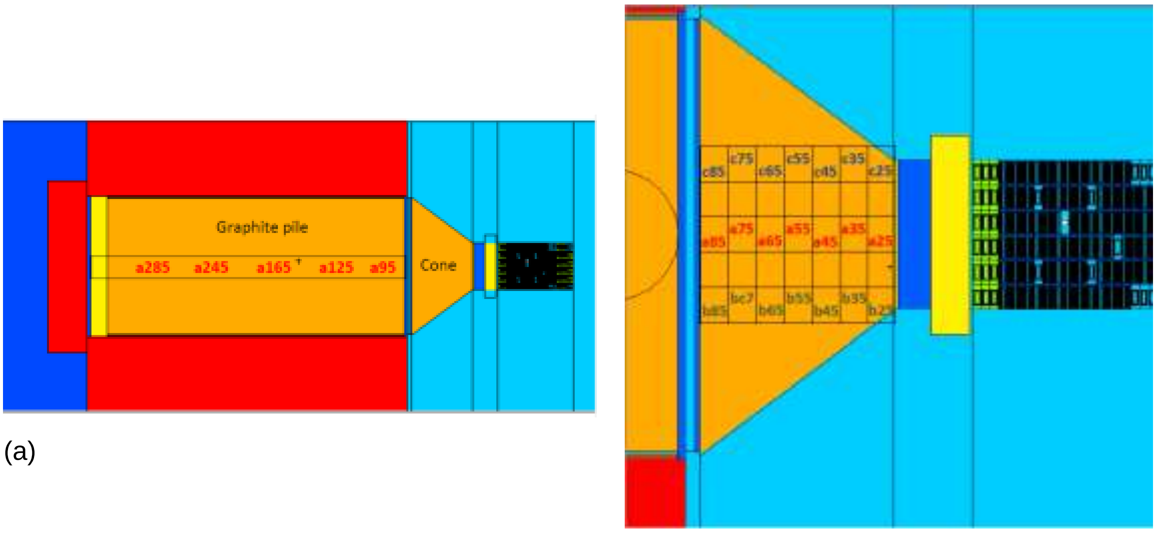
The off-gas was led through three washing bottles: The first bottle using acidic gas scrubbing in order to restrain Tritium and ^{36}Cl separation and the second and third bottle for alkaline gas scrubbing in order to restrain ^{14}C. These off-gas samples were analysed using liquid scintillation counter (LSC).

The residues of the incineration were disintegrated in acid. Subsequent options for characterisation are:

- Inductively coupled plasma - mass spectrometry (ICP-MS)
- Alpha sepctrometry
- X-ray detector (^{55}Fe)
- Further separation using high performance liquid chromatography (HPLC) and subsequent LSC (e.g., ^{59}Ni, ^{63}Ni, ^{90}Sr/^{90}Y, ^{93}Zr, ^{94}Nb, ^{241}Pu)

Greece

The thermal column of the Greek Research Reactor (GRR-1) is the moderator to slow down fast neutrons to thermal energies. It consists of a square steel chamber (graphite pile) (Figure 1a), lined by boral sheet. This chamber encases 7.77 Mg graphite blocks. A thermal pyramidal column (cone) extension is also provided (Figure 1b). The extension consists of 0.87 Mg graphite, encased in aluminum can. It is located in the operation section of the pool, positioned between the core and the inside end of the square thermal column chamber.



(a)

(b)

Figure 1 - GRR-1 thermal column (horizontal cross- section): a) the square steel chamber which encases graphite blocks; b) the thermal pyramidal column.

The preliminary radiological characterisation of the GRR-1 thermal column was performed by Monte Carlo neutron transport simulations and analytical radionuclide inventory calculations [9]. The spatial distribution of neutron fluxes and spectra were derived by an implicit Monte Carlo N-particle Radiation Transport Code (MCNP) thermal column model [10]. The thermal column graphite was subdivided in volume elements of (10x10x10) cm^3. The radionuclides were produced by activation of the impurities in the graphite blocks. It was assumed that the graphite is high purity reactor-grade graphite (Pile Grade A - PGA type) and the nominal impurities concentrations were used for the calculations. The specific activities of the thermal column in each square cell were evaluated.

The major radionuclides and the range of their activities in the thermal column cells, 14 years after last operation of the reactor, are presented in Table 1. The validation of the modelling results by measurement as well as the determination of the scaling factors (SFs) are pending.

Thermal pyramidal column central parallelepiped (see Figure 1b) (Bq/g)			**Pile axis (see Figure 1a) (Bq/g)**		
	MIN	**MAX**		**MIN**	**MAX**
^{3}H	5.22E+03	1.10E+05	^{3}H	3.12E+00	3.55E+03
^{14}C	1.58E+02	4.11E+03	^{14}C	9.41E-02	1.07E+02
^{60}Co	7.72E+01	2.08E+03	^{60}Co	4.59E-02	5.25E+01
^{154}Eu	4.54E+01	1.50E+03	^{154}Eu	2.17E-02	3.12E+01
^{55}Fe	3.25E+01	7.86E+02	^{55}Fe	1.92E-02	2.23E+01
^{36}Cl	5.56E-01	5.35E+01	^{36}Cl	1.30E-03	1.48E+00
^{152}Eu	4.72E+01	1.21E+03	^{152}Eu	2.41E-01	4.82E+02

Table 1 - The major radionuclides and the range of the specific activities in the cells.

Slovakia

Radioactive graphite represents a significant waste stream that arises during the decommissioning of certain types of nuclear installations. In case of Slovakia, the only source of radioactive graphite is the NPP A1 reactor (type KS 150) pending for decommissioning in a near future. Graphite in the NPP A1 reactor was used as a shielding material, its main task was to slow down and absorb neutron fluxes from the reactor core, which prevented undesired radiation effects on the internal reactor components and the reactor pressure vessel. Total mass of irradiated graphite in a reactor is 86 metric tons. Initial sampling and radiological characterisation of this kind of RAW was carried out and it was found that key radionuclides are ^{14}C, ^{36}Cl, ^{41}Ca, ^{59}Ni, ^{94}Nb and ^{152}Eu. Radiological characterisation was performed by means of gamma spectroscopy system and liquid scintillation detector.

Problems and challenges: A specific problem with irradiated graphite is Wigner energy. Up to now, Slovakia has only limited skills how to measure Wigner energy. As well, it is not specified what level of Wigner energy (threshold) is safe for disposal and how to perform waste pre-conditioning to achieve safe values.

Therefore, it is important that representative graphite samples be taken at low temperature with activated graphite and that the following measurements be made:

- total stored energy;
- the rate of release of stored energy;
- thermal conductivity;
- reactivity with air (oxidation rates in air).

These can then be used to model the behaviour of graphite during the period of "secure closure", disassembly, processing, packaging and disposal.

Because it is not acceptable to store or dispose graphite that contains releasable stored energy, such graphite should be annealed to remove energy and thus prevent from spontaneous heating. The annealing temperature above 250 ° C should be sufficient to protect against any subsequent fluctuations in ambient temperature during transport and storage.

Limited scope of graphite sampling was conducted at KS-150 reactor recently. Wigner energy was measured using differential scanning calorimetry. In 50 measurements, the presence of stored Wigner energy was not demonstrated. Thus, the absence of deposited Wigner energy in graphite confirms the assumptions of a minimal probability of the presence of Wigner energy due to the construction, operation time, irradiation, design and temperature gradients in the KS 150 reactor.

Based on the data obtained from the radiological characterisation, it was possible to perform safety analyses of graphite storage in the repository. The analyses confirmed that the current repository design and barriers allow the storage of low-activity graphite. However, studies have confirmed that the properties of graphite may vary within a particular reactor according to the position of the component within the reactor. Activated graphite is an inhomogeneous material that can be described as an amorphous-crystalline porous composite containing inhomogeneously distributed radionuclides. Therefore, it will be necessary to address this issue in future when removing the graphite shielding from other parts of the reactor; particularly in areas of high neutron flux the situation may be considerably different.

4.2.2 Radioanalytical characterisation of graphite

Non-conditioned waste

Graphite waste is problematic due to high volume of waste, although in general it has a low-activity. ^{14}C, ^{36}Cl and ^{3}H, the major radionuclides in graphite, undergo a beta minus decay.

NDA – Non-destructive analysis

The following Table 2 summarises the non-destructive radioanalytical characterisation methods for non-conditioned graphite. Countries providing input to this section were France, Germany, Slovakia, Spain and Ukraine. The non-destructive analysis of non-conditioned graphite waste mainly relies on gamma spectrometry.

Parameters	**Radioanalytical characterisation methods**
Dose rate	• Dosimetry (France, Ukraine)
RN inventory (incl. SL and LL)	• Gamma-Spectrometry (Ukraine)
Beta-/Gamma-emitting RN	• Gamma-Spectrometry (^{59}Fe, ^{59}Ni and ^{129}I) (Germany, Slovakia, Spain)
Reactive materials	• Gamma-Spectrometry with low-energy HPGe (^{55}Fe) (Germany)

Table 2 - Radioanalytical characterisation methods (NDA) for non-conditioned graphite

DA – Destructive analysis

The following Table 3 summarises the destructive radioanalytical characterisation methods for non-conditioned graphite. The information in this section were provided by France, Germany, Slovakia, Spain and Ukraine.

Graphite waste has a high quantity of beta-emitting radionuclides, which encourages destructive analysis for radioanalytical characterisation. Common methods are liquid scintillation counting and mass spectrometry for the determination of, e.g., beta-emitting radionuclides such as ^{3}H and ^{14}C, as well as alpha spectrometry for the determination of alpha-emitting radionuclides.

Parameters	**Radioanalytical characterisation methods**
RN inventory (incl. SL and LL)	• Isotope specific analysis (France[1]) • Radiochemistry (Spain[2]) • Mass-Spectrometry (Ukraine) • Radiochemistry (Ukraine) • Extraction chromatography (Ukraine) • Scaling Factor (Ukraine)
Alpha-emitting RN	• Liquid scintillation counter (Germany) • Alpha spectrometry after separation (ion exchange chromatography and liquid-liquid extraction) (Slovakia, Spain[3])
Beta-/Gamma-emitting RN	• Liquid scintillation counter (Germany, Spain[4]) • Beta-counting (Slovakia)
Fissile materials	• Alpha spectrometry (Slovakia, Ukraine)

1 ^{14}C, ^{3}H, ^{36}Cl, ^{41}Ca, ^{59}Ni, ^{60}Co, ^{55}Fe, ^{110m}Ag, ^{109}Cd, ^{90}Sr, ^{93}Zr, ^{129}I, ^{134}Cs, ^{137}Cs

2 ^{3}H, ^{14}C, ^{36}Cl, $^{41/45}$Ca, ^{54}Mn, $^{55/59}$Fe, $^{59/63}$Ni, ^{58}Co, ^{60}Co, ^{65}Zn, $^{89/90}$Sr, $^{93m/94}$Nb, ^{95}Zr, ^{99}Tc, ^{106}Ru, ^{108m}Ag, ^{110m}Ag, ^{125}Sb, ^{129}I, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, $^{239/40}$Pu, ^{241}Pu, ^{241}Am, ^{242}Cm & ^{244}Cm.

3 ^{241}Am, ^{238}Pu, $^{239/40}$Pu, ^{242}Cm, ^{244}Cm, ^{234}U, ^{235}U and ^{238}U

4 Separation by liquid-liquid extraction ($^{59/63}$Ni, ^{99}Tc), selective precipitation (^{36}Cl, $^{41/45}$Ca, $^{55/59}$Fe, ^{129}I), extraction chromatogrphy ($^{89/90}$Sr), ion exchange chromatography (^{241}Pu).

Parameters	Radioanalytical characterisation methods
	• Radiochemical release (Ukraine)
Reactive materials	• Inductively coupled plasma mass spectrometry ICP-MS (^{90}Sr, ^{55}Fe, ^{63}Ni) (Germany) • Liquid scintillation counter (^{90}Sr, ^{55}Fe, ^{63}Ni) (Germany)
^{3}H and ^{14}C release	• Liquid scintillation counter LSC (^{14}C, ^{36}Cl) (Germany, Spain) • Accelerator Mass Spectrometers AMS (^{14}C) (Germany)

Table 3 - Radioanalytical characterisation methods (DA) for non-conditioned graphite

Conditioned waste

Currently, only few countries have conditioned graphite waste. A major problem of graphite waste is the gas production due to CO_2 and mobility of ^{36}Cl and ^{14}C in a final repository [11]. Leaching tests have shown a high mobility of carbon and chlorine in clay [11]. Research for graphite waste is on-going.

The following Table 4 summarises the non-destructive characterisation methods of conditioned graphite waste. This information was provided by France.

Parameters	Radioanalytical characterisation methods
Dose rate	• Dosimetry (France)
Surface contamination	• Ionisation chamber (swipe test) (France) • Contamination meter (France)

Table 4 - Radioanalytical characterisation methods (NDA) for conditioned graphite

4.3 Identification of radioanalytical techniques: Sludges

Sludges presented by the different responding countries are of different types. In France, they mainly come from effluent treatment or from nuclear fuel reprocessing and are bituminized or cemented. In Greece, sludges are mainly at the bottom of liquid waste tanks and also inside the heat exchangers and delay tanks of the primary cooling system of the research reactor. In Germany some sludges are from the recycling foundries where metals from decommissioning are melt inside a control area. Subsequently, the secondary wastes are returned to the facility owner. In Bulgaria, the sludges are collected and stored under water in liquid radioactive waste storage facilities on the site of nuclear power plants (NPP). These sludges are mainly filtering materials (spent ions exchange filters) which are from special water treatment installations. Most challenging type of sludges in Slovakia comes from NPP A1. A special type of liquid (chrompik: aqueous solution of potassium chromate and dichromate) has been used as liquid heat transfer medium for cooling of the spent fuel assemblies. Sludge from these liquids is conditioned with geopolymers.

4.3.1 Approaches & Experience on characterisation of sludges

Bulgaria

In Bulgaria from the beginning of Kozloduy NPP (KNPP) operation there are activities for RAW management, in particular for sludges. They are developed taking into account that there are Special Water Treatment Installations, which are equipped with ion-exchange filters, intended for cleaning of technological media from corrosion products and chemical additives. During the operation of these facilities, spent filtering materials are generated that contain ion-exchange resins and sludges. The volume of the sludges is about 70 m^3. For their identification, sampling method and laboratory analyses are used. The main radionuclides contained in the sludges are ^{134}Cs, ^{137}Cs, ^{60}Co and ^{54}Mn. The activity of the sludges is about 10^{11} Bq.

Greece

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In petroleum engineering, the drilling mud is a heavy, viscous fluid mixture that is used in oil and gas drilling operations to carry rock cuttings to the surface and also to cool and lubricate the drill. By hydrostatic pressure it also prevents the collapse of unstable strata into the borehole and the intrusion of water. Usually oil-based muds (OBM) are used for great depths or in directional or horizontal drilling, which place greater stress on the drilling apparatus. A typical composition of OBM (w/w) is: Barite (69.5%), Base Oil (25.8%), $CaCl_2$ (2%), Emulsifier (1.8%) and others (0.9%) [12].

In general, spent drilling muds contain low activities of natural radionuclides and can be cleared after verification of clearance. The activities of gamma emitters in oil-based mud in Iraq seemed to depend on the drilling depths [13], where ^{226}Ra and ^{214}Pb partly exceeded the general clearance limits. Low activities were also observed in drilling mud samples from Greece, with activities of ^{226}Ra, ^{228}Ra; ^{228}Th and ^{232}Th partly exceeding the general clearance limits. The general clearance limit for all these radionuclides is 1,000 Bq/ kg except ^{40}K which is 10,000 Bq/ kg. It should be noted that usually the natural radionuclides of the same series are not in secular equilibrium in drilling muds. This makes their radiological characterisation challenging.

At NCSRD in Athens, a methodology for characterisation and clearance of spent oil-based muds was developed by using a $LaBr_3$(Ce) scintillator [14, 15]. The mud is put in common packaging (e.g. steel drum, Intermediate Bulk Container (IBC)) for measurement. MCNP-X simulations were carried out to evaluate the detection efficiency for selected source-detector configurations and estimate the optimum measurement parameters in the field. The measurement procedure combines MCNP-X simulations, non-destructive gamma spectrometry and sampling for determination of difficult to measure radionuclides. Detection efficiency, internal background of $LaBr_3$(Ce) scintillator, probability of emission and peak interferences, were considered in order to select the optimal natural radionuclides from uranium and thorium radioactive series and the corresponding emitting peak energies for the analyses. The activities of other radionuclides in the series, which come into radioactive equilibrium with those measured after a certain time from the last use of the mud, can be evaluated. Furthermore, the radionuclides which are not possible to be determined based on gamma spectrometry were identified. For these difficult to measure or to determine radionuclides, representative sampling and then radiochemical analyses can be carried out, if necessary.

The detection efficiency of the non-destructive gamma spectrometry for steel drum as well as IBC is of the order of 10^{-5}. Moreover, the density uncertainty of the mud was considered and activity study for strati form inhomogeneity in the waste containers was carried out. The technique was validated by using waste packages with homogeneous oil-based mud of known density and activity.

The proposed methodology can be effectively applied for fast and cost-effective clearance of spent oil-based muds originating from oil Industry. Specific activities at the general clearance levels can be determined by 30 min measurement and with total uncertainty 30-40 %.

Ukraine

Sludges at Ukrainian NPPs are generated as a result of sewage treatment. Sludges are collected and stored in storage facilities for liquid radioactive waste under a layer of water together with spent filter materials (SFMs), which are not currently treated. Today, the filling of temporary sludge storage tanks is quite significant at Ukrainian NPPs. Therefore, the priority task for NPPs is the introduction of technologies for immobilization of SFMs and sludge and the beginning of their processing. At the same time, Rivne and Khmelnitsky NPPs have centrifugal installation to treat small amount sewage from sludge. Dehydrated sludge is stored in 200-liter barrels in the solid radioactive waste storage without further treatment [16]. The classification of dehydrated sludge is uncertain, according to the Ukraine regulations unprocessed sludge is a liquid radioactive waste and dehydrated sludge is not classified at all [17].

Existing system of radwaste characterisation at NPPs provides determination of the specific activity of the main gamma-emitting radionuclides (^{134}Cs; ^{137}Cs; ^{60}Co; ^{54}Mn; ^{125}Sb; ^{110m}Ag). In order to free liquid radwaste storage facilities from sludge, technology for sludge immobilization is currently being developed. However, given the characteristics of dehydrated sludge, the possibility of disposal sludge containers without further processing is considered. The purpose of this work is to implement a set of measures to develop the optimal technology for immobilization of SFMs and sludge, testing of radwaste samples, and processing the experimental batch of sludge waste from tanks (approximately 6,000 to 12,000 liters) to obtain packages of radwaste in the form of 200-liter barrels. The method of fixing radwaste in a geopolymer or similar matrix with the help of a mobile installation should be used as a processing technology. Processing technology should allow obtaining the necessary characteristics of approved radwaste, acceptable for their safe storage at NPP sites and final disposal.

As part of a national project, sampling and physicochemical and radiochemical analysis (direct gamma spectrometry, radiochemical isolation + alpha, beta, gamma spectrometry, mass spectrometry) of samples for sludge were performed. The specific activities of radionuclides in this radwaste stream (mainly - ^{60}Co, ^{137}Cs, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{94}Nb, ^{99}Tc, ^{238}Pu, $^{239/240}Pu$, ^{241}Pu, ^{214}Am, ^{3}H, ^{14}C) were determined. Also, the preliminary nuclide vector for the selected radwaste stream was calculated and preliminary assessment of the radiation impact of direct disposal of containers with sludge was performed.

4.3.2 Radioanalytical characterisation of sludges

As presented in the national experiences above provided by Bulgaria, Greece and Ukraine, sludges contain generally gamma emitters as well as difficult to measure (DTM) radionuclides. So, non-destructive gamma spectrometry techniques are used and also sampling and radiochemical analyses are carried out for radiological; characterisation of sludge. Scaling factors (SF) are determined based on the results of samples analysis. Then, the isotopic vector (or isotopic composition) is determined through calculations by using the results of non-destructive gamma spectrometry measurement or dose rate measurements.

A good practice is to perform the characterisation of sludge before the conditioning. It is easier to collect samples from raw (primary) sludge for determination of the DTM radionuclides. The sludge consist of two phases: liquid and solid phases. The distribution of radionuclides might be different in these two phases. Therefore, this should be considered during sampling to collect representative samples.

Non-conditioned waste

As mentioned above, sludge contains gamma emitters and DTM radionuclides. Non-destructive techniques are used for determination of key radionuclides (e.g., ^{137}Cs, ^{134}Cs, ^{60}Co, ^{241}Am) and other gamma emitters in sludge. Also, sampling is necessary to determine DTM radionuclides.

NDA – Non-destructive analysis

Table 6 summarises non-destructive techniques for the characterisation of non-conditioned sludge. The information is provided by Bulgaria, France, Germany, Slovakia and Ukraine.

Parameters	**Radioanalytical characterisation methods**
Dose rate	• Dosimetry (Bulgaria, Germany, Ukraine) • Passive gamma scanner / Gamma spectrometry (Slovakia)
RN inventory (incl. SL & LL)	• segmented gamma scanner (Bulgaria, Ukraine) • Scaling factor (France)
Beta-/Gamma-emitting RN	• Gamma-spectrometry (Germany, Slovakia)
Topology	• Gamma spectrometry (Germany)

Table 5 - Radioanalytical characterisation methods (NDA) for non-conditioned sludge

DA – Destructive analysis

Table 7 summarises the applied destructive characterisation techniques for non-conditioned sludge, e.g. to determine DTM radionuclides. This information is provided by Bulgaria, France, Germany, Slovakia, Slovenia, Spain and Ukraine.

Parameters	Radioanalytical characterisation methods
RN inventory (incl. SL & LL)	• Gamma spectrometry (Bulgaria, Slovenia, Ukraine) • Low-energy Germanium (LEGe) gamma spectrometry (Slovakia) • Gross alpha/beta counting liquid scintillation (Bulgaria, Slovakia) • Isotope specific analysis[5] (Spain, Ukraine) • Extraction chromatography, (Ukraine) • Scaling factors (Slovenia)
Alpha-emitting RN	• LSC (Germany) • Alpha spectrometry after separation (e.g., Separation by ion exchange chromatography and liquid-liquid extraction. ^{241}Am, ^{238}Pu, $^{239/40}$Pu, ^{242}Cm, ^{244}Cm, ^{234}U, ^{235}U and ^{238}U) (Slovakia, Spain)
Beta-/Gamma-emitting RN	• LSC after separation (e.g., liquid-liquid extraction ($^{59/63}$Ni, ^{99}Tc), selective precipitation (^{36}Cl, $^{41/45}$Ca, $^{55/59}$Fe, ^{129}I), extraction chromatography ($^{89/90}$Sr), ion exchange chromatography (^{241}Pu) (Germany, Spain) • Gamma spectrometry after separation (^{59}Fe, ^{59}Ni and ^{129}I) (Spain)
Gross alpha/beta	• Gamma spectrometry (^{241}Am, ^{144}Ce, ^{125}Sb, ^{103}Ru, ^{106}Ru, ^{137}Cs, ^{154}Eu, ^{95}Zr, ^{95}Nb, ^{134}Cs, ^{60}Co) (France, Slovakia) • Alpha spectrometry / total alpha activity, (^{244}Cm) (France) • Scaling factors (France)
Fissile material	• Alpha spectrometry after separation or fixation (Pu) (France, Germany, Slovakia)
^{3}H and ^{14}C release	• LSC (Germany, Spain)

Table 6 - Radioanalytical characterisation methods (DA) for non-conditioned sludge

<u>Conditioned waste</u>

Table 7 summarises the applied radioanalytical characterisation methods for conditioned sludge by Germany, Slovakia and Slovenia.

[5] 3H, 14C, 36Cl, 41/45Ca, 54Mn, 55/59Fe, 59/63Ni, 58Co, 60Co, 65Zn, 89/90Sr, 93m/94Nb, 95Zr, 99Tc, 106Ru, 108mAg, 110mAg, 125Sb, 129I, 134Cs, 137Cs, 144Ce, 152Eu, 154Eu, 155Eu, 234U, 235U, 238U, 238Pu, 239/40Pu, 241Pu, 241Am, 242Cm & 244Cm.

Parameters	**Radioanalytical characterisation methods**
Dose rate	• Dosimetry (Germany, Slovakia, Slovenia)
RN inventory (incl. SL and LL)	• Gamma spectrometry (Germany)
Surface contamination	• Swipe test (Germany)

Table 7 - Radioanalytical characterisation methods (NDA & DA) for conditioned sludge

4.4 Identification of radioanalytical techniques: Organic Waste

A large variety of organic wastes exists, such as plastics, sorbents, paper, wood, oils, grease or scintillation cocktails. It also includes both liquid and solid waste streams. The management of these wastes, including the radioanalytical characterisation is highly dependent on the waste itself, but also on where and how the waste was generated. Depending on these waste characteristics, a waste management route has to be defined, including the selection of appropriate radioanalytical characterisation methods.

4.4.1 Approaches & Experience on characterisation of organic waste

Belgium

Regarding the processing of organic waste, a distinction is made between low-level waste (LLW) and intermediate or high-level waste (I/HLW).

Concerning LLW, solid organic waste is collected in 200l drums or 1m³ containers and typically includes cellulose, plastics and resins. Key and ETM radionuclides are determined via gamma spectrometry measurements (Q2, Low Level Waste Assay System; In Situ Object Counting System (ISOCS)), while the activity of DTM radionuclides is determined by a radionuclide vector. Organic liquids are collected in jerry cans from which a sample is taken and analysed by standard gamma spectrometry for the determination of the ETM radionuclides. Subsequently, a sample is taken for the determination of the total alpha activity and the total beta activity. The activity of the radionuclides is calculated via a radionuclide vector. Both solid and liquid waste types are characterised by the waste producer and are transported to Belgoprocess for incineration at CILVA. At Belgoprocess, the ashes are collected in 200l drums, from which samples are taken and analysed. The drums are eventually compacted and collected in 400l drums, which in turn are conditioned with cement, awaiting surface disposal (cAt project).

Solid organic I/HLW is collected in 200l drums and measured by gamma spectrometry (Q2 or 3AX, Segmented Gamma Scanner), followed by the application of a radionuclide vector. These drums are super compacted and conditioned in 400l drums poured with cement, awaiting geological disposal.

Further information on the determination and validation of the radionuclide vectors in Belgium can be found in [2].

Slovakia

Organic RAW typically includes plastics, sorbents, paper, wood and in case of Slovakia also dowtherm (an organic liquid used to cool down the stored spent nuclear fuel at the A1 nuclear power plant). According to waste acceptance criteria for RAW repository, organic RAW are not allowed for direct disposal, it must be pre-treated by incineration. Solid and liquid organic RAW are burned in the incineration facility at temperature 750 – 950°C followed by afterburning at temperature 1100°C in the post-combustion chamber. The facility is equipped with a device enabling taking ash samples during incineration process. Representative sampling has to be performed from the ash tank directly before its next treatment, after maximum possible homogenization of the tank contents. Ash arising from the incineration process is fixed in 200 l barrels by means of a fixation matrix, which is paraffin. Drums with ash are intended for conditioning by cementation into fibre reinforced concrete container, that is the only waste package allowed for disposal.

All incoming organic RAW is measured by gammascanner to determine total gamma/beta and specific radioactivity. Scaling factors (SF) for all key radionuclides have been developed for the ash coming from incinerator. According to [2], SFs are calculated as a linear regression of measured values, excluding low detection limit values. The only requirement to be met after identification of the outliers is that the regression coefficient should be greater than 0.8. However, in the case of poor correlation, linear regression of logarithms supported by statistical tests is used as the applicable calculation method.

Spain

In Spain, several management routes are considered:

- Scintillation cocktails (from non-nuclear producers) are incinerated at El Cabril repository to solidify them, and then mortar is used to create blocks from the ashes. The incinerator is of the excess air type, with a double combustion chamber. A temperature of 800°C is reached in the first, and 1000°C in the post-combustion chamber. At the chamber outlet there is a silicon carbide high-temperature filter. The fumes are cooled by dilution in fresh air to 140°C. The flue gases then pass through very high efficiency filters and once filtered are discharged through the stack.
- Oils and greases coming from the operational or dismantling equipment and tools, are stored in the interim storage of NPPs;
- Experiments are ongoing to treat liquid wastes used for decontamination abroad by incineration (slags and fly ashes will be sent back to Spain).

Gamma spectrometry is used to determine the RN inventory non-destructively, as well as the beta-/gamma-emitting RN.

4.4.2 Radioanalytical characterisation of organic waste

Non-conditioned waste

NDA – Non-destructive analysis

Table 8 summarises the non-destructive methods for radioanalytical analysis of non-conditioned organic wastes. The information in the following table is provided by Cyprus, Greece, Portugal, Slovakia, Spain and Ukraine. The methods include dosimetry, gamma scanning and spectrometry. In general, dosimetry is used to determine the dose rate of the organic waste. Gamma spectrometry is used to determine the RN inventory non-destructively, as well as the beta-/gamma-emitting RN. The topology as well as the RN inventory (via gamma-induced reactions) are determined using gamma scanning.

Parameters	**Radioanalytical characterisation methods**
Dose rate	• Dosimetry (Cyprus, Greece, Portugal, Slovakia, Ukraine)
RN inventory (incl. SL and LL)	• Gamma scanning / spectrometry (Greece, Ukraine)
Beta-/Gamma-emitting RN	• Gamma-spectrometry (Cyprus, Slovakia, Spain)
Decontamination factor (after treatment)	• Gamma spectrometry (Slovakia) • Dosimetry (Slovakia)

Table 8 - Radioanalytical characterisation methods (NDA) for non-conditioned organic waste

DA – Destructive analysis

Table 9 summarises the destructive radioanalytical methods based on sampling of organic wastes. The information is provided by Cyprus, Greece, Portugal, Slovakia, and Spain. Due to the liquid waste form sampling is easier than for solid waste and measurements can be done by mixing the sample with a scintillation cocktail. For solid waste, the sample must be dissolved and then extracted, e.g., by liquid-liquid extraction prior using the methods listed below. In case the sample contains a mixture of different RN, these can be extracted by liquid-liquid extraction (e.g., $^{59/63}$Ni, ^{99}Tc), selective precipitation (e.g., ^{36}Cl, $^{41/45}$Ca, $^{55/59}$Fe, ^{129}I), extraction chromatography (e.g., $^{89/90}$Sr) or ion exchange chromatography (e.g., ^{241}Pu). ^{3}H or ^{14}C can be measured after separation by oxidation in specific combustion ovens. After sampling the aliquots are dissolved/diluted in order to extract the RN and to measure them effectively. Further information can be found, e.g., in [18].

Parameters	**Radioanalytical characterisation methods**
RN inventory (incl. SL and LL)	• Liquid scintillation counter (Portugal, Slovakia, Spain[6])
Alpha-emitting RN	• Liquid scintillation counter (Cyprus) • Alpha spectrometry (Slovakia, Spain)
Beta-/Gamma-emitting RN	• Liquid scintillation counter (Greece, Portugal, Spain) • Beta counting (Slovakia)
^{3}H and ^{14}C release	• Liquid scintillation counter (Spain)
Gross alpha and beta	• Contamination monitor (swipe test) (Greece)

Table 9 - Radioanalytical characterisation methods (DA) for non-conditioned organic waste

The alpha-RN inventory is usually determined by liquid scintillation counting or alpha spectrometry. Tritium and ^{14}C are solely determined by LSC. Beta- and gamma-emitting RN are determined using LSC or beta counting (total alpha-beta-counter).

Additionally, mass spectrometric methods (e.g., ICP-MS) can be used to determine RN, especially low concentration RN with high half-life.

<u>Conditioned waste</u>

Organic wastes are generally treated by incineration, e.g., in Slovakia whereas this type of RAW is excluded from direct disposal according to valid WAC. Ash arising from the incineration process is fixed in 200 l barrels by means of paraffin. Final conditioning method is fixation in cement matrix. Conditioned RAW is inserted into a special fibre concrete (concrete reinforced with steel fibres) container (dimensions: 1.7 x 1.7 x 1.7 m) and cemented, which is the only waste form allowed for disposal at low-level RAW repository in Mochovce.

NDA – Non-destructive analysis

Table 10 summarises non-destructive methods for radioanalytical analysis of conditioned organic wastes. The information in the following table have been provided by Germany, Greece, Portugal and Slovakia. Most methods are based on gamma radiation measurements. For swipe tests, alpha and beta radiation are analysed.

6 ^{3}H, ^{14}C, ^{36}Cl, $^{41/45}$Ca, ^{54}Mn, $^{55/59}$Fe, $^{59/63}$Ni, ^{58}Co, ^{60}Co, ^{65}Zn, $^{89/90}$Sr, $^{93m/94}$Nb, ^{95}Zr, ^{99}Tc, ^{106}Ru, ^{108m}Ag, ^{110m}Ag, ^{125}Sb, ^{129}I, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, $^{239/40}$Pu, ^{241}Pu, ^{241}Am, ^{242}Cm & ^{244}Cm.

Parameters	**Radioanalytical characterisation methods**
Surface contamination (swipe test)	• Ionisation chamber (Greece, Portugal)
Dose rate	• Dosimetry (Greece, Slovakia)
RN inventory (LL)	• Gamma spectrometry (Portugal, Slovakia) • Ionisation chamber (Portugal)
Package integrity	• Dosimetry (Portugal) • Gamma spectrometry (Portugal) • Prompt gamma neutron activation analysis (Germany)

Table 10 - Radioanalytical characterisation methods (non-destructive) for conditioned organics

In general, dosimetry can be used as survey method to determine dose rates of high-activity organic waste. Gamma spectrometry is used to determine the RN inventory non-destructively. The topology as well as the package integrity are determined by active gamma scanning. Ionisation chambers are used to analyse surface contamination, as well as the RN inventory.

DA – Destructive analysis

Table 11 summarises the sampling-based radioanalytical methods used to analyse conditioned organic waste. The information is provided by Portugal. After sampling the aliquots are dissolved/diluted in order to extract the RN and to measure them effectively.

To ensure safe packaging, surface contaminations due to leakage are determined via swipe test and subsequent liquid scintillation counting. The package integrity is monitored by ionisation chambers or total alpha-beta counting after performing swipe tests.

Parameters	**Radioanalytical characterisation methods**
Surface contamination (swipe test)	• LSC (Portugal)
Package integrity	• Ionisation chamber (Portugal) • Total alpha-beta counting (Portugal)

Table 11 - Radioanalytical characterisation methods (sampling) for conditioned organics

4.5 Identification of radioanalytical techniques: SIERs

In a nuclear facility, circulating water and water released to the environment are filtered to remove radiological contamination. This filtration process results in wastes that may be composed of spent ion exchange resins (SIERs), zeolites and diatoms. After filtration, the spent ion exchange resins contain a variety of radionuclides making a characterisation necessary.

Once ion exchange resins are spent, they have to be conditioned for fixation and immobilisation by means of bitumization, cementation (Slovenia, Spain, France, Slovakia) or utilizing a matrix of epoxy polymers. Prior to conditioning, pre-treatment and treatment is necessary to avoid chemical reactions inside the waste matrix. Means of pre-treatment are dewatering inter alia by centrifugation, e.g., used in Germany, chemical treatment, e.g., used in France. Treatment methods are e.g., heat treatment/evaporation in casks (Germany, Slovenia) or geopolymerization (Slovakia).

4.5.1 Approaches & Experience on characterisation of SIERs

France

Spent ion exchange resins (SIERs) are a widespread waste stream derived from radioactive water treatment and filtration. In nuclear facilities, circulating water and water released to the environment are filtered to remove radiological contamination. Several treatments for the short-lived, low and intermediate level waste (LILW-SL) resins exist in France. This is depending on the waste producer. One conditioning process uses an epoxy-based polymer, the other a cement matrix. In the remainder of this section, we will focus only on cemented resins.

It should be noted that for conditioning in a cement matrix, the resins could be pre-treated to avoid any chemical reaction with the cement.

The knowledge of the activity of the resins allows the waste producer to manufacture packages that meet the waste acceptance criteria (WAC) of the storage facilities. Indeed, the cement-resin mixture is deposited in a 400-liter non-alloy steel drum whose thickness varies according to the activity of the resins. The drum is then placed in a fiber concrete container and immobilized by injection of a cement-based mortar.

The activity is determined from the results of radiological analyses carried out on samples of resins taken from the homogenization tank (before treatment and cementing), completed by the application of ratios. This scaling factor allows the measurement of pure beta emitters such as ^{60}Co, ^{90}Sr or ^{63}Ni.

Chemical characterisations are also carried out for Na, Mg, Cl, F, NO_3, NO_2 and PO_4 on raw resins before treatment to ensure the compatibility of the waste with the cement matrix.

For SIERs, one of the characterisation issues is essentially on the ILW-LL resins because, as organic compounds, the radiolysis of SIERs could lead to the production of hydrogen and complexing compounds.

Germany

The characterisation of SIERs in Germany is typically based on the dosimetry to determine the dose rate and gamma-spectrometry to determine the distinct beta/gamma emitters (e.g. ^{60}Co, ^{134}Cs, ^{137}Cs, ^{54}Mn). For further analysis, LSC is used to determine other alpha- and beta-/gamma-emitters diffusing from defects in fuel rod cladding such as ^{241}Pu or fission products, which are subsequently transported in the water circulation and captured by ion exchange in the resin. AMS is applied for ^{14}C determination.

For treatment, SIERs from NPPs in Germany are typically dewatered (e.g. by centrifugation) and dried (e.g. in-drum drying) in order to achieve a reduction of waste volume.

Greece

Spent Ion Exchange Resins (SIERs) were produced during the operation period from 1961 to 2004 of the Greek research reactor (GRR-1). The radiological characterisation of SIERs was carried out from 2003 to 2006 by collecting samples of primary waste from different depths of each waste drum. Then, the samples were analysed by gamma spectrometry by using NaI detector as well as HPGe detector (for intercalibration between the two detector systems). The waste drums were also measured by non-destructive gamma spectrometry based on NaI detector and the results were in good agreement with the sampling results [18]. This confirmed the homogeneous distribution of activities in each drum.

In addition, by studying gross beta and gamma spectroscopy analysis data of liquid wastes that were being produced during the regeneration procedure, the presence of pure beta emitters was ruled out. The gross beta and gross gamma analysis results of the regeneration liquid waste even during the time span in which the ^{137}Cs activity in resins reached the highest values did not show any significant difference and thereupon no evidence for the presence of ^{90}Sr or other pure beta emitters from fission. In general, the gross beta activity of liquid waste was up to two times greater than the gross gamma activity. So, the presence of pure beta from activation like ^{63}Ni is also negligible. Furthermore, the gamma spectrometry analysis results of regeneration liquid confirmed that the radionuclides, which should be taken into account in the summation formulas for verification of clearance are ^{108m}Ag, ^{137}Cs, ^{152}Eu and ^{60}Co.

4.5.2 Radioanalytical characterisation of SIERs

Non-conditioned waste

NDA – Non-destructive analysis

Table 12 summarises the non-destructive radioanalytical characterisation methods for non-conditioned SIERs. The information are provided by Bulgaria, France, Germany, Greece, Slovakia, Slovenia, Spain and Ukraine. Characterisation is done mostly prior to pre-treatment or treatment, although characterisation methods applicable after (pre-)treatment are available. Most frequently used characterisation methods include gamma spectrometry, gross alpha and beta counting and scaling factors.

Parameters	Radioanalytical characterisation methods
Dose rate	• Dosimetry (Bulgaria, France, Germany, Greece, Ukraine) • Passive gamma scanner/gamma spectrometry (Slovakia)
RN inventory (incl. SL and LL)	• Gamma-Spectrometry (Bulgaria, France, Germany, Greece, Slovakia, Slovenia, Ukraine) • Gross alpha/gross beta counting (Bulgaria)
Inventory of ^{226}Ra and ^{232}Th	• Gamma spectrometry (Greece)
Alpha-emitting RN	• Gross alpha counting (Bulgaria)
Beta-/Gamma-emitting RN	• Gamma-spectrometry (Bulgaria, Germany (^{60}Co, ^{137}Cs, ^{134}Cs, ^{54}Mn), Slovakia, Spain (^{59}Fe, ^{59}Ni and ^{129}I)) • Beta-counting (Bulgaria, Slovakia)
Scaling factor	• Scaling factor based on $^{60}Co/^{137}Cs$ activity determination (Slovakia, Slovenia)
Gross alpha and beta (after pre-treatment)	• Contamination monitor (Greece)

Table 12 - Radioanalytical characterisation methods (NDA) for non-conditioned SIERs

DA – Destructive analysis

Table 13 summarises the destructive radioanalytical characterisation methods for conditioned SIERs provided by Bulgaria, Germany, Greece, Slovakia, Slovenia, Spain and Ukraine. As for the non-destructive radioanalytical characterisation methods, most characterisation is done prior to pre-treatment of the waste. A common method is liquid scintillation counting for the determination of different parameters. The necessary pre-processing steps depend on the radionuclides to be determined. Additionally, alpha spectrometry is frequently used for the characterisation of different alpha-emitting radionuclides. Other methods are mass spectrometry, scaling factors or extraction chromatography.

Parameters	Radioanalytical characterisation methods
RN inventory (incl. SL and LL)	• Liquid scintillation counter (Bulgaria, Germany, Slovakia) • Sampling and radiochemical analyses for DTM radionuclides (Greece, Ukraine) • Scaling factors (Slovenia, Ukraine) [2]

Parameters	**Radioanalytical characterisation methods**
	• Radiochemistry[7] (Spain) • Mass-spectrometry (Germany, Ukraine) • Extraction chromatography (Ukraine)
Inventory of ^{226}Ra and ^{232}Th	• Alpha spectrometry after separation (ion exchange chromatography and liquid-liquid extraction / electrochemical plating) (Greece)
Alpha-emitting RN	• LSC (Germany) • Alpha spectrometry after separation (ion exchange chromatography and liquid-liquid extraction) / electro-chemical plating (Germany, Slovakia, Spain)
Beta-/Gamma-emitting RN	• Liquid scintillation counter after separation by liquid-liquid extraction ($^{59/63}$Ni, ^{99}Tc), selective precipitation (^{36}Cl, $^{41/45}$Ca, $^{55/59}$Fe, ^{129}I), extraction chromatography ($^{89/90}$Sr), ion exchange chromatography (^{241}Pu) (Germany, Spain)
Fissile material	• Alpha-spectrometry after electro-chemical plating (Germany)
^{3}H and ^{14}C release	• Liquid scintillation counter (Bulgaria, Germany, Slovakia, Spain) • Mass spectrometry (Accelerator MS & Noble gas MS) (Bulgaria, Germany)
Scaling factor	• Scaling factor based on ^{60}Co/^{137}Cs activity determination (Slovakia, Slovenia)

Table 13 - Radioanalytical characterisation methods (DA) for non-conditioned SIERs

Conditioned waste

Characterisation of conditioned waste might be necessary for ensuring the correct declaration of conditioned waste drums and the treatment and conditioning of waste works correctly. Additionally, regular checks of the conditioned waste drums might be necessary in terms of surface contamination and degradation, e.g., due to radiolysis and subsequent gas generation.

NDA – Non-destructive analysis

Table 14 summarises the non-destructive characterisation methods for conditioned SIERs used in Bulgaria, France, Greece, Slovakia and Slovenia. Different techniques are used to characterise parameters relevant for conditioned SIERs.

Parameters	**Radioanalytical characterisation methods**
Dose rate	• Dosimetry (Bulgaria, Slovakia, Slovenia)
RN inventory (incl. SL and LL)	• Scaling factor (France)
Free liquids	• X-ray technique (France)
Surface contamination (swipe test)	• Alpha-beta contamination monitor (Bulgaria, Greece, Slovakia)

[7] ^{3}H, ^{14}C, ^{36}Cl, $^{41/45}$Ca, ^{54}Mn, $^{55/59}$Fe, $^{59/63}$Ni, ^{58}Co, ^{60}Co, ^{65}Zn, $^{89/90}$Sr, $^{93m/94}$Nb, ^{95}Zr, ^{99}Tc, ^{106}Ru, ^{108m}Ag, ^{110m}Ag, ^{125}Sb, ^{129}I, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, $^{239/40}$Pu, ^{241}Pu, ^{241}Am, ^{242}Cm & ^{244}Cm.

Parameters	**Radioanalytical characterisation methods**
	• Gamma spectrometry (swipe test) (France, Slovakia)

Table 14 - Radioanalytical characterisation methods (NDA) for conditioned SIERs

DA - Destructive analysis

Table 15 summarises the destructive characterisation methods for conditioned SIERs used in Bulgaria, France, Germany, Slovakia and Spain. Different techniques are used to characterise parameters relevant for conditioned SIERs. It should be emphasised, that for conditioned waste sampling is more difficult than prior conditioning.

Parameters	**Radioanalytical characterisation methods**
RN inventory (incl. SL and LL)	• Scaling Factor (France, Slovakia)
Cement properties	• Leaching and diffusion resistance (Slovakia, Spain)
Gas generation	• Degassing control (France)
Surface contamination (swipe test)	• Liquid scintillation counter (Swipe test) (Bulgaria, Germany)

Table 15 - Radioanalytical characterisation methods (DA) for conditioned SIERs

4.6 Identification of radioanalytical techniques: U/Ra/Th bearing Wastes

In some countries there is U/Ra/Th bearing waste for example from oil, gas, phosphate/fertilizer industry with very high concentration in natural radionuclides and possibly in large amounts. These sometimes are considered as radioactive waste. The natural radionuclides are not in secular equilibrium because of chemical processing. Due to this, radiological characterisation is challenging. In this type of waste there are easy to measure radionuclides (i.e., gamma emitters) and difficult to measure radionuclides (i.e., alpha, pure beta and low energy gamma emitters). So, to characterise these wastes, destructive and non-destructive techniques should be combined.

4.6.1 Approaches & Experience on characterisation of U/Ra/Th bearing waste

Cyprus

Phosphogypsum (PG) is the by-product of the phosphoric acid industry and is obtained by reacting phosphate rock with sulphuric acid. Approximately 320,000 tons of PG produced by a former phosphate fertilizer industry in Vasiliko-Cyprus have been disposed at a coastal area of about 50,000 m^2. Radiometric measurements have shown that the PG contains increased amounts of uranium (21 – 320 Bq/kg) and radium (430 – 1050 Bq/kg), and emanates radon at levels that could be of radiological concern if the PG would be used as building material (e.g. gypsum boards). On the one hand, experimental investigations along with thermodynamic calculations have shown that increased salinity affects the solubility of PG resulting in increased uranium levels in the corresponding solutions. On the other hand, different composition of stack fluids and leachates results in significantly different uranium speciation in the corresponding solutions. Furthermore, changes in the redox conditions (e.g. after the application of a vegetative cover) affect the redox speciation of uranium and subsequently the mobility of uranium in the system.

For PG and stack fluid sampling there have been drilled four monitoring/probing wells into the PG body and samples were obtained at each meter with a maximum well depth of 5 meters. Radiological characterisation included on site γ-dose measurements, γ-measurements of PG drilling samples by high-resolution semiconductor detection systems (HPGe detectors, Canberra), alpha spectroscopy for uranium analysis in PG and stack solutions by (Alpha Analyst Integrated Alpha Spectrometer, Canberra) and radon emanation measurements and radium levels after edta-mediated sample dissolution by a radon monitoring system (Radon/Thoron monitor RTM1688-2, Sarad).

The mobility of uranium within the PG body was evaluated by radiochemical analysis of the uranium and thorium isotopes, and speciation calculations for uranium were performed using the chemical speciation software MINTEQA2 (Allison Geoscience Consultants Inc.). Calculations were performed for saturated gypsum solutions and 0.03% CO_2 atmosphere.

France

French uranium mining took place from 1948 to 2001. Tailings and heap leaching were generated through the treatment of uranium-bearing ores at approximately 250 sites. Due to the large quantities of tailings and heap leaching, about 50 million tons, the disposal of these wastes has been carried out as they were produced, in dedicated in-situ receptacles or depressions (open pits, basins, thalwegs) specifically designed. The former mine operator is responsible for the 17 tailings storage facilities in France.

The tailings have been characterised by operator gamma spectrometry and the radionuclide concentration is well documented. These mainly concern the radium series and the uranium series.

The current challenges in radioactivity measurements for mining tails concern the monitoring of the environment, the site, and the engineered barriers (coverage or dam). Indeed, one of the long-term issues is the disintegration of ^{226}Ra to ^{222}Rn, a gas that can accumulate in enclosed spaces like buildings or houses. The aim here is to measure the impact of radioactive gas emissions on individuals, especially in the event of loss of site memory. Another measurement problem is an accurate understanding of the radioactive carrier phase chemistry, in order to know the migration and release of radionuclides in the environment, over long periods of time.

Portugal

In Portugal there is a significant amount of U/Ra/Th bearing waste in raw form from phosphate/fertilizer industry, NORM found in scrap metal industry and some DU waste, which needs specific storage due to safeguards regime. Some of this waste was collected by the WMO, but most of these wastes are in the producers facilities. Some studies have been taken by the WMO, ID-RE and Agência Portuguesa do Ambiente (APA) (or Portuguese Environment Agency) to find a solution for this waste. The Portuguese RW facility is not prepared for this kind of waste. At this time, no treatment and conditioning is performed in Portugal.

4.6.2 Radioanalytical characterisation of U/Ra/Th bearing waste

In the next tables, the destructive and non-destructive techniques, which are used for characterisation of this non-conditioned U/Ra/Th bearing waste in different countries, are presented.

Non-conditioned waste

NDA – Non-destructive analysis

Table 16 summarises the NDA characterisation techniques for non-conditioned U/Ra/Th bearing wastes. The information has been provided by Cyprus, Greece, Portugal, Slovenia and Ukraine.

Parameters	**Radioanalytical characterisation methods**
Dose rate	• Dosimetry (Cyprus, Greece, Portugal, Ukraine) • Gamma spectrometry (Greece, Portugal, Slovenia, Ukraine) • Ionizing chamber (Portugal)
RN inventory (incl. SL and LL)	• Gamma spectrometry (Greece, Portugal, Slovenia, Ukraine)

Parameters	**Radioanalytical characterisation methods**
Inventory of ^{226}Ra and ^{232}Th	• Gamma spectrometry (when ^{222}Rn and ^{226}Ra are radioactive equilibrium) (Greece, Portugal)
Beta-/gamma-emitting RN	• Gamma-spectrometry (Cyprus, Portugal) • Ionizing chamber (Portugal)
Gross alpha/beta	• Contamination monitoring to help sampling (Greece)

Table 16 - Radioanalytical characterisation by non-destructive methods for non-conditioned U/Ra/Th bearing wastes

DA – Destructive analysis

Table 17 summarises the DA characterisation techniques for non-conditioned U/Ra/Th bearing wastes. The information has been provided by Cyprus, Greece, Portugal, Slovenia and Ukraine.

In Greece and Portugal, U/Ra/Th bearing waste is in raw form without any treatment and conditioning. Mostly, it is stored in drums for treatment and conditioning in the future. In Ukraine, Ra/Th bearing waste from the oil industry is already disposed.

In Portugal waste is previously characterised by gamma spectrometry (sometimes WMO works as technical support organisation (TSO) identity also) before collection as radioactive waste. Still, some of this waste can be excluded as radioactive waste, depending on gamma spectrometry characterisation and dose rate measurements.

Parameters	**Radioanalytical characterisation methods**
RN inventory (incl. SL and LL)	• Sampling and radiochemical analysis for DTM (Greece)
Inventory of ^{226}Ra and ^{232}Th	• Sampling, radiochemical treatment and measurement by alpha spectrometry for ^{232}Th, and ^{226}Ra (if no equilibrium) (Cyprus, Greece, Portugal)
Beta-/gamma-emitting RN	• LSC (Portugal)

Table 17 - Radioanalytical characterisation (DA) for non-conditioned U/Ra/Th bearing wastes

4.7 Identification of radioanalytical techniques: Decommissioning Waste

Decommissioning waste typically consists of metals (iron, coper, lead, aluminium etc.), concrete, plastic, filters and soil. For the decommissioning of nuclear reactors, the isotope composition depends on the type of reactor, lifetime of the facility and the operational incidents or accident if any. For other decommissioning waste, e.g. from laboratories, the generated waste volume, type and radiological characteristics depend on the former use of the facility. In decommissioning waste usually there are easy to measure radionuclides (i.e. gamma emitters) and DTM radionuclides, such as pure beta and alpha emitting radionuclides. So, for characterisation non-destructive and destructive techniques are combined.

Besides the radiological characterisation, other physical and chemical properties should be determined like pH for liquids, elemental analysis, organics, free liquids, gas production and strength tests of waste form.

4.7.1 Approaches & Experience on characterisation of decommissioning waste

Belgium

In the early '90s, when the first decommissioning projects in Europe were initiated, the BR3 (Belgian Reactor 3) PWR decommissioning project played an important role in the development and optimization of dismantling strategies through the decontamination of the primary loop followed by the dismantling of highly activated components. More recently, BR3 started playing a prominent role as an in-situ test facility for EU funded R&D projects related to the implementation of effective methods for the initial radiological characterisation process and the process of the building release. Before defining a dismantling strategy, it is essential to characterise the structure and compare results with the requirements for the various disposal options.

Metals collected during decommissioning do not mainly end up as radioactive waste, but the material can also be treated and recycled via decontamination and melting processes. Metallic low level waste can be processed with the aim of clearance. During the metal recycling processes, decontamination of certain fission products occurs (such as Cs, etc.), unlike the elements on the Table of Mendeleev close to Fe, such as Co, Mn, Ni, etc. which remain highly present in the metal. Regarding radiological characterisation, gamma spectrometry measurements are performed, followed by the application of a radionuclide vector. Determination of ^{60}Co is very important, because it plays a major role in defining the disposal route of the material, whether it will be recycled or disposed of as radioactive waste.

For the BR3 decommissioning, the initial material inventory consisted for nearly 90 wt. % of concrete. Basically two types of radiological problems occur for concrete structures:

- Contamination of the building structure, usually resulting from leakages during reactor operation, releases due to maintenance works or even during dismantling operations (raw estimated volume = 75 m^3); and
- Activation of the biological shield (or bioshield), due to rather high neutron fluxes during reactor operation (raw estimated volume = 150 m^3).

The use of an integrated methodology and advanced statistical data processing and modelling for the radiological characterisation process substantially improves the quality of the results and provides a better basis for the decision-making process related to the decontamination/separation and dismantling strategy, which is also in line with sustainability and economic objectives.

For contaminated concrete [19], initial radiological characterisation is essential to allow effective decontamination and serious reduction of the concrete waste production. First, data was gathered using gamma spectrometry measurements (ISOCS - In Situ Object Counting System) and quick dose rate and surface contamination scanning. Next, geostatistical analysis of the data was performed to reduce the number of measurements needed and to integrate different measurement supports and types. Intermediate sampling was performed followed by standard gamma spectrometry in the lab (control measurements). The results of the ISOCS measurements, the geostatistical mapping and the sampling and analysis in the lab were compared. In order to determine the amount of material removed at each location of the floor, laser scanner 3D mapping was performed before and after decontamination. As part of the final control measurements for unconditional release, the complete floor was measured using the ISOCS.

The BR3 biological shield mainly consists of high-density concrete (also known as heavy weight or barite concrete). The main goal of the radiological characterisation program is to economically optimize the biological shield dismantling strategy, using a waste-led approach [20]. Different diagrams for the data analysis and sampling design strategy are used [4]. After defining the objectives and assessing the constraints, available information is analysed and checked against the objectives. This check consists of the following steps: pre-processing, an exploratory step and the actual data analysis, and post-processing to transfer the obtained results into end-stage volumes. Apart from the available plans of the biological shield and the operational history of the reactor operation, results from neutron activation calculations and former characterisation programs were available for designing a preliminary 3D activity concentration distribution map, that includes uncertainty estimates. The second phase sampling strategy consisted of two types of data gathering: 1. Primary data - borehole sampling, sample preparation and in-lab measurements; 2. Secondary data - quick, straightforward and cheap non-destructive in-situ total gamma surface mapping. Subsequently, different end-stage volumes are quantified and localized among which unconditional release (aiming at conventional demolishing and recycling of the building materials), conditional release (for disposing the materials in a category 1 site for classical hazardous materials) and radioactive waste (for final disposal in a nuclear near surface disposal site). Next, test sections are defined, mainly for two purposes. On one hand to test and select on a dismantling strategy. On the other hand, to be used as verification of the modelled activity distribution which is initially based on a limited sampling size.

Germany

During the decommissioning of NPPs, large amounts of contaminated and irradiated metallic wastes are generated. In Germany, an in-situ dosimetry is used to determine the dose rate on these metallic wastes. Samples are taken for further radiochemical analysis in order to characterise the waste from the facility to be decommissioned. Alpha-emitting RN are determined using alpha-spectrometry, beta-/gamma-emitting RN are, e.g., determined using HPGe detectors. For activation calculations, radiation transport codes such as MCNP are used. Special attention is paid to hidden places, which become only accessible to sampling after dismantling and fragmentation of metallic wastes.

Greece

In the frame of T4.5.2 of the PREDIS project [22], two semi-empirical methodologies which are focused on optimization of characterisation of metallic waste are under development at the NCSRD: 1) monitoring of metallic segments; 2) monitoring for validation of the scaling factors. These methodologies are based on combination of non-destructive gamma spectrometry measurements and MCNP Monte Carlo simulations.

Monitoring of metallic segments: The proposed methodology concerns the monitoring by HPGe detectors of metallic segments after dismantling and cutting, aiming at significant reduction of the measurement uncertainties related to the density and activity inhomogeneity of the metallic segments [21].

After dismantling, in-situ characterisation is carried out to classify and package the generated waste [22]. This is usually achieved by using portable devices to measure dose rate or total counts. So far, the segments are put into packages, that are usually of 1-2 m^3 and monitored by the non-destructive gamma spectrometry or plastic scintillators for assessment of the activity and selection of the management route. The measurement uncertainty in this case is usually high, sometimes higher than 90%. The uncertainty is mainly due to the density inhomogeneity as well as the geometry that encompasses the geometry of the measurement package and the positioning of the activities. For localization of the activities and better estimation of radioactivity in waste packages, research based on the use of gamma camera [23] or a system of plastic scintillation detectors [24] is carried out.

For reduction of this uncertainty, a new measurement non-destructive gamma spectrometry layout is proposed by the NCSRD. This layout: 1) allows the reduction of the range of distance between metal segments and the detector; 2) allows the reduction of the range of the solid angles between metal segments and the detector; 3) is based on one layer of metal segments for measurement; 4) is based on the simultaneous use of four gamma ray detectors. The measurement is expected to be effective for determination activities of non-activated as well as of activated metallic waste. The specific activities inside and in the surface contamination of metallic waste will be determined by using the measurement results in combination with the use of the scaling factors for activation and/ or contamination.

For the proposed non-destructive gamma spectrometry layout, the efficiencies of the measurement for several segments geometries (i.e. straight & convex pipes, sheet metals and convex surfaces, etc.) are evaluated by simulations performed by the MCNPX code and the results are compared with the results of simplified geometries (e. g. pipes of specific diameter and thickness, slabs with homogeneous density distribution etc.). Sensitivity analysis against the parameters that affect the measurement efficiency are carried out (e.g. pipe wall thickness, metallic slab thickness etc.). Furthermore, the bias due to activity inhomogeneity for each segments geometry is determined [25].

By the proposed measurement layout, significant reduction of the measurement uncertainty, lower than 30%, can be achieved while the sensitivity of the key radionuclides ^{60}Co, ^{137}Cs is sufficient for acceptable measuring time. The activity of 100kg metallic waste at the level of general clearance, 0.1 Bq/ g, can be determined in less than 2 min because the detection efficiencies are of the order of 10^{-3}. Therefore, better selection of the management route as well as the selection of the appropriate decontamination techniques and clearance procedure can be achieved.

<u>Monitoring for validation of the scaling factors</u>: The methodology concerns the monitoring of metallic components or segments by HPGe detector for validation of the scaling factors. A non-destructive gamma spectrometry technique by using MCNP simulations is proposed for interpretation of the gamma-ray spectra (i.e. energy peaks and continuum) resulting from the radionuclides in the activated and/or contaminated components.

Many radionuclides contained in radioactive waste are difficult to measure (DTM) because they are low energy gamma or pure beta or alpha emitters. Identification of these DTM nuclides requires methods that involve analysis of samples by using radiochemical procedures to separate the various radionuclides for measurement. The approach is the scaling factor (SF) methodology [2]. It is based on developing of a correlation between easily measurable gamma emitting nuclides (key nuclides) and DTM nuclides. The activities of DTM nuclides are then evaluated by measuring the gamma emitting nuclides and applying the scaling factors.

The main key radionuclides which are easy to measure (ETM) are ^{60}Co and ^{137}Cs. ^{60}Co is an activation product radionuclide produced by the ^{59}Co(n,γ)^{60}Co reaction in the 100% abundant stable cobalt isotope ^{59}Co with a cross-section of 18.7 barns [26]. On the other hand, ^{137}Cs is a fission product and due to its high-water solubility is easily transported and settled as surface contamination.

Taking into consideration the uncertainties in SF determination, the proposed innovative non-destructive gamma spectrometry methodology is focused on the validation of semi empirical or theoretical determined SFs.

<u>Slovakia</u>

Main source of decommissioning waste in the Slovak Republic are three nuclear units at the Bohunice site that are currently under decommissioning:

- aged A1 nuclear power plant (gas cooled, heavy water moderated reactor KS-150)
- two units at the Bohunice V-1 NPP (WWER-440/V230 type reactors)

Types of radioactive waste from decommissioning typically include metals (iron, aluminium, coper), activated or contaminated concrete, contaminated soil, concentrates, graphite, plastics, SIERs and sludges. Radiological characterisation of decommissioning RAW is seen as an ongoing process of high priority and importance. That is why radiological characterisation plan is developed and implemented (sometimes referred to as a sampling and analysis plan). The characterisation plan typically includes detailed specifications which set out what characterisation work is required and what methods shall be applied.

The concept for radioanalytical characterisation of RAW is given by operational instructions. They comprise a set of waste streams, key radionuclides to be characterised and scaling factors for each radionuclide and a waste stream. This regulation sets out the basic rules, principles and procedures for declaring the content of radionuclides in RAW processed at nuclear facilities, depending on their origin, physico-chemical form and method of processing. It also defines the responsibility of the producer, processor and operator in declaring the content of radionuclides in RAW in the process of their origin, processing and final disposal.

Declaring the content of radionuclides is realized by gamma spectrometric measurement (determining the specific activity of reference radionuclides ^{137}Cs, ^{60}Co) and subsequent calculation of the activity of other radionuclides by recalculation based on knowledge of conversion (scaling) factors and technological process of RAW treatment.

Scaling factors are calculated based on measurements of radionuclides obtained through appropriate radiochemical analysis, through modelling code calculation or by a combination of both techniques. Conversion (scaling) factors are dependent on:

- type of waste stream,
- RAW origin, state, composition, transfer mechanism,
- type of nuclear facility where it was produced etc.

Gamma spectroscopy method is used for characterisation of gamma emitting nuclides as follows: ^{40}K, ^{54}Mn, ^{58}Co, ^{60}Co, ^{85}Sr, ^{94}Nb, ^{95}Nb, ^{95}Zr, ^{106}Ru, ^{109}Cd, ^{110m}Ag, ^{124}Sb, ^{125}Sb, ^{126}Sn, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{232}Th, ^{238}U.

Low energy photon spectroscopy is used for characterisation of gamma emitting nuclides as follows: ^{55}Fe, ^{59}Ni, ^{93}Mo, ^{93m}Nb, ^{129}I.

Alpha spectroscopy system is used for characterisation of alpha emitting nuclides as follows: ^{147}Sm, ^{229}Th, ^{230}Th, ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{242}Cm, ^{243}Cm, ^{244}Cm.

Liquid scintillation counter is used for characterisation of DTM nuclides as follows: ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{63}Ni, ^{79}Se, ^{90}Sr, ^{93}Zr, ^{99}Tc, ^{107}Pd, ^{147}Pm, ^{151}Sm, ^{204}Tl, ^{241}Pu.

Spain

The challenge of this massive waste coming from dismantling of nuclear facilities or workshop is to categorize properly in order to reduce the volume of the Medium low level waste (MLW), Low level waste (LLW) and Very low level waste (VLLW) in order to get a maximum of Excepted Waste (EW). On the other hand, the heterogeneity of this waste oblige to develop specific methods for radiological characterisation development of scaling factors and chemo toxic material concentrations in the generated waste (soil; rubble; debris; concrete). The uncertainties associated with the decommissioning waste are:

- Large volume pieces or workshop areas (e.g., hot cells) characterisation further than dose rate, surface contamination or dose to Curie methods (e.g. Microshield®)
- Heterogeneity in the determination of alpha and beta emitters in categorization processes
- Non-destructive techniques to apply together with a reliable scaling factors

4.7.2 Radioanalytical characterisation of decommissioning waste

Non-conditioned waste

Pre-treatment of decommissioning waste in Germany consists of dismantling and fragmentation. In Slovakia, decommissioning wastes are sorted, segmented and decontaminated by abrasive blasting. Both Germany and Slovakia use melting and super-compaction as treatment and conditioning for decommissioning wastes, e.g. metals.

NDA – Non-destructive analysis

Table 18 summarises the NDA characterisation methods used for non-conditioned decommissioning waste in Bulgaria, Germany, Greece, Slovakia and Ukraine. In general, these are dosimetry and gamma spectrometry. For RN inventory determination, gross alpha and beta counting is used additionally.

Parameters	Radioanalytical characterisation methods
Dose rate	• Dosimetry (Bulgaria, Germany, Greece, Slovakia, Ukraine) • Thermo-luminescence dosimetry (Ukraine)
RN inventory (incl. SL and LL)	• Gamma spectrometry (Bulgaria, Greece, Slovakia, Ukraine) • Gross alpha/beta counting (Bulgaria)
MCNP-modelling	• Activation calculation (Germany, Slovakia) • Gamma-spectrometry (Greece)

Table 18 - Radioanalytical characterisation methods (NDA) for non-conditioned decommissioning waste

DA – Destructive analysis

Table 19 summarises the DA characterisation methods used for non-conditioned decommissioning waste in Bulgaria, Germany, Greece, Slovakia, Slovenia Spain and Ukraine.

Parameters	Radioanalytical characterisation methods
RN inventory (incl. SL and LL)	• Scaling factor (Germany, Greece, Slovenia, Ukraine) • LSC (^{3}H, ^{90}Sr, ^{14}C) (Bulgaria, Slovakia) • Mass-spectrometry (Ukraine) • Radiochemistry[1] (Spain) • Extraction chromatography (Ukraine) • Statistical analysis of specific activities of key RN and DTM RN (Ukraine)
Alpha-emitting RN	• Alpha spectrometry after separation by ion exchange chromatography and liquid-liquid extraction (e.g., ^{241}Am, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Cm, ^{244}Cm, ^{234}U, ^{235}U and ^{238}U) (Bulgaria, Germany, Slovakia, Spain)
Beta-/Gamma-emitting RN	• Gamma spectrometry after separation liquid-liquid extraction (^{59}Ni), selective precipitation (^{59}Fe, ^{129}I) (Bulgaria, Germany, Slovakia, Spain) • LSC after separation by liquid-liquid extraction (^{63}Ni, ^{99}Tc), selective precipitation (^{36}Cl, ^{41}Ca, ^{45}Ca, ^{55}Fe), extraction chromatography (^{89}Sr, ^{90}Sr), ion exchange chromatography (^{241}Pu) (Bulgaria, Spain)
Fissile materials	• Alpha spectrometry (Germany, Ukraine)
^{3}H and ^{14}C release	• noble gas mass spectrometry (Bulgaria) • LSC (Bulgaria, Spain) • Accelerator Mass Spectrometry (Bulgaria)
Scaling factor	• DTM RN-specific analysis (Germany) • Preliminary RN vector (Ukraine)

Parameters	**Radioanalytical characterisation methods**
RN inventory (after treatment) (incl. SL and LL)	• Radiochemistry of slags and filters (secondary waste of metallic decommissioning waste after melting) (Germany)
Decontamination factor (after treatment)	• Gamma spectrometry (Slovakia) • Dose rate measurements (Slovakia)
Scaling factors (after treatment)	• Calculation e.g. for metals with Co due to ^{55}Fe (Germany)

Table 19 - Radioanalytical characterisation methods (DA) for non-conditioned decommissioning waste

<u>Conditioned waste</u>

NDA – Non-destructive analysis

Table 20 summarises the NDA methods for conditioned decommissioning wastes in Bulgaria, Germany and Slovakia. As most radioanalytical characterisation is before conditioning, methods for conditioned waste from decommissioning are mainly based on dosimetry or gamma spectrometry.

Parameters	**Radioanalytical characterisation methods**
Dose rate	• Dosimetry (Bulgaria, Germany, Slovakia)
RN inventory (incl. SL and LL)	• Gamma spectrometry (Bulgaria, Slovakia) • MCNP (Germany)
Surface contamination	• Alpha-beta contamination monitor (Bulgaria, Slovakia)

Table 20 - Radioanalytical characterisation methods (NDA) for conditioned decommissioning waste

DA – Destructive analysis

Table 21 summarises the DA radioanalytical characterisation methods for conditioned decommissioning waste in Bulgaria and Germany. The main aim of these methods is the determination of contamination, where alpha spectrometry is used to analyse swipes.

Parameters	**Radioanalytical characterisation methods**
RN inventory (incl. SL and LL)	• Alpha spectrometry (Bulgaria)
Surface contamination	• Swipe test (Bulgaria, Germany)

Table 21 – Radioanalytical characterisation methods (DA) for conditioned decommissioning waste

[1] ^{3}H, ^{14}C, ^{36}Cl, $^{41/45}Ca$, ^{54}Mn, $^{55/59}Fe$, $^{59/63}Ni$, ^{58}Co, ^{60}Co, ^{65}Zn, $^{89/90}Sr$, $^{93m/94}Nb$, ^{95}Zr, ^{99}Tc, ^{106}Ru, ^{108m}Ag, ^{110m}Ag, ^{125}Sb, ^{129}I, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, $^{239/40}Pu$, ^{241}Pu, ^{241}Am, ^{242}Cm & ^{244}Cm.

5. Analysis of radioanalytical characterisation

Within this chapter, the applied characterisation approaches discussed in the previous chapter for each selected waste type are analysed. Based on the analysed knowledge and experience, issues and underlying knowledge gaps have been identified in order to give recommendations for further R&D to eliminate them.

5.1 Analysis of existing approaches

This section summarises the characterisation approaches of the previous chapter for each of the selected waste types. The selection includes graphite, sludge, organic waste, SIER, U/Ra/Th bearing waste and decommissioning waste.

Graphite

For graphite, various approaches are chosen by MS. In general, radioanalytical characterisation is based on destructive measurements and radiation transport simulations, although some countries, e.g., Greece, only use simulations for a preliminary characterisation. In case of France, no WAC have been defined for graphite, therefore only preliminary characterisation is done. Initial sampling and radiological characterisation of irradiated graphite was carried out in Slovakia

Sludge

For sludge, the key RN identified by responding countries, such as ^{134}Cs, ^{137}Cs, ^{60}Co and ^{54}Mn, are characterised by gamma-spectrometry or mass spectrometry. Additionally, Monte Carlo simulations support the radioanalytical characterisation. For DTM radionuclides, which might be present e.g. in oil-based muds from petroleum engineering and are therefore the RN are not in secular equilibrium, different techniques for radiochemical analysis are applied.

Organic wastes

Organic wastes are either characterised prior or post treatment. In Slovakia and Spain, the ashes from incineration are characterised, e.g. by LSC or gamma spectrometry. Belgium characterises key RN and ETM RN by gamma spectrometry and utilises scaling factor and alpha spectrometry for DTM RN.

SIERs

Samples from SIERs are taken after homogenisation of tank content or from different depth of the tank, to confirm homogeneous distribution. Common characterisation techniques are the gamma-spectrometry. In France, scaling factors are utilised to determine pure beta emitters, while for Greece SIERs originating from a research reactor, beta emitters are negligible. Additional characterisation methods used for SIERs in Germany are LSC for the determination of fission products and Plutonium, as well as accelerator mass spectrometry to determine ^{14}C.

U/Ra/Th bearing wastes

Characterisation approaches for U/Ra/Th bearing wastes are highly depended on the specific origin of the waste. In Cyprus, samples of phosphogypsum containing U, Ra and Rn are taken by drilling. These samples are subsequently analysed using dosimetry, gamma-spectrometry, alpha-spectrometry as well as Rn emanation and Ra monitoring. France is analysing uranium mining tailings using gamma spectrometry and determination of Ra and U concentrations. Portuguese U/Ra/Th bearing waste originates from the phosphate and fertiliser industry, as well as imported contaminated metal scrap, for which currently no procedure has been established.

Decommissioning waste

Common characterisation approaches for all decommissioning wastes are the utilisation of dosimetry and gamma spectrometry. These techniques are both used for laboratory analysis and in-situ. In Belgium, metallic decommissioning waste is additionally characterised using scaling factors. In Germany, metallic decommissioning wastes are additionally analysed using alpha spectrometry and nuclear transport codes, such as MCNP. Concrete decommissioning waste is analysed by Belgium using surface contamination scanning and geostatistical analysis to reduce the amount of samples. In Slovakia, besides dosimetry and gamma spectrometry, low energy photon spectroscopy, alpha spectroscopy, LSC and scaling factors are used to determine concrete decommissioning waste. Spain additionally uses surface contamination measurements.

5.2 Analysis of existing issues

Existing issues have been gathered and analysed, in order to separate existing knowledge gaps from technical, organisational or financial issues. This section describes the issues, both for waste characterisation in general and waste type specific characterisation, raised by participating organisations of this task.

Common issues for liquid and solid waste characterisation are representative sampling, priorisation of wastes, which is especially an issue for legacy wastes, as well as legislative challenges.

Graphite

- Graphite is often used as moderator in research reactors, which need a specific decommissioning strategy due to its singularity. The dismantling and subsequent sampling of graphite therefore commonly provides a challenge.
- Another issue for the radioanalytical characterisation of graphite waste is the absence of WAC, both for storage and disposal, in order to facilitate target-oriented characterisation.
- Among others, WAC should define the limit for Wigner energy still acceptable for final disposal. In order to predict the release of Wigner energy, activation energy spectra can be derived from differential scanning calorimetry of graphite samples. ^{226}Ra and ^{232}Th inventory characterisation is required and usually measured by alpha spectrometry.
- The determination of ^{36}Cl content also appears as crucial in order to help identifying disposal options.

Sludge

Various issues of sludge wastes have been mentioned by member states.

- Due to the segregation, representative sampling is challenging.
- Issues also arise from chemical properties such as reactivity, inflammability or gas generation.
- Sludge from other industries such as oil- and gas-industry have the issue of transferability of regulations, as well as the big volumes to be handled.

Organic wastes

- Sampling is the main issue for organic wastes. Challenges provide the sampling of high active organic wastes due to radiolysis and subsequent gas production, as well as the sampling from two phase or unknown samples.
- Other issues concern the legislation for treatment of organic wastes and the volume of non-compacted organic waste in interim storage.

SIERs

- Issues in the predisposal route for SIERs commonly originate from missing legislation, e.g. undeveloped WAC.

- Additional issues arise, if SIERs are either part of legacy wastes or mixed wastes, challenging the sampling as well as the radioanalytical characterisation process.
- Specific issues mentioned for the characterisation of conditioned waste were the incident analysis and the gas generation due to radiolysis.
- For non-conditioned mixed waste containing SIERs, the challenged in the determination of ^{226}Ra and ^{232}Th inventories have been highlighted.

U/Ra/Th bearing wastes

- The variety of waste types containing U/Ra/Th bearing wastes is one of the challenges associated with it. Even for U/Ra/Th bearing wastes from the same industry, such as oil and gas, may largely differ in its scaling factors due to different geological settings.
- Another issue is the large volume of U/Ra/Th bearing wastes, especially from non-nuclear facilities.
- A specific issue raised, is the monitoring of ^{222}Rn release, especially for open pit storage of uranium mining tailings.
- For U/Ra/Th-contaminated metal scrap, the sampling might be challenging in specific cases.
- Additionally, in some countries the legislation is an issue for U/Ra/Th bearing wastes.

Decommissioning waste

Wastes from decommissioning is a broad category, therefore only general issues have been mentioned by participating countries.

- These can be subsumed under the challenge of representative sampling of decommissioning waste, both due to large volumes and mixed wastes.
- A challenge for decommissioning waste is the reduction of waste volume classified as LLW and VLLW and increase the volume classified as exempted waste (if the option of waste release is available in a country).

5.3 Analysis of knowledge gaps

Based on the issues presented in Section 5.2, knowledge gaps have been identified. The origin of most characterisation issues are of financial or legislative nature, only a minority is based on missing input from research and development.

One identified knowledge gap is **the optimal predisposal route of high activity liquids**. One common treatment of liquids is the incineration, which should not be performed for high activity liquids due to the risk of gas release. France is currently investigating new polymer matrices, which are applicable for high activity liquids.

For graphite waste, two knowledge gaps have been identified:

- An unsolved challenge is the **determination of a Wigner energy threshold for graphite waste**, which can be classified as safe for final disposal.
- Secondly, **scaling factors and their validation for graphite waste need to be improved**.

Identified knowledge gaps of sludge characterisation originate from the potentially large volumes of this waste, both unconditioned and conditioned, and the non-destructive characterisation of waste drums:

- **For characterisation of large amounts of sludge, methodologies need to be developed for representative sampling and characterisation for sludge where radionuclides in U/Ra/Th bearing wastes are not in an equilibrium**, e.g. as for sludge from oil and gas industry.
- **For the characterisation of sludge by gamma-spectrometry the correction factors need to be improved**, e.g. by validated determination of solid residues in sludge drums, which impact the analysis due to self-absorption caused by density inhomogeneity and inhomogeneity in activity.

For SIERs, techniques for the re-characterisation of solidified SIERs by non-destructive measurements are missing.

Two knowledge gaps for U/Ra/Th bearing wastes have been identified:

- First, **for the characterisation of U/Ra/Th bearing wastes by gamma-spectrometry the correction factors need to be improved**, e.g. by validated determination of solid residues in U/Ra/Th bearing wastes, which impact the analysis due to self-absorption caused by density inhomogeneity and inhomogeneity in activity.
- Additionally, **methodologies need to be developed for representative sampling for wastes where radionuclides in U/Ra/Th bearing wastes are not in an equilibrium**.

Due to the variety and potentially large structures, decommissioning wastes provide several challenges:

- **a methodology for representative sampling of large, inhomogeneous structures which cover both contamination and activation is missing for decommissioning waste.**
- **a methodology for in-situ measurements with low uncertainty is also missing for decommissioning waste.**
- **the validation of scaling factors for decommissioning wastes needs improvement.**

Finally, no knowledge gap has been identified for organic waste characterisation.

5.4 Recommendation for future R&D

Based on the identified knowledge gaps presented in the previous section and the discussions during the workshop in May 2022 (Month 36 of EURAD), R&D recommendations have been developed. These recommendations have been summarised in Table 22.

However, the limitations of this R&D recommendation work should be noted. Indeed, due to the absence of waste producers in the elaboration of these recommendations, some issues worth of future R&D activities might have not been included in the following table. Additionally, the significant representation of SIMS in the discussions may have induced biases concerning the priority of R&D recommendations that will need to be considered.

Field	Gap	R&D recommendation	Priority	Comment
Liquid waste	Incineration of high activity liquids not possible. New polymer matrix needs to be found	Development of new polymer resin	medium	already in development
Graphite	Wigner energy: threshold	Research on threshold for final disposal	medium	
	Improve scaling factors and validation of SF	Development of innovative validation technique	medium	already in development
Sludge	Handling of big volumes of sludge (Sampling (DTM, non-equilibrium of NORM-RN), Treatment/Storage)	Development of methodology for representative sampling	medium	
	Complex matrix needs correction e.g. in gamma-spectrometry (e.g., self-absorption), Determination of solid residues in sludge drums (inhomogeneous in activity and density)	Enhance correction factors via chemical/physical analysis of samples	low	Techniques available
SIERs	Re-characterisation of solidified SIERs by non-destructive measurements (would be useful to have techniques for this)	Development of innovative non-destructive measurement techniques for (DTM-)RN inventory (not only gamma-emitters)	high	
U/Ra/Th bearing waste	Complex matrix needs correction e.g. in gamma-spectrometry (e.g., self-absorption), determination of solid residues in U/Ra/Th bearing waste (inhomogeneous in activity and density)	Enhance correction factors via chemical/physical analysis of samples	low	Techniques available
	Methodology for representative sampling	Development of methodology for representative sampling	medium	
Decommissioning waste	Methodology for representative sampling (both contamination and activation)	Development of methodology for representative sampling	medium	
	Methodology for in-situ measurements with low uncertainty	Development of methodology for in-situ and non-in-situ measurements with low uncertainty / reducing measurement uncertainty (also for difficult-to-access parts)	high	Development on-going
	Validation of scaling factors	Development innovative methods for scaling factors validation	high	
Shared solutions		Development of a mobile facility/laboratory for rad. waste characterisation (both legacy and other wastes)	high	
SIMS		Development of guidance on radioanalytical, physical & chemical characterisation	high	
		Development of a forum for knowledge transfer for scaling factor application/determination	medium	

Table 22 - Recommendations for future R&D based on the analysis of identified knowledge gaps for radioactive waste characterisation

6. Recommendations for radioanalytical characterisation in countries with non-developed waste management concepts

For countries with non-developed waste management concepts, characterisation of radioactive waste according to waste acceptance criteria is often not possible, as no disposal site specific WAC exists yet. The approach of using foreign WAC as first attempt is in general not useful either, as these are generally waste- and site-specific, well developed and adjusted to the country's disposal concept. Additionally, countries with currently well-developed waste management concepts often have a big nuclear industry and thus the nuclear sector in general has no financial issues, providing all the means necessary to characterise the waste in-depth. On the other hand, for countries with no or only limited nuclear industry and SIMS in particular, financial restrains in the nuclear sector often make it necessary to only characterise the waste properties most important for waste handling and storage.

Table 23 and Table 24 provide a summary of NDA and DA radioanalytical characterisation techniques with high, medium and low benefit for SIMS. This table summarises the results of a questionnaire send to all task participants, asking to indicate which radioanalytical characterisation technologies for unconditioned waste they would recommend for SIMS. Based on the answers, the technologies have been categorised for each discussed waste type. The category "high benefit" (green) has been selected, if more than 2/3 of replies indicated this technology as recommendable. Equivalently, the category "medium benefit" (yellow) has been selected if more than 1/3 of replies recommended this technology. Categorised as "low benefit" (red) have been all technologies, with a recommendation from less than 1/3 of total replies.

Waste Type	**Dosimetry**	**Gamma-Spectrometry**	**Computer simulation (e.g. MCNP)**
Graphite			
Sludge			
Organics			
SIERs			
U/Ra/Th bearing wastes			
Decommissioning waste			

Table 23 - Summary of NDA radioanalytical characterisation techniques with high (green), medium (yellow) and low (red) benefit for SIMS.

Waste Type	**Mass-Spectrometry**		**Radio-chemistry**	**Ion-exchange and extraction**	**Scaling factor**	**Liquid scintillation counter**	**Alpha spectrometry**	**Beta counting**
	ICP-MS	**AMS**						
Graphite	red	yellow	red	red	yellow	green	red	yellow
Sludge	yellow	red	red	green	green	green	yellow	yellow
Organics	red	red	yellow	yellow	yellow	green	yellow	yellow
SIERs	yellow	red	yellow	yellow	green	green	yellow	green
U/Ra/Th bearing wastes	red	red	yellow	red	red	yellow	green	yellow
Decommissioning waste	red	red	red	yellow	yellow	red	yellow	yellow

Table 24 - Summary of DA radioanalytical characterisation techniques with high (green), medium (yellow) and low (red) benefit for SIMS.

Stated reasons for not recommending a specific technology are in general based on the costs of equipment, maintenance and specific know-how needed to operate the equipment. Additionally, the applicability of some technologies such as computer simulation, scaling factors or mass-spectrometry is limited and therefore the technology is assessed as having a low cost to benefit ratio for SIMS.

The obstacles for SIMS on radioanalytical characterisation can be condensed to two main reasons: Availability of know-how and availability of equipment. Therefore, three actions will be recommended in this deliverable:

- **Development of a guide on radioanalytical characterisation dedicated to SIMS:** This guide should specifically address waste types relevant to SIMS and provide in-depth approaches for their radioanalytical characterisation. It should provide solutions for SIMS-specific challenges, such as availability of know-how and equipment.
- **Knowledge transfer program on technology application:** This program should specifically tackle the challenge of know-how availability. One focus should be on the knowledge sharing concerning technique application such as scaling factors. Plausible formats might be webinars, trainings or personnel exchange programs between LIMS and SIMS facilities on specific issues.
- **Research project on the development of a mobile facility for characterisation:** This research project should tackle the challenge of equipment availability. It does not need to be limited to radioanalytical characterisation, but might be an all-in-one mobile facility enabling a complete characterisation of waste. It should additionally be applicable to handling of legacy waste.

7. References

[1] V. Wasselin, M. Maître and I. Kutina, “Overview of issues related to challenging wastes. Final version as of 18.08.2022 of deliverable D9.5 of the HORIZON 2020 project EURAD. EC Grant agreement no: 847593.,” 2022.

[2] International Atomic Energy Agency, “Determination and Use of Scaling Factors for Waste Characterization in Nuclear Power Plants, IAEA Nuclear Energy Series No. NW-T-1.18,” IAEA, Vienna, 2009.

[3] LGI, “The INSIDER project,” 2017. [Online]. Available: http://insider-h2020.eu/. [Accessed 8 April 2021].

[4] INSIDER, “Sampling Toolbox for Radiological Assessment To Enable Geostatistical and statistical Implementation with a Smart Tactic,” SCK CEN, 2019. [Online]. Available: https://strategist.sckcen.be/. [Accessed 12 08 2022].

[5] R. Tuerlinckx, T. Huys and K. Esbensen, “Representative Sampling and Radiological Characterization of Heterogeneous Legacy Waste,” in *WM2022 Conference*, Phoenix, Arizona, USA, 2022.

[6] International Atomic Energy Agency, “Processing of Irradiated Graphite to Meet Acceptance Criteria for Waste Disposal, IAEA-TECDOC-1790,” IAEA, Vienna, 2016.

[7] G. Nicaise and B. Poncet, “A reverse method for the determination of the radiological inventory of irradiated graphite at reactor scale,” EUROSAFE, 2016.

[8] ANDRA, “Catalogue descriptif des familles, inventaire national des matières et des déchets radioactifs,” 07 03 2019. [Online]. Available: https://inventaire.andra.fr/sites/default/files/documents/pdf/fr/export-familles-20190307-161729_0.pdf. [Accessed 12 08 2022].

[9] B. Bisplinghoff, M. Lochny, J. Fachinger and H. Brücher, “Radiochemical Characterisation of Graphite from Jülich Experimental Reactor (AVR),” Institut für Sicherheitsforschung und Reaktortechnik, Forschungszentrum Jülich GmbH, Jülich, Germany, 2013.

[10] T. Vasilopoulou, M. Savva, A. Savidou and I. Stamatelatos, “Radiological characterization of the irradiated graphite from the thermal neutron column of GRR-1 research reactor for decommissioning and waste disposal, Internal Technical Report,” NCSRD, Athens, 2018.

[11] D. Kontogeorgakos and I. E. Stamatelatos, “Validation of the Monte Carlo Model of the Greek Research Reactor Core,” *Nuclear Technology,* vol. 170, p. 460, 2010.

[12] N. Toulhoat, “Ion irradiation of 37Cl implanted nuclear graphite: Effect of the energy deposition on the chlorine behavior and consequences for the mobility of 36Cl in irradiated graphite,” *J. Nucl. Mater.,* vol. 464, p. 405–410, 2015.

[13] B. Roddie, “Project 1.2: Cuttings Pile Toxicity,” UKOOA and Rogland Research, UK and Norway., 1999.

[14] A. Sahar and A. Amin, “Assessment of naturally occurring radioactive material (NORM) in the oil In Situ Method Development for the Oil Based Mud (OBM) Radiological Characterization Originating from Oil Industry by Using a LaBr3(Ce) Scintillator,” *Environ. Earth Sci.,* vol. 75, p. 769, 2016.

[15] E. Ntalla, K. Tsirikos, A. Clouvas and A. Savidou, “Development of an effective technology for NORM Waste Characterization from Oil Industry,” in *European NORM Association (ENA) Workshop*, Virtual Event, 2020.

[16] E. Ntalla and A. Savidou, “Methodology for Clearance of Oil-based Muds Originating from Oil Industry,” in *12th International Symposium Release of Radioactive Materials –Provisions for Clearance and Exemption*, Frankfurt, Germany, 2022.

[17] Ukraine, “Management of radioactive waste during operation of NPP National Nuclear Energy Generating Company of Ukraine, Annual report,” 2019.

[18] OSPU, “Basic sanitary rules for ensuring radiation safety of Ukraine,” Kyiv, 2005.

[19] International Atomic Energy Agency, “Characterization of Radioactive Waste Forms and Packages, Technical Reports Series No. 383,” IAEA, Vienna, 1997.

[20] F. Tzika, A. Savidou and I. Stamatelatos, “Non Destructive Characterization of Radioactive Waste Drums by Gamma Spectrometry: A Monte Carlo Technique for Efficiency Calibration,” *Heath Physics Journal,* vol. 93(3), pp. 174-179, 2007.

[21] S. Boden, B. Rogiers, J. Dadoumont, L. Noynaert, M. Garcia-Miranda and D. Roudil, “R&D within the BR3 PWR decommissioning project,” in *DEM 2018 – Dismantling Challenges: Industrial Reality, Prospects and Feedback Experience*, 2018.

[22] W. Broeckx, S. Boden, B. Rogiers, J. Dadoumont, Y. Demeulemeester and R. Vandyck, “Decomissioning oft he BR3 biological shield: How a proper data analysis facilitates the D&D process,” in *DEM 2021 – International Conference on Decommissioning Challennges, Industrial Reality, Leassons learned and Prospects*, Avignon, France, 2021.

[23] EU PREDIS, “EU-project PREDIS - Pre-disposal management of radioactive waste,” VTT, [Online]. Available: https://predis-h2020.eu/. [Accessed 09 02 2023].

[24] D. Mavrikis, A. Markopoulos, E. Ntalla, A. Ioannidou and A. Savidou, “A Technique for Metallic Waste Characterization and Segregation in Management Routes,” in *29th Hellenic Nuclear Physics Society (HNPS)*, 2021.

[25] M. Duerr, K. Krycki, H. B. and T. Hansmann, “Radiological characterization from a waste and materials end-state perspective,” *NEA Radioactive Waste Management,* vol. 7373, 2017.

[26] A. Havenith, M. Fritzsche, D. Pasler and T. Hartmann, “Advance sectorial gamma scanning for the radiological characterization of radioactive waste packages,” *Atw. Internat. Zeitsch. fuer Kernen,* vol. 6, no. 3, pp. 160-166, 2019.

[27] M. Pastena, B. Weinhorst, G. Kanisch, E. Pérez Lezama, J. Radtke and T. Thomas, “A novel approach to the localization and the estimate of radioactivity in contaminated waste packages via imaging techniques,” *Measurement Science and Technology,* vol. 32, no. 9, p. 15, 2020.

[28] A. Savidou and I. E. Stamatelatos, “Non-destructive technique to verify clearance of pipes,” *Journal of Nuclear Technology Radiation Protection,* vol. 25, no. 2, pp. 133-1337, 2010.

[29] International Atomic Energy Agency, “Radiological characterization of shut down nuclear reactors for decommissioning purposes, IAEA Technical Report Series, no. 389,” IAEA, Vienna, 1998.

[30] Republic of Cyprus, “Department of Labour Inspection,” 12 08 2022. [Online]. Available: http://www.mlsi.gov.cy/mlsi/dli/dliup.nsf/All/E63D9A9AF63A76E4C2257E2A0024C929?OpenDocument.

[31] International Atomic Energy Agency, “The Joint Convention on the Safety of Spent Fuel Management and on the Safety of Radioactive Waste Management,” IAEA, Vienna, 1997.

[32] Greek Atomic Energy Commission, “National framework for the management of spent fuel and radioactive waste,” EEAE, 2015. [Online]. Available: https://eeae.gr/en/radiation-safety/management-of-radioactive-waste/national-framework-for-the-management-of-spent-fuel-and-radioactive-waste. [Accessed 12 08 2022].

[33] A. Savidou and J. Feinhals, “Clearance or Disposal? Management of contaminated resins,” in *8th International Symposium “Release of Radioactive Materials Requirements for Exemption and Clearance*, Hamburg Germany, 2013.

Appendix A. Member states input on motivation and criteria for characterisation

Motivation and criteria for characterisation: Belgium

In Belgium, ONDRAF/NIRAS (the Belgian Agency for Radioactive Waste and Enriched Fissile materials) is responsible for radioactive waste management. This includes among others the establishment of the inventory, collection, transport, processing, interim storage and long-term management of radioactive waste, as well as missions concerning decommissioning and management of enriched fissile materials. The national waste management policy is still in the process of being developed, in line with Directive 2011/70/Euratom. Nevertheless, some policy measures already exist. One of these measures is the disposal of the category A waste in a surface repository in the municipality of Dessel.

Radiological characterisation should ensure that the wastes are compliant with the acceptance criteria of the associated disposal facility. Verification of the declared inventory is one of the most important reason for waste characterisation, followed by operational and long-term safety, and the waste classification in view of disposal choices. Moreover, radiological characterisation is important at all stages of the nuclear waste life cycle, as the general flow "from prevention to final disposal" is valid.

The radiological characterisation methodology (and possibly a measurement facility and/or method) is proposed by the waste producer in a qualification file, which is reviewed and must be approved by ONDRAF/NIRAS. For each waste package, the documentation is checked to ensure that the waste package complies with the WAC. Moreover, regular audits and inspections are performed by ONDRAF/NIRAS to verify declared information and used methods.

Belgium has several characterisation methodologies that are approved by the national waste management organisation ONDRAF/NIRAS. In general, the methods are based on non-destructive analytical measurements such as gamma spectrometry or dose rate measurements and on numerical codes and models. The methods are:

- Determination of key nuclides through non-destructive analysis such as gamma spectrometry
- Measurement of dose rate on non-conditioned waste packages and calculation of radionuclide inventory through specific conversion factors (mSv/h → MBq). These factors are determined using software such as Microshield.
- Destructive analysis on samples of non-conditioned waste, such as mass spectrometry, gamma spectrometry, alpha spectrometry or liquid scintillation counting.

The results of these measurements focusing on easy-to-measure (ETM) RN will be combined with a radionuclide vector. This RN vector is based on models, calculations and/or on destructive measurements for the determination of difficult-to-measure (DTM) radionuclides and is approved by ONDRAF/NIRAS.

Another possible way to determine the radiological characteristics of a waste is by making a conservative estimation/calculation based on the well-known radiological characteristics of the radioactive materials from which the waste originated.

In general, characterisation is performed by the waste producer. On behalf of ONDRAF/NIRAS, the company Belgoprocess processes radioactive waste produced in Belgium, which is not processed by the waste producers themselves. In addition, Belgoprocess stores the processed waste pending disposal. Therefore, to the extent needed, Belgoprocess characterises the waste again after treatment and/or conditioning.

Motivation and criteria for characterisation: Bulgaria

The requirements for the characterisation of RAW are in compliance with the Updated Strategy for Spent Fuel and Radioactive Waste Management until 2030, adopted by the Council of Ministers, 2015, and are notably defined with the Ordinance on Safety in the Management of Radioactive Waste, adopted by the Council of Ministers, 2013.

For radioanalytical characterisation, there are specific waste characterisation methods, selected taking into account the legislative requirements and the categorisation of the RAW. In general, there is a universal strategy for the radioanalytical characterisation, but an additional specific characterisation approach and scaling factors apply for some listed waste types.

The State Enterprise for Radioactive Waste (SERAW) is responsible for characterisation. It is the licence holder and has the responsibilities for whole RAW management process, including pre-treatment, processing, conditioning, storage and disposal of RAW, as well as the decommissioning of RAW management facilities.

Motivation and criteria for characterisation: Cyprus

Due to missing legislation with regard to radioanalytical characterisation in Cyprus, no WAC have been defined yet. Therefore, treatment and reprocessing is currently not conducted. Additionally, as there are no WAC, there is no national concept for radioanalytical characterisation of RAW.

The Radiation Inspection and Control Service (RICS) is responsible for characterisation, which operates as one of the sections of the Department of Labour Inspection (Radiation Protection Section) of the Ministry of Labour and Social Insurance [27]. Guidelines are taken from “The Joint Convention on the Safety of Spent Fuel Management and on the Safety of Radioactive Waste Management” [28].

Motivation and criteria for characterisation: France

Law n° 2006-739 of 28 June 2006 on the sustainable management of radioactive materials and waste defines radioactive waste as radioactive substances that can neither be reused nor recycled. Radioactive waste management in France is governed by Articles R. 542-1 to R. 542-96 of the Environmental Code and the Ministerial Order of 9 October 2008, amended by the Ministerial Orders of 4 April 2014 and 16 March 2017. Concerning waste characterisation, the French Nuclear Safety Authority (ASN) specified in its Decision No. 2017-DC-0587 of 23 March 2017 the elements that must be described in the request for a packaging agreement, namely: radiological, physical, mechanical, chemical characteristics and properties of the package. These must be compatible with the demonstration of safety of the disposal facility during its operation and after its closure.

Moreover, the Order of 3 July 2019 on the radiological characterisation of materials, products, residues, or waste likely to contain radioactive substances of natural origin states that the objective of the radiological characterisations carried out by the accredited organizations is to determine the mass activity concentrations of potassium 40 and the radionuclides of the uranium-238 and thorium-232 chains. The radiological characterisations are carried out by gamma spectrometry and the radionuclides sought are metastable protactinium-234, thorium-234, radium-226, lead-214, bismuth-214, lead-210, actinium-228, lead-212, thallium-208 and potassium-40. The results of these characterisations are expressed in kBq/kg with an uncertainty determined with a broadening factor of two. The detection limits to be achieved allow the mass activity concentrations to be compared with the exemption limit values defined in Table 1 of Annex 13-8 of the Public Health Code.

The waste producer must define the activity of their radioactive waste packages to classify them in the corresponding waste streams. The methodology must be approved by Andra (the French Waste Management Organization) when operating waste disposal facilities or by the ASN for waste destined for disposal facilities under development. The packages must comply with the characteristics defined in their authorizations issued by ASN. In the case of waste for which the disposal is still under development, the waste producer draws up a conditioning reference system for these wastes and submit them to the ASN and Andra.

The evaluation of the quality control measures for the packages is carried out by Andra, which implement on-site monitoring (production control audits, technical visits, etc.) as well as destructive (core sampling, container inventory) and non-destructive (X-ray and degassing measurement, gamma spectrometry) controls. In the event of a discrepancy noted by Andra, the approval or acceptance is suspended, and this suspension can only be lifted if it is demonstrated that the deviation does not call into question the safety demonstration of the storage facility.

Motivation and criteria for characterisation: Germany

The legislative backbone of radioanalytical characterisation in Germany are the fulfilment requirements of WAC criteria, e.g. for LLW and ILW to be disposed in the Konrad mine.

Compliance with the WAC ensures good behaviour in the DGR, with limits for RNs undergoing fission by thermal neutron reaction (e.g. specific U and Pu RN as well as higher actinides). Special regulations apply for ^{220}Rn mother nuclides. In general, the declaration of RNs is important for incident analysis (ensuring safety during operation), thermal influence on the host rock via thermal reference nuclides (long-term safety) and the criticality safety (incl. ^{235}U, ^{239}Pu and ^{241}Pu). This resulted in a specific set of RNs specified in the WAC. These are in total 108 RNs with specific nuclide values for each type of waste package, as well as an additional list of 91 RNs with a general very low limit value for each waste package type.

The general workflow for a characterisation and treatment campaign starts with a global dose rate measurement. With this input, the waste producer or owner develops a concept for the characterisation, treatment and packaging in order to generate waste packages in compliance with WAC. This concept is then reviewed by a TSO and approved by the operator of the GDF in Germany, the BGE. Subsequently, the waste is treated according to the approved concept. The treatment of the waste is accompanied by waste characterisation based on:

- Dosimetry,
- Gamma-spectrometry,
- LSC,
- Isotope specific analysis (e.g. electrochemical plating and subsequent measurement with semiconductor detector),
- AMS (determining ^{14}C) and
- Swipe tests (surface contamination).

The workflow continues with the packaging of the waste according to the approved concept. The packaged waste is again measured by dosimetry and swipe tests to check for contaminations. The measurements are validated by software (e.g. “Abfallflussverfolgungs- und Produktkontroll-System (AVK)), which includes all scaling factors for DTM RN of standard wastes in a data bank. Finally, the documentation and declaration of compliance with WAC are reviewed by the TSO and approved by the BGE.

The waste owner is responsible for treatment, characterisation and packaging.

Motivation and criteria for characterisation: Greece

The Greek national framework for the management of spent fuel and radioactive waste is based on the Council Directive 2011/70/Euratom of 19 July 2011, establishing a community framework for the responsible and safe management of spent fuel and radioactive waste. This council directive is transposed into national legislation by the Presidential Decree no. 122 (Government Gazette no. 177/A/12.08.2013), as amended by the Presidential Decree no. 91 (Government Gazette no.130/A/01.09.2017). The management of the radioactive waste includes, among others, the characterisation of the radioactive wastes, as one of the initial activities, which should take place, in order for the radioactive wastes to be classified, according with the IAEA classification scheme (EW, VLLW, LLW, ILW) [29]. Some basic and relevant pillars of the national policy are:

- the generator of the waste has the primary responsibility for their management (including characterisation);

- scientifically accepted technical solutions are applied for the spent fuel and radioactive waste management (including characterisation);

Regarding the characterisation of radioactive waste in Greece, there is a strong motivation for the characterisation of the legacy or historical radioactive wastes, which are stored in the interim storage facility of the NCSR Demokritos. The updated National Program refers to a memorandum of understanding established between the regulator Greek Atomic Energy Commission (EEAE) and the operator NCSR Demokritos. In addition, the characterisation services for these legacy wastes will be requested through a tender, which will be part of a near future project to optimise the existing facilities. The characterisation concept (requirements on sampling, type of spectroscopy (γ, α), accuracy, etc) is directly determined by the classification needs, as described in the national policy.

These regulations outline the generic directions for a graded approach on the implementation of the characterisation and apply for all types of radioactive waste, including legacy waste.

Motivation and criteria for characterisation: Portugal

Instituto Superior Técnico (IST) is the engineering school of the University of Lisbon. On its *Campus Tecnológico e Nuclear,* IST operates the former Portuguese Research Reactor (a 1 MW pool-type reactor, currently being decommissioned), the Radiation Protection and Safety Laboratory, and the only RW Management facility in Portugal.

All former uranium exploration sites have been or are presently being remediated, as there are no further plans to resume this activity. There is no nuclear power plants and the spent fuel (SF) from the research reactor has been returned to the United States of America (USA) in 2019, under an agreement with the USA and the International Atomic Energy Agency (IAEA). As a result, the radioactive waste (RW) generated in Portugal is mainly composed of materials from past uranium and radium mining and milling activities, spent and/or disused sealed sources, smoke detectors, lightning rods, contaminated scrap metal, depleted uranium from aircraft counterweights, materials contaminated with unsealed sources produced from the applications of ionizing radiation in the fields of Medicine, Industry and Research.

The RW is of the very low, low and intermediate level waste types (VLLW, LLW and ILW) and is stored in a surface facility operated by IST at its *Campus Tecnológico e Nuclear* since the 1960s.

Decree-Law no. 156/2013, of November 5th, transposes Council Directive 2011/70/EURATOM into national law and sets the national framework for the management of spent fuel and radioactive waste. The RW management facility was licensed in 2016 by the former COMRSIN (Regulatory Commission for the Safety of Nuclear Facilities) as the regulatory authority at the time. In April 2019, Decree-Law no. 108/2018, of December 3rd, was enforced, the general framework of Radiation Protection in Portugal was reorganized. COMRSIN was extinguished and APA (Portuguese Environmental Agency) became the regulatory body superseding the activities related to RW management as well. APA renewed the license for the operation of the RW management facility in December 2021, in the framework with two decrees, Decree-Law no. 156/2013 and Decree-Law no. 108/2018.

Ministerial Ordinance no. 138/2019, of May 10th, updates Ministerial Ordinance no. 44/2015, of February 20th, adopting the clearance and exclusion levels as the same levels set by Council Directive 2013/59/Euratom. Prior to 2015, all radioactive material with no further use, including materials that activated the radiation detection portals at the entrance of scrap metal yards, steel and iron melting facilities, landfills for dangerous materials, or other, were collected and brought to the RW storage facility at IST.

In compliance with Decree-Law no. 156/2013, IST prepares an annual inventory of the RW stored in its facilities. The records registered after the year 2000 are reliable but there is a high degree of uncertainty regarding the waste collected before, which is considered as legacy waste requiring characterisation and classification.

The first National Programme for the Management of Spent Fuel and Radioactive Waste (2015-2019) was approved by the Government and published in the official journal as Resolution of the Council of Ministers no. 122/2017, on September 7th, following the strategic environmental assessment and public consultation. A second Programme has been prepared and is currently pending approval by the Government and publication in the official journal.

The National Programme specifically considers the following activities: characterisation and identification of legacy waste, eventual preparation of exclusion processes for waste that no longer require storage at such a facility, restoration of enough room for waste of concern, and the improvement of the overall inventory of radioactive waste. The operating license recently renovated also mentions these objectives.

IST WMO is motivated to characterise the historic waste stored in its facility for which there are no records (or could not be found), to carry out the treatment, and to optimize the volume of the facility.

The characterisation of RW at IST depends on the waste type and consists of dose rate measurement (at contact and at 1 m distance), the assessment of the activity concentration by gamma spectroscopy for gamma emitters, and wipe tests analysis by liquid scintillation counting for alpha and beta emitters.

The producer of the RW is responsible for its characterisation before inserting the corresponding data into a RW electronic platform managed by APA. The producer may ask IST to perform the characterisation of the RW before collection. Depending on the characterisation, which mainly consists of gamma spectrometry and dose rate measurements, part of the RW can be excluded provided that the activity concentration results are lower than the liberation values established in the above-mentioned Ordinance. Based on the description of the RW and the characterisation report, APA will classify the RW and define the waste stream for the destination of the RW waste.

Motivation and criteria for characterisation: Slovakia

The use of nuclear energy in Slovakia is governed by the Act No. 541/2004 Coll. on the peaceful use of nuclear energy (the Atomic Act). The general requirements for the RAW treatment, processing and WAC are specified in NRA (Nuclear Regulatory Authority) Decree No. 30/2012 Coll. Besides above, there are operating instructions that specify the methods for waste characterisation. The waste acceptance criteria are given in a specific document developed for each nuclear facility and approved by nuclear regulatory body. The elaboration of WAC is mandatory for each nuclear facility according to NRA Decree No. 58/2006, §14. As well, NRA Decree No. 30/2012, §12 requires that the limits and conditions for safe operation of radioactive waste management facilities be determined based on safety assessment (waste acceptance criteria). According to NRA Decree No. 30/2012, §3: characterisation of radioactive waste is the determination of its physical, chemical and radiological properties for further handling and verification, that the properties of radioactive waste meet the safety of further management. The radioanalytical characterisation is aimed to guarantee compliance with safety criteria of Mochovce near surface repository and related waste acceptance criteria limiting both total activity and the activity per waste package.

According to Slovak legislative provisions, all operated nuclear facilities must have waste acceptance criteria approved by Nuclear Regulatory Authority. These criteria provide pre-determined upper limits on radionuclide inventories and/or concentrations for individual waste packages. All WAC are specifically adopted for a particular nuclear facility according to its purpose (no generic WAC are used). Compliance with the WAC is a subject of regular inspection by a regulatory body.

A concept for the radioanalytical characterisation of RAW is given by a set of operational instructions. These include a set of waste streams, the key radionuclides to be characterised and the scaling factors for each radionuclide and waste stream. These instructions define the basic rules, principles and procedures for declaring the radionuclide content in RAW processed in nuclear facilities, depending on its origin, physico-chemical form and method of processing.

Graphite, toxic waste and contaminated asbestos are currently challenging radioactive waste - their way of treatment/processing/disposal is not yet fully established. Regarding these RAW types, research and development is needed, and the development of the WAC as well as licencing procedure must be completed.

There are 19 radionuclides important from the point of view of disposal that must be measured in all RAW intended for disposal at National RAW repository Mochovce as follows: ^{14}C, ^{41}Ca, ^{59}Ni, ^{60}Co, ^{63}Ni, ^{79}Se, ^{90}Sr, ^{93}Mo, ^{93}Zr, ^{94}Nb, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{135}Cs, ^{137}Cs, ^{151}Sm, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am. They represent those radionuclides important from both operational safety (during waste processing) and long-term safety (after disposal). Measurement of above radionuclides is assured by certified testing laboratory that performs of radioanalytical services using the following techniques:

- Gamma spectroscopy system
- Low energy photon spectroscopy
- Alpha spectroscopy system
- Low level alpha/beta counter
- Liquid scintillation counter

The test methods are guided by standards specification and are incorporated into the Standard Operating Procedures, are verified and regularly reviewed.

The legislative documents include common (general) provisions in terms of characterisation of various types of RAW, and thus do not recognize among specific types of RAW (sludge, organic wastes, graphite, SIERS, U/Ra/Th bearing wastes, decommissioning waste etc.). However, operational rules include specific procedures for above mentioned waste types. Each of these waste types represents a specific waste stream, therefore particular conversion (scaling) factors are developed for each of them, and the way the waste is treated is prescribed strictly.

The licence holder (nuclear power plant operator or waste producer) is responsible for the initial RAW characterisation, the application of the WAC and reporting how these criteria are met. The process qualification requirement are specified in operating rules of the facilities for solid waste characterisation, treatment/conditioning, pre-fabrication of e.g. waste containers. The RAW producer is obliged to ship the waste to JAVYS, a.s. (waste management organisation) for processing and treatment within 1 year after production. After receipt the waste, JAVYS is responsible for RAW characterisation during its processing, treatment and disposal.

Motivation and criteria for characterisation: Spain

In Spain, according to the legislation in force, radioactive waste management includes radioanalytical characterisation in order to guarantee compliance with safety criteria. "El Cabril" disposal facility has imposed a series of waste acceptance criteria limiting both total activity and the activity per waste package, beta and gamma, and a very low limit for activity concentrations from long-lived alpha emitters.

The general objective of radioanalytical characterisation is to obtain the inventory of necessary radionuclides for the radioactive waste management, which takes account of safety, traceability and volume reduction issues. For radioanalytical characterisation of different waste types, the Scaling Factor (SF) method is used to evaluate difficult to measure radionuclides in every specific waste stream (Sludges, Spent Ion Exchange Resins, etc).

For all types of waste, the producer is responsible for the characterisation of easy to measure radionuclides, while Enresa (Empresa Nacional de Residuos Radiactivos) is responsible for the characterisation of difficult to measure (DTM) radionuclides.

Motivation and criteria for characterisation: Ukraine

In Ukraine, the radiological characterisation of RAW is regulated by normative documents for general safety provisions for predisposal radioactive waste management. They require the determination of the requirements for characterisation and sorting of radioactive waste at any time and general safety provisions for disposal of the radioactive waste, which require the characterisation of RAW to justify the safety of disposal. Ukraine also has recommendations for the establishment of waste acceptance criteria for conditioned RAW for near-surface disposal facilities (RD 306.4.098-2004), which define the basic requirements for the development of WAC and, in particular, determines the radiation characteristics of RAW (e.g., basic list of radionuclides for characterisation).

The radiation characterisation of RAW is covered by a general approach (concept) in Ukraine. According to the above-mentioned documents, the RAW producer must agree on the main methodology of determining the RAW characteristics with the operator of the storage/disposal radioactive waste, as well as with SNRIU. Also, within the framework of INSC PROJECT U3.01 / 10 (UK / TS / 46), the manual on characterisation, accounting and control of radioactive waste was developed. This manual provides general methodological recommendations for characterisation, accounting and control of radioactive waste at different stages of their management.

In general, there are no different strategies for the radioanalytical characterisation of different waste types. The approaches to characterisation are defined by the characterisation methodology in a specific case for a particular RAW stream. The accuracy required to determine the radiological characteristics of radioactive waste is determined by the approach adopted for the safety assessment. The responsibility for ensuring the accuracy of the measurement of RAW characteristics relies with laboratories.

At the present time, sampling and characterisation methodologies were agreed for:

- Salt cake, sludge and SIERs of Ukrainian NPPs,
- Bituminized RAW of Rivne NPP and
- Radioactive materials of NPPs that potentially could be exempted from regulatory control.

In all cases, the owner of RAW is responsible for the characterisation.