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# Influence of thermal treatment on the disposability of spent ion exchange resins in a deep geological repository: a French case

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**Abstract**. The filtration of contaminated aqueous waste streams from nuclear applications produces spent ion exchange resins (IER) which can be classified either as low level Waste (LLW) or as intermediate level Waste (ILW). For the purpose of the work conducted in the framework of the European THERAMIN project, studies considered spent IER waste form to be routed to the French deep geological disposal facility in the Callovo-Oxfordian formation (Cigéo). This form of waste is known to release hydrogen by radiolysis degradation, reactive species and complexing compounds. Today, for disposability in Cigéo, direct cementation of IER is the main immobilization process. This work aims to evaluate the application of the incineration-vitrification with plasma process, SHIVA, on a mixture of zeolites, diatoms, and spent IER in regards to the reference immobilization process by cementation. Production of an alumina-borosilicate type glass using SHIVA incineration-vitrification process was considered in order to examine the impact of this process for managing the specificities of this IER waste form with the additional advantage of minimizing the disposal volume. The potential benefits that thermal treatment can provide in the context of Cigéo for such spent IER waste form are evaluated based on the physical characterizations and leaching experiments carried out by CEA on the resulting vitrified product. The influence of thermal treatment on several characteristics in line with a generic list of Waste Acceptance Criteria (WAC) defined within the THERAMIN project have been qualitatively evaluated considering their potential influences on operational and long-term safety.

## 1. Introduction

In a nuclear facility, circulating water and the water released to the environment are filtered to eliminate radiological contamination [1]. This filtration process induces waste that could be composed of ion exchange resins (IER), zeolites and diatoms. The direct cementation of this waste is the main immobilization process for disposability in Cigéo (French deep geological disposal project in the Callovo-Oxfordian formation, Figure 1).

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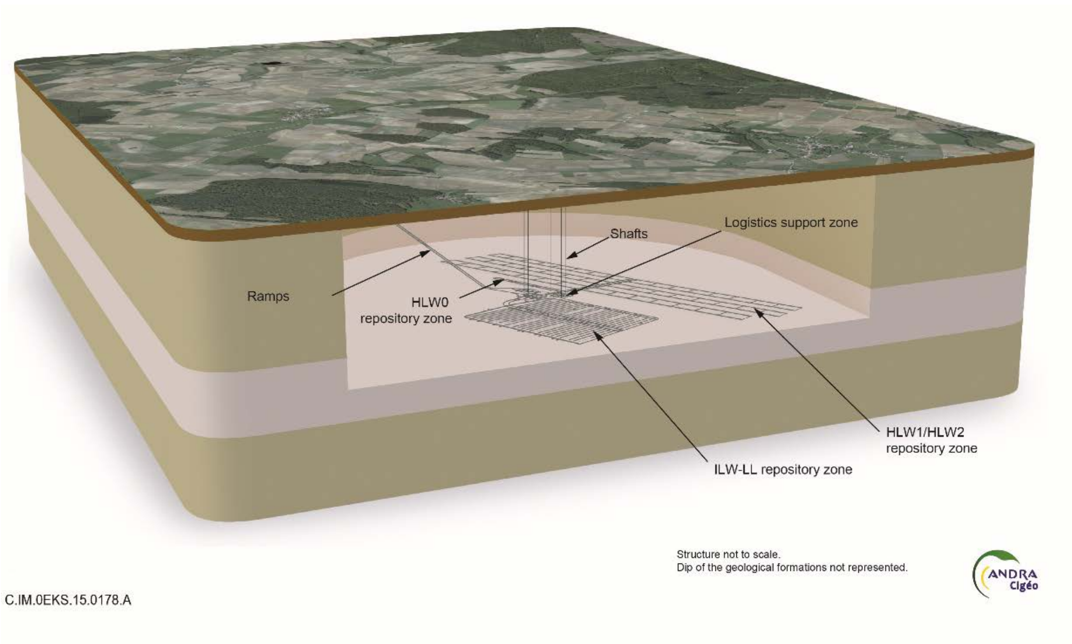


**Figure 1.** Schematic illustration of the French Cigéo project (extracted from [1]).

However, the weight ratio of such a process is around 10% of raw waste for 90% of cement, which significantly affects the disposal volume. Furthermore, as organic compounds, radiolysis of IER could lead to the production of hydrogen and complexing compounds. Therefore, vitrification of such waste could present an interesting alternative with a reduction of both volume and waste reactivity.

Spent IER waste forms in the French context may be categorised as Intermediate Level-Short Lived waste (ILW-SL), Low Level-Long Lived (LLW-LL) waste, or Intermediate Level-Long Lived (ILW-LL) waste. Considering the fact that in the French context, vitrified wastes are, so far, exclusively ILW-LL or HLW and therefore dedicated to deep geological disposal, this paper assesses the impact of vitrification on the disposability of a generic ILW-LL spent IER, mixed with zeolites and diatoms. This evaluation considers as baseline, a cementation process in concrete packaging.

In the framework of the THERAMIN project, an inactive mixture [2] composed of 45% of Zeolites, 44% of diatoms, 5.5% of anionic IER and 5.5% of cationic IER was vitrified with the inactive incineration-vitrification pilot process SHIVA developed by CEA [2][3]. The final product consists of an amorphous alumina-borosilicate glass (mainly composed of $SiO_2$, $B_2O_3$, $Nd_2O_3$ and $Al_2O_3$), which is homogeneous at the macroscopic level (Figure 2).

**Figure 2.** Waste glass sample from the SHIVA trial carried out in THERAMIN project [2].

Based on a list of generic WAC [4] to support analyses of the resulting product from thermal treatment, CEA performed physical characterizations and leaching experiments on the final product.

This assessment is carried out as part of WP4 of THERAMIN project. The article presents the main conclusions of this generic evaluation considering the main characteristics defined in the WP4 template, including the generic list of WAC.

## 2. Impact of thermal treatment on waste characteristics

### *2.1. Impact on radiological characteristics*

The mixture used for SHIVA vitrification was inactive. Therefore, no specific activity measurement was performed and the characterization focused on the chemical composition before and after treatment.

Mixed waste produced by the filtration of contaminated aqueous waste streams may contain volatile radionuclides, such as $^{3}H$, $^{14}C$, $^{36}Cl$, $^{106}Ru$, $^{137}Cs$ and $^{129}I$. A partial volatilisation of these elements is expected during the treatment. Most of them should be collected in the off -gas treatment system (which is not currently developed for active waste).

For a given waste volume, the SHIVA vitrification process leads to a higher concentration than the cemented IER waste form. From a qualitative analysis, it is likely that the concentration activity of the final vitrified waste form will increase.

Such evolution on radiological characteristics brings some elements to consider for the final product after thermal treatment:

- Heat generation and criticality: Even if the activity content of this type of IER waste does not usually cause criticality issues or heat generating problems, particular attention should be paid to activity concentration, heat production and fissile radioelements before and after processing due to volume reduction induced by the treatment.
- Waste classification: It should be noted that in France, the classification of radioactive waste is based on two important parameters to determine the appropriate management route and disposability: the level of waste activity and the half-lives of radionuclides. Depending on the impact of the thermal treatment on the concentration activity of the waste, the classification of the initial waste could be modified after thermal treatment (for example, a waste initially LLW-LL could be redirected to deep geological disposal if it becomes an ILW-LL waste). For the studied IER mixture, which is supposed categorised as an ILW-LL, there is no need to consider reorientation of disposability (i.e. Cigéo deep disposal).

### *2.2. Influence on the disposal volume*

The baseline for this waste, classified as an ILW-LL, would be cementation with a usual weight ratio around 10% of raw waste. The mass distribution of waste and glass frit for SHIVA vitrification is respectively 40% and 60%. Considering a similar density of cemented waste and vitrified waste, the vitrification induces a volume smaller than cementation (by a factor of about 4). The completely burned IER will imply a larger factor (this will depend on the initial amount of IER).

In addition, the packaging increases this difference: cemented waste is usually packaged in concrete containers while vitrified waste is packaged in smaller metallic containers, which optimises the packaging volume and its subsequent disposal in the cell. In this evaluation, it is intended that the final product will be packaged in vitrified waste canister (CSD-V type).

The disposal of ILW-LL and HLW vitrified waste will require an over packing in the context of Cigéo. The primary packages delivered by producers will be introduced into specific standardised disposal packaging.

In the context of Cigéo, ILW-LL vitrified waste canisters would be packaged in a metallic over pack as for vitrified HLW (Figure 3). They would be disposed in the HLW area. One option would be to use them as spacers between HLW packages in order to limit the level of thermal output in the cell. Anyhow,

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for the purpose of the current analysis of the SHIVA final product, it is considered that it will be disposed in the HLW area with no need to consider its exact localisation (used as spacer or not).

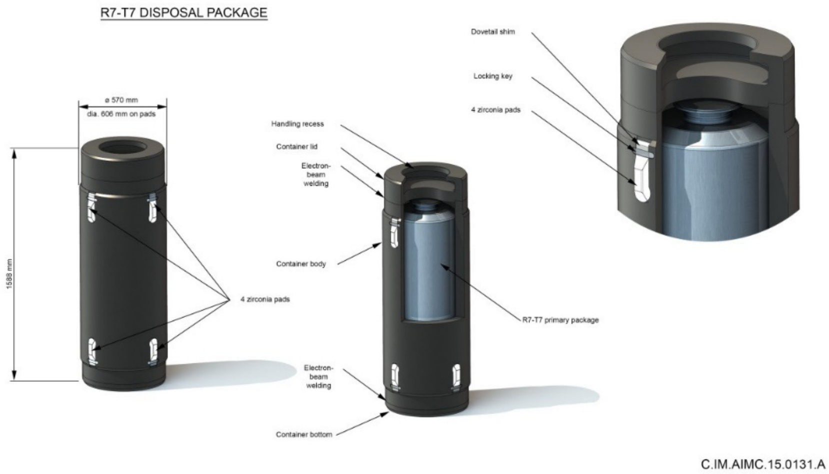


**Figure 3.** Schematic illustration of a vitrified high level waste package over pack (extracted from [5]).

### *2.3. Stability of the final glass product after thermal treatment*

The volatilisation of radionuclides induces secondary waste from the off-gas treatment system. This volume has not yet been evaluated and will depend on the industrialization of the treatment process. However, with the SHIVA process, the gas produced during incineration of organic matter (around 1 m3 of gas per kg of organic matter) is burned [2], which leads to the absence of gas in the final glass form product.

This thermal treatment process will prevent $H_2$ generation in the waste package by radiolysis due to the degradation of organic matter and the absence of water in the glass waste form (unlike in the baseline IER cemented form). In addition, the elimination of organic compounds during thermal treatment will lead to the absence of organic complexants in the final waste form (unlike in the initial cemented form).

It is also noted that since the final product consists of an amorphous alumina-borosilicate glass, the release of radionuclides will depend on chemical durability of the vitreous matrix. In order to get preliminary information about chemical durability and alteration mechanisms of the final waste form, CEA performed some standard leaching tests [6].

The results of the leaching tests have been compared with those relating to an international reference glass of nuclear interest, called ISG, which includes the six main oxides of the typical French borosilicate glass SON68 used to vitrify high-level waste [7].

The comparison of the first leaching test results obtained with the SHIVA-VDM1 and ISG samples shows a similar trend [6]. The hydrolysis rate of the SHIVA-VDM1 sample (based on boron B release) is lower by approximately one order of magnitude than the hydrolysis rate of the ISG sample. Boron is considered as a tracer of glass alteration whereas silicon can be partially retained at the surface of the glass. This is clearly visible in the ISG results in Figure 4: Si release is lower than B release and indicates the possible formation of an alteration layer on the surface of the glass. This phenomenon could also explain why the alteration rate of ISG drops earlier than for the SHIVA-VDM1 sample. However, concluding about the long-term behaviour of the SHIVA-VDM1 waste form would require further investigation in the geochemical context of Cigéo.

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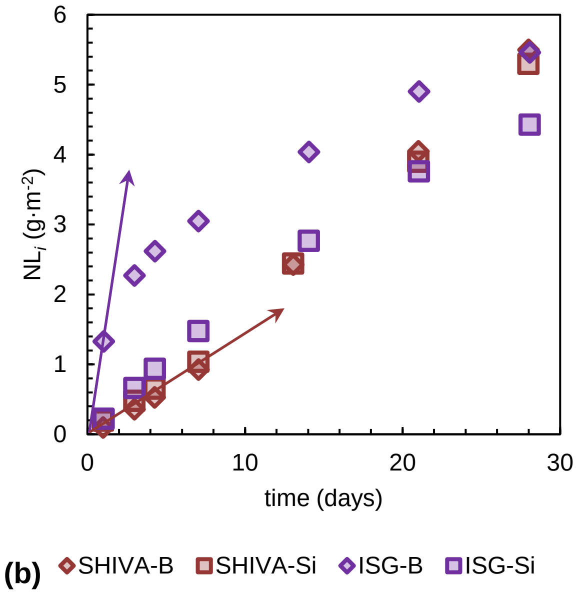


**Figure 4.** Compared evolutions of Normalized Leaching (NL) of Si and B during the leaching of ISG and SHIVA-VDM1 samples. The arrows are a guide for the eyes to estimate the hydrolysis rate of the matrices (extracted from [6]).

## 3. Impact of thermal treatment on disposability

### *3.1. Impact on disposability criteria*

In France, Waste Acceptance Criteria (WAC) are defined together with the progressive development of Cigéo. Currently, only preliminary specifications are available. However, the glassy waste form is already taken into account in the Cigéo concept and so has associated preliminary WAC.

Among the list of generic WAC proposed in the framework of THERAMIN WP4 [4], some criteria have been considered according to the actual state of the Cigéo preliminary WAC. No prohibitive elements have been identified for the final borosilicate glass, with in addition the added benefit of the absence of $H_2$ release. The SHIVA vitrification process being tested on an inactive sample, the analysis is qualitative and could not be exhaustive at this point. However, considering the potential radionuclide inventory of IER, there should not be any heat generation due to concentration by volume reduction and no impact is expected on critical safety.

### *3.2. Impact on operational safety*

The final product will be classified as an ILW-LL vitrified waste, which impacts on the packaging and overall disposal processes relative to the baseline spent IER waste.

The final product is intended to be packaged in the form of vitrified waste canister (CSD-V type), which is the main type of waste packaging defined for high-level vitrified waste to be disposed in Cigéo. The vitrified product obtained after thermal process of spent IER should therefore be disposed in the same conditions as other high-level waste [5].

However, due to a moderate initial activity of spent IER (classified as ILW), it is likely that high-level vitrified waste to be disposed in Cigéo present much higher values for (i) total activity per waste canister, (ii) mass of fissile material and (iii) heat generation. Therefore, the operational safety provisions that will be applied for disposal of high-level vitrified waste in Cigéo should cover operational safety to be considered for the final vitrified product obtained after thermal treatment of spent IER.

Vitrification resulting from the thermal treatment of the waste induced by the filtration of contaminated water (IER, zeolites, diatoms) offers, as would cementation, limitation to radioactive dispersion.

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One advantage of thermal treatment for the operational safety compared to cementation is the absence of $H_2$ release, which simplifies the ventilation constraints in a disposal cell. On the other hand, due to the risk of re-concentration of the original inventory, in particular of fissile material, it will require confirmation that it is covered by the hypothesis retained for high-level vitrified waste.

### *3.3. Impact on long-term safety*

The final product is an amorphous alumina-borosilicate glass macroscopically homogeneous in which radionuclides are integrated. From a qualitative point of view, analogies can be made with high-level vitrified waste already planned to be disposed in Cigéo [8].

The vitrified product obtained after thermal processing of spent IER will be disposed in the same conditions as other high-level vitrified waste (see Figure 3) and disposed in the high-level waste area of Cigéo. However, due to potential change of waste disposal area in Cigéo (from the ILW-LL area to HLW area), the redistribution of the inventory within the repository will have to be considered.

The glassy waste form produced after thermal treatment induces a slow release of radionuclides, which depends on the chemical durability of the vitreous matrix, compared to the instant release model associated to the baseline cemented spent IER waste form. This is more favourable even if long-term behaviour of the final product still needs to be assessed in more detail.

The long-term safety that will be applied for disposal of high level vitrified waste in Cigéo should cover long-term safety of the final vitrified product obtained after thermal treatment of spent IER. The overall long-term safety approach already taking into account high-level vitrified waste form can be applied (consideration of the same safety scenarios for example), only further knowledge on the chemical durability of the final product in the disposal conditions and new distribution of the inventory should be considered.

The absence of gas in the glass waste form after treatment leads to a reduction in the source term of gas after closure, which is favourable.

In addition, the characterisation results indicate that organic compounds have been removed leading to favourable characteristics for deep geological disposal due to the absence of organic complexants in the final product, although the Callovo-Oxfordian argillite offers good properties to limit radionuclide transfer.

## 4. Conclusion

This work, performed in the context of the European THERAMIN project, aimed at evaluating the application of the incineration-vitrification with plasma process, SHIVA, on a mixture of zeolites, diatoms, and IER, in regards to the reference immobilization process by cementation. A qualitative analysis was conducted in order to evaluate impacts of thermal treatment of a hypothetical l IER ILW-LL type of waste (baseline) into a vitreous product on disposability in Cigéo.

Results of the qualitative analysis indicate that the thermal treatment of a mixture of IER, zeolite and diatoms should induce less heterogeneous waste and a significant reduction of the waste and packaging volumes. The final product is an amorphous alumina-borosilicate glass with radionuclides integrated in a glassy matrix, which allows analogies with other vitrified waste to be disposed in the French deep geological disposal Cigéo.

Since the glassy waste form obtained with the SHIVA thermal treatment is already a type of waste taken into account in Cigéo, it is assumed that final glassy waste form should not require development of specific handling process and that operational safety applied for high level waste should cover the vitreous waste obtained by thermal treatment of spent IER.

From the generic list of THERAMIN WP4 WAC, qualitative analysis of some criteria according the actual state of the Cigéo preliminary WAC indicates no prohibitive elements for the final borosilicate glass with the added benefit of the absence of H2 release, thanks to the destruction of organic matter

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and the absence of water in the final waste form. This simplifies the ventilation constraints in disposal cell relative to the baseline IER cemented form.

Even if the activity content of this type of IER waste does not usually cause criticality issues or heat generation problems, particular attention should be paid to heat production and fissile radioelements before and after processing due to volume reduction induced by the treatment,.

Long-term safety already integrates such type of waste in Cigéo, which should not induce the development of specific approaches. In addition, the chemical durability of the glass appears more favourable than the instant release model associated to the baseline cemented IER waste form even if long-term behaviour of the final product needs to be assessed in more detail.

In addition, organic compounds have been removed which leads to favourable characteristics due to the absence of organic complexants although the Callovo-Oxfordian formation offers good properties which limit migration of radionuclides. Absence of gas in the glass waste form after treatment leads to a reduction in the source term of gas after closure, which is favourable.

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