

IODINE TRAPPING BY POROUS MATERIALS TO MITIGATE RADIOACTIVE RELEASES TO THE ENVIRONMENT

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Abstract

This paper deals with near past, ongoing and planned R&D works on iodine trapping behaviour to mitigate radioactive releases to the environment in case of potential severe accidents in nuclear power plants. These works were performed in the frame of the PASSAM and MIRE (Mitigation of outside Releases in the Environment) projects. These researches are mainly devoted to studying iodine trapping for Filtered Containment Venting System (FCVS) applications, linked to post-Fukushima management of severe accidents.

Two types of porous materials were tested: exchanged-zeolites and Metal Organic Frameworks (MOFs). The performance of different materials with respect to iodine filtering efficiencies has been studied at lab-scale experiments. In complement to this experimental work, some *ab initio* modelling approaches were developed for better understanding the influence of key parameters on trapping by using VASP (The Vienna *Ab initio* simulation package) which is a plane wave electronic structure computer code.

Various zeolites and MOFs were examined to make a link between the porous material characteristics, their chemical composition and their iodine filtration efficiency. These porous materials are characterised before and after iodine trapping by different techniques (XRD, HRTEM, GC, DR-UV-Vis spectroscopy, DRIFTS of adsorbed CO etc.) in order to establish relationships between the structural/chemical properties and their trapping capabilities. The main experimental parameters investigated are: temperature, gas composition (humidity) and irradiation for molecular iodine and methyl iodide filtering tests.

Silver zeolites appear to be suitable materials to trap volatile iodine species in severe accident conditions but some issues are still open, such as possible saturation by contaminants or ageing of the materials. Even if promising results were obtained for MOF, some open issues remains to investigate like to find formulation with good resistance to irradiation and humidity and good capacity of iodine trapping with no significant desorption.

1 INTRODUCTION

Since Fukushima accident, interest for mitigation means has renewed for NPPs. Volatile iodine, mainly I₂ and CH₃I [1], which can be released in case of severe accident (SA) contribute to high radiological consequences at short term, during the first month following the accident. In order to preserve the integrity

of the nuclear containment building, SA management guidelines aim at depressurizing this containment when the pressure reaches a threshold value. This depressurization occurs via a Filtered Containment Venting System (FCVS) in order to mitigate fission products (FPs) releases. These FPs are either under aerosol or gas forms. A recent OECD report [2] reviews the different types of FCVS used in the world. In France, after the TMI-2 and Chernobyl accidents, EDF decided to install passive FCVS composed of a sand bed filter plus a pre-metallic filter [3]. In term of filtering capacity, this FCVS was designed to trap aerosols.

Following the Fukushima Daiichi accident, many safety authorities recommend to utilities either to install FCVS on their Nuclear power Plants (NPPs) or to examine possible improvements of the filtering capacities of the existing FCVS and, noticeably, to extend their performance to trap volatile iodine species. Some R&D works were launched with the objective to propose some technical solutions to trap volatile iodine mainly via the EU PASSAM project (2013-2016) and the French program “investissement d’avenir” called MiRE (2013-2021), managed by the National Research Agency (ANR).

This paper will describe main works performed involving mainly specific porous materials with two classes tested: exchanged-zeolites and Metallic-Organic-Frameworks (MOFs). Zeolites are perfectly crystallized microporous aluminosilicates whereas MOFs are compounds consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures.

The first type of sorbents is already used in the nuclear industry and the second is a new type of porous materials whose potential applications are widely studied at that time [4].

2 LITERATURE REVIEW

A first work consisted in a literature reviews [5-6] to get a clear view of the existing works on the trapping of iodine by porous materials and define the needs of complementary works. It is also worth noticing that literature reviews were performed recently [7-8] in this topic of interest.

From a general point of view, many works were carried out for organic iodide trapping in what was called “standard conditions”, it means about room temperature and low relative humidity. The objective was to get efficient filters in order to reduce chronic releases in normal operating conditions. The SA conditions being more drastic, iodine should be trapped at high temperature, typically above 100°C, in steam/air carrier gas and under irradiation.

Metal-Organic Frameworks are crystalline hybrid materials constructed from inorganic nodes and organic ligands (cf. Figure 1). This association leads to the production of open frameworks usually composed of pores and/or channels, with diameters from few angstroms to several nanometers [9]. Theoretically, all the metals from the Mendeleev table and an infinite type of complexing organic ligands can be used for the generation of such compounds. De facto, prototypical MOFs are usually produced from carboxylic acids and transition metals (Cr, Cu, Zn, Zr) or block p elements (Al). This combination usually favours the synthesis of stable and well crystallized compounds, facilitating their study and characterization. The very low density of MOFs, coupled to an important porosity, explains why this family of materials usually exhibits higher specific surface areas (up to 7000 m²/g) than those observed with common porous purely-inorganic materials like zeolites.

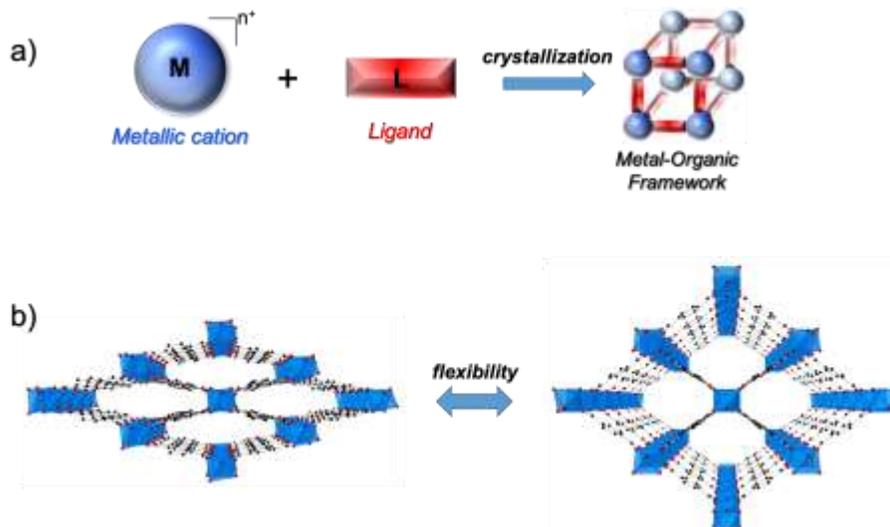


Figure 1: (a) Illustration of the MOF synthesis from metallic cation and organic ligand. (b) Illustration of the MOF flexibility in the case of MIL-53 (aluminium terephthalate).

In addition to their impressive porosity, some MOFs show another uncommon behaviour: their framework is capable of swelling (Fig. 1.) [10]. This flexibility without bonds breaking is triggered by guest adsorption/desorption, photochemical, thermal, and mechanical stimuli.

All these unique features offer to MOFs a huge academic interest and open the door to many industrial applications like gas storage, catalysis, biomedicine or sensing.

Compared to zeolites, one of the main restrictions of MOF applications remains their stability [11]. Indeed, hydrolysis reactions in presence of water weaken bonds between the metallic part and the organic ligand. Furthermore, the thermal stability of MOFs mainly depends on that of the organic part, which typically decomposes between 300 and 400°C. However, the literature gathers many examples of porous MOFs showing very good resistance in the presence of water (liquid or steam) or at high temperature (up to 500°C) [12].

If we focus the literature review to zeolites and MOFs, some trends can be draught.

- For zeolites, silver appears to be the most appropriate metal to trap iodine as illustrated in Table 1 because the chemisorbed amount is higher and guarantees low desorption. Silver has a good exchange affinity with Na⁺, H⁺, NH₄⁺ ions presents in the synthetic forms of zeolites. In comparison with other metals, silver is relatively non-toxic and has especially the faculty to form AgI phases thermally stable and chemically relatively stable [13].

As inconveniences of silver, we can quote its high price and also its marked trend to thermal caking and to changing of speciation under the influence of atmosphere and radiations (photo-reduction due to UV light).

Table 1. Effect of the cation type on the adsorption capacity at saturation of I₂ by zeolites type X at 150 °C [14].

Adsorbent	I ₂ amount (mg/g of adsorbent)		
	Iodine at saturation	Physisorbed amount	Chemisorbed amount
NaX	364	334	30 (8%)
AgX	349	135	214 (61%)
PbX	179	153	26 (15%)
CdX	374	329	45 (12%)

- For MOFs, in 2003, Abrahams et al [15] showed the possibility to insert some iodine into a saccharate of porous zinc. Since this precursory work, more than ten MOFs were tested as regards the insertion of iodine [16-20]. The most relevant works are the ones made by the team of Nenoff (Sandia Lab, Albuquerque) [16-18] on the capture of gaseous iodine in the ZIF-8 and the HKUST-1 MOFs.

Relevant results were obtained as displayed in Figure 2.

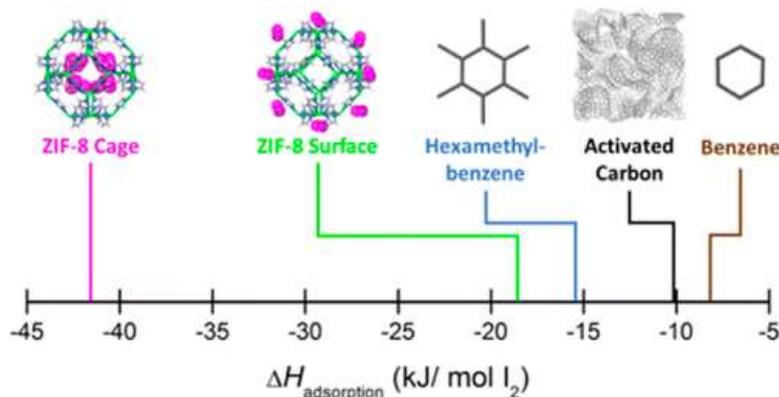


Figure 2: Adsorption enthalpy of molecular iodine for different materials including the ZIF-8 MOF.

Nenoff's team only focused on two MOFs with divalent cations (Cu^{2+} and Zn^{2+}). MOFs with divalent cations are generally less stable chemically than MOFs built from trivalent cations. Thus we chose to study radionuclide trapping by aluminum-based MOFs.

For nuclear applications, these preliminary works on I_2 sorption were followed by other studies involving other potential radioactive species involving iodine (CH_3I) or other elements (Th, U, Tc, Xe, Kr, Ru, ...) [21].

In the next paragraphs, experimental and theoretical works performed are summed up.

3 VOLATILE IODINE TRAPPING BY ZEOLITES

Some experimental works were carried out to study trapping of iodine according to the carrier gas composition, the nature of the zeolite, the amount of silver loading *etc.* In complement to experiments, theoretical modelling, at molecular scale, was performed to i) identify reactive sites ii) study the nature of the zeolite (Faujasite versus Mordenite) and iii) see potential impacts with contaminants.

Hereafter, the main results are summarized. Detailed results are available elsewhere [22-28].

3.1 Main experimental results

Different types of zeolites were prepared either by means of ion exchange with silver nitrate or by incipient wetness impregnation, which consists in saturating the pores of a sorbent with a known volume (i.e. the pore volume) of a silver nitrate solution whose concentration has been set to achieve a given silver content in the zeolite. Prior to adsorption and characterization studies, all zeolitic materials were calcined under static air in a muffle furnace with a heating rate of $5^\circ\text{C}/\text{min}$ from room temperature to 200°C (plateau of 1 hour) and then to 500°C (plateau of 2 hours). This procedure allowed to remove most of nitrates and ammonium impurities from the preparation and to obtain thermally stable materials for retention tests. Three experimental set-up were used, two lab-scale experimental lines located at University of Lorraine and the PERSEE line located at IRSN/Saclay (Figures 3 and 4). These set-ups are devoted to adsorption tests in dynamic gas-phase conditions for I_2 and CH_3I , respectively.

Different techniques were employed to characterize the zeolites and the state of silver, we can cite N_2 porosimetry at 77K, UV-Vis spectroscopy in diffuse reflectance mode (DR-UV-Vis) for which a large

amount of information on the nature of silver species in zeolites could be obtained and X-Ray Diffraction for silver-containing phases (Ag^0 and AgI).

At lab-scale, CH_3I quantification was made using infrared spectroscopy and important adsorption properties such as adsorption capacities at breakthrough and at saturation, as well as CH_3I desorption profiles were determined with good accuracy. In the PERSEE loop, labelled methyl iodide was used with γ -counting for iodine measurement. For I_2 , gas-phase concentrations were continuously monitored from UV-spectra absorbance measurements ($\lambda = 523 \text{ nm}$).

Refinement of experimental data provided information for capacity at saturation, percentage of AgI formed (Figure 5) and influence of gas composition.

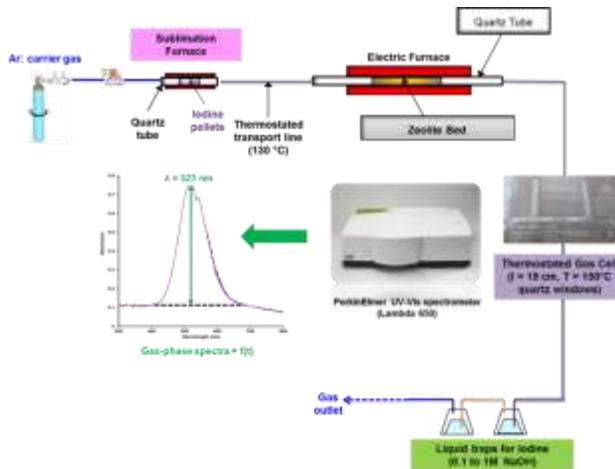


Figure 3: lab-scale experimental I_2 adsorption setup at University of Lorraine

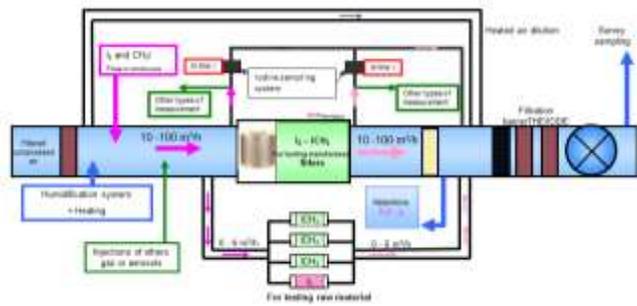


Figure 4: PERSEE pilot-scale CH_3I setup at IRSN (more representative of SA conditions in terms of gas velocity, humidity etc.)

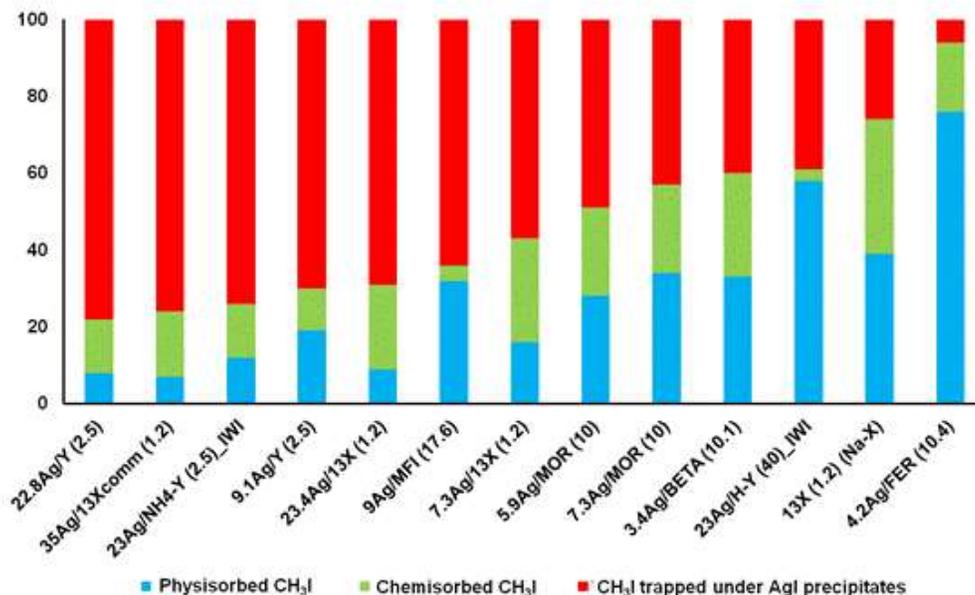


Figure 5: Ranking corresponding to the ability of the different studied sorbents to promote an irreversible trapping for CH_3I . The best sorbents are on the left side of the diagram [25].

The main results obtained can be summarized as follows:

- experimental results show that silver zeolites appear to be suitable adsorbents to trap irreversibly volatile iodine (I_2 and CH_3I) in severe accident conditions;
- the type of zeolite and the method of silver incorporation (impregnation or ion-exchange) influence the physico-chemical characteristics of silver species and the zeolite retention performances towards volatile iodine (this is especially valid for CH_3I , not or much less for I_2);
- in addition to a pore structure compatible with the size of CH_3I and I_2 ($> 0.5-0.6$ nm), a high amount and a high proportion of silver as dispersed species in cationic (at exchange sites) or cluster state seem to be mandatory in order to promote iodine retention as AgI;
- among a dozen of investigated silver zeolites, large-pore faujasite Y zeolite with silver content at least higher than 10%/w and with Si/Al ratio of 2.5 can be especially recommended.

The mechanism of CH_3I trapping at $100^\circ C$ was also investigated using *in situ* spectroscopic techniques. It was found that CH_3I could be either molecularly adsorbed or dissociated on silver or protonic sites, yielding methoxy species (and various kinds of hydrocarbons by thermal decomposition) and molecular AgI. In the course of adsorption process, AgI entities progressively grow in size. Upon return to ambient conditions, the embedded AgI clusters escape the porosity to form sintered AgI phases detectable by XRD.

3.2 Main theoretical results

In complement to experimental works, some molecular simulations were performed by Density Functional Theory (DFT) computations with the VASP software to investigate impact of zeolite structure (Faujasite vs Mordenite), possible effect of gas contaminants and also try to better identify reactive sites as well as the chemical mechanism of iodine trapping [28]. Figure 6 displays an example of computed results obtained.

It can be stated that:

- the simulations are consistent with experimental results showing that silver is the best metal to selectively trap methyl iodide;
- CO may interfere with iodine adsorption between 298 K and 523 K. The chemical affinity with silver-faujasite zeolites ranks as follows: $CH_3I > CO > I_2 > CH_3Cl > NO > H_2O > Cl_2$;
- The same trends are observed for the mordenite structure. We have shown that the Si/Al ratio (i.e. the silver content) is a key parameter driving the adsorption selectivity [27]. At low Si/Al ratio, the adsorption of iodine species is largely favoured compared to CO and H_2O . Therefore, the best compromise between resistance to steam and efficiency of iodine trapping has to be found. The mechanism of iodomethane trapping in a silver zeolite has been investigated using *ab initio* molecular dynamics. The formation of AgI aggregates inside the zeolites leading to an almost irreversible trapping has been evidenced in line with the experimental findings.

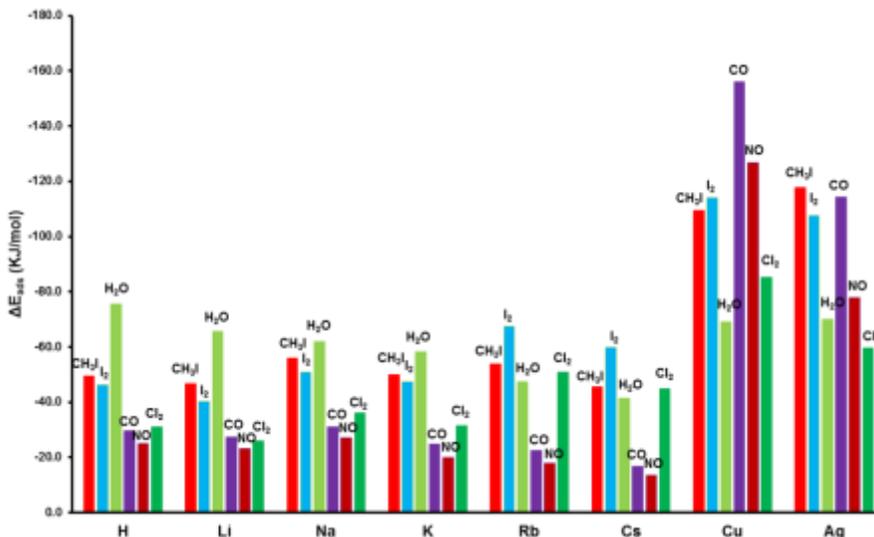


Figure 6: Interaction energies at 0K of I₂, CH₃I compared to CO, H₂O and NO for Faujasite exchanged with various monovalent cations [25].

The static DFT approaches at 0K used here are quite sufficient to propose zeolite formulations to be tested experimentally. However, they have several disadvantages: it does not provide the geometry of the adsorbate at a given temperature, the mobility of the cation induced by adsorption is poorly evaluated, and co-adsorption phenomena are difficult to evaluate. The use of more sophisticated *ab initio* molecular dynamics (AIMD) will allow tackling new issues such as co-adsorption (simulation with several molecules at the same time), refining the understanding of iodine trapping mechanisms and gaining confidence in extrapolations with experimental data.

4 VOLATILE IODINE TRAPPING BY MOFS

4.1 Characteristics and stability of MOFs under gamma irradiation

Prior to address the capture of radionuclides during a nuclear accident, MOFs have to prove their resistance to the drastic conditions encountered during this event. In the MIRE project, we evaluated for the first time the capacity of MOFs to resist to gamma radiation [29]. Due to their low ionizing power compared to alpha and beta particles, gamma rays are more penetrative and offer the easiest alternative for investigating the radiation damage of materials. Therefore, prototypical carboxylate-based MOFs (MIL-53[Al], MIL-100[Al], CAU-1[Al], UiO-66[Zr], HKUST-1[Cu] and ZIF-8[Zn]) involving different characteristics (metals, oxidation states and porosities) were selected, and submitted to calculated doses up to 2 MGy. These experiments were performed within the IRSN gamma irradiation cell called IRMA (IRadiation MAterials). This study proved the high resistance of aluminium-based MOFs (called MIL-53, MIL-100 and MIL-120) under gamma irradiation, which are stable at least up to 2 MGy. Under the same conditions, the other selected compounds synthesized from Cu²⁺, Zn²⁺ or Zr⁴⁺ (called HKUST-1, ZIF-8 and UiO-66, respectively) are partially decomposed by radiation. Based on these results, the better stability of Al-MOFs was assigned to the lower cross section of the metal involved in the structure (aluminium). While the hybrid framework is not damaged by the electromagnetic wave, trapped chemical species could be decomposed during the process, improving the porosity of the irradiated materials.

4.2 Capture of volatile iodine derivatives (I₂ and CH₃I) in prototypical MOFs

Due to their very high stability under severe conditions (high temperature, steam, and radiations), the efficiency of Al-based MOFs was also analysed for the capture of volatile iodine. For the immobilization of I₂ in MOFs, we selected a functionalized version of MIL-53[Al] decorated by thiol-groups associated to

the 2,5-dithiol-1,4-benzenedicarboxylate ligand [30]. This solid was submitted to a flow of gaseous iodine (0.87 mg of I₂ per hour at room temperature) diluted in argon, by using a home-made installation allowing the control of the iodine gas flow and the measurement of iodine trapped within the porous material. Iodine maximum uptake is reached after 2 days of impregnation and corresponds to a value of 325 mg of iodine trapped per gram of the functionalized version of MIL-53[Al]. Raman spectroscopy combined with sulfur K-edge XANES spectroscopy indicated the formation of sulfenyl iodide groups (S-I bond), cf. Figure 7, proving the chemisorption of iodine within the framework.

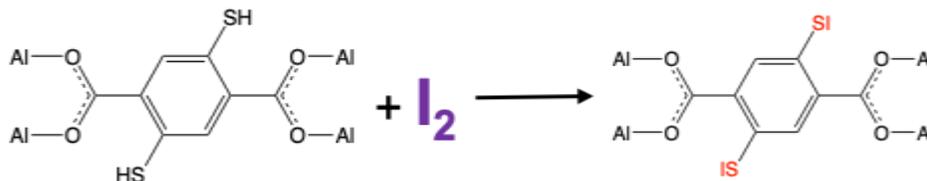


Figure 7: Strategy for the immobilization of volatile iodine in aluminium-based MIL-53-(SH)₂.

The capture of iodine derivatives was extended to methyl iodide (CH₃I), a volatile molecule produced either from the reaction between I₂ and epoxy paints usually covering the walls of the nuclear reactor buildings or from direct reactions with I₂ and organics present in the containment atmosphere. For this study [31], several prototypical MOFs were selected (MIL-53[Al], MIL-100[Al], CAU-1[Al], UiO-66[Zr], HKUST-1[Cu] and ZIF-8[Zn]), covering a large range of porosities and structural features, in order to highlight the factors driving the capture of CH₃I within this type of solids. The adsorption behaviour was studied using dedicated breakthrough experiments based on CH₃I dynamic sorption and its quantification by Infra-Red (IR) spectroscopy, cf. Figure 8. After impregnation, the MOFs were also submitted to a pure argon gas flow, in order to determine the affinity of adsorbed species within the porous framework.

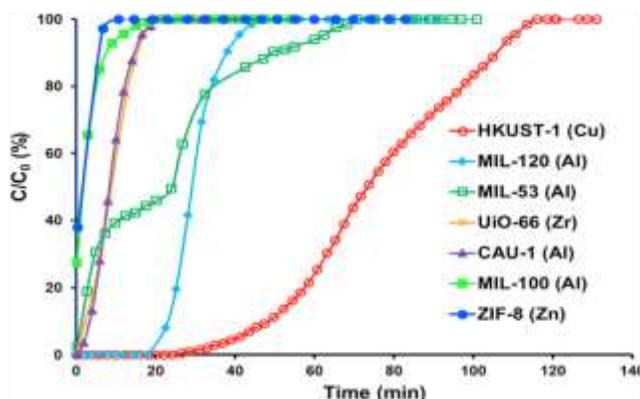


Figure 8: CH₃I breakthrough curves obtained at T = 35°C for the investigated MOFs.

Typically, the exploitation of the breakthrough curves reveals that the higher CH₃I sorption performances at 35°C (up to 425 mg/g for HKUST-1) are reached for materials showing pore size and geometry well-adjusted to CH₃I dimension. These experiments also revealed a particular two-steps breakthrough curve for MIL-53[Al], assigned to the swelling of the framework during CH₃I capture. Desorption experiments indicated that CH₃I retention is in most cases fully reversible at relative low temperature (35°C). The noticeable exception concerns MIL-120[Al], which retained 60% of CH₃I after the desorption process. DRIFTS (Diffuse Reflection Infrared Fourier Transform Spectroscopy) experiments have shown that this affinity is explained by strong Van Der Waals interaction between hydroxyl groups from the MOF and CH₃I.

5 CONCLUSION AND PERSPECTIVES

Experimental and theoretical results show that silver zeolites are the most suitable absorbents to trap volatile iodine (I_2 and CH_3I) in severe accident conditions. The type of zeolite and the method of silver incorporation (impregnation or ion-exchange) influence the physico-chemical characteristics of silver species and the zeolite retention performances for volatile iodine. In addition to a pore structure compatible with the size of CH_3I and I_2 (> 0.5 - 0.6 nm), a high amount of well dispersed silver cations is required to promote iodine retention. Under these conditions, most of the iodine can be trapped as highly thermally stable and insoluble AgI precipitates. Among a dozen of investigated silver zeolites, large-pore faujasite Y zeolite with silver content at least higher than 10%/w and with Si/Al ratio of 2.5 can be especially recommended.

At the laboratory scale, MOFs exhibit very attractive performances for their use as sorbent in nuclear SA conditions but the background of knowledge is less important than for zeolite. Yet, many other MOFs formulations could be investigated but for the iodine filtration application, no great improvement is expected because silver zeolites appear to be very suitable. Possible MOF applications in the future should be oriented towards selective decontamination for instance due to very flexible formula linked to its hybrid structure and infinite possibilities to make some functional groups.

Perspectives of iodine filtering tests in SA conditions are briefly proposed:

- **For zeolites**

Poisoning effect of gas contaminants and ageing effect of materials should be deeper investigated in priority.

- **For MOFs**

Some questions still remain to optimize iodine trapping. Indeed, accidental conditions usually involve a large panel of volatile molecules (e.g. H_2O , NO_x , CO) which can poison the capture of highly radioactive species by porous materials. Therefore, grafting of specific functional groups, can lead to the selective adsorption of iodine within MOF while reducing the sorption of undesired molecules.

- **For other porous materials**

In the meantime, R&D works with other kinds of innovative porous sorbents are still on-going in the frame of the MiRE project. Since their discovery in the early 90's, mesoporous silica constitute a class of ordered materials having tunable pore sizes (2-10 nm), high specific surface areas (500-1500 m^2/g) and existing under a variety of structures (ex: SBA-15, MCM-41, KIT-6...). Although silica alone is not efficient for iodine trapping, the affinity for iodine can be enhanced after insertion of metallic or organic functionalities of interest. Appropriate functional groups (containing for instance N or S atoms) can be introduced either by impregnation of molecules in the pores, post-reaction with silanol groups, or directly during the synthesis of the silica. Adsorption capacities in the range 0.5-2g/g for molecular iodine at 100°C were achieved using some of these strategies. In the case of silver-doped materials, mesoporous silicas are known to have pores 5-10 times larger than those of zeolites and are believed to be therefore less sensitive to pore blockage by AgI precipitates formed during reaction with iodine species. Nevertheless, further issues have to be solved for manufacturing such sorbents in industrial amounts and for increasing their stability under severe accident conditions.

Other materials doped with silver could be investigated with a cost lower than zeolite and easier to handle.

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