ROBATEL is a major actor in the French Nuclear Industry since the 1950s, with a clear focus on international development as a driver of new growth for the group. It is present in France with four ROBATEL Industries sites (Genas, La Hague, Cadarache, Marcoule) and in the USA with Robatel Technologies (Roanoke, VA). ROBATEL develops, licenses, manufactures and maintains transportation and storage casks for radioactive wastes/sources, spent fuels; LLW, ILW and HLW. We also provide custom design and fabrication of equipped Glove Boxes, Hot Cells, Shield Doors and Hatches for the nuclear industry and nuclear medicine. To provide the most reliable products, ROBATEL develop specific materials to ensure nuclear safety. Neutron shielding materials have been a long tradition at ROBATEL with trademark like PNT7™ for neutron shielding concrete or Compound 22™ for polymer based shielding. Thanks to its internal R&D program and collaboration with the European Center for Ceramic, new generation shielding materials are being developed with improved neutron shielding and temperature range of use. ROBATEL Industries R&D program is also active in the mechanical and fire protection, with the FENOSOL foam, a fire-proof, shock-absorbing foam for nuclear applications. The following article will present the R&D program currently held at ROBATEL Industry, with a focus on the safety materials.

1. Introduction

Heat, fire, fast neutron flux, thermal neutron flux, gamma flux, shock: many are the parameters to be considered for the safety of a nuclear installation. Nowadays, each of them can easily be handled through a specific solution and material. However, adding a new material to a design is always a source of complexity. Beyond the design aspect of additional weight and volume it requires, adding a new material involves additional work to design interfaces, ensure chemical, thermal, mechanical compatibility of the materials, many technical questions that induces additional safety demonstration. As a consequence, it translates in non-negligible additional costs. Thus today, the best material for a given application is not so much the best materials with respect to a given criteria, but the best tradeoff.

For example, a shock absorbing material has to have good mechanical properties at a reasonable price, but also good chemical properties during its whole service life. But if you need to protect a given equipment against both mechanical damage, heat and fire, having a same material able to fulfill reasonably these objective is much preferable than to have to append three different materials. Hence for the perfect shock absorbing material, mechanical performance is only one among many of its features (cf. Fig. 1).
As a consequence, ROBATEL Industries has focused its research program on the development of new multi-purpose safety materials. We quickly describe here the FENOSOL™ program, about a fire-proof shock absorbing foam, and the neutron protection program.

2. Neutron and Thermal Protection

The aim of a neutron protection material is to reduce the energy of a neutron flux. As the absorption cross section of most neutron poisons is high in the thermal part of the energy spectrum, the material only needs to be filled with such a poison to stop thermal neutrons, typically B, Cd or Gd.

However, in most cases the neutron flux will also include fast and epithermal neutrons. Reducing the energy of a fast neutron is simple in principle: you just need to collide it with light atoms to decrease its energy down to the thermal level. However, as many collisions are needed to substantially decrease this energy, high thicknesses of a light atom filled materials are necessary. From that point of view, the best candidates are water and High-density polyethylene (HDPE).

The hardships start to rise when these materials are put in real conditions. The service conditions are stringent: high service temperature, up to 160°C, γ-irradiation. The protection must be able to sustain this harsh environment during the decades of its service life. To these normal conditions are added extra requirements in accidental conditions with for several hours increases of pressure, and temperature beyond 200°C, the possibility of fire. Even in this degraded situation must the neutron protection be able to protect the sensitive equipment and lives on the other side from the neutron source.

Of course, HDPE cannot sustain such temperatures and requirements.

Thermal switch

As in normal operation thermal power needs to be extracted, the neutron wall cannot be a thermal insulator in normal conditions. But in accidental conditions, a neutron wall able to sustain high temperature and fire is required, and the equipment can be though to also provide a thermal protection in this specific situation. A material playing both the role of a neutron absorber and a thermal switch in then required.
The PNT7™ neutron and thermal protection has been developed for that purpose: As a boron-rich, highly hydrogenated concrete, it provides excellent neutron protection from both thermal and fast neutrons. However, its formulation also allows it to play a good role as a double thermal switch by releasing structural water at 120°C, and later at 280°C (cf. Fig: 2). At each of those temperatures, it dissipates heat and reduces its thermal conductivity. It thus also acts as an efficient fire retardant.

**Developments**

PNT7™ is a proven material that has been used in many applications. A current program is ongoing to develop a new generation of thermal switch materials based on a new generation of matrix materials.

3. **A fire retardant shock absorbing material**

Shock absorbers are a classical safety feature of products in the nuclear industry. They provide robust protection against mechanical damage of sensitive equipment. They are usually made of a shock absorbing material wrapped in a stainless-steel casing.

The aim of a shock absorber is to reduce the damage on a piece of equipment during an accident by dissipating a maximum amount of energy during its compression while keeping the acceleration below a desired threshold. As a consequence, the perfect shock absorber materials display a flat stress for any compressive strain between 0% and 100% (cf. Fig. 3). Certainly, a real shock absorber material cannot be compressed up to 100%; the real shock absorbing material has a stress-strain relationship that displays a fairly different profile, with an initial linear increase of the stress in the elastic regime, a long plateau at the required stress level with a little slope, and finally a stiff increase in the densification regime, as shown in Fig. 3. The efficiency of such a material, the energy absorbed below a stress threshold per unit volume, is then the area below the curve up to the stress threshold. The most compressible materials are cellular materials like wood, honeycomb or synthetic foam.
Looking for the perfect trade-off

A shock absorber material must not only fulfil a number of mechanical requirement, but also chemical, fire or operational ones, while staying perfectly reliable for the longest time at a minimum cost. An illustration describing some of these properties is shown in Fig 4. Many of the features are a trade-off; any given shock absorbing material will excel in some areas and lack in others.

In the case of multidirectional shock absorbers for mobile load, wood is often the best choice from a mechanical point of view. Very efficient along the main axis, it is still reasonably efficient in the transverse plane. However, its obvious drawback is its sensitivity to fire. This last point has been under sustained scrutiny recently [1][2], with chimney effects leading to complete post-combustion of wood based shock absorbers. Moreover, the use of wood induces other hardships; if its mechanical properties are excellent, they are highly sensitive to humidity, temperature, and may vary from one source to another. Honeycomb materials have good overall properties along their main axis but have negligible energy absorption capacity in the normal plane. As a consequence, their efficiency is extremely sensitive to their orientation during impact. Moreover, while they may be insensitive to fire, their geometry provides them with no fire retardation capacity along their main axis, and the aluminium honeycomb is even an excellent thermal conductor.

In comparison, synthetic shock absorbing materials have lesser mechanical properties, but they are less sensitive to environmental parameters, and are reliably consistent from batch to batch. A qualitative diagram describing some of the material trade-offs is shown in Figure 3. As a consequence, shock absorbers based on these materials do not need to be oversized in the design phase to compensate for this variability. Moreover, the hollow structure of these cellular materials can be used to provide thermal insulation and fire-retardancy properties to the material.
**FENOSOL™ form**

The FENOSOL™ program aim at providing nuclear-grade materials that would serve both for fire and mechanical protection. The current program, performed in collaboration with University Claude-Bernard – Lyon intend to optimize both properties through the investigation of the chemical and structural properties of phenolic foams.

The result of this program is the FENOSOL™ foam, a fire retardant, shock absorbing foam.

**Figure 5: Thermogravimetric analysis of Fenosol™ foam at 10°C.min⁻¹ in helium**

FENOSOL™ have excellent fire retardation properties. Figure 5 shows the results of thermal gravimetric analysis (TGA) of the FENOSOL™ foam. Below 200°C, no solid-state parts of the foam are affected by heat, as only free water and phenol are removed, preserving the
mechanical structure and properties. The phenolic carbon structure ensures its integrity even at high temperatures: at a 600°C exposure, 45% of the structure is left, maintaining the cellular structure and the thermal insulation properties. The micrometre-sized cell structure of FENOSOL™ shown in Fig. 6 provides it with excellent heat insulation properties and a conductivity of 0.037 Wm⁻¹k⁻¹ to 0.15 Wm⁻¹k⁻¹ depending on the chosen density. It can withstand direct exposure to a 600°C flame and self-extinguish.

From the mechanical point of view, synthetic foams like FENOSOL™ have isotropic mechanical properties that are only slightly less than the axial mechanical properties of the honeycombed structures along their main axis, but without any angle dependency. The main remaining mechanical trade-off is then between the stress threshold that has to be minimized and the energy absorbed to maximize.

The single-formulation, single-process of FENOSOL™ can be adapted to produce foams with the desired plateau stress level. Indeed, the plateau stress can be adjusted through the foam density as shown in Fig 7. Thus, FENOSOL™ can be used either as a highly insulating, low stress shock absorber, or as a less insulating, high energy shock absorber (cf. Fig. 8).
Conclusion

A good shock absorbing material has to present a specific stress-strain profile, with a long horizontal plateau at a chosen stress threshold. However, to be used in nuclear equipment and facilities, such material also has to be able to sustain the normal and accidental conditions that involve high temperature and fire exposition. Wood, the traditional shock absorbing material present excellent mechanical properties, but is anisotropic and fares poorly in front of fire. In comparison, synthetic foams such as FENOSOL™ foam combines isotropic mechanical properties and fire-retardant properties. Moreover, the repeatability of the production allowed to obtain an extensive knowledge of its properties based on laboratory tests and industrial feedback. Thus, the use of such a foam enhances safety-by-design for shock absorbers while remaining cost effective in most situations.

References