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## ZEOLITES AS POSSIBLE ADSORBENTS FOR EN 1948 STANDARD

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### Introduction

Waste incineration is an activity resulting in dioxin emissions on a quasi-continuous basis. To cut these emissions, the European Union legislation has set an emission limit value (ELV) of 0.1 ng/m<sup>3</sup> I-TEQ for dioxins from waste incineration and co-incineration plants<sup>1</sup>. Compliance with such ELV is usually checked through at least two short-term samplings per year. Monitoring of dioxin emissions at stationary sources is carried out using the EN 1948 standard, which consists in sampling, extraction /clean-up and identification/quantification<sup>2</sup>.

Since 2010, France has been the first country where a nation-wide legislation requires the use of a long-term sampling for waste incineration plants<sup>3</sup>. Semi-continuous sampling involves a time-integrated exposure of the adsorbent and then off-line analysis, whereas continuous monitoring would be more relevant in terms of both emission transparency and process control of the incineration plants.

The design of a field monitoring device can be possible through a set of adsorbents showing different adsorption specificities regarding dioxin congeners. Zeolites are adsorbents at molecular scale with large surface area and possible selective adsorption into pores<sup>4</sup>. Their pore surfaces are generally greater than 250 m<sup>2</sup>/g regarding the size of their pores and adsorbed molecules. Zeolites have already been used in dioxin adsorption from incinerator emissions<sup>5</sup> and some of them, with different pore sizes, have been chosen to obtain selective adsorption<sup>6</sup>.

In a first approach, zeolite adsorption properties are tested in a sampling device compliant with EN 1948 standard.

### Materials and methods

The base of the sampling device refers to EN 1948-1 standard: a continuously dust sampling train (from Cleanair Europe, France) equipped with a glassware set (from La Verrerie Villeurbannaise, France) according to the “filter/condenser method”, with flow division and solid absorbent downstream of the condenser.

Testing the adsorption properties of the selective materials requires modifications of the glassware set (Fig. 1). A second gas-sampling line with an adsorbent cartridge is added in parallel with the first one, requiring a three-neck balloon for recovering condensate. It is then possible to compare the adsorption properties of two different materials with the same stack gas. Furthermore, each line has two adsorbent cartridges in series: the first with the adsorbent being tested and the second (backup cartridge) with XAD-2 for breakthrough determination of the tested adsorbent.

Fig. 1: Adapted sampling device with two secondary lines. C11 and C12 cartridges packed with tested adsorbents.

The samples have been collected over a 6-hour period. The incinerator gas stream has been sampled between the electrostatic precipitator and fabric filter in order to reach high dioxin levels. With high dioxin concentrations, the specificity of adsorption can be tested between two different adsorbents: for instance, low-chlorinated congeners should be adsorbed into the micropores of one zeolite, while for another zeolite the adsorption should be limited to the external surface leading to a breakthrough of these congeners.

The adsorbent cartridges have been packed with 30 g of beads of 0.25-0.40 mm in diameter of \*BEA-Na and FAU-NaX zeolites, prepared with 5 wt. % of sodium metasilicate binder. The beads have mechanical performances sufficiently high for implementation in an in-line process<sup>7</sup>.

The zeolites have been activated at 350°C for 8 hours. The adsorbent cartridges have been spiked with a mixture of <sup>13</sup>C-labelled PCDD/F standards prior sampling, and then the toxic dioxin congeners have been measured by high-resolution gas chromatography and mass spectrometry according to EN 1948 standard.

## Results and discussion

The concentration profiles of the 17 toxic PCDD/F congeners adsorbed into beads of FAU-NaX and \*BEA-Na exposed to the same gas stream are given in Fig. 2.

A breakthrough of the \*BEA occurs for the PCDDs/PCDFs bearing 4 or 5 chlorine atoms and 2 chlorine atoms at one or both extremities, i.e. 2,3,7,8-TeCDD, 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF.

These congeners possess the highest vapour pressures<sup>8</sup>. In addition, diluted in isooctane, it has been observed that FAU-NaX adsorbs 2,3-DCDD with high affinity and capacity in the micropores, while the adsorption is limited to the external surface area of the \*BEA<sup>9</sup>. Regarding the size of the 2,3-DCDD and 2,3,7,8-TeCDD/F, it can be assumed that 2,3,7,8-TeCDD/F are adsorbed into micropores of FAU-NaX. Moreover, the surface area at meso- and macro-porosity scales of both materials has identical properties for dynamic gas adsorption.

Thus, the saturation of the external surface of the \*BEA has been reached with a breakthrough for the compounds having the highest vapour pressures, while a small part of 2,3,7,8-TeCDD/F has been adsorbed selectively into the micropores of FAU-NaX.

The specificity of adsorption of FAU13-NaX for 2,3,7,8-TeCDD/F is demonstrated. To be compliant with EN 1948 standard, the ice water was circulating at 2-3°C in the jackets of the condenser and cartridges. Other adsorption temperatures must be tested to favour adsorption into the micropores rather than external surface area.

Fig. 2: Concentration profiles of the 17 toxic PCDD/F congeners. (Top-left) Cartridge with FAU-NaX beads of 0.25-0.40 mm in diameter and (Top-right) backup cartridge with XAD-2. (Bottom-left) Cartridge with \*BEA-Na beads of 0.25-0.40 mm in diameter and (Top-left) backup cartridge with XAD-2.

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