Characterization of radioactive waste and packages

Peter Ivanov
Acoustics & Ionising Radiation
National Physical Laboratory, UK
Contents:

• Characterization objectives;
• Characterization strategy;
• Characterization process;
• Methods and techniques for characterization
• Scaling factors/nuclide vectors/nuclear fingerprints
• Conclusions.
CHARACTERIZATION OBJECTIVES:

The objective of radiological characterization is to provide a reliable database of information on:

- type of radionuclides
- quantity
- distribution
- physical properties
- chemical states

Characterization involves:

- survey of existing data
- calculations
- in situ measurements
- sampling
- analyses
CHARACTERIZATION OBJECTIVES:

Using characterisation results next stages can be planned:

• **operating techniques:** decontamination processes, dismantling procedures (hands on, semi-remote or fully remote working) and tools required;

• **radiological protection** of workers, general public and environment;

• **waste classification**;

• **resulting costs**.

Comparison and optimization of these factors will lead to the selection of a decommissioning strategy, i.e. typically, immediate or deferred dismantling
INITIAL CHARACTERIZATION

At the very beginning, the purpose is to collect sufficient information to assess the radiological status of the facility and identify any problem areas.

Data collected during this initial characterization step are generally based on available information, including historical operations documentation, and are used in:

- planning the overall decommissioning programme;
- prioritizing and sequencing major decommissioning activities.
Necessary and sufficient criteria for waste characterization must be identified as early as possible in the whole life cycle of waste management. The greatest benefits of waste characterization occur when the main investments and operating costs of characterization efforts are undertaken by the waste generator as early as possible rather than at later stages of the waste management life cycle.

Waste characterization uses **three main techniques**:

- Process knowledge
- Non-destructive examination and assay (NDE and NDA)
- Destructive analysis (DA)
- Scaling factors
WASTE CHARACTERIZATION

Process knowledge

Knowledge and documentation of the processes of waste generation is one of the most effective ways of assessing the characteristics of waste.

Process knowledge can help limit the range of characteristics possible and analysis methods to be used. In a fuel manufacturing plant, for example, uranium and its attendant products may be the only radionuclide species possible; therefore, broad analyzes to identify components in the nuclide vector will not be necessary, and specific methods to quantify the uranium present will be all that is required.

For new wastes, maximum benefit of process knowledge is being obtained by setting up effective waste stream control and segregation practices at the point of origin. A majority of the waste streams may fall into the simple and stable subcategories.

Process knowledge can also be valuable when considering historical wastes.
WASTE CHARACTERIZATION

Non-destructive assay

Non-destructive assay (NDA) involves analysis based on observing spontaneous or stimulated nuclear radiation (gamma rays of neutron flux),

NDA of radioactive waste often involves the characterization of the whole waste package.

Three different methods exist to perform non-destructive measurements: gamma methods, neutron methods and calorimetry.

- **Gamma methods** rely on capturing \( \gamma \)-photons emitted from the wastes as part of radioactive decay of the radionuclide species present.

- **Neutron methods** typically rely on capture of neutrons emitted either through spontaneous fission or \((\alpha,n)\) reactions and are primarily used to identify and quantify fissile or fertile isotopes in the wastes.

- **Calorimetry** relies on measuring the specific heat generated from radioactive decay to quantify the amount of activity present (SF and HLW).
WASTE CHARACTERIZATION

Non-destructive assay

When there is an abundance of process knowledge and the characteristics are stable and reproducible, the simplest (and cheapest) NDA methods (e.g. package dose rate) may be used with a high degree of accuracy.

If there is little prior knowledge or the package characteristics exhibit a high degree of variability, more sophisticated and complex (and hence, more expensive) methods must be employed, and accuracy will be severely limited.

The best and most accurate results occur when the process is highly controlled, the waste characteristics are uniform, and the simplest (and least expensive) methods are fully adequate.
Non-destructive assay

When **waste characteristics are relatively uniform** and a high degree of process knowledge exists, NDA may be effective with **larger package sizes**. When there is a high degree of variability or little specific process knowledge, accuracy may be limited by package size.

The more **sophisticated and complex the method**, the higher **knowledge and experience requirements** for the operator.
WASTE CHARACTERIZATION

Non-destructive assay

The simper methods tend to be used for routine waste processes. More complex methods tend to be used for research and development, for quality checking laboratories, or for very complicated and difficult waste streams such as historical wastes.

When the highest degree of accuracy is required for each individual package, more complex methods may be required. When the accuracy of a large population is more important than that of each individual package, simpler methods may be adequate. The statistics of averaging works in our favour in this regard.

The best approach is to try to develop a programme where by detailed process knowledge is obtained and the simplest, highest volume processes adequately meet accuracy requirements. The aim is to perform what is necessary and sufficient, no more and no less.
Non-destructive assay: **gamma methods**

Gamma ray scanning provides a non-destructive method to **measure the inventory of γ-emitting nuclides inside a waste package** where the specific nature of the matrix and the relationship between the radioactive nuclides and the matrix may be unknown. Two types of scan modes can be described:

— **Integral gamma scanning (IGS)**, which is a procedure to **measure an integral gamma** spectrum of an item. Integral gamma ray scanning can be performed with collimated or open detection geometry.

— **Segmented gamma scanning (SGS)**: A procedure to **measure one or more segment** spectra of an item. Segmented gamma scanning requires the **use of collimated detection** geometry.

To be representative for the complete waste package, gamma ray scanning **usually** involves a procedure that acquires an **integral gamma spectrum**.
WASTE CHARACTERIZATION

Non-destructive assay: **gamma methods**

Gamma scanning is used to apply for:

- **Inventory verification** before waste processing or transport,
- **Waste inspection** before interim storage or final disposal,
- **Quality checking** of waste conditioning processes,
- **Free release** measurements.

The γ-measurement procedures can be applied to different **types of waste packages**:

- **Raw or unconditioned waste**, including process waste (filters, resins, control rods, scrap etc.) and waste from dismantling or decommissioning;
- **Conditioned waste** in various forms and matrices (bitumen, cement etc.);
- **Broad range of activity levels**: low level, intermediate level and - with some restrictions - high level radioactive waste.
Non-destructive assay: **gamma methods**

**Dose rate:** Useful for a very stable nuclide vector; it does not specifically quantify individual radionuclides. **Simplest** of all gamma measurements and **very fast** process.

**Gross gamma counting:** Can be very fast and makes use of large scintillation detectors. Again, useful for very stable nuclide vectors; it is **not nuclide specific**. Simple process. **With large detectors can be very sensitive**, much more than dose rate measurement.

**Energy window or single channel analyser (SCA):** Useful when there is interference from naturals or other gamma emitters and you wish to focus on a key nuclide. **Biggest advantage is speed.** This does not require complex amplifiers or software, which quickly use up signal processing time.
Non-destructive assay: **gamma methods**

**Multi-channel analyser (MCA):** Specific for individual nuclides. Can independently **quantify each gamma emitter.** Requires more knowledgeable operator to interpret results. **Nuclear data issues still exist.**

**HR HPGe vs. LR γ-detectors (CdZnTe):** Resolution determines how clearly different nuclides can be discriminated from each other. **Higher resolution detectors** required when nuclide vectors are complex and many gammas of close energies are emitted. LRGS detectors are **more sensitive** on a size for size basis and **cheaper.**

**Modelling coupled with HRGe (e.g. CANBERRA ISOCS):** Very **complex technique,** difficult to operate and easy to abuse. Requires an operator with knowledge and experience.
WASTE CHARACTERIZATION

Non-destructive assay: **gamma methods**

**Tomography:** Potentially the **most accurate** technique; it corrects in 3 dimensions. Very **powerful** and no longer limited by computer processing time. Now it is limited by 3-D resolution of scan. More **expensive** and potentially **time consuming** process.

**Gamma imaging (gamma camera):** Routinely used in our days. Scans an area and overlays visual camera image with a survey of dose rate. Some systems incorporate spectroscopy. Very **powerful survey tool** that helps **identify hotspots** where more focused surveys should be taken. Can save planning time and staff dose.
Non-destructive assay: **gamma methods**

Two different system configurations are distinguished according to the detection geometry and type of scan procedure—**open detection geometry (A)** or **collimated detection geometry (b)**:

Open detection geometry

Collimated detection geometry
WASTE CHARACTERIZATION

Non-destructive assay: **gamma methods**

Complex and stable and complex and variable waste types require segmented **gamma-scanning** to determine the activity distribution in vertical, angular and radial mode in the waste form. The scanning mode should be selected depending on the expected spatial distribution of the radioactivity:

- **Vertical scanning**: vertical heterogeneous activity distribution (assuming radial and angular homogeneity in each segment);
- **Angular scanning**: in combination with vertical scanning characterizes coordinates and activity of the **hot spots in each vertical segment**;
- **Horizontal scanning**: in combination with vertical scanning, determines the radial radioactivity distribution.
Non-destructive assay: gamma methods

Based on the geometrical position of the $\gamma$-detectors towards the waste package there are three ways of scanning- vertical, horizontal and angular.
Non-destructive assay: **Neutron measurement**

**Passive total counting:** Every neutron emitted is counted. **Not specific to any individual actinide.** Can be very sensitive due to statistical precision but easily upset by interference from other neutron emitters.

**Active coincidence counting (ANCC):** An ever-present random neutron source induces prompt fission in fissile isotopes. Coincidence electronics rejects the random neutrons and only counts those from the fission. Useful for fissile isotopes, primarily **U-235** and **Pu-239**.

**Combined Passive/Active Techniques:** Where wastes contain both uranium and plutonium, a combined active/passive method can be used to individually quantify each component. The **passive** result indicates the **Pu-240** and **U-238** (if present in large quantity) and the **active** result indicates **U-235** and **Pu-239** content.
WASTE CHARACTERIZATION

Destructive analysis (DA)

Destructive analysis provides the most accurate and unbiased activity determination.

Chemical and radiochemical treatment of the primary waste or waste form allows measurements to be performed that assure the traceability of the determined activity.

This is not the case with NDA methods, which typically use standards calibration or modelling. As a consequence, there is greater uncertainty with NDA in terms of determining activity.
Destructive analysis (DA)

The DA process involves sampling, sample preparation and chemical separation methods.

• **Sampling** is a critical step in the characterization process. Designing the sampling procedures and checking the homogeneity and representation of the samples assures the reliability of the final results.

• **Sample preparation** by dissolution/mineralization has to be applied in accordance with the physicochemical characteristics of the matrix of waste forms or primary wastes and as a function of the behaviour of the specific element in the dissolution media (volatilization, precipitation).

In some cases, it is possible to do a direct measurement of the radionuclide after dissolution/mineralization if the determination technique has the resolution required for it.
WASTE CHARACTERIZATION

Destructive analysis (DA)

• **Chemical separations** involve the chemical strategy to eliminate chemical interference (e.g. Ca in Sr determination) and radiological interference in the measurement through a chemical process such as:

  • precipitation
  
  • solvent extraction
  
  • ion-exchange
  
  • extraction chromatography
WASTE CHARACTERIZATION

Destructive analysis (DA)

• Radiometric determination is performed by instrumental analysis. Sophisticated methods are used such as:

  • LSC that allow a/b spectrometry,

  • alpha spectrometry with semiconductor (PIPS) detectors,

  • high resolution gamma spectrometry for high and low energy gamma emitting nuclides,

  • mass spectrometry that gives an accurate and efficient response for the analysis of the prepared and/or separated waste samples.
SCALING FACTORS

DETERMINATION AND USE OF SCALING FACTORS FOR WASTE CHARACTERIZATION IN NUCLEAR POWER PLANTS
Difficult to measure (DTM) nuclides. A radionuclide whose radioactivity is difficult to measure directly from the outside of the waste package by non-destructive assay means. Example: Alpha emitting nuclides, beta emitting nuclides and characteristic X ray emitting nuclides.

Easy to measure (ETM) nuclides. Gamma emitting nuclide whose radioactivity can be readily measured directly by non-destructive assay means.

**Activation product (AP).** A radionuclide produced by neutron activation. For example, in decommissioning waste comprising structural materials from a nuclear facility, APs might typically be found primarily within the matrix of the material.

**Fission product (FP).** A radionuclide produced either by fission or by the subsequent radioactive decay of radionuclides thus formed. Example: $^{137}$Cs, $^{90}$Sr.
Corrosion product (CP). A radionuclide produced by neutron activation of products of material corrosion that are transported through the reactor core. Example: $^{60}\text{Co}$, $^{63}\text{Ni}$.

Correlation coefficient (CC). A CC is a number between $-1$ and 1 that measures the degree to which two variables are linearly related. If there is perfect linear relationship, with positive slope between the two variables, we have a CC of 1; if there is positive correlation, whenever one variable has a high (low) value, so does the other. A CC of 0 means that there is no linear relationship between the variables. Typically values of the CC above 0.6 have been taken to indicate evidence of significant positive correlation.

Scaling factor (SF). A factor or parameter derived from a mathematical relationship used in calculating the radioactivity of a DTM nuclide from that of an ETM key nuclide as determined from sampling and analysis data.
The SF method is based on developing a correlation between easily measurable gamma emitting nuclides (key nuclides) and DTM nuclides. The activities of DTM nuclides in waste packages are then estimated by measuring the gamma emitting nuclides and applying the SFs.

The international standard ISO 21238:2007 provides a general methodology for empirically determining SFs to evaluate the radioactivity of DTM nuclides in low and intermediate level radioactive waste packages.
SCOPE

The SF method has been developed from operating experience at nuclear power plants for low and intermediate level radioactive waste.

However, this method can be applied to a range of conditions and types of waste and facilities such as:
• Nuclear power plants, research reactors;
• Fuel manufacturing and processing;
• Nuclear decommissioning;
• Contaminated waste, activated waste;
• Historical waste.

This is because the basic methodologies described in the ISO 21238:2007 standard and IAEA NW-T-1.18 technical report can be used to demonstrate a correlation between DTM nuclides and selected ETM gamma emitting nuclides in virtually any situation where DTM nuclides and ETM nuclides are co-produced.
The SF method is a technique for evaluating the concentration of DTM nuclides, which are typically represented by beta emitting and alpha emitting nuclides, such as $^{14}\text{C}$, $^{63}\text{Ni}$ and $^{240}\text{Pu}$, which exist in these radioactive wastes.

In the reactor, key nuclides (gamma emitting nuclides such as $^{60}\text{Co}$ and $^{137}\text{Cs}$, which are measurable from outside of the waste package) are generated concurrently with DTM nuclides and transfer within the plant systems.

In the SF method, the concentrations of DTM nuclides in radioactive wastes are evaluated by multiplying the concentrations of the key nuclide by the coefficients calculated based upon radionuclide data obtained by sampling and radiochemical analysis (i.e. the SFs, which are the ratios of radioactive concentrations between DTM nuclides and key nuclides).
SCALING FACTOR METHOD

Radionuclide analysis data obtained from the study of actual radioactive wastes or other nuclear power plant radiological data are used in considering the various factors affecting the ratios of concentrations between DTM nuclides and key nuclides, which are expected during the course of radionuclide transport from the production stage into radioactive wastes as the final destination.

These factors include:

• Similarity in production mechanism;
• Similarity in transport behaviour within plant systems.

In applying the empirical SF method, however, it is necessary to judge its applicability through evaluation based on actual analysis of the target radioactive wastes.
Selection of the key nuclides
To establish representative correlations, KN are selected according to the following criteria:

• The KN must have a correlation with DTM nuclides;
• The KN must be present in the assay mixture in significant quantities;
• The radioactive half-life of the KN must be long enough for sampling, measurement, and physicochemical processing;
• The KN and DTM in the initial mixture should be formed by a similar mechanism: in nuclear fuel cycle facilities, the radionuclides arising from fission reactions in the fuel should be distinguished from radionuclides due to activation of structural materials;
• Similar chemical behaviour (e.g. solubility) of the KN and DTM;
• The KN can be non-destructively measured beyond the detection limit.
The following groups with similar chemical behaviour may be distinguished:

- $^{55}\text{Fe}$, $^{57}\text{Co}$, $^{58}\text{Co}$, $^{60}\text{Co}$, $^{59}\text{Ni}$, $^{63}\text{Ni}$. The most suitable tracer is $^{60}\text{Co}$ because of its abundance and radioactive half-life.

- $^{107}\text{Pd}$, $^{106}(\text{Ru+Rh})$, $^{103}\text{Ru}$: these are platinum-group metals with similar chemical behaviour. The radioactive half-life of $^{106}\text{Ru}$ makes it a better tracer than $^{103}\text{Ru}$, but it is poorly suitable for extended cooling times;

- $^{144}\text{Ce}$, $^{147}\text{Pm}$, $^{151}\text{Sm}$, $^{154}\text{Eu}$, $^{155}\text{Eu}$: these are lanthanides with comparable chemical behaviour. The radioelements $^{144}\text{Ce}$, $^{154}\text{Eu}$ and $^{155}\text{Eu}$ are directly measurable by γ spectrometry, but the half-life and γ spectrum emitted by $^{154}\text{Eu}$ make it a better tracer;

- $^{134}\text{Cs}$, $^{135}\text{Cs}$, $^{137}\text{Cs}$: these are all isotopes of the same chemical element. Because of its radioactive half-life and rate of formation in the reactor, $^{137}\text{Cs}$ is the best tracer here;

- $^{244}\text{Cm}$, $^{243}\text{Cm}$, $^{242}\text{Cm}$, $^{241}\text{Am}$, $^{242}\text{mAm}$, $^{243}\text{Am}$: these trivalent actinides exhibit similar chemical behaviour during spent fuel reprocessing. $^{241}\text{Am}$ is “directly measurable” by γ spectrometry, provided the 59.6 keV γ line characteristic of this radionuclide is measured under carefully controlled conditions.
A DTM nuclide such as $^{63}$Ni, which is produced by activation, can be expected to correlate with a key nuclide such as $^{60}$Co, which is also produced by activation and has physicochemical characteristics similar to it.

FIG. 5. Example of difference of SF between different plant designs.
Selection of DTM and key nuclide pairs

Similarly, an FP such as $^{129}$I has a production method and behaviour similar to the ETM nuclide of FP $^{137}$Cs. Therefore, $^{63}$Ni can be expected to correlate with $^{60}$Co, and similarly $^{129}$I with $^{137}$Cs. That is, if a reliable correlation can be developed between a DTM nuclide and a key nuclide, the SF method can be applied with reasonable certainty.

In practice, the available key nuclides, particularly those with sufficiently long half-lives, are limited to a select few, such as $^{60}$Co, $^{137}$Cs, $^{144}$Ce and $^{125}$Sb.

Therefore, only a few of the DTM nuclides can be logically paired with the available key nuclides based strictly on the similarity of their production mechanisms and their physicochemical characteristics.
Selection of DTM and key nuclide pairs

For the other DTM nuclides, the SF methodology reverts to purely empirical relationships. For example, $^{14}\text{C}$ and $^{90}\text{Sr}$ may be typically correlated with $^{60}\text{Co}$, even though the paired radionuclides do not have much in common with respect to their production route or chemical similarity.

In these instances, as long as a correlation can be demonstrated to exist, the DTM nuclide can still be inferred reliably from the concentration of the key nuclide.
It is broadly accepted that the vast majority of waste characterization applications will involve the use of scaling factors to some degree.

However, it must be recognized that the use of scaling factors is a serious and complex matter with many pitfalls and it is easy to be misled.
The following general guidance addresses many of these potential pitfalls.

Changes to chemistry or process is likely to change the distributions of nuclides, so scaling factors will need to be reassessed following any significant change, for example, changes to reactor power rating will change burn-up profile, changes to process chemistry, resin or filter types, etc.
Take into account the “log-log trap”. If logarithmic regression is necessary to produce a mathematical correlation, the uncertainty grows dramatically and may become several orders of magnitude.
Scaling factors are waste stream and case specific, not reactor type specific.
There is a trend in certain organizations to use scaling factors to assess ETM nuclides in addition to DTM and ITM.

In principle, this is not necessary because ETM nuclides can be directly measured.
If scaling factors are used to assess DTM in waste or waste forms, it is important **to validate these factors** through DA.

This is specially important **for the radionuclides affecting the long term dose to man** during the surface or geological disposal of the waste packages – e.g. I-129 and Se-79 in case of geological disposal of high-level waste.
A sufficiently large set of samples should be taken and analysed according to a sampling strategy.
Sampling strategy

The following sampling strategy is highly recommended when sampling is unsafe, difficult to perform, or expensive:

• define an initial sampling program taking into account the future necessity of analytical determinations (number and weight of the samples);

• clearly identify the traceability records;

• send the samples to the laboratory in order to realize representative subsamples;

• archive sufficient quantities of representative subsamples;

• process the initial analytical characterization programme to get data required to define the decommissioning strategy.
Sampling for establishing the decommissioning strategy

Sampling strategy

It may be possible to use aliquots of representative archived subsamples for the following needs:

• get more information relative to the waste stream to be decommissioned (special measurements required for safety, for design engineers);

• qualify the final waste form;

• determine the ratios for the DTM scaling factor.
CONCLUSIONS

- Characterization should not rely on the use of a single assessment method but requires the joint use of theoretical calculations, in situ measurements, sampling and analyses.

- Methods, techniques and equipment for performing characterization are available. Normal radiological survey techniques can be used to take measurements during the characterization process.
CONCLUSIONS

• The characterization is **complete when sufficient information is collected**, taking into account uncertainties.

• For a systematic approach to decommissioning planning, it is important that all relevant radiological characterization is in a **well documented** form consistent with QA requirements.
Literature:

- Radiological Characterization of Shut Down Nuclear Reactors for Decommissioning Purposes, IAEA TECHNICAL REPORTS SERIES No. 389.


- Determination and Use of Scaling Factors for Waste Characterization in Nuclear Power Plants (2004); IAEA Nuclear Energy Series No NW-T-1.18 (2009);