TITLE	**LEGACY WASTE CHARACTERIZATION PROJECT - TASK 4: CHARACTERIZATION TECHNIQUES OF RADIOACTIVE LEGACY WASTE**

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1. Introduction

The high-level objective of the ERDO Legacy Waste Characterization project (ERDO LWC project, hereafter) is sharing the state-of-the-art knowledge (i.e., information, techniques, methodologies, and experiences) for a thorough characterization of legacy waste, in view of future possible shared management activities or even multinational repositories, following the *dual-track* approach introduced by the EC Directive 2011/70/EURATOM.

Many countries are facing problems related to the management of legacy waste, with different approaches and applied standards. Performed activities may be considered as a technical support in the medium and long-term strategy for addressing the management of radioactive legacy waste; a sort of "first step" to develop a common system to be applied to the future management of these kind of waste. In this context, some organizations have already started to develop a methodology for its characterisation, while in other cases the characterisation methodology is still being developed.

The following tasks summarize the activities initially planned within the ERDO LWC project:

- task 1: survey of existing main legacy waste streams;
- task 2: minimum set of Waste Acceptance Criteria (WAC) for near-surface disposal of VLLW-LLW;
- task 3: main properties of ILW packages potentially suitable for geologic disposal;
- task 4: characterization of main legacy waste streams.

Unfortunately, it was not possible to carry out task 3 due to unavailability of data.

The first task of the project has regarded the analysis of the inventories of the main legacy waste generated in the countries that adhere to the ERDO association. In task 2, activities carried out has derived a common minimum set of WAC to be respected by the legacy VLLW-LLW streams for a near-surface disposal. Activities related to task 4 deal with the characterization techniques of legacy waste. The scope of the overall work is favouring future possible activities for the management of legacy waste up to a shared disposal, especially by means of information exchange and experience sharing.

The present deliverable illustrates the results of the activities performed within the framework of task 4. Its main goal deals with the physical, chemical and radiological characterization of VLLW and LLW legacy waste; ILW and HLW, unsuitable for near-surface repository, are not considered. In particular, the report illustrates the possible characterization techniques of some typology of legacy waste that belong to the ERDO members, much of which are stored in interim facilities and whose ages range from just a few years to several decades. Indications about chemical, physical, radiological characterization techniques and approaches of each technique are described, as well as the advantages and disadvantages.

The activities have been performed considering the results of previous tasks activities and the collaboration with ERDO members. As previously mentioned, the work performed in task 1 of the present project, has led to a survey among seven ERDO and non ERDO member countries, to analyse small inventories of legacy waste generated to date and their main characteristics (physical, chemical and radiological); one of the most important result concerns the fact that waste streams present strong similarities among countries. This led to common needs about the future waste characterization, as part of larger waste management and disposal activities; so, possible synergies in management of legacy waste are advisable, considered the context and the results of the studies performed in this project.

However, the conclusions obtained from this work cannot be considered definitive and exhaustive to solve the common problem of legacy waste management (and in particular of their characterization). A further joint effort is needed in the field of research, especially in the field of characterization techniques, in order to reduce the limits that are still present in current technologies. In fact, radioactive waste characterization is in constant evolution, taking into account the necessity of a continuous improvement of precision and sensitivity of measurements, but also considering the continuous technological progress in detectors, calibration sources, chemical and radiochemical analyses, radiological characterization, numerical simulations and so on.

2. The role of the legacy waste characterization

For the purpose of the present project, radioactive legacy waste is defined as the radioactive waste generated in past nuclear activities (e.g., energy production, medicine, research, industry) which has been treated and conditioned according to the rules in force at the time or simply stored pending a suitable management solution; such waste, with different properties compared with the waste generated in current nuclear activities under normal conditions, is often lacking sufficient physic-chemical and radiological characterization data (especially for the lack of documentation) for envisaging possible retreatment and reconditioning processes, in line with current regulatory requirements and checking compliance with current WAC of storage and disposal facilities. Furthermore, the current information about legacy waste is far behind the current state of the art; for example, in some cases, there is a misunderstanding on how the waste has been produced. This waste has been generally stored for a long time in different type of facilities, without a complete traceable characterization.

This is why the legacy waste characterization is one of the pivotal challenges among the countries managing this type of waste. Moreover, an incomplete waste characterization forces to rely on unduly conservative assumptions, which are costly; on the contrary, a characterization correctly performed in the early period of waste lifecycle guarantees a better accuracy and is cost saving.

Different types of legacy waste generally share common features, as the treatment processes, the properties of material used for conditioning or the radionuclide types and concentrations. Moreover, little information is available about non-radiological hazards and about possible damages caused by long storage, as the initial waste features has changed over time because of physic-chemical (and biological) degradation processes, as well as radioactive decay. The lack of information, due to poor or absent documentation, represents an important criticality for future management of this kind of waste. However, it is therefore important to precisely define their characteristics, to satisfy current regulatory requirements, and checking compliance with WAC of storage and disposal facilities. Therefore, it is necessary to evaluate the possible techniques and methodologies that have to be applied to gain the missing information.

The physical, chemical and radiological characterization of waste will then be developed around gaps in knowledge, reducing the associated uncertainties until all the waste streams have a sufficiently robust characterization approaches, assuring that the entire management and disposal system (processes, activities and final products) will satisfy given regulatory and safety requirements; moreover, addressing the correct classification of the same waste. No management and treatment activities should have started before completing at least the minimum characterization useful to gather a preliminary chemical and radiological framework of the waste, to plan the subsequent actions for the management, treatment and storage/disposal of the waste, establishing their suitability for processing possible transport to storage and disposal. On the contrary, the lack of characterization can lead to erroneous choices about the management approach, also underestimating the radiological and chemical hazard, leading to safety, possible non-acceptance at the final repository and economic issues.

The characterization of legacy waste can also support the analyses for assessment strategies, which are the base step useful to safety case and risk evaluation, in normal or accidental conditions, about future waste management and disposal (in particular to evaluate possible modifications of safety functions and to produce reliable input data for numerical simulations, sensitivity analysis, etc., reducing conservative assumptions in safety assessment). Characterization has a social importance too, that is to guarantee the right information for current and future generations, and for all the stakeholders.

As mentioned, the characterization techniques, that have to take into account the actual nature of waste and its package, is not only confined to the radiological aspects (radioactivity properties). Chemical and physical characterization (chemical and physical properties) is a fundamental step to guarantee the safety of the operators and correct application of the waste treatment processes; in some cases, biological properties are also important to analyze the future behavior of the waste. For example, these determinations may avoid the risk associated with the possible presence of chemical hazard, as asbestos, beryllium, etc., whose presence and risk has to be evaluated from qualitative and quantitative point of view, before assuming any decision about waste treatment and conditioning. In general, the most important physical, chemical and biological features of the waste determine how it will behave when it is managed, conditioned, transported and stored/disposed.

The determination of radiochemical and physical characteristics of radioactive waste is based on measurements, that are always affected by a measurement uncertainty; so that any representation of a measurement is complete only when such a value is associated to the corresponding measurement. There are many different sources of uncertainty; their identification, definition and quantification should be one of the step in the overall characterization process. This topic deserves a separate dissertation given its importance, but it is outside the scope of this work.

The survey performed in task 1 of the project, investigating legacy waste streams generated to date among the ERDO members, has showed that about the 80% of them lack or present a low reliability of the radiological characterization; for more than 40% of waste streams, the planned characterization methodology is not defined, while the remaining are planned to be characterized during the following sorting and treatment phases [R1]. Therefore, it is extremely useful to deal with the legacy waste characterization among the ERDO members.

3. Legacy waste analysed

The survey performed within the activities of the task 1 provided evidence of different types of legacy waste related to different ERDO member countries [R1]. In particular, the work has highlighted the main 9 waste streams in which the legacy waste may be grouped, which share similar features. The following description summarizes the main characteristics of the different categories, but also highlights the gaps present in the characterization of waste and the scarcity or low reliability of information about it.

1. Disused sealed radioactive sources: waste from medical, industrial and research applications. The characterization is partial or uncertain; the judgment of reliability of radiological characterization goes from low to medium and only in one case the reliability is defined as high. Chemical characterization is almost always absent.
2. Mixed waste: glass, plastic, clothes, rags, metal scraps, etc., in solid phase, classified as LLW and ILW, generally packaged or conditioned; the radiological characterization, when available, is considered poorly reliable (in two cases, the reliable is rated as high due to a reconditioning project); chemical characterization is not available.
3. Powdery waste: contaminated soil and zeolite, classified as VLLW and LLW (in one case, ILW); the radiological characterization, when present, is considered poorly reliable, while chemical characterization is not available.
4. Sludge: sediments and residues from water treatment, in some case cemented or bituminized, classified as VLLW, LLW and ILW. The radiological and chemical characterization, when present, is considered poorly reliable (except in one case, due to a project of reconditioning with characterization).
5. Ion exchange resins: IERs from research reactors power and reprocessing plants, in solid phase, classified as VLLW, LLW and ILW. The radiological characterization is judged poorly reliable, while chemical characterization is not available, except in one case where it is available, but its reliability is considered low.
6. Liquid organic waste: oil, detergents, solvents, kerosene, etc., mostly organic, and stored in metallic or plastic container. The radiological characterization is generally considered low reliable (only in one case is judged medium reliable), while chemical characterization is not available.
7. Graphite: blocks or bricks from moderator and reflector of power and research plants, classified as VLLW, LLW and ILW, in raw status. Reliability of radiological characterization is considered low or medium, while chemical characterization is not available.
8. Alpha-bearing solid waste: waste in solid phase containing uranium, plutonium, thorium, etc.; mostly classified as LLW and ILW, but in two cases, classified as HLW due to enrichment of original material. Reliability of radiological characterization is considered low (in only one case, high) while chemical characterization is not available.
9. Chemo-toxic materials: waste in solid phase containing asbestos, cadmium, beryllium, PCB, etc., classified as LLW and ILW (in one case, as HLW for waste belonging to research reactor). Reliability of radiological characterization is considered low, while chemical characterization is not available.

Other waste are metals or reactive metals, sharing the same features of the aforementioned categories. For almost all the categories, the radiological and chemical characterization is lacking and generally judged as low reliable and the current storing status is raw or conditioned.

On the other hand, in addition to a comparison analysis between the various waste streams of the various countries, carried out in task 1 of the project, the results [R2] of the task 2 activity were also examined. The task 2 had the purpose of verifying which were the main parameters of the waste, to which the WACs refer and to be considered, therefore, for defining a common characterization methodology.

4. Radiological characterization techniques

As already explained, a thorough and accurate assessment of the physical, chemical and radiological characteristics of the waste plays a fundamental role in the overall activities related to the management and disposal of radioactive waste. The characterisation activities, especially for what concern the measurement techniques, depend on many factors, as setting clear characterisation goals, the type of waste to be analysed, the regulatory regime, the WAC, the parameters to be measured, the amount of information already available.

From the radiological point of view, different techniques are used to assess the emitting radionuclides (identification of nature of radionuclides, their location in the waste and their concentration), so to evaluate whether the activities of waste management and disposal are performed in a safely and reliable manner. Non-destructive radiological analysis is performed by observing spontaneous (passive) or induced (active) nuclear radiation, to estimate the content of one or more nuclides in the waste under investigation; this type of investigation does not alter the physical and chemical form of the material. In this framework, it is possible to carry out measurements on site, relatively in short times, but with modest accuracy, using portable or transportable instrumentation. In this case, non-destructive technique may not provide conclusive characterization, requiring more detailed investigations and data interpretation; the accuracy of the results depends on these processes and on the complexity of the waste. Non-destructive characterization can be performed with higher accuracy and sensitivity in a laboratory, where gamma spectrometry can be carried out with an adequate collection time.

Destructive radiological analysis is always carried out in the laboratory, to search for those radionuclides whose emission is easily stopped by a small amount of material or even by the air. In particular, alpha- and beta-emitters usually requires destructive approaches for being detected and quantified. Destructive techniques are carried out by sampling the original waste and processing the sample with chemical methods. They must be carried out on uniform and sufficiently representative samples of the material so to lead to a precise and complete determination of the radionuclide inventory. Generally, these approaches are accurate, but the reliability of the determinations depend on the sample representativeness and its homogeneity. They require long measurement times and compromise the integrity of the sample (usually the sample is dissolved to obtain a homogeneous aliquot for the following process or measurement), a purification of the chemical element of interest or a chemical separation process (to isolate the element to be determined, eliminating the chemical interferences) and radiological measurement (measuring the radioactivity concentration of the radionuclides depending on their chemical and radioactive properties). All these operations may potentially put operators at risk, who must undergoes an appropriate radioprotection surveillance. The destructive techniques are usually complementary to the non-destructive techniques, particularly for legacy waste packages with scarce available data or documentation.

Waste sampling is an integral part of the characterisation process: the optimal characterization process must be supported by an effective and reliable sampling plan, to obtain a representative sample of the waste, if necessary for the specific analysis, especially in the case of destructive characterization techniques [R3]. In the case of destructive techniques, the correct choice of sampling has an important impact on the reliability and accuracy of the characterization; the results will determine whether is possible to scale them over the overall waste stream. Other preliminary activities might support the sampling plan and the future chemical and radiological measures, dose rate measurements, heterogeneity waste evaluation, etc.

The selection of the most appropriate radiological characterization techniques depends mainly on the type of waste, its physical phase, possible presence of fissile or fertile material, package size and geometry, objective of characterization and waste management strategy, legislative and regulatory framework. A combination of radiological techniques guarantees the most efficient approach for the best characterization of any waste. A limitation in radiological characterization regards the possibility to assess the type and quantity of the hard-to-measure-radionuclides (roughly defined as radionuclides with little-to-none gamma emission); in this case, if destructive characterization techniques cannot be adopted, they can be indirectly calculated by means of the scaling factors ratio, based on the relationship between key gamma-emitters and hard-to-measure-radionuclides, whose ratio is characteristic of the specific plant or installation.

The following is a summary of the main measurement techniques for radiological characterization, both non destructive and destructive, which are commercially available and adopted as golden standard in the field.

4.1. Gamma Scanning

This general term refers to an instrument performing gamma spectrometry on a radioactive waste drum. It is a non-destructive technique that allows the accurate determination of gamma emitting nuclides, useful to characterize activation products and gamma-emitting transuranic elements; that is, all the nuclides emitting gamma rays with a level of intensity and energy able to emerge the material surrounding the waste.

The procedure is based on gamma ray spectrometry, to identify and quantify radioactive material in the entire drum (i.e., Open Geometry, OG), separated drum slices (i.e., Segmented Gamma Scanner, SGS) or drum voxels (i.e., Tomographic Gamma Scanner, TGS). The instrumental system consists of a gamma spectrometer (usually a High-Purity Germanium detector) associated with some mechanical devices to manage the detector/waste movements; generally, the system uses a turntable to rotate the waste (i.e., a drum or another waste container) under investigation, during the measurement, to present to the detector the different portion of the drum (in case of SGS and TGS) or get an averaged measure for non-homogeneous waste (in case of OG). The waste is rotated along its vertical axis and horizontal segments are scanned, to acquire an integral gamma spectrum. This allows the building of a vertical profile of gamma ray transmission and nuclide concentration. The technique involves a procedure of calibration, for the correction of the attenuation taking place in the waste package material. The calibration process is generally performed by means of a Monte Carlo simulation code or using standard waste drum.

Gamma scanning is applicable to the radioactivity measurement from extremely low levels to high levels of activity and across a large range of densities. It may characterize waste in a variety of matrices and chemical phases; specifically, it is very useful when the relationship between the nuclide and matrix are unknown. When the system incorporates a radioactive source of adequate activity, which moves along with the detector on the opposite side of the drum, a transmission tomography of the drum can be carried out, resulting in an accurate evaluation of the density matrix distribution. This information greatly reduces the uncertainty associated to the mass and location of radionuclides identified inside the drum.

4.2. In-Situ Object Counting System (ISOCS)

In-Situ Object Counting System [R4] is a transportable non-destructive technique for quantifying gamma emitting radionuclides contained in samples, with different form and nature. It is equipped with lead collimators which reduce the detector field of view, making it able to focus on small samples, drums, or even large components. The instrument used in this technique is generally equipped with a semiconductor detector sensitive to gamma photons (the most common being a High-Purity Germanium, HPGe). The ISOCS main strength is its association to a companion calibration software. The operator must provide a geometrical description of the measurement and of the sample under consideration, this includes e.g., sample density, distances, collimator aperture; the calibration software interpolates the most suitable detector efficiency using a comprehensive matrix of pre-calculated efficiencies.

4.3. Laboratory Sourceless Calibration Software (LabSOCS)

This technique refers to a software analogue to ISOCS but applied to a fixed HPGe shielded in an appropriate well [R5]. The sample is placed inside the shielded well to reduce background radiation, maximizing the ability to detect radiation from the sample. The sample dimensions follow the size of the shielded well.

4.4. Multi-Group Analysis (MGA)

Non-destructive measurements of X-ray and gamma-ray emissions can be used to analyse a sample for plutonium or uranium. The Multi-Group Analysis (MGA) is a radiological characterization technique to quantify the isotopic composition of uranium and plutonium based on deconvolution of their low-energy gamma and X spectrum [R6]. This methodology requires no calibrations and can be used to measure virtually any size and type of plutonium or uranium sample. The detector adopted is a HPGe whose geometry is optimized to increase detection efficiency in the energy range where plutonium and uranium emissions occur, generally below 400 keV.

4.5. X-ray spectrometry

The X-Ray spectrometry is a technique based on X-ray sensitive detectors (e.g., CdTe) and can be non-destructive and carried out in situ, given the small size of these detectors. It is useful to detect the X-ray counterpart of the Auger electrons in those radionuclides decaying via electron capture (e.g., ^{55}Fe, ^{59}Ni) and the low-energy gamma emission from transuranic elements (e.g., U, Pu). This technique is particularly useful when radioactive material (emitting X-rays or low energy gamma rays) is occurring in a loosely shielded package, since such relatively low-energy photons may be stopped by surrounding material, preventing them to reach the detector. Self-absorption occurring in the sample itself might be also an issue [R7]. However, the technique should be considered when relatively high-activity waste is considered, for example activated metals in plant where a significant neutron flux occurs [R7].

The same detectors can be used in matrix, in analogy of sensitive pixels on a focal plane, to build a gamma camera. Spectral information is then overlapped on a conventional picture to identify the location of high-activity gamma source [e.g., 7].

4.6. Passive neutron counting

Neutron detection is generally applied to evaluate the presence of actinides, especially fertile materials in radioactive samples, in particular containing isotopes with even mass, such as ^{242}Pu, ^{240}Pu, ^{238}Pu because they undergo spontaneous fission, resulting in the emission of multiple neutrons for each disintegration [e.g., 8]. It is a non-destructive measurement widely applied in many nuclear fields, such as safeguards for the controls of nuclear materials or for radiological characterization of waste following the dismantling of nuclear facilities.

Passive neutron counting is a relatively low-sensitive technique (e.g., is potentially able to detect tens of mg of fertile material) with significant associated uncertainties due to the prompt interaction of neutron with hydrogen and other light elements occurring in the matrix that may surround the waste (i.e., the package). However, this technique may be complementary to gamma spectrometry, because provides evidence for the presence of fertile material which has some gamma emission at relatively low energy.

Passive neutron counting is effective if carried out by means of neutron detectors that typically surround the sample. This geometric constraint implies that the technique can be applied to samples whose dimensions are limited. Measurement systems are commercially available for radioactive waste drums.

4.7. Active neutron counting

Active neutron counting techniques generally use a neutron source to induce fission on fissile material potentially occurring in a sample. Fissile materials are actinides with uneven mass, such as ^{239}Pu, ^{235}U, ^{233}U, which have a low probability to undergo spontaneous fission. The neutron source is typically pulsed and is made by a compact linear accelerator which accelerates deuterium ions toward a target which contains tritium; the consequent fusion reaction generates neutrons with enough energy to induce fission. Neutrons from induced fission reactions reach the detectors at a later time with respect to those from the pulsed source. Such a time difference allows to discern the two signals and quantify the fissile material in the sample [e.g., 9]. This technique is generally more sensitive with respect to passive neutron counting (e.g., it's potentially able to detect a few of mg of fissile material).

The detector and the measurement geometry adopted are the same as in the case of passive neutron counting and they share the same limitations in terms of sample dimensions.

4.8. Alpha spectrometry

Alpha-particle spectrometry is a standard technique for assessing the sample content in terms of alpha-decaying isotopes [e.g., 10]. It is a destructive technique useful to determine the activity per mass unit of the natural and anthropic alpha-emitting radioisotopes contained in radioactive materials, e.g., polonium, uranium, thorium, americium, neptunium. In particular, the technique quantifies very low occurrence (down to fractions of mBq on the sample) of alpha-decaying isotopes; it is used to characterize different materials (soil, cement or iron-based materials, liquid samples, etc.) and it has been applied in different fields, as decommissioning of nuclear installations, nuclear decay data measurements, geological studies, environment, security.

Since alpha-particles promptly interact with matter by loosing energy, the measurement have to be carried out in vacuum for preventing alpha-particles to be stopped by the air between the sample and the detector. Furthermore, the sample itself has to be very thin, for minimizing self-absorption. The latter is usually accomplished by preparing the sample by electrodeposition [R12].

4.9. Liquid Scintillation Counting

Liquid scintillation counting (LSC), or liquid scintillation analysis (LSA), is a standard technique for the detection and quantitative measurement of activity due to alpha- and beta-emitters. It may also include nuclides that emit gamma radiation, as well as atoms that decay with the emission of X-radiation, and those that emit Auger and internal conversion electrons.

LSC is a destructive technique. It involves placing the sample containing the radioactivity, once dissolved, into a glass or plastic container, called a scintillation vial and adding a special scintillation cocktail containing organic fluors dissolved into suitable solvents. Then, the scintillation vial emits photons (usually in the visible range) which are detected by means of photomultiplier tubes [e.g., 12].

Before being mixed with the scintillation cocktail, the same usually undergoes a number of chemical processes like purification and separation of the different elements. Some of these are performed for preventing “quenching”. This effect can be loosely defined as the interference in the conversion of nuclear decay energy to photons of light emitted from the sample vial and can be the result of different physical and chemical phenomena and it is very common in LSC [R13].

However, LSC is a technique very sensitive to radioactivity, allowing to detect very low occurrence of alpha- and beta-emitting radionuclides (down to a few mBq in the scintillation vial).

4.10. Summary

Technique	Sample of interest	Measurement location	Information provided	Underlying measurement technique	Sensitivity (Bq)	Measurement time per sample (h)
Open geometry (par. 4.1)	Drum	Fixed laboratory instrument	Amount of γ-emitters in the drum	Non-destructive γ spectrometry	<100	>1
Segmented γ Scanning (par. 4.1)	Drum	Fixed laboratory instrument	γ-emitters vertical distribution	Non-destructive γ spectrometry	<100	10
Tomographic γ Scanning (par. 4.1)	Drum	Fixed laboratory instrument	γ-emitters volumetric distribution	Non-destructive γ spectrometry	<100	<48
Transmission tomography (par. 4.1)	Drum	Fixed laboratory instrument	Matrix density volumetric distribution	Non-destructive γ spectrometry	-	<48
ISOCS (par. 4.2)	Drum, package	Transportable instrument	Amount of γ-emitters in the sample	Non-destructive γ spectrometry	<100	>1
LabSOCS (par. 4.3)	Package	Fixed laboratory instrument	Amount of γ-emitters in the sample	Non-destructive γ spectrometry	<10	>1
MGA (par. 4.4)	Drum, package	Fixed laboratory instrument	Relative isotopic abundance of Pu and U	Non-destructive γ spectrometry	-	>0.25
X-ray spectrometry (par. 4.5)	Drum, package	Transportable instrument	Amount of X-ray emitters in the sample	Non-destructive, X-ray spectrometry	<10000	24
Passive neutron counting (par. 4.6)	Drum, package	Fixed laboratory instrument	Amount of fertile material in the sample	Non-destructive, neutron detection	(tens of mg)	<24
Active neutron counting (par. 4.7)	Drum, package	Fixed laboratory instrument	Amount of fissile material in the sample	Non-destructive, neutron detection	(a few mg)	<1
Alpha spectrometry (par. 4.8)	Aliquot	Fixed laboratory instrument	Amount of α-emitters in the sample	Destructive, α spectrometry	<0,001	48 (*)
Liquid scintillation counting (par. 4.9)	Aliquot	Fixed laboratory instrument	Amount of α-β- emitters in the sample	Destructive, β counting	0,01	48 (*)

(*) This includes sample preparation

5. Chemical and physical characterization techniques

Chemical and physical characteristics of the legacy waste should be thoroughly determined to choose and validate the appropriate subsequent actions, referred to the risk for human health (operators) and environment, but also to classify the waste from the physic-chemical point of view, in light of its future transport, storage and disposal. Moreover, it is important to analyse the non-radioactive substances, to understand their qualitative and quantitative characteristics, because they might have a substantial impact on the management and disposal activities, as on the final disposal system; the knowledge of the physical and chemical parameters of the waste support, among the others, the prediction of its future long-term behaviour in the repository, especially referring to its reactivity, corrosiveness, explosivity, gas generation, chemical toxicity. Another issue is related to the variability of the chemical characteristics of the waste. Some waste streams are complex, coming from complicated chemical and nuclear processes; in this case, the physic-chemical properties may remain relatively constant over the time because of their stability, but they may also be variable, so to become difficult to manage.

The goal of the physic-chemical characterization (as the radiological characterization) is assessing the source term of the waste, to verify compliancy with acceptance criteria and then to ensure that it is compatible with the management and disposal process and to assure their safety during operations. The physical-chemical characterization regards all the aspects that have a role in safety behaviour of the waste. Some parameters of interest are[1]:

- Density (determination of voids and waste distribution);
- Water content;
- Elemental composition;
- Organic molecules.

5.1. Density

Average density is a pivotal parameter both for storage and transport considerations and for modelling the waste to calculate the interaction of the radioactivity with the surrounding matrix. The latter being a fundamental step in gamma spectrometry, to model the sample for retrieving the most suitable efficiency for quantification of the occurring radionuclides (e.g., cfr. Par. 4.2). It is usually easily evaluated by estimating both mas and volume of the drum, package or component. In the latter case, when very complex geometries occur, such evaluations can be carried out by means of a specific modelling software.

Density distribution inside a waste matrix is also an important parameter, being the presence of voids (e.g., inside a waste drum) one critical parameter for repository WACs. A density volumetric distribution can be non-destructively carried out with radiographies, gammagraphies, or by means of transmission tomography (cfr. Par. 4.1).

[1] For a more exaustive list, see LWC task 2 Report.

5.2. Water content

The amount of water content in the waste or the matrix waste is one of the key parameters to assess for determining the correct treatment or process for waste conditioning. Generally, the amount of water in samples is carried out by means of Karl-Fisher titration method, a destructive technique very sensitive even to trace amount of water and typically based on the oxidation of sulfur dioxide with iodine. The reaction consumes exactly one molar equivalent of water against iodine. Iodine is added to the solution until it is present in excess, marking the end point of the titration, which can be detected by potentiometry [e.g., 13].

5.3. Elemental composition

For assessing the chemical nature of a waste or its associated matrix, destructive techniques are most common. There are two standard approaches: the first is detecting single chemical elements, the second to detect masses, therefore identifying specific isotopes.

The Atomic Emission Spectroscopy (AES) is a laboratory technique focused on determining the quality and the quantity of single elements in a sample. AES records the spectra of the elements in a way that would reveal the general nature of the spectra and offers a definitive summary of the most prominent spectral lines of the elements, i.e., those most likely to be useful for the determination of trace and ultratrace concentrations, down to ppm [R15]. It usually uses a plasma torch to ionize the sample in liquid state and compares the emitted radiation, specific for each element, to a reference library.

The Mass Spectroscopy (MS) is another laboratory technique able to discern between isotopes of different masses. Again, it usually makes use of a plasma torch to ionize the sample, resulting ions are accelerated by means electromagnetic fields. Ion trajectories bend based on their masses and collide to different detectors. This technique is extremely sensitive, being able to detect specific masses down to ppt [e.g., 15].

5.4. Organic molecules

Radioactive organic waste (e.g., contaminated oils) are a family of radioactive waste which shows several issues in terms of processing and conditioning. One of the main parameters for determining the organic content is the Chemical Oxygen Demand (COD), which is a measurement of the oxygen-depletion capacity of a water sample contaminated with organic waste matter [R17].

Assessing the nature of the organic compounds requires more complex analysis such as Gas Chromatography (GC; often the technique is associated to a mass spectrometer, GC-MS). GC-MS is very sensitive in quantifying volatile organic compounds. This destructive technique is based on an ionization process, such es electron ionization, where the gas analyte molecules are bombarded by energetic electrons leading to the generation of a molecular radical ion. This technique generally allows for the determination of both relative molecular mass and the structure of the molecule. One important feature of this technique is that resulting spectra are highly reproducible, which means that mass spectral libraries can be used for identification of unknowns [R18].

6. Characterization techniques applied to legacy waste

Taking into account the information obtained by ERDO members about the legacy waste, in this paragraph a primary analysis of the most suitable characterization techniques is suggested.

Characterization purpose		Characterization type	Applicability	Technique
Radiological	Gamma-emitter radionuclides	Non destructive	All waste	ISOCS
	Gamma-emitter radionuclides	Non destructive	All small size waste	LabSOCS
	Pu and U isotopic ratios	Non destructive	All waste	MGA
	Gamma-emitter radionuclides	Non destructive	Drums	OG, SGS, TGS
	Fertile material	Non destructive	All waste	Passive neutron counting
	Fissile material	Non destructive	All waste	Active neutron counting
	Alpha-emitter radionuclides	Destructive	All waste potentially contaminated by alpha-emitters; not applicable to sealed radioactive sources	Alpha spectrometry
	Alpha- and beta-emitter radionuclides	Destructive	All waste potentially contaminated by alpha- and beta-emitters; not applicable to sealed radioactive sources	LSC
	X-ray emitters; EC-decaying radionuclides (e.g., ^{55}Fe, ^{59}Ni, ^{99}Mo)	Non destructive	All waste	X-ray spectrometry
Physical	Density	Non destructive	All waste	Mass and volume
	Density distribution	Non destructive	All waste	Radiography, gammagraphy
	Density distribution	Non destructive	Drums	Transmission tomography

Characterization purpose		Characterization type	Applicability	Technique
Chemical	Water content	Destructive	All waste; not applicable to sealed radioactive sources	Karl-Fisher
	Elements	Destructive	All waste; not applicable to sealed radioactive sources	AES
	Isotopes	Destructive	All waste; not applicable to sealed radioactive sources	MS
	Organic Compounds	Destructive	All waste; not applicable to sealed radioactive sources	GC-MS

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