Toward a Lean Analysis for Waste to Support the Decommissioning Operation– 15321

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ABSTRACT

All over the world, several nuclear facilities have been shut down few years ago and are now under dismantling or will be dismantled in the future.

- Dismantling project takes place according to three major phases:
- Study and definition of the dismantling scenario
- Dismantling site operations
- Decommissioning and final state characterization.

Each step is lead in agreement with safety, security and waste management. This requires analytical tools appropriate to the radiological environment and aims. In the field of security, fissile products, explosives... will be researched and quantified while occupational safety requires quantification of radiological, carcinogenic, mutagenic and reprotoxic elements such as As, Se, Cr(IV) ... or even asbestos in order to follow more and more strengthened rules. For waste management, radiological and chemical quantification are necessary but must be completed by determining physical and chemical properties such as reactivity, stability or dissolution of the waste...

Required level of knowledge, analytical deadline, uncertainties, limits of detection and matrix varieties depend on the decommissioning phase.

Setting up a dismantling scenario requires the most possible accurate knowledge of the initial source term present in the facility, in order to establish waste management flow-sheets, define dismantling intervention modes, and prepare the associated safety demonstrations. As history is often not sufficient, in-situ investigations and off-site laboratories are necessary to assign an initial waste and radiological inventory and propose some strategy operations.

When a first scenario is chosen, more detailed samplings and analyses are required to fully prepare estimates of waste volumes and categories, and define and validate the waste recovery system that would be used during the dismantling operation. As the definition of the dismantling plan takes shape, data must be more and more accurate and reliable in order to define the waste outlet. The scaling factors for the waste must be defined in order to assure the refunding of the waste. This includes complete characterizations of various matrixes, with high precision, low detection limit in a limited time of few months, as sketchy data could lead to fix inappropriate plan.

Once site operations begin, it is necessary to control the safety operational conditions and waste production. Measurements requirement is under the safety threshold. Matrixes are often limited to filter. The most important factor is deadline, because operations delay is costly.

Finally at the end of dismantling operations, analyses must be performed to demonstrate the successful clean-up of the work site. Analytical methods with low detection limit are required.

Thus, characterization appears as a graded and iterative process and is a key issue for decommissioning and dismantling operations in term of efficiency and cost. In order to face this huge analytical demand, a strategy for sampling and characterization must be developed regarding the real needs.

On site measurements are usually performed with existing hand-held instruments. A basic first level of knowledge is obtained without delay, feeding the dismantling scenario. On these bases, a sampling strategy permits to select some representative specimens to be more precise, and accurate analysis is performed on off-site laboratories introducing an additional difficulty: the sampling on the site and sub-sampling in the laboratory itself. Whatever the level of sampling, aliquots are small considering the dimension of the dismantling area.

This step is crucial. Sampling strategy must be optimized according to objectives (scaling factors measurement, waste level). But in the particular case of high radioactive level waste, due to security manipulation constraints, the number and mass of samples collected are limited. At the opposite for low level waste, large number of samples is collected meaning that large analytical method capacity is necessary.

Optimization of the analytical plan is critical. The analytical strategy (including control of subsampling, analysis sequence according to analytical capability and performances, especially for pure beta emitters) developed for real case will be detailed.

INTRODUCTION

In the context of nuclear facility dismantling operations, waste characterization is vital for the main phases of any project: setting up scenarios, following up the work site, final site characterization.

These characterizations mean monitoring and follow-up of the 3 crucial aspects of running such operations, i.e. safety, security and waste management. The nature, number and performances of the analytical methods to implement are specific to each phase, as shown in Table 1.

Table 1. Nature, number and analytical performances required for the main phases of a dismantling project [1].

Dismantling phase		Definition and validation of the scenarios	Work site follow-up	Final state
Type of characterization	Sampling (number)	+++	++	+++
	Level of knowledge	+++	+	++
	Radioactivity level found	HL, IL, LL, VLL	HL, IL, LL, VLL	LL, VLL
	Matrix variability (sludge, concrete, graphite…)	+++	+	++
Analytical performance	Accuracy/uncertainty	+++	+	++
	Limit of detection	++	+	+++
	Time needed	++	+++	+

The characterizations expected are widely varied, and concern virtually all physico-chemical characterization disciplines, with a high knowledge level for analytical technics and matrices behavior.

The characterization measurements to be made depend on the final applications:

- ANDRA specifications, for existing waste route authorization purposes
- Treatment specifications, in order to ensure the waste is compatible with the existing waste routes
- Specifications related to respecting work safety regulations in conventional and nuclear environments (asbestos, toxics…).

The following needs can be found:

- physico-chemical measurements (physical state, viscosity, pH, conductivity, density, granulometry…)
- nuclear measurements (dose rate, all the radionuclides present),
- elementary analysis (inorganic),
- organic molecules (ligands, TBP…)
- solid (oxidation state) or liquid phase speciation analysis (CrVI, CeIV…)
- chemical or thermal reactivity study (pyrophoricity, stability etc.)

Apart from high-level technical and analytical skills, projects need to have available methods enabling the processing of the volume of samplings generated by dismantling operations. To meet the growing demand and the on-going changes to ever more demanding waste management specifications driven by quality accreditation situations, analysts from laboratories need to undertake studies, in collaboration with the primary contractors responsible for the dismantling operations order giving, in order to establish the best analytical strategy to meet the final objective (conformity for a waste route, scaling factors definition, work site intervention conditions, etc.) [2].

Thus the analyst's first task is to identify, understand and analyze the needs of the prime contractor and analysis order-giver, to then be able to define the analytical methods to implement, their sequencing and the options which will require a pause for decision-making. This situation examination is essential to ensuring the expected result can be obtained, using the most-suitably adapted analytical means.

Two often complementary types of intervention should be considered: in-situ work site characterizations and analyses to be carried out in appropriate laboratory conditions.

IN-SITU CHARACTERIZATION

In-situ characterization is an essential step. Coupled with the facility's historical records, its objective is to define the facility's radiological environment to settle the sampling strategy for the dismantling project. This is generally carried out using portable apparatus. The measurements are relatively fast and qualitative on raw samples with no prior preparation, enabling a tight sampling mesh. Furthermore, an immediate response is obtained

In the field of nuclear analyses, dose rate measurement detectors are commonly used. To analyze gamma and alpha emitters, specially-adapted cameras have been developed over recent years and are today widely used. For pure beta emitters, digital autoradiography has been used in LL situations, but to date its use in more highly contaminated environments has not been tested.

For elementary analyses, several devices based on different physical principles (LIBS and X Ray Fluorescence) are regularly used for geology purposes. In speciation analyses, new relatively cheap handheld devices based on spectroscopy RAMAN and IR analysis have also come onto the market. They are used in forensic or archeometry work. They can enable identification of asbestos or of organic products.

The use of these instruments in IL-HL environments requires:

- possible anti-radiation strengthening of the instrument's more fragile components (for example, the input/output window of the XRF, detectors, etc.)
- performance qualifications (spectral interferences, etc.) in the potential environment.

Feedback studies regarding physical measurements in HL environments must also be carried out.

In the case of final state in-situ characterizations, the instruments' detection limits may need to be improved.

Geostatistical processing of the analytical data thus acquired leads to a complete radiological (or other, depending on the type of measurement) mapping of the facility, which will help direct further samplings to be carried out for complementary analyses in a laboratory.

The sampling must be suitably dimensioned in location, number, volume and type, depending on the objectives to be reached. The optimal sampling plan is not always compatible with:

- The environmental constraints existing in the facility: in HL, radiological considerations impose the sample volume/mass, and certain zones are not physically accessible or for regulatory reasons it is not possible to carry out samplings there
- The analysis laboratory's capacities: the lab may not be able to manage the volumes and performances required
- The budget available – this may limit the number of analysis requests
- The time available to carry out the study must take into account the analytical delay and numbers of samples to measure.

A few rules to respect are listed below:

- Location: clearly distinguish the zones typically contaminated or activated; check for homogeneous or non-homogeneous zones (e.g. seek the optimal mixing time for a tank)
- Type: matrix (e.g. bulk mixed waste or specific waste – concrete, plastic etc.)
- Sample masses necessary to carry out all the test characterizations must be defined
- Sampling methods:
  - For measurements of volatiles (^{3}H, ^{14}C, Cs, Ru etc.), heating must be avoided (thread saw, shears..)
  - For measurements of metallic substances, avoid the use of metal cutting tools (saw, drill bits, etc.)
- The form of the sample (chips, thick metal pieces, powder, gravel, core drillings etc.) can considerably simplify laboratory measuring procedures
- Conditioning: the sample collection and storage containers must be suitable for the radiological level and processing location (Bag, remote handling in hot cell) and the storage time.

The samples collected are supposed to be representative of the entire zone of interest, which in fact has a much greater volume. None sampling is better than a badly-taken sampling (uncontrolled, with a poor procedure), which would lead to higher costs and possibly to unreliable data.

LABORATORY MEASUREMENTS

Experience has shown that laboratory analyses are a key point and expectation during the course of a dismantling project is large (slow performances and thus delivery times which may take several months). The analysis objectives are either:

- to define and/or confirm a dismantling scenario. As well as the need to characterize primary waste, the analysis laboratory is more and more subjected to requests to carry out

experiments simulating the procedures to be applied in situ, in order to optimize the process, quantify its performances and define the composition of secondary waste.
- or to define and/or validate the waste acceptability for its planned waste route (VLL, LL, IL, HL for Andra disposal site, Centraco …).

To achieve this, an evaluation or declaration for each of the radionuclides present in the waste needs to be carried out. The evaluations are based on knowledge of the facility and on the measurement of samples considered to be representative of the waste composition. The scaling factor reflects this information. In the context of cleanup and dismantling operations, the facility's initial scaling factors (or that for part of the facility) are likely to change following the implementation of treatment operations (rinsing etc.) It is then necessary for a new assessment to be carried out.

As an example, for waste accepted by the Aube facility (CSMA), 143 radionuclides are subject to be declared sometimes at very low limits (e.g. ^{41}Ca and ^{126}Sn must be declared as soon as their activities in the waste are higher 10^{-4} and 10^{-3} Bq/g respectively) and the maximum acceptability limits (MAL) have been defined by ANDRA for 40 radionuclides, of which about 75% are α or pure β emitters. Furthermore, these specifications can change drastically; for example the MAL for ^{36}Cl has been decreased by 3 magnitudes.

Analysis of these radioelements is very time consuming and requires the involvement of highly qualified personnel, all the more so given that the requirements regarding performance and quality for such characterizations are extremely demanding. In the U.S.A., the NRC (Nuclear Regulatory Commission) rightly recommends care to neither underestimate obvious safety and security risks nor overestimate the quantities and uncertainties for the radionuclides measured in waste, as an over-evaluation could lead to an immediate cost over-run and to the saturation of storage capacities. Similarly, ANDRA has specified that "The uncertainty associated with the activity declared for a package should lead to no more than a slight risk of exceeding the maximum acceptable limit (MAL). Consequently, all packages must respect the MAL, even if their activity is increased by the uncertainty corresponding to a confidence interval of 95 %)". Nevertheless, it is also specified that "the activity evaluation methodology retained must overall take on a leading role".

These recommendations mean that analysis methods with low detection limits are necessary in order to avoid overestimating the quantity of radionuclides present in the package, and the uncertainty associated with the measurement must be low when results are close to the threshold values. Given the complexity and duration of these characterizations, careful selection of the samples to be processed and the analytical strategy to implement are essential.

Apart from the chemical and radiochemical analyses, a set of easy physico-chemical analyses which could be necessary for treatments in order to make waste compatible with the requirements of a waste route is needed: granulometry, viscosity, specific surface, etc.

EXAMPLE OF A DISSOLUTION UNIT

A major program is in progress at Marcoule to dismantle the first French defense reprocessing complex, UP1. This complex was commissioned at the end of the 1950s and operated for 40 years. This extensive dismantling and waste recovery program must therefore cope with a large variety of waste and radiological situations. In many cases, operating events and poor documentation lead to a critical need for characterization activities prior to defining or initiating the dismantling operations. These characterization programs are supported by the tools, analyses and expertise of NucLab [3]. Most of the collected data are used in the safety reports, and the measurement, calibration and qualification techniques are part of the licensing process for each dismantling or recovery operation.

For the cleanup and dismantling of the continuous dissolver equipment, preliminary inspection confirmed the existence of sludge and deposits at the bottom of the dissolver. The in-cell counters confirmed the presence of Pu and provided a rough estimate of the activity. A specific program to collect 18 active samples was then defined and carried out.

Difficulties appeared in the sample collection as the sludge was located under the bottom support plate of the vessel. This perforated plate was about one inch thick and the preliminary rinsing test showed that the residues were partially blocked under the plate. In order to ensure fully representative sampling, the plate was removed by plasma cutting and specific systems were adapted to allow the collection of samples for analysis (Figure 12). The results obtained by the laboratory were taken into account on line for the definition of the interventions and the corresponding safety reports. The assessment of Pu content and its chemical and physical forms were of prime importance for defining of the sludge recovery technique. They were also considered in the safety report prepared for the future waste elimination route. The analytical laboratory provided the project with more than 200 physical, chemical and radiological data items under approved Q.A. conditions delivered in acceptable time. The required analyses included gamma spectroscopy, chemical analysis of U and Pu, quantification of hydrogen in Pu, Pu isotopic composition, ^{90}Sr measurement, graphite quantification, chemical analysis of cations, anions, acetate, formate as Pb, B, Ni, total Cr, Cr(VI), As, Sb, Hg, Be, Se, Cd, CN.

The wide variety of available analytical techniques in NucLab was necessary to address the uncertainties on the sludge content, chemical composition and physical behavior under transfer and filtration conditions. Based on these results the recovery and filtration of the sludge is currently in progress.

Fig 1. Perforation system to collect samples

CONCLUSIONS

To summarize, in order to meet the characterization needs for cleanup and dismantling work sites, and in particular to establish the scaling factors, the following are necessary:

- Analytical process enabling access to α or pure β radionuclides, which are difficult to measure. The radioelement looked for is often just present at a level of a few Bq or tens of Bq in a sample where ^{137}Cs and/or ^{60}Co can be present with activity levels from 10^7 to 10^8 Bq/g. Because of their radioactivity, it is necessary to isolate the radionuclide in a pure fraction without any chemical element and free from other radionuclide which could interfere with the measurement. The measurement must be accurate with a low uncertainty level, and efficient in terms of detection limits.
- Samples which are representative of the packages which will be produced, thus enabling extrapolation to scale. Their integrity throughout all the operations (sampling, storage…) must also be ensured. The results of in-situ measurement analyses constitute essential data for representative sample selection decisions.
- A high analytical processing capacity. The overall main role involves the analysis of several samples (5 to 7 samplings are typically recommended to establish a typical spectrum).

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