Context and objectives of the study

Fire is one of the most likely hazards in a nuclear facility and can lead to production of radioactive and toxic particles. One of the consequences of such an event is the clogging of the HEPA (High Efficiency Particulate Air) filters by solid particles produced during the fire and called soot. Those filters are the last barriers between the nuclear facility and the atmosphere.

Understanding and predicting the behavior of HEPA (High Efficiency Particulate Air) filters is essential to prevent their damaging during the clogging process and avoid the worst case which would be their breaching and the dispersal of combustion/radioactive products in the atmosphere.

IRSN researchers develop a clogging model adapted for HEPA filters (Mocho & Ouf, 2011) for simulating the ventilation in nuclear facilities during a fire. The clogging model currently used in the calculation codes has been empirically determined after fire and clogging experiments. The term of condensate rate highlights the influence of condensed vapours including water vapour on the aeraulic resistance of soot cake and HEPA filters. Another clogging model theoretically determined has been developed for dry soot cakes (Thomas et al., 2014) and takes into account different morphological parameters such as the overlap coefficient. Water sorption phenomenon actually takes place during clogging process but it is still not clearly taken into account in the current clogging model.

Soot are solid carbonaceous nanoparticles with different morphologies and physicochemical properties. It is formed during combustion by aggregation of single particles leading to aggregates of nearly 200 to 500 primary particles of 30 to 65 nm. These aggregates may present an organic coverage formed by condensed and adsorbed combustion substances. The primary particles are generally partially fused what is characterized by the overlap coefficient. Their microstructure consisting on portion of graphitic planes concentrically arranged makes soot material similar to the graphite’s one, the space between graphitic planes in soot and graphite is close.

The principal aim of this study is to:

- Obtain water sorption data on soot produced during fire experiments.
- Adapt a current water adsorption model based on the theory of multimolecular adsorption and capillary condensation (Ribeyre et al., 2014) to fire soot.

Indeed, this current Adsorption-Condensation model has been developed for ideal nanoparticles (spherical, smooth, dry and juxtaposed by contact points) whereas soot present a more complex structure and chemical composition as mentioned above.

Determining the most influencing physico-chemical parameters of soot on the water sorption phenomenon would enable to improve the current HEPA clogging models.

Experimental approach

Experiments consist first in producing and sampling soot during realistic fire experiments at different scales and dioxygen concentration. For the medium and small scales, separated fuels commonly found in nuclear facilities (polymers, solvents, hydraulic oils) are burned at different dioxygen concentrations thanks to an atmosphere controlled combustion chamber. For the large scale, whole flammable elements such as electric cables and cabinet or gloves box are burned at different ventilation conditions (over-ventilated or poorly ventilated room). This multi-scale soot production with different fuels would enable to compare the results from analytical experiments with those at large and medium scales in order to get closer to the realistic fire soot and evaluate the scale, dioxygen concentration and fuel nature effects on soot properties.

Then a soot characterization (physicochemical and morphological parameters) and finally water sorption measurements would enable to identify the most influencing parameters on sorption phenomenon thanks to a sensitivity study. Those parameters could then be added to the current adsorption and capillary condensation model (Ribeyre et al., 2014).

Materials and method

During the fire experiments at analytical scale, an online granulometric characterization of the emitted solid aerosols is carried out with different devices such as:

- The condensation particle counter (CPC) for the number concentration,
- The tapered element oscillating microbalance (TEOM) for the mass concentration,
- The scanning mobility particle sizer (SMPS) for the electric mobility diameter,
- The nanoparticle surface area monitor (NSAM) for the deposited surface concentration.

Moreover, the aerosols are online sampled on TEM grids and quartz filters for ex-situ analysis with different X ray characterization techniques and an OC/TC (organic carbon to total carbon) analyzer. This ex-situ characterization gives information about the morphology, the microstructure, the chemical and elemental composition and the OC/TC composition.

Finally, significant amount of soot are sampled on an acetate cellulose membrane in order to realize sorption measurement.

Water sorption measurements are carried out with the DVS (Dynamic Vapor Sorption) Vacuum microbalance supplied by Surface Measurement Systems. Samples are originally in the form of powder and compressed in the form of pellet in order to have enough mass for an optimal measurement. The particularity of this microbalance is to apply constant humidity steps in dynamic conditions by supplying a continuous vapour flow. This process is performed under vacuum so the physically adsorbed impurities coming from the ambient air are removed. Thus only the desired vapour is in contact with the sample surface.

The data table presents the current known properties of the samples tested in this study (the 6 first ones) and the one whose we have taken the sorption data in the literature (Popovicheva et al., 2008).

The primary particle diameter has been determined thanks to TEM pictures, the true density thanks to the buoyancy method (Archimedes' principle), the specific surface area thanks to BET measurements (manometric measurement of nitrogen sorption at 77°K) and elemental composition thanks to the X-ray spectroscopy method and OC/TC analysis.

Samples used in this study are commercial black carbons (PRINTEX 90 and FLAMMRUSS 101), provided by Orion (Engineered carbons) and have mean primary particle diameter of 15 and 95 nm respectively. Such materials exclusively composed of elemental carbon are morphologically similar to soot particles from fire flames.

Real "fire" soot particles have been produced by combustion of hydraulic oil, a gloves box and two types of electrical cables composed of PVC or halogen free fire retardant (HFFR) sheath. Those materials and elements represent potential fuels commonly handled in nuclear facilities.

Experimental results: water sorption

The microbalance good operating has been validated with a reference material called microcrystalline cellulose of which the water uptake is known for 10 water activities. Those data have been determined by 10 laboratories and published in an european standard (EN 12429). The results obtained with DVS microbalance are in good agreement with the standard data.

Than the repeatability of sorption measurements have been verified by performing five identical measurements with the same material (the carbon black PRINTEX 90) and the same protocol. The results enable to conclude that the repeatability is good since the dispersion between measurements is very low.

Figure on the lower left-hand corner of the poster shows the water adsorption isotherms on three different black carbons. These isotherms highlight the influence of the particle size on sorption measurement. The only varying parameter is the primary particle diameter since their chemical composition is essentially elemental carbon. The black carbon PRINTEX 90 which has the smaller particle diameter adsorbs much more water compared to the two other black carbons. Over 40% of relative humidity, isotherms present a rise of water uptake which corresponds to the multilayer adsorption. Those three isotherms are of type III according to the IUPCA classification and are characteristic of low interactions between sorbate and adsorbent. This is in accordance with the known low affinity of water with elemental carbon essentially composing the black carbons**.**

The last figure (on the right of the poster) presents adsorption isotherms of water on soot tested in this study and produced during fire experiments at large scale at different ventilation conditions (poorly or over ventilated room). It is compared with other sorption results for aeronautic and burner soot (Popovicheva et al., 2008). The most water adsorbing soot are these coming from burned electrical cables. The difference of water affinity between electrical cables soot with PVC sheath and the other with a halogen free fire retardant sheath may be due to surface chemical composition (presence of chlorine). Hydrocarbon fuels produced from similar flame type (Kerosene in an oil lamp, hydraulic oil in a confined room) present similar water sorption. Results for soot from propane burner are in good agreement with the literature data. Gloves box essentially composed of PMMA leads to soot adsorbing water as much as those from propane burner: this is consistent with the fact that PMMA soot and propane soot have similar morphologies and physico-chemical properties.

The combustion process and fuel nature strongly impact the water sorption properties of soot. A relative humidity of 40% has been identified as a critical limit above which the primary particle size is an influencing parameter on water sorption. This communication highlights the influence of fuel nature and soot morphology on the interaction between water and soot cake.