

NOCHAR polymers: an aqueous and organic liquid solidification process for Cadarache LOR (Liquides Organiques Radioactifs) - 13195

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ABSTRACT

To handle the Very Low Level Waste (VLLW) and the Low Level Waste (LLW) in France, two options can be considered: the incineration at CENTRACO facility and the disposal facility on ANDRA sites. The waste acceptance in these radwaste routes is dependent upon the adequacy between the waste characteristics (physical chemistry and radiological) and the radwaste route specifications. If the waste characteristics are incompatible with the radwaste route specifications (presence of significant quantities of chlorine, fluorine, organic component etc or/and high activity limits), it is necessary to find an alternative solution that consists of a waste pre-treatment process. In the context of the problematic Cadarache LOR (Liquides Organiques Radioactifs) waste streams, two radioactive scintillation cocktails have to be treated. The first one is composed of organic liquids at 13.1 % (diphenyloxazol, mesitylene, TBP, xylene) and water at 86.9 %. The second one is composed of TBP at 8.6 % and water at 91.4 %. They contain chlorine, fluorine and sulphate and have got alpha/beta/gamma spectra with mass activities equal to some kBq.g⁻¹. Therefore, tritium is present and creates the second problematic waste stream. As a consequence, in order for disposal acceptance at the ANDRA site, it is necessary to pre-treat the waste. The NOCHAR polymers as an aqueous and organic liquid solidification process seem to be an adequate solution.

Indeed, these polymers constitute an important variety of products applied to the treatment of radioactive aqueous and organic liquids (solvent, oil, solvent/oil mixing etc) and sludge through a mechanical and chemical solidification process. For Cadarache LOR, N910 and N960 respectively dedicated to the organic and aqueous liquids solidification are considered. With the N910, the organic waste solidification occurs in two steps. As the organic liquid travels moves through the polymer strands, the strands swell and immobilise the liquid. Then as the polymer-organic cure, over time, the polymer continues to collapse on the organic to create a permanent bond. The N960 has the ability to absorb aqueous waste up to 100 times its own weight. It creates a strong mechanical bond which permanently traps the contamination imbedded in the aqueous liquids. As a consequence, these two polymers seem to be able to constitute a suitable solidification matrix for a final acceptance in storage on ANDRA sites.

In order to validate the polymers as an acceptable aqueous and organic solidification process for Cadarache LOR, some solidification tests realized with N910 and

N960, have been carried out for different Waste/Polymer ratios. The determination of the best Waste/Polymer ratio and of the optimal experimental parameters has been made through an exudation test. Indeed, the process prevents leaching and it results in the absence of residual free organic or aqueous liquid which is forbidden in storage by ANDRA specifications. With these test results, we generated scientific data which are fundamental to obtain an ANDRA agreement.

As a conclusion, the aim of this study is to demonstrate that the solidification by polymers can constitute a pre-treatment solution for Cadarache LOR and more generally, for various organic and mixed organic/aqueous waste which can not be directly acceptable at CENTRACO facility or at ANDRA storage sites. This work is, therefore, a solid background to demonstrate the feasibility of the waste pre-treatment by solidification with polymers and to encourage the development of this process.

INTRODUCTION

The aim of this project is to identify and to realize the adapted pre-treatment of Cadarache LOR (Liquides Organiques Radioactifs) waste streams in order to obtain an ANDRA agreement which allows the waste disposal. Indeed, looking at the waste characteristics (physical chemistry and radiological), they are not in accordance with the specifications of the two usual facilities used in France (CENTRACO facility for incineration and ANDRA sites for disposal) to handle the Very Low Level Waste (VLLW) and the Low Level Waste (LLW).

Cadarache LOR waste streams which are two radioactive scintillation cocktails have been produced years ago in a Cadarache laboratory and are presently stored in the CEREES (CELLule de REconditionnement et d'Echantillonnage des fûts de Solvants radioactifs) cell implanted in the ICPE (Installation Classée pour la Protection de l'Environnement) 312. The Fig. 1 is LOR 20 photo and LOR 75 photo. The LOR 20 and LOR 75 characteristics are presented in the Table I.

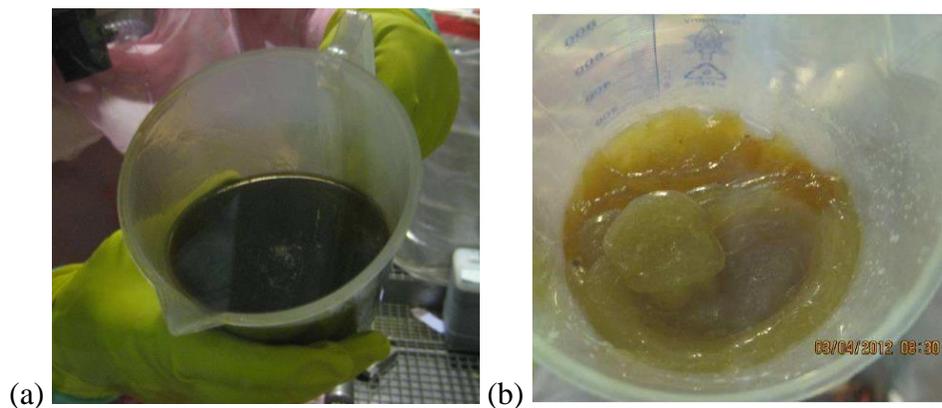


Fig. 1: (a) LOR 20 (b) LOR 75

Table I. Waste characteristics

		LOR 20	LOR 75
Volume (L)		208	137
Mass (kg)		206	137
Composition		11% Xylene (C ₈ H ₁₀) 1.6% Mesitylene (C ₉ H ₁₂) 0.4% Diphenyloxazole (C ₁₅ H ₁₁ NO) 0.1% TBP (PO(OC ₄ H ₉) ₃) 91.4% Water	8.6% TBP (PO(OC ₄ H ₉) ₃) 91.4% Water
Physical chemistry characteristics		1.7 mg.g ⁻¹ Chloride 0.61 mg.g ⁻¹ Fluoride 0.9 mg.g ⁻¹ Sulfate	1.3 mg.g ⁻¹ Chloride 0.23 mg.g ⁻¹ Fluoride 2.1 mg.g ⁻¹ Sulfate
Radiological characteristics	Spectra	Am-241 Co-60 Cs-137 H-3	Am-241 Pu-241 Cs-137
	Mass activity	A _{Alpha} = 3.78x10 ⁸ Bq.g ⁻¹ A _{Beta/Gamma} = 5.55x10 ⁵ Bq.g ⁻¹ A _{Tritium} = 3.47x10 ⁶ Bq.g ⁻¹	A _{Alpha} = 8.67x10 ⁸ Bq.g ⁻¹ A _{Beta/Gamma} = 8.62x10 ³ Bq.g ⁻¹

The LOR 20 corresponds to 206 kg i.e. 208 L, of a brown liquid characterised by a light viscosity. It is composed of water at 86.9 %, xylene at 11%, mesitylene at 1.6%, diphenyloxazol at 0.4% and TBP at 0.1%, and contains chloride, fluoride and sulphate. It has got an alpha/beta/gamma radiological spectrum related to the presence of Am-241 with an alpha activity equal to 3.78x10⁸ Bq.g⁻¹, of Co-60 and Cs-137 with a beta/gamma activity equal to 5.55x10⁵ Bq.g⁻¹ and of H-3 with a tritium activity equal to 3.47x10⁶ Bq.g⁻¹. The LOR 75 corresponds to 137 kg i.e. 137 L, of a beige liquid characterised by a high viscosity. It is composed of water at 91.4 % and TBP at 8.6 %, and contains chloride, fluoride and sulphate. It has got an alpha/beta/gamma radiological spectrum related to the presence of Am-241 and Pu-241 with an alpha activity equal to 8.67x10⁸ Bq.g⁻¹ and of Cs-137 with a beta/gamma activity equal to 8.62x10³ Bq.g⁻¹.

Base on this data, it is necessary to identify a process to pre-treat this LLW (mass activity equal to some kBq.g⁻¹) composed of organic and aqueous components with a presence of significant quantities of tritium, chlorine and fluorine in order to allow its handling in a dedicated facility. A pre-treatment by polymers as an aqueous and organic liquid solidification process seem to be an adequate solution.

METHOD AND EXPERIMENTAL DEVICE

In accordance with Cadarache LOR composition, N910 and N960 respectively dedicated to the organic and aqueous liquids solidification are considered [1, 2]. The polymers characteristics are presented in the Table II.

Table II. NOCHAR (N910 and N960) characteristics

		N910	N960
Composition		Polymer (Thermoplastic elastomer)	Polymer (Acrylic polymer)
Physical chemistry characteristics	Aspect	Granular	Granular
	Colour	White	White
	Density	0.3	0.8

The implementing of polymers technology which is safe and easy, is composed of 2 main steps: mixing waste/polymer (slow and constant addition of the waste on the polymer, then dynamic mixing) and curing during 24h to 48h. This process has some specificities for each polymer. With the N910, the organic waste solidification occurs in two steps. As the organic liquid travels moves through the polymer strands, the strands swell and immobilise the liquid. Then as the polymer-organic cure, over time, the polymer continues to collapse on the organic to create a permanent bond. The N960 has the ability to absorb aqueous waste up to 100 times its own weight. It creates a strong mechanical bond which permanently traps the contamination imbedded in the aqueous liquids. With all polymers, the final product is an immobilised solid waste which is stable under radiation, non-toxic, not dangerous, non-corrosive and non-biodegradable.

Based on this data, the polymer formulation adapted to the Cadarache LOR has been determined by study and tests in order to fix the polymer nature and quantity, and the waste/polymer ratio.

RESULTS AND DISCUSSION

For both Cadarache LOR, the approach has been the same. Based on the waste composition, firstly, the ideal polymer formulation has been identified. Then, the Waste/Polymer mass ratio has been increased. For all samples, observations, evaluations of residual liquid presence/absence and manual exudation tests have been carried out in order to evaluate the formulation validity.

Tests and Results for LOR 20

The tests carried out on LOR 20 are brought together in the Table III.

Table III. Tests realized on LOR 20

Test reference	m LOR 20 (g)	m N910 (g)	m N960 (g)	N910/N960 Mass ratio	Waste/Polymer Mass ratio
20-E-1	20	3	17	0.15 : 0.85	1 : 1
20-E-2	20	0	20	0 : 1	1 : 1
20-E-3	20	10	10	0.50 : 0.50	1 : 1
20-E-4	20	6	14	0.30 : 0.70	1 : 1
20-E-5	20	15	5	0.75 : 0.25	1 : 1
20-E-6	40	10	10	0.50 : 0.50	2 : 1
20-E-7	26.7	10	3.3	0.75 : 0.25	2 : 1

For each test presented in the Fig.2, sample observations have been realized.

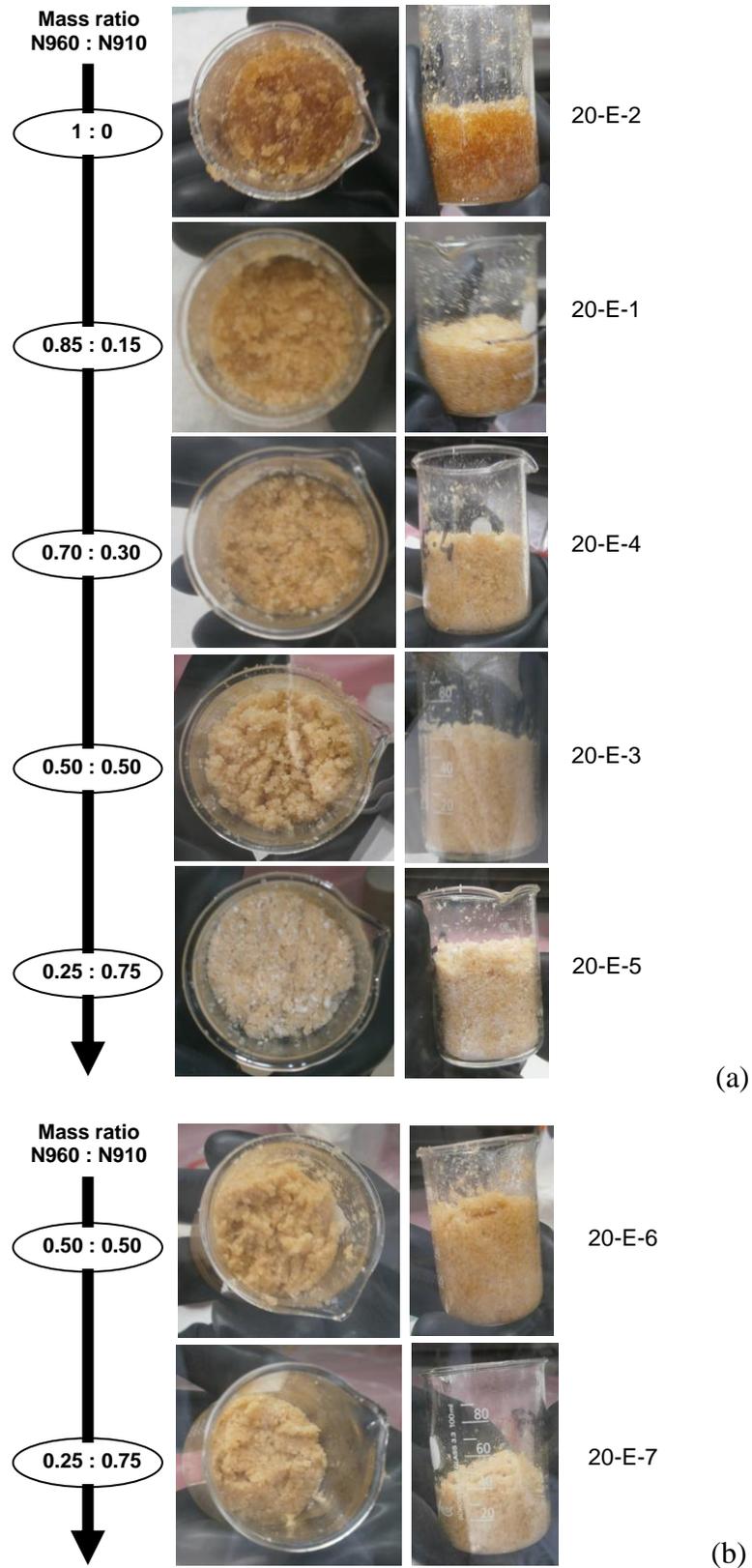
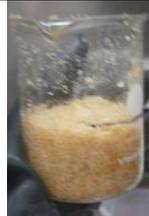


Fig.2: LOR 20 samples (a) with a Waste/Polymer mass ratio equal to 1 : 1 and (b) to 2 : 1

Firstly, in order to identify the adapted polymer formulation (nature and quantity), five tests have been carried out for a Waste/Polymer mass ratio equal to 1:1.

Table IV. Tests results for LOR 20 with a Waste/Polymer mass ratio equal to 1:1

Sample	Colour	Physical appearance	Picture
20-E-1	Caramel-colored	Sticky, doughy and glistening which is the sign of a residual moisture presence	
20-E-2	Dark caramel-colored	Sticky, very glistening and contains some waste which has not reacted	
20-E-3	Light caramel-colored	Dry sample has been obtained and all waste has reacted with polymer	
20-E-4	Caramel-colored	Sticky, doughy and glistening which is the sign of a residual moisture presence	
20-E-5	very light caramel-colored	Dry sample has been obtained and all waste has reacted. Presence of polymer excess which seems to be the N910	

Based on these results, the Waste/Polymer mass ratio has been increased to 2:1 for the formulation with a N910/N960 mass ratio equal to 0.75 : 0.25 and 0.50 : 0.50.

Table V. Tests results for LOR 20 with a Waste/Polymer mass ratio equal to 2:1

Sample	Colour	Physical appearance	Picture
20-E-6	Caramel-colored	Sticky, doughy and glistening (presence of residual moisture)	
20-E-7	Caramel-colored	Sticky, doughy and glistening (presence of residual moisture)	

To complete these observations, evaluations of the residual liquid presence/absence and the manual exudation tests after 1h and 20h of curing have been carried out. They are presented in the Fig. 3.

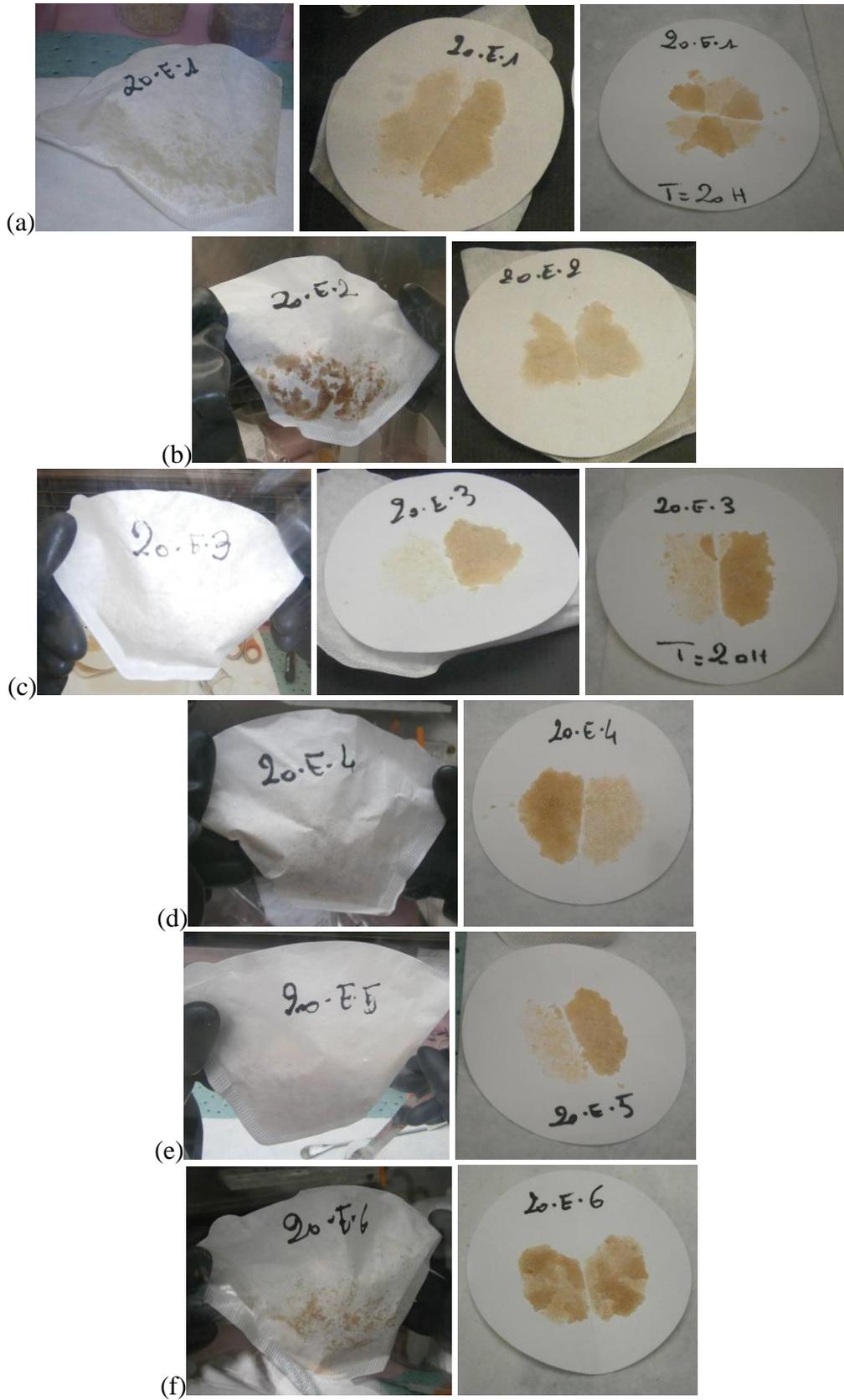




Fig.3: (a) 20-E-1, (b) 20-E-2, (c) 20-E-3, (d) 20-E-4, (e) 20-E-5, (f) 20-E-6 and (g) 20-E-7

For the samples which a Waste/Polymer mass ratio equal to 1:1, the obtained results are directly related to polymer formulation. For a N910/N960 mass ratio equal to 0 : 1 (20-E-2 sample), after a curing of 1h, the Waste/Polymer mix is characterised by a very important presence of moisture and an important waste desorption under exudation test. For the 20-E-1 and 20-E-4 samples, a presence moisture and a light waste desorption under exudation test have been observed after a curing of 1 and 20h. For the 20-E-3 and 20-E-5 samples, corresponding to N910/N960 mass ratio equal to 0.75 : 0.25 and 0.50 : 0.50, no moisture and no waste desorption under exudation test after a curing of 1 and 20h has been observed. For the two samples (20-E-6 and 20-E-7) characterised by a Waste/Polymer mass ratio equal to 2:1, an important presence of moisture and a waste desorption under exudation test have been observed.

With this study, and the one realized in 2007 only with polymer N910 and a Waste/Polymer mass ratio equal to 2:1 and 4:1, the adapted formulation has been identified. It corresponds to 20-E-3 and 20-E-5 samples i.e. a Waste/Polymer mass ratio equal to 1:1 and a N910/N960 mass ratio comprises between 0.75 : 0.25 and 0.50 : 0.50. The optimal Waste/Polymer mass ratio at 1 : 1 is related to the organic products nature. Indeed, the xylene and the mesitylene composed of a benzenic ring and methyl groups, present a limited number of free carbon atoms which negatively affects the reactive mechanism which occurs during the Waste/Polymer mixing to form covalent bonds between the two products. Concerning the N910/N960 mass ratio, it is explained by the fact that the N910 absorption power is higher than the N960 one.

Tests and Results for LOR 75

The tests carried out on LOR 20 are brought together in the Table VI.

Test reference	m LOR 20 (g)	m N910 (g)	m N960 (g)	N910/N960 Mass ratio	Waste/Polymer Mass ratio
75-E-1	20	0	20	0 : 1	1 : 1
75-E-2	18	4.5	13.5	0.25 : 0.75	1 : 1
75-E-3	20	10	10	0.50 : 0.50	1 : 1
75-E-4	16	12	4	0.75 : 0.25	1 : 1
75-E-5	36	9	9	0.50 : 0.50	2 : 1
75-E-6	31.7	12	4	0.75 : 0.25	2 : 1

Sample observations presented in the Fig.4, have been realized for each Waste/Polymer mix.

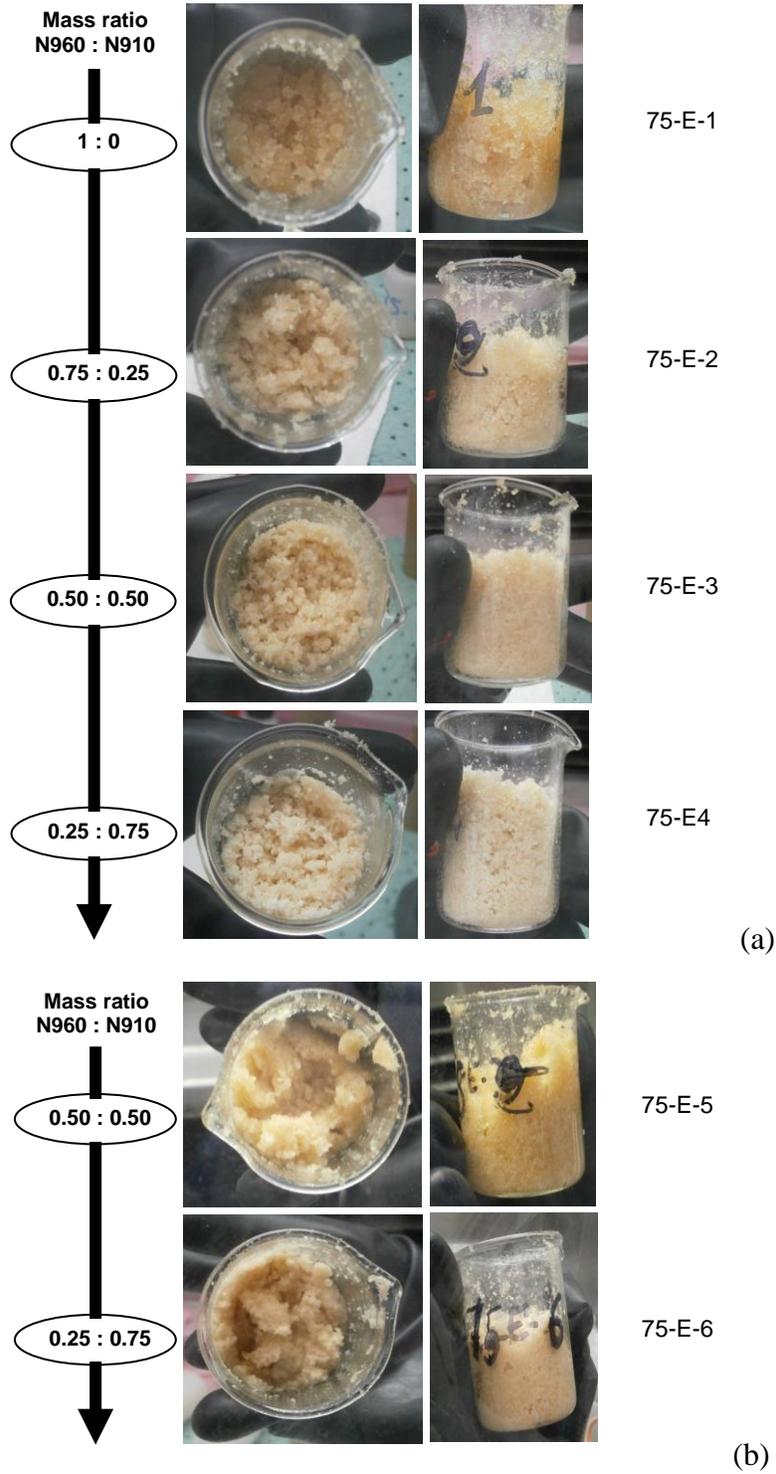


Fig.4: LOR 75 samples (a) with a Waste/Polymer mass ratio equal to 1 : 1 and (b) to 2 : 1

The tests have been carried out for LOR 75 like for the LOR 20. Firstly, the optimal formulation has been searched with a Waste/Polymer mass ratio equal to 1:1.

Table VII. Tests results for LOR 75 with a Waste/Polymer mass ratio equal to 1:1

Sample	Colour	Physical appearance	Picture
75-E-1	Beige	Sticky, doughy and very glistening. Presence of residual moisture with an important quantity of waste which has not reacted.	
75-E-2	Light beige	Sticky, doughy and lightly glistening	
75-E-3	Very light beige	Dry : all waste has reacted with a presence of a polymer excess which seems to be the N910	
75-E-4	Very light beige	Dry : all waste has reacted	

For the two more adapted formulation (75-E-3 and 75-E-4 samples), the Waste/Polymer mass ratio has been increased to 2:1.

Table VIII. Tests results for LOR 75 with a Waste/Polymer mass ratio equal to 2:1

Sample	Colour	Physical appearance	Picture
75-E-5	Light beige	Sticky, doughy and glistening (presence of residual moisture)	
75-E-6	Light beige	Sticky, doughy and glistening (presence of residual moisture)	

To complete the previous results, evaluations of the residual liquid presence/absence and the manual exudation tests after 1h of curing presented in the Fig. 5 have been realized.

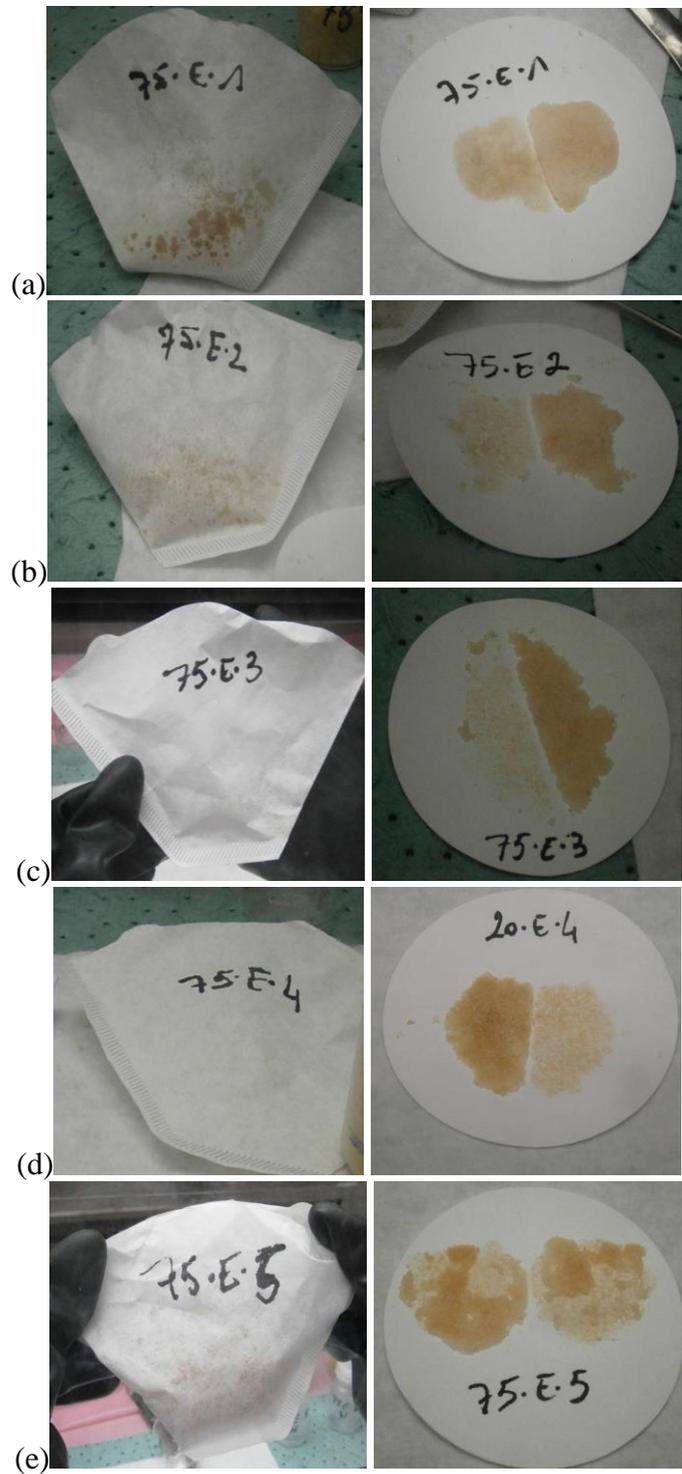




Fig.5: (a) 75-E-1, (b) 75-E-2, (c) 75-E-3, (d) 75-E-4, (e) 75-E-5 and (f) 75-E-6

The exudation tests have firstly been realized for the samples which are characterised by a Waste/Polymer mass ratio equal to 1:1. For the 75-E-1 and 75-E-2 samples, important presence of moisture and waste desorption under exudation test have been observed after 1h of curing. The best results have been obtained for a N910/N960 mass ratio comprises between 0.75 : 0.25 and 0.50 : 0.50 (75-E-3 and 75-E-4 samples). After a curing of 1h, little or no moisture and no waste desorption under exudation test have been observed. For the 75-E-5 and 75-E-6 samples characterised by a Waste/Polymer mass ratio equal to 2:1, the results are the same : presence of moisture and waste desorption under exudation test after a curing of 1h.

Like for LOR 20, the adapted formulation for LOR 75 has been identified by this study, and the one realized in 2007 only with polymer N910 and a Waste/Polymer mass ratio equal to 2:1 and 4:1. This one corresponds to a Waste/Polymer mass ratio equal to 1:1 and a N910/N960 mass ratio comprises between 0.75 : 0.25 and 0.50 : 0.50 i.e. respectively 75-E-3 and 75-E-4 samples. Like for the LOR 20, the optimal Waste/Polymer mass ratio is explain by the nature of the LOR 75 organic product (TBP) and the adequate N910/N960 mass ratio is related to the adsorption power difference between N910 and N960.

CONCLUSION

For both Cadarache LOR waste streams (LOR 20 and LOR 75), the pre-treatment by polymer i.e. an aqueous and organic liquid solidification process polymer seems to be adapted. As a consequence, polymers seem to be able to constitute a suitable solidification matrix for a final acceptance in storage on ANDRA sites.

In the future and in order to consolidate this conclusion, it seems to be necessary to refine the adapted formulations for each LOR by tests and to realize a waste field study. It will be based on the experimental data collected during this study, on the potential adequate between pre-treated Cadarache LOR waste streams characteristics and ANDRA specifications, and on the ANDRA agreement principle obtained by AREVA CL BU (Clean-Up Business Unit) on VLLW, LLW and ILW immobilised by polymers. Indeed, for LLW/ILW immobilised by polymers, they can be accepted in storage on ANDRA site if they are conditioned in homogenous waste package (waste immobilised by polymers placed in cement matrix) or in heterogeneous waste at 10% for the waste immobilised by polymers and at 20% for the waste immobilised by polymers placed in cement matrix.

After the waste field study and if the conclusions of this study are conclusive, the outlook of this study can be the preparation of an ANDRA agreement file for Cadarache LOR waste streams pre-treated by NOCHAR polymers.

REFERENCES

- [1] Pacific World Trade, Material Safety Data Sheet N910 (2007)
- [2] Pacific World Trade, Material Safety Data Sheet N960 (2007)