



Retardateurs de flamme et
Toxicité

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PolyFlame est une newsletter à destination des chercheurs et des industriels du domaine du «comportement au feu des matériaux organiques». Cette newsletter périodique est publiée via la Société Chimique de France (SCF).

Le débat lié aux risques toxicologiques et environnementaux des retardateurs de flamme halogénés a fait couler beaucoup d'encre depuis une quinzaine d'années. Quelques retardateurs de flamme halogénés ont déjà été interdits par des réglementations spécifiques telles que la directive RoHS et/ou le règlement REACH. Les avis sont encore partagés sur le sort des retardateurs halogénés, notamment bromés. Certains chercheurs considèrent que les risques doivent être évalués au cas par cas tandis que d'autres sont pour une interdiction générale des retardateurs de flamme halogénés.

D'autre part, l'utilisation des nanoparticules dans les systèmes ignifugeants suscite de nouvelles questions sur le devenir des nanoparticules lors de l'incinération des nanocomposites.

Le présent numéro, «PolyFlame N°9», est consacré à la toxicité des retardateurs de flamme et à la fin de vie des matériaux contenant des nanoparticules. Ce numéro est un premier numéro sur ce sujet. Par ailleurs, nous sommes ouverts à toutes propositions d'articles sur cette thématique.

Les articles publiés dans ce numéro n'engagent que leurs auteurs. Ils ne reflètent pas nécessairement les vues ou les opinions de l'équipe rédactionnelle de PolyFlame.

Le premier article concerne la toxicité des retardateurs de flamme. Son auteur est Marcelo M. Hirschler (GBH International). L'article a été publié pour la première fois par SPFE (Society of Fire Protection Engineers) dans le magazine «Fire Protection Engineering». Nous remercions Marcelo de nous avoir autorisés à le publier. Afin d'éviter toute erreur liée à la traduction, nous avons décidé de publier cet article en anglais. Le deuxième article est consacré à la fin de vie des nanocomposites et présente différentes études réalisées sur ce sujet.

Bonne Lecture,

Flame Retardants and the Associated Toxicity

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(GBH International)

Flame retardants are incorporated into materials, to improve their fire performance, normally by slowing fire development. They are either added into an existing polymeric material (natural or synthetic) or reacted with other raw materials to create a new material so that the resulting material exhibits improved fire performance. This typically results in a decrease in the amount of combustion products released in a fire [1].

Smoke toxicity and heat release are key factors in fire hazard, together with flame spread and ignitability. In fact, "inhalation of combustion products" is listed as the cause of death for

some 2/3 of all fire victims. It is rare for multiple fire fatalities to occur in fires that have remained small. In the United States more than 83% of fire deaths in building fires happen in fires that have become very large. Such fires are large enough that they extend beyond the room of origin, and thus generate too much toxic smoke for survival [2]. The inherent toxic potency of smoke resulting from burning most combustible materials falls within a narrow range, so that there is no non-toxic smoke. Therefore, releasing lower mass of combustibles is essential to lower the overall toxicity of a fire atmosphere. Moreover, the key fire property controlling

the loss of human tenability in fires is the heat release rate of the burning materials [3], which governs the intensity of a fire and can vary by orders of magnitude for common combustibles [4]. Thus, toxic hazard is a more direct function of heat release rate rather than of the toxic potency of the smoke.

Table 1 [3] shows predicted survival time from an upholstered

Product	Survival time
Chair (base case)	> 10 min
Chair igniting twice as fast	> 10 min
Chair with twice as high toxic potency	> 10 min
Chair with twice as high heat release rate	3 min

Table 1. Effects of Fire Properties on Survival Time

During the 1970'S and 1980's there was a belief that burning plastic materials produced smoke that was far more toxic than smoke from burning natural products such as wood, wool, or cotton. A number of studies have been done to compare the amount of carbon dioxide, carbon monoxide, and hydrogen cyanide produced by natural and synthetic materials under flaming and nonflaming conditions in order to model smoke toxicity. This work resulted in the development of multiple small-scale smoke toxicity test methods, all of which gave varied and narrow rankings for materials, resulting in limited applicability to predicting outcomes of fire events. Toxicologists studying toxicity data consider that ranges of toxicity are measured in orders of magnitude step changes, while most combustible materials produce data that are comparable and differences between materials is generally of minor importance to the overall toxicity of smoke [5]. In other words the smoke toxicity of virtually all materials, natural or synthetic, is almost identical, within the margin of error.

Effects of Individual Combustion Products on Fire Victims

A pair of studies involving over 5,000 fatalities (between fire victims and non-fire victims or carbon monoxide(CO) inhalation) addressed: (a) a period between 1938 and 1979 in a localized area (Cleveland, OH) and (b) a countrywide study in the early 1990s [6]. They found remarkable similarities between the populations of victims: they all died primarily of CO asphyxiation. Other studies have shown that the fraction of any combustible converted into CO in a large (typically flashover) fire is approximately 0.2 g/g [7-8]. By combining the

chair fire in a standard room. The data show the different results from varying toxic potency of smoke versus heat release and the dramatic survival time declines for the latter. This is a very important concept, because it puts into perspective the importance (or lack of it) of smoke toxic potency data in terms of fire hazard assessment, or simply of fire safety.

conclusions of the studies above and others it can be concluded [9] that:

- There is excellent correlation between fire fatalities and the concentration of carbon monoxide absorbed in blood as carboxyhemoglobin (COHb).
- COHb concentrations in blood are the same (when comparing populations of the same type) in fire and non-fire CO deaths (e.g. defective space heater incidents).
- Fatalities can be linked to COHb levels as low as 20%, and any COHb level above 30-40% is usually lethal.
- The toxicity of fire atmospheres is determined almost solely by the amount of CO, since there is no difference in the COHb levels in blood of victims of poisoning by pure CO or in fire victims, once other exposure factors have been considered.
- The concentration of CO in fire atmospheres is roughly 20% [10], irrespective of what materials have burnt.
- It is rarely important to measure individual toxic gases for hazard assessment purposes, for any materials, including flame retardant additives.
- The primary usefulness of measuring toxic gases issued by burning materials is usually in terms of material development so as to understand its fire performance.
- The most immediately dangerous chemicals produced during all fires are those that behave as chemical asphyxiants, such as CO, responsible for most deaths in fires, and hydrogen cyanide, along with smaller contributions by irritants such as hydrogen halides or oxides of nitrogen.
- Moreover, the smoke toxicity of virtually all materials is almost identical [9-10].

The overall conclusion from a large body of research is clear:

fire fatalities are overwhelmingly associated with heat release since when heat release rate increases it leads to more CO generated. Thus, as fires become bigger, they have higher smoke toxicity, while other causes of fire deaths are of minor importance.

Types of Flame Retardants and their Effects

Seven key chemical elements are known to interfere or disrupt combustion: chlorine, bromine, phosphorus, aluminum, boron, antimony and nitrogen [11]. These elements are not used as such but provide the essential functionality into substances known as flame retardants. A flame retardant could contain one or more of these elements. Flame retardants act by various mechanisms, including free radical gas phase quenching, physical barrier formation by charring or contribution of water. Flame retardants improve fire performance by interfering with the availability of fuel, oxygen or ignition source (fire triangle components). Effective flame retardant designs are rarely composed of a single flame retardant and may (depending on the substrate) contain a multiplicity of chemicals.

Two of the elements mentioned (chlorine and bromine) are known as halogens (another halogen exists, fluorine, which is not used in flame retardant additives but is found as part of polymers known as fluoropolymers). Halogenated flame retardants are generally considered the most effective and can be used at some of the lowest concentrations. During combustion free radicals containing bromine or chlorine quench the fuel source in the gas phase. On the other extreme, some purely inorganic materials (such as metal hydroxides: alumina trihydrate or magnesium hydroxide) are used to provide water, released during combustion to lower gas phase temperatures. Such flame retardants are the highest volume products used commercially but have limited applicability because they need to be used at very high concentrations, often resulting in deleterious effects to properties of the substrate material, such as flexibility. Between these extremes are phosphorus-containing materials, which can form protective char barriers on the surface of a burning material. Their performance and applications is often improved by including other elements, such as nitrogen or a halogen. Flame retardants are also used in combination with other additives (to improve the functionality of the base flame retardant) that affect fire performance or lower smoke release. They include materials based on molybdenum, tin, zinc and sulfur compounds.

Flame retardants cannot make materials “fire proof”. Flame retardants are an important first line of defense in the case of fire by slowing the combustion process (or even preventing it) and by lowering the resulting heat release and flame spread. A large and sustained heat input can overwhelm the effect of flame retardants and the material can still burn. Flame retardant materials are being developed continually, and the total number of flame retardant additives that have been used commercially can be counted in the thousands, since the first one used commercially in the 1700s [12-14].

Smoke Toxicity of Flame Retarded Materials

The overall smoke toxicity of materials containing flame retardants is not significantly different from that of materials that do not contain flame retardants (as discussed above). In fact, properly flame retarded materials will generate less mass of smoke and combustion products, thus causing fire atmospheres to be less toxic (as shown in a famous NBS study [15]). Thus, the use of flame retarded materials will not alter the smoke toxicity in fire atmospheres. The basic function of flame retardants in interfering with the combustion process means that there will be more incomplete combustion. However, as discussed above, in large fires the fraction of burnt material converted into CO is fairly constant, at 20% [7-9] so that there is no significant effect of flame retarded materials in actual fires.

Halogenated materials (including ones with halogenated flame retardants) will contribute halogenated effluents, including acid gases, which will contribute to the acute toxicity of fire atmospheres, although it is normally overwhelmed, as discussed above, by the toxicity of CO. In some cases, the thermal decomposition or combustion of halogenated materials generates small amounts of polyhalogenated dioxins and furans as components of the associated smoke. The composition of emitted gases will depend not just on the material burnt but also on the presence of catalysts (including metals like copper) and the fire intensity. The concentrations of these gases are so small that they are not associated with acute smoke toxicity but with the chronic effects resulting from fires. In fact, the advances in analytical and detection techniques mean that scientists can now detect the presence of materials, or derivatives of materials, at levels so small as to not be meaningful. Thus, they may affect primarily those facing repeat exposures like firefighters.

Some of these halogenated dioxins and furans fall into the

category of known human carcinogens, and thus research has analyzed smoke and soot residues to determine their concentrations during and after fires. A plethora of research has shown that all fire atmospheres contain large amounts of known carcinogens, especially polynuclear aromatic hydrocarbons (PAH), including benzo[a]pyrene [BAP], formed by all burning materials. In fact, BAP is the one combustion product with the highest level of toxic carcinogenicity. Therefore, work has been done comparing the toxic effects of dioxins and furans with those of PAHs. It was found that the concentrations of dioxins and furans in particulate residues were at levels 4,000 times lower than those of PAHs [16-19]. Moreover, analysis of pollutant data gathered from two well-documented German catastrophic fires found that PAH levels were thousands of times higher than those of polyhalogenated dioxins and furans [20]. Essentially, all reports to date indicate that dioxins and furans pose only a very minor exposure risk while the exposure risk to known human carcinogenic components, like PAHs, is extremely high and unaffected by the presence of halogenated compounds in a fire.

Inherent Toxicity Issues Associated with Individual Flame Retardants

The vast majority of flame retardants are not carcinogens, mutagens or reproductive toxins, and are neither bio-accumulative nor have acute toxicity. In 2000, the US National Research Council (Committee on Toxicology, Subcommittee on Flame-Retardant Chemicals, NRC) presented findings to the US Consumer Product Safety Commission (CPSC) and the US Congress [21-22]. The work analyzed the inherent toxic effects of individual flame retardants or flame retardant classes, both on their immediate effects (acute) and on their long-term effects (chronic), with primary focus on the latter. This was done by analyzing the toxicological and exposure data on 16 key flame retardant chemicals to assess potential health risks to consumers (primarily in residential furniture). The subcommittee was also asked to identify data gaps and make recommendations for future research. NRC made assessments to determine whether causal relationships existed between the dose of each chemical and each adverse health effect by reviewing human (epidemiological studies, clinical observations, and case reports) and laboratory animal data on neurotoxicity, immunotoxicity, reproductive and developmental

toxicity, organ toxicity, dermal and pulmonary toxicity, carcinogenicity, and other local and systemic effects. NRC also reviewed *in vitro* data to determine the potential for genotoxicity as well as other toxic effects and to understand the mechanisms of toxic action. Toxicokinetic studies were also reviewed to understand the absorption, distribution, metabolism, and excretion of the FR chemicals. For some types of toxic effects, notably most cancers, the subcommittee conservatively assumed that no threshold for a dose-response relationship exists or that, if one does exist, it is very low and cannot be reliably identified. Therefore, the subcommittee's risk-estimation procedure for carcinogens was different from that for non-carcinogens: the relationship between the incidence of cancer and the dose of a chemical reported in an epidemiological study or an experimental animal study was extrapolated linearly to much lower doses at which humans might be exposed in order to overestimate conservatively the excess lifetime risk of cancer resulting from lifetime exposure to a chemical at a particular dose rate. This procedure does not provide a "safe" dose with an estimated risk of zero (except at zero dose), although at sufficiently low doses, the estimated risk becomes very low and is regarded to have no public-health significance. The actual risk is also highly likely to be lower than the upper bound, and it might be zero. In the final phase of the risk-assessment process, NRC integrated the data to determine the probability that individuals might experience adverse effects from a chemical under anticipated conditions of exposure, by calculating a hazard-index to judge whether a particular exposure would be likely to present a non-cancer toxicological risk.

Without going into detail, for most of the most widely used flame retardants, NRC concluded that the hazard indices for non-carcinogenic effects are less than 1 for all routes of exposure for all flame retardants studied, meaning that they are not a concern. Carcinogenic risk assessments performed on the flame retardants that were found to be or likely to be carcinogenic indicate that some of the estimated excess cancer risks may be greater than 1×10^{-6} . However, the NRC committee concluded that actual carcinogenic risk is likely to be much lower because of the extremely conservative (high) exposure estimates. Several of the flame retardants analyzed were actually chemical classes rather than single compounds.

In those cases one chemical was selected as a surrogate on the basis of representativeness and conclusions were based on the properties of the surrogate and the risk from other members of the class might be different from the risk from the surrogate. It is important to point out that this study (as opposed to many other studies) did not focus exclusively on halogenated flame retardants but discussed all types of chemistries.

NRC intentionally overestimated exposure levels as a precautionary approach to the protection of public health and concluded that the following flame retardants can be used on fabrics for residential furniture with minimal risk, even under worst-case assumptions:

- Hexabromocyclododecane,
- Decabromodiphenyl oxide,
- Alumina trihydrate,
- Magnesium hydroxide,
- Zinc borate,
- Ammonium polyphosphates,
- Phosphonic acid (3-[[hydroxymethyl]amino]-3-oxopropyl)-dimethyl ester,¹
- Tetrakis hydroxymethyl phosphonium salts (chloride salt)

They also recommended that additional exposure studies be made on the following flame retardants to determine whether toxicity studies need to be conducted:

- Antimony trioxide,
- Antimony pentoxide and sodium antimonates,
- Calcium and zinc molybdates,
- Organic phosphonates (dimethyl hydrogen phosphite),
- Tris (monochloropropyl) phosphates,
- Tris (1, 3-dichloropropyl-2) phosphate,
- Aromatic phosphate plasticizers (tricresyl phosphate), and
- Chlorinated paraffins.

In conclusion, the NRC committee found no significant risk concern with any of the flame retardants assessed, which covered a broad range of chemical compositions.

For some of these materials additional studies were performed after the NRC work, much of which was done for European Union risk analyses, and it filled in some of the gaps identified. Two brominated flame retardants, not directly studied by NRC, have been clearly associated with potential health issues and withdrawn from the market: pentabromobiphenyl oxide (pentaBDE) and octabromobiphenyl oxide (octaBDE). In the case of neither chemical have proven health effects (including carcinogenic effects) on humans been published but the fact that the chemicals are bioaccumulative and do have proven health effects on animals mean they should not be used.

PentaBDE and octaBDE may enter the body by ingestion or inhalation and they are stored mainly in body fat. EPA studied pentaBDE in detail in 2008 [23]. Following a comprehensive risk assessment the European Union banned the use of both pentaBDE and octaBDE since 2004 [24]. In the US, as of 2005, “no new manufacture or import of” pentaBDE and octaBDE “can occur... without first being subject to EPA evaluation” and in May 2009, both were added to the Stockholm Convention on Persistent Organic Pollutants as it meets the criteria for the so-called persistent organic pollutants of persistence, bioaccumulation and toxicity.

In December 2009 all manufacturers voluntarily phased out production of a flame retardant in the same family as the last two, decabromobiphenyl oxide (decaBDE), in spite of the lack of proven health effects. The main reason for this action by the manufacturers is that many of the properties of decaBDE are similar to those of pentaBDE and octaBDE even if the health effects are not.

Much earlier, the first flame retardant found with negative health effects (carcinogenicity), and voluntarily withdrawn from the market (for children’s sleepwear) in the 1970s, was brominated tris [tris (2,3-dibromopropyl) phosphate], which has not been used commercially since. It is important to note that it is a different material from the chlorinated tris flame retardant used more recently for furniture, and which is being misidentified in the press as the same material.

Hexabromocyclododecane (HBCD) has been found to have the potential for ecotoxicity but no demonstrated effects on humans have been reported. The Stockholm Convention recommended its inclusion in a list of persistent organic pollutants, an action not completed as of 2015. However, in 2014 manufacturers of HBCD, extensively used as a flame retardant for polystyrene thermal insulation, in conjunction with the manufacturers of the polystyrene foam itself, have decided to replace HBCD in the foam by a polymeric brominated flame retardant (polyFR) [25], which has very low bioavailability and intrinsic toxicity and is, thus, not bioaccumulative.

No other flame retardant has, at least until 2015, been demonstrated to have such an effect on risk to humans that it was deemed necessary to eliminate it from the market.

Health Effects of Flame Retardants in Actual Fires

Flame retardants, as discussed above, do not significantly contribute to acute toxicity in fires. Toxicologists comparing acute toxicities use a toxicity classification scale for inhalation that places LC50 (toxic potency) values of 10 to 100 in the highly toxic category and values of 10 or less in the extremely toxic category [26]. The smoke toxic potency values of flame retarded materials are so similar to those of the same materials without flame retardants that they are not statistically significantly different. Moreover, as properly flame retarded materials will generate lower masses of combustion products they will often cause fire atmospheres to be less toxic [15]. Thus, the use of flame retarded materials will not alter smoke toxicity in fire atmospheres.

With regard to the effects on the health of firefighters, it is undoubtedly true that firefighters should have special concerns because the rates of many chronic diseases, including cancers, are higher among firefighters than among the general population. These health effects on firefighters will be minimized by: (a) the continued use of self-contained breathing apparatus both during firefighting and during overhaul operations (after the fire has been brought under control) and (b) improvements in the effective treatments of firefighter protective clothing after each use. However, there is no evidence that this is associated with the use of flame retardants. In fact, there is significant evidence that the added effect of the combustion or thermal decomposition products of flame retardants have an insignificant added effect on toxicity.

With regard to halogenated flame retardants, the data discussed above showed the extremely minor contributions to the concentrations of carcinogens in smoke and soot which polyhalogenated dioxins and furans (resulting from halogenated flame retardants) make relative to the extremely large contributions from PAH.

Conclusions

Flame retardants are based on many individual chemical components, including not just halogens. Some of them are also used in household applications unrelated to fire safety. Thus, any scientifically-based discussion of the toxicity and/or health effects flame retardants needs to address the specific material of potential concern and not a generic catch-all. While it is essential to ensure that materials with negative health

effects not be used, this cannot be interpreted as a blanket attack on flame retardants in general or even on brominated and/or chlorinated flame retardants. Every flame retardant offered for commercial use should always be investigated and those materials proven to be toxic or harmful should be prohibited from use.

However, flame retardants are an important way to maintain robust fire safety in product and building designs. They are an essential first line of defense in terms of passive fire protection. Flame retardants are a broad class of materials with unique functionality, hazard characteristics, and impacts on fire events.

In conclusion, published data overwhelmingly shows that flame retardants do not contribute significantly contribute to either acute or chronic fire toxicity in real fires. While some flame retardants have been removed from the market in recent years the vast majority in commercial use do not present significant toxicological concerns.

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Fin de vie de matériaux nanocomposites

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Les matières plastiques sont utilisées dans de multiples applications de notre vie quotidienne, et par conséquent, une quantité considérable de plastiques et composites se retrouve dans les flux de déchets solides. Dans les pays de l'Union Européenne, jusqu'à 250 Mtonnes de déchets solides sont ainsi produits chaque année, avec une augmentation annuelle chiffrée à 3%. Les matières plastiques représentent entre 7 et 15% du flux de déchets selon les pays considérés [1] (5,111 Mtonnes en 2008 pour la France [2]), soit une estimation moyenne de 25 Mtonnes de plastiques par an (1,025 Mtonnes en 2007 pour la France). Par ailleurs, de nouvelles solutions consistant à adjoindre des nanoparticules (Al₂O₃, TiO₂, SiO₂, nanotubes de carbone (NTC), nanoargiles) dans ces matériaux polymères apparaissent de façon croissante, notamment pour améliorer leurs propriétés mécaniques, barrière et leur réaction au feu. Un inventaire réalisé en 2011 dans le cadre de l'initiative américaine

« Project on Emerging Nanotechnologies » [3] avance le chiffre de plus de 1 300 produits commerciaux dans lesquels des nanoparticules sont incorporées. Néanmoins, du fait de l'absence de marquage spécifique, aucun chiffre n'est disponible au sujet des quantités collectées pour ces matrices polymères incorporant des nanoparticules. La présence de substances nano particulières dans les produits en fin de vie, et donc dans les déchets, peut constituer un risque pour la santé, l'environnement et pour les procédés de traitement eux-mêmes. Dans le cadre du projet NORMAN [4], les nanoparticules, et au sens large les nano-objets, ont été identifiés comme une des familles de polluants émergents prioritaires pour lesquelles il est nécessaire d'acquérir de nouvelles données significatives concernant leurs sources d'émission, leur devenir et les seuils d'émission. De nombreuses études tendent à prouver que certaines nanoparticules peuvent avoir des effets néfastes sur

l'homme [5], [6]. La gestion de la fin de vie de ces produits et des matériaux qui les constituent est par conséquent une problématique d'actualité.

Le recensement des travaux scientifiques réalisés jusqu'alors met en évidence le faible nombre d'études menées sur le lien entre nanoparticules et recyclage, et plus particulièrement concernant la fin de vie des nanocomposites. Le Tableau 3 récapitule les projets connus abordant cette question en France et en Europe. Il apparaît que la voie de l'incinération et les conséquences associées y sont peu représentées, alors que la présence de nano-objets dans les matériaux est susceptible de modifier les

mécanismes de dégradation thermique mis en jeu lors de l'incinération et les mécanismes d'émission associés. Le fait que cette question soit rarement abordée dans les projets en cours indique clairement le caractère émergent de la problématique liée à l'incinération des nanomatériaux. Ainsi, il s'avère crucial d'évaluer les conséquences associées à l'incinération de nanocomposites, en termes d'émission de nanoparticules dans l'air, de leur dispersion dans les zones proches des sites de traitement des déchets et de leur toxicité éventuelle.

	Titre des travaux	Période	Pays (Porteur)	Nanoparticules considérées (NPs)	Incinération
NANOFlueGas (ADEME)	Caractérisation des émissions de NPs provenant de l'incinération de déchets contenant des NM	2011-2014	France (INERIS)	3 « nano-déchets »	OUI
INNANODEP (ADEME)	Incinération de nanomatériaux et relargage de particules	2012-2014	France (LNE/ARMINES)	- <u>Matrices</u> : PA6, PC, Epoxy - <u>Charges</u> : SiO ₂ , Al ₂ O ₃ , TiO ₂ , MMT, Sépiolite, NTC	OUI
NANOEMI (ADEME)	Etude des émissions liées à l'incinération de matériaux nano-structurés et incidence éventuelle sur les procédés industriels	2012-2015	France (LNE/INERIS/ARMINES)	- <u>Matrices</u> : PA6, Silicone, EVA - <u>Charges</u> : SiO ₂ , MMT, Sépiolite, Halloysite, NTC	OUI
NANOSUSTAIN (FP7)	Relargage possible de NTCs pendant l'incinération de composites-NTC	2010-2013	Suède	- <u>Matrices</u> : papier, Epoxy, peinture - <u>Charges</u> : nanocellulose, TiO ₂ , NTC, ZnO	OUI
NANOPOLYTOX (FP7)	Impact toxicologique de NMs issus du vieillissement, de l'entreposage ou du recyclage de polymères nano-composites	2010-2013	Espagne	- <u>Matrices</u> : PP, EVA, PA6 - <u>Charges</u> : SiO ₂ , TiO ₂ , NTC, ZnO, nano-argiles	NON
NANOMICEX (FP7)	Fin de vie pour encres et pigments via l'entreposage	2012-2014	Espagne	- <u>Charges</u> : Al ₂ O ₃ , TiO ₂ , ZnO, Fe ₃ O ₄ , Ag, CoAl ₂ O ₄	NON
NANOFATE (FP7)	Devenir des NPs et exposition dans les eaux et les sols suite à un entreposage de nano-déchets	2010-2014	UK	- <u>Charges</u> : Ce ₂ O, ZnO, Ag	NON
NEPHH (FP7)	Relargage de NPs suite à l'usage de NMs et à l'incinération de nano-déchets	2009-2012	Espagne	- <u>Matrices</u> : PP, PA, PU, Silicone - <u>Charges (5%)</u> : SiO ₂ , MMT	OUI

Tableau 1 : Projets connus traitant de la fin de vie des nanomatériaux

Les méthodes d'identification et de tri utilisées actuellement lors du recyclage des matières plastiques ne permettent pas de détecter la présence de nano-objets inclus dans la matrice polymère, ce qui conduit à traiter de la même façon les composites dopés et non dopés en nano-objets. L'incinération peut donc être une voie qui sera privilégiée dans l'avenir pour la fin de vie des pièces de composites comportant des nano-objets, ce qui est à même de conduire à l'émission potentielle de nanoparticules et de particules ultrafines lors de leur dégradation thermique [7]. Ces produits de dégradation sont dispersés dans l'atmosphère et augmentent la concentration en aérosols,

entraînant un impact toxicologique potentiel encore mal caractérisé. Cette problématique à elle seule constitue un enjeu de santé publique majeur comme l'a souligné un récent rapport de l'OCDE [8]. Par ailleurs, les réglementations concernant la gestion de la fin de vie de ces matériaux nanocomposites ne sont pas toujours établies.

Ainsi, en 2008, le projet français NANOFEU financé par l'ANR et concernant l'étude de l'impact des nanoparticules sur le comportement au feu des matériaux a été réalisé lors d'une collaboration entre l'INERIS, le LNE, l'EMA, l'ISMANS et PlasticsEurope. C'est le premier projet mené en France à

avoir considéré l'impact de l'utilisation d'additifs retardateurs de flamme combinés avec des nanoparticules sur le comportement thermique des matériaux et l'émission de polluants.

Deux projets ADEME montés en réponse à l'appel CORTEA (NANOFlueGas, 2011-2014 ; INNANODEP, 2012-2014) ont ensuite contribué à la caractérisation des émissions de nanoparticules dans l'air. Le projet INNANODEP avait plus particulièrement pour objectif de réaliser un bilan de matière entre la fraction résiduelle solide formée et la fraction de gaz et de particules aérosol émise lors de l'incinération de nanocomposites. Le projet NANOFlueGas visait quant à lui à caractériser les émissions de nano-objets dans les fumées d'incinération de déchets contenant des nanomatériaux manufacturés et de dégager, si nécessaire, des pistes d'amélioration des procédés industriels pour minimiser les risques potentiellement associés à l'incinération de tels matériaux.

En complément de ces deux projets, une thèse ADEME, celle de Ghania Ounoughene, a été lancée et soutenue en novembre 2015 (NANOEMI, 2012-2015, cf. Tableau 3). Son sujet consistait à étudier les émissions liées à l'incinération de matériaux contenant des charges nanométriques et leur incidence éventuelle sur les procédés industriels (tels que la filtration). Les objectifs étaient a) d'élaborer un outil d'aide à la décision basé sur une classification

des produits (matrice ; nanoparticules) et b) de mettre en place une démarche de réduction des risques liés à l'émission de « nano-déchets », notamment en adaptant les systèmes de traitement des fumées pour traiter également ces derniers. Cette collaboration entre l'INERIS, le LNE et ARMINES s'est inscrite au cœur des préoccupations 46 et 50 du Plan National Santé Environnement 2 (PNSE2). Elle avait pour but de répondre au manque d'outils métrologiques capables de caractériser de manière fiable les émissions (notamment dans l'air) de nanoparticules par les produits contenant des nanomatériaux, tout au long de leur cycle de vie.

Suite à ces études le projet Nano Tox 'In qui a été déposé par l'Ecole des Mines d'Alès, le LNE et l'Ecole des Mines de Saint-Etienne a débuté en janvier 2016. Ce dernier repose sur les connaissances acquises et sur l'exploitation des outils développés dans le cadre des projets NANOFEU, INNANODEP et NANOEMI.

Nano Tox'In viendra s'articuler plus spécifiquement à la suite de la thèse de Ghania Ounoughene en y ajoutant une évaluation de la toxicité intrinsèque des nanoparticules primaires (i.e. introduites initialement dans la formulation du nanocomposite) ainsi que celle des nanoparticules issues de l'incinération de nanocomposites.

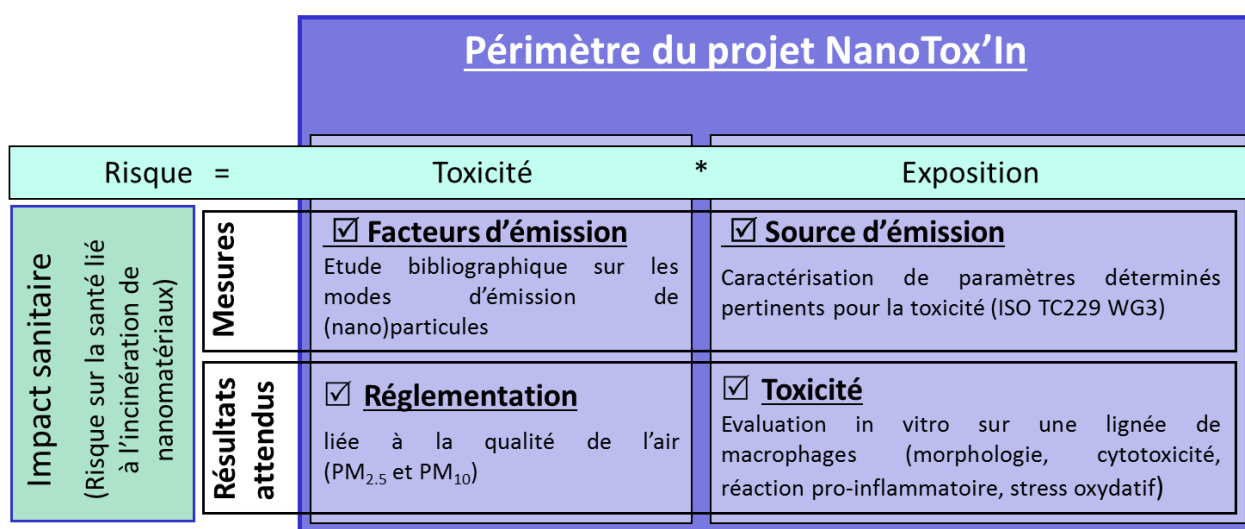


Figure 1 : Périmètre du projet NanoTox'In

Les projets réalisés jusqu'alors portant sur l'incinération de nanocomposites n'ont considéré que la caractérisation des aérosols et « nano-déchets » issus de l'incinération. La question de la dispersion des produits de dégradation, pourtant cruciale dans le cadre de l'évaluation des risques sanitaires associés, n'a jamais été prise en compte.

Depuis quelques années, la nécessité d'étudier le comportement des nanoparticules tout au long du cycle de vie du produit dans lequel elles sont incorporées a bien été intégrée. Toutefois, la majorité des études réalisées s'intéresse aux étapes de production (projet FP7 NanoImpactNet [9]) ou à l'usure de ces nanomatériaux (projet Nano-Data financé par

l'ANSES [10]), délaissant la plupart du temps la question de leur fin de vie, telle que le stockage ou l'incinération. Dans le cas de l'incinération, les nanomatériaux peuvent libérer dans l'air une grande quantité de particules fines et ultrafines (c'est-à-dire de taille inférieure respectivement à 1 μm et à 0,1 μm). L'exposition de l'homme aux nano-objets (nanoparticules) par les voies respiratoires apparaît comme l'une des plus préoccupantes, puisque selon leur diamètre aérodynamique, les particules peuvent se déposer dans la région thoracique, pouvant entraîner une toxicité pulmonaire en cas de biopersistance. Dans certains cas, en atteignant les alvéoles pulmonaires, les particules peuvent passer dans la circulation sanguine en franchissant la barrière alvéolo-capillaire. La connaissance des propriétés toxicologiques spécifiques aux aérosols issus d'incendie demeure globalement insuffisante à cause du faible nombre d'études, de la courte période d'exposition, ou encore de la composition différente des aérosols testés (composition chimique, diamètre aérodynamique, morphologie, état d'agglomération).

Un état des lieux de la production française de nano-objets a été réalisé en 2011 dans le cadre de l'étude pilotée par la DGCIS (Délégation Générale de la Compétitivité, de l'Industrie et des Services) et montre qu'un total de 135 000 tonnes de nanoparticules sont produites annuellement pour un chiffre d'affaire (CA) de 500 M€ [11]. Il apparaît par ailleurs que 90% des nanoparticules produites sont des oxydes métalliques de type TiO_2 , SiO_2 et CeO_2 ou des boehmites [12], [13]. Les nanotubes et les nanofibres représentent quant à eux plusieurs dizaines de tonnes produites pour un CA d'environ 100 M€. L'ensemble de la filière, depuis la production des nanoparticules, leur intégration dans les matériaux, jusqu'à leur utilisation par l'industrie, concerne en France environ 3 000 personnes. A ces effectifs exposés au risque engendré par la manipulation de nanoparticules s'ajoute bien évidemment les travailleurs sur sites de traitement de déchets, les personnels des laboratoires de recherche ainsi que les populations voisines de ces derniers.

Dans les cadres réglementaires actuels relatifs aux déchets, il n'existe cependant aucune définition officielle des « nano-déchets ». Ces derniers ne disposent par ailleurs d'aucun marquage propre et ne sont à ce jour en France visés par aucune réglementation spécifique. Bien que quelques études aient pu considérer la question, très peu d'informations sont disponibles concernant la quantification des flux de ces « nano-déchets ». Des scénarii ont ainsi été proposés à partir de modèles

stochastiques en utilisant différentes hypothèses et extrapolations appliquées à des données d'entrée, telles que les volumes de production de certains nanomatériaux. Toutefois, les incertitudes résultant des hypothèses utilisées s'avèrent difficiles à évaluer et il est délicat de transposer d'une région à une autre les champs d'étude et les cibles considérées.

Il y a un intérêt de santé publique à porter à la connaissance des fabricants le risque sanitaire et environnemental engendré par l'utilisation de nanocomposites dont la fin de vie est l'incinération.

Les réflexions en cours ont conduit l'ensemble du consortium à s'interroger sur la fin de vie des matériaux comportant des nano-objets, notamment vis-à-vis des risques sur la santé ou la sécurité, mais également vis-à-vis de l'intégration de ces matériaux dans les démarches d'analyse du cycle de vie des produits et de développement durable.

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