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# Delayed Ettringite Formation Thermal Management in Cement Grout for Long-Lived Intermediate-Level Radioactive Waste Conditioning

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## Introduction

Activated long-lived medium or intermediate-level metallic radioactive waste (LL-ILW) from dismantled or in operation French nuclear power plants are conditioned since 2021 in a new EDF<sup>1</sup> facility (ICEDA) located in the Middle East of France.

The conditioning consists in blocking waste in a cement grout inside a long-lasting and confining concrete container. Due to the waste radioactivity, the process is carried out remotely, in hot cells.

Containers must have confining properties to be disposed without any additional packaging in the future French final geological repository studied by ANDRA<sup>2</sup>. The goal is to demonstrate that confinement properties of the concrete container are preserved during manufacturing and storage stages in the EDF facility and then after transfer to the ANDRA repository.

Many phenomena, such as irradiation and radiolysis, shrinkage induced by drying, carbonation and corrosion, can alter confining properties of the container. This paper focuses on the manufacturing stage and especially on industrial operating conditions that have been defined in order to limit the temperature rise and thus control the risk of Delayed Ettringite Formation in the packages. Temperature of the blocking grout is directly influenced by the thermal residual power of the metallic waste and by the exothermic reaction taking place during the hydration phase of the blocking grout.

To verify that the core temperature of packages stays below the 75°C threshold during the manufacturing process, experiments have been carried out with full scale package prototypes instrumented with thermocouples. Then, a thermal numerical model of the mock-up has been developed and validated based on the measurements. At last, an experimental campaign, including 5 instrumented packages with inactive waste, has been carried out in the industrial facility. Again, numerical model comparisons between measurements and calculations indicate that the numerical model is predictive and ultimately makes it possible to perform a sensitivity study. This study leads to identify manufacturing parameters required to ensure that the package core temperature will stay under 75°C: initial grout temperature and manufacturing cell temperature have to be controlled according to the nature and the mass of the waste in the packages.

## ICEDA facility

EDF commissioned a long-lived intermediate-level metallic radioactive waste conditioning facility in 2020.

This facility (Figure 1) has four main areas which are (i) the receipt area of radioactive waste transport packaging, (ii) the waste conditioning area in confining concrete container, (iii) the radioactive package storage area with a capacity of around two thousand packages arranged on three levels, (iv) conventional areas that include a cement matrix manufacturing plant. The first radioactive waste package was conditioned in ICEDA in September 2021.

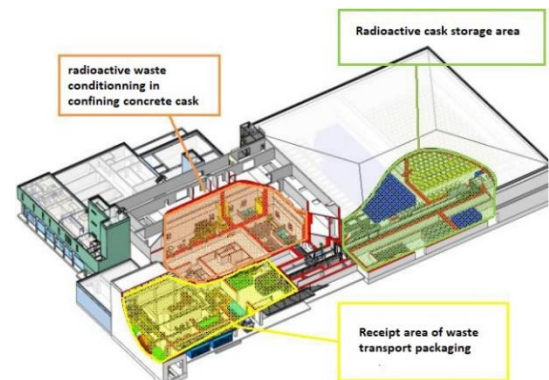


Figure 1 : ICEDA facility

<sup>1</sup> Electricité de France, main Electric industrial actor in France.

<sup>2</sup> ANDRA is responsible for identifying, implementing and guaranteeing safe management solutions for the entire French radioactive waste, in order to protect present and future generations from the risks inherent in such substances.

## C1PG<sup>SP</sup> Long-lived Intermediate-Level Waste package (LL-ILW)

C1PG<sup>SP</sup> (Figure 2) is a cylindrical EDF package design made with high performances concrete :

- Diameter : 1.4 m
- Height : 1.3 m
- Volume : 2 m<sup>3</sup>

The inner part, delimited by a steel basket, receives the waste and the blocking grout. The outer envelope of the package consists of a pre-fabricated concrete container and a plug, added at the end of manufacturing process by pouring the same type of concrete than the container.

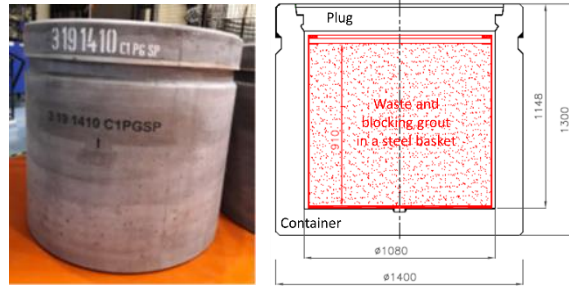


Figure 2 : C1PG<sup>SP</sup> package photo (l) and schematics (r)

Three main steps lead to a final package :

- blocking of radioactive waste by gravity casting of a cement grout into the basket,
- wedging of the waste basket in the container with the same cement grout,
- plugging the package with the same high performance concrete as the container.

### Delayed Ettringite Formation

In order to mitigate the risk of Delayed Ettringite Formation (DEF) in the cement matrix around LL-ILW in a C1PG<sup>SP</sup> package, we have to:

- choose the right components for grout and concrete formulations,
- respect a maximum temperature criteria of 75°C everywhere in the cement matrix (which leads to maintain specific operating conditions in hot cells during each operation described above)

This temperature criterium is defined by LCPC<sup>3</sup> for concrete applications but is also extrapolated for our grout application even if the relevance of this extrapolation is not obvious. This 75°C criteria is considered to be the most severe level of prevention (Ds, III) among several exposure classes related to civil engineering buildings. It requires the use of a low hydration heat cement, such as Le Teil HTS cement (CEM I 52,5 SR5 PM) from LAFARGE-HOLCIM group (used for grout and concrete). Indeed, this cement is known for its non-reactivity relating DEF.

In addition, another component in grout and concrete is silica fume that is included in formulations in proportions known to be effective in preventing reaction.

DEF laboratory carried out penalizing tests on wrapped grout samples, considering different temperature and relative humidity (RH) conditions representative of the waste package conditions found in the ICEDA facility :

- 75°C-100%RH during 4 days then storage at 50°C-80%RH during 28 days,
- 85°C-100%RH during 4 days then storage at 50°C-80%RH during 28 days,
- 75°C-100%RH during 4 days then storage at 50°C-80%RH during 28 days, then storage at 70°C-80%RH during 10 days.

Observation under a scanning electronic microscope of the wrapped specimens demonstrates the absence of any DEF index up to 85°C of heating when setting. Specifically, the average longitudinal deformation of specimens is less than 0.04% and no individual value exceeds 0.06% at the end of a 12 months period.

### Industrial penalizing input data

Even if the objective is to fill the useful volume of the basket with a large amount of radioactive waste in order to limit the number of containers in the deep geological repository, the penalizing mass chosen for the study is the industrial minimum authorized limit of 400 kg of waste per basket. Indeed, the aim is to maximize the blocking grout volume and consequently the exothermic energy due to setting. Likewise, radiological activity considered for the study is equal to 400 TBq <sup>60</sup>Co equivalent corresponding to the industrial maximum authorized activity for a  $\beta/\gamma$  emitting radionuclides group. The corresponding residual waste power is equal to 170 W.

<sup>3</sup> Laboratoire Central des Ponts et Chaussées (France)

## Experimental data

### Grout hydration heat

The hydration heat of the grout has been determined experimentally by Langavant calorimeter measurements [1]. These measurements led to define the Arrhenius law parameters [2] in order to estimate the hydration heat released by the grout during setting.

This law has been subsequently integrated into the thermal behavior model of the LL-ILW package.

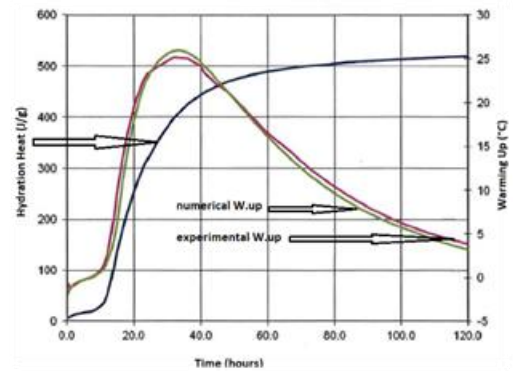


Figure 3 : Hydration heat as a function of time

### Scale one prototype experiments

To develop a numerical model of the LL-ILW package thermal behavior, several scale one prototype experiments have been carried out in an insulated room considering variable parameters:

- grout temperature when filled in the basket,
- air temperature in the room,
- amount of stainless steel waste in the basket,
- thermal power of 170 W in the waste represented by an electric heating cord.

Each prototype was equipped with thermocouples measuring the temperature at different points of the package.

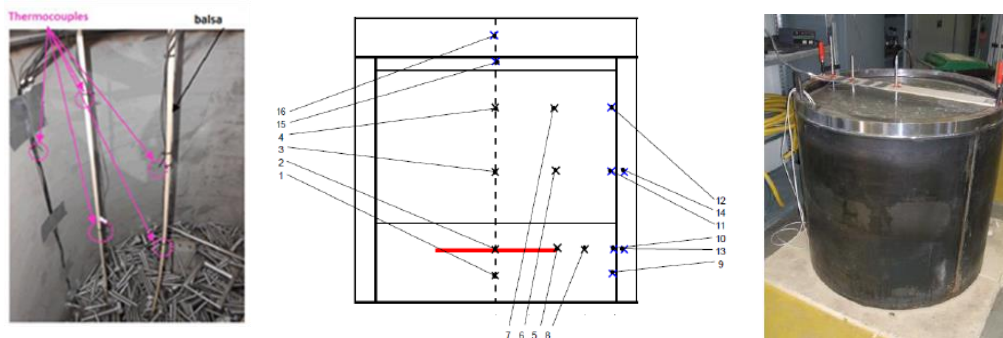


Figure 4: Metallic waste simulant - Positions of thermocouples in the package – Waste blocked in the steel basket

Temperatures registered by the thermocouples during 11 days are presented Figure 5. Conclusions of scale one prototype experiments are:

- The thermal peak is observed during the grout setting phase corresponding to the waste blocking operation in basket,
- Along the operation, energy dissipated by the grout hydration reaction is much higher than the residual heat of the waste. The increase of the inner temperature of the grout is for more than 80% due to the exothermic effect during setting grout.
- Therefore, without a large amount of waste in the basket (waste mainly located at the bottom), the maximum temperature is observed in the grout upper part area only.
- A large amount of waste means less grout and thus less exothermic effect. Furthermore, metallic waste thermal conductivity allows better heat dissipation.

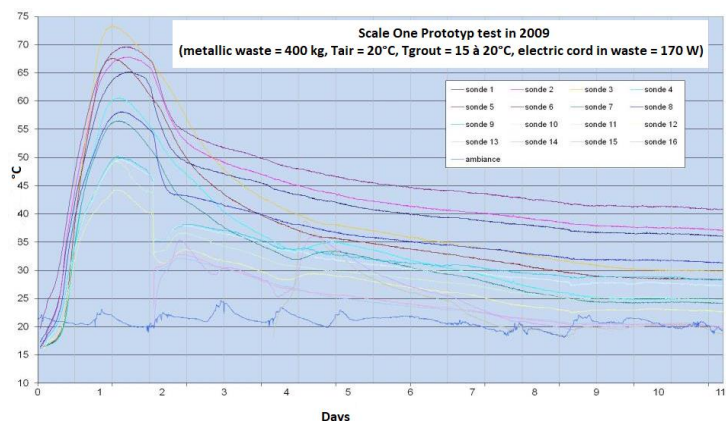


Figure 5 : Evolution of temperature measured by the thermocouples

- Initial grout temperature and room temperature significantly influence the temperature in the package.

### On-site scale one experiments

Finally, experiments were carried out in 2019 in the ICEDA blocking cell, under the operating conditions of the facility:

- Five baskets filled in one day, with stainless steel and 170 W electric cord in each basket powered 48 hours before the experiment first filling (Figure 6),
- 400 kg of stainless steel inactive waste in geometrical agreement like future radioactive waste (10 cm length and 10 mm diameter cylinder, Figure 6),
- Grout temperature under 10°C at the filling time,
- A set air temperature in the cell equal to 25°C,
- Thermocouples in and around baskets record temperatures throughout the experience (Figure 7)

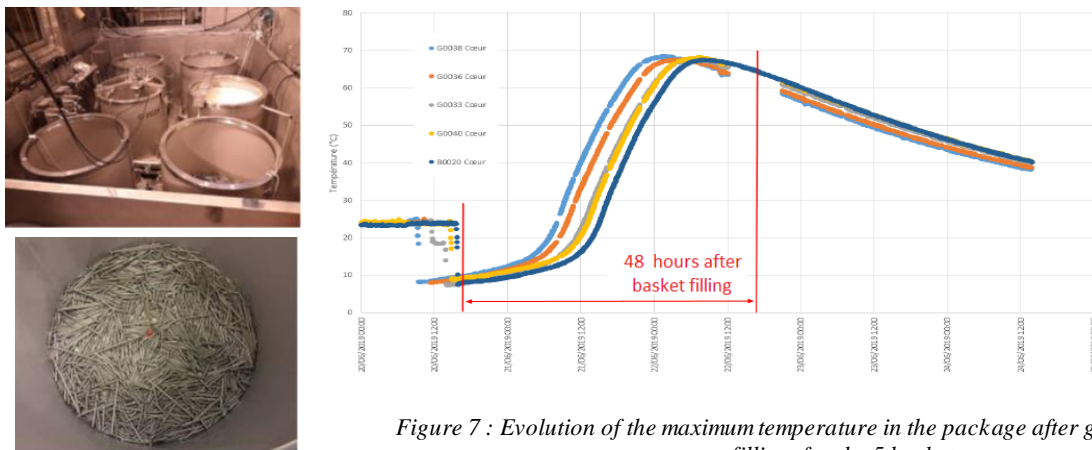


Figure 7 : Evolution of the maximum temperature in the package after grout filling, for the 5 baskets

Figure 6 : 5 side-by-side packages – Inactive waste

A first important result is the reproducibility and homogeneity of the in-box grout temperature for all five baskets.

Considering industrial and also penalizing waste conditions, another result is that grout temperature in each basket does not exceed 69°C, which is far from the 75°C DEF mitigation criteria.

It demonstrates that industrial conditions lead to a 6°C margin for core temperature peak into the grout inside the basket. This is due, firstly, to a lower grout temperature at filling (around 7 to 9°C instead of 10°C) and, secondly, to a lower air temperature at the cell outlet (around 22°C while air temperature was set to 24°C).

These results confirm the importance of operating conditions and the need to develop a numerical model representative of the thermal behavior of radioactive packages during manufacturing. This model will make it possible to define precisely the industrial operating parameters required to ensure an inner temperature below 75°C in the packages. The available parameters are: grout temperature when filling the basket, air temperature in the blocking operation cell, air temperature in the plugging operation cell, waiting time between operations.

## **Numerical thermal behavior model of LL-ILW C1PG<sup>SP</sup> package during manufacturing**

### Description

Using the EDF thermal code SYRTHES [3], three numerical models have been developed (Figure 9), one for each operation: blocking, wedging, plugging. They take account two distinct volumes in the basket: one with a mixture of grout and waste (in the lower part of the basket) and one consisting only of grout, in green on Figure 9. The ratio of the 2 parts is variable. In a preliminary study, the waste and grout mixture has been modeled in detail and equivalent physical properties have been determined (Figure 8).



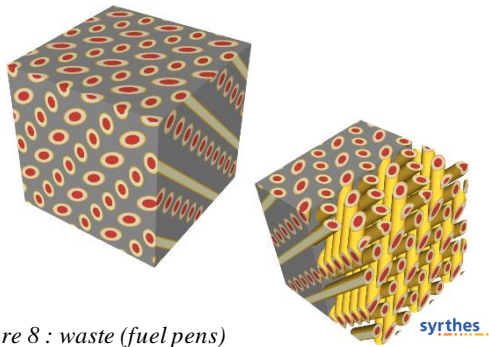


Figure 8 : waste (fuel pens) and grout (in grey) mixing sample to calculate equivalent physical properties

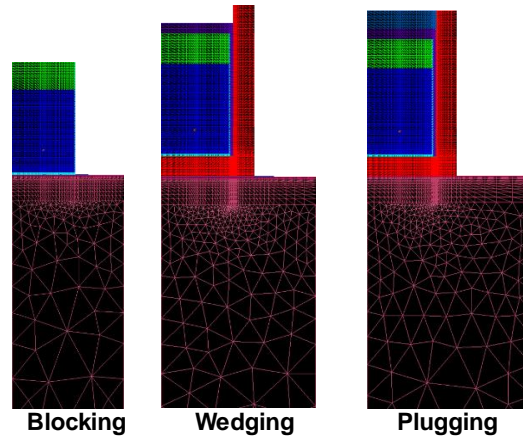


Figure 9 : Numerical models for the 3 manufacturing stages

SYNTES models conduction in waste, grout and package concrete and even in the cell ground. It takes into account convection and radiation around the package thanks to a global heat exchange coefficient and air temperature. Finally, hydration heat of cement is modeled based on adiabatic calorimeter measurements.

### Model validation

Calculation/experiment comparisons have been conducted considering two 2009 prototypes packages for which grout temperature and air temperature around each basket/package were known. In-package temperature profiles comparison between experiment and numerical calculation show good agreement (Figure 10).

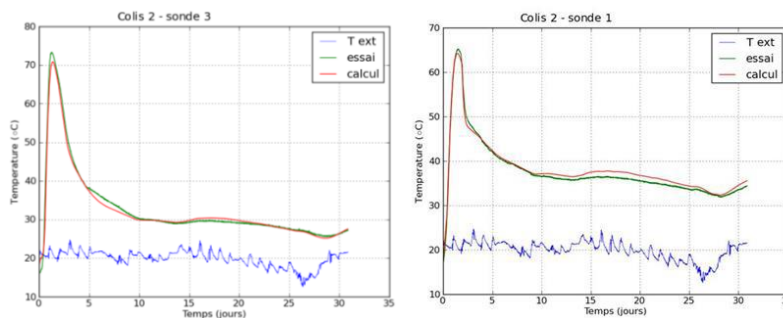


Figure 10 : Temperature evolution in the packages. Experiment in green, calculation in red, temperature in the grout only (left), temperature in the waste/grout mixing (right). In blue, the recorded external temperature.

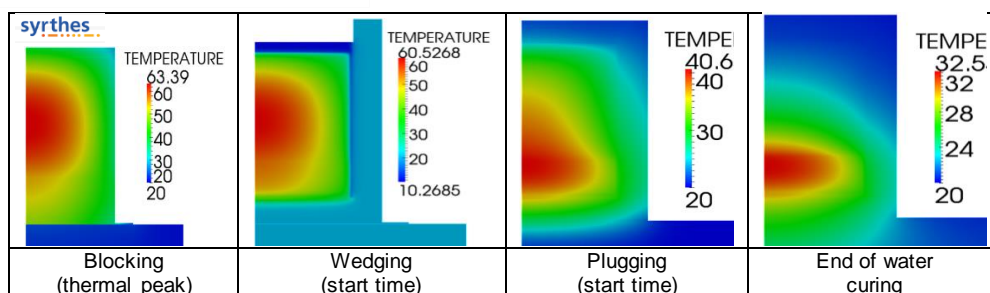


Figure 11 : Temperature fields of the package for each operating phase considering 20°C as ambient temperature in blocking, wedging and plugging cells

Measures/calculation mean deviations stay under 0,74°C while measures/calculation mean standard deviations stay under 0,8°C. The maximum is located at the thermal peak into the grout during the blocking operation : for 2009 tests, its value was 3°C. For the 2019 tests, a better knowledge of the environmental conditions of the package (industrial conditions in the ICEDA blocking cell) has given a reduction of the discrepancies to less than 0,5°C for 3 baskets and less than 1°C for the 2 others.

**In conclusion, the EDF thermal behaviour model of radioactive metallic waste packages during manufacturing operations is considered as a predictive model.**

### Sensitivity study

With this predictive model, maximum and average temperatures can be evaluated during the whole process for many parameter sets (initial grout temperature, initial waste temperature, air cells temperature, waste power, waste volume). Thus, transient temperature during the process can be compared to the 75°C criteria (minus 1°C to take into account model uncertainties), (Figure 12).

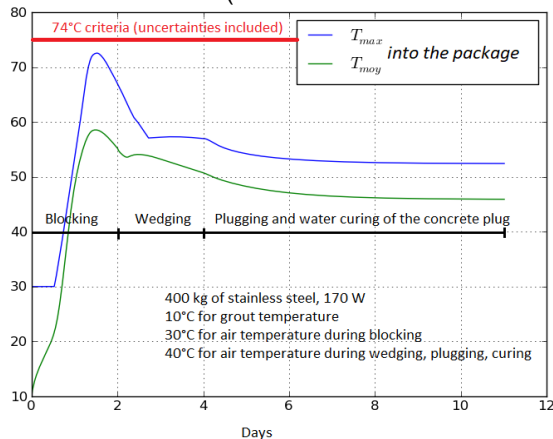


Figure 12: Maximum and average temperature

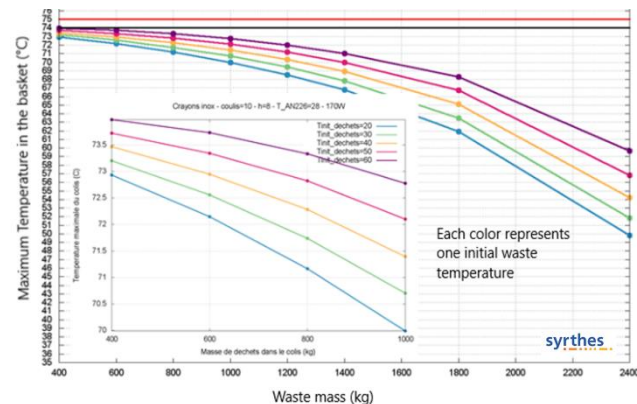


Figure 13: Maximum temperature during blocking stage, depending on waste mass in the package and initial waste temperature

As thermal peak is observed during the blocking stage, many calculations were conducted depending on different values of waste mass, initial grout temperature when filled in the basket, air temperature in the blocking operation cell and initial waste temperature. Figure 13 shows the envelope cases theoretically available in the ICEDA facility.

As a conclusion, the grout must be cooled under 10°C before being poured into the packages. Taking into account the uncertainties of the thermocouples (0,6°C), this means that grout temperature is actually between 7 and 9°C. Considering this condition, the ambient air temperature in cells near the basket must be at most at 28°C which means that temperature of air in the cell outlet has to be at most at 24°C including 1°C of industrial thermocouples uncertainties. Indeed, last tests performed in 2019 on 5 baskets, with industrial conditions in the ICEDA blocking cell, show a maximum gap of 3°C between the air temperature around the baskets and the air temperature in the cell outlet.

### Conclusions

EDF commissioned a long-lived intermediate-level metallic radioactive waste conditioning facility in 2020. The conditioning consists in blocking the waste in a cement grout inside a durable and confining concrete container. Due to its confining properties, this package can be disposed in the future french deep geological repository without any additional packaging. The entire process is carried out remotely inside hot cells due to the high radiation level of waste set up into the package.

Industrial operating conditions have been defined in order to mitigate the risk of Delayed Ettringite Formation (DEF) in the packages by limiting the temperature rise due to the thermal residual power of the metallic waste inside and the exothermic reaction taking place during hydration phase of the blocking grout. Experiments have been carried out at full scale on package prototypes instrumented with thermocouples to verify that the inner temperature stays below the 75°C threshold during the manufacturing process. At last, an experimental campaign, including 5 instrumented packages with inactive waste, has been carried out in the industrial facility.

A numerical model has been developed and validated by measurements. The numerical model is predictive and ultimately makes it possible to perform a sensitivity study. It leads to identify manufacturing parameters required to ensure that inner package temperature stays under 75°C. Hence, admissible combinations of initial grout temperature, mass of waste, air cell temperature have been calculated.

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