Fire Toxicity of Construction And Building Materials

Presented by:-

Prof Anna A Stec
Leader Fire Toxicity
Centre for Fire and Hazard Science
University of Central Lancashire
Preston, PR1 2HE, UK
Fire toxicity assessment

- The growing need to address the flammability of synthetic polymeric materials, as substitutes for natural-based materials, has led to an increase in the use of fire and flame retardant (FR) systems.

- Most of the recent research in development of fire safe materials is focussed on preventing ignition and fire growth, shifting the focus of the fire safety towards reducing peak heat release rates.

- It is important to understand the range of concentrations of chemical species likely to be present in any fire and can have a negative effect on the environment as well as posing a serious hazard to human health.

- Quantitative data on environmentally hazardous components of fire effluent cannot routinely be obtained from accidental fires, data is obtained from real-scale fire tests and simulations involving physical fire models.
Issues – Regulatory Guidance


The building shall be designed and constructed so that there are appropriate means of escape from the building to a place of safety capable of being safely and effectively used at all material times.

FACTORS AFFECTING FIRE COMBUSTION AND TOXICITY

Harmful Effects
FACTORS AFFECTING
FIRE COMBUSTION AND TOXICITY

Harmful Effects

Fire Scenarios and Combustion Conditions
FACTORS AFFECTING FIRE COMBUSTION AND TOXICITY

- Harmful Effects
- Fire Scenarios and Combustion Conditions
- Experimental Methods
FACTORS AFFECTING FIRE COMBUSTION AND TOXICITY

Harmful Effects

Fire Scenarios and Combustion Conditions

Experimental Methods

Toxicity Assessment
FACTORS AFFECTING
FIRE COMBUSTION AND TOXICITY

Harmful Effects

- Asphyxiants
- Irritants
- Smoke
- Particulates
- PAH
- Dioxins

Fire Scenarios and Combustion Conditions
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Fire Scenarios and Combustion Conditions
- Oxidative Pyrolysis
- Well-Ventilated
- Under-Ventilated
Immediate effects, less than 30 s.

Some disorientation because of smoke obscuration, sensory irritation, impaired normal breathing, etc., but the natural reaction for the unimpaired individual is to attempt to extinguish the fire, warn others, and try to escape.

Immediate effects, within 2 min.

All of the above present and intensifying.

Spreading smoke, accumulating and forming a hot layer at the ceiling level but rapidly descending toward the floor.

-The combination of low O₂ and heat are extremely fast acting and above smoke also contains carbon dioxide and carbon monoxide.

-If the burning material contains nitrogen (as in PU foam, nylon, PAN) the smoke will contain hydrogen cyanide (HCN), nitrogen oxides (NO, NO₂), ammonia etc.

-If the burning materials contain chlorine, bromine, or fluorine (as PVC), hydrogen chloride (HCl), hydrogen fluoride (HF), and hydrogen bromide (HBr) are released.

-These inorganic irritants are always present, and exacerbate the irritating and choking effects of the smoke.
Harmful Effects

- **Smoke obscuration**
  - Impaired vision due to the smoke and particulates presence
  - HCl, HBr, HF, NOx, Acrolein, Formaldehyde
  - Depending upon the concentration cause painful stimulation of the eyes, nose, mouth, throat and lungs with some hypoxia due to breathing difficulties which impedes escape and can be fatal

- **Irritant gases**
  - CO, HCN, CO₂, Low Oxygen
  - Cause confusion and loss of consciousness followed by death from asphyxia when a sufficient dose has been inhaled
  - Depending upon dose inhaled cause lung inflammation and oedema which may be fatal usually some hours after exposure

- **Asphyxiation gases**
  - For asphyxiant effects depend upon an exposure dose. There is little effect until a threshold dose is inhaled after which confusion occurs rapidly followed by collapse
Analysis of Polish Fire Statistics

Deaths/million

Injuries/million

Stec et al. Forensic Science International, Volume 277, August 2017, Pages 77-87
Analysis of Polish Fire Statistics

Year

2003 2004 2005 2006 2007 2008 2009 2010 2011

Fire Deaths /%

Soot Presence: Yes  No  Unknown/Not tested

Stec et al. Forensic Science International, Volume 277, August 2017, Pages 77-87
Emission pathways from fires

Direct gaseous and particulate emissions to the atmosphere
- carbon dioxide
- carbon monoxide
- other gases
- soot
- water
- other condensates

Spread of atmospheric emissions
- distribution
- dilution

Deposition of atmospheric emissions
- sedimentation

Ground and surface water contamination from fire debris/residues

- extinguishing agents
  - water
  - foam
  - powder
  - gases

- burning object
- fire residues
- fire debris

- recycling
- waste

- soil / waters
- sewerage system
- ground / groundwater
- surface waters

ISO TC92 SC3 - PWI 26367-2: Guidelines for assessing the adverse environmental impact of fire effluents
Identification of potential environmental impact

Ecotoxicants with acute effects

Ecotoxicants with long-term effects

Metals

Particulates

Polycyclic aromatic hydrocarbons (PAHs)

Perfluorooctanesulfonates (PFOS)

Polychlorinated and polybrominated dioxins and furans (PCDD/PCDF, PBDD/PBDF)
What’s in Smoke and what are the Impacts

Smoke particles: small, less than one micron in diameter; behave like a gas

Penetrate indoors and deep into the lung

Have high surface area: adsorb other combustion products, catalytic surface

Solid and liquid aerosols are characterized by:

• Concentration,
• Particles size distribution,
• Chemical nature
• Morphology (depending on aerosol chemical nature)
<table>
<thead>
<tr>
<th>Cyclic and Polycyclic Aromatic Hydrocarbons</th>
<th>Structure</th>
<th>IARC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzene</strong></td>
<td><img src="image" alt="Benzene" /></td>
<td>1 (2012)</td>
</tr>
<tr>
<td><strong>Benzo[a]pyrene</strong></td>
<td><img src="image" alt="Benzo[a]pyrene" /></td>
<td>1 (2012)</td>
</tr>
<tr>
<td><strong>Dibenzo[ah]anthracene</strong></td>
<td><img src="image" alt="Dibenzo[ah]anthracene" /></td>
<td>2A (2010)</td>
</tr>
<tr>
<td><strong>Styrene</strong></td>
<td><img src="image" alt="Styrene" /></td>
<td>2B (2002)</td>
</tr>
<tr>
<td><strong>Naphthalene</strong></td>
<td><img src="image" alt="Naphthalene" /></td>
<td>2B (2002)</td>
</tr>
<tr>
<td><strong>Benzo[a]anthracene</strong></td>
<td><img src="image" alt="Benzo[a]anthracene" /></td>
<td>2B (2010)</td>
</tr>
<tr>
<td><strong>Chrysene</strong></td>
<td><img src="image" alt="Chrysene" /></td>
<td>2B (2010)</td>
</tr>
<tr>
<td><strong>Benzo[b]fluoranthene</strong></td>
<td><img src="image" alt="Benzo[b]fluoranthene" /></td>
<td>2B (2010)</td>
</tr>
<tr>
<td><strong>Benzo[k]fluoranthene</strong></td>
<td><img src="image" alt="Benzo[k]fluoranthene" /></td>
<td>2B (2010)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group</th>
<th>General description</th>
<th>Bases of evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carcinogenic to humans</td>
<td>Sufficient evidence of carcinogenicity in humans.</td>
</tr>
<tr>
<td>2A</td>
<td>Probably carcinogenic to humans</td>
<td>Limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals.</td>
</tr>
<tr>
<td>2B</td>
<td>Possibly carcinogenic to humans</td>
<td>Limited evidence of carcinogenicity in humans and less than sufficient evidence of carcinogenicity in experimental animals.</td>
</tr>
</tbody>
</table>
What strategies are in place to minimise risk of getting cancers?
Firefighters and routes of exposure: Inhalation or Absorption or both?

Firefighting clothing is contaminated with carcinogens

Hazardous Contamination “follows” firefighters

Absorption via skin is one of the main exposure routes

AA. Stec, et. al Scientific Reports, volume 8, Article number: 2476(2018)
PAHs Release

- New sofas, meeting the UK furniture flammability regulations, were used either solely or with additional furnishings (carpet, curtains, television set).
- The ventilation conditions were varied (well- to under-ventilated) by varying door and/or window openings (in bedrooms/lounge).
- Two sheets of newspaper were ignited on the sofa.
- Gaseous effluents and particulate deposits were measured.

OPFRs and PAHs Release During House Fires

The most toxic PAH: benzo[a]pyrene was identified in the gas phase samples.

Phosphorus-based compounds were detected in both gas and condensed phases from burning sofas or the fully-furnished lounge.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tris (1-chloro-2-propyl) phosphate</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>4-Methylphenyl diphenyl phosphate</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>Triphenyl phosphate</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>Bis(4-methylphenyl) phenyl phosphate</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
<tr>
<td>Tri-m-cresyl phosphate</td>
<td><img src="image5.png" alt="Structure" /></td>
</tr>
<tr>
<td>Tri-p-cresyl phosphate</td>
<td><img src="image6.png" alt="Structure" /></td>
</tr>
<tr>
<td>Isopropylphenyl diphenyl phosphate</td>
<td><img src="image7.png" alt="Structure" /></td>
</tr>
</tbody>
</table>

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- Bench and Large scale methods
The sofa was constructed from polyurethane (PU) foam and was timber framed. The label showed that it conformed to UK fire-safety regulations.

Ignition source – 4 sheets newspaper

# Equivalence Ratio-Classification of the fire stages

\[ \phi = \frac{\text{Actual fuel / Air ratio}}{\text{Stoichiometric fuel / Air ratio}} \]

<table>
<thead>
<tr>
<th>Combustion condition</th>
<th>Temperature (°C)</th>
<th>Equivalence ratio</th>
<th>Oxygen from fire %</th>
<th>CO\textsubscript{2}/CO ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smouldering</td>
<td>350</td>
<td>not applicable</td>
<td>&gt;21</td>
<td>1-5</td>
</tr>
<tr>
<td>Well-ventilated flaming</td>
<td>650 or 700</td>
<td>$\phi &lt; 0.75$</td>
<td>5 to 21</td>
<td>2-20</td>
</tr>
<tr>
<td>Under ventilated flaming:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>small vitiated fires</td>
<td>650</td>
<td>$\phi &gt; 1.5$</td>
<td>0 to 12</td>
<td>2-20</td>
</tr>
<tr>
<td>post-flashover fires</td>
<td>825</td>
<td>$\phi &gt; 1.5$</td>
<td>0 to 12</td>
<td>2-20</td>
</tr>
</tbody>
</table>
How is Fire Toxicity Measured?

3 general approaches:
- Well-ventilated (e.g. Cone calorimeter)
- Closed box tests (e.g. NBS Smoke Box, ASTM E1678, NES 713)
- Tube furnaces (e.g. NFX 70-100, DIN 53436, IEC 60695-7-50, Fire Propagation Apparatus)

<table>
<thead>
<tr>
<th>Heat flux (kWm²)</th>
<th>Pilot flame</th>
<th>ISO fire stage depends on test material and thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>400°C</td>
<td>Oxidative Pyrolysis (?)</td>
</tr>
<tr>
<td>25</td>
<td>600°C</td>
<td>Well-ventilated (?)</td>
</tr>
<tr>
<td>50</td>
<td>800°C</td>
<td>Under-ventilated (?)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3b) Post flashover (?)</td>
</tr>
</tbody>
</table>

3 Conditions: each with air flow 2 litres min⁻¹

ISO 19700
The steady state tube furnace method

Polyamide 6

Equivalence ratio (phi)

CO, particulates, HCN, NO g/g.

CO2 g/g

CO Particulates HCN NO CO2
Yields g/g CO, particulates

Equivalence ratio (phi)

PVC

yields g/g CO2 and HCl

CO Particulates CO2 HCl
Fire Toxicity FR polyamides (20 g/m³)

PA 6 Polyamide 6 with 30% glass fibres (PA6+GF)

PA 6/AIPiM with 20% Aluminium phosphinate (OP1230) and Melamine polyphosphate (Melapur 200/70)

PA 6/BrSb with 20% Brominated polystyrene (Saytex HP 3010G) and 6% Antimony Trioxide (Campine 2617)

S Molyneux, A A Stec and T R Hull,, Polymer Degradation and Stability, In Press, September 2013
http://dx.doi.org/10.1016/j.polymdegradstab.2013.09.013
SEM-EDAX showing non-carbon in airborne particles Si, Al etc.

44% Polyamide 66
30% Glass fibres
20% Brompolystyrene
6% Antimony Trioxide
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Toxicity Assessment
- Animal and Chemical Assessment
- FED
- FEC
Estimation of fire toxicity - ISO 13344

**FED** - the fraction of a lethal dose (for 50% of the population)

*When FED = 1 then 50% of the population will die.*

\[
FED = \frac{m[CO]}{[CO_2] - b} + \frac{21 - [O_2]}{21 - LC_{50,O_2}} + \frac{[HCN]}{LC_{50,HCN}} + \frac{[HCl]}{LC_{50,HCl}} + \frac{[HBr]}{LC_{50,HBr}} + \frac{[SO_2]}{LC_{50,SO_2}} ....
\]

\[
FED = \frac{m[CO]}{[CO_2] - b} + \frac{21 - [O_2]}{(21 - 5.4) \%} + \frac{[HCN]}{150} + \frac{[HCl]}{3700} + \frac{[HBr]}{3000}
\]
Fire toxicity of Common Polymers at 20 g/m³ loading
The fire toxicity of six insulation materials (20 g/m³)

Glass Wool (GW)  Expanded Polystyrene Foam (EPS),
Stone Wool (SW)  Polyurethane Foam (PUR)
Phenolic Foam (PhF)  Polyisocyanurate Foam (PIR)

Estimation of fire toxicity

ISO 13571

\[
\text{FED} = \sum_{t_1}^{t_2} \frac{[\text{CO}]}{35000} \Delta t + \sum_{t_1}^{t_2} \frac{\exp([\text{HCN}]/43)}{220} \Delta t
\]

\[
\text{FEC} = \frac{[\text{HCl}]}{IC_{50, \text{HCl}}} + \frac{[\text{HBr}]}{IC_{50, \text{HBr}}} + \frac{[\text{HF}]}{IC_{50, \text{HF}}} + \frac{[\text{SO}_2]}{IC_{50, \text{SO}_2}} + \frac{[\text{NO}_2]}{IC_{50, \text{NO}_2}} + \frac{[\text{acrolein}]}{IC_{50, \text{acrolein}}} + \frac{[\text{fomaldehyde}]}{IC_{50, \text{fomaldehyde}}} + \sum \frac{[\text{irritant}]}{IC_{50, \text{irritant}}}
\]

Gases and smoke in lounge
Chair: CM foam, FR Dronon covers Test CDT18

Time to incapacitation in Lounge
Chair: CM foam, FR Dronon covers Test CDT18
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- Animal and Chemical Assessment
- FED
- FEC

Toxic product yield and Toxic Potency
CONCLUSIONS

- Fire toxicity is dependent on both material and fire conditions.
- Yields depend on conditions, and underventilated fires are the most toxic.
- Fire toxicity data is best related to ventilation conditions in terms of equivalence ratio $\phi$.
- CO is a good indicator of incomplete combustion however, it is not always the major toxicant. CO and HCN are much more prevalent in developed flaming.
- Irritants (HCl, organics and smoke particles) can prevent escape, but CO will be recorded as the cause death. HCl is independent of fire condition and NOx is favoured by well-ventilated conditions.
- Fire retardants which act in the gas phase often increase fire effluent toxicity. Brominated flame retardants increase the yield of both CO and HCN.
- Bench-scale methods rarely distinguish particular fire conditions. SSTF and FPA show acceptable agreement with large scale data over the range of fire conditions.
- Toxicity is often seen as too complex for fire safety assessments: a methodology to incorporate it at the design stage has already been under development.
Thank you for your attention

aastec@uclan.ac.uk