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In-Can vitrification of ALPS slurries from Fukushima Daiichi effluent treatment using DEM&MELT technology

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Abstract. After the accident at the Fukushima Dai-ichi Nuclear Power Station, a large amount of contaminated water was treated using several decontamination systems with different natures of adsorbents and chemicals. The resulting wastes, called Fukushima Effluent Treatment Wastes (FETW), were stored at the Fukushima Dai-ichi site. Vitrification could be the most promising treatment method to package these wastes. The consortium gathering CEA, Orano, ECM Technologies and ANDRA, implemented an in situ, robust, simple and versatile In-Can vitrification process, the DEM&MELT technology. Since 2018, the applicability of this technology for FETW treatment and conditioning has been evaluated. In 2021–2022, studies focused on one particular waste, coming from the ALPS system (Advanced Liquid Processing System-Multi Radionuclides Removal) generating around 70%vol. of FETW. This waste is composed of two co-precipitation slurries: one mainly composed of iron hydroxide, and one of calcium carbonate and magnesium hydroxide. The purpose of this article is to highlight the feasibility of ALPS slurries vitrification with DEM&MELT, relying on tests performed from laboratory-scale to full-scale. Macroscopically homogeneous glasses were produced using the DEM&MELT demonstrator, with a waste loading of 60 wt.% (expressed as waste dry mass) and microstructural analyses were performed. It gives promising results for FETW conditioning with the DEM&MELT process.

1 Introduction

A large amount of waste, called Fukushima Effluent Treatment Waste (FETW), has been stored on the Fukushima Daiichi site. Among this waste, ~80%vol. consist of sludge and slurries that have been generated by three decontamination systems: ACTIFLO[®], ALPS and evaporative concentration apparatus. Among the volume, about 70% is generated by the ALPS system which produced two types of co-precipitation slurries: an iron hydroxide slurry and a calcium carbonate/magnesium hydroxide slurry. For now, ALPS slurry is stored in liquid form, but a dewatering process by filter press is planned for the stabilization of the slurry. The pasty and sticky texture of the dewatered slurry (after filter press operation) as well as its chemical composition make this waste very challenging to treat.

Vitrification is a promising method to condition such waste. A dense and durable final wasteform is produced thanks to a thermal treatment with the addition of vitrification additives to the radioactive waste

[1–3]. Atomistic bonds are created between the elements of the radioactive waste and the glass formers, which enables to reduce the waste reactivity and enhances passive safety. Vitrification is already implemented by many countries, especially for high-level waste, and the glassy wasteforms long-term behaviour with regard to the deep geological repository that has been studied since the 1950s.

The goal of the study reported in this article is to highlight the feasibility of the vitrification of ALPS slurries with the In-can vitrification process [4–6] DEM&MELT. The DEM&MELT technology has been developed by the consortium gathering CEA (French Alternative Energies and Atomic Energy Commission), Orano, ECM Technologies and ANDRA (French national radioactive waste management agency, acting as the operator of the French call for proposals resulting in the DEM&MELT pilot construction), and is an in situ, robust, simple and versatile In-Can vitrification process (see scheme in Fig. 1) [7]. This study was performed through funding from the Japanese Ministry of Economy, Trade and Industry as The Subsidy Program “Project of Decommissioning and Contaminated Water Management”.

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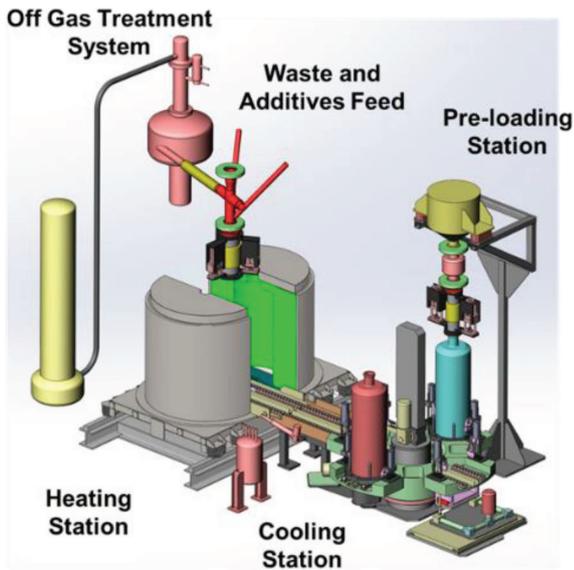


Fig. 1. Schematic diagram of the DEM&MELT process.

The applicability of the In-Can vitrification to the FETW is evaluated following some baseline treatment objectives [8]:

- the production of a solidified and dense vitreous matrix, in which the presence of non-labile crystallizations is accepted,
- the production of a waste form which is not subject to radiolysis,
- a significant volume reduction,
- chemical stabilization of radionuclides in the waste form,
- a suitable treatment capacity regarding the amount of waste.

This article aims to present the study of the In-Can vitrification of ALPS slurries, from laboratory-scale to full-scale, to produce inactive industrial canisters of vitrified ALPS slurries (as non-radioactive surrogates) using the DEM&MELT demonstrator operated on the CEA Marcoule site.

2 Experimental method and data

This experimental program is performed in a non-radioactive environment [9]. This is a classic and important methodological step in the vitrification study of any radioactive waste stream. Indeed, it is a powerful tool for increasing the technical and economic efficiency of studies. Although the radioactive nature of the waste is important, the major challenges related to its vitrification can be studied, and at least partly solved, in a non-radioactive environment. After the non-radioactive studies, studies with radionuclides using the CEA facilities can be considered, if necessary, to verify the results obtained on the materials and their evolution under irradiation. This methodology has been successfully applied to the qualification of various vitrification processes and glass matrices.

Table 1. Composition in wt.% of mixed ALPS slurries surrogates.

Dry composition (wt.%)	Surrogate ALPS slurry mix (5:1)
CaCO ₃	47.30
Mg(OH) ₂	29.47
Na ₂ CO ₃	3.52
SiO ₂	2.98
SrCO ₃	1.90
FeO(OH)·H ₂ O	11.97
Al ₂ O ₃	0.94
Co(OH) ₂	0.50
Ti(OH) ₂	0.45
Zn(OH) ₂	0.38
Ca(OH) ₂	0.32
Cl	0.26

First, representative surrogates of both ALPS ferric slurry and ALPS carbonated slurry were manufactured by a co-precipitation process. In order to be physically representative of the real waste, filter press operations were used to obtain a water content close to 50 wt.%. Although these two slurries can be vitrified independently, preliminary scoping studies (not shown) demonstrated the interest in mixing these two slurries for vitrification. Therefore, the waste studied is a 5:1 mix of carbonated and ferric surrogate slurries expressed as dry mass (Tab. 1). Slurries are doped with non-radioactive Sr, a surrogate of their main radionuclide.

To vitrify these ALPS slurries, borosilicate glass additives were selected because the properties of borosilicate glasses are recognized in the nuclear field. They enable high Waste Loadings (WL: waste fraction in the final wasteform) while meeting processability requirements such as chemical reactivity with the waste, appropriate melting temperature, limitation of the volatility of some species and corrosion issues.

In order to ensure the course of full-scale tests with the DEM&MELT demonstrator, various experimental steps were implemented. First, the study started at a laboratory scale (≈ 100 g of glass) in order to test some of the main parameters and search for an acceptable final wasteform, using a muffle furnace. Then a test at bench-scale was made (≈ 1 kg of glass) with a furnace integrating an Off Gas Treatment System (OGTS) to evaluate the volatility of species during the glass production and consolidate operational parameters. The last step was the full-scale tests with the DEM&MELT demonstrator (≈ 300 kg of glass). The present article focused on laboratory-scale and full-scale tests.

One of the goals of the study was to obtain a high WL to reduce the volume of waste and so the number of containers to be produced and stored while having a suitable final wasteform. In the following, the waste loading is

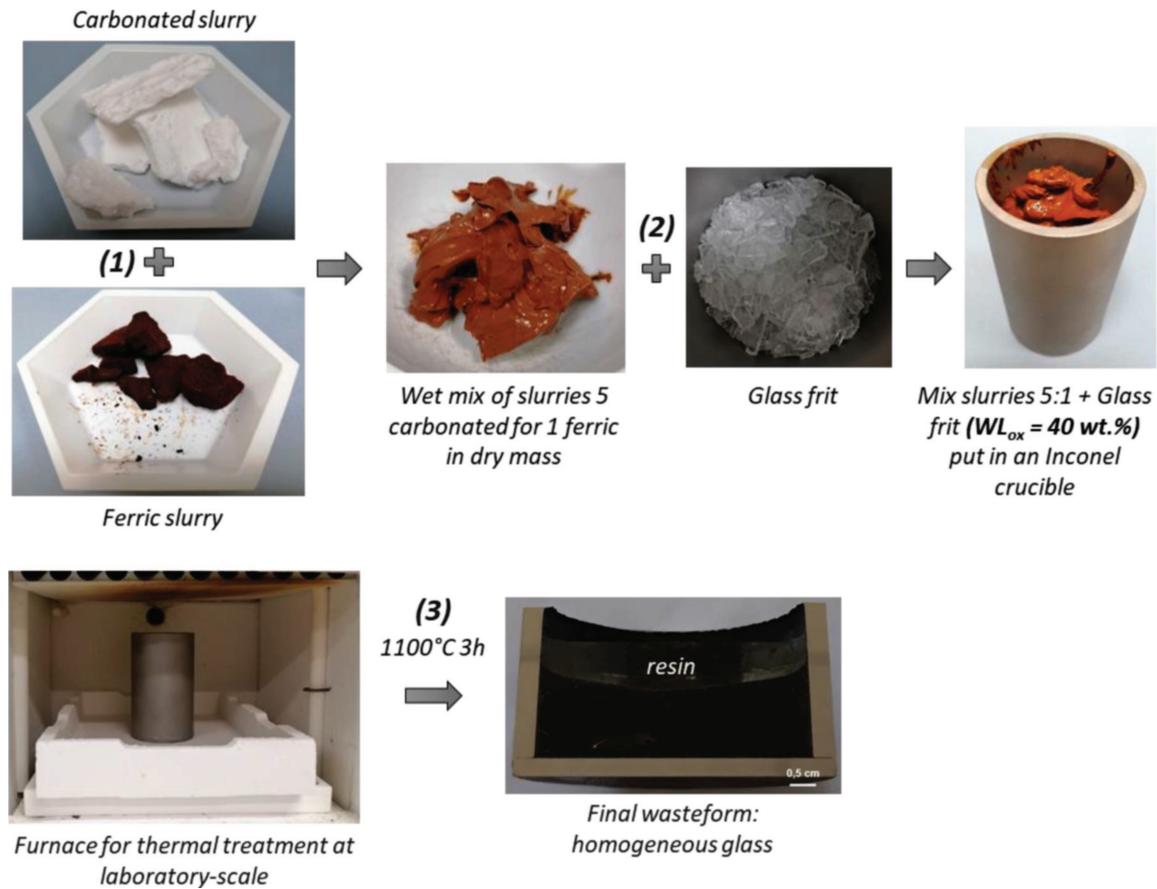


Fig. 2. (1) Mixture of the two slurries, (2) mixture of mixed slurries with the glass frit placed in a crucible (3) thermal treatment in a muffle furnace and crucible cut in the height direction to see the material. An epoxy resin is poured after the thermal treatment to maintain the material during cutting.

expressed in two ways: (i) as a function of the masses of dry waste and final wasteform (WL_{dry}, Eq. (1)), remembering that there is 50 wt.% of water inside the slurries, or (ii) as a function of the masses of oxides forming the waste and final wasteform (WL_{ox}, Eq. (2)). WL_{ox} calculation requires the conversion of the waste mass into an equivalent mass of oxides (e.g. CaCO₃ converted in CaO) so that chemical species discharged to the OGTS (e.g. water, carbonates, nitrates, etc.) are not taken into account. To calculate the mass of slurries in oxide form, a batch of slurry is heated to 1000 °C to remove all gases, and masses before and after thermal treatment are compared.

$$WL_{dry} (\%) = \frac{\text{mass of dry waste (kg)}}{\text{mass of wasteform (kg)}} \times 100 \quad (1)$$

$$WL_{ox} (\%) = \frac{\text{sum of oxide masses composing the waste (kg)}}{\text{mass of wasteform (kg)}} \times 100. \quad (2)$$

3 Laboratory-scale tests

After previous investigations (not shown), a glass frit additive composed of SiO₂, B₂O₃ and Na₂O was selected for the vitrification of ALPS slurries surrogate. It can be

noted that this study was not focused on glass frit formulation, so a deeper material study could have led to a higher WL than the one found in the presented study. The laboratory-scale study focused on sensitivity tests covering the process main parameters:

- refining temperature,
- reactivity between the glass frit and the slurries as a function of the shape of each component and their mixing procedure,
- reactivity at high temperature of a mix of slurries and glass frit put into a high-temperature molten glass,
- WL.

3.1 Nominal tests – glass production and characterisation

The different preparation steps of a typical test are shown in Figure 2. The mixture of slurries and glass frit is placed into a crucible. The crucible is then put inside a muffle furnace and follows a thermal treatment up to 1100 °C, with dehydration and decarbonation steps due to the quantity of water and carbonates composing the slurries. After the thermal treatment, the crucible is gently cooled at 60 °C·h⁻¹. The glass sample shown in Figure 2 is the

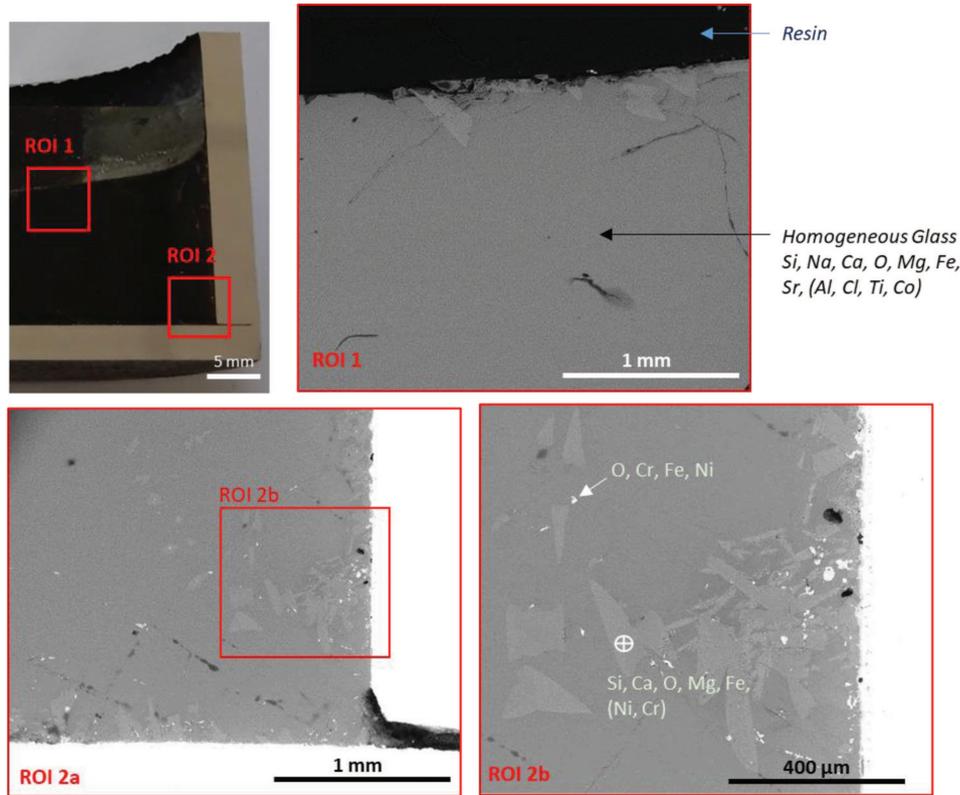


Fig. 3. SEM imaging of the wasteform, $WL_{ox} = 40$ wt.%.

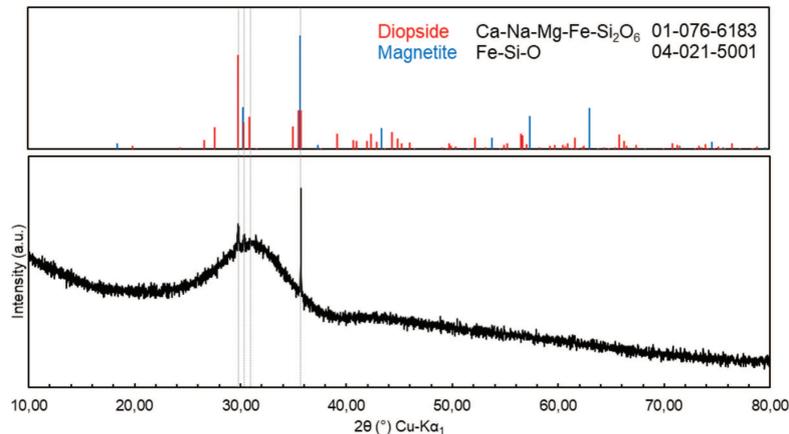


Fig. 4. X-Ray diffractogram of the wasteform $WL_{ox} = 40$ wt.%.

wasteform obtained with the nominal parameters selected for the study: $WL_{ox} = 40$ wt.%, a homogeneous mixture of ALPS slurries with the glass frit supplied as flakes, and a refining temperature of 1100 °C. After each test, the crucible is cut to characterise the vitrified material. Visual and microstructural analyses are performed.

Scanning electron microscopy (SEM) (Fig. 3) and X-ray crystallography (Fig. 4) are performed and are presented here for the nominal sample shown in Figure 2. The SEM observations of the cross-section show a homogeneous glass in a major part of the sample, composed of Si, Na, Ca, O, Mg, Fe, Sr, Al, Cl, Ti, Co, and B. The

amorphous state of the wasteform is also confirmed by the X-ray diffractogram. Very few grey crystals are visible on the surface and especially near the metallic crucible wall. These crystals are silicates of Ca, Mg, Fe, a diopside phase according to the X-ray diffractogram, and contain also some Ni or Cr. These two last elements are not present in the initial material composition, they come from the crucible. Some small crystals, in white colour, are present near the big grey crystals and contain Cr, Fe, and Ni. These particles, coming from a very slight crucible corrosion, could act as nucleating agents for the silicate crystals, favouring their growth, and are localized in the

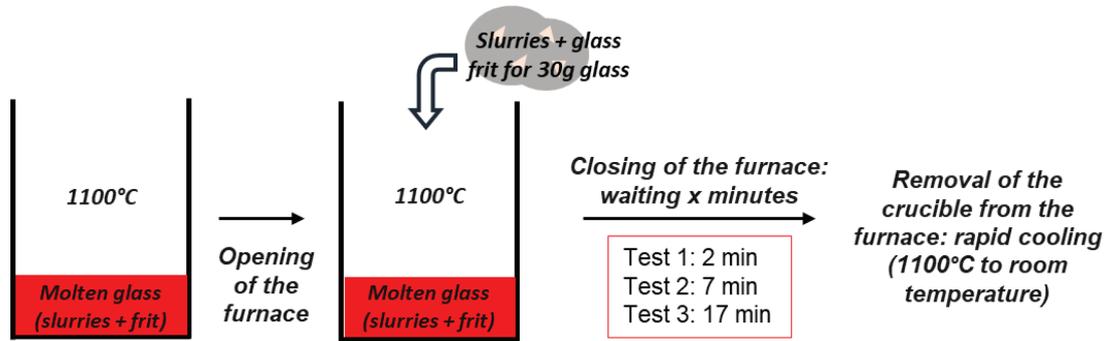


Fig. 5. Principle of the reactivity tests at high temperature.

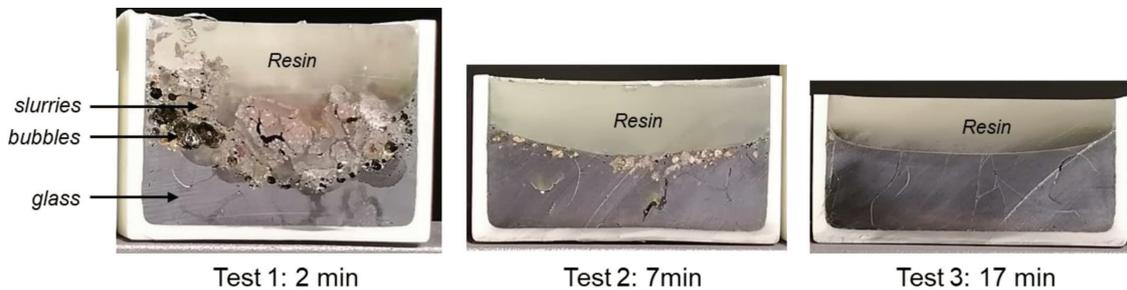


Fig. 6. Half-cut crucibles after the tests to see the evolution of the material with the time of digestion.



Fig. 7. Photo of the DEM&MELT inactive pilotdemonstrator at CEA Marcoule (© Y. Audic/CEA).

interface areas which favour heterogeneous nucleation. So a glass matrix is obtained with very few crystals which do not impact the durability of the matrix and which are not containing Sr.

3.2 Study of the reactivity between slurries and glass frit

During the course of an In-Can treatment, raw material (waste and/or glass additive) is first preloaded into the canister at ambient temperature and then heated until the

selected treatment temperature. Then, waste and/or glass frits are usually fed on the molten glass in order to fill the canister. At the laboratory-scale usual tests in muffle furnaces are made under static conditions, with no material feeding during the thermal treatment. The so-called “reactivity tests” at high temperatures described in the following aimed to mimic material feeding and to estimate the time of fed material digestion in the molten glass.

The principle of the test is described in Figure 5. A mix of slurries and glass frit ($WL_{ox} = 40$ wt.%) is poured on a molten glass (corresponding to a $WL_{ox} = 40$ wt.% waste-form) at 1100°C . After waiting x min ($x = 2$ min for Test

1, 7 min for Test 2 and 17 min for Test 3), the crucible is removed from the furnace to “freeze” the state of the material by rapid cooling from 1100 °C to the room temperature. The goal is to follow the reactivity steps between the fed material and the glass bath as a function of time and to look at the evolution of the microstructure at the interface between the molten glass and the added mixture.

Visual observations presented in Figure 6 show fast digestion of the slurries under static conditions (<20 min at 1100 °C). After two minutes at 1100 °C, the addition of mix slurries + glass frit is not assimilated. Large bubbles are visible at the boundary between the glass and the added material, coming from the decomposition process of the slurries. After 7 min at 1100 °C, the reaction of slurries + glass frit with the molten glass has begun but some fragments of slurries are still present on the glass surface, associated with the presence of very small bubbles. After 17 min at 1100 °C, the added slurries + glass frit are completely digested: a homogenous glass is visible at the macroscopic scale.

Reactivity tests at high temperatures showed fast digestion of the slurries inside the molten glass bath, meaning that a good reactivity between constituents at 1100 °C can be expected at full-scale.

3.3 Results of the sensitivity tests

The other tests made in the sensitivity study are not shown in detail but they showed that a homogeneous glass was obtained with a WL_{ox} of 40 wt.% in a temperature range between 1050 and 1130 °C. The glass frit shape, tested with three different shapes (flakes, beads and fine powder), did not affect the wasteform quality.

Therefore, the feasibility of the vitrification of ALPS slurries was validated at the laboratory scale and nominal operation parameters were selected for the full-scale test.

4 Full-scale

4.1 DEM&MELT In-Can vitrification demonstrator

Test at full-scale was performed on the DEM&MELT demonstrator located at the CEA Marcoule site. A picture of the prototype is shown in Figure 7. In the In-Can vitrification process, the canister is directly used as a melter and renewed after each batch. The container is first preloaded with waste and/or glass additives, then placed into the resistive furnace composed of two half shells. During the heating, glass frit and slurries are added. A special feeding system was developed to be able to continuously feed this constraining waste. Indeed, slurries are very hard to process regarding feeding function: their rheology is penalizing (high viscosity) and it has a high tendency to stick. An OGTS enables stopping volatilized species released from the melt and recycling them into the melter in order to increase the radionuclides trapping in the glassy confinement matrix.

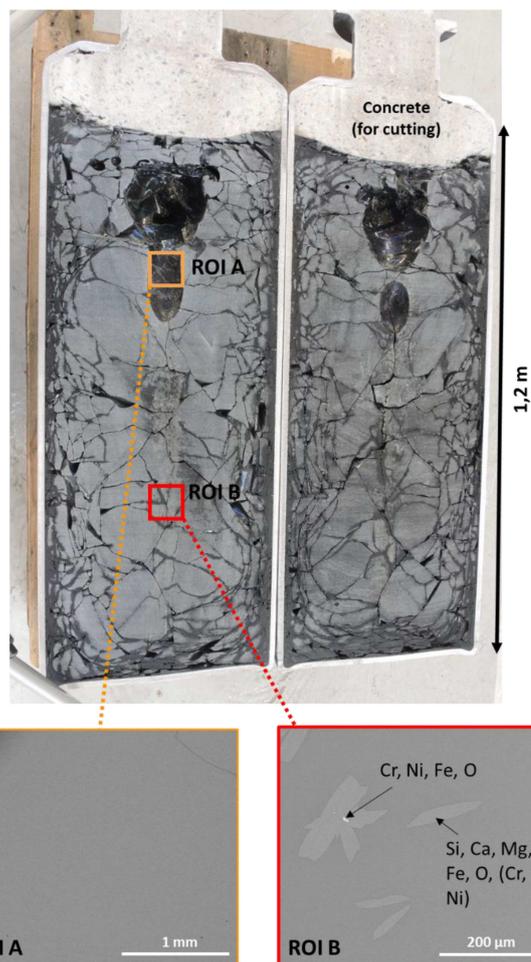


Fig. 8. Half-cut container obtained after vitrification of ALPS slurries using DEM&MELT prototype ($WL_{ox} = 40$ wt.%) and SEM pictures of its microstructure.

4.2 Vitrification of ALPS slurries

A vitrification test of ALPS slurries surrogates was performed on the DEM&MELT full-scale demonstrator at a melting temperature of around 1100 °C. A full container was produced (~280 kg of material) containing ALPS slurries with a WL_{dry} of 60 wt.% (corresponding to a WL_{ox} of 40 wt.%). The measure of Sr volatility gave very good results with a low value of 7×10^{-3} wt.%. A picture of the container cut in two parts is shown in Figure 8.

Such as observed at the laboratory scale, the final wasteform is a black homogenous glass. Microstructural SEM analyses on different locations of the canister were performed: results are consistent with the laboratory scale result. As confirmed also by X-ray diffraction (not shown, but similar to laboratory-scale), the wasteform is an amorphous glassy material. Very few crystals are visible inside the glass matrix for some locations and are composed of Si, Ca, Mg, Fe, O and a bit of Cr and Ni, such as diopside crystals seen at the laboratory scale. No Sr was identified in these crystals, it was located in the glass matrix.

5 Conclusion

The feasibility of ALPS slurries conditioning into a borosilicate glass wasteform was studied using the DEM&MELT In-Can process. The upscaling methodology enabled us to find the best parameters such as the optimal waste loading or the melting temperature before operating full-scale tests using the DEM&MELT demonstrator.

The vitrification demonstration of ALPS slurries was successfully performed, with a high waste loading. Good homogeneity of the glass melt was ensured with the DEM&MELT In-Can vitrification process, thanks to the natural thermo-convection loop triggered inside the molten glass that ensures a good reactivity between the waste and the glass additives.

The final wasteform is a homogeneous, monolithic and dense vitrified material exhibiting only a few isolated crystallizations. The high waste loading achieved of 60 wt.% (in dry mass of slurries) leads to a significant volume reduction of ALPS slurries: volume of waste reduced close to 1/12 considering ALPS slurries in the liquid form before the filter press process. The volatility of Sr was low, less than 0.007%, meaning that nearly the whole amount of Sr coming from slurries was confined into the wasteform. A formulation study could still allow for increasing this WL.

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Conflict of interests

The authors declare that they have no competing interests to report.

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Data availability statement

This article has no associated data generated and/or analysed.

Author contribution statement

Aliénor Vernay performed laboratory-scale tests and material analysis and wrote the manuscript. Hélène Nonnet supervised laboratory-scale tests with Aliénor Vernay and reviewed the manuscript. Caroline Michel and Jean-François Hollebecque performed the full-scale test and reviewed the manuscript. Maxime Fournier and Régis Didierlaurent performed the project management and reviewed the manuscript.

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