**Characterisation and Preliminary Study for Solidification of Organic Alpha-Contaminated Liquid Waste**

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**Abstract**

 Management of Organic Alpha Contaminated Liquid Waste can pose significant challenges during the pre-disposal and disposal phases: their dual nature of organic and radioactive compounds can affect nuclear safety and have harmful effects on health and environment. These kinds of contaminated liquids must be immobilized into a waste forms to limit their long-term release and collected into appropriate waste packages to avoid the contact with water and any loss of containment. Due to their chemical and radiological characteristic there are very few official analyses to design reliable solidification protocols specially when their volume is too low for complex treatments, however a proper management of radioactive wastes requires their definition and classification: to do this it is necessary to apply destructive and non-destructive techniques.

Destructive techniques need a chemically processing of the sample before being analysed by specific techniques. Non-destructive techniques are able to identify and quantify the intensity of radiation (spontaneous or induced) emitted: the samples don’t require any physical and chemical treatments, but they have a low accuracy and are strongly influenced by the matrix composition.

. The paper summarises the results of the characterisation activities of a batch of samples made up of organic alpha contaminated liquid wastes, produced in the past activities of the IPU (Plutonium fuel experimental facility) plant, a Sogin facility (Rome, Italy) and the very preliminary trials carried out for their solidification..

## INTRODUCTION

The characterisation of radioactive waste is one of the fundamental keys of waste management for the following reasons: safety assessments during transport or storage, determination of waste treatment and conditioning methods. It also significantly improves the quality of controls during the aforementioned operations. A correct management of radioactive waste, which takes into account the necessary health protection and environmental protection safeguards, makes it necessary the definition and the classification of radioactive waste, as well as that of the legal determination of limits below which waste can be unconditionally release without restrictions on the destination or restrictions on their use.

 From a radiological point of view, waste characterisation can be performed through different methods, destructive and non-destructive. Destructive techniques are used to analyse samples that need to be chemically processed before appropriate measurements are carried out. They are more accurate and sensitive than non-destructive techniques, but they are time consuming and highly linked both the quality (e.g., homogeneity) than the representativeness of the material. Non-destructive techniques identify and quantify the intensity of sample emitted radiation, spontaneous or induced. These methods do not require any physical and chemical modifications, but, show lower sensitivity and might strongly depends on the matrix composition.

Samples of organic alpha contaminated liquid waste produced in the past activities of the IPU plant, a Plutonium fuel experimental facility managed by Sogin, the Italian State owned company responsible for the decommissioning of Italian nuclear plants and the radioactive waste management, have been fully characterised by physical and radiochemical analyses.

Such characterisation activities were the first essential step to synthetize simulants and design experimental tests to evaluate the properties of the solidified waste form in terms of stability and durability, with reference to its physical-chemical behaviour and, if available, the waste acceptance criteria.

## DESCRIPTION OF THE EXPERIMENTAL CAMPAIGN

**2.1 Description of the samples**

 Historical activities carried out at the IPU Plant facility have produced about 500 liters of alpha contaminated liquid organic waste, currently stored at the Sogin Casaccia site in Rome.

They are composed of:

* Extraction solvents (CMPO[[1]](#footnote-2) and TBP in Dodecane) used in the PUREX and TESEO[[2]](#footnote-3) processes to remove all alpha emitter actinides from the liquid waste
* Organic solutions containing pyridine, MIBK and scintillation liquids coming from past analytical activities
* Liquids containing CCl4 (carbon tetrachloride), originating from the mixed Pu-U oxide fuel fabrication
* Other organic liquids produced during the analytical activities of the IPU Plant and by previous activities carried out at the Casaccia site

The liquids have been stored in bottles of different volumes (2, 5, 10, 20, 25 and 30 liters), confined in a double PVC bag and saved in stainless steel containers (i.e. Sant'Andrea type). Their total activity was 2,26E+11Bq (alpha: 1,75E+08 Bq/l - beta-gamma: 2,76E+08 Bq/l). The main radionuclides occurring in these liquid waste are: Pu-238, Pu-239, Pu-240, Am-241, U-238, U-235. The presence of an aqueous phase may not be excluded.

Starting from historical data available, 5 groups of different samples have been identified on the basis of matrix homogeneity and chemical-physical characteristics:

* Group 1: CMPO and TBP matrix, from TESEO and PUREX processes;
* Group 2: alkaline organic miscible with water, from analytical activities;
* Group 3: acid organic miscible with water, from analytical activities (not included in the analyses);
* Group 4: neutral Aggressive and non, from analytical activities;
* Group 5: carbon tetrachloride matrix, from mixed oxide fuel manufacturing activities.

 Aliquots (50 ml) of 24 samples packaged in a special glass container, were extracted and underwent radiological characterisation.

2.2 **Description of the characterisation activities**

*2.2.1Non-Destructive characterisation methods*

Before the chemical-physical and radiological characterisation of the samples was carried out by means of destructive analysis techniques, a preliminary radiological analysis was performed with non-destructive methods.

The radioactive liquid waste (Fig. 1) has been previously characterised through gamma analysis technique by an ORTEC-MGA system to determine the Uranium and Plutonium relative isotopic composition [2].

 

 *Fig.1 Radioactive liquid waste*

A data file for each sample has been realized containing the sample physical information (e.g., volume, apparent density, weight), the isotopic composition data and the intrinsic efficiency curve relative to each sample. In order to carry out a coherent evaluation of the uncertainty associated with the isotope fractions, confidence intervals have been identified for each isotope, which take into account the geometrical measurement parameters (i.e., materials, shape and nature of the sample, thickness of the absorbers involved, geometry of the positioning of the sample on the detector) along with the statistical spectral distribution.

To demonstrate a relationship between the activity distribution within the sample and the efficiency curve calculated by the MGA algorithm, emission measurementswere carried out for each sample as a function of the height of the vial, assuming that it is possible to record a change in the count rate measured on a reference energy peak identified in the known source spectrum.

The system operates with a High-Purity Germanium coaxial detector with about 50% relative efficiency and high energy resolution. The objective of such measurements was fundamental to identify the physical phase which the sample activity is concentrated in. The reference nuclide considered wasAm-241. Emitted gamma radiation was collimated by means of a 5 mm through hole in a lead slab. Each vial was then moved in height by means of a lab-jack, for looking at the desired section of the sample. To prevent extremely long measurements, the most active samples (16 out of the 24) were analysed. For each selected sample, a spectrum of each section of interest was acquired in the energy range 0 ÷ 400 keV. The data collected were then compared to the measurement geometry and the intrinsic efficiency curve calculated by the MGA.

To demonstrate, however, the non-homogeneity of the sample matrix, and therefore differential characteristics in the self-attenuation of the sample as a function of the height, transmission measurementswere performed by measuring the intensity of a gamma source through the different sample sections characterised by different phases. For each section identified, the attenuation characteristics as a function of energy were obtained, in the range of energies of interest of the energy spectrum analysed by MGA.

By considering the same collimation procedure, a 133Ba source is placed on the opposite side of the sample and the reduction of the gamma lines in the range 0 ÷ 400 keV is evaluated to retrieve the attenuation factors and therefore densities of the different sample sections.

*2.2.2 Destructive characterisation methods*

The quantitative radionuclides determination in complex matrices requires its destruction by chemical methods of homogeneous samples which are representative of the original material.

In order to improve the homogeneity of the samples, they have been shacked mechanically, quickly picking up 20 ml aliquots then placed into ceramic pots for evaporating the liquid fraction. Solid residues have been mineralized by a mixture of nitric acid-hydrogen peroxide to obtain the complete destruction of the matrix. Each residue has been divided in 3 batches of sub-aliquots which have been analysed respectively with Inductively coupled Plasma Mass Spectrometer (ICP-MS), Gas Chromatography mass spectrometer (GC-MS) and alpha spectrometry techniques.

The amount of water in the radioactive waste has been determined, on a sub-aliquots diluted in dimethyl sulfoxide (DMSO) through GC-MS Agilent model 7890B, equipped with AGILENT 5977B Series MSD mass spectrometry detector. Significant amounts of ammonia in most of the samples have prevented the use of the most common Karl Fischer titration. This equipment has been also used to determine organic residues, using another batch of sub-aliquots diluted in Acetone. The results are compared resulting consisted with a certified calibration curve.

The heavy metals content has been determined through ICP-MS analyses. Sub-aliquots, diluted in acidified ultrapure H2O have been analysed using an ICP-MS Agilent 7700x system with magnetic Quadrupole detection and equipped with Collision/Reaction Cell ORS3. The last sub-aliquots batch has been used to quantify alpha emitters using a spectrometer equipped with a Canberra 600 mm2 PIPS detector, with a total efficiency of about 3% and a FWHM of 25 keV. Electrodeposition has been carried out following the method “Eichrom\_ Analytical Procedures (2014) Electrodeposition of Actinides [1]

## DISCUSSION

The lack of homogeneity has strongly influenced the overall radiological characterisation of the samples, both for non-destructive and destructive methods. The variability of the efficiency calibration curves, due to both to irregular distribution and self-absorption, claimed additional and unexpected measurements such as emission measurements. The objective of the measure was essentially to verify the physical phase in which the sample activity is concentrated, following the content in Am-241.

Referring to destructive methods, the simple shaking of the samples has only partially overcome the inconvenient. After the mineralization described above residues have been further diluted (less than 1g l-1) In order to obtain reliable results to perform by ICP-MS the metal contents and a sufficiently thin electrodeposition.

 Also, the measurement of the water content has been severely influenced by the lack of homogeneity and by a low level of representativeness. Since the solutions were predominantly made up by organic and organic solvents, which are generally poorly miscible or totally immiscible with water, it has been calculated that the representativeness of the aliquots was affected by at least an additional 10% relative error.

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**3.1 Definition of the reference simulants to be used for the laboratory solidification tests**

The composition of the surrogates to be used for the subsequent laboratory solidification tests is built upon the characterisation analytical results. The percentage of the aqueous phase in most of the bottles ranged from 2 to 20 %.

It was observed that the chemical data were not always coherent with the available historical data for all bottles. Chemicals identified in the organic phase consist mainly of:

* Methyl isobutyl ketone (MIBK)
* Tributyl phosphate (TBP)
* Dodecane
* Pyridine
* Potassium hydrogen phthalate (KHP)
* Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)
* Scintillation liquids
* Kerosene

In order to define a limited number of reference surrogates that should have been used for the solidification tests, some basic assumptions have been fixed: organic components with a concentration below 5% were excluded from the simulation and cations in the aqueous phase were considered relevant only for concentrations up to 1000 µg/kg. Based on the analysis of the data (see Table 1), it was possible to identify 8 groups of bottles with similar composition (i.e., one or more than one in common components with similar concentration

TABLE 1 CHEMICAL COMPOSITION OF RADIOACTIVE WASTE

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Group | Bottle | Aqueous phase% | Organic phase% | Organic phase composition % |
| MIBK | TBP | Dodec. | Pyrid | KHP | CMPO | ScintiL.cocktail | kerosene |
| **1** | *1* | 2 | 98 | 52 |   |   |   |   | 48 |   |   |
| *16* | 2 | 98 | 31 |   |   |   | 14 | 51 |   |   |
| *17* | 2 | 98 | 5 |   |   | 17 |   | 62 |   |   |
| **2** | *2* | - | 100 | 24 | 25 | 51 |   |   |   |   |   |
| 9 | - | 100 | 21 | 41 | 20 |   |   | 15 |   |   |
| 3 | 3 | 3 | 97 | 15 | 13 |   |   |   |   |   | 66 |
| 4 | 2 | 98 | 22 | 14 |   |   |   |   |   | 56 |
| 4 | 5 | 19 | 81 | 31 |   |   | 69 |   |   |   |   |
| 11 | 2 | 98 | 69 |   |   | 25 |   |   |   |   |
| 15 | 0 | 100 | 76 |   |   | 22 |   |   |   |   |
| 20 | - | 100 | 73 | 10 |   | 17 |   |   |   |   |
| 5 | 6 | 13 | 87 | 36 |   | 11 | 23 | 28 |   |   |   |
| 8 | 4 | 96 | 36 |   | 11 | 22 | 29 |   |   |   |
| 6 | 7 | 6 | 94 | 17 | 38 | 26 |   | 13 | 6 |   |   |
| 21 | 5 | 95 | 19 | 40 | 28 |   | 13 |   |   |   |
| 22 | 0 | 100 | 32 | 37 | 21 |   | 10 |   |   |   |
| 23 | - | 100 | 13 | 38 | 19 |   | 8 |   |   |   |
| 24 | 17 | 83 | 18 | 34 | 14 |   | 34 |   |   |   |
| 7 | 10 | 6 | 94 | 59 |   |   | 27 |   |   | 14 |   |
| 13 | 13 | 87 | 69 |   |   | 13 |   |   | 31 |   |
| 8 | 12 | - | 100 | 9 | 5 |   |   |   |   | 83 |   |
| 14 | 10 | 90 | 8 | 18 |   |   |   | 11 | 52 |   |
| 18 | 2 | 98 | 10 |   |   |   |   |   | 86 |   |
| 19 | 4 | 96 | 11 |   |   |   |   |   | 85 |   |

8 surrogated enveloping solutions were defined considering for each component within a group, the maximum concentration (%) present in one of the different bottles and then calculating the percentage of that component in the final enveloping solution (see. Table 2).

TABLE 2 DEFINITION OF THE SURROGATED SOLUTIONS

|  |  |  |  |
| --- | --- | --- | --- |
| Envelopingsolutions | Aqueous phase% | Organic phase% | Organic phase composition % |
| MIBK | TBP | dodecane | pyridine | KHP | CMPO | Scintillationcocktail | kerosene |
| 1 | 2 | 98 | 36% |  |  | 12% | 9% | 43% |  |  |
| 2 | 0 | 100 | 18% | 31% | 39% |  |  | 11% |  |  |
| 3 | 3 | 97 | 21% | 14% |  |  |  |  |  | 65% |
| 4 | 19 | 81 | 49% | 7% |  | 45% |  |  |  |  |
| 5 | 13 | 87 | 37% |  | 11% | 23% | 29% |  |  |  |
| 6 | 17 | 83 | 23% | 29% | 20% |  | 24% | 4% |  |  |
| 7 | 13 | 87 | 54% |  |  | 21% |  |  | 24% |  |
| 8 | 10 | 90 | 9% | 14% |  |  |  | 8% | 68% |  |
| MIX | 11 | 89 | 32% | 11% | 7% | 16% | 7% | 11% | 12% | 5% |

An additional enveloping solution (MIX) was added: it includes the composition of the total volume of liquids analysed (about 170 litres), in the hypothesis of a preliminary mixing of the content of the different bottles. The percentage of the different components was determined considering the relative percentage of the volume of the different groups as reported in Table 3.

TABLE 3 volume relative percentage of the different groups

|  |  |  |
| --- | --- | --- |
| Group | volume tot (l) | % |
| 1 | 32,2 | 19% |
| 2 | 15 | 9% |
| 3 | 12,5 | 7% |
| 4 | 40,7 | 24% |
| 5 | 10,6 | 6% |
| 6 | 20,5 | 12% |
| 7 | 12 | 7% |
| 8 | 24,3 | 14% |
|  | 167,8 | 100% |

##  PRELIMINARY SOLIDIFICATION TESTS

Different approaches are currently being studied for the solidification tests. They include:

1. Solidification with the use of NocharTM polymers
2. Direct conditioning with the use of Cement
3. Direct conditioning with the use of geopolymers or alkali activated materials

The preliminary results for the first two options are summarised below, while the third option is not yet started.

**4.1 Solidification with the use of NocharTM polymers**

A preliminary investigation of the NocharTM polymers capacity to solidify single components was carried out. Different Polymer / Liquid ratios have been investigated [3,4,5]. The polymers used were N910 for organic compounds and N960 for water. Some visual observations on the samples were performed and the weight loss during the first week was evaluated.

These are the obtained results.

* A complete polymerisation was observed only for hydrocarbons (n-dodecane and kerosene) with a Nochar N910/liquid ratio equal to 0.3;
* TBP and scintillation cocktails showed not clear polymerisation even with increasing amount of Polymer from 0.3 to 0.7 (N910/liquid ratio). No weight loss was determined during time.
* Pyridine and MIBK evaporate totally or almost completely, demonstrating in fact that polymerisation, for these compounds (polar and volatile), does not occur;
* The water temporarily absorbs on the N960 polymer but evaporates completely over time, regardless of the amount of polymer used confirming that the interaction between polymer and water is based on a physical and not chemical absorption

**4.2 Absorption tests on the 9 surrogated solutions**

Additional tests were performed on the 9 solutions as defined in table 3. Different Polymer/liquid ratios were tested and the weight loss during time were checked. Moreover, the order of addition (liquid to polymer or polymer to liquid) with or without mixing were analysed.

The results are summarized below:

* Only solution 3 showed a complete polymerisation without release of liquid
* Solutions containing hydrocarbons show a partial polymerisation;
* The volatile compounds present in the solutions evaporate almost completely form the semisolid product
* The order of addition or the mixing of the solutions with the polymer didn’t have a significant impact on the results.

**4.3 Direct conditioning with the use of Cement**

In order to quantify the necessary amount of water to obtain a complete solidification of the cement some preliminary tests have been run. For each of the 9 surrogated solutions some preliminary tests were carried out in order to define the quantity of water to be added to have a complete solidification with cement. 4 different water dilution were tested: 60%-80%-90%-95%. Any exudation and/or leakage of liquid on the surface of the samples (Cylindrical specimens) was checked. All tests were carried out by sealing the containers after cementation to prevent evaporation of the surface liquid (the volatile compounds would otherwise evaporate quickly).

The obtained results are showed below:

* direct cementation does not appear to be suitable for conditioning the different type of liquids because even adding large quantities of water the organic phase is not easily incorporated;
* The best result was obtained with the MIX solution (n.9) where, with a water addition of about 80% -90%, no bleeding or liquid exudation occurred.
* Further studies were based on the optimisation of the direct cementation of the MIX solution.
* Different types of cement and different Water/cement ratio (directly related to the Waste Loading) were tested.
* For the optimised recipes compressive strength tests, thermal cycling tests and leaching tests were performed. The results are summarised in the following table:

TABLE 4 OPTIMIZATION OF DIRECT CEMETATION PARAMETERS

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Cement Type | Water/Cement | Sol MIX Waste loading(% vol.) | Compressivestrength | Thermalcycling test | Leaching |
| III-B | 0.35 | 12 | 29 MPa | No cracks and Fc = 42 MPa | Li (Cs-137)=7.90 |
| IV-A | 0.35 | 12 | 33 MPa | No cracks and Fc = 28 MPa | Li (Cs-137)=8.59 |

## CONCLUSION

The definition of a reliable management strategy of radioactive organic waste must be based on their chemical and radiochemical characterisation. Simulating liquid waste can be prepared on the bases of the characterisation results in order to test in laboratory the feasibility of different treatment and conditioning.

Radiological characterisation results have been strongly influenced by the inhomogeneity of the samples. Such an issue has requested modifications to the standard procedures: the chemical data allowed to reproduce some surrogated enveloping solutions that were used to perform some preliminary screening tests on the possibility of solidifying the liquids with the use of NocharTM polymers or cement.

The outcomes achieved are summarised below:

a) NocharTM polymers showed good solidification results only when the amount of hydrocarbon in the solution is sufficiently high (up to 60%) and the volatile compounds tend to be lost from the matrix during time.

b) Direct solidification with the use of cement showed different results with the different surrogated solutions with a maximum waste loading achieved of 12% (vol.) for just one of the 9 solutions tested.

The final goal is to increase the waste loading and, for this reason, additional test will be performed using geopolymer or alkali activated materials.

Nowadays, geopolymers are one of the most promising material to replace Portland cement, because of their powerful characteristics including good mechanical properties, low permeability to liquids, resistance to high temperatures and acidic attack, etc [6].

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1. Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide [↑](#footnote-ref-2)
2. Effluent Treatment by Extraction with Organophosphors [↑](#footnote-ref-3)