



## Experimental study on the feasibility for noble gases (Xe, Kr) trapping using Metal-Organic Framework

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### ► To cite this version:

Julie Nguyen Sadassivame, Philippe Nerisson, Laurent Cantrel, Jérémy Dhainaut, Sébastien Royer, et al.. Experimental study on the feasibility for noble gases (Xe, Kr) trapping using Metal-Organic Framework. ERMSAR2022 - The 10th European Review Meeting on Severe Accident Research, May 2022, Akademichotel, Karlsruhe, Germany. hal-03902397

**HAL Id: hal-03902397**

**<https://hal.science/hal-03902397>**

Submitted on 15 Dec 2022

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## Development of an experimental test bench for dynamic adsorption of noble gases (Xe, Kr) by porous Metal-Organic Framework materials

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### ABSTRACT

Xenon and krypton are noble gases produced from fission reactions in nuclear fuel. During accidental situations, their potential releases can lead to significant radioactive doses in the short and medium terms, particularly for on-site operators. These radioactive isotopes have various half-lives, from few days (5.3 days for <sup>133</sup>Xe, short term nuclear accident tracer) to several years (10.8 years for <sup>85</sup>Kr). Due to their low reactivity and very high volatility, these gases are difficult to trap (nuclear mitigation) and separate (industrial applications).

Until recently, the capture of these noble gases had never been thoroughly investigated because only complex and expensive methods or processes were accessible, making them difficult to implement in industry. However, since a decade, relatively new porous materials named Metal-Organic Frameworks (MOFs) have demonstrated efficient trapping capacities towards volatile compounds, notably the capture of gaseous fission products such as volatile iodine or ruthenium tetroxide, as well as trapping of CO<sub>2</sub>. Indeed, these 3D hybrid metal-ligand materials, showing structural flexibility and variable pore diameters, can be functionalized in order to improve gases sorption.

The objective of this work is to study the feasibility of noble gases trapping by innovative porous materials such as MOFs in a nuclear context. This will contribute to better characterize the efficiency of filtration or purification devices (mitigation processes), to reduce radioactive releases under normal and accidental operations.

A first study has been carried out on a reference copper-based MOF called HKUST-1. Its efficiency for Xe and Kr sorptions, along with Xe/Kr selectivity, have been examined under static conditions as well as under dynamic conditions on the SAFARI homemade experimental bench at IRSN. This is an essential step before testing other promising materials less described in the literature. Thanks to SAFARI test bench, we can also analyze the effect of thermohydraulic conditions representative of accidental situations (flow velocity, temperature, humidity...) over the capture of noble gases. First results with HKUST-1 are presented.

### KEYWORDS

Noble gases, Metal-Organic Frameworks, trapping, severe nuclear accident, experimental study

## 1. INTRODUCTION

Xenon and krypton are noble gases naturally present in the atmosphere at concentrations around 0.087 ppmV and 1.14 ppmV, respectively. They are produced industrially as by-products of the cryogenic distillation of air, (nitrogen-oxygen separation, widespread technique though very energy consuming). In industry, xenon and krypton have different uses such as lighting or insulation. These gases also find medical uses, for imaging and anesthesia. In addition, xenon is used as a probe for NMR (Nuclear Magnetic Resonance) or as a fuel for space propulsion (ion engine). The capture and separation of xenon and krypton is therefore an economic issue but also a nuclear safety issue. Indeed, radioactive isotopes such as <sup>133</sup>Xe and <sup>85</sup>Kr are produced by nuclear fission of uranium and have half-lives of 5.3 days and 10.8 years respectively. These gases are not toxic as such, but they contribute to an accumulation of significant radioactive doses in the environment following nuclear tests, spent nuclear fuel reprocessing, production of medical isotopes or during a hypothetical nuclear severe accident on a NPP (Nuclear Power Plant).

Noble gases chemical inertia and high volatility make them difficult to trap and separate. Their capture using porous materials such as activated carbons or zeolites is reported in literature [1-4]. Moreover, for the past ten years, a new class of hybrid materials called Metal-Organic Frameworks (MOFs) has demonstrated remarkable performance in gas capture, selectivity and storage [5]. It concerns notably CO<sub>2</sub> [6] and fission products such as volatile iodine [7-8] or ruthenium tetroxide [9]. MOFs are crystalline materials made up of organic ligands and metal clusters (hence hybrid). They offer advantages such as high porosity (up to 7000 m<sup>2</sup>/g) [10], an infinity of possible structures and an unlimited functionalization by the choice of organic ligands or by doping with metallic particles. A judicious choice of the metal cluster (Al, Zr) can also make them resistant to radiations [11]. Different studies have been conducted for the capture of noble gases by MOFs under static and dynamic conditions (gas flow through MOF, less frequently studied) [12-13]. However, very few studies have been carried out under conditions representative of a nuclear accident: flow velocity through material, temperature, humidity, gas mixture, etc... Such data would be critical in the long term, notably to contribute to improve Filtered Containment Venting Systems (FCVS) [14] implemented on NPPs for mitigation of airborne releases, or equivalent devices in reprocessing plants.

To contribute to this latter point, after a state of the art in static and dynamic conditions, this paper presents the development of an experimental test bench allowing the dynamic study of noble gases adsorption (Xe, Kr) by MOFs and selectivity, under nuclear accident conditions listed above. This device named SAFARI, initially used for volatile iodine and RuO<sub>4</sub>(g) capture [15-16], is adapted for the study of noble gases capture, notably with the development of an online analysis method for noble gases by gas chromatography coupled with a mass spectrometer. In this work, the reference copper-based material HKUST-1 was synthesized. This MOF compound has two different pore sizes (5 Å and 15 Å) offering opened and polarizing metal sites, favorable for Xe and Kr adsorptions [17]. Its trapping capacities for noble gases in dynamic conditions will be compared to those obtained in static conditions in a previous step of this work. This experimental campaign with reference material will permit to validate SAFARI for noble gas studies, in order later on to test other promising MOF materials less described in the literature.

## 2. STATE OF THE ART ON NOBLE GAS TRAPPING

### 2.1. Static studies

Numerous studies discuss the adsorption of noble gases in porous materials such as MOFs [13] [18]. These studies are carried out under so-called static conditions, using a gas adsorption analyzer. This consists in inserting pure gas (Xe or Kr) into the material at fixed temperature; then gas-phase pressure variation is measured as a function of the adsorbed gas volume. Literature has highlighted the main parameters for optimizing the adsorption of noble gases in porous materials:

- Temperature: as it increases, the adsorption capacities are reduced due to the fact that gases become more volatile [19], thus limiting solid-gas interactions;

- Pressure: the adsorption capacities strongly increase with pressure. It is notably highlighted by Mueller *et al.* [20] for noble gases adsorption in MOF-5 at high pressure;
- Specific surface area: the general trend in the literature shows that the maximum adsorption capacities of noble gases are obtained for materials with high specific surface area (SSA), generally greater than 1000 m<sup>2</sup>/g. For example, xenon adsorption record is 7.1 mmol/g in PCN-14 (SSA = 2138 m<sup>2</sup>/g) and 1.4 mmol/g for krypton in NOTT-100 (1619 m<sup>2</sup>/g) at ambient temperature and pressure [21];
- Pore size: this important parameter can influence the selective adsorption of Xe/Kr. Selectivity S under static conditions is defined such as:

$$S_{Xe/Kr} = \frac{k_H(Xe)}{k_H(Kr)} \quad (1)$$

$$q = k_H P \text{ and } k_H = B q_m \quad (2)$$

With q the adsorbed amount (cm<sup>3</sup>/g), P the pressure (bar), k<sub>H</sub> the Henry constant (cm<sup>3</sup>/g/bar), B the Langmuir constant (bar<sup>-1</sup>) and q<sub>m</sub> the monolayer or saturated amount adsorbed (cm<sup>3</sup>/g).

Indeed, when this size is close to the kinetic diameter of Xe atom (4.10 Å), interactions are favored between the gas and the framework or the unsaturated material sites. Therefore, this makes it possible to create an induced dipole between the electronic cloud of the gas and the MOF. The kinetic diameters of the other gases (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, etc.) being smaller, they interact less with the material. On the other hand, MOFs belonging to this category do not have high adsorption capacities due to their low specific surface (generally less than 500 m<sup>2</sup>/g) [12]. Material SBMOF-1 is a good example since it holds the record of 16 for Xe/Kr selectivity, at 298 K and 1 bar [22]. Indeed, this solid has no unsaturated sites or high porosity (145 m<sup>2</sup>/g) but it presents pore sizes (4.5 Å) very close to the kinetic diameter of Xe atom;

- Functionalization of the ligand by specific groups: Lee *et al.* [23] presented the adsorption of Xe and Kr in functionalized UiO-66-X (with X = -NH<sub>2</sub>, -(OMe)<sub>2</sub>, -NH<sub>2</sub>(OMe)<sub>2</sub> and -F<sub>4</sub>) at 283 K and 1 bar. Xe adsorption capacity obtained in UiO-66-NH<sub>2</sub> (SSA = 1274 m<sup>2</sup>/g) is 2.3 mmol/g, greater than the original UiO-66 (1.3 mmol/g) while its specific surface is higher (1706 m<sup>2</sup>/g). This functionalization of the ligand also has an impact on Xe/Kr selectivity [23] since it modifies functional groups electron density: -NH<sub>2</sub>(OMe)<sub>2</sub> (14.4) > -NH<sub>2</sub> (11.4) > -(OMe)<sub>2</sub> (9.5) > -F<sub>4</sub> (7.4). The adsorption mechanisms involved are the Van der Waals forces because noble gases are uncharged and non-polar while they remain polarizable (Xe more than Kr). This is also shown by Meek *et al.* [24] on the adsorption of Xe and Kr at ambient temperature and pressure on halogenated IRMOF-2 [Zn<sub>4</sub>O(2-X-1,4-BDC)<sub>3</sub>] with X = F, Cl, Br or I. Thus, Xe/Kr selectivity increases with halogen size and so its polarizability: -I (4.17) > -Br (3.9) > -Cl (3.7) > -F (3.4). Perry *et al.* [21] studied noble gases adsorption in MOF-74-M (M = Co, Mg, Ni or Zn), containing open metal sites. They showed that adsorption and interaction energies increase with the polarizability of the gas. MOF-74-Co achieved the best selectivity (10.4), but no clear trend was defined between interaction energies and the nature of the open metal sites. On the other hand, this type of material obtained overall better performance due to the charge density of the unsaturated sites and its cylindrical and uniform structure (pore size of 11 Å).

## 2.2. Dynamic studies

As mentioned before, these works are much less conducted than static studies [12]. Dynamic breakthrough experiments allow concluding on the real potential of adsorbents. Breakthrough experiments involve a gas-mixture flow at different concentrations through a material, under fixed conditions of temperature and pressure (around 298 K and 1 bar for all reported studies). For a porous material, dynamic studies generally lead to adsorption capacities lower than under static conditions. Parameters influencing static adsorption,

mentioned in section 2.1, also have an impact on the breakthrough time (*i.e.* time when the target gas is detected downstream the material, at the outlet of the device).

Liu *et al.* [25] carried out dynamic breakthrough experiments on HKUST-1 and MOF-74-Ni materials. These materials were selected for their open metal sites, favorable to noble gases adsorption, and also for their different structures and pore sizes. A gas-mixture flow containing 1000 ppmV Xe or 1000 ppmV Kr in air was flowed through the material. The breakthrough times were around 8 min with xenon through the 2 solids, while krypton was detected downstream the MOF almost immediately after injection. Besides, Xe adsorption capacity was slightly higher in MOF-74-Ni (9.3 mmol/kg) than in HKUST-1 (8.5 mmol/kg), due to the stronger interaction between open metal sites of MOF-74-Ni and Xe. Conversely, Kr adsorption was slightly higher in HKUST-1 (2.0 mmol/kg) than in MOF-74-Ni (1.8 mmol/kg), owing to its bimodal pore sizes. In addition, this study showed that the gas-mixture concentration influences Xe/Kr selectivity, regardless of the material. Indeed, with a 80/20 (V/V) Xe/Kr gas-mixture, the relating Xe/Kr selectivity was lower than with a 20/80 (V/V) Xe/Kr gas mixture Xe/Kr. Selectivity  $S$  under dynamic condition is defined such as:

$$S_{Xe/Kr} = \frac{x_{Xe}/y_{Xe}}{x_{Kr}/y_{Kr}} \quad (3)$$

With  $x_i$  the adsorbed mole fractions and  $y_i$  the mole fractions in the upstream bulk gas for each species  $i$ . Material SBMOF-1 [22], mentioned previously, achieved a record breakthrough time of 55 min for Xe and 8 min for Kr, with a 400 ppmV/40 ppmV Xe/Kr gas-mixture in air. Moreover, this solid presented an exceptional Xe adsorption capacity of 13.2 mmol/kg. In addition, its low porosity and the absence of unsaturated sites give it great stability even in the presence of water. Finally, the breakthrough time can be increased by the doping of MOF structures with metallic particles, as conducted by Wang *et al.* [26] on MOF-303 which was silver-doped. Despite a reduced specific surface of MOF-303@Ag (716 m<sup>2</sup>/g) compared to the initial MOF-303 (1343 m<sup>2</sup>/g), the breakthrough time of Xe (20/80 (V/V) Xe/Kr gas mixture, room temperature and pressure) was increased by 25 min/cm<sup>3</sup>, thanks to the silver doping. Indeed, its pore size becomes close to the kinetic diameter of Xe atom, which favors Xe retention as mentioned in section 2.1.

All these dynamic breakthrough experiments were conducted at ambient temperature and pressure, which is not representative of a nuclear accident. In contrast, herein, the objective is to be able to evaluate the effect of severe thermohydraulic conditions over the capture of Xe and Kr by MOF materials.

### 3. MATERIAL AND METHODS

As mentioned above, copper-based MOF HKUST-1 has been chosen for this first step of noble gases trapping study, given it is a reference material, which synthesis in large-scale quantities is mastered and well referenced. Besides, previous studies exist in the literature for standard conditions (Liu *et al.*, cf. section 2.2), to compare the results.

#### 3.1. Synthesis of HKUST-1 material

The HKUST-1 large-scale synthesis conducted in the present study was derived from the protocol proposed by Giovine *et al.* [27]. 238,56 g (1,03 mol) of Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O and 143,14 g (0.68 mol) of trimesic acid were dissolved in 5 L of 50/50 (V/V) water/ethanol liquid mixture, inside a 8 L autoclave (Figure 1). The solution was heated at 110 °C during 23 h under stirring. The obtained suspension was thereafter centrifuged 3 times with ethanol à 60 °C, to recover blue crystals. These latter were dried at 70 °C during 12 h, prior to be activated at 110 °C during 12 h under vacuum then kept in glove box. The activated material was dark blue/purple, attesting that the material was effectively dried.



Figure 1. Picture of the 8 L autoclave used for the synthesis of HKUST-1 in which the solution is stirred and thermostated.

### 3.2. Characterization of HKUST-1 material

Powder X-ray diffraction diagram has been registered at ambient temperature using a diffractometer Bruker D8 Advance A25. N<sub>2</sub> adsorption-desorption isotherm at 77 K until 1 bar has been measured with a Micromeritics ASAP 2020 porosimeter. BET specific surface is calculated on the range  $0.015 \leq P/P_0 \leq 0.30$ . Before each measurement, the material is heated under a primary vacuum (5 Pa) at 110 °C during 12 h. Figure 2 presents both PXRD diagram and N<sub>2</sub> adsorption-desorption isotherm obtained for as-synthesized HKUST-1.

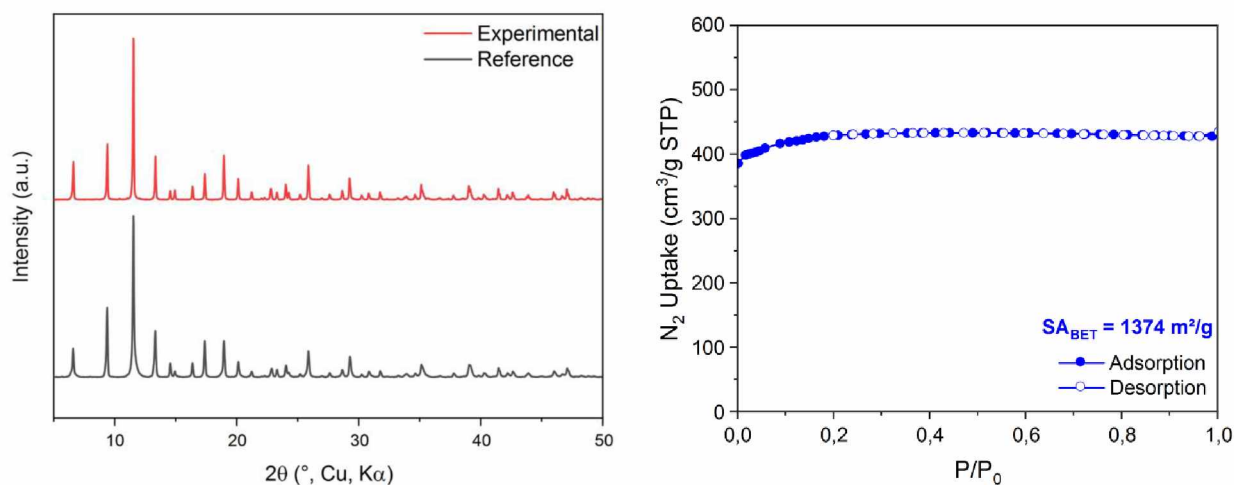


Figure 2. Left: PXRD patterns of activated HKUST-1 (top) and reference (bottom); Right: N<sub>2</sub> adsorption-desorption isotherm, related to a BET specific surface area value of 1374 m<sup>2</sup>.g<sup>-1</sup>.

### 3.3. Noble gases (Kr, Xe) analysis

Noble gases analysis is performed continuously online by gas chromatography coupled to a mass spectrometer (GC-MS). Gas chromatography module (Agilent 7820A, injection split/splitless) is made up of a pre-column (Agilent J&B PoraBond Q with two particle traps) of sizes  $3\ \mu\text{m} \times 0.25\ \text{mm} \times 25\ \text{m}$ . This permits heavy gases to be evacuated through a 6-way valve and allows light gases to reach the second column with molecular sieve (Agilent J&W CP-Molsieve 5 Å) of sizes  $30\ \mu\text{m} \times 25\ \mu\text{m} \times 25\ \text{m}$ . Isotherm analysis is done at 130 °C, with a carrier gas flowrate (helium) of 1 mL/min in the first column and 5 mL/min in the second column. The sampling loop volume, driven by a 6-way valve, is 1 mL and the split ratio is 150:1. The sampling loop is continuously swept by the SAFARI bench outlet gas flow. The 6-way valve is then programmed to inject the volume of the loop into the separation columns using the carrier gas. The uncertainty of the measurement is 10 %.

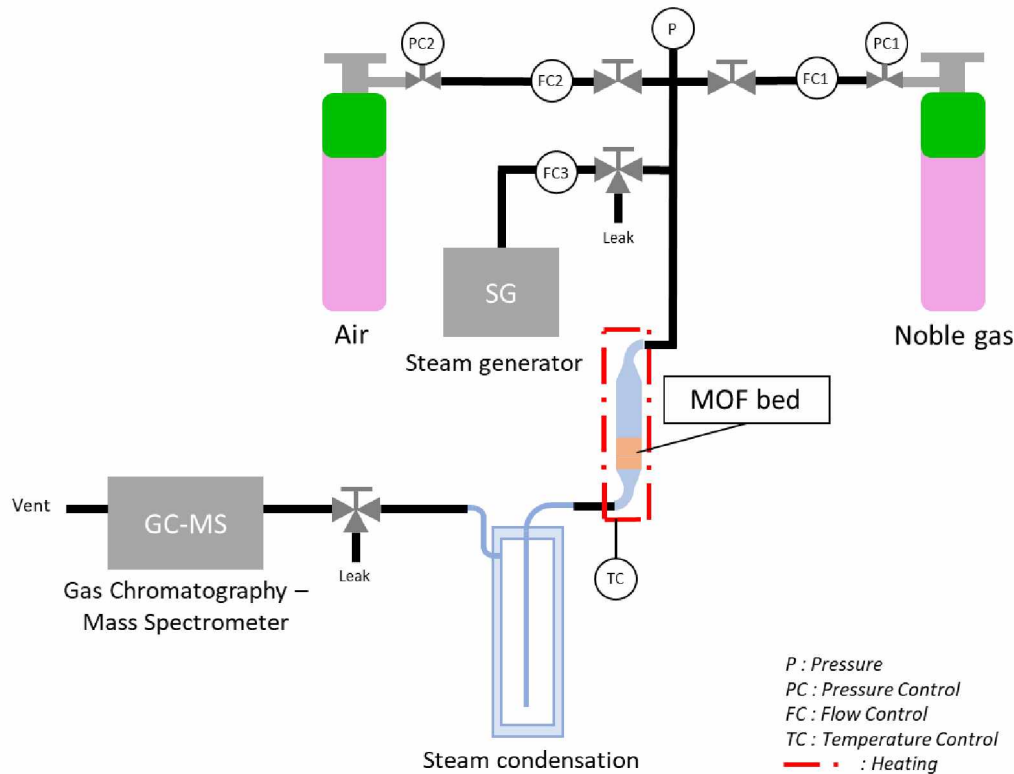
The mass spectrometry module (Agilent 5977B GC/MSD) allows ionization of the sample by electron impact (EI) at 230 °C and mass analysis by a quadrupole at 150 °C.

Commercial gas cylinders titrated at 1000 ppmV and 100 ppmV in Xe and Kr separately are diluted on a dedicated dilution bench, to obtain standard samples for apparatus calibration. High purity helium (99.99%) is used as carrier gas.

### 3.4. Experimental test bench SAFARI

Dynamic breakthrough experiments are carried out on the SAFARI test bench (Figure 3), at IRSN (Institute for Radioprotection and Nuclear Safety, Cadarache, France). This experimental device allows the injection of xenon and/or krypton diluted in air through a bed of adsorbent material. The flow downstream the adsorbent bed is analyzed online by GC-MS (see section 3.3). Before each gas adsorption experiment, the material is activated at 110 °C for 1 hour. Then, the cylindrical glass column (diameter 2 cm) containing a 1 cm height bed of dried adsorbent (1.8 g of HKUST-1) on a sintered filter, is placed in SAFARI test bench, as shown on Figure 3. Heating cords and heat insulators are placed around the column, as well as a thermocouple to regulate the temperature. Before and after each xenon and/or krypton breakthrough experiment, the line is swept with dry air at 1 cm/s. This procedure is applied for each test. Steam can also be added to the gas stream at a desired flowrate, to reach the target relative humidity. In dynamic experiments, xenon (or krypton) diluted in air at 500 ppmV or 400/40 ppmV Xe/Kr gas mixture, are injected at a rate corresponding to 1 cm/s in the glass column through the material. Gases are injected from the top of the column and a glass bubbler is placed at the outlet to condense the water vapors (for tests involving steam) before injection into the GC-MS. Improving the online GC-MS analysis for Xe and Kr is part of this work: the GC-MS outflow gas sampler is programmed to inject a known volume into the separation columns, at periodic intervals. This permits to obtain a more regular sampling (every 3 min) and a curve with more points.





**Figure 3. Experimental test bench SAFARI for dynamic adsorption of noble gases into a MOF sample.**

## 4. RESULTS AND DISCUSSION

The first dynamic experiments series performed on SAFARI bench for noble gases adsorption in HKUST-1 have permitted to investigate:

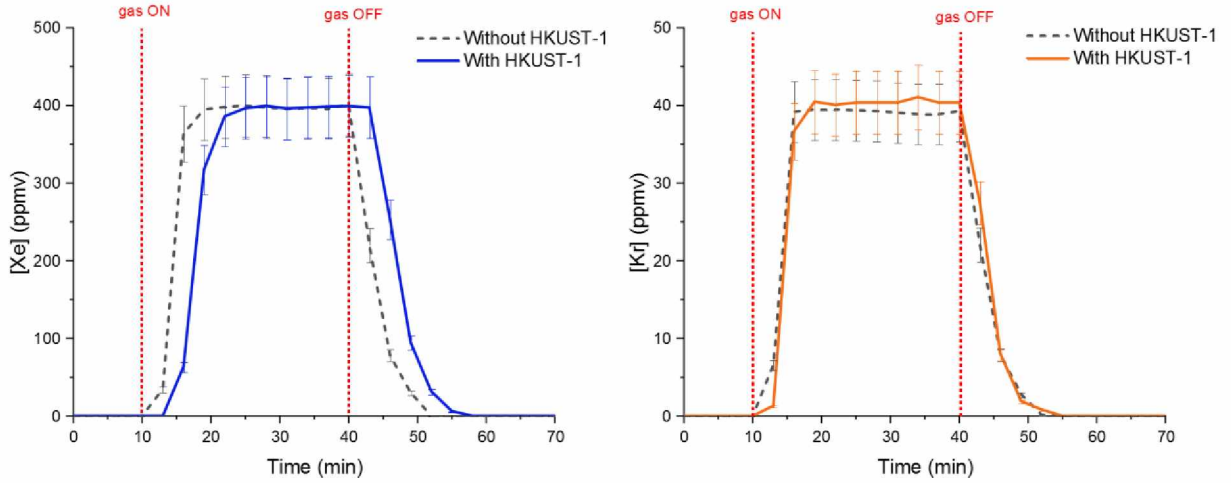
- Selectivity of Xe/Kr adsorption in HKUST-1 at ambient temperature;
- Influence of temperature on noble gases adsorption;
- Influence of humidity on noble gases adsorption;
- Comparison with results obtained in static conditions.

These points are detailed below.

### 4.1. Selectivity of Xe/Kr adsorption in HKUST-1 at ambient temperature

Figure 4 below presents the monitoring of Xe and Kr concentrations, measured with GC-MS downstream the MOF HKUST-1 bed as a function of the experiment time. The test is performed at ambient temperature with a dry airflow such as  $[Xe] = 400$  ppmv and  $[Kr] = 40$  ppmv upstream the MOF. The dash curves correspond to the experiment without material (blank test) and the line curves are the breakthrough test with MOF HKUST-1.





**Figure 4. Xe (left) and Kr (right) breakthrough curves in HKUST-1 material on SAFARI test bench.**  
[Xe]<sub>upstream</sub> = 400 ppmV, [Kr]<sub>upstream</sub> = 40 ppmV, 22 °C, 1 bar. Velocity: 1 cm/s.

According to breakthrough curves on Figure 4:

- Breakthrough time (*i.e.* time when the signal attesting noble gas presence is detected downstream the HKUST-1, compared to this time in blank test, taking into account injection and timeout due to GC-MS measurement) is around 5 min for Xe and 0 min for Kr;
- Trapping capacities are estimated at 5.68 mmol<sub>Xe</sub>/kg<sub>MOF</sub> and 0.064 mmol<sub>Kr</sub>/kg<sub>MOF</sub> (integration method, equation 4).

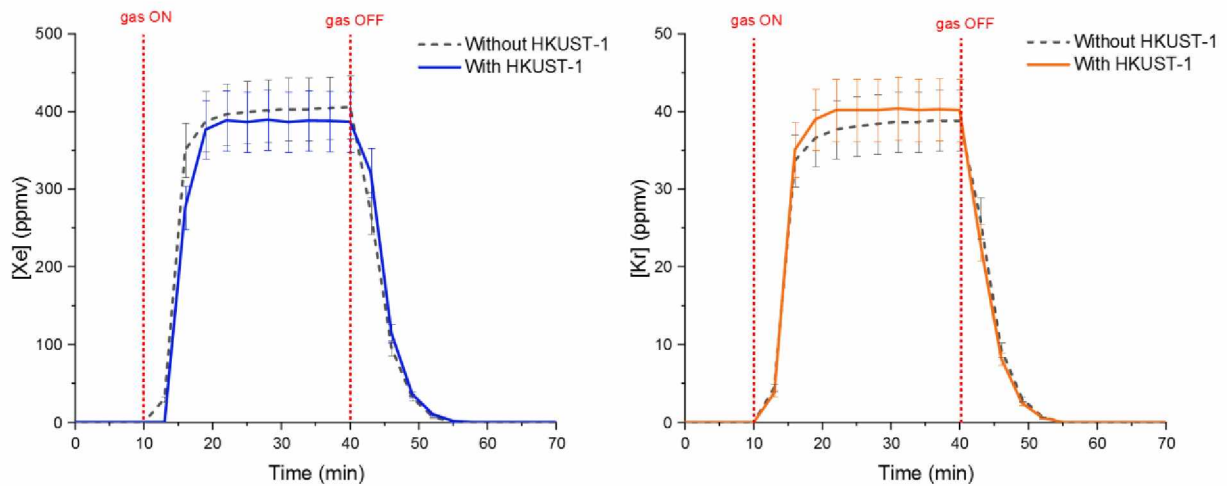
$$q = \frac{Q_v \int_0^{t_s} (C_{blank} - C) dt}{V_m W} \quad (4)$$

With  $q$  the adsorbed amount of the gas (mol/g),  $Q_v$  the injected gas flow rate (cm<sup>3</sup>/min) in the Standard Temperature and Pression (STP),  $t_s$  the time of bed saturation (min),  $C_{blank}$  and  $C$  the Xe or Kr concentrations in the flow respectively for blank test and test with MOF (ppmV),  $V_m$  the molar volume (m<sup>3</sup>/mol) in the STP and  $W$  the mass of the activated adsorbent material (g).

These results confirm the selectivity of Xe over Kr in HKUST-1, noted  $S_{Xe/Kr}$ , (cf. equation 3 in section 2.2). Indeed, with trapping capacities determined above,  $S_{Xe/Kr} = 8.9$  in HKUST-1. This selectivity can be associated to gas atomic diameters compared to pore sizes. This value is higher than data provided by Liu *et al.* [25], where  $S_{Xe/Kr} = 4.3$  is obtained experimentally using HKUST-1. This gap can be explained by differences in experimental conditions, especially upstream concentrations ( $[Xe] = [Kr] = 1000$  ppmV for Liu *et al.*), gas velocity through the MOF and MOF properties such as shaping. Liu *et al.* also mention a selectivity of 2.6 obtained with Xe/Kr mixture of pure gases (volume ratio 20:80), and the corresponding value predicted with GCMC simulation by Ryan *et al.* [28], where  $S_{Xe/Kr}$  was determined to be of 8.1 in HKUST-1 (higher than experimental results of Liu *et al.*). These values confirm the strong dependence of selectivity on the operating parameters, even if the order of magnitude remains the same.

## 4.2. Influence of temperature

Figure 5 presents the breakthrough curves obtained for Xe and Kr in HKUST-1 at 50 °C in dry air.

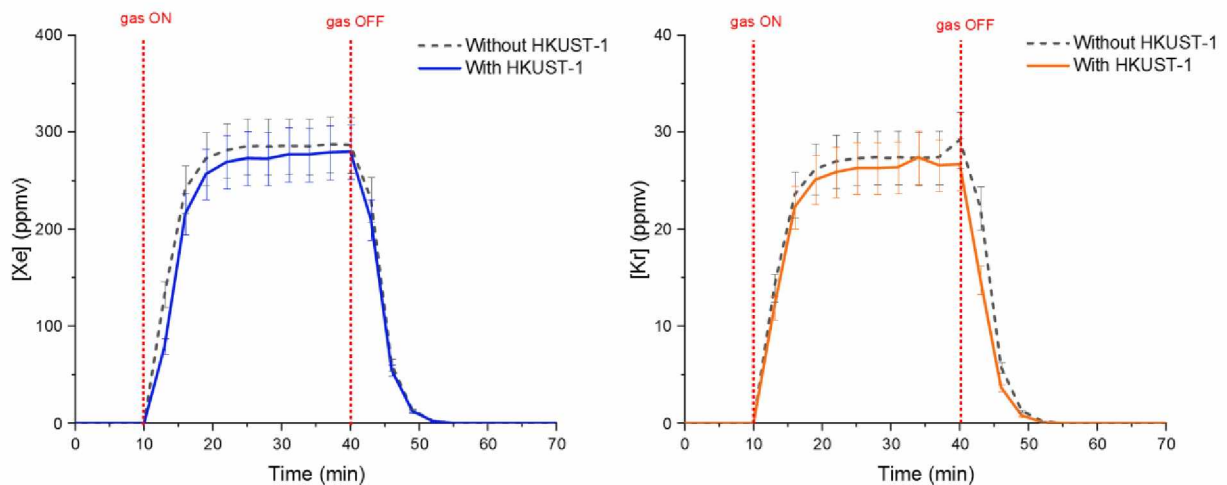


**Figure 5. Xe and Kr breakthrough curve in HKUST-1 material on SAFARI test bench. Influence of temperature.  $[Xe]_{\text{upstream}} = 400 \text{ ppmV}$ ,  $[Kr]_{\text{upstream}} = 40 \text{ ppmV}$ ,  $50^\circ\text{C}$ , 1 bar. Velocity: 1 cm/s.**

The breakthrough curves on Figure 5, compared to curves presented on Figure 4, show that breakthrough time of Xe in HKUST-1 decreases from 5 min to 3 min when temperature increases (0 min for Kr in both cases). It highlights that adsorption capacities of Xe decreases with temperature as expected. This can be explained by the increase in volatility of gases with temperature.

#### 4.3. Influence of humidity

Figure 6 presents the breakthrough curves obtained for Xe and Kr in HKUST-1 at  $50^\circ\text{C}$ , for a relative humidity  $\text{RH} = 30\%$ . It corresponds to a steam flowrate of  $0.28 \text{ g}\cdot\text{h}^{-1}$ .



**Figure 6: Xe and Kr breakthrough curve in HKUST-1 material on SAFARI test bench. Influence of humidity.  $[Xe]_{\text{upstream}} = 300 \text{ ppmV}$ ,  $[Kr]_{\text{upstream}} = 30 \text{ ppmV}$ ,  $30\% \text{ RH}$ ,  $50^\circ\text{C}$ , 1 bar. Velocity: 1 cm/s.**

The breakthrough curves on Figure 6, compared to curves presented on Figure 5, show breakthrough time of Xe in HKUST-1 decreases to zero min when RH increases (0 min for Kr in both cases). It highlights that

adsorption capacities of Xe decrease when RH increases. This can be explained by the competition between Xe and water molecules to fill the pores.

#### 4.4. Comparison to static tests

As mentioned in the introduction, HKUST-1 trapping capacities for noble gas have been tested in static conditions in a first step of this work. More precisely, adsorption isotherms of Xe and Kr in HKUST-1 have been established (Figure 7), thanks to the same apparatus as that used for BET specific surfaces measurements (see section 3.2), with pure Xe or Kr gas instead of N<sub>2</sub>. These curves allow to determine Xe and Kr adsorption capacities CS and selectivity  $S_{Xe/Kr}$  in HKUST-1 in static conditions. Some of them are, reported in Table 1, to compare with dynamic conditions.

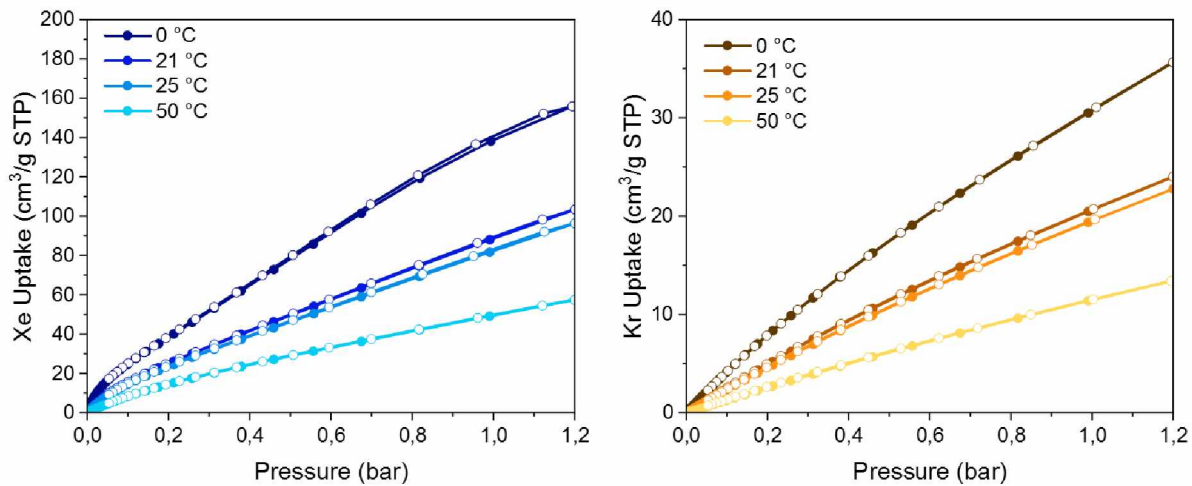


Figure 7 : Adsorption isotherm of Xe (left) and Kr (right) under static conditions in the temperature range of 0 to 50 °C.

Table 1: Comparison of Xe and Kr adsorption capacities (CS) and selectivity in HKUST-1 in dry gas, in static and dynamic conditions (1 bar). Influence of temperature.

Température (°C)	$CS_{Xe}$ (mmol/g) static	$CS_{Xe}$ (mmol/kg) dynamic	$CS_{Kr}$ (mmol/g) static	$CS_{Kr}$ (mmol/kg) dynamic	$S_{Xe/Kr}$ Static Equation 1	$S_{Xe/Kr}$ Dynamic Equation 3
22	3.64	5.68	0.84	0.064	9.7	8.9
50	1.83	1.94	0.43	0.00	9.1	-

Results listed in Table 1 show the same trend linked to temperature increase between static and dynamic tests, namely that adsorption capacities decrease while temperature increases. It also highlights the most important quantities of noble gases adsorbed in static conditions. It is logically explained using pure gases under pressure for static experiments, compared to diluted flows used in dynamic studies.

## 5. CONCLUSIONS

This work aims to determine the feasibility of trapping noble gases using a new class of so-called "hybrid" materials named Metal-Organic Frameworks (MOFs). Literature review made it possible to highlight the

main parameters influencing the adsorption capacities of noble gases into MOFs, as well as their Xe/Kr trapping selectivity. Up to now, very few studies reported adsorption studies under dynamic conditions, representative of a hypothetical accidental scenario impacting nuclear plants (noble gases concentrations, temperature, humidity, etc.).

So, objectives of this work were to identify and characterize a reference MOF, and to evaluate its noble gas adsorption capacities under dynamic conditions. For this latter point, described in this paper, a method has been developed and improved on SAFARI test bench. Thereby, the reference MOF called HKUST-1 has been synthesized and characterized. The Xe and Kr adsorption study performed with HKUST-1 provides very encouraging results, allowing the test bench validation. Indeed, Xe retention inside the MOF and selectivity of Xe over Kr are confirmed, in accordance with literature results. Besides, influences of temperature and humidity have been investigated to reach more representative conditions of the nuclear severe accidents context. Thus, the increase in temperature or RH lead to a decrease in the adsorption of noble gases. In line, additional experimental tests are in progress, dealing with more severe conditions (up to 150 °C, higher RH, higher velocity through the MOF).

The next step of this work is to perform static tests with new MOFs, to select potential promising compounds for noble gas trapping. It concerns notably MOFs such as MIL-100 or MOF-303, given their suitable synthesis processes, pore sizes and Ag-doping possibilities. The most efficient MOFs in these conditions will be tested later in dynamic and representative conditions (T, RH,...) on SAFARI test bench. Results obtained with HKUST-1 will be presented at ERMSAR 2022.

## ACKNOWLEDGMENTS

This work was performed in the French Institut de Radioprotection et de Sûreté Nucléaire (IRSN) and Unité de Catalyse et Chimie du Solide (UCCS, Lille), with the financial support of NUVIA Company.

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