Setting an Optimal Procedure for Transfering Intermediate Radioactive Effluents: Contribution of Laboratory Experiments – 15234

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ABSTRACT

The INB35 nuclear facility at the CEA Saclay center is in charge of collecting and treating radioactive effluents generated from site's research activities. The first step of the process consists of an evaporation. The concentrate is an IL radioactive suspension with high salt concentration and suspended matter content. Until the 1990s, the resulting effluents were bitumen coated and since 2012 they have been cemented. During the 1990s, concentrates were stored in 7 tanks, named MA50X with X from 1 to 7. With today's changes to safety regulations, the effluents must now be transferred before tank dismantling.

According to the site records, the compositions of the liquid wastes MA501, MA502, MA503, MA504, MA506 and MA507 are similar. From 2013 to 2014, effluents contained in MA502, MA503, MA504 tanks have been transfered.

Several difficulties have been encountered:

- The tanks were historically different, especially manhole tank access
- Since the 1990s, effluent composition has changed due to water evaporation. The salt concentration has increased and insoluble elements have formed a deposit in the bottom of the tanks resulting in high composition heterogeneity
- In some tanks, a wall breeze-blade exists dividing the tank into two zones, which complicates the interventions.

Major challenges have been met and will be described in the presentation.

- To obtain an effluent which is as homogeneous as possible, the duration of mixing has been optimized.
- To pump the liquid, it has been necessary to treat the effluent with nitric acid. This step has been optimized thanks to experiments in laboratory and hydrodynamic modelling.
- A mobile workshop has been designed in order to perform the effluent transfer. It is set up directly above the tanks and can be moved from one tank to another on rails.
- Laboratory experiments have been carried out to characterize the suspension and sludge in order to understand its chemical behavior.
- The treatment of the effluent has been studied in the laboratoy and is now mastered.
- The analytical strategy has been optimized.

The close collaboration between the analytical laboratory and the dismantling project was a real advantage. Thanks to this, the duration of the last transfer on MA 504 was reduced by half, compared to the first operations.

Transfer operations will be described and the differences and similarities between laboratory and in-situ observations will be pointed out.

INTRODUCTION

The CEA Saclay site includes a Liquid Waste Treatment Plant (LWTP) named facility INB 35.

This facility includes Medium Level Liquid Waste (MLLW) storage units dating from the 1970s, which operated until the end of the 1990s. At the end of their lifetime, technical issues arose: a compressed air stirring system no longer worked and emptying rods were clogged. Moreover, new regulations were published at that time, particularly concerning radioactive liquid waste storage, under which the storage tanks were no longer in conformity. Consequently, the CEA decided to shut down the operation of the storage unit and to transfer the MLLW to a new storage workshop which met the regulatory requirements.

Emptying the tanks meant creating a new mobile workshop to carry out the stirring and emptying functions necessary due to the sedimentation of the radioactive liquid waste over time. The objective was to retrieve most of the source term. Chemical treatments were therefore implemented in order to ensure a maximum transfer of the source term present. The effluent retrieval equipment also had to include a system ensuring that particle diameters would be less than 1mm (INB35 requirement).

PRELIMINARY STUDIES

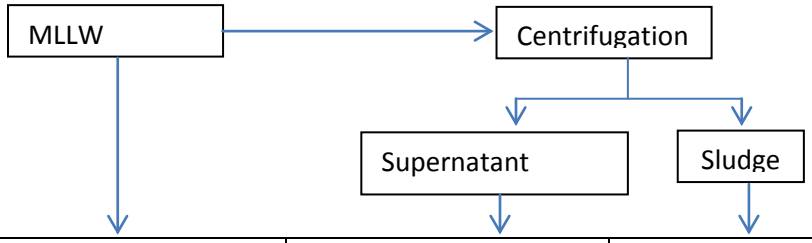
Faced with the issues involved in retrieving the liquid waste, the project team requested assistance from a laboratory to:

- radiologically and chemically characterize the complex MLLW with a heavy salt content

- carry out tests to help plan the MLLW transfer operations.

The effluents were collected in the same period of the research center's activities, so the composition and behavior of the different tank contents were expected to be similar.

During the radiological characterization campaign, analysis results showed that the source term, particularly alpha, was mainly present in the solid phase of the effluents, see Figure 1.



Gross Alpha activity	100%	1%	99%
Gross Beta activity	100%	35%	65%

Fig.1: Distributions of the gross alpha and beta activities

In order to retrieve as much as possible of the source term, and given the issues related to the liquid waste particle extraction from the tanks (due to their sedimentation), it appeared that dissolution would facilitate the operations**.** This type of liquid waste modification has to respect the operating rules which permit the addition of HNO_3 acid at a maximum concentration of 6N to the tanks, while maintaining a pH $\geq$ 2 throughout the operation.

Dissolution studies were carried out, adding variable quantities of 6N nitric acid to the effluents. The supernatant pH, activity and composition in major elements were monitored.
These tests showed that:

- The addition of HNO3 acid 6N (initial pH of the concentrates ≈ 7) enabled the percentage of insolubles to decrease by a factor of 2 as from pH = 4 (Figure 2). The laboratory therefore recommended adjusting the effluent pH to a value of around 2.

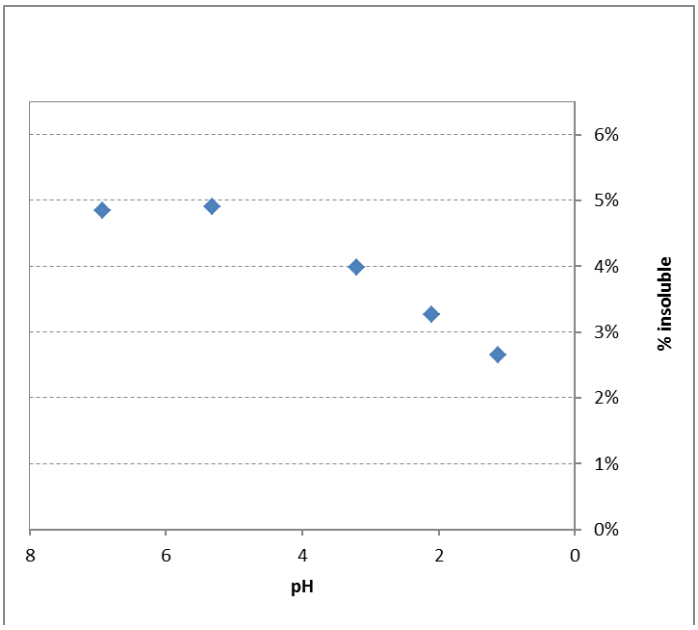


Fig.2: Changing percentage of insolubles depending on the pH

– The sludge dissolution meant an increase in the concentrations of magnesium, calcium and phosphate in the liquid phase (supernatant obtained after centrifugation) (Figure 3). The date is consistent with the solubilizing of a calcium phosphate salt with a stoichiometry of 1/1 (CaPO4), as the numbers of calcium and phosphate moles released during the dissolution are equal. However, the quantity of insoluble solubilized was higher than the mass of calcium and phosphate solubilized, indicating that one or several other salts made up the insoluble fraction.

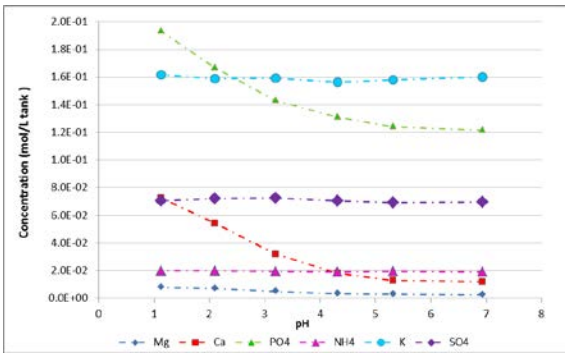


Fig.3: Evolution in the composition of the liquid phase obtained after waste centrifugation, depending on pH

In order to check for the absence of particles larger than 1mm, a filtration test on a 1mm grid was carried out in the laboratory on the suspension. No clogging was observed.

On the basis of this information it was decided that before any emptying operations commenced, a treatment of the liquid waste should be carried out under stirring with HNO_3 6N at a pH of between 2 and 3, to obtain a maximum dissolution of the solid phase and thus enable the removal of the source term by pumping.

IMPLEMENTATION OF EFFLUENT RETRIEVAL

The storage unit consists of 5 horizontal tanks, each in a semi-underground pit. The 316L stainless steel tanks are cylindrical, have a capacity of 50 m^3, and are 3 m diameter x 7.5 m long). They have 2 manhole-type accessways (figure 4).

Retrieving the liquid waste required equipment which able to carry out:

- Tank stirring with submerged devices,
- Sample taking,
- Acidification in order to dissolve the salts,
- Removal into a tanker for transfer to the new storage workshop, named RESERVOIR.

Given these requirements, a mobile workshop which could be located above each tank in turn was designed. It can be moved from tank to tank by rolling along beam supports and is placed two metres above the tanks, to limit the dose rate for operators working from it. The workshop design incorporates containment features, with two barriers associated with a suitable ventilation system.

The position of the tank and in particular of the two manhole-type accesses defined the structure's positioning. The original biological protection slabs above each access were replaced by equvialent metallic plates, ensuring the protection was replaced. These plates had openings through which connections with the mobile unit were fitted via linking shafts.

The equipment was inserted into the tank via the two accesways, linked to the mobile workshop with the two shafts. Two submerged stirrers were thus set up with the help of support rods (Figure 4).

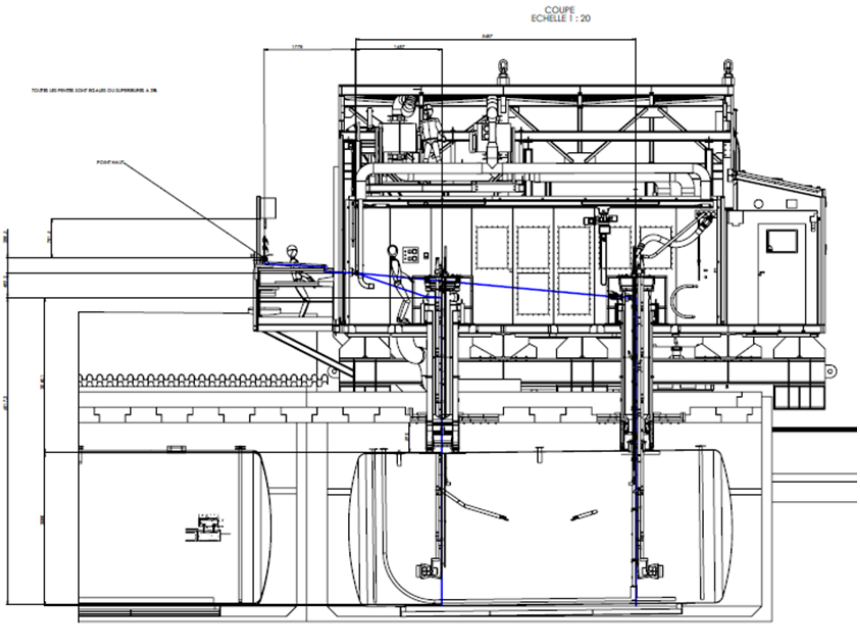


Fig.4: Positioning of the mobile workshop unit above a tank

One rod enabled samples to be taken via a glove box. Another rod was used to transfer nitric acid, as recommended by the laboratory, to dissolve the salts. A pH meter monitored the pH in order to ensure the range of 2 to 3 was respected, bearing in mind the pH 2 limit for the tank leaktightness. This monitoring overcame the laboratory scale effect. Finally, a pump rod linked to an appropriate mast structure carried out the vacuum transfer of the MLLW into a tanker.

Carrying out the operations meant two challenges had to be met:

- Efficient homogenization of the effluent, which had not been stirred for 15 years

- Pumping through a strainer which would limit the diameter of particles transferred to the tanker.

To check the stirring efficiency, samples were taken at different heights within the tank at different times during the homogenization operations. The parameters followed were the dry extract, the pH, and the gross alpha/beta and gamma activities. The main anion and cation analyses were carried out on the first tank.

It was then possible to demonstrate that a minimum of 7 days of stirring was necessary to obtain suitable effluent homogeneity.

During the first tank emptying trials, it was noticed that the 1 mm strainer had clogged and the operations had to be halted. Given the trials were carried out in the laboratory, this situation had not been expected.

The CEA asked an external supplier to carry out hydrodynamic modeling in order to understand and optimize these two steps. The studies showed that:

- A particle agglomeration phenomenon occurred on the strainer when high-speed stirring was running,

- There was a localized homogenization of the liquid around the periphery of the stirrers, because of the tank geometry and the diameter of the submerged stirrer action zones.

Translating this study into practical terms, the stirring rate was reduced at the end of the tank where the pumping rod had been set up. A homogenization scenario was defined in order to lift as much sludge as possible, to enable its dissolution by the nitric acid.

The MLLW analyses showed that as the acid was injected and the pH decreased, the concentrations of phosphate, calcium and magnesium increased (Figure 5) in conformity with what had been recorded in the laboratory. The total alpha and beta indexes also increased, whereas the gamma activity (mainly ^{137}Cs) remained constant (Figure 6). This data was also in agreement with the information obtained from the laboratory.

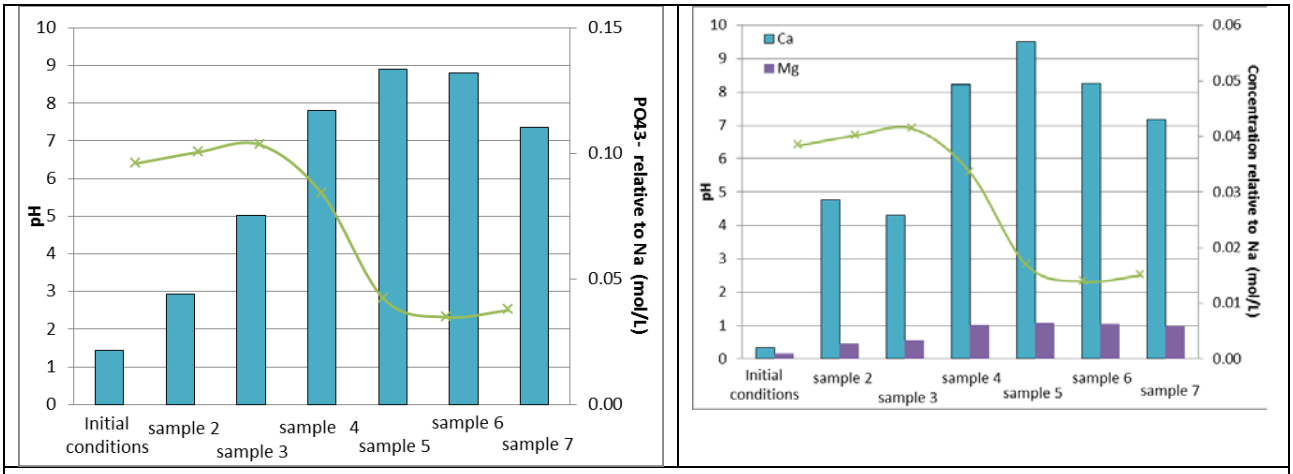


Fig.5: Evolution of the phosphate, magnesium and calcium concentrations as the acid was injected

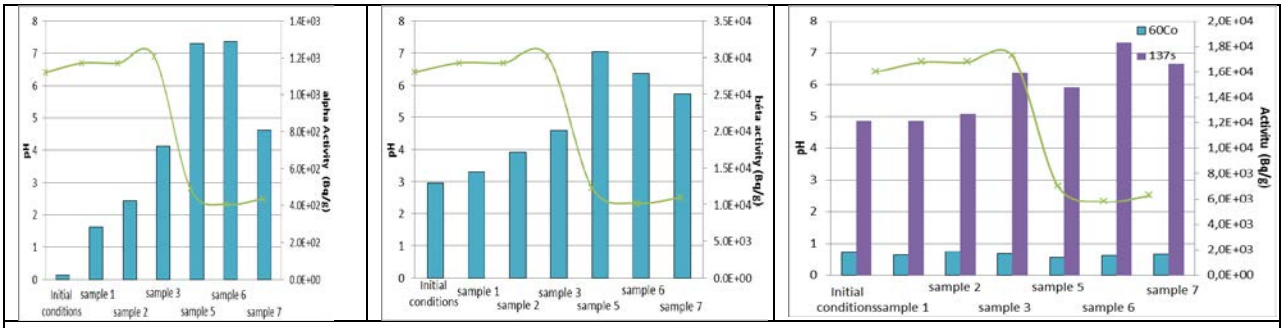


Fig.6: Evolution of the radiological activity as the acid was injected

However, the volume of nitric acid added to the tank in order to reach the required pH level was higher than that calculated in the laboratory. This point can be explained by the impossibility of stirring at the bottom of the tank and therefore of putting the entire solid sludge which had settled there into suspension. The first samples which had been taken and processed in the laboratory in order to estimate the amount of acid to be added had not in fact been representative of the actual amount of sludge present in the tank. It was therefore going to need more acid than expected to dissolve.

The radiological and chemical characterizations carried out during the MLLW tank treatments with HNO_3 6N before emptying showed that the procedures implemented to solubilize the solids present in the concentrates performed well.

FINAL STATE OF THE TANK

After pumping was completed, the procedure which had been used revealed a certain number of constraints. The stirrers used were not able to homogenize beyond a height of around 30 cm**.** Because of this, where the stirring had no impact, the acidification became less efficient. This observation was confirmed by laboratory tests.

The presence of the strainer made the pumping more difficult, particularly at the bottom of the tank where the solid phase sludge remained.

When most of the liquid had been pumped out, the nitric acid added had to be at a concentration of 0.01N in order to meet the level of pH allowed (higher than 2). This treatment is no longer efficient enough to dilute the remaining sludge.

The on-site observation was confirmed by laboratory tests under hydrodynamic conditions close to those in the tank (without stirring). These tests were carried out for variable sludge compaction rates (heights from 5 mm to 4 cm).

It was found that in such conditions (absence of stirring, compacted sludge) as close as possible to those of the tank, the pH which was initially at 2 increased slowly to reach 2.6 after 20 days. There was no sludge de-structuring and only 15 to 30% of the solid matter dissolved (or even more so as sludge thickness increased). Radiological measurements showed that the radioactivity remained concentrated in the sludge. For one of the tanks, the MLLW retrieval by addition of acidified water continued, but the volume of sludge retrieved, and consequently the reduction of the source term, is low compared to the amount of acidified water added.

At the same time, the laboratory found insoluble salts were present, which had not been able to be put into suspension.

Given the final state situation, the amount of sludge initially present was 10 to 15% of the total effluent volume. The material remaining after the retrieval operations represents about 2.5% of the total initial

effluent volume (Figure 7). Thus at the end of the operations described, 10 to 15 cm of sludge and a few liters of liquid were still present in the tank.

Fig.7: Final state of the tank after the emptying operations

Concerning the source term, the treatment implemented enabled the retrieval of 95% of the beta-gamma activity, and 75 % of the alpha activity, which were present throughout the tank.

CONCLUSIONS

The process developed for the retrieval of the MLLW in these storage tanks enabled most of the term source present to be removed. The close partnership between the teams on-site and in the laboratory was a major factor in optimizing the methodology.

From a qualitative point of view, the laboratory results were consistent with the situation actually observed. Nevertheless, quantitatively speaking the laboratory information was not directly transferable given the effect of the differences in scale and in particular once hydrodynamics came into play in the phenomenon studied. Calling on assistance from chemical engineering modeling enabled the phenomena related to the circulation of liquid within the tank to be understood. From this, the practices necessary for the optimization of stirring and pumping conditions were able to be deduced.

The MLLW retrieved, once treated chemically, will be immobilized in a cementary matrix. Consequently, a compromise must be found between the amounts of liquid added compared to the source term removed, as well as the direct immobilization of the sludge material during the clean-up phase.

ACKNOWLEDGEMENTS

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