CHANCE project

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Synthesis of CHANCE project

DELIVERABLE (D6.6)

Work Package 6

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1. Introduction

The CHANCE project aimed to address the specific issue of the characterization of conditioned radioactive waste. The characterization of fully or partly conditioned radioactive waste is a specific issue because unlike for raw waste, its characterization is more complex and therefore requires more advanced non-destructive techniques and methodologies. There are different and varying reasons for this: 1) conditioned waste may no longer be in its initial form (e.g., due to incineration), 2) conditioned waste is typically embedded or surrounded by a matrix which might obscure or shield radiological spectra and/or physico-chemical compounds, 3) conditioned waste may contain wastes coming from different primary sources and therefore the radiological spectrum might become more complex.

CHANCE focused on these categories of waste as described in [1]:

- Very Low Level Waste (VLLW);
- Low Level Waste (LLW);
- Intermediate Level Waste (ILW);
- High Level Waste (HLW).

The first objective of the CHANCE project was to establish at the European level a comprehensive understanding of current conditioned radioactive waste characterization and quality control schemes, as well as already identified needs across the variety of different national radioactive waste management programmes, based on inputs from end-users members such as Waste Management Organizations and storage operators.

The second objective of CHANCE was to further develop, test and validate techniques that will improve the characterization of conditioned radioactive waste, namely those that cannot easily be dealt with using conventional methods. Specifically, the work on conditioned radioactive waste characterization technology will focus on:

- Calorimetry as an innovative non-destructive technique to reduce uncertainties on the inventory of radionuclides;
- Muon Tomography to address the specific issue of non-destructive control of the content of large volume nuclear waste;
- Cavity Ring-Down Spectroscopy (CRDS) as an innovative technique to characterize outgassing of radioactive waste.

The present report has been produced within the context of the project's Work Package 6. It describes the organisation of the project, the objectives of the different Work Packages, and the main results of the project.

2. Project Organisation

The CHANCE project was structured into six work packages as illustrated in the Figure 1 :

- Management and coordination (WP1)
- Methodology for conditioned radioactive waste characterization: Problematic wastes and R&D proposal (WP2)
- Calorimetry associated with non-destructive assay techniques and uncertainties study (WP3)
- Muon imaging for innovative tomography of large volume and heterogeneous cemented waste packages (WP4)
- Innovative gas and outgassing analysis and monitoring (WP5)
- Dissemination activities (WP6)

WP2 was related to the first objective of the Chance Project and it was dedicated to the establishment at the European level of a comprehensive understanding of current conditioned radioactive waste characterization and quality control schemes across the variety of different national radioactive waste management programmes, based on inputs from end- users. This WP was closely linked to the End-users group comprised of 20 members coming from Waste Management Organisations, Nuclear Facility Operators, Technical Support Organisations and research entities from ten European countries.

WP3, WP4 and WP5 were dedicated to technological developments associated to the calorimetry, muon tomography and CRDS studies.

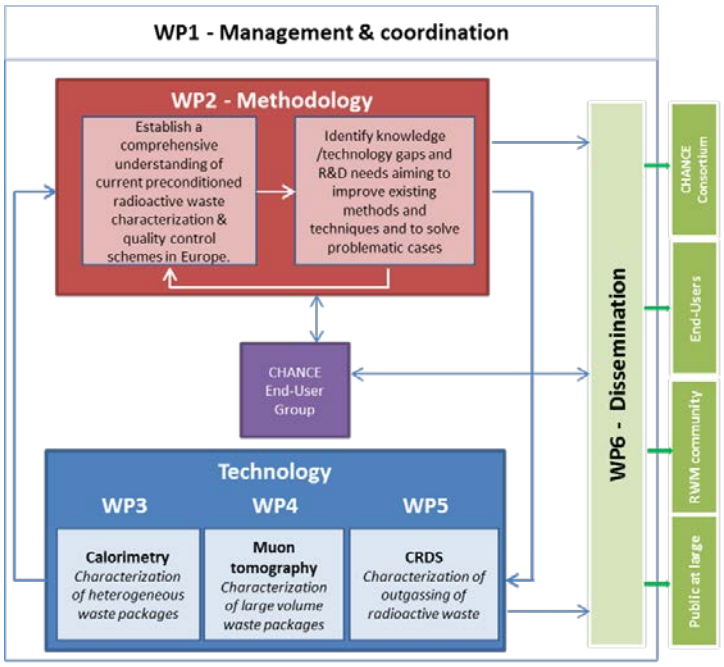

FIGURE 1 - CHANCE STRUCTURE

3. Work-Package Overview

3.1. Methodology for CRW characterization: Problematic waste and R&D proposal (WP2)

The approach of this WP was to be driven by the end-user requirements for the characterization of radioactive waste (VLLW, LLW, ILW or HLW) and specific waste acceptance criteria (WAC) for each disposal concept (surface, sub-surface or geological). One of the tasks of WP2 was dedicated to the identification of links and overlaps between WAC and actual waste characterization technologies available in order to allow CHANCE to identify specific methodological and/or technical knowledge gaps. In order to enhance the efficiency of conditioned radioactive waste characterization methodology, CHANCE proposed to identify:

- key parameters that need characterization;

- technologies commonly used for conditioned waste characterization;
- specific problematic issues for the characterization of conditioned radioactive waste;
- knowledge and technology gaps for radioactive waste package characterization methodologies.

To obtain a broad overview of the end-users needs for the characterization of conditioned radioactive waste, a questionnaire comprising 18 questions was elaborated and distributed to the CHANCE End-User Group [1]. The list of questions included the following subjects: i) existing and planned disposal solutions for radioactive waste; ii) waste acceptance specifications for each solution; iii) technologies used for conditioned radioactive waste characterization; iv) ongoing R&D programs (if any) on the topic of conditioned radioactive waste characterization; v) interest on R&D actions included in CHANCE; vi) socio-ethical and technical frameworks of radioactive waste characterization practices and policies.

13 responses were received from the EUG and the CHANCE WP2 members, including data from Belgium, France, Italy, Germany, Poland, Romania, Spain, Sweden and UK. 8 of these were from national waste management organizations and 5 were from research institutes. The information received was synthesized and complemented with information from the NEA general reports [2, 3, 4] and country specific reports [5] on their waste inventory and waste management programs.

The analysis of answers received allowed to identify some key parameters that need characterization. These parameters, which depend on the disposal/storage and country considered, can be grouped in four categories:

- Radiological parameters such as radionuclide activity, dose rate, surface contamination, content of fissile materials, heating power
- Chemical parameters such as inventory of toxic species, complexing and chelating agents, accelerators of leaching processes, organic substances, pyrophoric, flammable, corrosive, oxidizing materials
- Mechanical parameters such as compression resistance, drop resistance, matrix behaviour (swelling, diffusivity and leachability)
- Other parameters such as hydrogen production, homogeneity of the waste, parameter associated to disposal container (physical dimensions and weight)

Regarding the methods used for characterization of conditioned RW, nuclide vector and scaling factor (SF) methodologies are widely used in many European countries for the characterization of standardized RW streams, and direct information about the origin of waste streams under consideration is also used in many cases. Gamma spectrometry (open-geometry for the whole RW package, or segmented/collimated) is the most widely used non-destructive technique in the characterization of conditioning RW. Some other countries are using dose rate conversion to derive radionuclide activities, but this methodology requires good knowledge of the origin and/or history of the waste, which can be problematic for legacy wastes. Spectroscopic techniques (alpha, beta and gamma spectrometry) are applied in the majority of the institutions involved in RW characterization either for inspection or in the process of SF development. More advanced methods such as active and passive neutron measurements, calorimetry and X-ray inspection are used in some specific cases to identify the fertile and fissile materials, or to analyse the matrix and its density distribution.

Some challenges regarding characterization were mentioned, namely:

- The proper characterization of conditioned legacy/ historical waste packages
- The determination of alpha and beta activities in conditioned RW due to signal attenuation by the waste packages and backfill (compacted drums, concrete)
- The detection of difficult to measure isotopes and sealed radioactive sources
- The limited traceability of the chemical content of waste packages

- The accessibility of the waste for sampling, difficulties in monitoring waste drums packed deeply in a storage facility
- The characterization and reconditioning of the waste already stored in a storage facility

R&D needs are described mainly related to the development of novel non-destructive methods capable to detect the radiological (including α and β emitters) and fissile mass content as well as the chemical content. According to the answers, the newly developed methods should be able to be applied for homogeneous and heterogeneous waste on waste packages of different sizes, including spent nuclear fuel (SNF) casks. All detailed results are described in the Chance deliverable D.2.2 [6].

Based on the identified gaps and needs on waste characterization, the deliverable D2.3 [7] was produced. This deliverable describes the state of the art regarding (RD&D on) waste characterization techniques and methodologies. It also highlights the techniques that can be improved/further developed in the future to improve characterization of conditioned radioactive wastes.

The emphasis of the document [7] is on non-destructive waste characterization methods. The techniques discussed in the document are the following:

- Imaging methods allowing to obtain a visual inspection of the inside and contents of a (conditioned/shielded) waste form.
- Passive measurement techniques, including gamma-based and neutron-based methods. Both techniques are well-established and routinely used to obtain information on easy-to-measure isotopes present in the waste. From these sections onwards, it is detailed how the complete radiological inventory of a waste form can be obtained, e.g., through scaling factors or calorimetry.
- Technical more high-end techniques where developments are still very active in order to allow these techniques to tackle more challenging waste forms and/or isotope quantification. These include active interrogation techniques, cavity ring-down spectroscopy, coupling of different methods and Bayesian approaches that can greatly enhance insights and reduce uncertainties in waste form characterization.
- Mobile and transportable characterization techniques frequently encountered when dealing with heterogeneous wastes or wastes with unknown physico-chemical content.

New developments are underway and are still needed to overcome problems encountered with currently available techniques. To this end, important R&D challenges include:

- high energy and dual energy X-ray imaging to characterize the physico-chemical content and structure of large and dense waste packages;
- photofission (active photon interrogation with high energy X-rays) to measure and identify nuclear materials in large and dense packages;
- neutron coincidence counting with alternatives to ^{3}He detectors (now too expensive);
- active neutron interrogation to measure the fissile mass in high-level waste (high gamma irradiation and high neutron emitters like curium isotopes);
- neutron activation analysis to characterize the chemical elements (including toxic chemicals) or the long-lived isotopes that are difficult or impossible to measure by gamma-ray spectroscopy;
- attenuation corrections (combined matrix and localization effects) based on machine learning techniques and intensive calculations (e.g. Monte Carlo simulations) to establish predictive models of the searched parameters (activity, position of the radionuclides, etc.);
- bayesian approaches to take advantage of all the available information (measurements, expert knowledge, X-ray radiographic or tomographic pictures, etc.) in view to iteratively adjust the prior distributions of the activity, radionuclide location, matrix density and composition, etc. until the model

fits as well as possible the available measured data: for instance the different net peak areas of a radionuclide in a gamma-ray spectroscopy (e.g. ^{239}Pu), the neutron counts of individual detection blocks distributed all around the package, the signals measured with different angles, different fields of view, or at different heights with respect to the package, etc.

- mobile measurement systems: The transport of radioactive waste packages, in particular those with high activity or limited knowledge of their radiological, physical and chemical characteristics, is very complex and obtaining the necessary authorizations is time-consuming, with unguaranteed success. In this context, bringing the characterization device to production or storage sites is often easier. The mobile measurement system can significantly increase the number of waste package characterizations.

3.2. Calorimetry associated with non-destructive assay techniques and uncertainties study (WP3)

The objective of this WP was to complement existing, widely used techniques for characterization of waste packages (gamma spectrometry and passive neutron measurement) with an exhaustive study of uncertainties related to such characterization methods in conjunction with calorimetry.

In the beginning of the project, an overview of the existing calorimeters was carried out [8]; the main designs of calorimeters and specific parts of the calorimetric system were detailed with their advantages and drawbacks. Their performances were evaluated depending on their mode of operation. A review of the main characteristics concerning alternative mature NDA techniques that can be used for characterizing plutonium and other radioactive nuclides in 200 L radioactive waste drums has also been produced. The following techniques have been considered:

- Gamma methods: Gamma spectrometry, Segmented Gamma Scanning, Tomographic Gamma Scanning
- Neutron methods: Passive Neutron Coincidence Counting, Active Neutron Interrogation

MCNP simulations were performed to quantify the percentage of particles (mainly gamma and neutrons) that would leave a waste drum, for a generic and specific source and matrix composition. The results suggest that the most interesting study cases would be polyethylene, bitumen and concrete matrices. While escaping radiation can be largely hampered with these matrices, the heat flux is unaffected, thus demonstrating the usefulness and complementarity of calorimetry in these cases and in general.

Further simulations with heterogeneous and homogeneous distribution of activities within the drums showed that the neutron and gamma measurements are very sensitive to the source distribution, leading to uncertainties that can reach two orders of magnitude, depending on the matrix composition. In case of gamma emission, the two orders of magnitude are obtained for concrete, while for neutron emission it is only a factor of two, leading to a factor four in the neutron coincidence rate measurement. The first MCNP simulations of the calorimeter suggest that the uncertainty related to the energy deposition, based on uncertainty on the distribution of activities within a drum, is much smaller than the two orders of magnitude. Therefore, the usefulness of calorimetry was also demonstrated in cases with unknown distribution of activities within a drum.

3.2.1. Calorimeter development

A large calorimeter with an optimized detection limit to host a 200L drum (10-3000mW range) was developed specifically for the CHANCE project by KEP Technologies. This equipment is composed of a measurement cell opening in two half shells, based on the calorimetric principle using measuring and reference sensors surrounding the sample to be studied (drum) and collecting all the heat released by the sample [9]. The sensors are Peltier elements generating a differential signal proportional to the deviation of the heat flux going through the measuring sensors compared to the reference sensors. The calorimeter is shown in Figure 2.

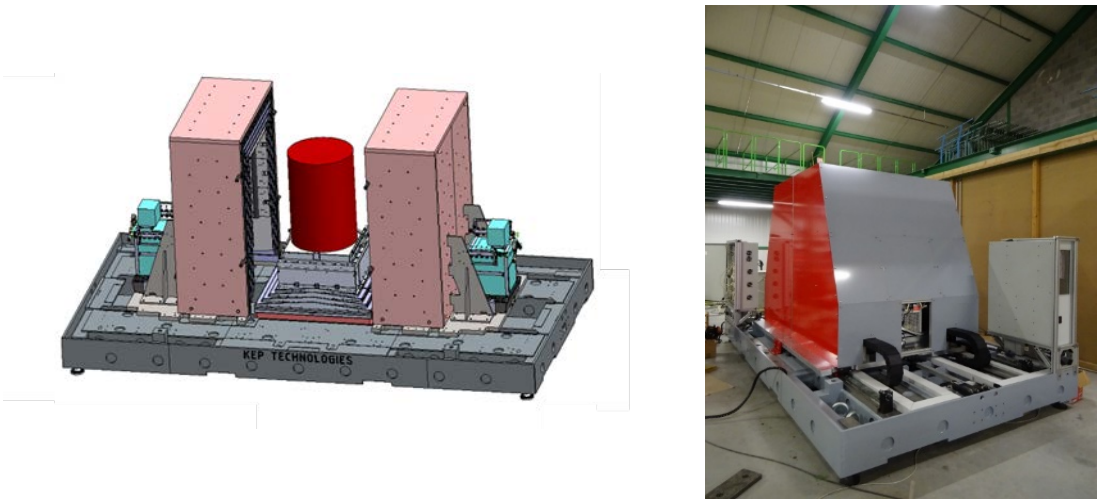

FIGURE 2 - CAD VIEW AND REAL PICTURE OF THE CHANCE CALORIMETER

3.2.2. Measurements

Measurements with mock-up 200 litres drums and a real drum were performed in CEA and SCK CEN facilities with gamma spectrometry, passive neutron counting and using the calorimeter developed by KEP Technologies. The detailed results are described in the deliverable D3.3 [10].

In CEA, calorimetric measurement was carried out with a muck-up drum with Pu pellets in the centre of a concrete matrix not favourable to heat transfer. Energy deposition simulations were also performed for a Pu source located at the $\left(\frac{H}{2}; 0\right)$ position according to the real measurement. Calculations showed that for this case the gamma radiation carries only around 0.03% of the total energy, so more than 99.9% of the energy produced is deposited in the drum and wall of the drum and can thus potentially be detected by the calorimeter. The energy deposition for the sample used, determined by Monte Carlo simulation (code MCNP), corresponded to a thermal power of 106 mW while the measured value equalled 99.7 mW, with an experimental uncertainty being 16.4 mW. Thus, the expected value is in line with the measurement within the uncertainty range.

In CEA some measurements with the mock-up drum with Pu pellets in different positions inside the concrete drum were analysed by gamma ray spectroscopy and Passive Neutron Measurement Counting (PNMC). However, only one measurement in this drum was done using the KEP Technologies calorimeter with Pu pellets in the centre due to a technical breakdown of the device.

The measurement campaign at SCK CEN was focused on three targets:

- Measurement of a real waste drum,
- Exploration of the effect of the spatial distribution of radioactive sources with mock-up drums/reference sources
- Exploration of the effect of matrix composition and density with mock-up drums/reference sources.

The corresponding list of setups, that was investigated at SCK CEN with both the NDA and calorimeter measurements is the following:

- Real unconditioned waste drum
- 7 pins (21 sources) inside a mock-up with a central section with extruded polystyrene and outer layer of mortar
- 1 pin (single source) in the centre of a mock-up with a central section with extruded polystyrene and outer layer of mortar
- 1 pin (single source) at the border of a mock-up with a central section with extruded polystyrene and outer layer of mortar
- 7 pins (21 sources) inside a mock-up homogeneously filled with ethafoam (polyethylene foam)
- 7 pins (21 sources) inside a mock-up heterogeneously filled with ethafoam, PVC, and steel

The results obtained with the measurements coupled with modelling indicated that the gamma spectroscopy and passive neutron coincidence counting (PNCC) measurements may show punitive uncertainties due to radiation attenuation effects in dense waste matrices, when the position of plutonium inside the waste package is not known, which is the case for most heterogeneous technological waste. We observed for instance a discrepancy larger than a factor 10 between the PNCC signals, depending on the source position inside a 220 L concrete mock-up drum. In this frame, calorimetry measurements have shown to be far less sensitive to coupled matrix and source position effects. A more detailed analysis of all uncertainties in the performed measurements and calculated efficiencies, possibly also resulting in more accurate estimates, and a corresponding theoretical assessment of a series of different isotopic vectors, will be provided in D3.4, in view of further quantifying the usefulness of calorimetry for 200L radioactive waste drums.

Concerning the potential benefits of a calorimetric measurement technique added to existing gamma and neutron measurements, we can highlight the following lessons learned that will be extremely valuable for a future application:

- The central block misses a part of the heat emitted by the drum in regards of how the calorimeter is calibrated.
- Therefore, it is important to take into account the heat going through the centre, right and left parts of the calorimeter considering the way how the calorimeter is calibrated.
- The calorimeter is very sensitive to the fast room temperature variation and the thermal inertia does not make it possible to compensate for this effect.
- The reference system (Peltier modules) on the left and right does not see the perturbation coming from the outside in the same amplitude than the measurement system (Peltier modules). When processing the data measured in SCK CEN, a correction coefficient was applied on the reference signals to follow the same amplitude of measurement signal, which gives good results without bringing a bias on the true mean measured power.
- Baseline determination is very important for real drums. For mock-up drums it is very precise as we introduce Pu samples in the same drums used for baseline measurements, but for real drums baseline depends on the mass and thermal conductivity of the waste matrix. Therefore, building a quantitative relation between drum properties and baseline signal would be recommended in the future.

- The minimum detectable power can be as low as 5 to 15 mW under good conditions, meaning a representative baseline is available, temperature fluctuations are limited, and the measurement time is sufficiently long.
- On the other hand, without a representative baseline, the minimum detectable power quickly increases towards values in the range of 100 to 200 mW.

The improvements necessary to study large waste drums and improve the detection limit would be to:

- Adapt the ghost cell to the mass and thermal conductivity of the drum.
- Have a better differential measurement for the left and right blocks, aiming at similar amplitudes of the measurement and reference signal variations with room temperature.
- Insulate the drum more from the outside and let the heat only go through the central block (no more measurements by the right and left will then be necessary), which will also simplify the manufacturing of the calorimeter.

3.3. Muon Tomography

The objective of this Work Package was to develop a mobile muon tomography system to address the as-yet unsolved problem of the non-destructive assay of large volume nuclear waste packages, such as large spent fuel (storage/transport) casks and large concrete waste packages with heterogeneous waste.

In CHANCE it was chosen to produce a system based on both Resistive Plate Chambers (RPCs) and Drift Chambers (DCs). The design is shown in Figure 3. The system consists of 30 RPCs, 18 DCs, and trigger panels. The panels are located in two perpendicular orientations, namely X and Y: each orientation detects hits in the (X, Z) and (Y, Z) planes, respectively, together forming a 3D track. It was chosen to operate the detector in a non-laboratory environment. The detector, which is shown in figure 4, was hosted at the Fenswood Farm, 5 miles south-west of Bristol, UK.

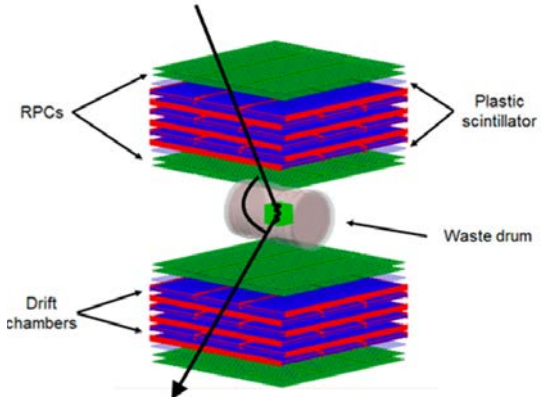

FIGURE 3 - THE DESIGN OF CHANCE MST DETECTOR WITH AN EXAMPLE OF A MUON SHOWING THE ANGLE BETWEEN THE INCOMING AND OUTGOING DIRECTION.

FIGURE 4 - THE CHANCE MUON DETECTOR: THE CONFIGURATION A (RIGHT) AND CONFIGURATION B (LEFT).

Both of the tracking subsystems of the CHANCE detector require an external trigger to know when the muon crossed through the detector and initiate a readout cycle. To provide an external trigger to the CHANCE subsystems, scintillator trigger paddles are used.

During the projects, there were 2 different experimental configurations used. Configuration A corresponds to trigger panels, 2 layers of DCs and 4 layers of RPCs, and Configuration B consists of trigger panels, 1 layer of DCs and 5 layers of RPCs. Figure 4 (right) shows the Configuration A of the system, while Configuration B is presented in Figure 4 (left). Figure 4 (left) also shows a mock-up drum during the experimental program. The 300 L drum was positioned in the centre of CHANCE muon tomograph system.

An RPC essentially consists of a chamber filled with gas under a high voltage (HV). When a charged particle traverses the gap chamber, ionization takes place. Under the influence of the high voltage, a current pulse is produced. This induces a signal on pick up strips on the outside of the sensor. These signals are read out to detect the particle and reconstruct where it traversed the detector. The RPC drift achieved spatial resolutions better than 500 µm and efficiency above 95% when flushed at a rate of 25 ml/min with a mixture of Tetrafluoroethane R-134a (95%) and Iso-butane (5%) at a pressure of about 500 Pa above the atmospheric pressure [5]. R-134a is a very good gas for RPCs. Unfortunately, due to stricter environmental regulations coming into force during the CHANCE project, it was forbidden to use R-134a. It was then decided to switch to CO_2 instead until an environmentally friendly version became available. The signal in the CO_2 filled RPCs is much lower (around 5–10 times) than R-134a. This leads to a low efficiency per layer and since the analysis requires a registered hit in all layers, a very low track efficiency. An environmentally friendly gas alternative was published in November 2021 but is still not available to buy in the UK. A detailed description of the equipment is described in deliverable D4.1 [11].

3.3.1 Global Tracking

Due to differences in the control software between the RPC and Drift Chamber subsystems data acquisition was kept separate up until the global matching and track fit stage. Data is obtained independently from both systems, while their trigger indices are kept approximately synchronized by sharing a common global trigger from the discriminator unit. This allows an additional data processing stage to be run offline to match up the data from both subsystems before reconstructing global tracks of the muons' trajectory above and below the imaging volume. The offline process is split into 3 stages: trigger matching, locale track fitting, final global point-of-closest approach calculation.

Figure 5 shows an overview of the tracking performance for each RPC for the configuration with 5 layers of RPCs. It shows for each RPC how often it was part of a full 5 hit track, how often it was part of a 4 hit track, how often it was missing on an otherwise good 4 hit track, how often it was part of a 3 hit track, how often it was missing on an otherwise good 3 hit track. Ideally, all RPCs are only part of good 5 hits tracks, but this is clearly not the case. Some RPCs were not responding well and are often not recording a hit, for example RPC 16 and 17, while RPC 2, 6 & 7 are showing a lot of hits on 4 hit tracks. The results indicate that we have recorded a small but good sample of tracks, but also that there are parts of the detector system that do not provide (many) hits.

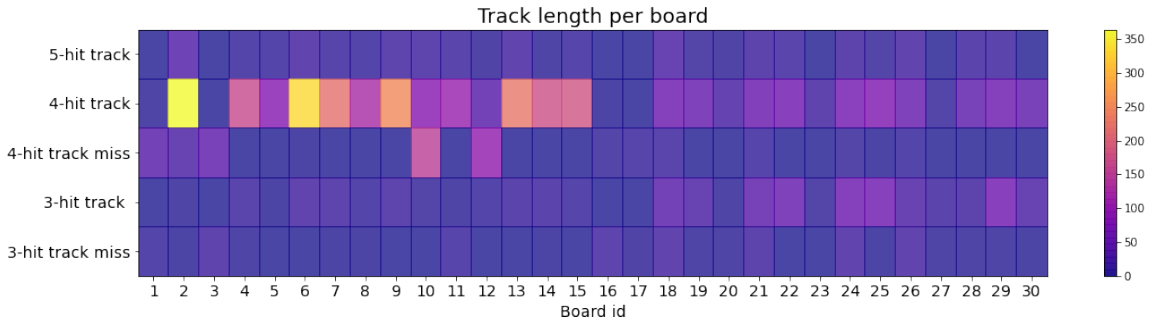

FIGURE 5 - HEATMAP SHOWING FOR EACH BOARD THE LENGTH OF THE TRACK IT BELONGS TO. MOST TRACKS HAVE 4 HITS, AND THE Y LAYERS HAVE A HIGHER DETECTION EFFICIENCY THAN THE X ONES. MISSING HITS ARE ALSO SHOWN IN THE 5-HIT TRACK AND 4-HIT TRACKS CASE.

Several major challenges severely affected the development of the muon system and experimental programme of WP4, see [11] for details. We have tried to mitigate their effects to the best of our abilities and pushed to get the best possible results out of the system before the end of the project. Unfortunately, we have only managed to obtain a small sample of muon tracks, too small to do detailed imaging.

In November 2021, an environmentally friendly Freon alternative with good performance was reported. We have tried to source this. However, it is still not available to purchase in the UK, see [12] for more details.

3.3.2 Simulation studies

An exhaustive series of simulations were performed to assess the expected size and position resolution of any expected feature in a waste drum as a function of the system parameters for a system analogous to the commissioned CHANCE muon detector [13]. The simulations were done using GEANT4 simulations with the detector performance tuned to the expected performance of the CHANCE system. The muons were generated using the CRY library, see e.g. [12b] for details.

Figure of merit tests were developed to enable the imaging performance of standard muon tomography algorithms to be compared to one another. A feature resolution test was developed to understand an algorithm's ability to separate and distinguish high density objects in close proximity to one another. A size resolution test was also developed to understand the smallest object that can be observed by a given tomography algorithm. In each case 3 different algorithms were considered, namely: the simple Point-of-Closest Approach (POCA), the Angle Statistics Reconstruction (ASR), and the Binned Clustering (BC) Algorithm. To understand feature resolution, an array of 20 cuboid uranium target objects was simulated, each with sides of 10 cm in the Y and Z dimension embedded in a concrete-filled nuclear waste drum of dimensions 88 cm high and 57 cm in diameter. The results show, for example, that the PoCA algorithm is only capable of clearly resolving objects larger than 0.95 cm. In contrast, the ASR and BC algorithms both are resolving the presence of a target object down to 4mm.

Several methods for the identification of objects in the radioactive waste packages were developed. These methods allow for the recognition of the blocks of material, both high-density and low-density ones, and finding their size (or volume) and location [14].

A method for high-Z material identification was developed that uses multivariate analysis techniques to locate and identify materials in nuclear waste drums [15]. To evaluate the performance of the method for material identification, we simulated objects made of uranium, lead, and iron of different shapes and sizes dispersed throughout the waste drum. For each test case, we simulated muon track data corresponding to a 10-day exposure. The quantitative analysis showed the method for high-Z material identification perform well in the recognition of blocks of uranium, lead and iron in the conditioned nuclear waste packages. We found the method sensitivity to uranium is $0.90^{+0.07}_{-0.12}$ and a false positive rate of $0.12^{+0.12}_{-0.07}$ (quoted as 95% Clopper-Pearson confidence intervals).

A new approach to gas bubble and void detection was developed as well. It is based on voxel-by-voxel identification of low-density materials and allows for the detection of the location of gas bubbles (or voids) and calculation of their volume. To evaluate the precision of the method and its detection limits, different hydrogen volumes within a waste container filled with bitumen were simulated. Initial investigations indicate that the relative uncertainty on hydrogen volume measurement using muon scattering tomography and voxel-by-voxel approach is below 10% for bubbles larger than 0.85 L. The detection limit of this method is estimated to be 0.55 litre at a 95% confidence level.

In conclusion it is clear can be stated that the forced replacement of Freon by CO_2 in the RPC system lead to a much lower hit efficiency. In order to reconstruct tracks, hits in all traversed layers are required. Hence, the efficiency to detect tracks reduces by the product of the efficiency of all layers. This led to a very small track sample. Due to limited statistics, we were not able to perform more differential experimental studies of the performance of methods of material identification we had developed for the CHANCE muon scattering tomography system. However, in the simulation part of the CHANCE program a lot of scientific progress was made. We published 10 papers in the field, 1 more was submitted recently and 1 more is in preparation, gave 14 conference talks and three PhD theses are in preparation. In addition, many new projects and discussion with new partners, both industrial and academic, has come as a result of the CHANCE project, see [12b] for details.

As such, despite the issues with the experimental program, we achieved a lot of scientific outputs and expect many future muon tomography projects.

3.5. Cavity Ring-Down Spectroscopy (CRDS)

The objectives of this Work Package were to advance the use of CRDS as an innovative technique to characterize the outgassing of radioactive waste by 1) developing a new instrumentation for ^{36}Cl measurement, as $H^{36}Cl$ molecule, and 2) to demonstrate an application of the technique to the monitoring of radiocarbon outgassing from graphite samples and spent ion-exchange resins.

Cavity ring-down spectroscopy is a laser spectroscopy method, where a gas sample is placed in an optical cavity to increase the interaction length between light and the target molecules and allow the detection of extremely small amount of gases. Each molecules has specific absorption features that can be used for this purpose based the knowledge of their rotation-vibration transition energies.

3.5.1 Developing a new instrumentation for ^{36}Cl measurement

^{36}Cl outgasses from nuclear graphite waste packages in the form of Cl_2 and HCl. However, only HCl has strong enough absorption lines to be detected by CRDS.

As $H^{36}Cl$ was never measured with such a technique, its spectroscopic characteristics are unknown. Using the spectroscopic characteristics of isotopologues $H^{35}Cl$ and $H^{37}Cl$, available in literature and especially in the HITRAN database, it was possible to calculate the $H^{36}Cl$ rotation-vibration transitions (D5.1) with a good accuracy. $H^{36}Cl$ transitions are positioned between the $H^{35}Cl$ (5739.26 cm^{-1}) and $H^{37}Cl$ (5735.11 cm^{-1}) ones, so the theoretical peak of $H^{36}Cl$ is situated at 5737.15 cm^{-1} [16].

Fourier-transform infrared spectroscopy (FTIR) method was used to detect and characterize the fundamental and first overtone rotational-vibrational bands of $H^{36}Cl$ [17]. The fundamental band lies in the mid infrared part of the electromagnetic spectrum and the first overtone band in the near infrared. The gaseous $H^{36}Cl$ sample for the experiments was prepared from ^{36}Cl-enriched NaCl-solution.

Experimental work confirmed a line transition lying at 5737.113 cm^{-1}, near to the laser emission range of the PROCEAS $H^{36}Cl$ analyser estimated theoretically. PROCEAS is a commercial CRDS instrument which was first tested for this application but did not perform as expected. Unfortunately, the obtained experimental data for the first overtone transition (in near infrared region) was of too low quality to make meaningful estimation of the spectral line intensity for the $H^{36}Cl$ transition at 5737.113 cm^{-1}.

On the other side, spectral line intensities of the fundamental band of $H^{36}Cl$ rotational–vibrational transition band in the mid infrared spectral region are typically ten times stronger than first overtone line intensities. The determination of these lines was the crucial first step for the development of CRDS equipment. It is advised to design the instrument so that it probes these transitions in the mid infrared spectral region. In this region, it should be also possible to find transitions, which do not suffer so much from spectral interference caused by water molecules. The latest development in instrumentation in this wavelength range can provide the required components (mainly lasers, detectors and high-reflectivity mirrors) to build a suitable CRDS system.

In the framework of the Work Package 5, the potential for $H^{36}Cl$ detection from irradiated graphite by using optical methods, such as CRDS, and other methods such as ICP-MS [18], was also evaluated. Literature studies indicated that the release of HCl (at least at room temperature) is very small, and therefore heating of the samples is necessary to generate enough sample to fill the measurement cavity and allow the measurement. Other gaseous species, such as CO_2 and CO, will be release in much larger amounts which will dilute the HCl and there is therefore no real alternative to concentrating the HCl using a trapping method.

A CRDS system built for HCl detection can achieve a limit of detection of 1 ppb (in the near-infrared) or even 0.1 ppb (in the mid-infrared wavelength region). Those limits are assuming no significant interferences from other species such as water. CRDS will be suitable of HCl monitoring assuming that HCl can be purified and almost pure HCl can be directed into the measurement cell.

If HCl can be trapped efficiently it is clearly feasible to detect it with CRDS. If the HCl can be collected and purified this will enhance the measurement sensitivity. While purification of HCl is challenging due to its highly reactive nature, a few possible approaches can be described:

- HCl can be trapped in a liquid medium using a bubbler and subsequently release by heating up the liquid sample. However, one has to consider also interfering species such as water which can interfere with the measurement due to overlapping absorption lines. Other liquid trapping media than water can also be considered if they have less interfering lines.
- Other trapping methods can be explored where trapping into a liquid medium is not required. A cryogenic trap can be used to concentrate HCl below its boiling point (-85 °C) and then release it by heating the trap. With such an approach high concentration of HCl can possibly be achieved. An adsorbent material can be used to trap HCl and subsequently release it.

Chemical methods were also applied for determination of the ^{36}Cl concentration in samples of irradiated graphite. They were based on the sample decomposition by acid digestion followed by determination by a Liquid Scintillation counter (LSC). The main limitations are that only very small sample quantities can be treated in this way, leading to possible underestimates of the real chlorine content. Furthermore, this method is not sensitive to other gases that may contain active isotopes.

A new approach would be to sample directly the gas released from graphite by using the mass spectrometer ICP-QMS for total Cl and ^{36}Cl content. This technique could be explored in the future as a complement to optical detection methods.

3.5.2 Application of CRDS to the monitoring of radiocarbon outgassing

The detection of radiocarbon (^{14}C) outgassing was based on the detection of $^{14}CO_2$ molecule P(20) absorption line at mid-infrared at 2209.109 cm^{-1}. The CRDS measurement requires concentrating the CO_2 to enable detection of low ^{14}C concentrations at good accuracy. Therefore, an on-line sample processing unit was built for the CO_2 purification and used together with CRDS with is shown in Figure 6. A diaphragm pump is used to flow the air through the sample processing unit. The gas flows through a particle filter to a catalyser, which converts methane and other hydrocarbons to CO_2. The conversion occurs on a palladium catalyst which is kept at 500 °C temperature. Conversion of hydrocarbons to CO_2 allows detecting ^{14}C also originally present in other molecular species than CO_2 (e.g., organic molecules such as methane). The catalyser can also be bypassed to get the ^{14}C content only in CO_2. The detailed description of the processing unit can be found in the deliverable D5.4 [19].

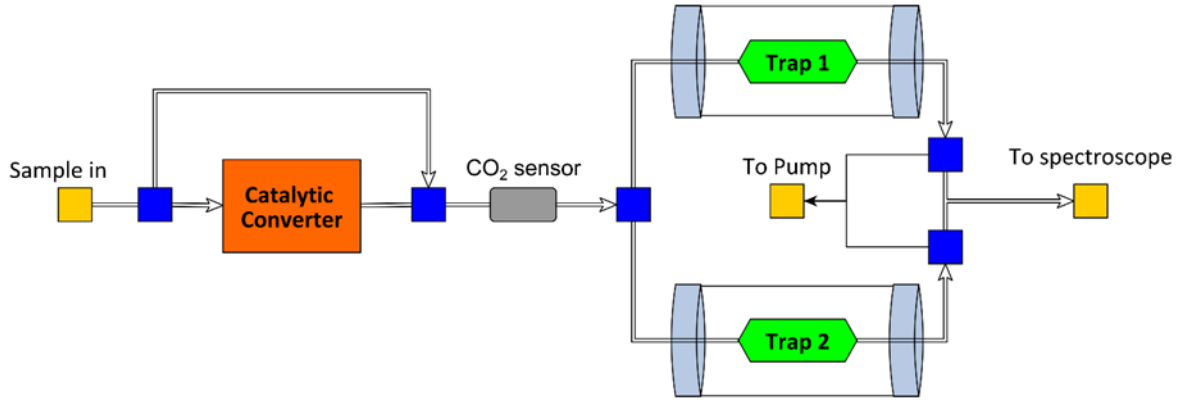

FIGURE 6 - SAMPLE PROCESSING UNIT

^{14}C graphite outgassing

Gas samples were collected into 50 litre gas cylinders from four sealed steel crates containing graphite from the thermal column of the FiR1 research reactor (VTT, Finland). The research reactor was disassembled in 1995 and the graphite in the steel crates was stored in research wells in VTT laboratories.

The samples from the gas cylinders were measured using the sample processing unit together with the CRDS. For each cylinder, measurements were done to measure the total ^{14}C and to measure ^{14}C that was originally in the form of CO_2. This required trapping two samples with the sample processing unit: first one trapping with catalyst, and second one without, and measuring them separately in the CRDS.

The CRDS measurements gave valuable information on the behaviour of ^{14}C in the gaseous form in the stored graphite samples. The measurements showed that significant amount of ^{14}C is released in the air during storage of graphite. The measured ^{14}C activity concentrations from the air sampled from the storage crates mostly followed the ^{14}C activities estimated from scaling factor based on ^{152}Eu measurements. The ^{14}C distribution in different molecular species was also studied, and the measurements showed that there were differences in the distribution between the samples. However, CO_2 is the most abundant airborne carbon species in the samples (74 – ~99 % of all carbon), and therefore contains most of the ^{14}C in the sampled air. The outgassing of ^{14}C from irradiated graphite had not been studied before in such accuracy.

Graphite samples were also analysed with both CRDS and LSC. For CRDS, the measurements on the graphite pieces considered combustion of a sample. The results showed little variation between the measured ^{14}C activity concentration within single samples. The variation is mostly due to variation of the actual activity within the graphite, which depends on the location on the graphite block. In addition, the distance from the graphite block surface affects the activity, as the radiation is strongest at the surface. The same samples have been characterized by LSC 15 months earlier.

Spent Ion Exchange Resin

CRDS was used to measure the production of ^{14}C production from spent ion-exchange resins [20]. The resin samples used originate from the VTT FiR1 research reactor. The resin was an Amberlite IRN150, which is a 50:50 mix of the IRN77 and IRN78 types.

In order to accelerate the outgassing of the spent resin, the samples were heated at 160°C. The total amount of ^{14}C of spend resins were measured. The ratio of CRDS measured ^{14}C concentrations of the two samples was 7.6 ppb / 35.1 ppb = 0.217. This value is close to the ratio of activity concentrations 33.6 Bq/g / 176.3Bq/g = 0.190 detected with LSC, which supports the validity of the CRDS method. In addition to CO_2, N_2O was also observed and the N_2O outgassing increased with the temperature.

4. Conclusions

The characterization of conditioned radioactive waste has been improved in the last years but there are still important challenges in this field, namely for a better characterization of radiological and physico-chemical characteristics particularly for historical wastes.

The studies carried out in the framework of CHANCE contributed to increase the knowledge on the characterization of conditioned wastes through the development of three innovative techniques, calorimetry coupled with more widely used radiological characterization techniques, muon tomography and the cavity ring-down spectroscopy (CRDS).

Results obtained in the framework of WP3 show that calorimetry can significantly reduce the uncertainty when characterizing the mass of plutonium compared to neutron and gamma measurements. Indeed, these last suffer from large waste matrix and Pu (or more general activity) localization effects resulting in punitive uncertainties when measuring large, dense and heterogeneous waste packages, like concrete drums containing technological waste. In such cases, the use of calorimetry in combination with gamma and neutron measurements, and the various experiments interpreted in the project reveal improvements both in bias and precision.

Calorimetry measurement times are long for radioactive waste packages (a few days, plus a few days for the baseline measurement for a 200-L drum) and this technique should be used when gamma spectroscopy and passive neutron coincidence counting are not conclusive, making another reference measurement with smaller uncertainties necessary to guarantee an acceptance criterion.

A muon system was commissioned but unfortunately a number of unforeseen challenges, in particular the ban on the use of Freon, which is the key ingredient for our detectors, have led to a very small track sample, too small for detailed imaging. A lot of progress was done on reconstruction methods addressing the issues of material identification of objects in waste drums, the detection of gas bubbles in drums and detection of irregularities in filling CASTOR V52 drums. These methods were developed using Monte Carlo simulations that were tuned to the expected performance of the CHANCE system based on the measured performance of very similar detectors operated by our group.

A new environmentally friendly Freon alternative have been found, but not on item for a deployment in CHANCE. The inventors reported very similar detector performance as we pre-Freon ban achieved with very similar detectors. Therefore, we are confident that with more data with the new gas, the capabilities demonstrated in our simulation studies, in terms of materials identification, void location, material location and material differentiation would be reflected in our empirical findings.

The implementation of CRDS method in measuring outgassing of ^{14}C from graphite was demonstrated successfully. The measurements showed good repeatability and accuracy. The technique was also successfully used to measure small amount of ^{14}C of spent ion-exchange resins in real-time.

We have shown that $H^{36}Cl$ detection is possible with laser spectroscopy as suitable absorption lines were experimentally measured. A strategy for the development of a more advance laser spectroscopy system (e.g., CRDS) capable of detecting trace amount of $H^{36}Cl$ is outlined in the work performed in the project. More research work is however required to achieve this goal, which is particularly challenging due to the low concentration of ^{36}Cl expected in the outgasses from, e.g., irradiated graphite waste.

CRDS and the LSC measurements have been compared, and both techniques show benefits but also limitations in radiocarbon measurements. To reach the best measurement performance, the best suited technique should be selected depending on measurement circumstances and requirements. The LSC works best, when low detection limit is required, and samples can be prepared properly for the measurement. The CRDS performs better in field measurements, in continuous monitoring, and where flexibility of the measurement is important, or information of the radiocarbon speciation in different carbon species is required.

Besides the experimental developments, the overviews related to the waste characterization issues, produced in the project, allowed to clarify and identified the further needs, challenges and methodologies applied or in development through Europe.

Great improvements have been done in the development of innovative detection and characterisation systems, reconstruction algorithms, data acquisition and modelling in the framework of CHANCE project but future needs remain namely:

- For Muon tomography:
  - experimental confirmation of the new algorithms using the existing system but with the new gas;
  - development of algorithms for the monitoring of even smaller gas bubbles in bituminized waste to study the formation and behaviour of the gas bubbles and assess the safety risks of the bubbles;
  - improvements in the algorithms for material identification for objects inside the waste drums to limit the data taking time and identify smaller objects;
  - imaging of the contents of CASTOR drums; not only to verify that the fuel rods are present, but also their structural integrity and imaging the contents of waste silos.
- For calorimetry:
  - developments to improve the insulation of the calorimeter allowing to measure smaller effects more reliably and to be able to work in facilities with important room temperature fluctuation
  - developments to decrease measurement time and to increase accuracy in the quantification of radioelements emitting high gamma ray activity
- For CRDS for outgassing monitoring, future developments will focus on validating the method in real industrial conditions. Characterization of the method in different gas matrices will also be needed to ensure that the CRDS works in all situations. Finally, simultaneous detection of different radionuclides of interest (e.g. C-14, tritium, Cl-36) will be implemented in order to have a single system capable of detecting all relevant radioactive species present in outgasses.

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