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Investigating the Properties of Fireproofing Materials for an Advanced Design of Equipment Protection

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Fire scenarios in process industry have a high potential to cause severe asset damage. Fireproofing is a consolidated technique for passive fire protection for units and supporting structures. Since several materials are available for passive fire protection, it is important to choose the best solution for the protected equipment and critical fire scenarios. Current practice in rating fireproofing materials does not provide sufficient information about the protection granted to process equipment: for example, the 'time-to-failure' of pressurized vessels protected by fireproofing materials cannot be predicted from the results of standardized fire tests. This study investigates the key properties (e.g. density, geometrical structure, thermal degradation and thermal conductivity) of representative fireproofing materials, in order to better understand the elements underlying the actual protection performance. An experimental activity was focused on the definition of fundamental models to describe the thermo-physical properties of the materials. The investigation cast the foundations of a better understanding of the dynamics underlying the effective design for passive fire protection, identifying the criticalities and limits of the alternative fireproofing options. The changes in the physical properties of materials during fire exposure were confirmed to play a major role on the protection performance. Such effects could not be accounted for complex geometries by conventional simplified approaches alone: thus, the proposed approach paves the way for a safer and more cost effective design of passive fire protection systems.

1. Introduction

Fire was responsible of several severe accidents in the process industry. Accidental fire may lead to the escalation of severe secondary scenarios (domino effect) when it involves pieces of equipment containing significant inventories of flammable materials (Landucci et al., 2009a; Demichela et al., 2004). In order to reduce the severity of domino escalation, consequence mitigation is a key issue in plant design (Tugnoli et al., 2008). Several active and passive strategies are commonly applied to reduce and/or avoid such events (see e.g. SCI, 1992; API, 2007). Passive fire protection (PFP) avoids the rapid increase of temperature in the protected items and the deterioration of the mechanical properties of the structural components. Thermal coatings, known as fireproofing materials, are suitable solutions for the application of PFP in both mobile and fixed installation (see e.g. Paltrienieri et al., 2009). The protection performance in fireproofing layers is achieved by characteristics as high thermal stability and low thermal diffusivity. The PFP delays the heat-up of fired units for a sufficient time lapse for the deployment of emergency teams and for starting fire suppression measures (see e.g. Tugnoli et al., 2012; Di Padova et al., 2011). Several approaches are available to assess the performance of a PFP material. While a complete assessment is provided only by real scale experiments, where the test is carried out on vessels exposed to fire (see e.g. Landucci et al., 2009b; VanderSteen et al., 2003), these should be avoided because of risks, complexity and costs. As an alternative, simulation analysis and/or smaller scale tests can be effectively used to investigate the properties and to understand the technological issues (e.g. preparation, formulation and design) of innovative materials (Argenti et al., 2014).
However, it is crucial to collect detailed information and to be able to model the thermodynamic and transport

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Table 1: Experimental test protocols

Instrument	Application	Test conditions
Thermogravimetric analysis (TGA Q500 from TA instruments)	• Weight loss analysis • Development of an apparent kinetic model	• Temperature ramps up to 800 °C • Constant heating rates: 5÷45 °C/min • Inert gas (N_2) atmosphere • Sample mass: 1÷45 mg
Differential Scanning Calorimetry (DSC Q2000 from TA instruments)	✓ Thermal effect of reaction ✓ Heat capacity ✓ Validation of TG runs	✓ Temperature ramps 550 °C ✓ Constant heating rates: 5÷45 °C/min ✓ Inert gas (N_2) atmosphere ✓ Sample mass: 1÷20 mg
Fixed bed tubular reactor (FBR) heated by Carboline HST 12/300 furnace equipped with W301 controller	• Analysis of sample swelling • Validation of TG runs • Produce solid residue for other tests	• Temperature ramps up selected final T • Constant heating rates: 10 °C/min • Inert gas (N_2) atmosphere • Sample mass: 1÷20 g
Thermal conductimeter (TPS1500S from Hot Disk AB)	✓ Thermal conductivity ✓ Heat capacity	✓ 80x80 mm slab samples ✓ Tests from RT to 700 °C ✓ Time residence in furnace 150 min ✓ Inert gas (N_2) atmosphere, 500 L/h ✓ Sample mass: 50÷120 g
Liquid pycnometer	• Density • Void fraction	• Sample mass: 1÷20 g • Liquids reference: water, xylene

Table 2: Apparent thermal conductivity: epoxy intumescent coating and lightweight cement

Model	Main equation	Notes
Bulk thermal conductivity	$k_{bulk} = (1-\phi)k_{solid} + \phi k_{pore}$	• k_{bulk} bulk thermal conductivity • k_{solid} thermal conductivity of solid fraction • k_{pore} thermal conductivity of the pores • $\phi = 1 - \frac{\rho_{app}}{\rho_{real}}$ pore fraction
Thermal conductivity of solid fraction	$k_{solid} = \sum_{p=1}^{j} \varpi_p k_{S,p}$	✓ $k_{S,p}$ thermal conductivity of the p-th solid pseudo-material ✓ ϖ_p mass fraction of pseudo-material p
Thermal conductivity of pores	$k_{pore} = k_g + k_{rad}$	• k_g thermal conductivity of the gas contained inside pores • k_{rad} thermal conductivity of the radiative heat transfer
Thermal conductivity of radiative heat transfer	$k_{rad} = \frac{4\sigma d}{(2/\varepsilon)-1} T^3$	✓ σ Stefan-Boltzmann constant ✓ d mean pore diameter ✓ ε emissivity of pore surface ✓ T absolute temperature

properties of PFP materials when exposed to fire: only this way a reliable evaluation of PFP performance by advanced simulation techniques is possible. In the current study, three materials were chosen as a representative reference set of PFP materials: intumescent resin, lightweight concrete and inorganic fiber. A methodology for investigating and modelling the properties of fireproofing materials is presented. The approach relies on the experimental characterization of properties such as thermal conductivity, density, porosity and thermal effect of the degradation. Constitutive equations are proposed for these data, based on the experimental findings. The discussion of the result will show as significant variations of these properties occur and should be accounted, by the proposed models, in the advanced design of equipment protection by PFP systems.

2. Experimental activity

2.1 Materials

The reference materials considered in this study are an epoxy intumescent coating, a lightweight cement-based coating and a silica fiber blanket. The epoxy intumescent coating (supplied by International Protective

Coatings) is formed by an epoxy resin, ammonium polyphosphate (APP), boric acid, and fillers (e.g. glass fibers, magnesium silicates, limestone, etc.). It is a spray-applied coating; the analysed specimens were prepared by the conventional procedure with average thickness approximately equal to 9 mm. Intumescent coating are defined by the American Petroleum Institute (API) as an active insulator: it was recently confirmed (Gomez-Mares et al., 2012a) that the analysed coating undergo a significant physical and/or chemical change when exposed to heat.
The lightweight cement coating (supplied by Cafco), is constituted principally by Portland cement, vermiculite and other inorganic fillers. It is a spray-applied coating with a density lower than the one of common cement; in typical industrial applications, the average thickness applied is about 24 mm. The silica blanket (supplied by Insulcon) represents the family of synthetic insulating fibers and is formed by silicon dioxide, aluminium dioxide (together constitute 97 % of the mass), and binders; its nominal thickness is equal to 12 mm. Both the two latter materials are defined inactive insulators, because they are not inherently designed for modification during fire exposure.

2.2 Experimental characterization

The experimental analysis investigated the thermo-physical properties of the materials, focusing in particular on thermal conductivity, a key property for the insulation performance. A set of different experimental techniques was used. Table 1 reports the main references of the small-scale tests carried out.

Table 3: Effective thermal conductivity: synthetic fibers

Contribution model	Main equation	Notes
Effective thermal conductivity	$k_{eff} = k_{conduction} + k_{radiation}$	• k_{eff} effective thermal conductivity • $k_{conduction}$ thermal conductivity through fiber and gas phase • $k_{radiation}$ thermal conductivity radiation
Conductivity of gas and solid	$k_{conduction} = (1-\phi)k_{fiber} + \phi k_{gas}$	✓ k_{fiber} thermal conductivity of fiber ✓ k_{gas} thermal conductivity of gas
Thermal conductivity of fiber insulating	$k_{fiber} = Fsk_S^* f_v^b$	• Fs geometrical parameter • k_S^* thermal conductivity of the bulk fiber material • f_v solid fraction ratio: 1- ϕ • b power varying between 1 and 3
Thermal conductivity of gas phase	$k_{gas} = \frac{2k_g^0}{\Phi + \Psi\left(\frac{2-\alpha}{\alpha}\right)\left(\frac{2}{\gamma+1}\right)\left(\frac{1}{Pr}\right)Kn}$	• k_g^0 gas thermal conductivity • Φ, Ψ parameters depend on Knused number • α accommodation coefficient equal to 1 • γ specific heat ratio • Pr Prandtl number • Kn Knused number
Knused number	$Kn = \left(\frac{K_B T}{\sqrt{2}\pi d_g^2 P}\right) / \left(\frac{\pi D_f}{4 f_v}\right)$	✓ K_B Boltzmann constant ✓ T absolute temperature ✓ d_g gas collision diameter ✓ P pressure ✓ D_f fiber diameter
Thermal conductivity radiation	$k_{radiation} = -\frac{16\, n^2 \sigma_B}{3\beta} T^3$	• T absolute temperature • n refraction index • σ_B Stefan-Boltzmann constant • $\beta = \frac{c_e}{L} f_v$ extinction coefficient, $c_e > 2$ constant parameter and L characteristics length

Table 4: Apparent kinetic for epoxy intumescent coating

Model	Main equation	Notes
Apparent kinetic	$\frac{d\xi_j}{dt} = A_j e^{\frac{-E_j}{RT}} (1-\xi_j)^{m_j}$	• ξ_i mass conversion in region j • A_j apparent pre-exponential factor for j • E_j activation energy of region j • R gas constant • T absolute temperature • m_j reaction order of region j
Real density	$\rho_{real} = \left(\sum_j \omega_j \cdot \frac{1}{\rho_{S,j}} \right)^{-1}$	✓ ρ_{real} real density of the solid fraction ✓ $\rho_{S,j}$ density of pseudo-material j ✓ ϖ_j mass fraction of pseudo-material j
Swelling factor	$\psi = \exp\left(\sum_j \ln(a_j) \cdot \xi_j \right)$	• ψ swelling factor • a_j swelling empirical material
Apparent density	$\rho_{app} = \frac{\left(1 - \sum_j \alpha_j \cdot \xi_j\right)}{\rho_0 \cdot \psi}$	✓ ρ_{app} apparent density ✓ α_j weight loss in region j ✓ α accommodation coefficient equal to 1 ✓ ρ_0 density of virgin sample

3. Property models

The future activities of simulation of the behaviour of insulating materials exposed to fire require the definition of reliable constitutive equations for the main material properties (density, thermal conductivity, thermal stability, etc.). Focusing on thermal conductivity, this is mainly a function of three key physical parameters: material porosity, thermal conductivity of the solid matrix and thermal conductivity of the gas inside the pores (Gomez-Mares et al., 2012b). Table 2 reports the simplest bulk thermal conductivity model proposed to predict conductivity of epoxy intumescent coating and lightweight cement, as applied by several earlier researches (Kantorovich et al., 1999) for porous materials. The same model was applied to the reference fireproofing materials analysed in current study.

In materials with an high gas fractions (i.e. high porosity), such as the silica blanket, the radiative contribution to apparent thermal conductivity may pay a significant role at higher temperatures, as shown by Moricone et al., 2014. In this case the generic model proposed above may provide inadequate results. A specific effective thermal conductivity developed for synthetic fibers is presented in Table 3. This model embeds advanced equations for heat transport in the gas phase (Kennard, 1938), for radiative heat transport (Siegel and Howell, 1992) and for solid conduction in a fibrous media (William et al., 1993).

Reactive materials, such as the epoxy intumescent coatings, need a kinetic model to be integrated into the constitutive equations for physical and transport properties. Apparent kinetics can be obtained by various techniques: Gomez-Mares et al. (2012b) used TGA runs to develop a kinetic model for this kind of material. The swelling mechanism of the material, and therefore apparent density and pore fraction can be connected to the conversion term by the approach described in Table 4.

4. Results and discussion

4.1 Thermal stability during heating

As for Table 1, the thermal decomposition of the representative PFP materials was studied by TG and DSC analysis. Figure 1-A shows the weight losses determined in nitrogen atmosphere. The silica blanket (curve c) presents moderate weight losses (about 10 %) mostly due to water evaporation and degradation of binders, so the material was considered thermally invariant up to temperatures as high as 800 °C. The lightweight concrete (curve b) shows some weight loss, which becomes relevant (about 27% of the initial weight) only at temperatures above 600 °C. These can be interpreted as losses of carbon dioxide and water (Alarcon-Ruiz et al., 2005; Villain et al., 2007), and correspond to endothermic effects in DSC analysis (Figure 1-B). The epoxy intumescent coating (curve a) clearly demonstrate the need of a kinetic model in order to track property variation: degradation starts at low temperatures with dehydration of boric acid (completed at 260 °C, with losses about 12 % of initial weight) and continues in several steps up to total weight losses of about 65 % of initial weight at 800 °C. The DSC data show as the dehydration of boric acid is an endothermic process (about 202 mJ/mg, indicated in Figure 1-B with point 1a), while the weight loss between 260 °C and 550 °C, associated to the degradation of epoxy resin and APP (point 2a of the DSC signal) is an exothermic process (about 142 mJ/mg). In the latter step, the degradation generates the swelling phenomenon with char formation. These phenomena are in agreement with the results of studies on similar materials (Jimenez et al., 2009; Jimenez et al., 2006) and they were confirmed by test conducted in FBR. The char residue at 800°C is equal to 35% of the initial mass. These deep modifications of the material and the thermal phenomena associated are expected to have a significant role in the definition of the fireproofing performance.

4.2 Fireproofing materials properties

The experimental characterization according to the protocols defined in Table 1 allowed the identification of the parameters of the models discussed in section 3. The results for the major properties are shown in Figure 2-A and Figure 2-B, considering a temperature ramp at constant heating rate (10°C/min).

The apparent density and porosity of silica blanket remains almost constant with temperature (around 95 %) due to the lack of degradation phenomena. On the other hand, the lightweight cement coating shows a density reduction at high temperatures due to the increasing of pore fraction as a consequence of calcination processes. The epoxy intumescent coating suffers a dramatic change in density due to the swelling and significant weight loss; the porosity changes from initial 0.13 to 0.93 when the material is exposed to final temperature.

Figure 2-B shows the results obtained from experimental measuring, using TPS method, and thermal conductivity models for three different fireproofing materials. As shown in the figure, a good agreement is present between experimental data and model predictions for all the reference materials. The thermal conditions affect the properties of materials, it has been observed that the drastic increase of porosity, in the case of active fireproofing materials , leads to a decrease of effective conductivity, favouring the its protective action. This increase, however, is linked to the degradation of the material that leads to problems of failure of the structure. In inert materials, instead, as silica blanket, a high degree of porosity allows maintaining a low

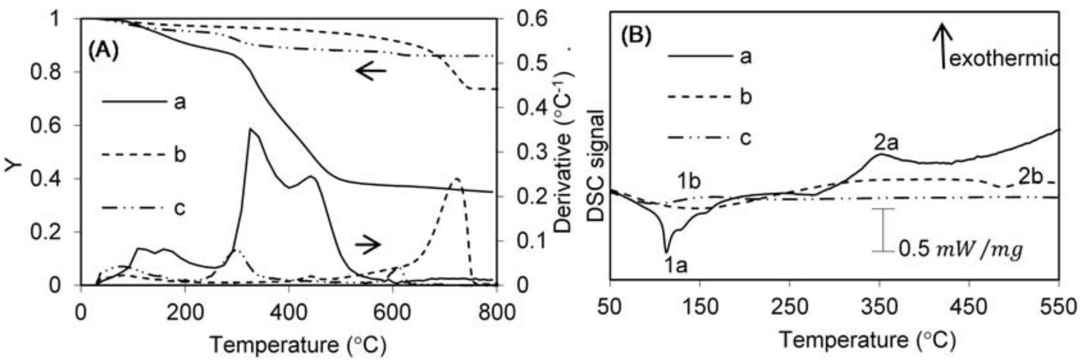

Figure 1: (A) Results of the constant heating rate (10°C/min) in TG runs on the reference samples (a) epoxy intumescent coating, (b) lightweight cement and (c) silica blanket. (B) Results of DSC test.

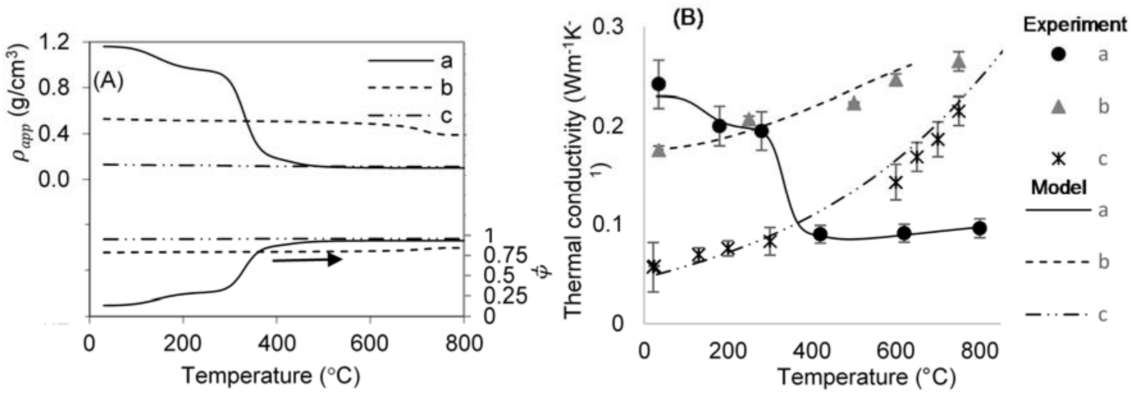

Figure 2: (A) Apparent density and Pore fraction in thermal trend for the reference samples (a) epoxy intumescent coating, (b) lightweight cement and (c) silica blanket ; (B) Thermal conductivity results as a function of the temperature during constant heating rate (10 °C/min) .

thermal conductivity in the range of temperatures considered. In the case of the fibrous material has also been noted that the contribution of the radiation is not negligible for temperatures higher than 500 ° C, while it is for the intumescent material.

5. Conclusions

The thermal behaviour of three different commercial fireproofing materials was investigated. The key properties defining the performance of the fireproofing were experimentally measured by an array of laboratory-scale techniques. Constitutive equations were proposed for modelling these properties, in view of future application in advanced simulation of the fireproofing system (e.g. FEM). The behaviour of the material during simulated fire exposure evidenced large changes in the values of key parameters such as thermal conductivity and apparent density. The role of these changes, frequently unrecognized or inadequately modelled, is expected to pay a primary role in the effectiveness of the passive fire protection system. The investigation method proposed in current paper, avoiding expensive large-scale tests, paves the way to an improved analysis of PFP based small-scale tests and performance simulation.

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