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Abstract

Mortars based on geopolymers have been proposed for the conditioning of magnesium-alloy scraps. The qualification of the immobilization process requires the confirmation that, during the setting of the geopolymer matrix, the temperature in the waste container would not exceed a threshold where adversarial consequences could be observed, such as increased scrap corrosion (accompanied with hydrogen production) or structural matrix disorders.

An experimental campaign has culminated in 2020 with the pouring of a large geopolymer mortar quantity (2.7 m^3) in an industrial-size cubic container, and the monitoring of the ensuing temperature transient inside the mortar and on the package walls. We present a numerical thermal model based on finite elements, we justify the hypothesis and adopted material parameters, and we compare the obtained numerical simulation with the experimental result.

The comparison between the measured temperatures and the calculated ones is rather acceptable. The agreement regarding the maximum temperature inside the mortar is especially satisfactory. Sensibility analyses have shown that the temperature peak is not dependent on the external cooling fluxes (irradiance and atmospheric convection), but only on the mortar thermal properties.

Introduction

Mortars based on geopolymers are considered for the conditioning of several nuclear waste kinds, including magnesium-alloy scraps that are presently stored in legacy nuclear facilities (in France, Marcoule and La Hague). The qualification of the embedding process requires the validation that, during the setting of the geopolymer matrix, the peak temperature does not exceed a threshold where adversarial consequences could occur. The two main issues associated with the temperature rise are the hydrogen generation caused by the increased scrap corrosion, and the loss of mechanical properties due to amplified structural disorders.

This internal temperature rise depends on a variety of contingencies and parameters, including the heat generation capacity of the geopolymer mixture, the package geometry, and the thermal characteristics of the package constituents (the mortar and the embedded metallic waste).

The metallic scraps to be conditioned come from the reprocessing of irradiated Natural Uranium Graphite Gas (UNGG) fuel, originating from nine French and one Spanish reactors. UNGC uranium fuel used to be fit inside a magnesium-based alloy cladding, either <0.6% Mg-Zr> alloy or <1.2% Mg-Mn> alloy. At Marcoule (France, Gard), more than 1600 tons of metal scraps are currently stored in interim repositories, and waiting for a definitive conditioning and disposal.

For this solid and definitive conditioning, a geopolymer mortar is an envisaged embedding matrix. Geopolymers are aluminosilicate materials with an amorphous structure, which are synthesized by alkaline activation of silicate materials. They are composed of cross-linked chains mainly consisting of silicon and aluminum tetrahedrons sharing one atom of oxygen between them, with the presence of balancing alkaline cations. The setting generates heat, with adversarial consequences as increased scrap corrosion (which leads to hydrogen generation) and structural matrix disorders (cracking and fracturing of the

material, leading to increased permeability and decreased mechanical strength). An empirical (and somewhat informal) temperature threshold has been estimated from small-scale setting experiments: large-scale trials and numerical simulations must demonstrate that during industrial operations the temperature inside the proposed package will not exceed this value.

Several experimental campaigns have culminated in 2020 with the pouring of a large geopolymer mortar quantity (2.7 m^3) in an industrial-size cubic container, and the monitoring of the ensuing temperature transients inside the paste and on the package walls. In this paper, we present a numerical thermal model based on finite elements, we justify the adopted material parameters and we compare the obtained simulation with the experimental result.

Basics of geopolymer thermo-chemistry

The geopolymer mortar is made up of sand (45 % mass ratio) mixed with a geopolymer binder, prepared by the activation of metakaolin with a polysilicate solution ($Na_2O.nSiO_2$ with small additions of soda and water). The reaction begins with a dissolution of the solid alumino-silicate (the metakaolin); the oversaturation of oligomers in the solution leads to their condensation, and the creation of a solid and porous monolith.
The whole dissolution-polymerisation process generates a significant amount of heat; the setting temperature peak can have adversarial consequences, notably increased waste scrap corrosion (accompanied with hydrogen production) and structural matrix disorders (due to the differential dilatation between the gaseous, liquid and solid parts in the material). Sand addition leads (among other consequences, especially cost reduction) to setting heat-up decrease; previous formulation endeavours at the laboratory scale have established an optimal sand ratio and an approximate temperature threshold.
We have to insure that this temperature threshold will not be exceeded during future industrial operations, inside the planned 2.7 m^3 container, under any circumstances. The numerical model has been build to complement and analyse the results of a nominal-size trial.

Justification of the thermal model and of the parameter values

We represent the setting kinetic of the geopolymer mortar with the equation:

$$\dot{\xi} = \tilde{A}(\xi).e^{\left(-Ea(\xi,T)/RT\right)}$$

where

- ξ is the reaction advancement, deduced from the cumulated heat by $\xi(t) = q(t)/q(\infty)$.
- $\tilde{A}(\xi)$ is the normalized affinity, and is deduced from a semi-adiabatic Langavant measurement.
- $Ea(\xi,T)$ is the apparent activation energy of the setting. We have verified that a fixed value (not depending on reaction advancement and temperature) was an acceptable proposition, so further it is noted Ea.

The activation energy Ea has been inferred from the observation of the elastic modulus G' and viscous modulus G'' during the setting of a geopolymer paste (without sand), using dynamic rheology at different temperatures. In the frame of a general study <1> on the viscoelastic properties of different types of geopolymers, the temperature dependence of the geopolymerization reaction (for our geopolymer kind) has been estimated ($Ea \sim 74.5 kj/mol$) by plotting the time necessary to reach the maximum of the loss function $tan(\delta) = G''/G'$.

This Ea value has been consolidated with the results of semi-adiabatic Langavant tests, where the input materials were conditioned at various temperature levels. The input materials of the geopolymer mortar (metakaolin, silicate, sand) were put into an environmental chamber, then mixed and brought into the Langavant box. We calculate the affinity function $\tilde{A}(\xi)$ for all these different thermal transients; the fact that the evaluated $\tilde{A}_i(\xi)$ are rather close to each other confirms our proposal regarding temperature non-dependence.

We studied different thermal transients with the help of the equation $Ea(\xi) = \frac{-R}{\left({}^{1}/_{T_2(\xi)} - {}^{1}/_{T_1(\xi)}\right)} Ln[\dot{q}_2(\xi)/\dot{q}_1(\xi)]$ deriving from the thermo-kinetic hypothesis (<2>).

It seems that the apparent activation energy tends to decrease with the on-going reaction; but the experiental values at near-completion ($\xi > 0.8$) are not relevant as the reaction is hampered by the mortar heterogeneity.

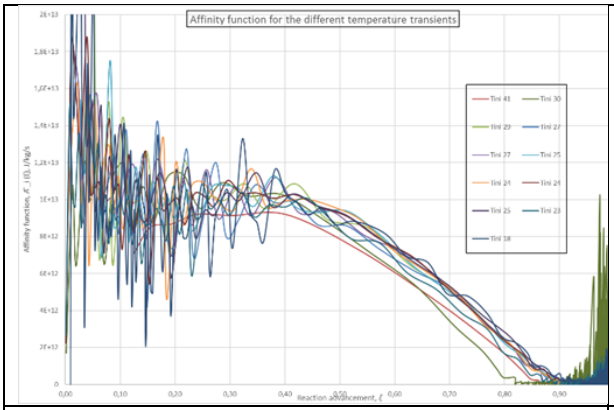

Figure 1 : Affinity function deduced from several tests

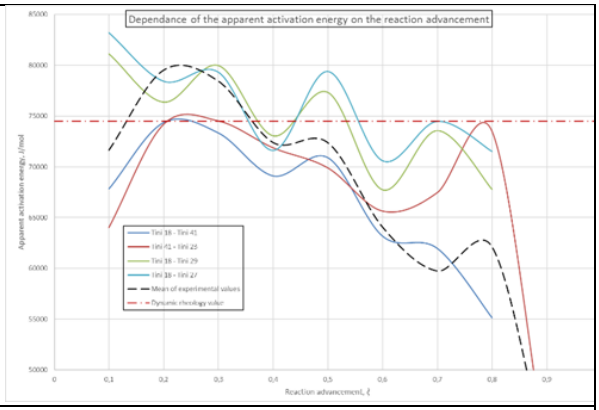

Figure 2 : Activation energy during setting

We have investigated the influence of Ea on the simulation results, by considering three different values {upper value 84 kJ/mol; nominal value 74.5 kJ/mol, lower value 65 kJ/mol}, the affinity $\tilde{A}(\xi)$ being accordingly corrected. In both extremal cases, deviation of the maximal temperature (inside a virtual industrial container) stays under 0.2 °C. We conclude that a constant value $(Ea{\sim}74.5kj/mol)$ is acceptable.

The setting heat generates a transient temperature field via conduction in the mortar monolith; external fluxes (irradiance and atmospheric convection) and internal fluxes (through a PTFE internal basket) are considered and modelled. The specific heat capacity of the mortar has been measured in the LCBC laboratory with a micro-calorimeter. For the heat conductivity we consider a value proposed by a research team of INSA-Rennes led by Aveline Darquennes (in the frame of the associated R&D project 'DECIMAL'), who has used a 'Hot disk' device.

Experimental campaign with a 2.7 m^3 package, and comparison with numerical simulation

In September 2020, a real-size pouring trial has been performed. In an industrial concrete facility (company 'Charpentier' at Pont-Saint-Esprit, France) the R&D and project CEA teams have tested the manufacturing sequence leading to the solidification of an industrial-sized mortar package. A vast set of technological and operating features have been tested; to record the thermal transients the metallic 2.7 m^3 cubic box (with an internal PTFE basket, and closed with a lid) was equipped with 37 internal and external thermal sensors.

Figure 3 : Container (red) with the mortar injection apparatus

Figure 4 : Container with the external thermal sensors

The box (with its lid), its mortar content and the small air gap at the apex are geometrically modeled (symmetry conditions being exploited) with a 10125-node mesh. The PTFE basket is modeled with a thermal resistor.

We calculate the thermal transient by considering the heat generation, the conduction inside the box and the external fluxes to the environment. The comparison between the measured temperatures and the calculated ones is rather acceptable; the differential remains (except on eight sensors) smaller than 5°C.
The agreement regarding the maximum temperature inside the mortar is especially satisfactory.

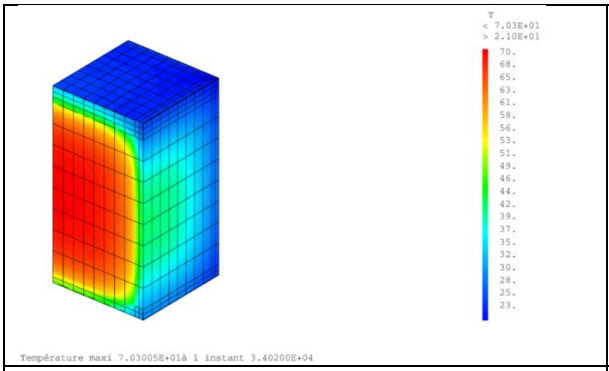

Figure 5 : Temperature map at the peak time (after 9 hours 30 minutes)

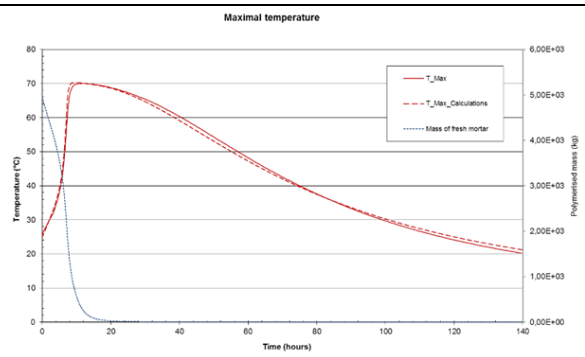

Figure 6 : Maximal temperature in the mortar, measured and simulated, during the first 140 hours

We have completed this simulation with a sensibility analysis, which shows that the most influential parameter is by far the specific setting enthalpy. All the thermal parameters that are related to the external fluxes (irradiance and atmospheric convection) or internal fluxes (through the PTFE internal basket) are non-influential. Thus, our numerical model with its parameters is validated.

In fact, the temperature peak is not influenced at all by the environmental conditions. Due to the quick heat generation, the maximal temperature is only governed by the thermal mortar properties (specific enthalpy, specific heat capacity, thermal conductivity).

Conclusions

The definitive qualification of the geopolymer immobilization process requires a performance check on a wide span of technical topics, considering different operational circumstances. Using the results of a large solidification trial, we have developed and validated a numerical model. Our thermal analysis shows that our set of hypothesis (heat generation model, thermo-kinetics parameters of the setting reaction, thermal properties, ..) is rather adequate for simulating the real transients that are experienced in geopolymer mortar packages.
The 2020 experiment has been performed only with geopolymer mortar, without any metallic waste or surrogate. Therefore, this experience maximizes the temperature peak that could occur during the future industrial operations. Our numerical model will be used to extrapolate the available data to regular operation when metal scraps are conditioned inside the container.
This model can also be used to evaluate the thermal transient for any irregular situation (deviation of the sand ratio, of the waste ratio …), as during the future industrial operations, there will be inevitably some fluctuations on the operational parameters.

References

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