Retrieval and Conditioning of Powder Waste: Investigations Carried Out in a Storage Pit to Consolidate Input Data Prior to Conditioning – 14207

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ABSTRACT

The decladding facility was built in the early 1980s to store spent fuel elements pending reprocessing. In the context of final shutdown operations, waste initially present in various pits was transferred to a temporary storage pit, originally used to manage effluents sent to the Marcoule liquid effluent treatment station. A waste conditioning matrix has been developed by the CEA and requires input data in order to be optimized. The information available to date allowed certain physicochemical characteristics of the waste to be estimated, but is not sufficiently detailed to provide a basis for waste treatment. Further analytical investigations are necessary. This paper describes the analysis program.

INTRODUCTION

Marcoule was the home of the first French electricity-generating nuclear reactors (3 gas-graphite reactors operated between 1956 and 1984) and spent fuel reprocessing plant (UP1 and various ancillary facilities operated between 1958 and 1997). The reprocessing plant was shut down nearly fifteen years ago and decontamination, dismantling and waste retrieval activities have been in progress since then.

The MAR 400 decladding facility was built in the early 1980s to receive various types of spent fuel elements intended for reprocessing. The MA-EST pit in MAR 400 was originally an interim storage pit for effluents before they were sent to the Marcoule liquid effluent treatment station (STEL). The pit has a useful volume of 53 m^3 and a total volume of 113 m^3.

During the final shutdown operations in the decladding facility, the waste initially stored in pits 7 and 14 was transferred to pit MA-EST. The volume of transferred to the pit was estimated at 52 m^3 in April 2009 after a video survey.

A waste conditioning matrix is being developed by the CEA as part of the waste retrieval and treatment project for the materials stored in pit MA-EST, and it requires input data for optimization. The data available to date allowed some physicochemical characteristics of the waste to be estimated, but is not sufficient for waste treatment. Investigations were carried out in the pit to obtain further information. Two types of investigations were carried out:

In situ investigations

- Video surveys in the headspace of the pit to confirm the waste volume,
- Video surveys in the actual waste volume to assess the waste breakdown,
- Gamma spectrometry measurements in the waste volume to assess the overall activity distribution,
- Interpretation of the results (data cross-checking and coupling) to identify suitable sampling points,
- Assessment of the most relevant samples taking into account the difficulty of the operations.

Laboratory analyses of representative samples

- Exhaustive characterization of the physical and chemical properties of the flowable solid waste,
- Radiological and radiochemical characterization of the waste.

The main technical difficulty in implementing this program is access to the pit. The only available access is through a plug 50 mm in diameter. The investigation and sampling techniques had to be adapted to these dimensional constraints in order to fulfill the project.

All of the in situ investigations have now been completed. The samples were sent to the NucLab Laboratory at Marcoule and the first analysis results are now available. Complete characterization of all the samples will be completed by February 2014.

Investigation program

The investigation program includes three phases:

- Video examination via the selected access point(s) for sampling,
- Assessment of the level and volume of sludge in pit MA-EST,
- Localized representative sampling of the materials for characterization in the NucLab analysis and investigation laboratory.

INVESTIGATIONS IN PIT MA-EST (OBSERVATIONS AND SAMPLING)

Access to pit MA-EST

The existing access points to the pit are limited. The central access provision is encumbered by a large number of inoperative equipment items that prevent easy access to the sludge in the pit.

For these investigations the creation of new access provisions was not considered given the short deadlines and the necessary authorizations. The selected access route was therefore the drain pump penetration, which is situated 1.6 m from the pit filling port. The access plug is 50 mm in diameter (Figure 1).

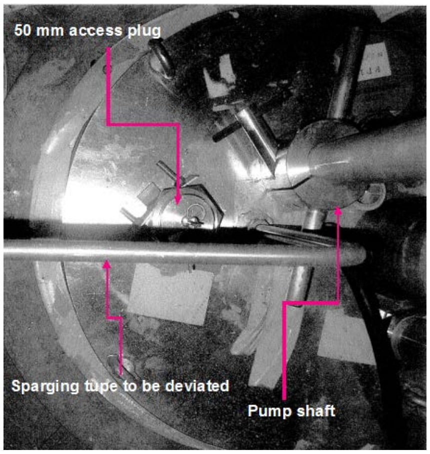


Figure 1. View of selected access plug

Video examination via the selected access port for sampling

The main objective of the video survey was to confirm that access to the sludge was possible through the selected port, and that sampling was technically feasible (unobstructed by equipment or piping).

The video investigation was carried out in July 2012. It revealed the presence at the pit access point (Figure 2) of the drain pump (retracted at the top of the pit), a sparging tube, and the measuring rod (retracted to safe position). Better accessibility was obtained by deviating the sparging tube to allow access to the plug and by removing the measuring rod.

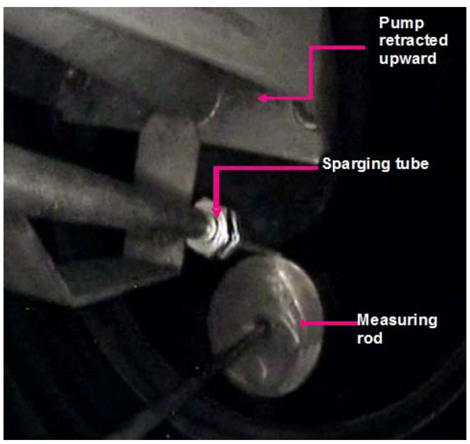


Figure 2. Video examination: location of sparging tube and measuring rod

Confirmation of the level and volume of sludge in pit MA-EST

In the July 2012 video examination, the height of the sludge layer was determined relative to the access point in the pit headspace, and the image was compared with the visual examination performed in 2009. The physical state of the pit is shown in Figure 3. Based on the available drawings, the sludge volume was estimated at 40 m^3.

Figure 3. View of sludge surface in pit MA-EST

The consistency and nature of the sludge was also evaluated by means of a transparent tube in November 2012 (Figure 4).

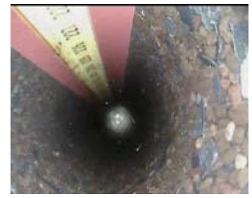
Figure 4. Tube inserted in the sludge

The tube was inserted in the sludge until it touched the bottom of the pit:

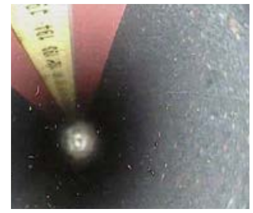
- to visualize the layers of waste in the pit,
- to obtain collimated gamma spectrometry measurements at different depths for a nondestructive assessment of the layers.

Visualization of waste layers

A camera was inserted in the tube positioned in the sludge. Three distinct zones were clearly visible (Figure 5). The positions of the sampling points were determined from these observations:



Upper layer: a layer about 10 cm thick with coarse, heterogeneous waste particles.



Intermediate layer: a thicker layer (30-50 cm) containing a large fraction of graphite fines, and other coarse particles in decreasing amounts toward the bottom of the layer.

Main layer: the bottom sludge is 190 cm thick (83% of the total height of waste) of homogeneous appearance comprising finer particles.

Figure 5. Images in the sludge taken through the transparent tube

Collimated gamma spectrometry measurements

Ambient dose rate and collimated gamma spectrometry measurements were carried out through the transparent tube. The collimator is shown in Figure 6.

Figure 6. CdTe detector and collimator

The measured ambient dose rate ranged from 750 to 900 mGy/h over the full height of the sludge. Gamma spectrometry measurements were carried out with a CdTe detector, because its compact size was suitable for the poor access conditions and because of its compatibility with high flux levels. The measurements show that ^{137}Cs is the major element. The dose rate measurements and physical observations were used to construct a radiological model with Mercurad dose-rate modeling software. The model is used to determine the total radiological activity of the sludge. Assuming a layer of coarse elements at the top of the pit and graphite fines at the bottom, the total activity is 182 TBq of ^{137}Cs equivalent:

- Coarse elements (29 TBq) at the top,
- Graphite fines (153 TBq) for the remainder.

The number of samples and their positions were determined from the values measured in situ.

Location of sampling points

Access to the pit is limited, and all the sampling points must be situated on the same centerline. Considering the poor accessibility and representativeness of the samples, and based on the measurements carried out in the pit, six sludge samples and one liquid sample were taken. The sampling points are indicated in Figure 7.

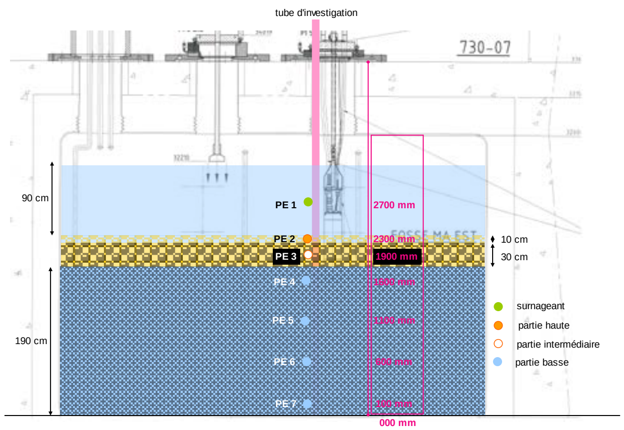


Figure 7. Location of sampling points

Sampling equipment

The sampling equipment had to have the following characteristics:

- less than 50 mm in diameter because of the access constraints,
- sludge sampling capacity between 100 and 200 g (the mass necessary for the all the requested analyses),
- capable of being opened by a telemanipulator arm in a shielded cell of the analysis laboratory,
- capable of penetrating into the sludge to a depth of 2 m to obtain all the requested samples,
- a mechanical system to avoid modifying the sludge composition.

Based on these criteria, studies and tests were carried out in surrogates representative of the observed sludge composition. The resulting sample head is shown in Figure 8.

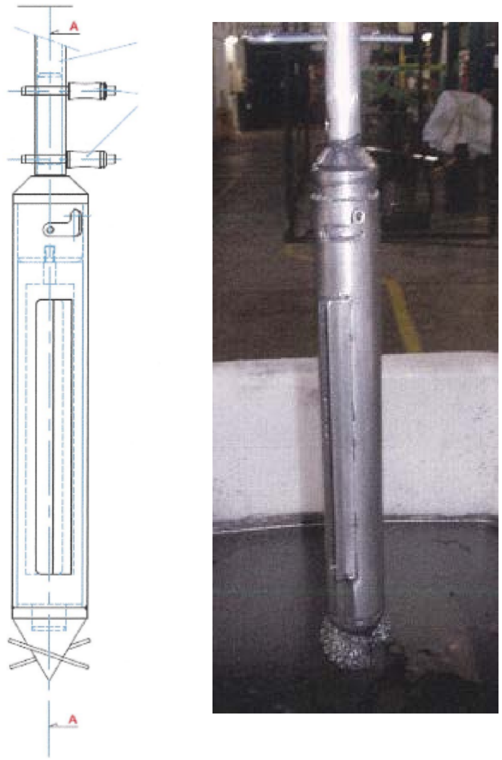


Figure 8. Sampling head

Sampling

Six sludge samples were taken in February 2013 and received by the NucLab analysis laboratory in March 2013. The characteristics and results of analyses already performed on the samples are indicated in Table I. Despite the “average” sampler content (50% full), the sampled volumes are sufficient to carry out the defined characterization program.

Table I. Summary of sample characteristics and first analysis results

Sample	PE01	PE02	PE03	PE04	PE05	PE06
Volume (mL)	100					
Mass (g)		156	75	129	79	64
Visual appearance	Supernatant	Similar to resins	Granular sludge	Granular sludge	Granular sludge	Granular sludge
^{137}Cs activity of wet sludge (10^6 Bq/g)		4		3.8		
Water content (wt%)		21.6		25.2		22.6
Bulk density		1.52		1.36		
Macroscopic examination		in progress		Graphite (70%), Zeolites (30%)		Graphite (60–70%), Metal particles (20–30%), other (10%)
Particle size distribution (wt%)		in progress				17% <800 µm 18%: 500−800 µm 27%: 200−500 µm 11% > 200 µm
Cations		Al, Mg, Fe, Cr, Ca, Ba, Si		Al, Fe, Cu, Ca, Si, U, K		Al, Mg, Fe, Na, B, U
Anions						nitrates, chlorides, sulfates, fluorides
^{238}U isotope (wt%)		99.6		99.6		
^{239}Pu isotope (wt%)		75		69		
^{240}Pu isotope (wt%)		22.6		27.6		
βγ emitters ^{137}Cs (wt%)		99.9		99.9		99.8
βγ emitters ^{60}Co (wt%)		0.1		0.1		0.1
βγ emitters ^{154}Eu (wt%)				0.1		0.1

ANALYTICAL CHARACTERIZATION PROGRAM

The objectives of the characterization program are to specify the physical and chemical properties and the radiological characteristics of the flowable solid waste in pit MA-EST with a view to incorporating it in a dedicated cement matrix.

On receipt of the samples by the analysis laboratory, the ^{137}Cs activity of the wet sludge will be estimated by gamma spectrometry measurement combined with a model developed with Mercurad. This basic data will be the benchmark value for the specific activity of a significant volume of wet sludge.

The wet samples will be submitted to visual observation and macroscopic examination. The wet sludge sample will then be divided into three subsamples:

- a wet sludge sample of significant volume to determine the rheological characteristics of the sludge,
- a wet sludge sample to determine the properties of the dry solids,
- a wet sludge sample for dissolution and physicochemical characterization of the sludge.

An “average” sample will be prepared from a fraction of each sample taken. All the analyses will be performed on this sample.

Rheological characteristics of the sludge

The sludge will be analyzed:

- to determine the settling kinetics in a graduated test cylinder by visual observation,
- to determine the bulk density (ratio between wet mass and wet volume),
- to check the representativeness of the sample after settling compared with the initial sample.

Characteristics of dry solids

The sample will be dried at constant weight at 60°C to determine the free water content of the waste and the dry solid content. After drying, the following operations will be carried out:

- macroscopic examination of the dry sample and estimation of the nature and size of the particles observed,
- sieving to determine the dry particle size distribution between 50 mm and 1 mm, and macroscopic examination of different size fractions.

Dissolution

The sample will first be homogenized and dissolved. An aliquot of about 1 g will be sampled for dissolution. The dissolution solution will be filtered to 0.45 µm. The insoluble dissolution residues will be dried and weighed to determine the residual insoluble content. The solution will be measured by gamma spectrometry to evaluate the solubilized activity and to calculate the residual specific activity of the insolubles. If the residual insoluble content is greater than 5% *and* the residual specific activity exceeds 10%, a second dissolution will be performed.

Physicochemical characterization of the sludge

The dissolution solutions will be characterized as follows:

- uranium and plutonium isotopic compositions
- uranium and plutonium concentrations,
- activity concentrations of alpha emitters,
- activity concentrations of beta-gamma emitters,
- concentrations of major cations: Al, Mg, Na, Fe, Ni, Mn, Cu, B, Ca, Ba, Mo, Zr, Rh, Pd, Tc, La, Sr, Eu, Pr, Nd, Gd, Ce, Sm, Th, Zn, Ag, Li, P, Cd, Si, U, Be, Pu,
- concentration of toxic elements: As, Hg, Pb, Cd.
- concentrations of anions: nitrates, nitrites, sulfates, chlorides, fluorides, oxalates, formates, acetates, phosphates.

To minimize the number of characterizations and the duration of the analysis program, the uranium and plutonium isotopic compositions will be determined for only two samples and the toxic element concentrations will be determined for only three samples.

INITIAL ANALYSIS RESULTS (TABLE I)

Samples PE02 and PE04 are now being analyzed. An average sample was prepared from samples PE04, PE05, PE06 and PE07 (25% from each sample) and is now being analyzed.

Estimated ^{137}Cs activity of wet sludge

The entire sample was measured. The activity is given with an uncertainty of 30%.

Characteristics of dry solids

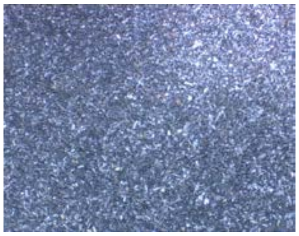
Four particle size fractions will be determined from the dry samples. The objective is essentially to identify the finest fraction (< 50 µm) and the coarsest fraction (> 1 mm). Based on visual observation of the sampled waste, the size fractions were defined as follows:

Sample PE-02/03: 4 mm, 1 mm, 800 µm, 500 µm,

Samples PE-04 to 07 and PE-08: 800 µm, 500 µm, 250 µm, 100 µm.

Figure 9 shows macroscopic images of two samples.

PE04, 800 µm screen (×1)



PE08, 100 µm screen (×2)

Figure 9. Macroscopic images of samples

Physicochemical characterization of the sludge

After dissolution of a fraction of the samples (about 5 g/sample) the requested characterizations were carried out or are now in progress. The gamma spectrometry measurements on the whole sample gave values equivalent to those determined after dissolution (with allowance for the water content and density). This result demonstrates the representativeness of the 5 g sample compared with the complete sample.

CONCLUSION AND OUTLOOK

The data currently being determined are essential for validating the formulation of the encapsulation matrix for the waste recovered from pit MA-EST developed by the CEA waste containment R&D teams.

Further investigation will be necessary, but the initial results are sufficient to validate the encapsulation matrix. The final objective is to define the matrix formulation by the beginning of 2015, as its characteristics will be taken into account by the studies in progress for installing a cement encapsulation unit for the flowable solid waste recovered in the MAR 400 program. All the analytical data should be available in April 2014 to envisage the treatment of the sludge.