Scaffold Public Documents – SPD8

Innovative strategies, methods and tools for occupational risks management of manufactured nanomaterials (MNMs) in the construction industry

EMISSION OF TOXIC GASES AND MANUFACTURED NANOMATERIALS (MNMs) DURING A FIRE OF CONSTRUCTION PRODUCTS CONTAINING NANO-OBJECTS

Scaffold Public Documents - Ref.: Scaffold SPD8

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EXECUTIVE SUMMARY

The aim of this report is the assessment of the risk associated with the exposure of construction products containing nano-objects to an accidental fire. The report summarizes the activities carried out in the task 3.5 *Developing strategies and methods for exposure assessment in accidental situations: Fire* of the Scaffold project. Therefore, the different products developed in the project (FRpanels, mortar, concrete, insulation, etc..) have been tested in different fire scenarios in order to evaluate the influence of the nano-additives in the reaction to fire of the samples. As benchmarks, control samples of its material were compared with the modified ones. Properties of reaction to fire (inflammability, fire spread, additive nanoparticles in effluents, smoke opacity and toxicity) were compared with reference materials.

The main conclusions are:

1. As expected, inorganic materials (concrete and mortar) have good performance and only in the case of nanoSiO_2 worsen the smoke parameters of the concrete.
2. For the insulation product (PUR foam) the presence of nanocellulose crystals improves the heat release parameter (MARHE) and the smoke opacity (Ds). The figures for all the parameters are moderates.
3. For glass reinforced composites (FRPANEL and COMPOSITE) the values are very high, particularly smoke related parameters. The effect of the CNF in COMPOSITE fire performance is despicable. Regarding FRPANEL, the nanoclay improves the heat release parameters and decreases the smoke parameters.
4. Two methods for the identification of nanoparticles in the effluents of combustion products have been developed in qualitative and quantitative approaches.
5. Concerning qualitative approach, only evidences of nano-objects (nanoclay) was observed for FRPANEL but just few particles attached to the soot.
6. Concerning quantitative approach (applied to the FRPANEL), it is showed that the emission of submicronic particles (< 1µ) is higher for the control material than for the formulations doped with nanoclay. Analysis of the morphology of the particles released showed no differences between formulations control and doped. The particles released are mainly soot accompanied with other metal particles and also silica in some cases; the origin of these particles is difficult to determine and could be impurities from cone calorimeter or from the glass fiber or the nanoclays from the material. No free particles of nanoclay have been identified.

1. INTRODUCTION

The target of this report is the assessment of the risk associated with the exposure of construction products containing nano-objects to an accidental fire. The report summarizes the activities carried out in the task 3.5 *Developing strategies and methods for exposure assessment in accidental situations: Fire* of the Scaffold project. Therefore, the different products developed in the project (FRpanels, mortar, concrete, insulation, etc..) have been tested in different fire scenarios in order to evaluate the influence of the nano-additives in the reaction to fire of the samples. As benchmarks, control samples of its material were compared with the modified ones.

During a fire, there are different hazards associated with the materials involved on it: heat, smoke opacity (solid and liquid particles) and smoke toxicity.

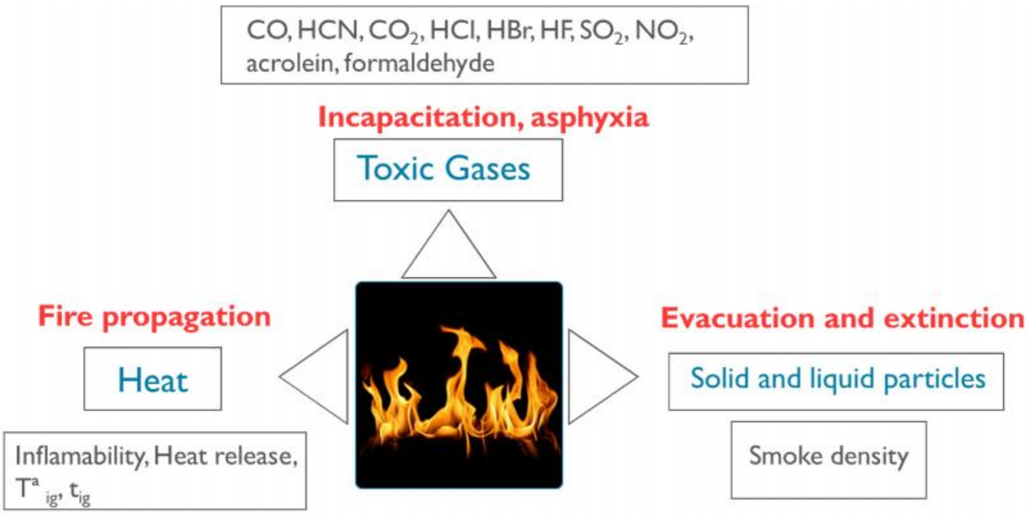


Figure 1. Fire hazard and related reaction to fire parameters.

The measurement of the most of these parameters is well established and has been used in this study:

- Heat related parameters: Cone calorimeter (CONE)
- Smoke opacity: Smoke density chamber (SDC)
- Smoke toxicity: Infrared spectroscopy (FTIR)

However, the identification and quantification of the amount of nano-objects realised by a sample in combustion conditions is not defined and there are no standardized methods to accomplish them.
Taking this into account, one of the aims of this task was the development of new methods for the identification of nano-objects in fire effluents. Two different approaches were following:

1. Qualitative method: Analysis of cone calorimeter effluents by collecting the emissions in filters and subsequent EDX analysis as a screening of the samples.
2. Quantitative method: Coupling of CONE with an equipment to characterize particles: number and size distribution (CPC, SMPS, ELPI) for selected materials.

2. OBJECTIVES AND SCOPE

The main objective of this report is the evaluation of the fire hazards associated with construction products containing nano-materials. Information about the key parameters related with fire reaction properties (MARHE, Ds, toxic gases concentration and presence of nanoparticles in the effluents) will be provided. These results will be used as input data for the risk assessment and included in the Scaffold report SPD 9 - *Best Practice Guide for Risk Assessment of manufactured nanomaterials (MNMs) in the construction sector.*

3. FIRE PERFORMANCE CHARACTERIZATION METHODS

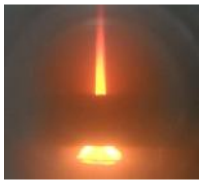
Cone calorimeter:

Bench scale test for reaction to fire

Cone Calorimeter[1] is probably the most popular bench-scale heat release method at the moment. The main advantage of the cone calorimeter is the simulation of different fire scenario by the variation of the thermal attack levels (0-100 kW/m^2). The principle of the technique (oxygen consumption calorimetry) is the same used in full-scale fire test method SBI for *euroclass* classification. The fire performance of the products will be tested in order to obtain the most important parameters: Heat Release Rate (HRR: kW/m^2), maximum average rate of heat release (MARHE, MJ/m^2), time to ignition (TTI, s), mass loss rate (MLR, g/s), effective heat of combustion (EHC, MJ/Kg), total smoke production (TSP, m^2) in a fire scenario similar to that reflected in EN 13501-1[2] (50 kW/m^2).

Smoke Density Chamber:

Smoke Opacity test



The main parameter to estimate the Smoke opacity is the *specific* optical density (D_s). The method to measure it is described in the standard ISO 5659-2[3], and the equipment used is the smoke density chamber (SDC). D_s is related, by definition, to the transmission by equation:

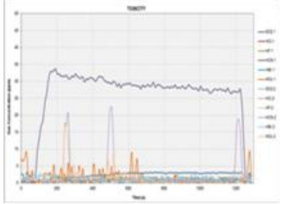
$$D_S = \frac{V}{A \cdot L} \log_{10}\left(\frac{100}{T}\right)$$

Where,
D_S is the specific optical density
V is the chamber volume (m^3)
A is the specimen area (m^2)
L is the light path length (m)
T is the *actual* transmission or relative intensity (%)

The fire scenario selected was a heat flux of 50 kW/m^2 in horizontal position in **no flame** conditions.

FTIR:

Smoke Toxicity test.



The method consists of a sampling procedure and analysis of gases present in the fire effluents by the discontinuous or continuous way using spectroscopy in the Fourier transform infrared technique (FTIR)[4]. This method is based on the classification system for fire effluents from railway products, specified in EN 45545-2:2013[5]. It is based on the use of FTIR spectrometry to measure 8 common fire toxic gases (CO, CO_2, HCN, HCl, HF, HBr, SO_2 and NO_x) after they have been generated in the ISO 5659-2 smoke chamber (SDC) into the smoke test. The conditions used in the ISO 5659-2 tests are selected on the basis of the type of fire that may be expected.

For the estimation of the toxic gases hazard, it is necessary to do a correlation between the conditions of the laboratory test (SDC) and the final application of the product. The main parameter used is the conventional toxicity index (CIT) which is defined by the next model:

$$\text{CIT} = [\text{Precursor Term}] \times [\text{Summation Term}]$$

The precursor term is a system parameter (or scaling factor), which defines the area of a product that is estimated to burn and the volume of the space into which the smoke and gaseous effluents flow. Taking into account that currently the smoke toxicity is not a requirement for construction products, there are no construction models that correlate the smoke test with the final application of the material. So, for application in this research, the model used in railway applications has been used. This model is based on simple assumptions such as the exposed area of many products is 0.1 m^2 and the volume of the space is 150 m^3.

$$CIT_G = \frac{0{,}51\ \mathrm{m}^3 \times 0{,}1\ \mathrm{m}^2}{150\ \mathrm{m}^3 \times 0{,}004225\ \mathrm{m}^2} \times \sum_{i=1}^{i=8} \frac{c_i}{C_i}$$

So as simplified form, the equation to use in the calculations is:

$$CIT_G = 0{,}0805 \times \sum_{i=1}^{i=8} \frac{c_i}{C_i}$$

The reference concentrations (Ci) are expressed in mg/m^3 and the following data has to be used:

Table 1. Reference values based on IDLH (Immediately Dangerous to Life and Health), recognized as a limit for personal exposure to the gas component by NIOSH (National Institute for Occupational Safety and Health) (1997 version).

Gas component	Reference concentration [mg/m^3]
CO_2	72 000
CO	1 380
HBr	99
HCl	75
HCN	55
HF	25
NO_x	38
SO_2	262

SDC+FTIR Continuous Vs discontinuous method:

Different conditions were checked for reference **FRPANEL-control** to analyse the concentration of hazardous gases (CO, CO_2, HCN, NOx, HBr, HCl, HF and SO_2). Best correlation has been getting for a sampling flow of 4 L/min and recirculation of the gases to the chamber in order to avoid underpressure conditions.

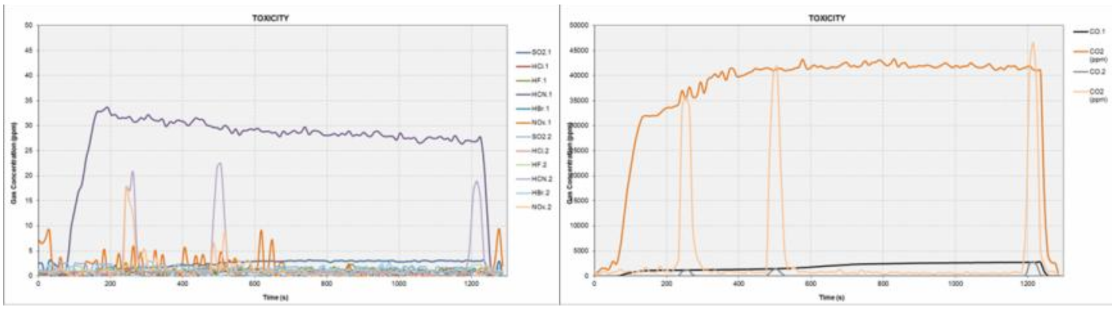


Figure 2 Comparison of gases concentration in continuous and non-continuous FTIR.

As can be observed in the graphs, the results are comparable for the continuous method. Although, in a continuous measurement we reduce the uncertainty in the measure because parameters like time to retention and time to response play a secondary role so the results are more reproducible.

Therefore, the method to be used for the rest of the samples was: SDC 50kW/m^2 thermal attack, no flame conditions and FTIR coupled in continuous mode (4L/min) with recirculation. For quantification of the smoke toxicity, the value of $\mathbf{CIT_{8min}}$ was used.

3.1. Development of a method to analyze nano-objects in fire effluents

3.1.1. Introduction

There is no standardized method for the quantification of nanoparticles suspended in effluents from fire. There are some studies in the literature[6] using the cone calorimeter (modified) as fire scenario for the measurement of the particles released during combustion products. However, these tests require especial equipment and a modification of the cone duct. Then, the aim of this task is the development of a method to analyse emissions of particles of materials and to evidence the release/non release of the nano-objects.

3.1.2. Results

Cone calorimeter was selected as the equipment for the combustion of the materials due to its versatility and the information about reaction to fire parameters. The smoke generated during the combustion of the materials is conducted by a duct with a flow of 24 L/min thanks to a fan located after the sampling point. In these conditions, the effluents can be considered as homogeneous and laminar.

Qualitative method

For the collection of the effluents, a sample probe was introduced in the duct so manner as the sample point was in the middle of the duct. After the sample point, two filters were located in series. The first filter (10µm PC filter supplied by Hahnemühle) acts as a soot remover to avoid the collapse of the second filter (0.1µm PC filter supplied by Hahnemühle) due to the amount of soot released by the samples. A schematic view of the material flow can be observed in the next graph:

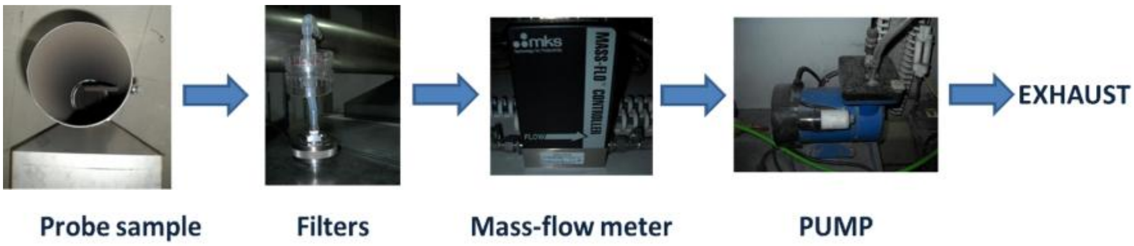


Figure 3. Particle path from the cone calorimeter duct to the exhaust.

In the centre of the second filter, a carbon adhesive tab was placed to capture the particles with diameters up to 0.1µm. This kind of tabs is suitable for further analysis by electron microscopy.

Figure 4. Second filter with C adhesive tab.

A schematic view of the method is showed In the figure 5.

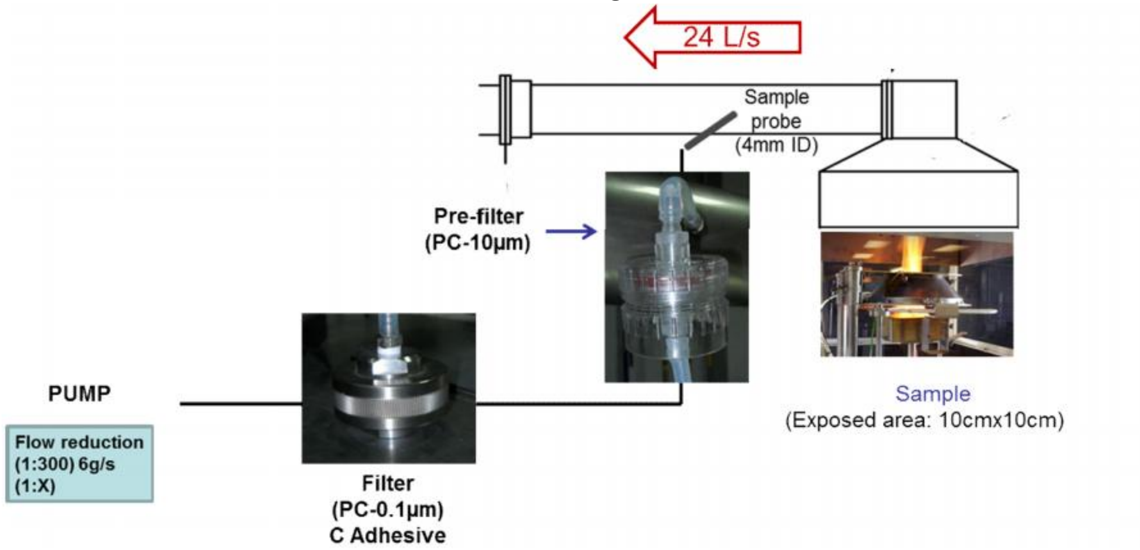


Figure 5. Experimental setup of the qualitative method.

The dilution factor can be changed with a pump (1:300 for these experiments).

After the test, the filters and the residue were analysed by X-Ray spectroscopy (EDAX) for the identification of nano-objects both in the gas phase (fumes) and in the solid phase (residue).

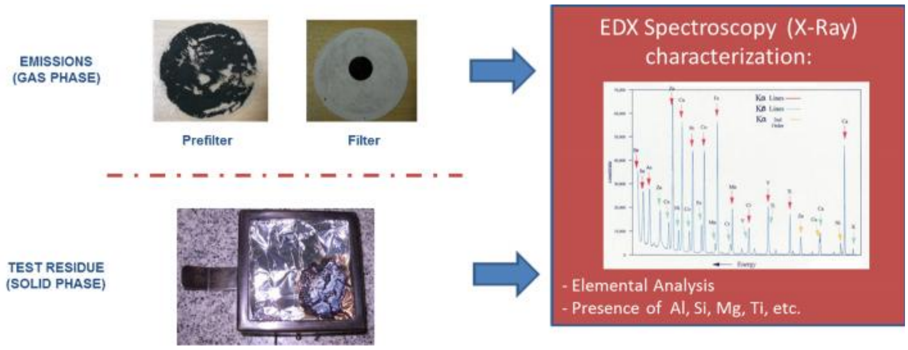


Figure 6. Scheme of the characterization.

Microscopic inspection was performed with a scanning electron microscope (model 200 of Quanta EIF). Elemental analysis was also performed using a fluorescence spectrometer for X-ray dispersive energy (EDAX). The particle sizes and counter were made by image analysis with the XT Pro v3.2 software (Soft Imaging System GmbH).

This method allowed a quick screening of the samples and qualitative analyse of the effluents.

Tuning up the method:

First step of the method has been carried out using references from NETCOMPOSITES of FR panels and FR panels charged with nanoclays (5%) made ad hoc for the identification of the nanoclays in the effluents and for the testing of the filters system. For this propose, no glassfiber was used to simplified the combustion process and to ensure the worst conditions.

Samples:

Table 2. EDAX spectrum and image of the FR PANEL-Control.

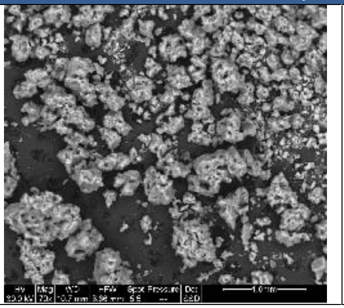
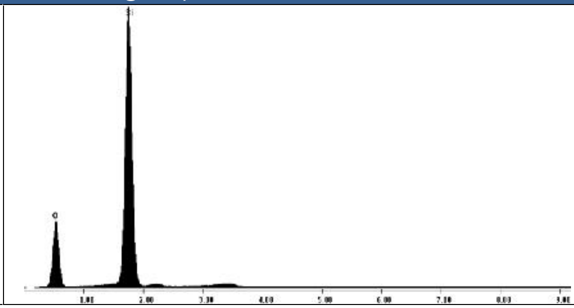
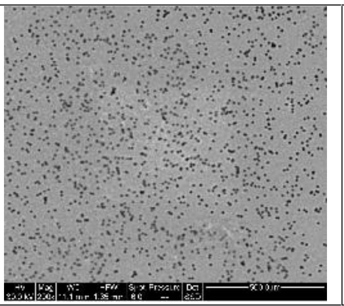
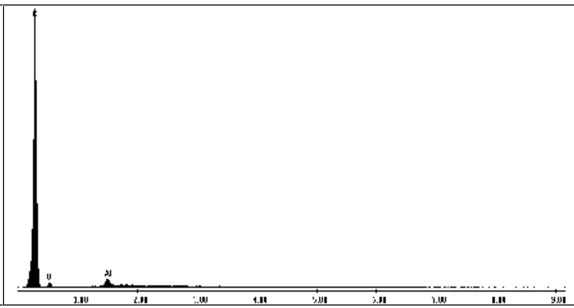
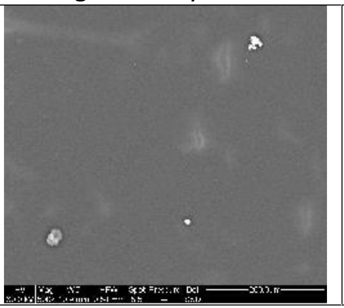
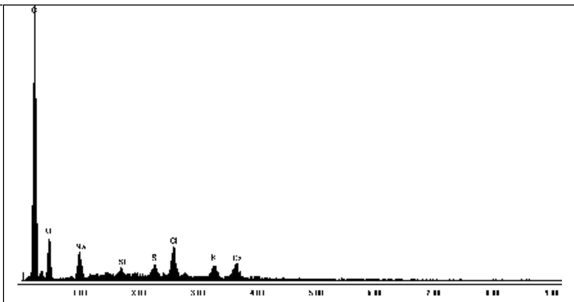
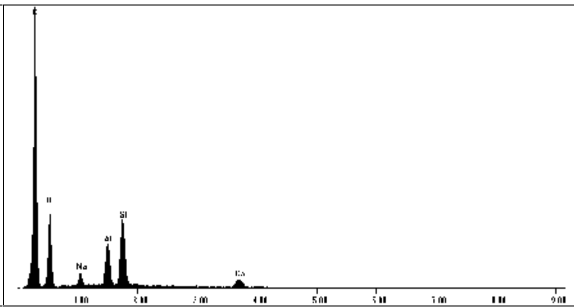
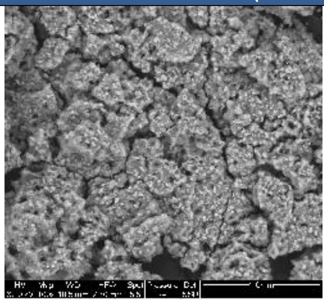
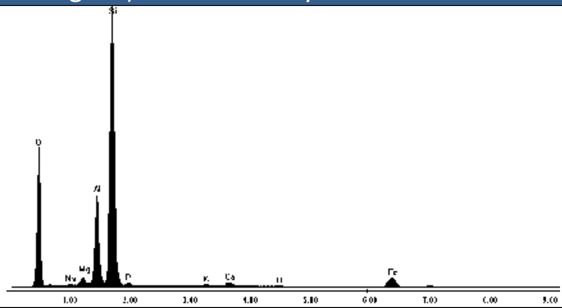
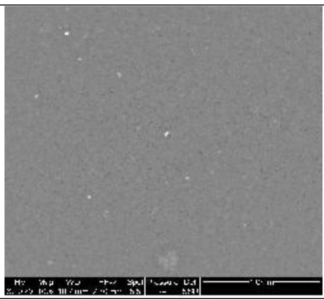
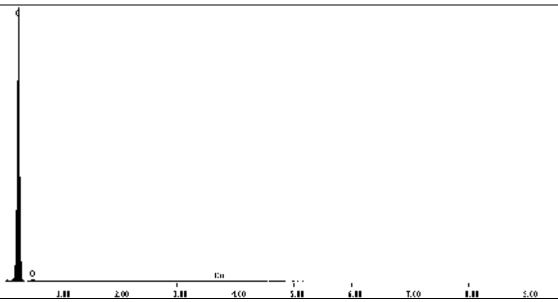
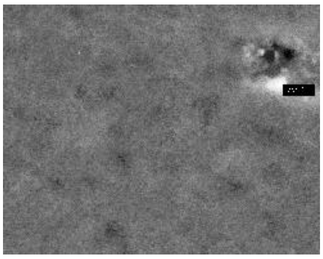
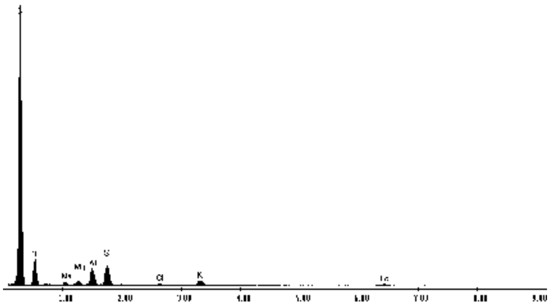
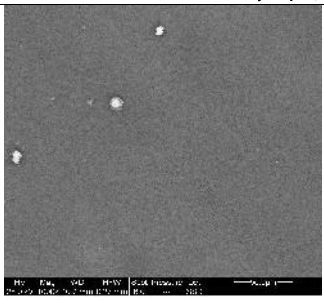
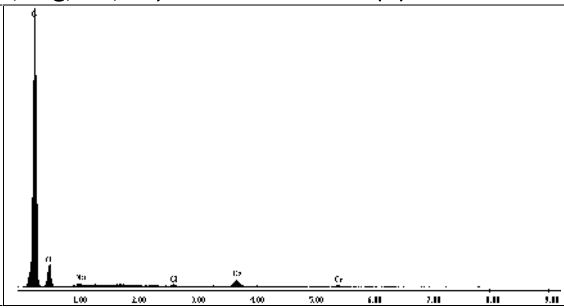
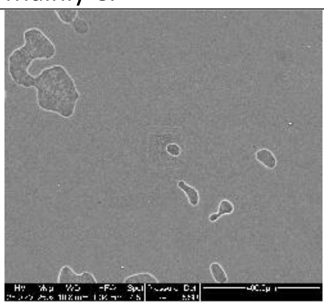
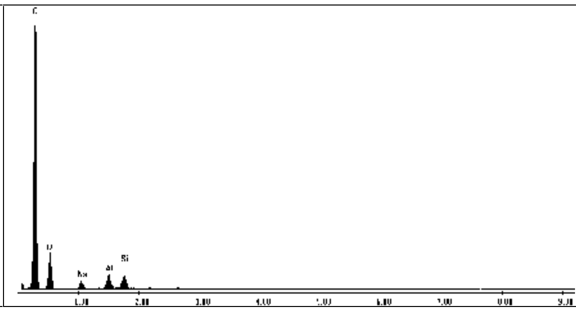
<table>
<tr><th colspan="4">FR Panel (without fiberglass) control</th></tr>
<tr><td colspan="2" rowspan="2">Residue:</td><td></td><td></td></tr>
<tr><td colspan="2">Si and O.</td></tr>
<tr><td colspan="2" rowspan="2">Filter 1 (PC 10µm)</td><td></td><td></td></tr>
<tr><td colspan="2">homogenous layer of soot covers the surface of the filter.</td></tr>
<tr><td rowspan="3">Filter 2</td><td rowspan="2">PC 0.1µm</td><td></td><td></td></tr>
<tr><td colspan="2">Mainly C.</td></tr>
<tr><td>C Adhesive</td><td></td><td></td></tr>
</table>

Table 3. EDAX spectrum and image of the FR PANEL+5% Nanoclay.

<table>
<tr><th colspan="4">FR Panel (without fiberglass) + 5% Nanoclay</th></tr>
<tr><td rowspan="2" colspan="2">Residue:</td><td></td><td>
</td></tr>
<tr><td colspan="2">Si and O.</td></tr>
<tr><td rowspan="4" colspan="2">Filter 1
(PC 10µm)</td><td></td><td>
</td></tr>
<tr><td colspan="2">Homogenous layer of soot covers the surface of the filter.</td></tr>
<tr><td></td><td>
</td></tr>
<tr><td colspan="2">Evidences of nanoclays (Si, Al, Mg, Na, Fe) attached to soot (C).</td></tr>
<tr><td rowspan="4">Filter 2</td><td rowspan="2">PC 0.1µm</td><td></td><td>
</td></tr>
<tr><td colspan="2">Mainly C.</td></tr>
<tr><td rowspan="2">C Adhesive</td><td></td><td>
</td></tr>
<tr><td colspan="2"></td></tr>
</table>

- No evidence of nanoclays in the second filter was observed.
- Nanoclays indications were found in the first filter attached to particles of soot.

According to the results observed for the selected material, the method variables were defined:

- A dilution factor of 1:300 (6g/s) seems to be enough to avoid the saturation of the filters.
- No evidences of nanoclays were observed in the FILTER 2 (neither in C adhesive zone nor in PC filter). For the other products only **FILTER 1 (10µm) + C adhesive tab** will be used.

Quantitative method

The aerosol released from the combustion has been characterized in *number concentration and size distribution* with appropriate measurement devices: ELPI+ (9 nm-7,3 µm) and CPC3775 (4 nm- >3 µm) jointly with devices to collect sample for off-line analysis in microscopy SEM/TEM (NAS and Dekati PM10 Impactor) (ISO/TR 27623:2007[7]).

The goal is to study potential differences among the materials concerning these metrics.

The effluents from the combustion have been collected in a sample probe introduced in the duct (sample point in the middle of the duct). The aerosol is diluted with a double ejector dilutor (Dekati Diluter L7) which avoids the oversaturation of the measurement devices. The dilutor works at 2 bars pressure and includes two modules: first one works at 100-120º to avoid condensations and second module operates at ambient temperature.

Figure 7 shows a scheme of the experimental set-up. It should be pointed out that a limit of this experimental system is that conditions are not isokinetic (the cone calorimeter is a standard device that did not allow modifications to assure isokinetic measurements). Considering this limitation, measurements of particles above 1 µm should be considered with caution. However, this fact is not a limitation for this study because gravimetric analysis is not done (where particles > 1µm are the relevant ones) and because its focus is the analysis of particles in the small range (<1µm).

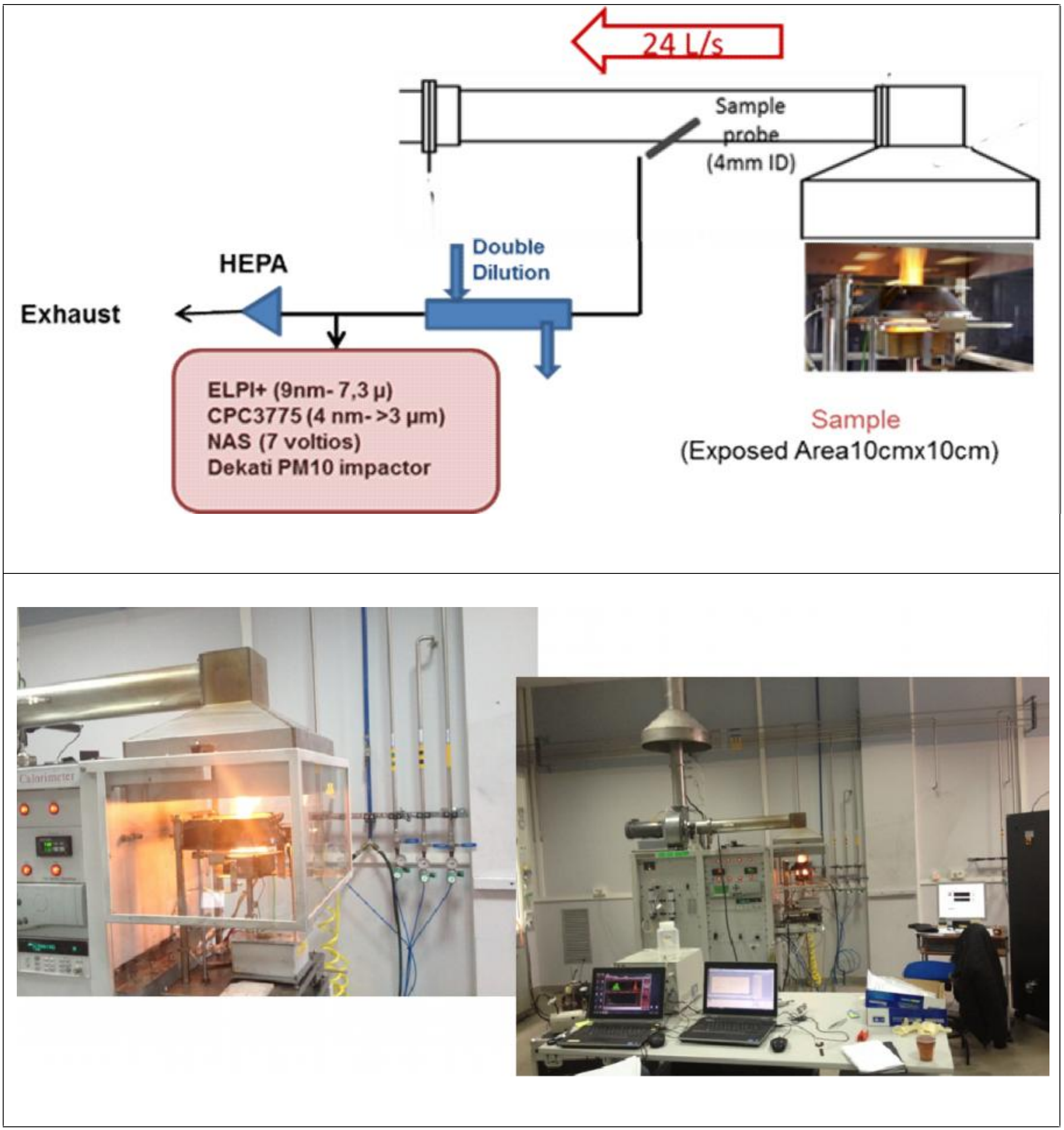


Figure 7. Experimental setup of the connection of Cone with measurement devices ELPI/CPC, jointly with some pictures during experiments.

4. RESULTS

4.1. CONCRETE

Two formulations of concrete were analysed according to the previously described methods.

- CONC-A: Self-compacting concrete by ACCIONA
- CONC-C: Self-compacting concrete + 5% of nanoSiO_2 by ACCIONA

4.1.1. Heat Release

As we would expect, concrete samples did not ignite so all the parameters related with the heat emission were negligible. The total amount of mass loss was the evaporation of the water which produces small amount of smoke. The slight differences between the TSP and SEA of the samples were not representative.

Table 4. Cone calorimeter results for CONCRETE.

Ref.	t_{ig}	HRRmax (kW/m^2)	THR (MJ/m^2)	MARHE (m^2)	Mass loss (%)	TSP (m^2)	SEA (m^2/kg)
CONC-A	-	-	-	-	5.5	1.7	63.44
CONC-C	-	-	-	-	6.3	2.8	92.86

4.1.2. Smoke opacity

The behaviour of the samples was similar to that observed in cone calorimeter. The samples did not ignite but release certain amount of smoke.

Table 5. SDC results for CONCRETE.

Ref.	$Ds_{(4min)}$	Ds_{max}	VOF_4
CONC-A	5.30	67.42	3.52
CONC-C	41.64	243.96	40.06

Sample treated with nano-SiO_2 (**CONC-C**) emitted more smoke than control material.

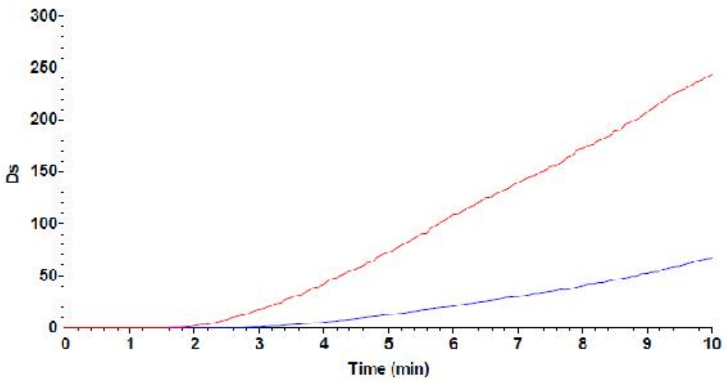


Figure 8. Ds curve of concrete samples; control (blue) and +nanoSiO_2 (red).

4.1.3. Smoke toxicity

Table 6. FTIR results for CONCRETE.

Ref.	CO_2 (ppm) (40000)	CO (ppm) (1200)	SO_2 (ppm) (100)	HCl (ppm) (50)	HF (ppm) (30)	HCN (ppm) (50)	HBr (ppm) (30)	NO_x (ppm) (20)	CIT_g (8min)
CONC-A	1100	5	0	0	0	0	3	0	0.009
CONC-C	900	34	1	0	0	0	2	16	0.063

The figures of toxic gases are very low. The sample treated with nanoSiO_2 showed slightly worse results.

4.1.4. Nano-objects in effuents

Conc A-Filter1

In the surface of the filter, different particles were observed with a range of diameters (1-33 µm). The density of the particles is around 175 particles/mm^2. The particles found are:

- Concrete particles: the most abundants. Composed of Ca, Si and O with traces of Na, Mg, Al, P, S, K and Ti.
- Calcium carbonate particles: composed of Ca, C and O.
- Gypsum particles: composed of Ca, S and O.
- Aluminium particles: composed of Al and O.
- Barium sulphate particles: composed of Ba, S and O.

Table 7. EDAX spectrum and image of the CONCRETE-Control.

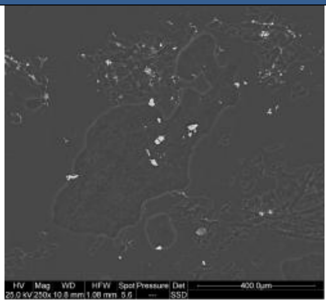
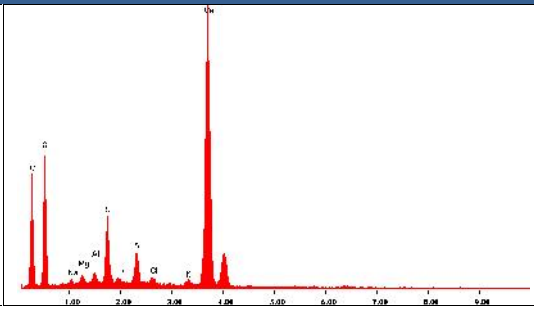
CONC-A		
Filter 1 (PC 10µm)		

Figure x. Image and spectrum of a concrete particle in the filter1.

Conc-C Residue

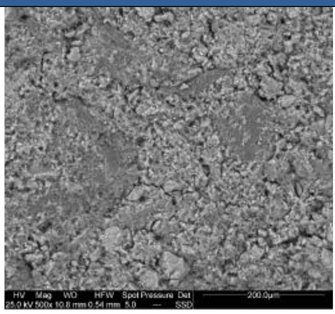
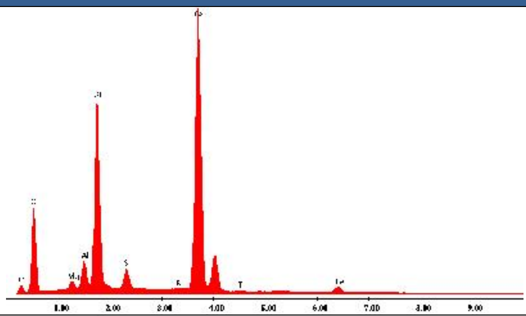
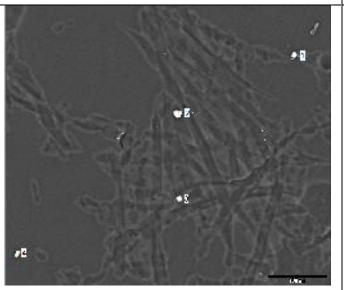
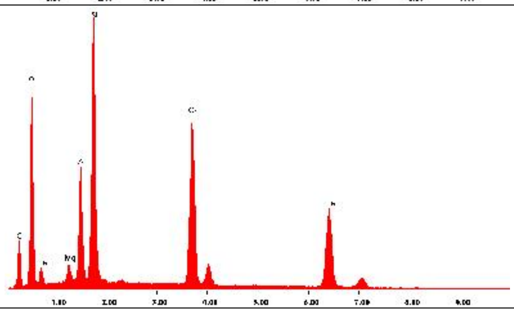
Two types of zones could be identified:

- Cement matrix: In order of abundance Ca, Si and O; C, Al and S; Mg, K, Ti and Fe.
- Aggregate: Si and O together with Al.

Conc-C Filter 1

In the surface of the filter, different particles were observed with sizes from 1 to 43 µm. The average density of the particles in the surface was around 66 particles/mm^2. The particles were similar than observed in the Control-Filter1 (concrete, $CaCO_3$, gypsum and metallic particles).

Table 8. EDAX spectrum and image of the CONCRETE-Control.

CONC-C		
Residue:		
Filter 1 (PC 10µm)		

4.2. MORTAR

The following formulations of mortar were analysed:

- MORTAR-A: Mortar by ACCIONA
- MORTAR-C: Mortar + 1% nanoTiO_2-sepiolite by ACCIONA

4.2.1. Heat Release

As inorganic material, mortar samples did not ignite so all the parameters related with the heat emission were negligible. The total amount of mass loss was the evaporation of the water which produces small amount of smoke. The values of TSP and SEA were very low.

Table 9. Cone calorimeter results for MORTAR.

Ref.	t_{ig}	HRRmax (kW/m^2)	THR (MJ/m^2)	MARHE (m^2)	Mass loss (%)	TSP (m^2)	SEA (m^2/kg)
MORTAR-A	-	-	-	-	7.8	1.6	39.77
MORTAR-C	-	-	-	-	1.5	0.1	10.50

4.2.2. Smoke opacity

The behaviour of the samples was similar to that observed in cone calorimeter. The samples did not ignite but release certain amount of smoke.

Table 10. SDC results for MORTAR.

Ref.	$Ds_{(4min)}$	Ds_{max}	VOF_4
MORTAR-A	3.91	77.92	2.55
MORTAR-C	0.64	31.37	0.68

Sample treated with nanoTiO_2-Sepiolite (MORTAR-C) emitted less smoke than control material. Although, the values of the two samples were very low.

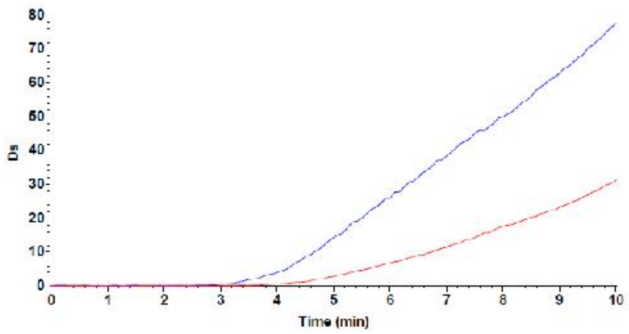


Figure 9. Ds curve of mortar samples; control (blue) and +nanoTiO_2 (red).

4.2.3. Smoke toxicity

The results of the smoke toxicity of the two mortars are comparable and very low.

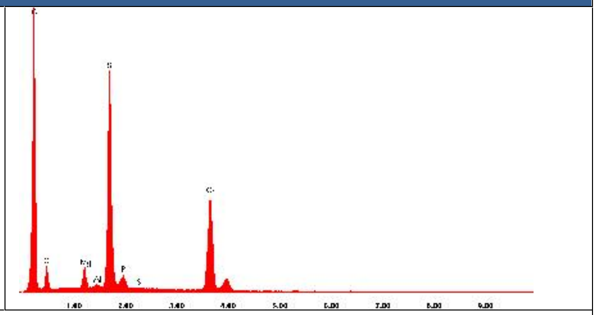
Table 11. FTIR results for MORTAR.

Ref.	CO_2 (ppm) (40000)	CO (ppm) (1200)	SO_2 (ppm) (100)	HCl (ppm) (50)	HF (ppm) (30)	HCN (ppm) (50)	HBr (ppm) (30)	NO_x (ppm) (20)	CIT_g (8min)
MORTAR-A	**600.00**	**4.87**	**0.00**	**0.35**	**0.00**	**0.00**	**0.84**	**3.03**	**0.014**
MORTAR-C	**1400.00**	**2.99**	**0.49**	**0.01**	**0.00**	**0.00**	**1.52**	**1.76**	**0.012**

4.2.4. Nano-objects in effluents

Only the filter was analysed for MORTAR-control. Some complex microparticles were found composed of Si, Ca and Al with small amounts of Na, Mg, K and Fe.

Table 12. EDAX spectrum and image of the MORTAR-A.

	MORTAR-A	
Filter 1 (PC 10µm)		
	.	

Regarding sample MORTAR-C-Residue, it was composed of Si, O and Ca, together with C, Al, S and traces of Mg, K, Ti, Cr and Fe.

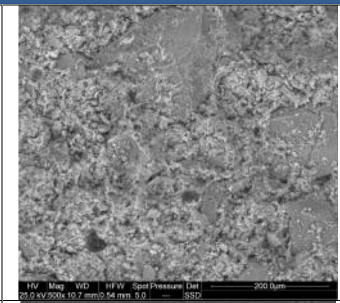
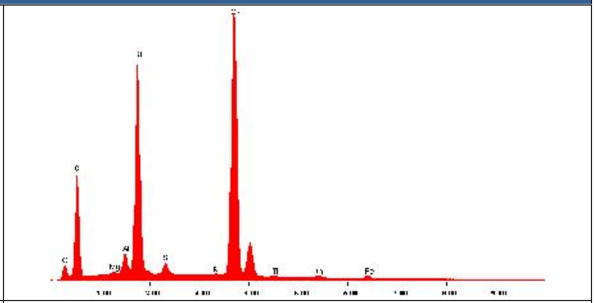
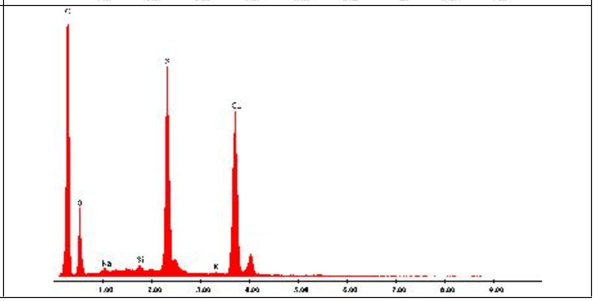
In the surface of the filter1, different particles were observed with sizes from 1 to 20 µm. The average density of the particles in the surface was around 18 particles/mm^2.

The particles found were:

- Mortar particles: the most abundants. Composed of Ca, Si and O with traces of Na, Mg, Al, P, S, K and Ti.
- Calcium carbonate particles: composed of Ca, C and O.
- Gypsum particles: composed of Ca, S and O.
- Aluminium particles: composed of Al and O.

- Siliceous aggregate particles: composed of Si and O.

Table 13. EDAX spectrum and image of the MORTAR-C.

MORTAR-C		
Residue:		
Filter 1 (PC 10µm)		

No evidences of TiO_2 were observed in the filter.

4.3. FRPANEL

The following formulations of glassfiber reinforced composite used as FRPANEL were analysed:

- FRPANEL-Control: Glassfiber reinforced composite by NETCOMPOSITES.
- FRPANEL-1.25%Dellite: Glassfiber reinforced composite + 1.25% nanoclay (Dellite) by NETCOMPOSITES.

4.3.1. Heat Release

Parameters measured in the cone calorimeter are included in the next table:

Table 14. Cone calorimeter results for FRPANEL.

Ref.	t_{ig}	HRR_{max} (kW/m^2)	THR (MJ/m^2)	MARHE (m^2)	Mass loss (%)	TSP (m^2)	SEA (m^2/kg)
FRPANEL-Control	**33**	**271.27**	**85.39**	**191.68**	**59**	**46.5**	**1026.84**
FRPANEL-1.25%Dellite	**30**	**203.39**	**87.62**	**154.85**	**64**	**49.7**	**1034.52**

The samples had comparable results for ignitability (t_{ig}), total heat release (THR) and smoke parameters (TSP and SEA). However parameters related with the spread of flame and fire growth (HRR and MARHE) were improved with nanoclay.

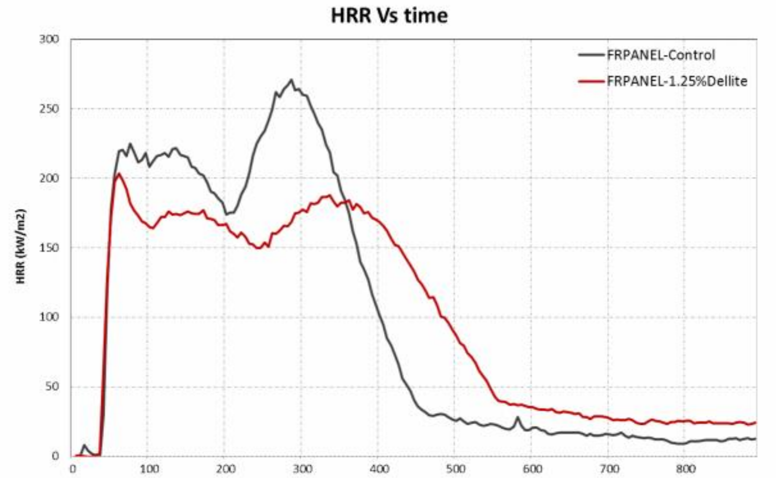


Figure 10. HRR curves of FRPANEL control (black) and +1.25%nanoclay (red).

If we pay attention to the HRR curve, initially both formulations ignite quickly and release important amount of heat. Nevertheless, nanoclay containing sample reach a peak (aprox. 200 kW/m^2) and keep stable in the range of 150-200 kW/m^2 up to 400s when drop. This trend could be justified by the barrier effect of the nanoclay that reduces the total amount of heat received by the composite and the combustion is more constant. In the control sample, the sample reach bigger values of HRR and a second peak (270 kW/m^2) was reached at 300s.

This effect is more noticeable in the case of the ARHE curve:

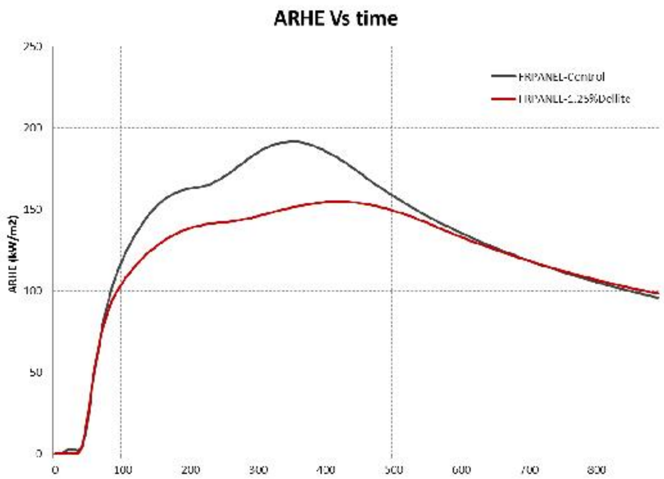


Figure 11. ARHE curves of FRPANEL control (black) and +1.25%nanoclay (red).

As these parameters outline the tendency of the samples to spread and contribute to a fire, the presence of the nanoclays moderately improves the fire performance of the composite.

4.3.2. Smoke opacity

Regarding smoke opacity results in SDC test, the following table shows the main parameters:

Table 15. SDC results for FRPANEL.

Ref.	Ds $_{(4min)}$	Ds_{max}	VOF_4
FRPANEL-Control	**972.07**	**1094.16**	**1796.95**
FRPANEL-1.25%Dellite	**12014.93**	**1320**	**3012.21**

Sample with nanoclay (FRPANEL-1.25%Dellite) emitted more smoke than control material and reach the measurement limit of the equipment (1320).

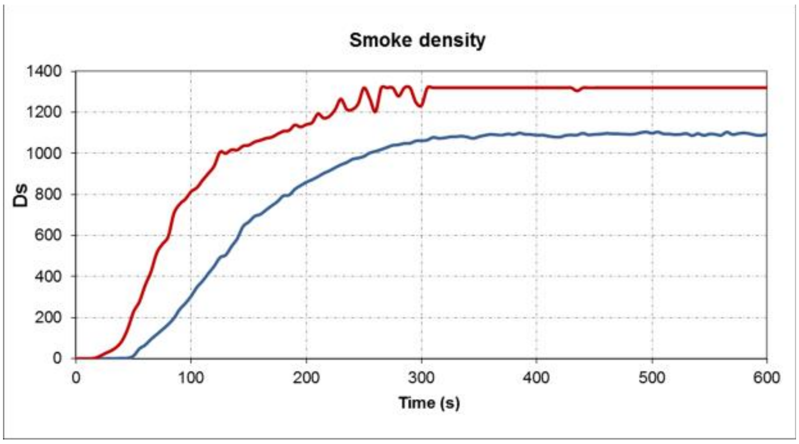


Figure 12. Ds curves of FRPANEL control (blue) and +1.25%nanoclay (red).

The values of VOF_4 and Ds were very high for all the samples and the Ds vastly increase in the first period of the test reaching the maximum value quickly.

4.3.3. Smoke toxicity

The CIT results of the FRPANEL are showed in the following table:

Table 16. FTIR results for FRPANEL.

Ref.	CO_2 (ppm) (40000)	CO (ppm) (1200)	SO_2 (ppm) (100)	HCl (ppm) (50)	HF (ppm) (30)	HCN (ppm) (50)	HBr (ppm) (30)	NO_x (ppm) (20)	CIT_g (8min)
FRPANEL-Control	**37600**	**2154**	**0**	**4**	**2**	**49**	**2**	**21**	**0.338**
FRPANEL-1.25%Dellite	**21600**	**7506**	**7**	**1**	**1**	**197**	**0**	**32**	**0.887**

The toxic gases that contribute significantly to the CIT value were CO, CO_2, HCN and NO_x. In the case of control material, the most oxidized species (CO_2 and NO_x) predominate while for nanoclay composite CO and HCN [1].

In the following graphs, the evolution of the species can be observed at 4min and 8min.

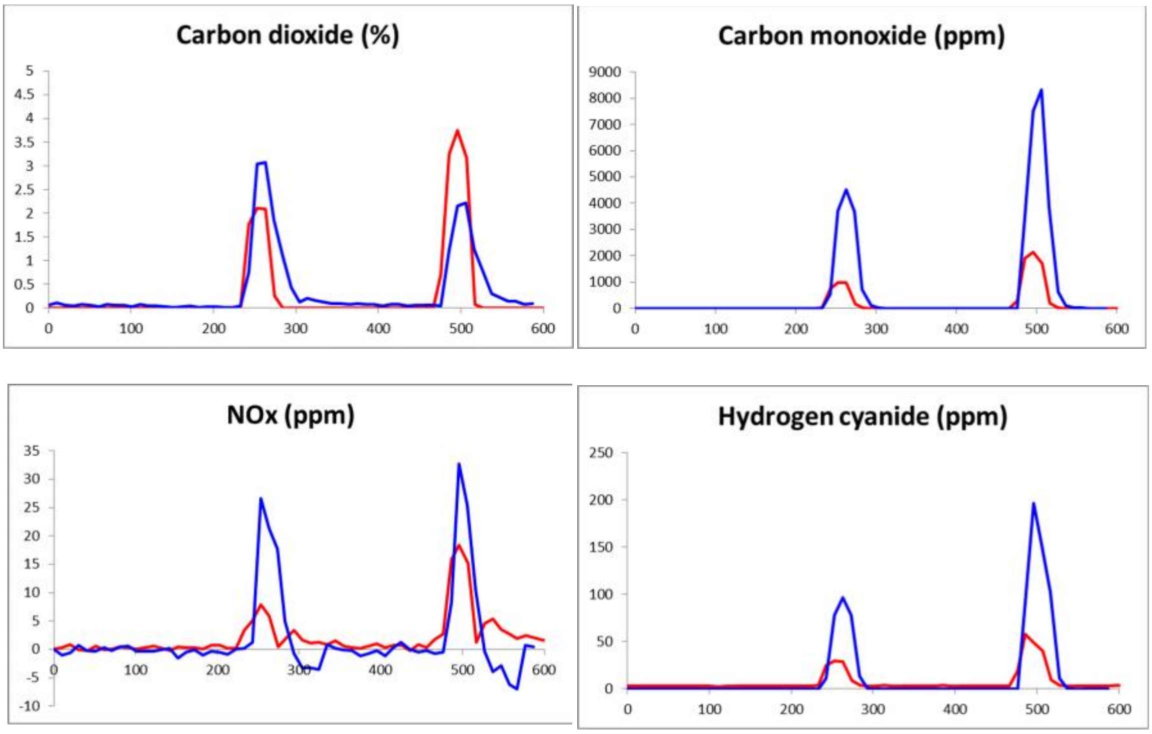


Figure 13. Gas curves of FRPANEL control (blue) and +1.25%nanoclay (red).

Due to the lethality of CO and HCN the toxicity index is double for the nanoclay composite.

4.3.4. Nano-objects in effuents

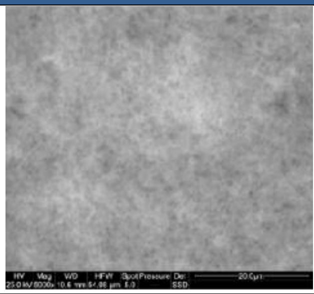
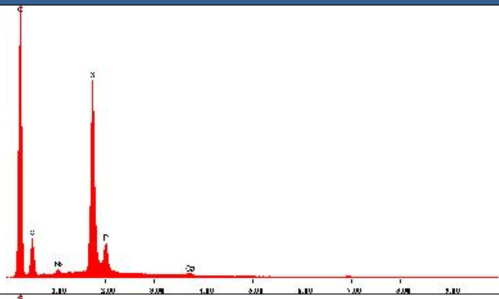
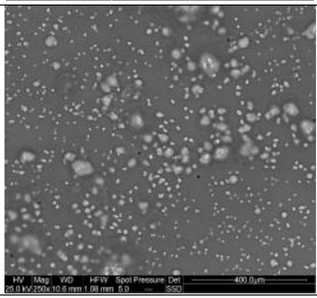
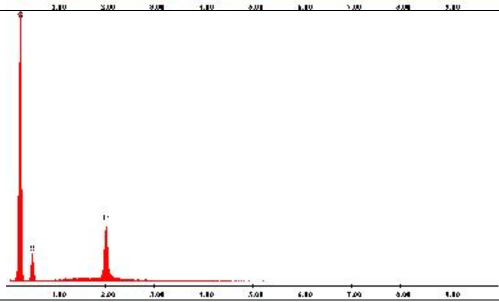
FRPANEL-Control

The residue of the FRpanel–Control sample was a massive and very homogeneous material with a spongy microtexture given by very fine micropores (Ø < 1 µm).
This residue is mainly composed of carbon and oxygen, accompanied by phosphorus.

The filter1 surface contains many heterometric particles (10 <Ø< 100 µm) occupying 15% of the filter surface.
These particles have a very spongy and porous microtexture. Its elemental composition is characterized by the presence of abundant carbon, accompanied by phosphorous and oxygen.
The images in the following tables illustrate the discussed features in addition to the elemental composition of the particles in the residue and the filter.

[1] It is important to note that the contribution of each gas to the total toxicity value is the ratio between the concentration and the limit concentratcion.

Table 17. EDAX spectrum and image of the FRPANEL-Control.

FRPANEL-Control		
Residue:		
Filter 1 (PC 10µm)		

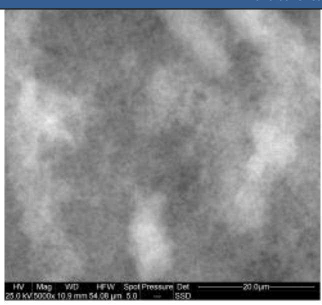
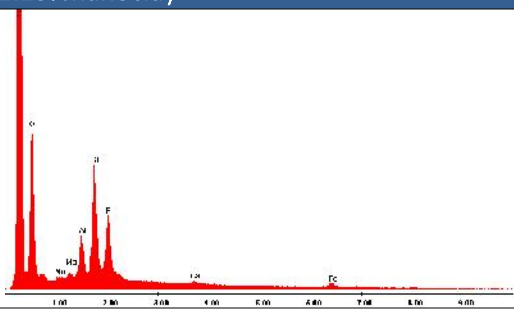
FRPANEL-1.25%Nanoclay

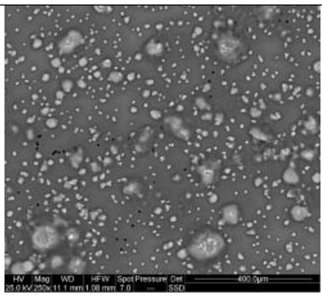
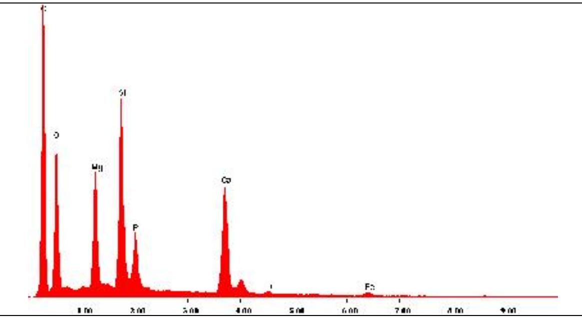
The Residue of FRPanel-1.25%Dellite had a spongy microextructure similar to control material. This residue is mainly composed of carbon and oxygen, accompanied by phosphorus. Occasionally, microparticles were detected (Ø< 10 µm) in which the predominant presence of Si and Al, accompanied by several minor elements such as Na, Mg, Ca and Fe. These particles have a greater relative abundance of aluminium than those found in the residue of the control sample. This fact can be attributed to the presence of clay in the material, so that some of these particles, particularly those containing Mg and Fe, are remnants of Dellite clay.

By the other hand, filter surface contains many heterometric particles (10µm < Ø< 500 µm) distributed occupying 25% of the filter surface.

These particles have a very spongy and porous microtexture. Its elemental composition is characterized by the presence of abundant C, accompanied by P and O.
The images in the following tables illustrate the discussed features in addition to the elemental composition of the particles.

Table 18. EDAX spectrum and image of the FRPANEL-1.25%Nanoclay.

FRPANEL-1.25%nanoclay		
Residue:		

Filter 1 (PC 10µm)		

According to the spectrum of the particle showed in the filter, the presence of Si, Mg, and Fe suggest the possibility of be nanoclay remains. Due to the great amount of C in the filter is complicated to assess the total amount of these particles in the filter. Therefore, FRPANEL was selected as one of the materials to evaluate according to the quantitative method.

4.3.5. Nano-objects in effluents (Quantitative method)

Three tests have been repeated for each formulation; the goal is to analyse potential differences for the two formulations of FR panels concerning *total number concentration* of particles released and *size distribution*, jointly with off line analysis of samples in SEM.

Total Particle Concentration (#/cm^3).

The table 19 collects the results concerning total number concentration (#/cm^3) of the measurements performed with the ELPI+ and the CPC3775.

Table 19. Summary of data measured with ELPI+ and CPC (total number concentration) during the tests.

Ref.	CPC 3775 (#/cm3)	ELPI (#/cm3)
	Prom	Prom
FRPANEL-Control A1	1.44E+05	7.81E+05
FRPANEL-Control A2	1.50E+05	7.33E+05
FRPANEL-Control A3	1.31E+05	5.53E+05
MEAN (FRPANEL-Control)	**1.41E+05**	**6.89E+05**
FRPANEL-1,25%Dellite B1	1.23E+05	5.82E+05
FRPANEL-1,25%Dellite B2	1.20E+05	5.65E+05
FRPANEL-1,25%Dellite B3	1.17E+05	5.31E+05
MEAN FRPANEL-1,25%Dellite B3	**1.20E+05**	**5.59E+05**

As can be observed in the table, the results of the three tests are very consistent and repetitive for each material.

Comparing both formulations, the data from ELPI and CPC show that FRPANEL-Control releases slightly more particles than the formulations with nanoclays. For instance, considering the measurements from ELPI+ the mean concentrations for each one are 6.89E+05 and 5.59E+05 (#/cm^3) respectively. This can be also observed in next figure 14 where it is represented the number concentration for the two materials measured with the CPC3775 (data for the second test in both cases).

NOTE: differences among the data reported by CPC3775 and ELPI may be due to constrains in the experimental set-up; however the results are consistent and valid to establish differences among materials.

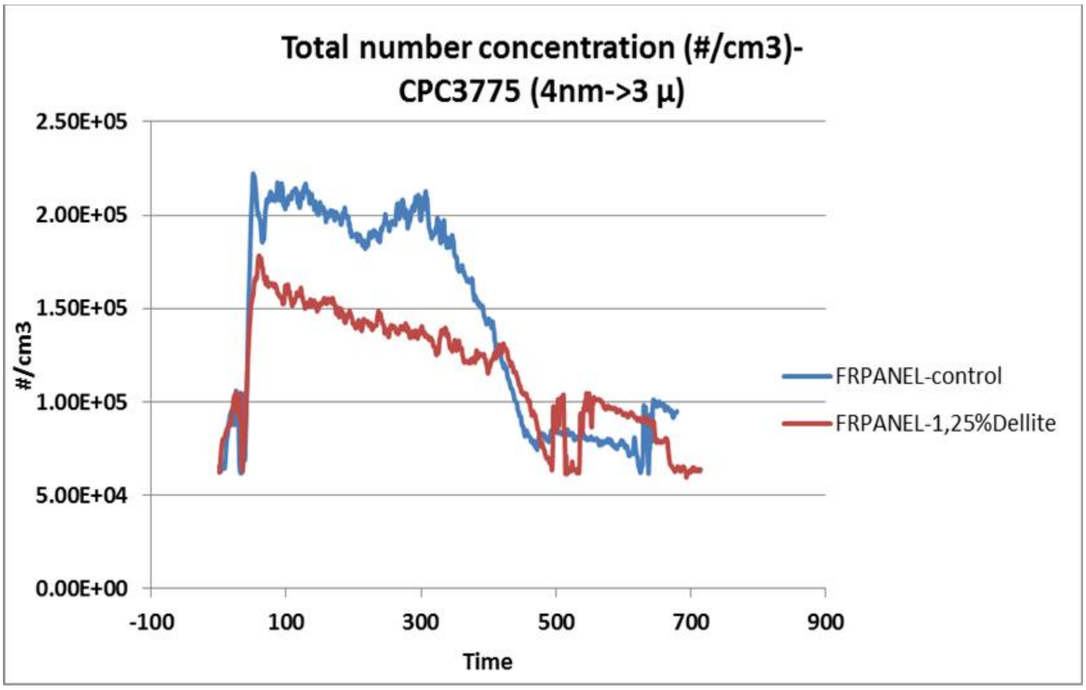


Figure 14. Total number concentration for formulations FRPANEL-control and FRPANEL 1,25%Dellite (data from CPC3775).

This result is in coherence with the data by Motzkus[8] who also reported that the particle number concentration measured with a CPC for submicronic particles (< 1µm) was lower for formulations with nanoparticles (combustion of PMMA matrix with silane).

Size Distribution

Data from ELPI have been analysed to study the size distribution of the particles released for the two materials (see figure 15). As can be observed in the figure, the particles released show a mode around 200 nm, similarly for both materials (although the control material show a higher pick due to the higher concentration of particles released).

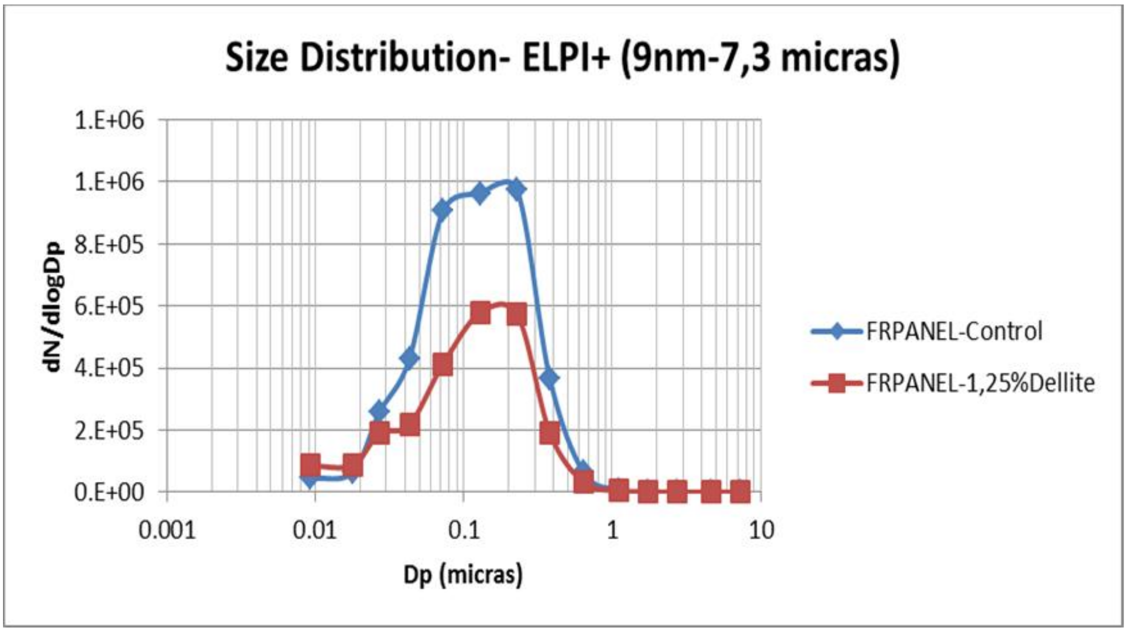


Figure 15. Size distribution of the particles released (data from ELPI+).

SEM Analysis

It has been analysed the stage 3 of Dekati PM10 impactor ("cut-point" 1µ based on specifications) for the two materials (see Figure 16). As can be observed:

- The particles observed are mainly soot particles (aggregates of elemental soot particles around 100 nm size) for both materials. Figure 17 shows and example of soot particle for the control material.

- In both materials, the soot particles are commonly accompanied with other particles with metal elements ((Zn, Pb, Fe, Mn, Cr, etc) and also silica (see figure corresponding to the FRPANEL-1,25%Dellite). These metal particles may be impurities from the cone calorimeter.

- It has not been identified free particles of nanoclay in the FRPANEL-1,25%Dellite; however, the analysis does not allow to discriminate in the mix of metal particles mentioned above, and also clay particles may be included.

FRPANEL-Control A1

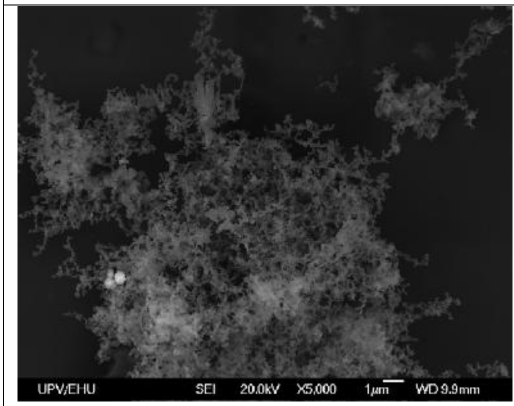
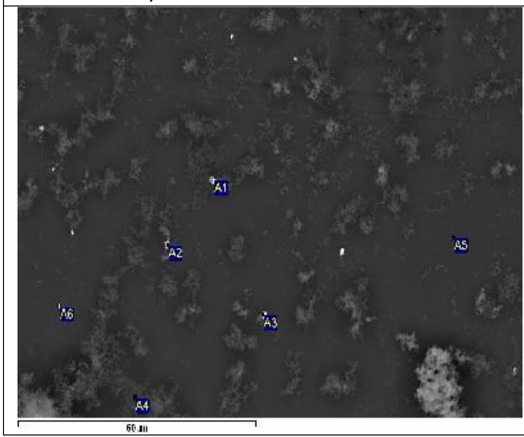


Figure 16. SEM image of FRPANEL-Control A1.

FRPANEL-1,25%Dellite



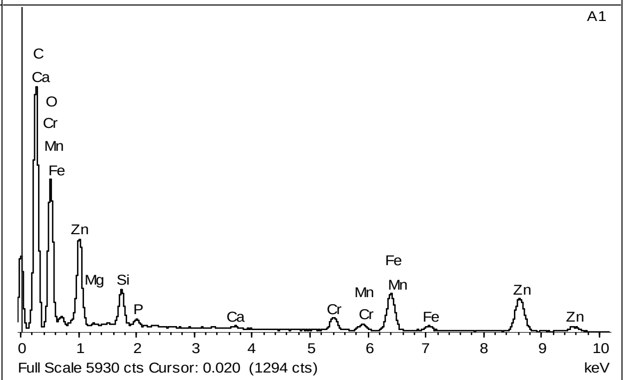


Figure 17. SEM image of FRPANEL-1,25%Dellite.

4.4 INSULATION FOAM

The following formulations of insulation foam were analysed:

- PUR-FOAM-Control: Polyurethane foam by ACCIONA
- PUR-FOAM+0.5%NCC: Polyurethane foam + 0.5% nanocellulose crystals by ACCIONA.

4.4.1 Heat Release

It was complicated to obtain samples with the same dimensions and the same weight due to the problems for cutting the foams and obtain similar thickness. Furthermore, the low density of the foams gives it a very low mass and small differences lead to large differences in the cone calorimeter. Parameters measured in cone are included in the next table:

Table 20. Cone calorimeter results for FOAM.

Ref.	t_{ig}	HRRmax (kW/m^2)	THR (MJ/m^2)	MARHE (m^2)	Mass loss (%)	TSP (m^2)	SEA (m^2/kg)
FOAM-Control	**5**	**232.47**	**16.13**	**164.15**	**79**	**8.1**	**1005.90**
FOAM-0.5%NCC	**6**	**182.68**	**10.43**	**124.24**	**79**	**4.5**	**819.68**

Despite the small concentration of nanocellulose (0.5%), heat release and smoke parameters were improved significantly.

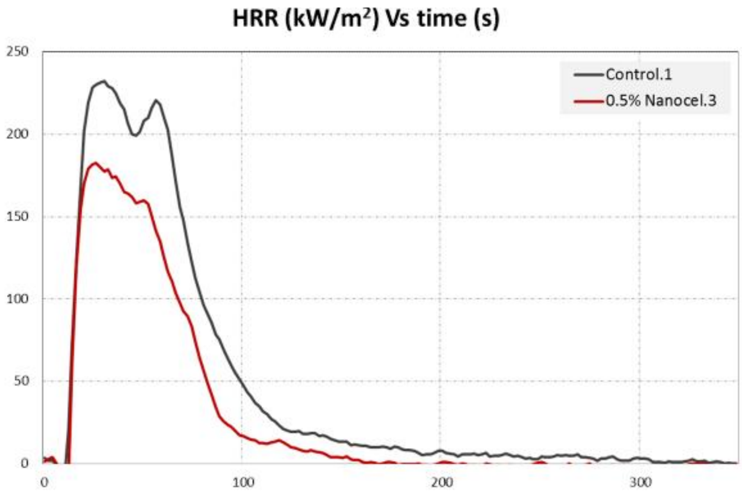


Figure 18. HRR curves of FOAM control (black) and +0.5%NCC (red).

pHRR was reduced by 28% and THR by 38%. Nevertheless, ignitability parameter (t_{ig}) was not improved and maintain very high (5-6 seconds).

4.4.2. Smoke opacity

Table 21. SDC results for FOAM.

Ref.	Ds $_{(4min)}$	Ds_{max}	VOF_4
FOAM-Control	**205.98**	**210.81**	**648.70**
FOAM-0.5%NCC	**180.95**	**188.15**	**634.49**

As observed in cone for smoke parameters (TSP and SEA), smoke density of nanocellulose treated foam was lower than control foam. Ds values were improved by 10%. This trend can be observed in the next graph:

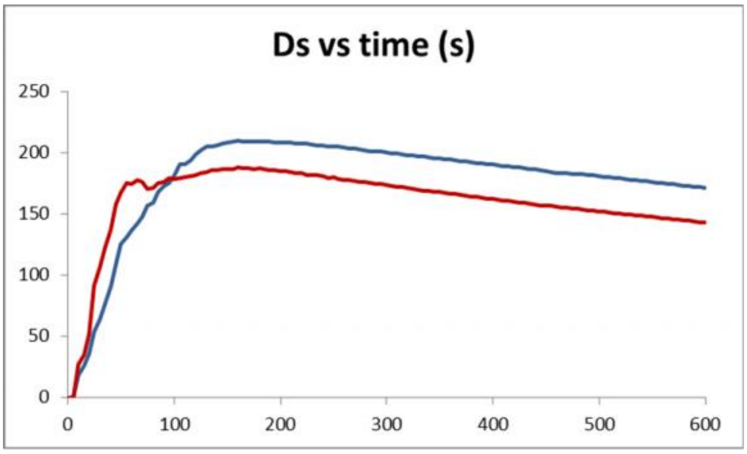


Figure 19. Ds curves of FOAM control (blue) and +0.5%NCC (red).

4.4.3. Smoke toxicity

The CIT values of the two formulations are comparable.

Table 22. FTIR results for FOAM.

Ref.	CO_2 (ppm) (40000)	CO (ppm) (1200)	SO_2 (ppm) (100)	HCl (ppm) (50)	HF (ppm) (30)	HCN (ppm) (50)	HBr (ppm) (30)	NO_x (ppm) (20)	CIT_g (8min)
FOAM-Control	**14400**	**253**	**0**	**1**	**0**	**20**	**1**	**17**	**0.131**
FOAM-0.5%NCF	**23000**	**175**	**0**	**1**	**0**	**5**	**0**	**22**	**0.134**

Due to the low density of the material (foam), the total amount of toxic gases released was moderate so the values of CIT were quite low.

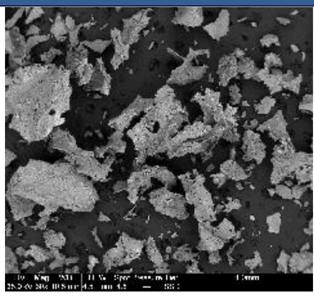
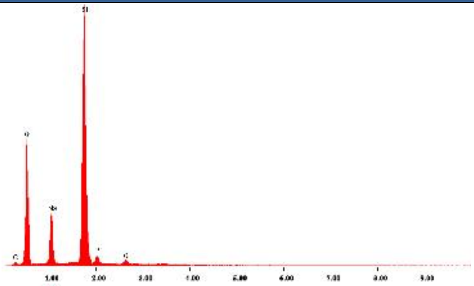
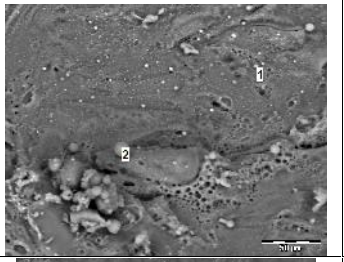
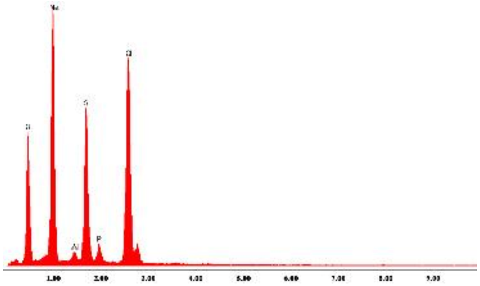
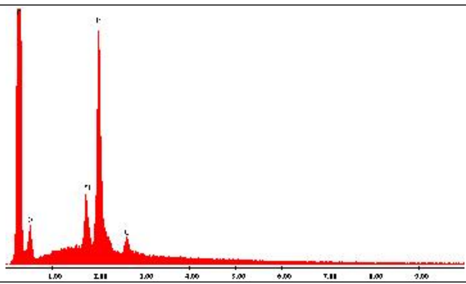
4.4.4. Nano-objects in effuents

FOAM-Control

FOAM-Control residue is mainly composed of Si, O and Na, accompanied by Cl, P and C. Tiny particles (Ø < 5 µm) of sodium chloride were also detected, together with O, Si, Al and P.

The material of the Filter1 was a spongy, massive and very homogeneous with a very porous microtexture (Ø < 1 µm). This material is composed mainly of C, accompanied by P, Cl, Si and O. In this fluffy residue were microparticles (Ø < 300 µm) of various kinds. The most common were rich in P, usually Si, O and Cl. The diameter of these aggregates was not usually exceed 100 µm maximum and the aggregates were randomly distributed.

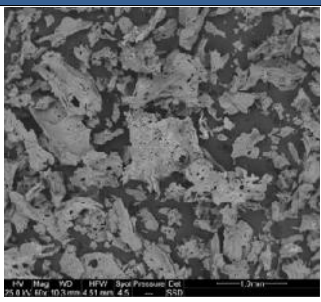
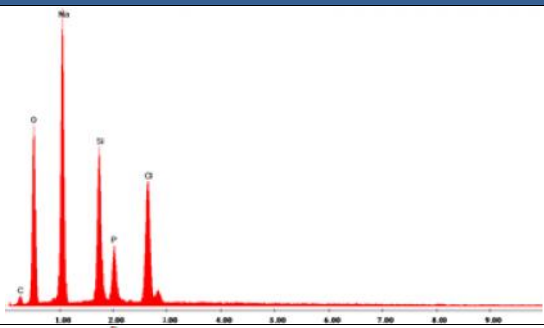
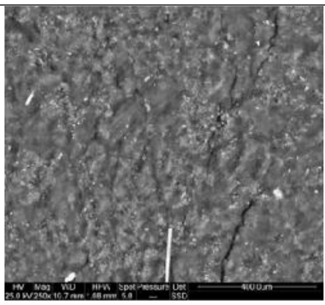
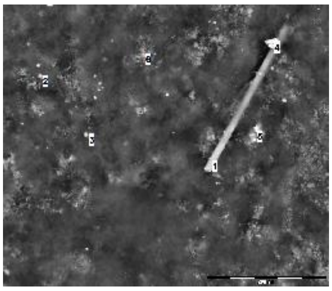
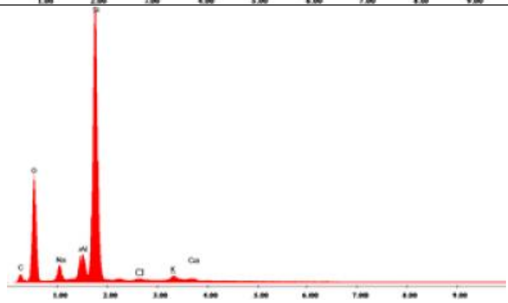
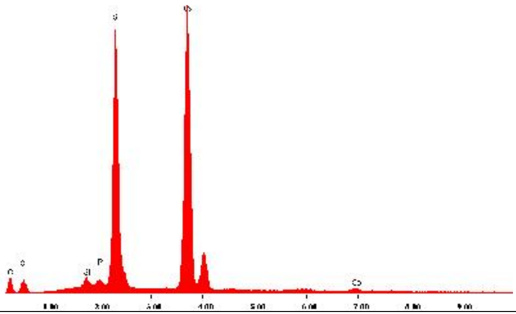
Table 23. EDAX spectrum and image of FOAM-Control.

FOAM-Control		
Residue:		
		
Filter 1 (PC 10µm)		
	.	

FOAM-0.5%NCC

The residue and the filter of FOAM+0.5%NCC were very similar to FOAM-Control one and no remarkable differences were observed.

Table 24. EDAX spectrum and image of FOAM-0.5%CNF.

FOAM-0.5%NCF		
Residue:		
Filter 1 (PC 10µm)	 	 

As could be expected, the combustion temperatures reached by the sample (>600ºC) completely decompose the nanocellulose and no residue was observed. This data corroborate the comparable data of mass loss (79%) for both samples in cone

4.5. COMPOSITE

The following formulations of COMPOSITE were analysed:

- COM-Control: Composite by ACCIONA
- COM+0.5%CNF: Composite + 0.5% carbon nanofibers by ACCIONA.

4.5.2. Heat Release

The following table summarizes the data obtained in cone calorimeter:

Table 25. Cone calorimeter results for COMPOSITE.

Ref.	t_{ig}	HRRmax (kW/m^2)	THR (MJ/m^2)	MARHE (m^2)	Mass loss (%)	TSP (m^2)	SEA (m^2/kg)
COM-Control	**78**	**656.29**	**156.81**	**286.16**	**34**	**52.7**	**981.78**
COM-0.5%CNF	**61**	**644.76**	**164.74**	**296.27**	**34**	**55.6**	**1052.02**

The samples had comparable results with small differences within the uncertainty of the test.

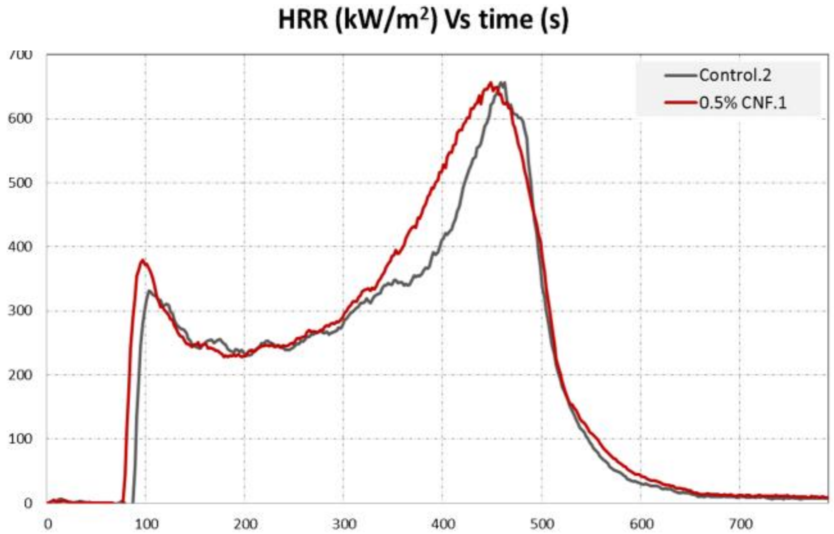


Figure 20. HRR curves of COMPOSITE control (black) and +0.5%CNF (red).

As can be observed in HRR graph, the shapes of the two curves were analogous with slight differences in the t_{ig} and the THR which were worse for the CNF formulation. This trend was better represented by the ARHE curve:

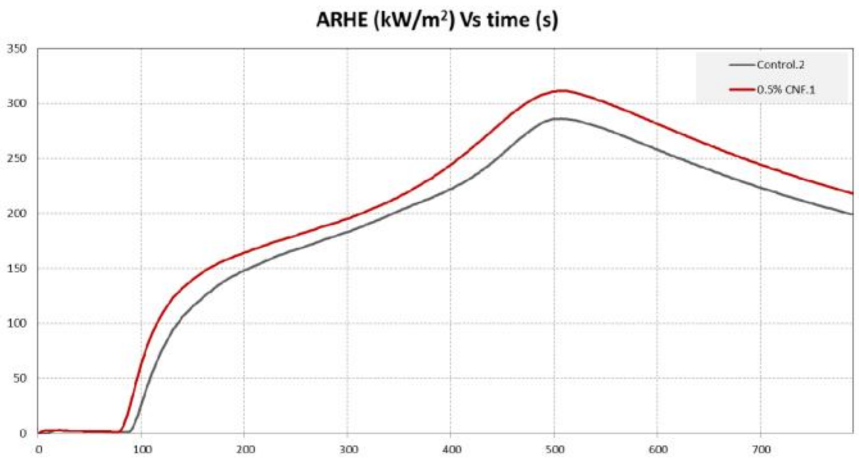


Figure 21. ARHE curves of COMPOSITE control (black) and +0.5%CNF (red).

4.5.3. Smoke opacity

Table 26. SDC results for COMPOSITE.

Ref.	$Ds_{(4min)}$	Ds_{max}	VOF_4
COM-Control	695.03	1320	677.30
COM-0.5%CNF	765.02	1320	1109.46

Smoke opacity parameters are comparable instead of the values of VOF_4. The peaks observed in the two curves are caused by the ignition of the samples and the change in the chamber pressure rather than a "real" opacity change.

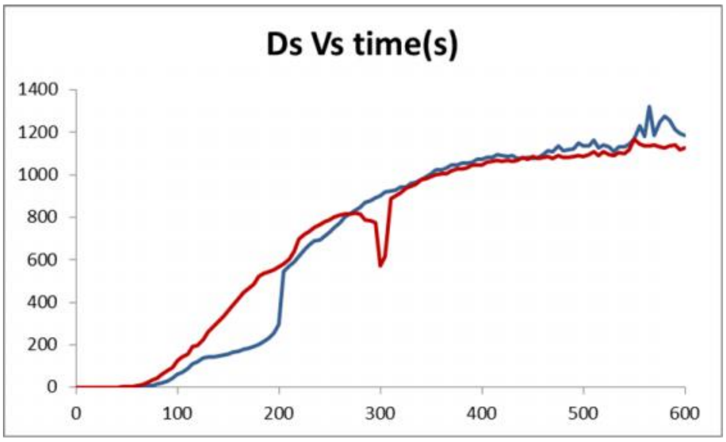


Figure 22. Ds curves of COMPOSITE control (blue) and +0.5%NCC (red).

4.5.4. Smoke toxicity

Table 27 shows the results obtained for the composites formulation.

Table 27. FTIR results for COMPOSITE.

Ref.	CO_2 (ppm) (40000)	CO (ppm) (1200)	SO_2 (ppm) (100)	HCl (ppm) (50)	HF (ppm) (30)	HCN (ppm) (50)	HBr (ppm) (30)	NO_x (ppm) (20)	CIT_g (8min)
COM-Control	**30200**	**2029**	**0**	**8**	**1**	**113**	**5**	**136**	**0.750**
COM-0.5%CNF	**25500**	**1941**	**0**	**14**	**0**	**97**	**3**	**110**	**0.637**

The toxic gases that contribute significantly to the CIT value were CO, CO_2, HCN and NO_x. The two samples released similar amounts of each gas being slightly higher for the control material.

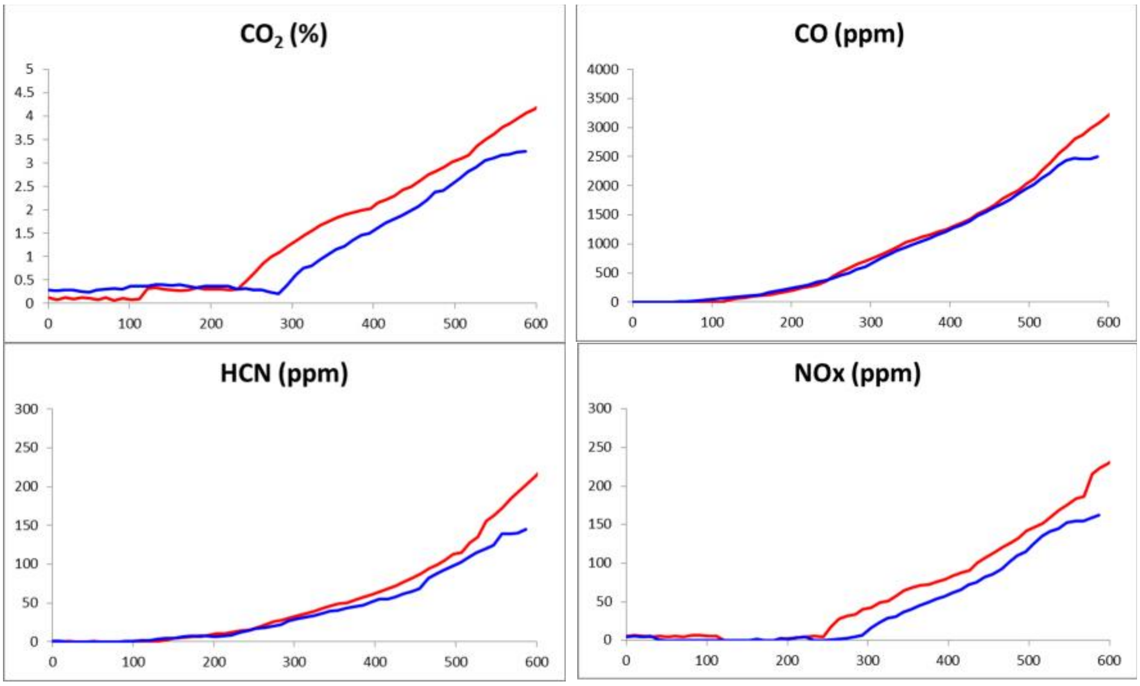


Figure 23. Gas curves of FRPANEL control (blue) and +1.25%nanoclay (red).

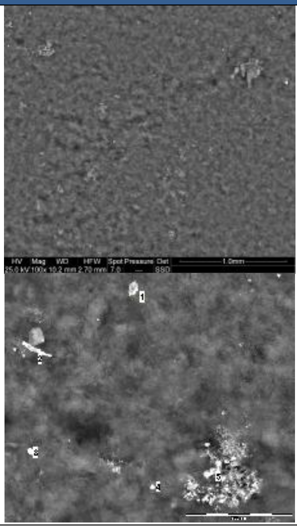
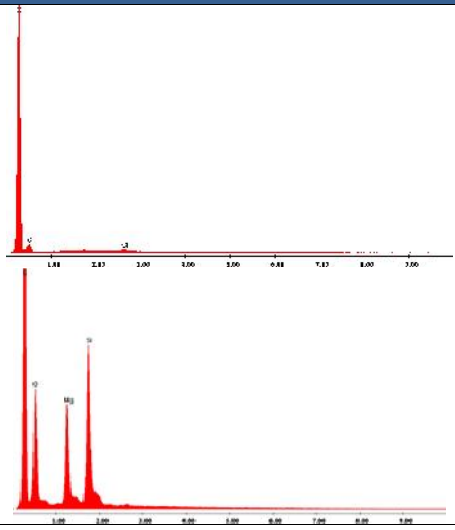
As well as toxicity values of FRPANEL, COMPOSITE samples showed very high figures for CIT_8.

4.5.5. Nano-objects in effuents

COMPOSITE-Control

Apart from the glassfiber, no combustion residue was identified for EDAX analysis.
The filter surface of COMPOSITE-control was composed mainly of C. In this fluffy residue various kinds of microparticles (Ø <100µm) were observed. The most common were rich in P, usually associated with Si and Ca, and often occur in irregular lumpy and very porous aggregates. These aggregates did not exceed 180µm maximum diameter and were randomly distributed.

Table 28. EDAX spectrum and image of COM-Control.

COM-Control		
FILTER 1 (PC 10µm)		

COMPOSITE-0.5%CNF

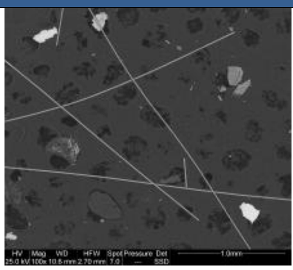
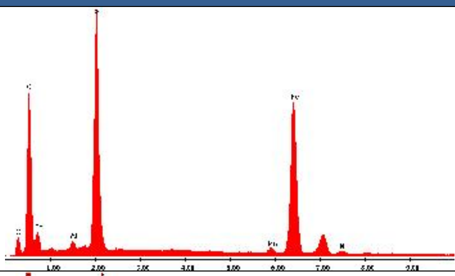
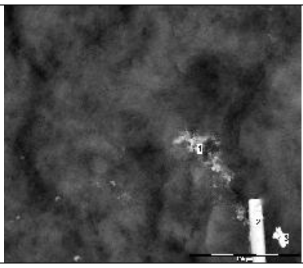
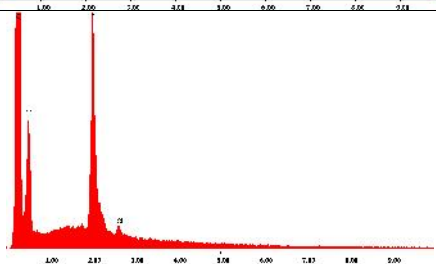
In the residue of COMPOSITE+0.5 %CNF sample there were two morphological types of particles: needle (Ø<2.5µm) and granular. The acicular particles found rarely exceed 2.5 mm length and 20µm thick. They were composed mainly of Si, Ca, Al and O.

Different types of granular particles were identified:

- C rich particulate. Have rounded edges and appear to be remnants of unburned organic material.
- Si rich particles. Si was usually associated with Na and O, also have associated Cl and P.
- Metallic particles. Typically rich in Fe with Cr, Mn and Ni associated in varying proportions.

The images in the following table illustrate the discussed features and EDX spectrum of the most representative particles was plotted.

Table 29. EDAX spectrum and image of COM-0.5%CNF.

COM-0.5%CNF		
Residue:		
Filter 1 (PC 10µm)		

5. CONCLUSIONS

This report includes the results for the study of the impact of the nanoparticles in some selected construction products exposed to an accidental fire. Properties of reaction to fire (inflammability, fire spread, additive nanoparticles in effluents, smoke opacity and toxicity) were compared with reference materials. Table 30 summarizes the results obtained for each parameter and the impact of the nano-objects on them (Table 31 shows the criteria for risk assessment).

Table 30. Reaction to fire results of the SCAFFOLD products.

Ref.	FIRE PROPAGATION		SMOKE DENSITY		PARTICLES IN EFFLUENTS*		SMOKE TOXICITY	
	MARHE		Ds		Nano-objects		CIT_g (8min)	
CONC-A	-		67.42		-		0.009	
CONC-C	-		243.96	↑	n.d.		0.063	
MORTAR-A	-		77.92		-		0.014	
MORTAR-C	-		31.37	↓	n.d.		0.012	
FRPANEL-Control	191.68		1094.16		-		0.338	
FRPANEL-1.25%Dellite	154.85	↓	1320		Indication		0.887	↑
FOAM-Control	164.15		210.81		-		0.131	
FOAM-0.5%NCC	124.24	↓	188.15	↓	n.d.		0.134	
COM-Control	286.16		1320		-		0.750	
COM-0.5%CNF	296.27		1320		n.d.		0.637	

**Particles in effluents related with the release of the nanoparticles used in the material (CNF, TiO_2, SiO_2, NCC, nanoclay). It is possible that other nanoparticles of combustion but they are not the aim of this study.*

Table 31. Risk assessment criteria for the selected parameters.

PARAMETER	RISK LEVEL			
MARHE	0-75	75-150	150-225	>225
Ds	0-150	150-300	300-600	>600
Nano-objects	n.d.	Low conc	Mid conc.	High conc.
CIT_8	0-0.1	0.1-0.3	0.3-0.5	>0.5
↓	Presence of nano-object improve the parameter			
↑	Presence of nano-object worsen the parameter			

The main conclusions are:

- As expected, inorganic materials (concrete and mortar) have good performance and only in the case of nanoSiO_2 worsen the smoke parameters of the concrete.

- For the insulation product (PUR foam) the presence of nanocellulose crystals improves the heat release parameter (MARHE) and the smoke opacity (Ds). The figures for all the parameters are moderates.

- For glass reinforced composites (FRPANEL and COMPOSITE) the values are very high, particularly smoke related parameters. The effect of the CNF in COMPOSITE fire performance is despicable. Regarding FRPANEL, the nanoclay improve the heat release parameters and decrease the smoke parameters.

- Two methods for the identification of nanoparticles in the effluents of combustion products have been developed in qualitative and quantitative approaches.

- Concerning qualitative approach, only evidences of nano-objects (nanoclay) was observed for FRPANEL but just few particles attached to the soot.

- Concerning quantitative approach (applied to the FRPANEL), it is showed that the emission of submicronic particles (< 1µ) is higher for the control material than for the formulations doped with nanoclay. Analysis of the morphology of the particles released showed no differences between formulations control and doped. The particles released are mainly soot accompanied with other metal particles and also silica in some cases; the origin of these particles is difficult to determine and could be impurities from cone calorimeter or from the glass fiber or the nanoclays from the material. No free particles of nanoclay have been identified.

6. REFERENCES

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