Transactions, SMiRT-26
Berlin/Potsdam, Germany, July 10-15, 2022
Division VIII

AGEING OF INTUMESCENT FIRESTOP SYSTEMS

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INTRODUCTION

Firestop systems (intumescent-based materials) in nuclear power plant are essential to prevent fire spreading. They must be utilized in numerous situations to comply with the "nuclear safety first" principle especially since fire is considered as a major nuclear threat.

Intumescent materials are a class of firestop products that are employed to protect equipment or sectors against the spread of fire. They are used as reactive caulking items (opened in normal situation, closed in fire) and protect equipment that shall not fully be insulated due to overheating risks (i.e. insulation housing or cable trays wrapping). They are also frequently used as gasket in smoke damper or as removable piece intended to close cable entries through walls.

While highly efficient and versatile, intumescent products are still organic materials (or at least hybrid) and therefore are subjected to ageing. Ageing is a normal process occurring in materials while exposed to ambient heat and humidity. To some extent, the material's chemical and physical may be affected over time which may ultimately lead to a loss of functional properties (i.e. intumescence).

In the context of the upcoming life extension for various power plants, it becomes crucial to figure out whether intumescent products under scope, after several decades of operating, are still capable of meeting fire resistance requirements.

An intumescent material as part of a nuclear power plant assembly system is here examined. The material endured various artificial ageing. Spectroscopic, thermal as well as rheological analyses have been performed afterward to highlight physico-chemical modifications taking place inside the material. An attempt was made to relate these internal modifications to an eventual modification of the expansion factor - considered as an end-life criterion that would reasonably explicate a loss in insulating capabilities. Yet, testing the intumescent material according to some regulatory test standards surprisingly showed that the expansion factor – especially in the present case – could not necessarily be a relevant end-life criterion for characterizing durability.

EXPERIMENTAL SECTION

The material tested, a RTV-2 silicone, was provided by Nuvia Protection. Specimens were prepared by injection-molding and the material allowed to dry under ambient atmospheric conditions for at least 3 days.

An advanced rheometric expansion system (ARES 20A, Rheometric Scientific, TA Instruments, New Castle, DE, USA) with a concentric cylinder sample holder was used to evaluate the char expansion of the intumescent material as a function of temperature. The samples of circular shape with 25 mm diameter and of 1 mm thickness were used. All tests were performed under dynamic temperature ramp from 25 to 500 °C in strain-controlled mode over 1.5–3.0 gram-force range with 5 and 10 °C/min heating rates,

1.0 rad/sec frequency range and 1% strain limits. Three replicate specimens of the material were tested and the results were averaged.

A bench scale furnace was previously developed in our laboratory to evaluate the fire performance of intumescent coatings (Figure 6). This test is designed to mimic the UL1709, ISO and others normalized temperature-time curves related to a given fire. Refractory fibers stable up to 1300°C covers the insides of the furnace (1). Two burners (2) fed by propane have a capacity of 20kW each and the flow is regulated (3) to mimic UL1709 curve. IR pyrometer (4) is used to record the temperature at the backside of the coated steel plate (10cm x 10cm x 3mm). Burner control and pyrometer readings are controlled by the attached computer (5). Coated plates (6) are sprayed with black paints of known and constant emissivity on the uncoated side and the plate is fixed in the window and sealed the sides with glass-fiber wool. Through a quartz window (7), the intumescent behavior of the char can be viewed inside the furnace during the fire test and movies can be recorded.

^{29}Si solid state nuclear magnetic resonance (NMR) was used to determine the changes of the chemical composition and of the structure of the material. These techniques can distinguish several kinds of structures including D, T and Q structures which characterize silicone network. ^{29}Si NMR spectra were recorded on a Bruker Advance II 400 operating at 9.4T and using a 7 mm probe. Zirconia rotor and caps were used. NMR spectra were acquired with MAS (magic angle spinning) of 5 kHz. The reference used for ^{29}Si NMR was tetramethylsilane (TMS). A delay of 180s between the $\pi/2$ pulses (pulse of 180s) were used and 128 scans were accumulated to get an acceptable signal to noise ratio.

Thermogravimetric analysis (TGA) was performed on a TA Instrument TGA Q50 0 0IR with alumina crucibles under nitrogen atmosphere. 5 mg sample underwent an isotherm at 40 °C for one hour under nitrogen atmosphere (purge flow of 50 mL/min), then was heated from 40 to 800 °C with a constant heating rate of 10 °C/min under nitrogen atmosphere.

RESULTS

Intumescent materials, as they belong to the class of reactive products, are particularly known to be sensitive to ageing [1],[2]. Hence, their fire resistance properties would need to be scrutinized after a long period of time so as to ensure they can still perform their insulating function under fire after a specified time.

Accelerated ageing is a way of evaluating the durability of materials through shorter period of time. Artificial exposures can accordingly be applied to intumescent products, nevertheless, these materials exhibit proper onset of expansion temperature (depending on the nature of the intumescent technology) that should not be overtaken. For this reason, any ageing program implemented shall be appropriately adapted to the type of investigated system.

In this study, the ageing of an intumescent raw material to be used in nuclear power plant assembly system was assessed. The material is composed of a silicone based elastomeric binder and contains near 50 wt% of an amorphous hydrous sodium silicate filler as intumescent agent.

Figure 1 shows a superimposition of the mass loss (TGA) and the expansion curve (rheometer) of the material as a function of temperature. The latter starts releasing water (due to silicate decomposition as well as native water) around 120-130°C which causes it to expand up to 4 time from its starting thickness (expansion factor) until 200°C.

The expansion proceeds then gradually from 200°C to 350°C and the material finally deflates to lower expansion rate due to decomposition of the silicone matrix. A crusty silicate residue is observed at 800°C.

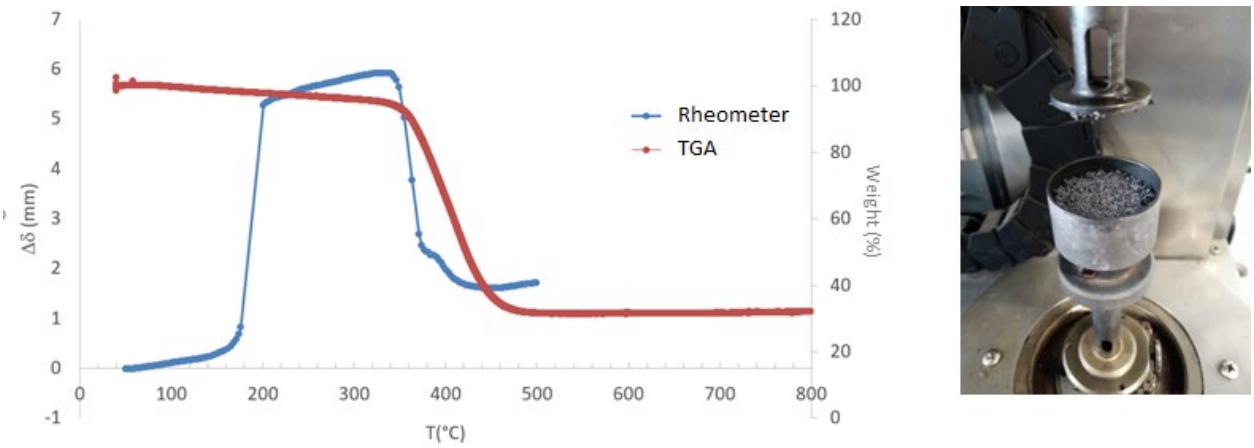

Figure 1: superimposition of the TGA curve and the expansion curve of the material. The expansion curve was obtained using rotary rheometer. The photograph shows the assembly sample basket / measurement plate of the rheometer

A first insight on the ageing resistance of this material was evaluated through the fire test standard UL1479[3]. In Accordance to the standard, the material underwent ageing at elevated temperature (70°C, 270 days) as well as under damp conditions (97-100 % RH (relative humidity), 35°C, 180 days). One of the main criteria to succeed the test is that the aged material – while heated 30 min in an oven at 300°C - shall exhibit an expansion factor within 3 standard deviations of the mean of the maximum expansion factor of the "as received sample".

The material finally failed to achieve the ageing requirement especially since the pass criteria under high humidity environmental exposure was not reached (Figure 2). UL1479 ultimately intends to be applied to assess the fire performances of the material through a ISO 834 fire test scenario (cellulosic fire). In this case, the tested specimen is subjected to a fire up to 1100°C. One major drawback of the UL1479 ageing pass/fail criteria (through measurement of the expansion factor) is that it relies on a reactive expansion occurring at only 300°C which is far below the end range temperature to which is subjected the material during the final standard fire test ISO 834. This means that the conditions to which the expansion factor is measured are not quite representative to ISO 834 fire test conditions.

Further analyses are therefore needed to ensure that this failure obtained to the standard test - failure viewed as a potential end-life criterion to establish an ageing model - reflects a loss of firestop performances.

Figure 2 : intumescent material tested according to the UL1459 standard. The "as received" and aged specimens were expanded in an oven at 300°C for 30 min

As UL1479 testing program implies too long environmental exposures which is not appropriated for a quick evaluation of the material, other standards or specifications providing artificial ageing condition guidelines of shorter terms were followed (Table 1).

The programs implemented covered various ageing situations going from high hydric or thermal stresses to moderated ageing conditions: accelerated ageing at 120°C for 55 days (V1) as well as ageing at 95% relative humidity for 48h (V2) were drawn from an internal technical specification [4] providing guidelines to evaluate ageing of intumescent gaskets for smoke dampers. V3 exposures was drawn from a European report[5] that provides methods to assess reactive products and V4 ageing - corresponding to moderate ageing conditions - was arbitrary define (inspired from the EOTA report though) for comparison. The mass gain / loss of specimens as well as their aspect after ageing are given in table 1.

Table 1 : ageing programs underwent by the intumescent material

	Reference	Ageing program	Aspect of specimen	Mass variation
V1	UK-DITSCV-EN-0177[4]	55 days, 120°C	Unchanged	-2,5% to 3%
V2	UK-DITSCV-EN-0177	**2 cycles of 24h :** - 80-95 %RH - 25 to 40 or 55°C	White spots on the surface	+ 7,1% (1,5 mm) + 4,5% (3 mm)
V3	EOTA TR 024 (2019)[5]	**21 cycles of :** - 4h at 10°C, 50%RH - 4h at 23°C, 80%RH - 16h at 40°C, 50%RH	Unchanged	+ 2,5%
V4	Insp. EOTA TR 024 (2019)	21 days, 40°C, 35%RH	Unchanged	+1 to 2%

After ageing, the mass of the sample changed depending on the type of conditioning. After the high temperature exposure (V1), a mass loss of about 2.5-3 %, corresponding to water release was observed and confirmed by DSC and pyrolyser GC-MS. On the contrary, mass gain due to water uptake was obtained after damp conditions (V2, V3, V4), especially after V2 (high humidity exposure) for which a water uptake of more than 4.5% was measured. Samples recovered from this last conditioning exhibited surface mottled with white spots which were attributed to silicate exudation (Figure 3).

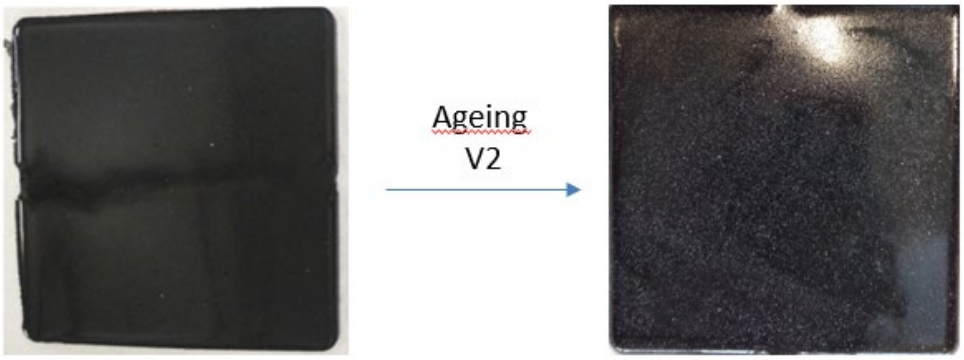

Figure 3 : photograph of the samples before and after V2 ageing

The aged materials were analyzed through ^{29}Si solid state NMR[6] (Figure 4). The results showed that the silicate filler underwent structural modifications while the silicone binder remained unchanged.

With high temperature ageing (V1), structural profile of the silicate went from a majority of Q^3 units to a mix of Q^3 and Q^4 units meaning that the dehydration noticed was indeed resulting from the condensation of silanol units (≡Si-OH or ≡Si-ONa) into siloxane groups. Structural rearrangement of the silicate was also observed through damp conditions and was particularly pronounced under high humidity (V2). In this case, structures changed from a majority of Q^3 units to a mix of Q^1 (small amount), Q^2, Q^3 and Q^4 proving both rehydration and dehydration (through condensation) of the silicate. NMR signals of the Si units also appeared thinner which indicates an increase of order in the structural arrangement of silicate molecules.

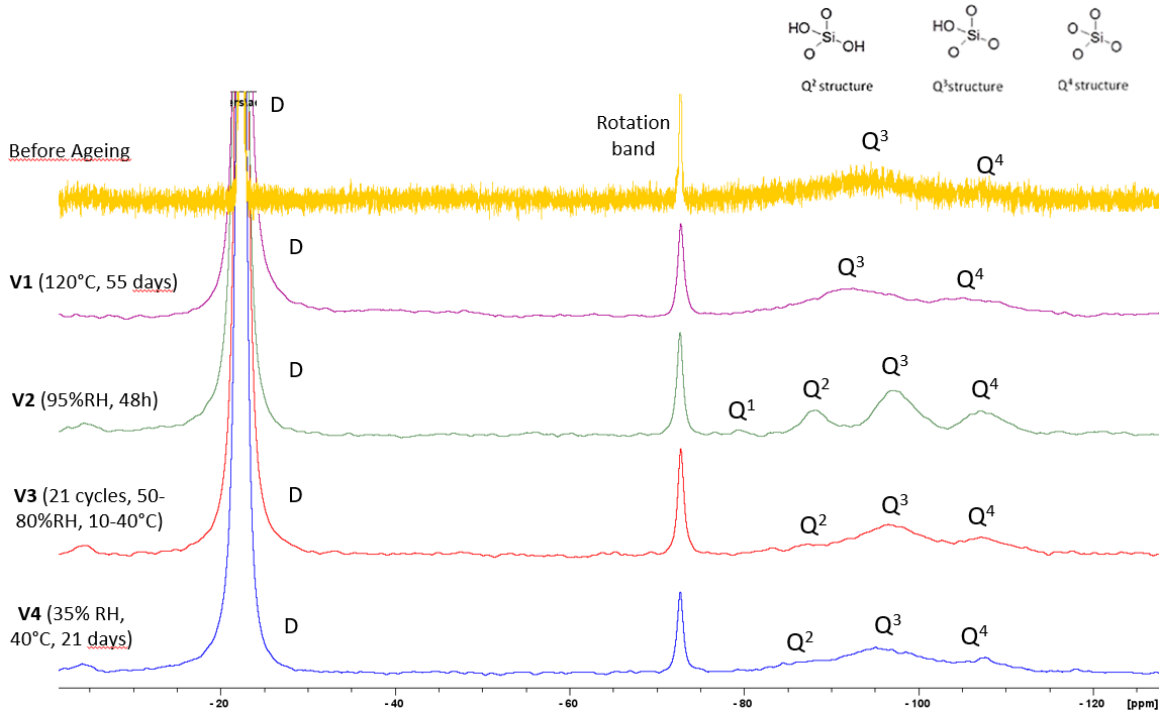

Figure 4 : 29Si solid state NMR spectra of the intumescent material before and after ageing. The signal at -23 ppm is attributed to D units (-SiO(CH_3)$_2$) from the silicone binder. Q units belongs to the silicate filler. A description of the various Q forms is given at the top right of the figure.

Chemical and structural changes of the intumescent silicate fillers as well as some extent of blooming (at high humidity) have been clearly evidenced after ageing.

The expansion factor of aged materials - that was so probed and used as one of the pass/fail criteria through the UL1479 standard (Figure 1) - was yet investigated by rheological analyses (Figure 5). These have revealed that the materials had partly (for the less severe conditioning V4) or drastically lost their expansion ability between 200°C and 350°C. Besides, two distinct phenomena could be observed throughout the measurements: a short inflating effect attributed to the release of water from 130°C to 200°C (not for the sample exposed to high temperature conditioning since water was already removed from the material) and a transitional expansion phenomenon between 350°C and 450°C (only for samples that did not inflate between 200°C and 350°C) attributed to the release of gases from the decomposing silicone.

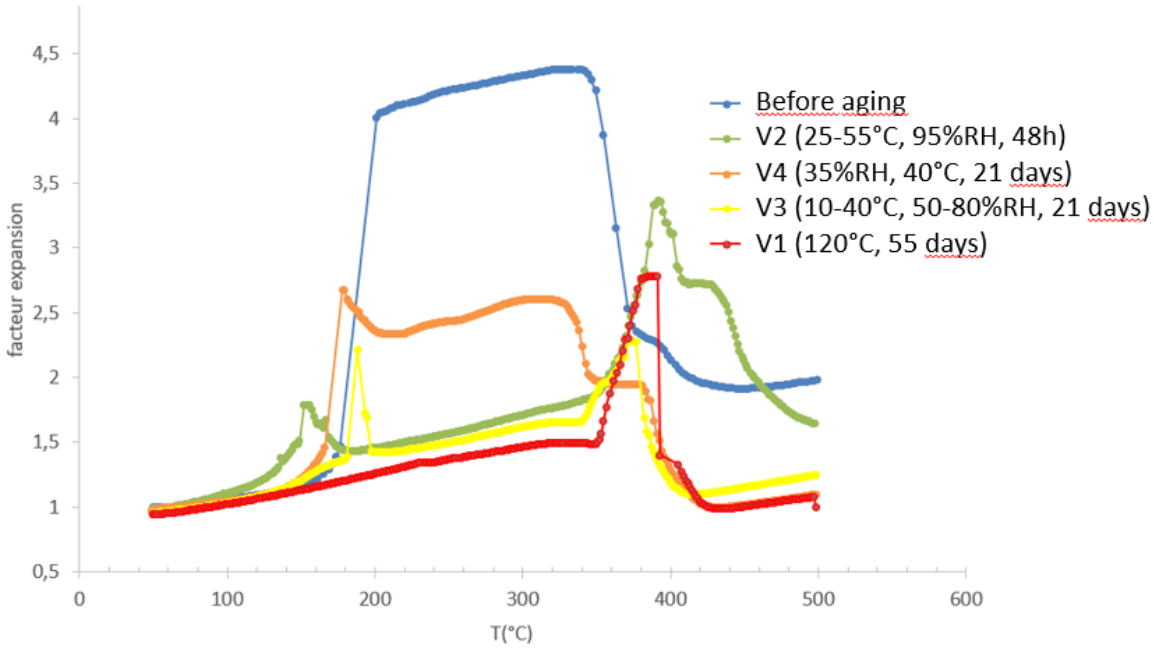

Figure 5 : Expansion curve (expansion rate) measured by rotary rheometer

It makes thus no doubt that high temperature and damp ageing of the intumescent material lead to a significant change in its expansive behavior (at least in the temperature range investigated), and that this modification is related to the modifications undergone by the silicates fire resistant filler.

One of the primary purposes of this work is to find a correlation between the material transformation after ageing and subsequent decrease of its fire resistance properties. In this respect, ISO 834 fire resistance tests were performed on a bench-scale oven (Figure 6). As observed on Figure 6, the “as received” intumescent material provided efficient insulation allowing a strong reduction of the temperature to about 275°C at the back of the specimen holder (compared to the blank). 440°C were reached after 75 min of testing. Temperature curves of the same material after ageing exhibited the same profile meaning that various exposures had no significant impact on the thermal insulation properties of the material.

Only a small alteration was observed for the high temperature aged sample (V1) for its curve exhibited no inflection (from endothermal release of water) at 4 min contrary to that of other samples but this did not influence the heating profile afterward.

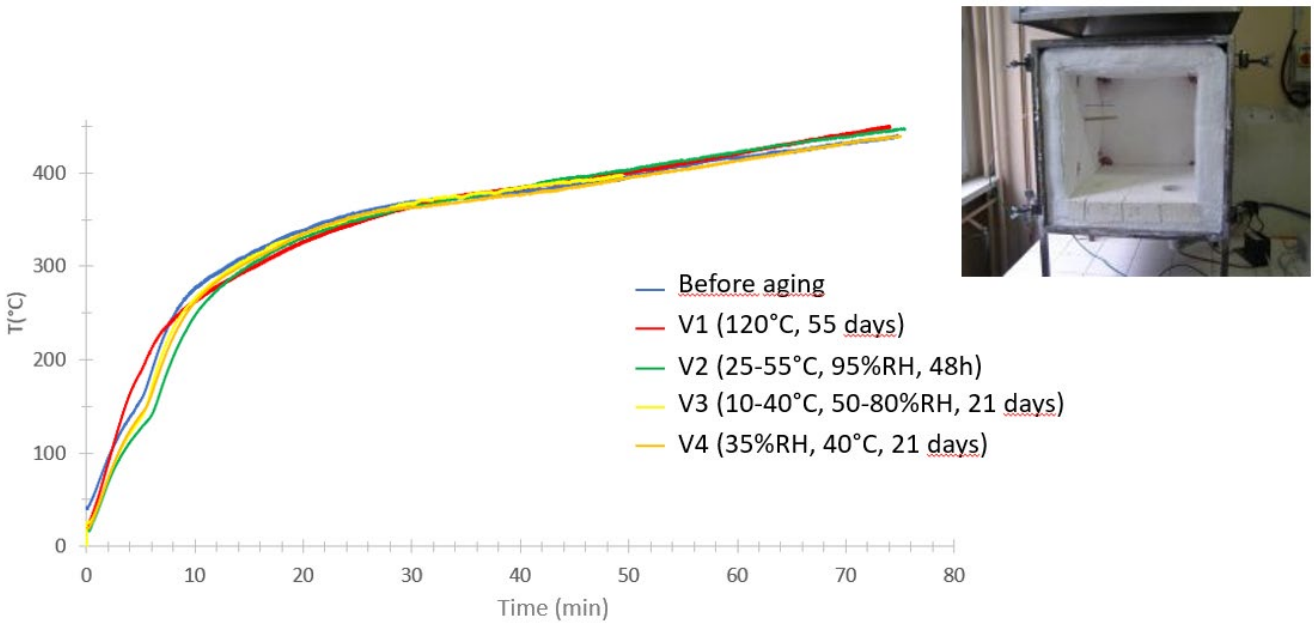

Figure 6: Temperature curves from ISO814 fire tests. The photograph shows the bench-scale test where the fire tests have been performed

The crusty residue obtained after the test (Figure 7), whatever the material was aged or not, exhibited the same aspect and an expansion factor of about 3 or nearby was found for all samples.

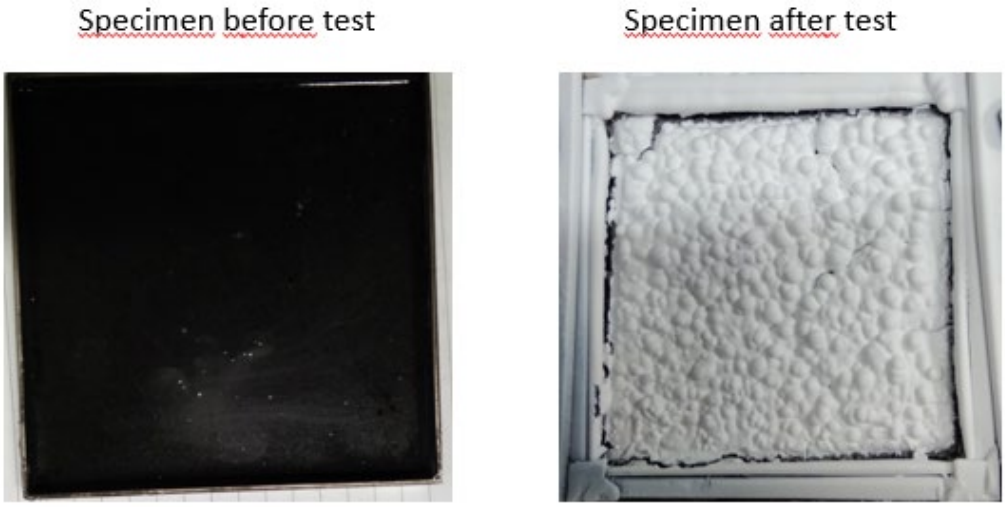

Figure 7: photograph of a sample before and after the fire test ISO834

While thermal and damp exposures brought about notable structural and rheological (especially expansion rate) changes in the intumescent material, the latter could still provide insultation to the substrate through ISO 834 fire scenario without its efficiency being affected.

These results bring to the fore that standard guidelines such as UL1479 should be regarded with caution when it comes to evaluate durability of intumescent materials. Since measurement of the expansion factor at 300°C appears to be irrelevant to depict a loss in the firestop properties of the material under investigation further research need to be done to identify the effective end-life criteria that will allow establishing a practical model to determine durability.

CONCLUSION

In this study, ageing of an intumescent product filled with a silicate based expansive agent was assessed. The product underwent several accelerated ageing and analyses were performed to identify mechanisms possibly responsible for a loss in firestop performances. It was showed that even though physical and chemical modifications occurred in the material and led to a loss of expansion ability at moderate temperature heating (300°C), the insulating properties of the material to higher temperature were still maintained.

A few more features, such as impact of the specimen size (especially thickness), the heating rate, the material conductivity profile, the expansion development at high temperature and longer-term ageing have still to be investigated so as to fully understand the mechanisms involved in the material insulating performances and how these performances may be affected by the material structural modification. Such an understanding will be the key to determine the durability of the material.

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