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Doctoral dissertation submitted to obtain the degree of Doctor of Engineering Technology, to be defended by

## **Christophe Gueibe**

## **DOCTORAL DISSERTATION**

Improving the noble gas detection capability for the verification of the Comprehensive Nuclear-Test-Ban Treaty



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D/2025/2451/34

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*"If I have seen further it is by standing on the shoulders of Giants" Isaac Newton (1642-1727)* 

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### List of abbreviations

AC	Activated Carbon
AgZ	Silver-exchanged zeolite
ARIX	Automatic Radioanalyzer for Isotopic Xenon
ARSA	Automated Radioxenon Sampler/Analyzer
BET	Brunauer-Emmett-Teller
СТВТ	Comprehensive Nuclear-Test-Ban Treaty
DFT	Density Functional Theories
DPRK	Democratic People's Republic of Korea
DR-PSA	Dual Reflux Pressure Swing Adsorption
EDX	Energy-Dispersive X-ray
EPDM	Ethylene Propylene Diene Monomer
GM	Geiger-Müller
HEU	High Enriched Uranium
HPGe	High Purity Germanium
IMS	International Monitoring System
INGE	International Noble Gas Experiment
IRE	Institute for RadioeElements
LEU	Low Enriched Uranium
MARDS	Movable Argon-37 Rapid Detection System
MAS	Magic Angle Spinning
MDC	Minimum Detectable Concentration
MIPF	Medical Isotope Production Facility
MOF	Metal-Organic Framework
MS	Mass Spectrometer
MSieve	Molecular Sieve
MTZ	Mass Transfer Zone
NG	Noble Gas
NLDFT	Non-Local Density Functional Theory

NMR	Nuclear Magnetic Resonance
NPP	Nuclear Power Plant
NPT	Treaty on the Non-Proliferation of Nuclear Weapons
NRR	Nuclear Research Reactor
OSI	On-Site Inspection
PNNL	Pacific Northwest National Laboratory
PSA	Pressure Swing Adsorption
PTBT	Partial Test Ban Treaty
PXRD	Powder X-Ray Diffraction
QSDFT	Quenched-Solid Density Functional Theory
RH	Relative Humidity
ROI	Region Of Interest
RT	Room Temperature
SAUNA	Swedish Automatic Unit for Noble gas Acquisition
SEM	Scanning Electron Microscopy
SPALAX	Système de Prélèvement d'Air en Ligne avec l'Analyse des radioXénons atmosphérique
TEM	Transmission Electron Microscopy
TGA	ThermoGravimetric Analysis
TPNW	Treaty on the Prohibition of Nuclear Weapons
TSA	Temperature Swing Adsorption
UNE	Underground Nuclear Explosion
VPSA	Vacuum Pressure Swing Adsorption
XRF	X-Ray Fluorescence

## **Chapter 1**

# Context, objectives and outline

#### 1. Context, objectives and outline

In this first chapter, the context is introduced, starting from the first man-made nuclear reaction up to the implementation of the verification regime for the Comprehensive Nuclear-Test-Ban Treaty (CTBT). The discovery of the fission reaction just before World War II led to the unfortunate race for the nuclear weapon. Testing of nuclear weapon prototypes is an integral part of nuclear weapon development. Following the devastating consequences of the Hiroshima and Nagasaki bombings, as well as public concerns about the radioactive fallouts of nuclear weapon testing, international efforts took place to ban nuclear weapon tests. These efforts resulted ultimately in the CTBT with the aim to constrain any further development of nuclear weapons. One method used for the verification the CTBT is to monitor the atmosphere for traces of radioactive noble gases, specifically xenon and argon, that can be released by nuclear weapon tests. Radioactive xenon (radioxenon) monitoring in the atmosphere is facing a complex background from civilian nuclear facilities, which limits the detection capability for traces of nuclear weapon tests. Research is necessary in this field to improve the detection capability for CTBT verification. Beside radioxenon, radioargon can be used as well to verify the compliance with the CTBT. Radioargon measurements are complex and are currently only used for the inspection of a suspected test site. Research is needed to simplify these measurements. The overarching goal of the PhD is to improve the noble gas (*i.e.* xenon and argon) detection capability of the verification system of the CTBT, by investigating the potential of new porous materials or new process designs for the adsorption and desorption of xenon and argon. As presented further in this first chapter, four sub-objectives, related to the improvement of the noble gas component of the verification regime, are identified. Finally at the end of the chapter, the objectives of the research are summarized, and the outline of the thesis is given.

#### 1.1.Nuclear weapon tests and their prohibition

In 1919, Ernest Rutherford reported the first, man-made, nuclear reaction by bombarding nitrogen with alpha particles emitted by a naturally occurring radioactive source [1]. This was followed by many experiments where target atoms were bombarded with naturally emitted alpha particles. In 1932, Ernest Walton and John Cockcroft, colleagues of Rutherford at Manchester University, produced the first fully artificial nuclear reaction by artificially accelerating protons towards a lithium target liberating two alpha particles [2]. James Chadwick discovered a neutral particle, the neutron, during his experiments with alpha particles on a beryllium target, which he reported in 1932 as well [3]. These discoveries, and others, paved the way for Enrico Fermi and his team in 1934 to use neutrons, instead of naturally emitted alpha particles or artificially accelerated protons and deuterons, for bombarding atoms [4, 5]. During their experiments with neutrons bombarding uranium-containing targets, Enrico Fermi concluded that new, heavier, elements were created after excluding the presence of elements with a mass between lead and uranium [6]. Ida Noddack was the first to suggest that some of Fermi's experiments might have produced large fragments, but lighter than lead, rather than new heavier elements [7]. Otto Hahn and Fritz Strassman confirmed the presence of a lighter element, barium, after neutrons interacting with uranium [8]. In 1939, Otto Frisch called this reaction 'fission' of the uranium nucleus [9]. Together with Lisa Meitner, they calculated that the energy released by this new reaction was about 200 MeV [10]. Their work also provided an experimental confirmation of Albert Einstein's famous mass-energy equivalence  $E = mc^2$  that he published in 1905. Hans Von Halban, Frédéric Joliot-Curie and Lew Kowarski estimated in 1939 that more than one neutron was liberated during a nuclear fission event [11]. This demonstrated that a self-sustaining chain reaction could be obtained and confirmed Leo Slizárd's idea that a neutron chain reaction could generate power as already patented in 1934 [12]. These discoveries, with many others during the 30s, were the basis for the first man-controlled and self-sustaining nuclear chain reaction at the end of 1942 in Chicago (USA) as well as the rather sombre race towards the conception of a nuclear weapon during World War II.



*Figure 1-1. Color photograph taken by Jack W. Aeby after the detonation of the first nuclear weapon test (Trinity, USA) on July 16, 1945. From [13].* 

Nuclear weapon testing is an integral part of nuclear weapon development. The first nuclear weapon test, performed in the United States of America in July 1945, called Trinity (Figure 1-1), aimed at testing an implosion-design plutonium weapon device [14]. This design was used for the "Fat Man" nuclear weapon that was later dropped on Nagasaki. After the Trinity test, and the Hiroshima and Nagasaki bombings in August 1945, about 2000 nuclear weapon tests were performed throughout the world (Figure 1-2), despite international efforts to ban nuclear weapon testing and prevent the spread of nuclear weapons [15]. These tests were performed by eight countries (USA, USSR/Russia, UK, France, China, India, Pakistan and North Korea) mainly to: develop a nuclear weapon (including increasing the knowledge in nuclear physics, the effectiveness and the effects of nuclear weapons in different environments), or develop new nuclear weapon designs (*e.g.* fusion-boosted fission and two-stage thermonuclear), or to investigate the aging behaviour of nuclear weapons in their stockpile [16]. Next

to the devastating use of nuclear weapons, some of the nuclear weapon tests had important radiological consequences, such as the Castle Bravo test (about 1000 times more powerful than the Hiroshima bomb) conducted in the Bikini Atoll (Marshall Islands, USA) in 1954, resulting in radioactive fallout and exposure of the people living in northern atolls (closest affected atoll was about 150 km away) [17].



## Number of world-wide nuclear tests

120

Note: Number of nuclear explosions from 1945 to 2006 are estimatesSources: Comprehensive Nuclear-Test-Ban Treaty Organization (1945-2006);staff reports (North Korea data)THE WALL STREET JOURNAL.

Nuclear weapon testing in the atmosphere, in outer space and under water was **banned** by the Partial Test Ban Treaty (PTBT) that was signed by the Soviet Union, the United Kingdom and the United States of America in 1963 [18]. Resulting from the PTBT, mainly underground nuclear weapon tests were performed after 1963. France and China did not sign the PTBT and performed atmospheric nuclear weapon tests until 1974 and 1980, respectively. In 1996, the Comprehensive Nuclear-Test-Ban Treaty (CTBT), banning also underground nuclear weapon tests, was opened for signatures [19]. Since then, India and Pakistan performed each two underground nuclear weapon tests in 1998, and the Democratic People's Republic of Korea (DPRK) performed six underground nuclear weapon tests in the period from 2006 to 2017 [20]. The CTBT has now been signed by 187 states, out of which 178 states (*i.e.* 91% of all UN recognized states) have ratified the Treaty [21].

Figure 1-2. Nuclear weapon tests in the period from 1945 to 2017. From [15].

With regard to efforts preventing the spread of nuclear weapons, the Treaty on the **Non-Proliferation** of Nuclear Weapons (NPT) entered into force in 1970 [22]. In the NPT, non-nuclear weapon states agree to never acquire or manufacture nuclear weapons. Whereas nuclear-weapon states agree not to transfer nuclear weapons, to assist or encourage non-nuclear weapon states to acquire such weapons. Nuclear-weapon states also agree to pursue nuclear disarmament. Verification of the compliance with the Treaty is performed through safeguards inspections by the International Atomic Energy Agency. Currently, the NPT has 191 states parties (*i.e.* 98% of all states) [23].

In 2021, the Treaty on the Prohibition of Nuclear Weapons (TPNW) entered into force [24]. The TPNW globalizes the prohibition and non-proliferation of nuclear weapons. The treaty prohibits states parties to develop, test, produce, manufacture, acquire, possess, or stockpile nuclear weapons. States parties are also not allowed to use or threaten to use nuclear weapons. Finally, states parties cannot allow stationing, installing, or deploying nuclear weapons in their territory. In opposition to the CTBT and the NPT, the TPNW does not contain any verification regime [24]. Since the Treaty was opened for signature in 2017, 97 states have currently signed the TPNW, amongst which 69 are states parties (*i.e.* 35% of all states) [25]. Next to the younger age of this treaty, the low number of signatures is due to a strong opposition to the TPNW by all states parties of the North Atlantic Treaty Organisation (NATO), as the Treaty prohibits the current arrangements of nuclear deterrence within the members of the NATO [25].

These arms control efforts have reduced the total number of nuclear warheads worldwide, which was at his highest point in 1986 with about 70 000 nuclear warheads worldwide [26]. As of 2024, the estimated global inventory gives a total of over 12 100 nuclear warheads [26]. About 20% of this total accounts for nuclear warheads that have been retired and are awaiting dismantling [26]. About 90% of the nuclear warheads belong to Russia and the United States of America [26]. Other countries that possess nuclear warheads are: United Kingdom, France, Israel, Pakistan, India, China and DPRK [26]. The trend over the last four years for Russia and the United States of America is that the military stockpiles are increasing again. Whereas the global trend on all nuclear warheads remains approximately at a status quo due to the dismantling of retired warheads [26]. Efforts on arms control should thus continue on all fronts, including banning nuclear weapon tests. A universal comprehensive ban for nuclear weapon testing would prohibit non-nuclear-weapon states to develop their own nuclear weapon and nuclear-weapon states to further develop their arsenal. Such a ban would also hamper investigations on the aging behaviour of nuclear weapons in military stockpile to ensure their effectiveness.

The **CTBT** is currently the only treaty banning tests with a verification framework. To enter into force, the Treaty still requires the ratification of 9 specific states (China, DPRK, Egypt, India, Iran, Israel, Pakistan, Russia, and the United States of America) that possessed nuclear power or research reactors in 1996 [21]. The verification regime of the CTBT foresees the operation of an International Monitoring System (IMS), which consists of 321 monitoring stations distributed worldwide to monitor the Earth for clandestine nuclear weapon tests (Figure 1-3).
For this purpose, four different types of monitoring stations are foreseen: seismic, hydroacoustic, infrasound and radionuclide. The seismic, hydroacoustic and infrasound stations are monitoring the Earth for waveform signatures of underground, underwater and atmospheric nuclear weapon tests, respectively. The radionuclide monitoring stations are crucial to provide evidence on the nuclear nature of an anthropogenic explosion. The Treaty foresees 80 radionuclide monitoring stations. All stations need to be capable to measure radioactive particulate matter in the atmosphere (called IMS particulate stations) and half of the stations need also to be capable to measure relevant noble gases (called IMS noble gas stations). After entry into force and at the first regular annual session of the conference of the states parties, a plan shall be decided to implement noble gas monitoring for all 80 radionuclide stations [19]. Even though the CTBT has not yet entered into force, about 90% of the stations were in operation in 2024 and have proven their effectiveness by detecting signals from all six underground nuclear weapon tests performed by DPRK [27].



+ Radionuclide - Noble Gas 🔸 Radionuclide - Particulate 🔺 Hydroacoustic 🔍 Infrasound 🔳 Seismic Auxiliary 🔲 Seismic Primary



Next to the IMS, On-Site Inspections (OSI) can be performed as ultimate verification measure under the Treaty. Currently, the preparatory commission for the CTBT Organization (CTBTO) is charged with building up the OSI capability. As part of the building up for OSI, field-deployable techniques for monitoring radionuclides in air samples (surface air and soil gas) are being developed [28].

#### 1.2. Radionuclide signature of nuclear weapon tests

During a nuclear fission event, such as a nuclear weapon test, a large variety of radionuclides are produced due to fission and activation events. From the fission of <sup>235</sup>U and <sup>239</sup>Pu, the first fission fragment is very likely to have a mass number between 80 and 110, whereas the second one is very likely to have a mass number between 125 and 155 (Figure 1-4).



*Figure 1-4. Cumulative fission yield for* <sup>235</sup>*U and* <sup>239</sup>*Pu in function of mass number for fast fission neutrons. Data from ENDF/B-VIII.0 [29].* 

Considering only radionuclides with sufficiently long half-lives, at least 6 hours, to be sampled at some distance away from the fission event, and with a fission yield higher than 0.1%, only 45 and 54 radionuclides remain for  $^{235}$ U and  $^{239}$ Pu, respectively. These criteria were used together with the detectability (presence of gamma radiation with a primary gamma energy > 50 keV having an emission intensity > 0.1%) to define a list of radionuclides relevant for CTBT verification [30]. The resulting list contains 51 fission radionuclides (Table 1-1). In addition, neutrons generated by the fission reaction will activate nuclei in materials (from the nuclear weapon itself or the environment) surrounding the explosion. Based on observations from past nuclear weapon tests, the list was extended with 41 neutron-activation radionuclides (Table 1-1) by using the previous criterion on the half-life [30]. The list was limited to activation products for which: i) the relevant production cross sections for non-fuel bomb materials is higher than 0.1 barn, ii) the abundance (either in the Earth's crust or the Sea) is larger than 0.1% and iii) the product of the cross section (in barns) for radiative capture, the abundance (maximum value for either the Earth's crust or the Sea in ppm) and the isotopic abundance (normalised to 1) is higher than 100 [30]. Finally, four radionuclides resulting directly from the decay of the fuel itself were included in the list as well [30]. Amongst the fission radionuclides, four noble gas radionuclides (specifically, isotopes of xenon) are of relevance for the CTBT. Regarding noble gases radionuclides, isotopes of krypton, which are also produced in significant quantities from fission (in particular for masses between 85 and 90) as shown in Figure 1-4, have a half-live that is not well suited for IMS. All isotopes, except <sup>85</sup>Kr, have a very short half-life (the longest half-life is 4.48 h for <sup>85m</sup>Kr), which does not allow monitoring over long distances. <sup>85</sup>Kr has a half-life of 10.75 years, which in turn is too long as there is a build-up of <sup>85</sup>Kr in the atmosphere from nuclear fuel reprocessing plants [31].

Specifically for OSI, the list of relevant radionuclides is limited to radionuclides that allow a discrimination of a nuclear explosion from other radiation sources (*e.g.* nuclear power plants and medical isotope production facilities) in a period from one week to two years from the detonation, whilst avoiding disclosure of confidential information not related to the OSI [32]. The list contains 16 particulate radionuclides with half-lives ranging from 17.3 minutes to 30.1 years. In addition to the particulate radionuclides, the same four Xe isotopes are of relevance for OSI together with <sup>37</sup>Ar. As will be discussed in the following, the PhD thesis focusses on improvements of the noble gas component of the IMS and for OSI.

Table 1-1. List of CTBT-relevant radionuclides for IMS monitoring. Adapted from [30]. Noble gas radionuclides are highlighted in bold. The half-life (from ENDF/B-VIII.0 [29]) is colour coded with the following coding: grey for  $T_{1/2} \in [0; 1d[$ , blue for  $T_{1/2} \in [1; 31d[$ , green for  $T_{1/2} \in [31d; 1y[$ , orange for  $T_{1/2} \in [1; 10y[$  and red for for  $T_{1/2} \in [10; 500y[$ .

Fission	products	Activation products		Fuel product
<sup>91</sup> Sr	<sup>130</sup> I	<sup>24</sup> Na	<sup>106m</sup> Ag	<sup>224</sup> Ra
<sup>91</sup> Y	<sup>131m</sup> Te	<sup>42</sup> K	<sup>108m</sup> Ag	<sup>237</sup> U
<sup>93</sup> Y	$^{131}I$	<sup>46</sup> Sc	<sup>110m</sup> Ag	<sup>239</sup> Np
<sup>95</sup> Zr	<sup>131m</sup> Xe	<sup>47</sup> Sc	<sup>120m</sup> Sb	<sup>241</sup> Am
<sup>95</sup> Nb	<sup>132</sup> Te	<sup>51</sup> Cr	<sup>122</sup> Sb	
<sup>97</sup> Zr	<sup>133</sup> I	<sup>54</sup> Mn	<sup>124</sup> Sb	
<sup>99</sup> Mo	<sup>133m</sup> Xe	<sup>57</sup> Co	<sup>132</sup> Cs	
<sup>99m</sup> Tc	<sup>133</sup> Xe	<sup>58</sup> Co	<sup>133</sup> Ba	
<sup>103</sup> Ru	<sup>135</sup> I	<sup>59</sup> Fe	<sup>134</sup> Cs	
<sup>105</sup> Rh	<sup>135</sup> Xe	<sup>60</sup> Co	<sup>152m</sup> Eu	
<sup>106</sup> Ru	<sup>136</sup> Cs	<sup>64</sup> Co	<sup>152</sup> Eu	
<sup>109</sup> Pd	<sup>137</sup> Cs	<sup>65</sup> Zn	<sup>168</sup> Tm	
<sup>111</sup> Ag	<sup>140</sup> Ba	<sup>69m</sup> Zn	<sup>170</sup> Tm	
<sup>112</sup> Pd	<sup>140</sup> La	<sup>72</sup> Ga	<sup>187</sup> W	
<sup>115m</sup> Cd	<sup>141</sup> Ce	<sup>74</sup> As	<sup>190</sup> Ir	
<sup>115</sup> Cd	<sup>143</sup> Ce	<sup>76</sup> As	<sup>192</sup> Ir	
<sup>123</sup> Sn	<sup>144</sup> Ce	<sup>84</sup> Rb	<sup>196</sup> Au	
<sup>125</sup> Sn	<sup>147</sup> Nd	<sup>86</sup> Rb	<sup>196m</sup> Au	
<sup>125</sup> Sb	<sup>149</sup> Pm	<sup>88</sup> Y	<sup>198</sup> Au	
<sup>125m</sup> Te	<sup>151</sup> Pm	<sup>89</sup> Zr	<sup>203</sup> Pb	
<sup>126</sup> Sb	<sup>153</sup> Sm	<sup>102</sup> Rh		
<sup>127</sup> Sb	<sup>155</sup> Eu		-	
<sup>127m</sup> Te	<sup>156</sup> Sm			
<sup>127</sup> Te	<sup>156</sup> Eu			
<sup>128</sup> Sb	<sup>157</sup> Eu			
<sup>129m</sup> Te				

#### 1.3.Noble gas measurements for CTBT verification

Depending on the type of nuclear weapon test (*i.e.* atmospheric, underwater, or underground), the quantity of produced radionuclides that will be released in the atmosphere will be different. In case of an **atmospheric** nuclear weapon test, most of the radionuclide inventory will be released to the atmosphere and could be picked-up, depending on the explosive yield, by IMS radionuclide stations. On the other hand, in case of an **underground** nuclear explosion, particulate matter will in most cases remain contained and noble gases are more likely to seep out from the test cavity. For instance from the 340 underground nuclear weapon tests performed at the Semipalatinsk test site (Kazakhstan) and from the 39 underground tests performed at the Novaya Zemlya test site (Russia), about 40% and 60%, respectively, of the tests were followed by a detectable seepage of radioactive noble gases whereas other radioactive radionuclides were released in only about 4 to 5% of the tests [33]. The behaviour of radioactive matter from underwater nuclear explosions is less known as only 8 tests have been conducted underwater [34]. It is expected that most of the radionuclide inventory will be retained in the water, but a fraction will reach the water surface. Calculations were performed for the Wigwam underwater nuclear weapon test (30 kton, USA) and showed that about 1% of the radionuclide inventory would have been released [34]. Noble gases will be released in larger quantities due to their inert gas nature. The estimated release fraction for noble gases is generally considered as 100% [35].

The four radioxenon isotopes of relevance for CTBT verification in the IMS are  $^{131m}$ Xe,  $^{133m}$ Xe,  $^{133}$ Xe and  $^{135}$ Xe, with half-lives of 11.93 days, 2.19 days, 5.24 days and 9.14 hours, respectively [30]. Monitoring these four radioxenon isotopes is important to maximize the likelihood of collecting evidence on the nuclear nature of a suspected underground nuclear weapon test. A 1 kt TNT-equivalent nuclear weapon test could emit about 10<sup>15</sup> Bq of  $^{133}$ Xe for an atmospheric test with more than 90% of the fission products released to the atmosphere [36]. Whereas it would be anything between 0 and  $10^{14}$  Bq for an underground test with a release of 0 to 10% of the fission products, 12 hours after the detonation [36].

For OSI, the relatively short half-life of the relevant radioxenon isotopes might make their detection difficult, depending on the time between the detonation and the OSI itself. It was demonstrated by Haas et al. [37] that an underground nuclear weapon test would yield detectable levels of <sup>37</sup>Ar in subsurface soil gas, by neutron activation of Ca through the <sup>40</sup>Ca(n, $\alpha$ )<sup>37</sup>Ar reaction in geologic structures, even in soils with a low Ca-content. The longer half-life of <sup>37</sup>Ar (34 days) makes it an important complementary noble gas candidate for OSI. As shown in Figure 1-5, its activity will surpass the activity of the radioxenon isotopes at 163 days after the test for a geologic structure with low Ca content (halite), and at 34 days for a geologic structure with high Ca content (carbonate). Accordingly, this radionuclide was included to the specific list of radionuclides for OSI.



Figure 1-5. Evolution of the radioargon (<sup>37</sup>Ar) and radioxenon (<sup>131m</sup>Xe and <sup>133</sup>Xe) activity concentration at the surface after a 1 kton underground nuclear weapon test . A dilution factor is used to convert the activity produced by the test to the activity concentration at the surface. Adapted from [37].

It has to be noted that <sup>39</sup>Ar (half-life of 269 years) is also investigated as a potential long-term indicator of underground nuclear explosions (UNEs) for OSI [38]. It is produced by neutron activation of K through the <sup>39</sup>K(n,p)<sup>39</sup>Ar reaction in geologic structures. The produced initial activity of <sup>39</sup>Ar is lower than for <sup>37</sup>Ar, but after 200 to 700 days (depending on the geology) post-detonation, the activity of <sup>39</sup>Ar will surpass that of <sup>37</sup>Ar [39]. The downfall of the longer half-life is that its use for verification of a fresh UNE would be difficult at test sites where UNEs have already been performed in the past due to the build-up.

The thesis aims at improving the noble gas detection capability of the verification regime for the CTBT. As will be discussed in the following sections, this is achieved by addressing three challenges: (1) improving the detection capability of IMS radioxenon monitoring stations, (2) simplifying <sup>37</sup>Ar sampling and measuring systems for OSI and (3) reducing the radioxenon background from civilian sources. Sections 1.3.1 to 1.3.3 are describing the development of radioxenon monitoring systems (specifically for CTBT verification) and the observed radioxenon background. The current status regarding the collection and measurement of <sup>37</sup>Ar for OSI is given in Section 1.3.4.

#### 1.3.1. First generation radioxenon monitoring systems

Radioxenon isotopes released from a nuclear weapon test will be transported in the atmosphere where they can be monitored by the noble gas component of the IMS. For this purpose, IMS noble gas stations are collecting large volumes of air to retrieve a small volume of purified xenon gas. The radiation emitted by this purified xenon gas can be measured to determine the activity of the four CTBTrelevant radioxenon isotopes.

Criteria	Minimum requirement	
Air flow	0.4 m <sup>3</sup> h <sup>-1</sup>	
Total volume of sample	10 m <sup>3</sup>	
Collection time	≤ 24h	
Measurement time	≤ 24h	
Time before reporting	≤ 48h	
Reporting frequency	Daily	
Isotopes measured	<sup>131m</sup> Xe, <sup>133m</sup> Xe, <sup>133</sup> Xe and <sup>135</sup> Xe	
Massurament mode	Beta-gamma coincidence or	
	high resolution gamma	
	1 mBq m <sup>-3</sup> for <sup>133</sup> Xe	
Minimum detectable concentration	(95% confidence level for	
	not measuring a false positive)	
State of health	Status data transmitted to	
	the International Data Centre	
Communication	Two-way	
Data availability	95%	
Downtime	≤ 7 consecutive days or	
Downtime	≤ 15 days annually	

Table 1-2. Minimum requirements for IMS noble gas monitoring. From [40].

At the opening for signature of the CTBT in 1996, only very few laboratory systems existed for atmospheric radioactive xenon measurement. These systems were far from meeting the minimum requirements (Table 1-2) that were defined for noble gas monitoring in the IMS [41]. Accordingly, the International Noble Gas Experiment (INGE) was created to bring together experts from Member States and the Preparatory Commission for the CTBTO, and to adapt laboratory systems for field deployment [42]. Resulting from the launch of INGE, 4 countries (France, Sweden, USA and Russia) developed a noble gas monitoring system that could be used in the IMS [41, 43-45]. The developed systems, called SAUNA (Sweden), SPALAX (France), ARIX (Russia), and ARSA (USA), all operate in a similar way with 4 main stages: air sampling, Xe purification, Xe enrichment and Xe detection. Following these developments, the French, Swedish and Russian systems have been deployed in the IMS.

The air sample (ranging from 7 to 80 m<sup>3</sup> depending on the system) is fed by a compressor, for 8 to 24 hours, into a dryer, to remove some of the moisture, and is then directed towards the Xe **purification** stage. Seven stable xenon isotopes ( $^{126}$ Xe,  $^{128}$ Xe,  $^{129}$ Xe,  $^{130}$ Xe,  $^{131}$ Xe,  $^{132}$ Xe and  $^{134}$ Xe) and two very long-lived xenon isotopes ( $^{124}$ Xe and  $^{136}$ Xe with half-lives of 1.8 10<sup>22</sup> years and 2.2 10<sup>21</sup> years,

respectively) are naturally present in ambient air [46]. The Xe concentration in ambient air is 87 ppb by volume [47]. In the Xe purification stage, residual moisture and CO<sub>2</sub> are further removed by Molecular Sieves (MSieves), zeolites, alumina, or polymeric membranes, depending on the system. The purified gas. containing mainly Xe and Rn, is then further enriched in Xe through collection and separation on Activated Carbon (AC) columns, Depending on the system, these columns are operated either at low temperature (between 100 and 173 K) or at Room Temperature (RT). Next to enriching the gas in Xe, by concentrating Xe on the AC columns, it is crucial to remove as much as possible Rn from the gas using these columns. Rn is present in ambient air with activities that are about 5 orders of magnitude higher than the Minimum Detectable Concentration (MDC) of 0.1 mBg  $m^{-3}$  that can be achieved for Xe [44]. If not sufficiently removed from the Xe enriched gas, the decay products of Rn would provide a significant background component in the detector. Depending on the system, a final enrichment can occur on AC or MSieve columns. The final volume of Xe recovered from the process, by thermal desorption with He or  $N_2$ , lies between 0.04 and 0.31 cm<sup>3</sup> per hour of sampling, which can then be measured with a dedicated radiation detection system.



*Figure 1-6. Most relevant decay modes of* <sup>131m</sup>*Xe and* <sup>133m</sup>*Xe. Adapted from* [48] *with data from* [49]*.* 

<sup>131m</sup>Xe isomeric state decays to <sup>131</sup>Xe (Figure 1-6) by a strongly converted gamma transition (163.9 keV with a gamma emission probability of 2.0%) [49, 50]. Conversion electrons are emitted (most likely emission with 129.4 keV), leading to a vacancy in the electron orbitals, which is directly reoccupied with the emission of a characteristic X-ray (average energy of 30.4 keV).

Similarly, <sup>133m</sup>Xe decays to <sup>133</sup>Xe (Figure 1-6) by a strongly converted gamma transition (233.2 keV with a gamma emission probability of 10.1%) [49, 50]. Conversion electrons are emitted (most likely emission with 198.7 keV), leading to a vacancy, which is again directly reoccupied with the emission of a characteristic X-ray (average energy of 30.4 keV).



*Figure 1-7. Most relevant decay modes of* <sup>133</sup>*Xe and* <sup>135</sup>*Xe. Adapted from* [48] *with data from* [49]*.* 

<sup>133</sup>Xe decays to three excited states of the stable <sup>133</sup>Cs nuclide by  $\beta$  decay (branching ratio of 98.5% for the most likely decay) [49, 50]. The most likely resulting excited state gives rise to a gamma transition of 81 keV (gamma emission probability of 36.9%) to the <sup>133</sup>Cs ground state (Figure 1-7). Here also the gamma transition is internally converted, and in most of the decay cases (52.8%), conversion electrons will be emitted (with 45.0 keV) followed by a characteristic X-ray (average energy of 31.6 keV).

Finally, <sup>135</sup>Xe decays to excited levels of the long-lived radioactive <sup>135</sup>Cs radionuclide (half-life of 2 10<sup>6</sup> years) by  $\beta$  decay (Figure 1-7) [49, 51]. The most likely excited state will give rise to a gamma transition (249.8 keV), which is not often converted (less than 10%). When converted, conversion electrons will be emitted (most likely emission with 213.8 keV) followed by a characteristic X-ray (average energy of 31.6 keV).

Two approaches were used in the developed systems for the **detection** of the four CTBT-relevant xenon isotopes: high resolution gamma spectrometry and betagamma coincidence spectrometry. In the **first approach**, an electrically cooled high purity Ge (HPGe) crystal is used with a counting time of about 24 hours. This allows to reach a MDC of about 0.15 mBq m<sup>-3</sup> for <sup>133</sup>Xe [43]. However, the MDCs for the two metastable isotopes were initially one order of magnitude higher, due to their lower gamma emission probabilities coupled with a lower detector efficiency at their respective gamma energies, as the detectors were optimized for the 81 keV peak of <sup>133</sup>Xe. During further developments of this approach, the MDC for <sup>131m</sup>Xe and <sup>133m</sup>Xe was improved by a factor 16 and 4, respectively, by measuring and quantifying the emitted X-rays [52]. The **second approach** implements beta-gamma coincidence with a system containing cylindrical plastic scintillator cells surrounded by two NaI(TI) crystals in a 4 $\pi$  configuration [44].

In the 2D beta-gamma spectra (Figure 1-8), Regions Of Interest (ROIs) are defined for each beta-gamma coincidence region characteristic of the four Xe isotopes (ROIs 2 to 6) as well as of <sup>214</sup>Pb (ROI 1), as daughter product of <sup>222</sup>Rn.

The number of counts in the ROIs are used to determine the activity of each isotope, taking also into account the interference between ROIs (*e.g.* contribution of <sup>214</sup>Pb in ROI 1 to all other ROIs) [53]. The MDC for <sup>133</sup>Xe in this configuration is about 0.1 to 0.9 mBq m<sup>-3</sup> depending on the system [41, 44, 45]. For beta-gamma coincidence, the MDCs for the three other isotopes are of the same order of magnitude as the one for <sup>133</sup>Xe [41].



*Figure 1-8. Regions of interest in the 2D beta-gamma energy spectra as defined for the Swedish radioxenon monitoring system. Adapted from [54].* 

After testing the developed systems extensively in the period from 2000 to 2010, the certification of the first radioxenon monitoring station in the IMS, USX75 (Charlottesville, USA), took place in 2010 [42].

# 1.3.2. Worldwide radioxenon background

Before the opening for signatures of the CTBT, it was shown that relatively high **atmospheric** <sup>133</sup>Xe **background levels** (*i.e.* 1 to 22 mBq m<sup>-3</sup>) could be observed in regions with a high density of nuclear reactors [55, 56]. This was confirmed during the first intercomparison experiment for IMS noble gas monitoring systems in Freiburg, Germany [57]. An important conclusion from this experiment, using such very sensitive systems with high temporal resolution, is the strong variability of the <sup>133</sup>Xe background ranging over two orders of magnitude (1-100 mBq m<sup>-3</sup>) over periods of one to two days [57]. The background was, at that moment, thought to be mainly coming from nuclear reactors. Further measurements at other locations around the world indicated that the background had a strong geographical dependency [48, 58, 59]. It soon became clear that another background source had to contribute significantly to the observations to explain the sharp and intense radioxenon peaks measured by these monitoring systems.

The measurements performed in Ottawa (Canada) showed, by using the xenon isotopic ratios, that the observed radioxenon background had two contributions: a) the collective emissions of Nuclear Power Plants (NPPs) and b) the emission from the fission-based Medical Isotope Production Facility (MIPF) located 180 km northwest of the monitoring station [58]. This was further highlighted when a European MIPF was temporarily shut down in 2008, resulting in a drop by two orders of magnitude (from a few hundred mBq m<sup>-3</sup> to a few mBq m<sup>-3</sup>) of the <sup>133</sup>Xe background peaks (Figure 1-9) in a nearby monitoring station [60].





A <sup>133</sup>Xe release from the 1<sup>st</sup> announced underground **nuclear weapon test** performed by DPRK was very likely picked-up, based on the explosion timing determined by seismic measurements and atmospheric transport modelling, by a CTBT radioxenon monitoring station that was in operation in Yellowknife, Canada [61]. It demonstrated that nuclear weapon tests could be observed in fairly low background IMS radioxenon monitoring stations, as is the case in Yellowknife with a yearly average <sup>133</sup>Xe activity concentration of about 0.05 mBq m<sup>-3</sup> in 2004 [59]. However, it also confirmed that such an observation in a high background location, in Europe for instance (above 1 mBq m<sup>-3</sup> on average for <sup>133</sup>Xe [62]), would be much more challenging as it was compared to "finding a needle in a haystack"

[48]. In this context, investigations were performed to list and understand radioxenon background emissions in order to discriminate a radioxenon signal of a nuclear weapon test from the ones of the background sources. They resulted in a number of publications addressing the following topics: i) atmospheric radioxenon background measurements around the world, ii) identification of radioxenon background sources and estimation of their emissions, iii) comparison of simulated background contributions at IMS stations with observations and iv) discrimination between nuclear weapon tests and background sources.

• Atmospheric radioxenon background measurements

Concerning the atmospheric radioxenon background measurements, the IMS was further populated with radioxenon monitoring stations yielding 26 certified stations (out of the 40 foreseen) as of 2024. The 26 certified stations are highlighted in Figure 1-3. The observations collected with these stations were regularly reported over the years, and analyses of comprehensive datasets have been reported [36, 62-65]. In addition, mobile noble gas monitoring systems were used at different locations in the world to improve the understanding of radioxenon background sources [66, 67].

# • Identification of sources and estimation of their emissions

Several studies focused on the identification of background sources (including the estimation of their average emissions) contributing to observations at specific IMS stations [63, 68-70]. These studies allowed to develop a comprehensive list of background sources (Figure 1-10) with their emissions.



+ Radionuclide - Noble Gas 🛨 Medical isotope production facilities 🔺 Nuclear research reactors 🔳 Nuclear power plants

Figure 1-10. Location of IMS noble gas stations and most important background sources. Locations for MIPFs and NPPs are from [36]. The list of MIPFs was updated with the data from [71]. Locations of NRRs (operational in 2014 and with a power of at least 10 MW) are retrieved from [72]. The first comprehensive dataset for **NPPs** was developed by Kalinowski et al. [73]. This study highlighted the strong variability of radioxenon emissions from NPP to NPP, even for the same NPP type, with variations up to 4 orders of magnitude for the annual <sup>133</sup>Xe emissions and with an average of about  $10^{12}$  Bg y<sup>-1</sup> per NPP [73]. Similarly, Achim et al. [64] listed the known **MIPFs** (9 facilities distributed around the world) with their best estimated <sup>133</sup>Xe releases showing emissions in the range of 0.4 to  $6 \ 10^{15}$  Bg y<sup>-1</sup> per facility. The average releases of MIPFs were complemented (for 6 facilities already reported by Achim et al. [64] and for one additional facility) with best estimates for the three other radioxenon isotopes [36]. It was shown by Hoffman and Berg that a particular Nuclear Research Reactor (NRR), the NRU reactor in Chalk River, Canada, was contributing significantly to some regional IMS observations after the closure of the nearby MIPF [74]. Accordingly, a list of **NRRs** with their reported or estimated emissions was developed by Kalinowski et al. [75] to take their contribution into account. The study showed that the reported <sup>133</sup>Xe emissions (available for only a few reactors), for reactors operating at more than 10 MW, are typically ranging from about  $10^9$  to  $10^{11}$  Bg y<sup>-1</sup>, except for the NRU reactor that had an emission of almost 10<sup>15</sup> Bg y<sup>-1</sup> [75]. Recently Kalinowski [71] compiled a list of radioxenon emissions from MIPFs (with new and updated data), NPPs (updated data) and NRRs, specifically for the year 2014 as a reference year. The author added a first estimation of radioxenon releases from **spent fuel reprocessing** (9 10<sup>10</sup> Bg y<sup>-1</sup> for La Haque) and **spallation neutron sources** (3  $10^9$  Bg v<sup>-1</sup> for the Japan Spallation Neutron Source), as it was highlighted in previous research that activation sometimes dominate over fission for radioxenon releases in NRRs due to activation of air [71]. Releases of <sup>133</sup>Xe from medical use in **hospitals** are lower than all previous background sources as they are in the  $10^6$  Bg d<sup>-1</sup> range [70]. Medical use of <sup>133</sup>Xe is not approved in all countries. It is for instance approved in the USA (about 5000 patients per week), but not in the EU [76]. As discussed previously, a 1 kt TNT-equivalent underground **nuclear weapon test** could emit anything between 0 and  $10^{14}$  Bg. Considering these figures, traces of radioxenon released from a partly contained 1 kt underground nuclear weapon test are difficult to find within the current radioxenon background.

#### • Comparison of simulated background contributions with observations

In 2016, Achim et al. [64] produced a map of the annual average <sup>133</sup>Xe activity concentration (Figure 1-11) based on simulations, using best estimates of radioxenon releases from MIPFs and NPPs at that moment, highlighting the complex worldwide radioxenon background. In their comparison with the <sup>133</sup>Xe observations in the IMS, more than 80% of the estimated annual averages were within a factor 2 of the observations [64]. Even day to day variations in the observations were fairly well represented by most of the simulated concentrations. For annual averages that were not within a factor 2, the assumption of a yearly average release might not well represent the actual source(s), or the atmospheric transport modelling might not well represent the actual wind pattern between the source(s) and the IMS station (specifically for short distances) [64]. Gueibe et al. [36] highlighted that the simulated concentrations for the three other xenon isotopes, based on best estimates of releases, were significantly lower (even for yearly averages) than the IMS observations.



*Figure 1-11. Simulated annual average* <sup>133</sup>*Xe activity concentration at ground level (for the period 2013-2014) based on reported or estimated releases from civilian nuclear installations. From* [64].

Since 2016, the knowledge on radioxenon sources has improved by refining the release estimates and adding new sources that can contribute to IMS observations [71]. It is likely, as demonstrated by the necessary updates on the list of sources and their emissions, that the location and number of sources as well as their intensity will change over time, making it a clear challenge to maintain an up-to-date list of sources and their emissions. In addition, the processes in MIPFs might change over time and require changes in the best estimates. A way to overcome this issue is to use stack monitoring data of radioxenon releases, which would allow to estimate continuously and more accurately their contribution to IMS observations [77, 78]. A project was started in 2018 to install radioxenon stack monitoring systems at background sources to transmit the collected data (a.o. radioxenon emissions) to a central location and develop algorithms to better

detect potential nuclear weapon test observations within the radioxenon background [79].

#### • Discrimination between nuclear weapon tests and background sources

Finally, some researchers investigated the use of the xenon isotopic composition for discriminating between nuclear weapon tests and background sources. It was already clear in the early days of the CTBT that nuclear weapon tests could be discriminated from NPP releases based on xenon isotopic ratios [80]. Using ratios from observations (at NPPs and IMS locations) and simulations (from NPPs and nuclear weapon tests), a discrimination line, Equation 1-1, in the 4-isotope plot (Figure 1-12) was proposed, separating isotopic ratios of nuclear weapon tests (illustrated by the blue and black lines in Figure 1-12) from nuclear reactors (*e.g.* green line and yellow diamonds in Figure 1-12) [81, 82]. During the operation of a reactor (*e.g.* green line for a Light Water Reactor), the isotopic composition will change during start-up, shut-down and revision. In particular at start-up with fresh fuel, the isotopic signature is on the nuclear weapon test domain [82].



Figure 1-12. Four-isotope plot used for the discrimination between nuclear weapon tests (right side of the discrimination line) and nuclear reactors (left side of the discrimination line). Adapted from [82]. An example of the range of ratios measured by stack monitoring at a MIPF in Belgium is given using the data from [83].

At that time, the impact of MIPFs on atmospheric radioxenon observations was not yet fully known. When it became clear that MIPFs were contributing to most IMS observations, investigations on the isotopic signature of MIPFs started. Stack measurements, showed that MIPFs (magenta area in Figure 1-12) can have a xenon isotopic signature on the nuclear weapon test side of the discrimination line, due to the short decay time between irradiation and release [70, 83, 84]. Their signature is not systematically on the nuclear weapon test side of the discrimination line due to the complex processes and corresponding radioxenon release patterns [84]. When the discrimination line was proposed, all except one observation in the IMS were outside the nuclear weapon test domain [82]. An isotopic analysis of IMS observations from 2010 to 2016 was performed using the proposed discrimination line and showed that only two of the 4-isotope observations were in the nuclear weapon test domain [85].

However, detections with 4 isotopes in the IMS are rare and are also unlikely for an underground nuclear weapon test. In the period from 2012 to 2020, only 0.6% out of 45 326 detections observed in SAUNA systems contained the four isotopes. As shown by the likely radioxenon detections from four of the six underground nuclear weapon tests performed by DRPK [61, 86-88], only one or two Xe isotopes could be detected in the IMS. For the two other underground nuclear weapon tests, no radioxenon observation could be linked to the corresponding test. Eslinger et al. [89] calculated with thousands of release simulations that the probability of detecting 4 isotopes in the IMS network with the currently best performing monitoring systems would be 0.4%, 6.2% and 0.0% for a radioxenon release of 10% of the inventory of a 1 kt underground nuclear weapon test that would be contained (with ingrowth from the precursors) for 1 hour, 1 day and 10 days, respectively, before being released to the atmosphere. Recognizing this difficulty, Kalinowski et al. [82] proposed also discrimination lines for cases with only three isotopes observed (e.g.  $^{135}$ Xe/ $^{133}$ Xe against  $^{135}$ Xe/ $^{131m}$ Xe when  $^{133m}$ Xe is missing). For two of the four cases, when  $^{135}Xe$  or  $^{131m}Xe$  is missing, a significant fraction (25% and 87%, respectively) of IMS observations were in the nuclear weapon test domain making the discrimination less powerful for these combinations [82]. In practice, a large fraction of the observations in the IMS contains only <sup>133</sup>Xe, as is also likely for an underground nuclear weapon test, making any isotopic discrimination very challenging. MDCs can be used for discrimination but can only provide an upper or lower bound. In the period from 2012 to 2020, 37% of the SAUNA samples with a radioxenon detection (57% of all samples) contained only <sup>133</sup>Xe, whereas 23% of the samples contained 2 isotopes, and 4% contained three isotopes. As recalled recently by Bowyer [90], the proposed discrimination line in the four isotope plot works well with observed isotopic ratios from a single source. In practice the radioxenon signature from a nuclear weapon test will very likely be mixed with the isotopic signature of background sources yielding an altered radioxenon signature potentially located in the nuclear reactor domain [90].

All the accumulated experience during the building-up of the IMS showed that the noble gas monitoring systems could be further improved to increase their verification capability. The first aspect is the sampling time, which was between 12 and 24 hours for the first generation of certified systems. It was shown that decreasing the sampling time (for instance to 6 hours) would allow to better locate the origin of a radioxenon detection by atmospheric transport modelling, and improve the isotopic information that can be obtained, as <sup>135</sup>Xe would have less time to decay [91]. In addition to shorter sampling times, lower detection limits

for all four isotopes would also increase the likelihood to have a multi-isotope detection from an underground nuclear weapon test, which would allow isotopic discrimination [92].

# 1.3.3. Second generation radioxenon monitoring systems

During the operation of IMS noble gas stations, the systems were improved over the years without major process changes until 2013. At the INGE 2013 workshop, a new generation system, with major process changes, for the American radioxenon monitoring system, called Xenon International, was presented [93]. Similarly at the INGE 2015 workshop, the new generation of the Swedish and French radioxenon monitoring systems, called SAUNA III and SPALAX NG, respectively, were presented [94, 95]. A new generation system for the Russian radioxenon monitoring system, called MIKS, was also developed in the same period [96]. The current information on the MIKS system is scarce and will not be discussed further. Based on the latest available reports, significant improvements have been achieved compared to the previous generation (Table 1-3) [97-100].

As can be seen in Table 1-3, the new generation systems have **shorter sampling times** (between 6 and 8 h) and allow to retrieve more stable Xe per hour of sampling (0.38 to 0.50 cm<sup>3</sup>). This is achieved by more efficient Xe collection and separation in the different adsorption columns. The major improvement in the gas processing part of the SPALAX NG system is the replacement of the MSieve columns, used for the final Xe purification and enrichment, by a much more efficient adsorbent, namely a silver-exchanged aluminosilicate porous material called Ag-ZSM-5 [97]. The SPALAX NG can operate with different sampling times: 4, 8 or 12 h [97]. SAUNA III brings two major improvements in the gas processing part, compared to its previous generation, by: i) adding two Pressure Swing Adsorption (PSA) stages to pre-purify and pre-enrich the gas stream by removing CO<sub>2</sub> and H<sub>2</sub>O, and ii) replacing AC in the purification and enrichment part by a much more efficient adsorbent, namely a silver-exchanged titanosilicate porous material called Ag-ETS-10 [98].

Next to these process changes, the **reliability of the gas processing part** of all systems has been significantly improved as well, using the operational experience in the IMS.

In addition, improvements have been done on the **detection part** of the system and all systems are now using beta-gamma coincidence spectrometry. In the SPALAX NG, a HPGe is still used in combination with two silicon pin detectors on the surface of a gas cell as well as a cosmic veto to reduce the cosmic radiation background [97]. The new generation systems allow to reach MDCs for <sup>133</sup>Xe in the range of 0.15 to 0.2 mBq m<sup>-3</sup>. The MDCs are in the same range as for the first generation, but they are achieved with shorter sampling times. More importantly, the MDCs for the three other isotopes have been significantly reduced and are all, even for <sup>135</sup>Xe, below 0.5 mBq m<sup>-3</sup>. The improved MDC for the short-lived <sup>135</sup>Xe is the result of a shorter processing time in the systems minimizing the loss of <sup>135</sup>Xe activity [98]. Table 1-3. Summary of the main features of the first (black text) and second (orange text) generation radioxenon monitoring systems. Silver-exchanged zeolites (or alike) are highlighted in bold. NK: Not known. NA: Not applicable.

	First generation / second generation			
	ARIX /	ARSA / Xe	SAUNA II /	SPALAX/
	MIKS	International	SAUNA III	SPALAX NG
V <sub>air</sub> (m³)	12 / 10	29 / <mark>30</mark>	7 / 40	80 / <mark>45</mark>
t <sub>sampling</sub> (h)	12 / NK	8 / 6	12 / 6	24 / 8
Xe purification	NaA and CaA zeolites followed by AC / NK	13X and alumina followed by AC / Alumina followed by AC	4A followed by AC / 13X and a 2 <sup>nd</sup> MSieve followed by Ag-ETS-10	Polymeric permeation membrane followed by activated carbon
Final purification		5A, mixture of ascarite and silica gel, and AC / MSieve followed by AC	3A and 5A / MSieve followed by carbogenic MSieve	MSieve / <b>Ag-ZSM-5</b>
V <sub>Xe</sub> (cm <sup>3</sup> ) per sampling hour	0.07 / NK	NK / 0.42	0.04 / 0.50	0.31 / 0.57
t <sub>acquisition</sub> (h)	10 / 14	16 / 12	11 / 6	24 / 6.5
Detection mode	β-γ	3-γ coincidence spectrometry		High resolution γ spectrometry / High resolution β-γ coincidence spectrometry
MDC <sup>133</sup> Xe (mBq m <sup>-3</sup> )	0.50	0.10 / 0.23	0.60 / 0.15	0.15 / 0.20
Carrier gas	He / NK	N <sub>2</sub>	He / N <sub>2</sub>	Self-purified N <sub>2</sub>
T <sub>Cryogenic</sub> (K)	100 / NK	173 / 100	NA	NA
Reference	[45] / [100]	[44] <mark>/[99]</mark>	[41]/[98,101]	[43] <b>/ [97]</b>

The testing phase of three of the four systems demonstrated that these improvements allow to better locate the origin of radioxenon observations as well as to obtain more information on the origin through radioxenon isotopic ratios as multi-isotope detections are more likely [97, 98, 102]. As an example the comparison of co-located SAUNA II and SAUNA III systems in Stockholm (Sweden) showed an increased detection rate from 59% to 75% for <sup>133</sup>Xe, from 17% to 36% for two isotopes, 1.6% to 12% for three isotopes and 0.2% to 2.9% for four isotopes [98].

For all observations with 4 isotopes during this measurement period in Stockholm, no isotopic ratio was in the nuclear weapon test domain (Figure 1-13). One should here remember that the observed isotopic ratios can be the result of air mixtures from different radioxenon sources. Achim et al. [83] were able to more precisely characterize the radioxenon background in Paris (France) through the use of the SPALAX NG system owing to its shorter sampling time and lower MDCs. The new generation systems will pick-up more background observations, but they will also allow to better discriminate the source of these observations by atmospheric transport modelling and by analysis of the isotopic ratios. In 2021, the first new generation radioxenon monitoring system was put in operation in the IMS at SEX63 (Stockholm, Sweden).



Figure 1-13. Isotopic ratios from samples collected in Stockholm (Sweden) in the period 2017-2019 with both generations of the Swedish radioxenon monitoring system. From [98].

In summary, the noble gas monitoring stations of the IMS have significantly improved (detection limits, sampling duration and reliability) with the second generation. This will increase the discrimination power of the IMS as a whole. However, mixing of air masses or weak and remote nuclear weapon tests will still challenge the IMS even with the new generation systems.

Accordingly, research should aim to further reduce the detection limits and/or the sampling duration, by for instance reducing the processing time, allowing to detect even lower signals and better discriminate between different sources. Research should also aim at reducing the energy consumption of the systems by minimizing the number of purification steps. In this context, further research on the application of silver-exchanged zeolites or silver-exchanged zeolite-like materials (such as titanosilicates) for IMS systems is of relevance. More specifically for the whole process instead of specifically for the final part of the purification and

enrichment process. In addition, investigating new porous materials, as will be discussed further in the following sections, for further improvements of the purification and enrichment process might support these objectives. The first research objective of this work addresses the potential of new porous materials for IMS, in particular when working directly with ambient air.

Research objective			
1	Investigate the potential of new porous materials for collecting and separating Xe directly from ambient air in the context of the international monitoring system		

It is also important to note that radioxenon measurements are also foreseen for OSI. Field radioxenon sampling and measuring systems have been developed for this application [101, 103]. Here also the development of a more efficient Xe collection and separation process from air and soil gas samples is of relevance for improving their detection and isotopic discrimination capability.

#### 1.3.4. <sup>37</sup>Ar measurement systems

Following the demonstration of Haas et al. [37] in 2010 on the detectability of <sup>37</sup>Ar in subsurface soil gas (discussed in Section 1.3), research on sampling and detecting <sup>37</sup>Ar from atmospheric and subsoil air was intensified [104-106]. Research is also being performed to assess the <sup>37</sup>Ar background, from natural production in the atmosphere and in the soil as well as from anthropogenic releases, and its impact on the use of <sup>37</sup>Ar measurements for CTBT verification during an OSI [107-109]. In opposition to the radioxenon background, current research does not suggest a significant anthropogenic background contribution to <sup>37</sup>Ar measurements [109]. The natural production in the atmosphere and in the soil can be well modelled [107, 110].

Currently two systems have been developed for <sup>37</sup>Ar measurements during OSI: the Chinese MARDS system and the American <sup>37</sup>Ar Field System. The MARDS system is operating with the following steps: air drying, nitrogen separation, oxygen separation, deoxidization, argon separation, argon collection and <sup>37</sup>Ar counting [106]. This allows to produce a 99.999+% Ar-pure sample. Liquid nitrogen cooling is used in the separation process and the developers of the MARDS system identified several research topics to improve the system, one of the topics was further research on Ar separation [111]. The <sup>37</sup>Ar Field System is operating, similarly to the MARDS system, through the following steps: air drying, nitrogen removal, oxygen removal, purification and <sup>37</sup>Ar detection [105]. This system is using Pressure Swing Adsorption (PSA) for nitrogen removal, high temperature (about 873 K) oxygen removal systems and low temperature Ar adsorption (about 173 K) for final purification. It produces a sample of about 2 L of pure argon from about 400 L of air (containing 0.9 vol% of Ar), yielding a concentration factor of about 100.



Figure 1-14. <sup>37</sup>Ar decay scheme. Data from [112].

The purified Ar sample, containing <sup>37</sup>Ar, is measured by a proportional counter in both systems. <sup>37</sup>Ar decays by electron capture (813.9 keV) to the stable <sup>37</sup>Cl radionuclide (Figure 1-14) and emits only low energy Auger electrons, neutrinos, and X-rays. For OSI measurement, two K-shell capture decay channels are relevant [105]. The first decay channel yields Auger electrons in 81.5% of decays with a total energy of 2.82 keV. For the second decay channel, 8.7% of the decays give rise to 2.82 keV mostly or completely from X-rays.

In the American  ${}^{37}$ Ar Field System, the proportional counters, each filled with a purified Ar sample, are housed in active and passive shields against cosmic-ray backgrounds and count for 12 hours [105]. The achieved MDC is lower than 10 mBq m<sup>-3</sup>. A similar design is used in the MARDS system and is also achieving a MDC lower than 10 mBq m<sup>-3</sup>.

The development of field systems for <sup>37</sup>Ar measurement is very recent and efficient adsorbents for separating Ar from subsurface soil gas are looked for. In particular, field-deployable systems could benefit from less energy demanding processes for the separation of Ar from atmospheric air and subsoil gas. Accordingly, for the second research objective, an adsorptive separation process working at or close to ambient conditions is investigated.

Research objective			
2	Investigate the collection and separation of Ar using a single adsorbent operating at or close to ambient conditions for on- site inspections		

Such research could potentially also be of relevance for IMS noble gas monitoring stations as there are recently discussions on the inclusion of <sup>37</sup>Ar to the list of IMS relevant radionuclides [113]. For IMS, simplification on the processing system and reduction of the energy consumption would be beneficial as well.

# 1.4.Radioxenon emissions at medical isotope production facilities

Returning to the radioxenon background issue, which is both relevant for IMS and OSI, an alternative approach to reduce the influence of MIPFs and other background sources on the verification capability of the IMS is to further reduce

their radioxenon emissions. These emissions are well below the national regulations and do not pose any health or environmental issue [114]. For instance, the MIPF in Belgium (Institute of RadioElements – IRE, Fleurus) released about  $9 \ 10^{14}$  Bq of noble gases in the atmosphere in 2023 [115]. The release limits are based on the exposure limit, in terms of dose, of the population, which in Belgium is set at 1 mSv per year. Considering all releases from IRE (all radionuclides, and both atmospheric and liquid releases), the maximum exposure of the population was about 0.7% of the regulatory limit in 2023 [115]. The regulations at national level are different from one state to another, but they are all based on dose limits. The frequent observations in the IMS are the result of the ultra-low detection limits of the systems as necessary for detecting potential traces from underground nuclear weapon tests over long distances.

Name	Country	<sup>133</sup> Xe (Bq y <sup>-1</sup> )	
CNEA	Argentina	9.00 10 <sup>13</sup>	
ANSTO	Australia	8.60 10 <sup>14</sup>	
IRE	Belgium	5.53 10 <sup>14</sup>	
CNL/MDS Nordion	Canada	7.80 10 <sup>15</sup>	
Nordion	Canada	1.50 10 <sup>13</sup>	
HFETR	China	3.65 10 <sup>14</sup>	
PT INUKI	Indonesia	3.80 10 <sup>12</sup>	
Curium	The Netherlands	7.30 10 <sup>11</sup>	
PINSTECH PARR-1	Pakistan	3.65 10 <sup>14</sup>	
Karpov Institute	Russia	3.01 10 <sup>14</sup>	
NIIAR	Russia	2.01 10 <sup>15</sup>	
NTP/NECSA	South Africa	2.30 10 <sup>16</sup>	
Lantheus Medical Imaging	USA	1.15 1010	

Table 1-4. Most comprehensive list to date of medical isotope productionfacilities in operation in 2014. Data from [71].

As discussed previously, the most important radioxenon background sources are MIPFs, producing, amongst others, <sup>99</sup>Mo as generator of <sup>99m</sup>Tc, which is used intensively in medical diagnostic imaging [116]. There are only a few MIPFs around the world (Table 1-4 lists the MIPFs in operation in 2014), but their emissions are significantly higher than any other background source. One should note here that the release figures have changed since 2014 as: i) some facilities stopped the production of <sup>99</sup>Mo (*e.g.* CNL/MDS Nordion [74]), ii) some companies increased their <sup>99</sup>Mo production (*e.g.* ANSTO with a brand-new facility [117]) and iii) the production process changed (*e.g.* IRE converting from High Enriched Uranium (HEU) to Low Enriched Uranium (LEU) [118]). This makes it difficult to maintain an up-to-date list of facilities with up-to-date radioxenon emissions. Accordingly, stack monitoring (as described in Section 1.3.2), to estimate their contribution in the IMS observations, and mitigation, to minimize as much as possible their contribution in IMS observations, are crucial for the future of the CTBT verification.

Bowyer et al. [119] performed a study on the impact of MIPFs on the IMS and concluded that a release rate of 5 GBq  $d^{-1}$  per facility would be an acceptable

upper limit for a minimal impact to IMS monitoring stations as well as for mitigation at MIPFs. If we assume a constant release over the full year, this would mean a decrease by up to 4 orders of magnitude for the most emitting sources. For <sup>133</sup>Xe, this would mean an additional decay time of about 70 days before being released to the atmosphere. In practice, the emissions are not constant, and some days have higher releases than others. As shown in Figure 1-15, working days have typically a few sharp peaks of a few hours and a decreasing residual radioxenon release in between peaks [78]. Meaning that for some releases, even longer decay times would be necessary.



*Figure 1-15.* <sup>133</sup>*Xe releases from the IRE (Belgium) as measured by stack monitoring during a production week in September 2019. From [78].* 

For the production of <sup>99</sup>Mo, uranium targets are typically irradiated for 2 to 14 days in a high neutron flux reactor [84]. There have been major international efforts to convert all uranium targets from HEU to LEU as LEU poses less proliferation risks than HEU [120]. These targets are then dissolved in a hot cell to separate the fission products from the uranium target. During the dissolution, fission noble gases are released in the ventilation of the facility, which provides the first radioxenon release pathway. Then in successive separation steps to recover the <sup>99</sup>Mo from uranium and other fission products, other radioxenon release pathways, with different isotopic composition, exist as radioiodine is decaying to xenon [121]. Concerning the isotopic composition, stack monitoring data of the MIPF in Belgium indicate a large variability in the 4 isotope plot, with a range of about three orders of magnitude both on the <sup>135</sup>Xe/<sup>133</sup>Xe and <sup>133m</sup>Xe/<sup>131m</sup>Xe ratios, and a limited number of stack data are in the nuclear weapon test domain (as shown in Figure 1-12) [83]. For the three isotope screening without <sup>131m</sup>Xe, almost all stack data is in the nuclear weapon test domain [83]. This highlights again the need to have four isotopes to be able to discriminate a nuclear weapon test from the background sources. Even with four isotopes, MIPFs can sometimes have an isotopic signature that is similar to a nuclear weapon test. In addition, one should here recall that mixing of air masses from different sources, including a potential nuclear weapon test, makes isotopic discrimination very difficult. Accordingly, a significant reduction of the radioxenon background will enhance the CTBTverification capability of radioxenon measurements in the IMS and during OSI.

Currently at MIPFs, radioxenon released during the production is contained in decay tanks, or on adsorbents, or in cryotraps, or in a combination of these

methods before being released to the atmosphere [114]. To achieve lower radioxenon emissions, the gas streams carrying radioxenon from the production process (including from radioiodine decay) should be held longer in the facility to allow for sufficient decay. This could be achieved by adsorbents being able to retain radioxenon longer before releasing it to the atmosphere. Retaining radioxenon for a longer time requires either larger volumes of adsorbent or new adsorbents with a higher adsorption capacity. In this context, silver-exchanged zeolites might provide an efficient adsorption solution for a longer retention of radioxenon in MIPFs. The third research objective focuses on this aspect.

#### **Research objective**

Examine the potential of silver-exchanged zeolites for trapping radioactive Xe more efficiently at fission-based medical isotope production facilities to reduce radioxenon emissions

#### 1.5.Adsorption, adsorbates and adsorbents

#### 1.5.1. Adsorption of noble gases

As shown previously, the efficient adsorption of noble gases is a crucial aspect for CTBT verification, in particular for: i) radioxenon monitoring, ii) <sup>37</sup>Ar measurements, and iii) mitigation of background radioxenon releases. Both xenon and argon are noble gases that have very limited interaction with their surroundings. Their adsorption process concerns the adhesion of a gas, called the adsorbate, by weak Van der Waals and electrostatic interactions onto the surface of a solid material, called the adsorbent. This weak adhesion on the surface is called physisorption, in contrast to chemisorption where a chemical bond is formed. In some cases (*e.g.* interaction of Xe with Ag aggregates), the interaction between the adsorbate and the adsorbent can contain both a chemical and physical contribution [122]. Depending on the concentration of the adsorbate and the specificity of the adsorbent, the gas molecules can be adsorbed in one or multiple layers on the surface of the adsorbent (Figure 1-16).



Figure 1-16. Adsorption process on a solid material. From [123].

Other gas species can be present in the gas stream (moisture,  $N_2$ , etc.) and the competition of different gas species will be discussed in Section 1.5.2.

Typically, the number of molecules of a specie that are adsorbed on a unit mass of adsorbent is proportional to the pressure of the corresponding specie. In isothermal conditions, the curve representing this relation is called an adsorption isotherm as shown in Figure 1-17. The removal of the adsorbed molecules is called desorption. In addition to the pressure dependence, the number of adsorbed molecules per unit mass of adsorbent increases with decreasing temperature [124].



*Figure 1-17. IUPAC classification of adsorption isotherms. From [125]. Both the adsorption and desorption curves are shown. B is an inflection point differentiating type II and type III isotherms.* 

More specifically in porous materials, the adsorption can occur on the external surface of the material and internal surface of the pores. Importantly, the size of the pores plays a crucial role in the number of molecules of a specie (with its molecule specific dimensions) that can reach the interior of the pore and be adsorbed on its internal surface. The pores are classified as follows: i) pores smaller than 2 nm are called micropores, ii) pores with dimensions between 2 and 50 nm are called mesopores and iii) pores with dimensions larger than 50 nm are called macropores [125]. The International Union of Pure and Applied Chemistry

(IUPAC) classifies the adsorption isotherms in 6 categories depending on the shape of the adsorption (upward arrow in Figure 1-17) and desorption (downward arrow in Figure 1-17) isotherm. Each category corresponds to a specific pore structure.

Type I is a reversible isotherm given by microporous solids with relatively small external surfaces [125]. Solids with narrow micropores (< 1 nm) are Type I(a), whereas Type I(b) corresponds to solids with wider micropores and possibly narrow mesopores (< 2.5 nm). Type II is a reversible isotherm given by nonporous or macroporous adsorbents on which physisorption of gases occur [125]. The isotherm results from the unrestricted monolayer-multilayer adsorption up to high  $p/p_0$  values. The type III reversible isotherm occurs when no monolayer formation can be identified [no inflection point B at low relative pressure (Figure 1-17)] [125]. In this case, weak adsorbent-adsorbate interactions take place. The adsorbed molecules are aggregated in the surrounding of the most favorable sites. Type IV isotherm, given by mesoporous adsorbents, can contain an hysteresis (a) during the desorption or be fully reversible (b) [125]. The adsorbent-adsorbate interactions and the interactions between the molecules in the condensed state (from capillary condensation) determine the adsorption behaviour in mesopores. A hysteresis, Type IV(a), occurs when the adsorbent has pores exceeding a certain critical width (dependent on the adsorption system and temperature) at which the adsorption and desorption properties of the condensed state differs [126]. Adsorbents with mesopores of smaller width have the reversible type IV (b) isotherm. Type V is an isotherm with hysteresis, which is typically given by water adsorption on hydrophobic microporous and mesoporous adsorbents [125]. The adsorption isotherm in the low  $p/p_0$  range is typically due to weak adsorbent-adsorbate interactions. Pore filling follows molecular clustering at higher  $p/p_0$ . Finally, Type VI is a stepwise reversible isotherm, which is representative of layer-by-layer adsorption on a highly uniform nonporous surface [125]. Each adsorbed layer has a capacity represented by the step-height. The degree of curvature of the step depends on the system and the temperature.

Type I is typically the pore structure that is relevant for Ar and Xe adsorption at RT and in the range of concentration investigated. It is generally well described with the Langmuir adsorption isotherm model [127], which will be described in the following chapter. In addition to micropores, some adsorbents have a significant quantity of mesopores. In this case, the adsorption of a probing molecule (like N<sub>2</sub> at 77 K) will be driven by mesopores and these adsorbents have thus a type IV (a) or (b) isotherm.

#### 1.5.2. Multi-component adsorption

In practice, the noble gas to be adsorbed will be present in a gas mixture. Depending on the application investigated in this work, the gas mixture can be air, a mixture of Ar or Xe in a carrier gas ( $N_2$  or He), or more complex mixtures with contaminants. In the presence of multiple gas species, preferential adsorption of a specie over another on the surface of the material can occur, which allows the separation of the different gas species. This is called equilibrium

separation and is the most common adsorption process. In case the adsorbent is used to sieve the feed gas by blocking, by pore size, some of the gas species, the process is called steric separation. Finally, separation can also be obtained by kinetic separation in porous materials where a difference in diffusion rate of the relevant gas species allows their separation. Steric separation can only occur in porous adsorbents with uniform aperture size in the crystalline structure (*e.g.* zeolites), whereas kinetic separation can only occur for adsorbents with a distribution of pore sizes avoiding exclusion of any gas specie (*e.g.* molecularsieve carbons). The presence of contaminants can significantly affect the adsorption of the targeted gas specie (*i.e.* Xe or Ar), depending on their concentration and the strength of their adsorption in the investigated adsorbent, due to competition in the adsorbent. An example of such strong competition is the presence of moisture for the adsorption of a targeted gas specie in zeolites [128].

These separation processes can be performed in cycles by desorbing the adsorbed gas species by heating or decreasing the pressure. The first case is called Temperature Swing Adsorption (TSA), whereas the second case is called Pressure Swing Adsorption (PSA). The latter provides the advantage of being less time consuming than heating-cooling cycles. A combination of temperature and pressure for the desorption is also possible to optimize the separation process.

#### 1.5.3. Adsorbents for radioactive noble gases

Looking at adsorbents, Activated Carbon (AC) was already a well-known adsorbent to capture radioxenon, in particular at cryogenic temperatures, in the nuclear industry in the early 50s [129]. AC is generally manufactured through the following steps: preparation of the raw material (*e.g.* wood, peat, coconut shells), carbonization and activation [130]. Pelletizing of the material can be done in any step of the process. Carbonization is generally done under an inert atmosphere and can be done at different temperatures to reach the desired pore structure and mechanical strength. Activation can be of chemical or physical nature. During chemical activation, mostly performed jointly with the carbonization, a chemical activating agent (e.g. KOH) is applied on the precursors allowing for instance dehydration and oxidation reactions to alter the pore structure and surface properties [131]. In case of physical activation, the resulting char after carbonization is treated under oxidizing gases (steam,  $CO_2$  or  $O_2$ ) at high temperature altering again the pore structure [131]. For the capture of impregnated potassium radioiodine, AC is with iodide (KI) and/or triethylenediamine (TEDA) to improve the retention of methyl iodide ( $CH_{3}I$ ) in humid conditions by dedicated interactions (chemisorption or isotopic exchange) [132]. Precautions need to be taken when using AC due to the fire hazard [114]. AC is a common and cheap adsorbent. However, ACs are non-selective and have a low Xe adsorption capacity at RT. This is the result of the large pore size distribution, as shown in Figure 1-18, and the lack of surface polarity of most ACs [133]. Research is ongoing to further improve the pore size distribution as well as the surface functionality of ACs specifically for the adsorption and separation of Xe [133]. As it is currently the standard adsorbent for xenon adsorption in the nuclear industry, it is used as reference material in the PhD research.



Figure 1-18. Pore size distribution of activated carbon. Adapted from [134].

In the 50s, incombustible adsorbents, specifically **silica gel** and **zeolites**, were also considered for trapping radioactive xenon, but none of the investigated adsorbents, at that time, was more efficient than AC [135]. Silica gel is a partially dehydrated form of polymeric colloidal silicic acid having chains and nets of linked  $SiO_4$  tetrahedra, which aggregate to form spherical particles of 2 to 20 nm [134]. These spherical particles form the microporous structure in silica gel and their size can be controlled by the synthesis conditions such as pH and the presence of other cations [134]. Zeolites are porous materials formed by crystalline aluminosilicates consisting of an assemblage of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra joined together by shared oxygen atoms [134]. The regular arrangements of these assemblages form an open crystal lattice with pores of molecular dimensions [134]. Since the pores are defined by the crystal lattice, the pores of a specific zeolite have fixed dimensions as shown with the first peak in Figure 1-19. Intra-crystalline pores have larger dimensions as indicated by the second peak in the same figure. The framework is negatively charged, as each Al atom introduces a negative charge, which is balanced by an exchangeable cation located at specific sites within the framework and plays an important role in the adsorption properties [134].



*Figure 1-19. Pore size distribution of a binderless 5A molecular sieve. Adapted from [134].* 

Zeolites can be found naturally or can be synthetized. Zeolites are often referred to as MSieves due to their sieving ability resulting from the fixed pore dimensions. The various polyhedra that can be formed by arrangements of  $SiO_4$  and  $AIO_4$  tetrahedra can be assembled by what are called secondary building units (Figure 1-20) and are used to describe zeolites.



Figure 1-20. (a) Secondary building units and (b) commonly occurring polyhedral units in zeolite framework structures [134].

The first studies on the use of zeolites for radioxenon adsorption were performed on zeolites A (composed of  $\beta$  units and four-membered oxygen rings, S4R) and zeolites X (composed of  $\beta$  units and six-membered oxygen rings, S6R) [135]. Other zeolites were studied, such as Mordenite (stacked  $T_8O_{16}$  units), but they did not provide better Xe adsorption properties than AC [136]. In 2003, it was shown for the first time by Munakata et al. [137] that a **Ag-exchanged** Mordenite, by exchanging the extra-framework cations, showed higher Xe adsorption capacities than AC at low Xe partial pressure. A few years later, Kuznicki et al. [138] demonstrated that Ag-exchanging a crystalline titanosilicate, called (Ag-)ETS-10, provided a significantly higher Xe adsorption capacity than the unexchanged sample. Titanosilicate MSieves have a similar structure as zeolites except that they are formed by SiO<sub>4</sub> tetrahedra and TiO<sub>x</sub> (x = 4-6) polyhedra joined together by shared oxygen atoms [139]. For simplicity, titanosilicates will be referred to as zeolite or zeolite-like materials in the remainder of the thesis due to their similar structure. In 2016, Deliere et al. [140] reported a very high Xe adsorption capacity on a silver-exchanged (Ag-)ZSM-5 zeolite (Zeolite Socony Mobil-5, belonging to the pentasil family formed by stacking double five-ring units, D5R). In 2019, Monpezat et al. [141] demonstrated that both Ag-ZSM-5 and Ag-ETS-10 were far superior, certainly at low Xe partial pressure, in terms of Xe adsorption capacity compared to AC. As shown in Figure 1-21, the Xe breakthrough at 50% of the inlet concentration occurs in these Aq-zeolites about 20 times later than in AC. It was demonstrated that this strong adsorption affinity at low pressure on silverexchanged zeolites is due to the interaction of Xe with Ag sites [142-144]. There is currently no consensus on the nature of the Ag adsorption sites [143-146].



Figure 1-21. Breakthrough curves obtained for a mixture of 400 ppm Xe and 40 ppm Kr in air at 298 K for similar masses of activated carbon (top), Ag-ETS-10 (middle) and Ag-ZSM-5 (bottom). Adapted from [141]. The flow rate was 33% higher for Ag-ETS-10 and Ag-ZSM-5 than for activated carbon.

In this thesis, commercial Ag-zeolites or Ag-zeolite-like materials, in particular Ag-ZSM-5 and Ag-ETS-10, are investigated as a potentially more efficient porous material for Xe adsorption and separation. At the start of the PhD, no peer-reviewed literature existed on the potential of these Ag-zeolites for radioxenon mitigation nor for Xe collection and separation directly, *i.e.* without pre-purification, from atmospheric air.

In 2006, investigations on a new type of porous material, called **Metal-Organic Framework** (MOF), for Xe adsorption were reported [147]. MOFs are constructed by organic linkers and metal ions or clusters. MOFs are characterized by a large surface area and a high porosity compared to other adsorbents. They can be tailormade due to the theoretically unlimited number of possibilities for organic linkers to be linked with a large variety of metal nodes [148]. By 2018, many MOFs were investigated for the adsorption of Xe, and for Xe/Kr separation [149]. Molecular models and simulation methods are crucial to screen hypothetical MOFs for a specific application [150]. Promising results were reported for the adsorption of Xe and the separation of Xe from Kr at high Xe partial pressure (*i.e.* > 1000 Pa) and at RT. However, no investigation was performed on their use for lower Xe partial pressures as would be encountered for CTBT verification. Accordingly, commercial MOFs were explored in this thesis for Xe adsorption for CTBT verification. For Ar collection and separation from air, the most challenging part is the  $Ar/O_2$  separation. The following adsorbents were considered in the past for  $Ar/O_2$  separation at RT: Carbon MSieves [151, 152], zeolites or zeolite-like frameworks [153-158], MOFs [159] and other ultra-microporous solids [160]. Studies on zeolites showed that silver-exchange increased significantly the  $Ar/O_2$  separation performance due to a strong Ar-Ag interaction [161]. In 2008, a year after reporting the high Xe adsorption capacity on Ag-ETS-10, Ansón et al. [162] showed that Ag-ETS-10 had also a high  $Ar/O_2$  selectivity. Since then, its application for oxygen production has been investigated [156, 163, 164], but its application for Ar collection and separation for OSI was not yet investigated. In this thesis we explore the potential of a commercial Ag-ETS-10 sample for such an application.

# 1.6.Adsorption and desorption measurements

Adsorption and desorption isotherms on porous adsorbents are commonly obtained by volumetric (also known as manometric) or gravimetric measurements [125]. These measurement methods are specifically designed to measure the amount of gas adsorbed on the adsorbent in function of pressure after an equilibrium is reached. The adsorbent is kept at constant temperature during the measurement. As represented in Figure 1-22, the volumetric measurement method monitors the pressure change (PI, Pressure Indicator), when a known pressure  $(P_d)$  and volume  $(V_d)$  of gas is allowed to equilibrate in an uptake gas cell of known volume  $(V_u)$ , which contains the adsorbent  $(V_s)$  to be investigated [165]. The difference between the pressure without adsorption or desorption, known by the equation of state, and the measured pressure allows to determine the amount of gas adsorbed or desorbed. The isotherm is constructed point by point by successively increasing or decreasing the pressure of the gas that is allowed to equilibrate with the adsorbent at constant temperature. The gravimetric method first measures the mass of the adsorbent free of any adsorbates. Then by increasing successively the gas pressure and measuring the resulting mass, *i.e.* the adsorbent with the adsorbed molecules, the adsorption isotherm can be constructed. The desorption isotherm can then be measured by decreasing the gas pressure.

The measurement of adsorption and desorption isotherms of small and inert probing molecules allows to characterise the porous structure of adsorbents.  $N_2$  adsorption and desorption at 77 K is generally the accepted standard method for analysing the mesoporous and microporous structure [125]. The saturation pressure of  $N_2$ , about 1 bar at 77 K, allows to cover the full pressure range of the gas phase without specific pressure needs. However, the quadrupole nature of  $N_2$  results in specific interactions with surface functional groups and exposed ions, which affect the orientation of the adsorbed molecule as well as the micropore filling pressure [125]. Such effects are observed in many zeolites and MOFs. For these adsorbents, Ar adsorption at 87 K is recommended by the IUPAC for the analysis of the microporosity, due to the absence of a quadrupole moment of Ar [125].  $N_2$  and Ar both suffer from slow equilibration in small pores at cryogenic temperatures, which limits their use for very narrow micropores. This can be

addressed by the adsorption of the smaller  $CO_2$  molecule at 273 K, which allows measurements at a moderate pressure range for micropore analysis due to the very high saturation pressure (about 35 bar at 273 K). Adsorption of  $CO_2$  at 273 K can probe pores as small as 0.4 nm [125]. As the maximum relative pressure that is readily achievable for adsorption measurements is about 3% of the saturation pressure, the method is generally restricted to pores smaller than 1 nm. The quadrupole moment of  $CO_2$  is even higher than that for N<sub>2</sub>. Care has to be taken when using  $CO_2$  for micropore analysis in zeolites and MOFs [125]. Despite the quadrupole moment of N<sub>2</sub> and  $CO_2$ , both molecules are still useful for assessing the pore volume and porosity of small micropores in MOFs and zeolites [166].



*Figure 1-22. Working principle of the volumetric gas adsorption measurement method.* From [165].

Volumetric adsorption and desorption measurements are performed in this work to characterise the mesopores and micropores of different types of adsorbents. As will be detailed in Chapter 2,  $N_2$  at 77 K and  $CO_2$  at 273 K are used as probing molecules. The combination of both probing molecules allows to cover the range of pore size that is expected in the investigated adsorbents. Even though the quadrupole moment will affect the analysis, both probing molecules are used to investigate zeolites and MOFs, as they can still provide helpful micropore information and can be compared to existing literature data, which does currently not exist for Ar.

Next to the characterisation of the porous structure with the previously described probing molecules, the evaluation of an adsorbent for a specific application can initially be assessed through single-component adsorption and desorption isotherms with the gas species of interest. The measurement of single-component adsorption at different temperatures allows to determine the energy of adsorption of an adsorbate on the investigated adsorbent [167]. Single-component measurements can be complemented with multi-component adsorption and desorption isotherms to extend the investigation towards more realistic conditions

for the considered application. As discussed in Section 1.5.3, such an initial evaluation exists for most of the adsorbents that are investigated in this work.



Figure 1-23. Example of a breakthrough curve (top) and desorption curves (bottom) from a packed adsorption column.

For further assessment of the potential of an adsorbent for a specific application, dynamic adsorption and desorption measurements need to be performed in a range of conditions (temperature, pressure, concentration, gas mixture, flow rate, etc.) that can be encountered for the relevant application. These dynamic measurements can also be used to collect single-component adsorption and desorption isotherms, when the gas specie can be mixed with a carrier gas that has negligible adsorption on the adsorbent [125]. In particular, dynamic adsorption and desorption measurements on a packed adsorption column are a necessary step for investigating adsorbents in conditions close to industrial applications [168]. As shown for Xe in the top part of Figure 1-23, such measurements can record the breakthrough of the gas components of a mixture

from a regenerated adsorbent, by monitoring the concentration of the investigated gas species at the outlet of the packed adsorption column until the inlet concentration is reached. Similarly, the outlet of the packed adsorption column can be monitored during its desorption to investigate the regeneration of the adsorbent or the separation capabilities during the desorption of gas species, as shown for Ar, O<sub>2</sub>, CO<sub>2</sub> and Xe during a thermal desorption in the bottom part of Figure 1-23. Such a measurement technique allows to investigate the behaviour of the adsorbent in cyclic conditions (TSA or PSA), as would be encountered in industrial processes [169].

In this work, the focus is on bridging the gap between initially reported promising adsorption results, in idealized conditions, and the industrial application of the relevant adsorbents. For this purpose, a dynamic gas adsorption and desorption measurement set-up was designed, as described in Chapter 2, to meet the three research objectives presented previously. Meeting these objectives requires a versatile set-up having the following capabilities:

- i. a large concentration range (from 87 ppb Xe in air up to 100% Ar);
- ii. complex gas compositions (for instance with a Rn tracer or different moisture levels);
- iii. temperatures at and below RT (down to 213 K) for the adsorption and higher temperatures (up to 523 K) for the thermal desorption;
- iv. a large range of applicable flow rates (30 to 2000 cm<sup>3</sup> min<sup>-1</sup>); and
- v. adsorbent column volumes ranging from 30 to 300 cm<sup>3</sup>.

For research objective 2 (argon collection and separation), the set-up was adapted to reach higher inlet pressures (up to 340 kPa) to investigate the PSA method as well as to recover adsorbates by pulling a vacuum on the adsorbent.

# 1.7.Durability of adsorbents

In the current global environmental context, it is crucial to reuse materials as long as possible under sustainable conditions, which is evidently also applicable to adsorbents. In addition, some adsorbents, such as AqZs, are quite expensive, partly due to the cost of the raw materials (*e.g.* Aq), and their **reusability** is thus even more critical. Adsorbents can be reused through a desorption step by increasing the temperature or by decreasing the pressure. In IMS noble gas stations, the adsorbents are undergoing one to four regeneration steps per day. This is more demanding than for radioxenon trapping in MIPFs were at maximum (depending on the mode of operation of the trap) one to two regeneration steps per week would occur. The reusability of two AqZs, Aq-ETS-10 and Aq-ZSM-5, is investigated in this work. No peer-reviewed literature exists on the durability of Ag-ETS-10 against thermal regeneration cycles, whereas an initial investigation with 25 cycles was reported on Aq-ZSM-5. Only general system durability has been reported so far for the SAUNA III system [170], which uses Ag-ETS-10 in part of the gas processing. Resulting from the initial investigation with Ag-ZSM-5, it was shown that pre-purification of air enriches the gas in Cl-containing volatile organic compounds, which degrade the Xe adsorption properties of Ag-ZSM-5 due to deactivation of silver nanoparticles and silver sintering during the thermal regeneration [171]. In the current work, the focus is on atmospheric air (without pre-purification) and on extending the knowledge on the durability against thermal regeneration cycles to a higher number of cycles. The focus will be laid on thermal regeneration as pressure swing adsorption systems are to be avoided in nuclear installations such as MIPFs. The effect of contaminants, for instance released during the dissolution, on the durability are not considered as there is currently a lack of peer-reviewed information on the gas composition from the dissolution.

Next to these considerations, more volume-efficient adsorbents for trapping radioxenon will concentrate the activity in a smaller volume compared to reference adsorbents. This has two implications: i) a more intense radiation field in and out of the adsorbent and ii) a higher concentration of decay products by unit of volume.

For the first implication, a more efficient adsorbent needs to be able to withstand higher radiation doses and will potentially need (depending on its location in the facility) to be more shielded to limit the exposure of workers in the surrounding. Specifically for MIPFs, the adsorbents need to retain a large amount of radioxenon, about 10<sup>14</sup> Bq per weekly <sup>99</sup>Mo production [121]. At the start of the PhD, no peer-reviewed literature existed on the radiation resistance of both AgZs. The focus is laid on <sup>133</sup>Xe as the radioxenon gas coming out of the dissolution process in MIPFs is mostly composed of <sup>133</sup>Xe (Table 1-5). The irradiated targets also contain krypton isotopes, which are present with an activity that is about two orders of magnitude lower than for Xe isotopes. In addition, the Xe/Kr selectivity on both adsorbents for a partial pressure of about 100 Pa is higher than 10, which further limits the content of krypton in AqZs [141]. It is also important to note that the activity of the radioxenon isotopes present in the ventilation pathways in MIPFs is much higher than in the ones of any other nuclear installation in normal operation. Accordingly, achieving relevant radiation doses for durability studies for operational use in MIPFs is a significant undertaking as will be demonstrated further in the PhD thesis.

Table 1-5. Activity of radioxenon isotopes 24 hours after irradiation of LEUbased targets used for a typical production of 3.4 10<sup>14</sup> Bq of <sup>99</sup>Mo. Data from [121].

	<sup>131m</sup> Xe	<sup>133m</sup> Xe	<sup>133</sup> Xe	<sup>135m</sup> Xe	<sup>135</sup> Xe
Activity (Bq)	8.7 10 <sup>10</sup>	4.1 10 <sup>12</sup>	9.7 10 <sup>13</sup>	2.2 10 <sup>12</sup>	3.8 10 <sup>13</sup>

For the second implication, the **decay products** of the radioxenon isotopes will accumulate with higher concentrations in more efficient adsorbents. Five radioxenon isotopes are of relevance in MIPFs: <sup>131m</sup>Xe, <sup>133m</sup>Xe, <sup>133</sup>Xe, <sup>135</sup>Xe and <sup>135m</sup>Xe. The metastable isotopes decay to the ground state isotopes. <sup>131</sup>Xe is one of the stable xenon isotopes and will be desorbed during the regeneration of the adsorbent. <sup>133</sup>Xe decays to <sup>133</sup>Cs, which is the only stable Cs isotope. The decay of <sup>135</sup>Xe gives rise to <sup>135</sup>Cs, which is a long-lived radionuclide (half-life of 2.3 10<sup>6</sup> years). The behaviour of Cs after decay of radioxenon in AgZs, operating at RT and then exposed at a higher temperature during the regeneration step, is currently not known. If the Cs remains immobile in the AgZs, it could decrease

the number of available adsorption sites for radioxenon in the long term. The decay of the typical <sup>133</sup>Xe activity, present during a dissolution (Table 1-5), produces about 10<sup>-4</sup> mol of <sup>133</sup>Cs. To put this figure in perspective, it is about 0.02% of the adsorption capacity for Xe at 2 kPa and RT on Ag-ETS-10 [138]. The long-lived <sup>135</sup>Cs decay product can also pose potentially a waste issue in the long term. The exemption level in Belgium for <sup>135</sup>Cs is 10 MBq kg<sup>-1</sup>, as defined in the Royal Decree of 20/07/2001 on the protection of the population, the workers and the environment against ionising radiation. According to the activities typically present during a dissolution (Table 1-5) and assuming that Cs is immobile in the adsorbent, about 500 dissolution properties over time). The effect of Cs on the availability of adsorption sites and the potential waste issue are long term aspects that will not be investigated.

Both for trapping radioxenon and for collecting and separating Xe from air, a degradation of the adsorbent would result in a significant decrease in the verification capability of the IMS. In MIPFs, a sudden and significant loss of Xe adsorption properties would give rise to a major radioxenon release with a potential impact on safety. Accordingly, their use for these applications requires a dedicated investigation of their durability in the relevant conditions, which corresponds to the fourth research question.

# Research objective 4 Assess the durability of Ag-ETS-10 and Ag-ZSM-5 after multiple thermal regeneration cycles as well as after irradiation

# 1.8.Objectives

The CTBT is an important treaty for a world without nuclear weapons, as it will inhibit their further development and is supporting the 16<sup>th</sup> sustainable development goal of the UN on the promotion of peaceful societies. It is thus crucial that the IMS network has an adequate verification capability for nuclear weapon tests.

The overall objective of the PhD is to improve the noble gas detection capability for the verification of the CTBT through different means: i) decrease the radioxenon emissions at civilian facilities contributing to the radioxenon background, ii) lower the detection limits or shorten the sampling time of Xe sampling and measuring systems to increase the detection probability of a nuclear weapon test and obtain more information on the origin of the detection by isotopic discrimination, and iii) simplify the Ar separation process of <sup>37</sup>Ar sampling and measuring systems for OSI to optimize their operationalisation the field. To achieve this, four research questions related to adsorbents (in particular AgZs) were identified based on the state of the art on noble gas monitoring for CTBT verification, as presented in the previous sections.

The four research questions are summarized in Table 1-6. As indicated in the table, each research question will be dealt with in a dedicated chapter. For the first research question, the results on new adsorbents (AgZs and MOFs) will be evaluated using two metrics: the collection efficiency (*i.e.* adsorption capacity in the relevant gas mixture) and the separation efficiency (*i.e.* purity of the recovered Xe gas). The Ar collection and separation at or close to ambient conditions on a single adsorbent (Ag-ETS-10) is compared to the current process using the Ar yield and the relative Ar enrichment. For the reduction of the radioxenon emissions using AgZs, the Xe adsorption capacity in relevant conditions is used as a metric for the comparison with AC. In addition, the regeneration conditions are also considered for the reusability of AgZs. For the last research question, the durability of the two AgZs is evaluated through the Xe adsorption capacity as well as by means of six structural characterization techniques.

	Research objectives	Main evaluation metrics	Related chapter
1	Investigate the potential of new porous materials for collecting and separating Xe directly from ambient air in the context of the international monitoring system	Xe collection and separation efficiency	3
2	Investigate the collection and separation of Ar using a single adsorbent operating at or close to ambient conditions for on-site inspections	Ar yield and relative enrichment	4
3	Examine the potential of silver- exchanged zeolites for trapping radioactive Xe more efficiently at fission-based medical isotope production facilities to reduce radioxenon emissions	Xe adsorption capacity and regeneration conditions	5
4	Assess the durability of Ag-ETS-10 and Ag-ZSM-5 after multiple thermal regeneration cycles as well as after irradiation	Xe adsorption capacity and structural characterization	6

Table 1-6. Research objectives an	nd corresponding	evaluation	metrics	addressed
	in the PhD.			

# 1.9.Outline

After this introduction, the second chapter will describe the materials and methods that were used for multiple research objectives. Materials and methods that are specific to a particular research objective will be described in the corresponding chapter. After the second chapter, the two first research objectives addressing the CTBT monitoring systems are described in Chapter 3 and Chapter 4 for radioxenon and radioargon, respectively. In Chapter 5, the use of more efficient adsorbents
for mitigating the radioxenon background is investigated (third research objective). The durability of AgZs, as evaluated for the fourth research objective, is discussed for the relevant applications (CTBT monitoring systems and radioxenon mitigation) in Chapter 6. The last chapter of the PhD thesis will provide a summary, general conclusions and an outlook for the work performed within the PhD. The outline of the PhD thesis is presented in Figure 1-24.

# IMPROVING THE NOBLE GAS DETECTION CAPABILITY FOR THE VERIFICATION OF THE COMPREHENSIVE NUCLEAR-TEST-BAN TREATY



*Figure 1-24. Outline of the thesis. Chapters 3 to 6 are linked directly with the four research objectives discussed in previous sections.* 

Chapters 3 to 6 are structured in the same manner with first an introduction going deeper in the specific subject, a materials and methods section limited to the materials and methods specifically relevant for the specific research objective, a results and discussion section, a conclusion section on this specific subject, and, if relevant, supplementary material.

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# **Chapter 2**

# Materials and methods

# 2. Materials and methods

Throughout the PhD research a variety of materials and methods were used, which are all listed for each chapter in Figure 2-1. Some materials and methods were used in multiple chapters, as highlighted by the yellow box in the figure, and will be described in this chapter. All other chapter-specific materials and methods will be described in a dedicated materials and methods section in the relevant chapter.



Figure 2-1. Materials and methods used throughout the PhD thesis.

Throughout the research, various adsorbents (activated carbons [ACs], silverexchanged zeolites [AgZs] and metal-organic frameworks [MOFs]) were investigated and are described in Section 2.1. On all adsorbents, breakthrough measurements were performed to assess their performance for the collection and separation of Xe and/or Ar. These breakthrough measurements as well as their analysis are described in Section 2.2. A description of the analysis of adsorption isotherms is given in Section 2.3. Some of the adsorbents were further characterized by powder X-ray diffraction, scanning electron microscopy,  $N_2$ sorption at 77 K and CO<sub>2</sub> adsorption at 273 K. These characterization techniques are described in Section 2.4.

# 2.1.Adsorbents

Table 2-1. Density, mesh size, and, when applicable, Ag content of investigated adsorbents. Together with the reported Xe adsorption capacity (± 100 Pa, room temperature).

Supplier	Material name	Density (g cm <sup>-3</sup> )	Mesh size (mm)	Ag (wt.%)	Xe adsorption capacity (mol kg <sup>-1</sup> )
	Ac	tivated car	bons		
Cabot Norit Nederland B.V.	Norit RKJ 1	0.52ª	Pellets: 1.7-3.4	NA	-
NUCON International Inc.	Nusorb® GXK	0.48 <sup>b</sup>	Granules: 1.7-3.4	NA	0.061° [172]
Chemviron Carbon	Nuclearcarb® 203C	0.57ª	Granules: 0.71-4.8	NA	0.052 <sup>d</sup> [173]
	Silver-	exchange	d zeolites		
Sigma Aldrich Co.	Ag-Mordenite	1.07ª	Pellets: 1.7-4.8	10-15	-
Extraordinary Adsorbents	Ag-ETS-10_1 Silica bound	0.90ª		25-30	0.46 <sup>e</sup> [138]
	Ag-ETS-10_2 Silica bound	1.10ª 0.90 <sup>b</sup>	Granules:	25-30	-
	Ag-ETS-10 Self-bound	1.03 <sup>b</sup>	0.30-	25-30	-
	Ag-Chabazite_1	0.57ª		10-15	-
	Ag-Chabazite_2	0.63ª		25-30	-
CEA	Ag-ZSM-5	0.59 <sup>b</sup>	Granules: 0.30- 0.50	10.6% [174]	0.70 <sup>f</sup> [141]
Metal-Organic Frameworks					
Technische Universität Dresden	Ni-DOBDC	0.41 <sup>b</sup>	Granules: / 0.30-1.7 /		0.008° [175]
MOF Technologies	HKUST-1	0.29 <sup>b</sup>	Pellets: 1 x 10 mm	/	0.012 <sup>c</sup> [175]

<sup>a</sup> As reported by the supplier.

<sup>b</sup> As measured from a 50 cm<sup>3</sup> column filling.

<sup>c</sup> From the Xe Henry's adsorption constant at room temperature and at 100 Pa.

<sup>d</sup> From the Xe Henry's adsorption constant at 273 K and at 100 Pa.

<sup>e</sup> Xe adsorption capacity at 298 K and 67 Pa.

<sup>f</sup> Xe adsorption capacity at 298 K and 100 Pa.

Three ACs, seven AgZs and two MOFs were investigated throughout this research. Their supplier, commercial name together with their density, mesh size and silver content, as provided by the supplier of the acquired sample, are presented in Table 2-1. Whenever available, the reported Xe adsorption capacity at about 100 Pa and Room Temperature (RT) is listed in the table.

#### 2.1.1. Activated carbons

The selected ACs are commercially available adsorbents especially developed for the capture of radioactive gases in the nuclear industry. Both the Nuclearcarb® 203C and Nusorb® GXK samples are coconut based granular ACs specifically designed for noble gas adsorption. The Nuclearcarb® 203C material was used for xenon retention in a transportable Xe monitoring system for verification of the Comprehensive Nuclear-Test-Ban Treaty (CTBT) [176]. Norit RKJ 1 is a potassium iodide impregnated and extruded AC, which has specifically been designed for iodine trapping. This AC has been investigated for iodine adsorption [177], but not yet for Xe adsorption.

#### 2.1.2. Silver-exchanged zeolites

The selected silver-exchanged Mordenite is commercially available. Munakata et al. [137] showed that this type of AqZ had a higher Xe adsorption capacity than a reference AC at Xe partial pressures lower than 1 kPa and at 273 K. The two samples of silver-exchanged Chabazite, with different silver loadings (10-15 wt.% and 25-30 wt.% for Aq-Chabazite 1 and Aq-Chabazite 2, respectively), were prepared, as reported in [178], by Extraordinary Adsorbents Inc. Such a silverexchanged Chabazite was reported to have a Xe adsorption capacity ranging from 0.79 to 0.88 mol kg<sup>-1</sup>, depending on the synthesis process, at 1 kPa and 298 K [179]. Aq-ETS-10 is a commercially available silver-exchanged titanosilicate, which will be classified as AqZ in this work due to its strong similarity with zeolites. This AgZ was developed and investigated by Kuznicki et al. [138]. A steep Xe adsorption isotherm at low partial pressure was demonstrated. A sample of this AqZ was obtained; this sample is called Aq-ETS-10 1 in the following sections. The synthesis method of the Aq-ETS-10 was further developed to improve its adsorption properties, as reported by Shi et al. [163], leading to the development of the denser Ag-ETS-10\_2 sample, which is also investigated. It has to be noted that the previous study reported a higher bulk density, *i.e.* 1.45 g cm<sup>-3</sup>, by using two different particle sizes [163], which is not the case for the sample used in the current work. As described in Section 1.3.3, Ag-ETS-10\_2 is being used in a dedicated subprocess, after reducing the  $H_2O$  and  $CO_2$  content, in one of the second generation IMS systems (SAUNA III). All analyses performed on Ag-ETS-10\_1 and Ag-ETS-10\_2 are using the composition including the silica binder. Self-bound Ag-ETS-10 was synthetized based on the same procedure as for Ag-ETS-10 2 [163], but the granules were formed without the use of a binder. Aq-ZSM-5, which is being used in another second generation IMS system (SPALAX-NG), was kindly provided by the Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA, France), and was synthetized according to a previously described procedure [174].

Kuznicki's group demonstrated the presence of silver nanoparticles on the surface of the Ag-ETS-10 and the Ag-Chabazite after synthesis [138, 178]. Another research group showed that the observed experimental Xe adsorption isotherms

on various AgZs contained two clear adsorption steps and could be represented by the sum of two independent Langmuir isotherms [142]. The strong Xe adsorption at low Xe partial pressure in a particular silver-exchanged Pentasil, Ag-ZSM-5, was demonstrated to be likely due to the presence of silver nanoparticles on the external surface of the zeolite [143]. As discussed in Section 1.5.3, the adsorption mechanism is currently not known [143].

#### 2.1.3. Metal-Organic Frameworks

Ni-DOBDC, aka Ni-MOF-74 or CPO-27(Ni), and HKUST-1, aka Cu-BTC, were selected based on their commercial availability in hundreds of grams of pellets or granules and their reported Xe adsorption properties. Their Xe adsorption capacity at low Xe partial pressure is expected to be low, but they have promising Xe separation properties with Xe/Kr selectivities of 5.8 and 8.5, respectively [175]. It has to be noted that other MOFs with higher Xe/Kr selectivities and higher Xe adsorption capacities have been reported. However at the start of the PhD research, these were not yet commercially available in hundreds of grams of pellets or granules as would be required for the investigated applications.

# 2.2.Breakthrough experiments

#### 2.2.1. Measurements

As explained in Section 1.6, an experimental set-up was developed to measure the breakthrough of gases in different adsorbents. In comparison with typical volumetric or gravimetric gas adsorption instruments, used to measure adsorption isotherms, it allows to determine dynamic properties based on breakthrough curves. The set-up, presented in Figure 2-2, is composed of three main parts: the gas management system, the adsorption column, and the detection and acquisition system.

Chapters 3, 5 and 6	Chapter 4
He BIP®	N <sub>2</sub> BIP® Plus
N <sub>2</sub> BIP®	He BIP <sup>®</sup> Plus
99.9% He / 0.1% Xe Experis®	Ar BIP®
99% N <sub>2</sub> / 1% Xe Experis®	O <sub>2</sub> UltraPure Plus
99.995% N <sub>2</sub> / 0.005% Xe Experis®	99.9% He / 0.1% Ar Experis®
	99.9% N <sub>2</sub> / 0.1% Ar Experis®
	99% N <sub>2</sub> / 1% Ar Experis®

Table 2-2. Composition of the high purity gases in function of chapters.

In the gas management system, the different high purity gases used in the experiments were obtained from Air Products. The gases are listed in Table 2-2 in function of the chapters in which they were used. Air was sampled, compressed and dried on site to a frost point of about 223 K. The necessary Xe or Ar in a carrier gas mixture for an experiment is controlled by two mass-flow controllers (Voëgtlin, red-y smart series). The investigated Xe concentrations are ranging from 87 ppb to 10 000 ppm in the carrier gas for a pressure of 120 to 180 kPa,

whereas the investigated Ar concentrations are ranging from 5 ppm in the carrier gas to 100% for a total pressure of 120 to 150 kPa.

As a comparison, the natural Ar and Xe concentrations in air are 0.933 vol.% and 87 ppb, respectively [47]. In contrast, the xenon concentration during the dissolution at MIPFs is in the range of 200 ppm. This corresponds to a typical flow rate of 1000 cm<sup>3</sup> min<sup>-1</sup> at Standard Ambient Temperature and Pressure and a <sup>133</sup>Xe activity of 4.4  $10^{14}$  Bq as reported by Braekers et al. [180] released over one hour.

A gas humidifier system can be connected in the gas management system when necessary. The humidifier consists of a double-walled concentric tube with the central pipe being a specific semi-permeable membrane (PermaPure, Nafion®), which is fed by a deionized water column. The necessary humidity level is obtained by adjusting the fraction of the flow rate passing over the humidifier as the water column height and temperature are fixed. The two selected relative humidity (RH) levels, 5 and 50%, corresponded to a dew point of  $255 \pm 3$  K and  $283 \pm 3$  K respectively, for a column temperature of 294 K. A pressure sensor (General Electric, UNIK 5000) is monitoring the pressure just after the mass flow controllers.



Figure 2-2. Schematic representation of the experimental set-up for the measurement of breakthrough curves. V1-7 and VHB are ball valves and VR1 is a needle valve. From [181].

The adsorption column is a stainless steel column filled with the adsorbent to be investigated. The adsorption column is positioned vertically and the gas is fed through its upper part. Six different adsorption columns with different geometries were used and their characteristics are summarized in Table 2-3. The experiments on the collection and separation of Xe from air (Chapter 3) were performed on column C3, whereas the ones on the collection and separation of Ar from air (Chapter 4) were performed on columns C4 and C5. During the investigations on the applicability of AqZs for radioxenon mitigation, described in Chapter 5, columns C1 to C3 were used. Finally, columns C3 and C6 were used for the research on the durability of AqZs (Chapter 6). Columns C1 to C3 have a stainless steel sintered wire mesh on both ends to retain all adsorbent particles in the column, whereas for the other columns, a borosilicate glass fibre filter was used. During the filling of the adsorption column with the adsorbent, mechanical vibrations are applied on the external surface of the column to ensure a good packing of the material. For adsorbent packings that were not fully filling the adsorption columns, glass wool is used on both ends of the column to have the adsorbent in the middle of the column and to ensure a good packing. A differential pressure sensor (KELLER, PD-23 series) is monitoring the pressure drop across the adsorption column. The temperature of the adsorbent is continuously monitored with a thermocouple (type K) connected to a digital indicating controller (CHINO, LT300 series).

Column #	Internal diameter (mm)	Internal length (mm)	Used in:	
C1	30	45	Chapter F	
C2	20	80	Chapter 5	
C3	20	200	Chapters 3, 6 and 5	
C4	28	300	Chapter 4	
C5	34	380	Chapter 4	
C6	19.5	200	Chapter 6	

Table 2-3. Internal diameter and length of the adsorption columns together withthe chapters in which the columns were used.

The detector system is either a Thermal Conductivity Detector (SRI Instruments, 110 GC TCD), where the carrier gas is used as reference, or a Mass Spectrometer (Analytical, HPR-20 R&D) depending on the experiments. The detector system is calibrated for Xe or Ar at least every week in the range of Xe or Ar concentrations, in the relevant carrier gas, necessary for the experiments. For experiments with air, the N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> and Kr measurements were based on their reported concentration in air: 78.1 vol.%, 20.9 vol.%, 0.933 vol.%, 414 ppm and 1.14 ppm, respectively [47]. For experiments with varying mixtures of N<sub>2</sub>, O<sub>2</sub> and Ar, dedicated calibrations were performed with the ternary mixture in the relevant range of concentrations. The dew point sensor (Michell, Easidew Online) is monitoring the dew point in parallel of the detector system.

Most breakthrough measurements were performed at RT (294 K). For investigating the effect of temperature on the Ar collection and separation from

air (Chapter 4), the adsorption column was placed in an ultra-low temperature freezer (Haier, DW-86W100) at temperatures ranging from 213 to 248 K. Before each breakthrough experiment, the adsorbent is regenerated at the desired temperature, typically about 473 K, under a He or N<sub>2</sub> flow, depending on the carrier gas used for the following experiment. The regeneration is performed until the Xe or Ar partial pressure in the mass spectrometer reaches the background level (about  $10^{-13}$  mbar for Xe and about 5  $10^{-11}$  mbar for Ar). The process is controlled by a temperature controller (West Control Solutions, KS20) in combination with a thermocouple (type K) on the external surface of the column. The heating system is either a 180 W e-glass textile heating wire (Eltherm, ELK-HS) wrapped around the column or a 1200 W infrared lamp (Heraeus, SW/1200W), with a gold reflector, directed towards the column.

In case moisture is added to the gas stream, the desorption in  $N_2$  is performed until the water partial pressure in the mass spectrometer reaches the level for dry  $N_2$ . Before each breakthrough measurement with air, the adsorbent is thermally desorbed with He until the partial pressure of each air component in the mass spectrometer reaches the background level in He. The temperature used during the regeneration was in the range from 294 to 543 K depending on the experiment. The flow rate for the experiments ranged from 30 to 2000 cm<sup>3</sup> min<sup>-1</sup>.

The following parameters are continuously recorded on a PC: flow rate on both mass flow controllers, inlet pressure, pressure drop across the adsorption column, temperature of the test bed and dew point. All values reported in this work correspond to the median value over the duration of the experiments. The partial pressure of each gas component in the gas stream is calculated based on the inlet pressure and its concentration. All breakthrough measurements, except the breakthrough measurements with 50% relative humidity, were duplicated to ensure reproducibility. The average values are used in the results, except when otherwise specified. For 50% relative humidity, only one breakthrough curve was recorded, as an explorative investigation, due to the strong water uptake on some adsorbents and the challenges to remove the moisture from these adsorbents as well as drying all the gas tubing of the experimental set-up after the experiment.

#### 2.2.2. Analysis

From the experiments, two parameters are directly extracted: the adsorption capacity and the retention time. The adsorption capacity (q [mol g<sup>-1</sup>]) corresponds to the amount of a gas specie retained in the material until full breakthrough ( $t_b$  [s]), as shown in Equation 2-1. It is determined based on calibrations made on beforehand with the relevant concentrations (C [mol m<sup>-3</sup>]). The mass of adsorbent (M [g]) is measured with a mass balance (METTLER, AE240) after the set of experiments performed in the adsorption column, which always ended by a desorption. The median flow rate (F [m<sup>3</sup> s<sup>-1</sup>]) over the duration of the experiment is used in Equation 2-1.

$$q = \frac{F \int_0^{t_b} (C_{inlet} - C_{outlet}) dt}{M}$$
 Equation 2-1

For the measurement of adsorption isotherms of a gas specie, the adsorption capacity at each partial pressure is measured successively. The retention time  $(t_{XX\%}$  [s]), which can be defined at any percentage of the breakthrough curve (XX%), is corresponding to the time required to have a certain percentage of breakthrough of the gas specie (*i.e.* percentage of the inlet concentration).

In addition, the notion of Mass Transfer Zone (MTZ) is used to quantify the overall mass transfer kinetics (diffusion, dispersion and adsorption-desorption) of the gas specie during each experiment, which is in the current work defined as the zone going from 10% to 90% breakthrough ( $t_{10\%}$  and  $t_{90\%}$  [s]). This is the percentage of the adsorbent bed where active adsorption occurs. The relative length of this zone is calculated based on the definition in Zhou et al. [182]. The definition of the MTZ percentage is given in Equation 2-2.

$$MTZ (\%) = \frac{2 (t_{90\%} - t_{10\%})}{(t_{90\%} + t_{10\%})} \cdot 100 \%$$
 Equation 2-2

For gas separation, the equilibrium selectivity  $S_{A/B}$  [-] was calculated according to Equation 2-3

$$S_{A_{B}} = \frac{q_{A}/y_{A}}{q_{B}/y_{B}}$$
 Equation 2-3

where  $q_A$  and  $q_B$  [mol g<sup>-1</sup>] denote the adsorption capacity, as measured by the breakthrough experiments, of gas component A and B, respectively, at their respective partial pressure, and  $y_A$  and  $y_B$  [-] are the molar fractions in the gas phase of gas component A and B, respectively.

The uncertainty on the Xe adsorption capacity and retention time at 10% of the overall experimental system was evaluated through ten successive measurements of breakthrough curves on a sample of Nusorb® GXK in the same conditions, which are given in Table S 2-1 in Supplementary material. The average adsorption capacity in these conditions was  $1.2 \ 10^{-2} \ mol \ kg^{-1}$  and the minimum and maximum values were  $1.1 \ 10^{-2} \ mol \ kg^{-1}$  (-8.3%) and  $1.3 \ 10^{-2} \ mol \ kg^{-1}$  (+8.3%), respectively. The average retention time at 10% was 36 minutes and the minimum and maximum values were 35 (-2.8%) and 39 minutes (+8.3%), respectively. The average MTZ percentage was 66% and the minimum and maximum values were 63% (-4.0%) and 70% (+6.6%), respectively. This can be considered as a worst-case uncertainty as the same sample was used throughout the ten breakthrough curves and a desorption step was performed in between the adsorption runs so that a potential degradation of the material cannot be excluded. An uncertainty of  $\pm 10\%$  is used for the reported adsorption capacities, the retention times at 10%, and the MTZ percentages.

## 2.3.Analysis of adsorption isotherms

The adsorption isotherms collected with the breakthrough experimental set-up were fitted with the Langmuir equation described in Section 2.3.1 as this is a well-

known isotherm equation for Type I adsorption isotherms (as shown in Figure 1-17). The BET method described in Section 2.3.2 was used to determine the surface area of the adsorbents using the adsorption of N<sub>2</sub> at 77 K. As detailed in Section 2.3.3, the micropore volume of the adsorbents was determined using the Dubinin-Radushkevitch equation on N<sub>2</sub> and CO<sub>2</sub> adsorption data. Finally, the pore size distribution was determined from the N<sub>2</sub> adsorption isotherm at 77 K using Density Functional Theory (DFT) models.

#### 2.3.1. Langmuir isotherm

The experimental Xe adsorption isotherms, measured at RT with the breakthrough measurement set-up, were fitted with the single-site Langmuir adsorption isotherm in Equation 2-4

$$q = \frac{q_s \, b \, P}{1 + b \, P}$$
 Equation 2-4

where q [mol kg<sup>-1</sup>] is the adsorption capacity for the relevant gas specie,  $q_s$  [mol kg<sup>-1</sup>] is the saturation capacity of the adsorption site, b [Pa<sup>-1</sup>] is the adsorption coefficient of the adsorption site and P [Pa] is the partial pressure of the gas specie.

In case the measured adsorption isotherm is showing two adsorption sites (*i.e.* two saturation levels), the previous Langmuir isotherm is extended by a second term with a dedicated saturation capacity and adsorption coefficient for the second site, resulting in the so-called dual-site Langmuir isotherm. In case the adsorption isotherm is linear in the investigated pressure range, the linear form (*i.e.* when b P << 1), known as Henry's law, is used with slope K [mol kg<sup>-1</sup> Pa<sup>-1</sup>], Henry's adsorption constant, being the multiplication of  $q_5$  and b in Equation 2-4.

Ar in He adsorption isotherms were collected at different temperatures to determine the heat of adsorption, as it was not yet reported for the material investigated. The heat of adsorption was obtained by fitting the isotherms with the temperature dependent Langmuir isotherm, where the temperature dependence of the adsorption coefficient, b(T) [Pa<sup>-1</sup>], is expressed by Equation 2-5 [183]. In this equation,  $b_{\infty}$  [Pa<sup>-1</sup>] is the adsorption coefficient at infinite temperature, Q [J mol<sup>-1</sup>] is the heat of adsorption, T [K] is the temperature and R [8.314 J mol<sup>-1</sup> K<sup>-1</sup>] is the ideal gas constant.

$$b(T) = b_{\infty} exp(\frac{Q}{RT})$$
 Equation 2-5

#### 2.3.2. BET method

The Brunauer, Emmet and Teller theory, as initially described in Brunauer et al. [184], is often used to calculate a specific surface area, expressed in  $m^2$  per gram of adsorbent, by analysing gas adsorption data using a specific probing molecule, such as N<sub>2</sub> at 77 K. The specific surface area is the surface area, per unit mass of adsorbent, where the first adsorption layer can be formed by the probing molecule [185]. Multilayer adsorption of the gas specie on the surface of the adsorbent is

assumed in the BET theory and requires a careful selection in the measured adsorption data to avoid data in the capillary condensation pressure range [186]. Typically, the reduced pressure (p/p<sub>0</sub>, where p<sub>0</sub> is the saturation pressure of the relevant gas specie) range is restricted from 0.05 to 0.35 [187]. The BET theory assumes that each adsorbed molecule in the first layer corresponds to one adsorption site for the second layer (by sorbate-sorbate interaction) and similarly for the subsequent layers. The molecules in the second and subsequent layers are considered to behave like the saturated liquid, whereas the first layer, in contact with the surface of the adsorbent, has a different behaviour with a specific equilibrium constant [187]. The BET theory is applicable to Type II and Type IV adsorption isotherms (Section 1.5). The BET equation is given in Equation 2-6, where q<sub>m</sub> [mol g<sup>-1</sup>] is the monolayer adsorption capacity and b [-] is here the BET constant.

$$q = \frac{q_m b (p/p_0)}{(1 - p/p_0) (1 - p/p_0 + b p/p_0)}$$
 Equation 2-6

For the analysis of the BET isotherm, the previous equation is generally reorganized as follows:

$$\frac{p/p_0}{q(1-p/p_0)} = \frac{b-1}{q_m b} p/p_0 + \frac{1}{q_m b}$$
 Equation 2-7

By plotting the left term  $(p/p_0)/[q(1-p/p_0)]$  in function of  $p/p_0$ , the BET constant, b, and the monolayer capacity can be retrieved, using Equation 2-8 and Equation 2-9, by fitting the isotherm with a linear equation where A is the slope, and I is the intercept.  $q_m$  can be converted to a surface area using the Avogadro constant [6.022 10<sup>23</sup> molecule mol<sup>-1</sup>] and the cross sectional area of the probing molecule [16.2 10<sup>-20</sup> m<sup>2</sup> molecule<sup>-1</sup> for N<sub>2</sub> at 77 K].

$$q_m = \frac{1}{A+I}$$
 Equation 2-8  
 $b = 1 + \frac{A}{I}$  Equation 2-9

The BET method can also be applied for all other types of adsorption isotherms by further restricting the data selection to meet the following five criteria (the so-called Rouquerol-criteria) [188]:

- A linear fit should be obtained for the BET transformed data;
- The BET constant (b) must be positive;
- The Rouquerol transform  $[q (1 p/p_0)]$  must continuously increase with  $p/p_0$ ;
- The monolayer capacity (q<sub>m</sub>) must be within the limits of selected data;
- $1/(\sqrt{b}+1) \approx p/p_0$  at the monolayer capacity.

As the calculated BET surface area is dependent on the data selection, the pressure range used for this calculation will always be reported in the following chapters.

#### 2.3.3. Dubinin-Radushkevitch equation

The Dubinin-Radushkevitch (D-R) equation was initially developed for investigating the microporosity of activated carbon [189], but it can be used for any microporous material [190]. The D-R equation is derived from the Polanyi potential theory of adsorption [191]. It considers the filled volume, by adsorption,  $V_a$  [cm<sup>3</sup> g<sup>-1</sup>] at a given p/p<sub>0</sub> pressure to be a function of the adsorption potential E [J mol<sup>-1</sup>] [191]. The filled volume is a part of the total micropore volume  $V_{micro}$  [cm<sup>3</sup> g<sup>-1</sup>]. The obtained empirical relation is given in Equation 2-10.

$$V_a = V_{micro} e^{-\left[\left(\frac{RT}{\beta E_0}\right)^2 ln\left(\frac{p_0}{p}\right)^2\right]}$$
Equation 2-10

In this equation,  $E_0$  [J mol<sup>-1</sup>] is a characteristic energy,  $\beta$  [-] is called the structural constant, R [8.314 J K<sup>-1</sup> mol<sup>-1</sup>] is the ideal gas constant and T [K] is the temperature. The equation can be reorganized (Equation 2-11) to plot  $\log V_a$  against  $[\log(p_0/p)]^2$  to fit the so-called D-R isotherm with a linear equation. V<sub>micro</sub> is then directly obtained by the ordinate intercept. The micropore surface area can be calculated from V<sub>micro</sub>.

$$\log V_a = \log V_{micro} - \left[2.303 \left(\frac{RT}{\beta E_0}\right)^2\right] \left[\log \frac{p_0}{p}\right]^2$$
 Equation 2-11

#### 2.3.4. Pore size distribution

Density Functional Theories (DFTs) are used in physisorption to model pore structures by a rigorous theoretical treatment [192]. DFTs are very powerful for determining the pore size distribution. However, they require to solve the statistical mechanical Hamiltonian, which in turn requires to know the position of the force centres in the adsorbent and the potential functions governing the adsorbent-adsorbate and adsorbate-adsorbate interactions. Most applications of DFT have focused on the adsorption of small, spherical molecules in pores of uniform geometry (mostly cylindrical or slit-shaped pores) [192]. Two DFTs are widely used for the analysis of adsorption data: the Quenched-Solid Density Functional Theory (QSDFT) and the Non-Local Density Functional Theory (NLDFT). The NLDFT is particularly well suited for ordered porous structures such as zeolites and MOFs, whereas the QSDFT is particularly well suited for disordered pore

Accordingly, pore size distributions were determined by applying the QSDFT to the  $N_2$  adsorption isotherm of ACs whereas the NLDFT was applied for AgZs and MOFs. The pore shape (cylindrical or slit pores) used in the DFT models depends on the adsorbents and will be given in the corresponding chapters.

#### 2.4.Adsorbent characterisations

Some of the adsorbents were characterized, after crushing the pellets and granules back to powder, by powder X-ray diffraction (PXRD), scanning electron

microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX), and  $N_{\rm 2}$  adsorption isotherms at 77 K as well as CO\_2 adsorption isotherms at 273 K.

# 2.4.1. Powder X-ray diffraction

PXRD measurements were performed at SCK CEN (Belgium). Diffractograms were collected at RT using a Bruker D8 Advance diffractometer, operating in Bragg-Brentano configuration and using a Cu X-ray tube (Cu Ka1 = 0.154060 nm). Diffracted X-rays were detected with a Lynxeye detector (linear position-sensitive detector). The incident beam was collimated by a variable divergence slit set to an illumination length of 15 mm. A small amount of the sample powder was dispersed on top of a zero-background silicon single crystal holder. Diffractogram acquisitions were performed by scanning from 5° - 90° with a step size of 0.02° (20) and a dwell time of 0.4 s/step.

# 2.4.2. Scanning electron microscopy

The morphology of the adsorbents was studied by SEM (Phenom ProX Desktop model) at Hasselt University (Belgium). The images were acquired at RT, applying an acceleration voltage of the primary electron beam of 15 kV. SEM images were obtained in backscatter electron imaging mode. Elemental analysis was performed with the complementary EDX detector of the SEM.

# 2.4.3. N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms

 $N_2$  adsorption isotherms at 77 K were recorded on a volumetric sorption instrument Autosorb IQ (Quantachrome) in the relative pressure range of 0 – 0.96 at the Wrocław University of Science and Technology (Poland). Prior to analysis, the samples were degassed at 473 K for 24 h at pressures below 0.1 Pa. The specific surface area ( $S_{BET}$ ) was calculated using the Brunauer-Emmett-Teller (BET) equation method in a relative pressure range meeting the Rouquerol BET consistency criteria as described in Section 2.3.2. The volume of  $N_2$  adsorbed, considering its liquid density, at the relative pressure of  $p/p_0 = 0.96$  was used to determine the total pore volume ( $V_T$ ). The micropore (size < 2 nm) volume ( $V_{DR}$ ) was estimated by applying the Dubinin-Radushkevitch equation as described in Section 2.3.3. The mesopore (size 2-50 nm) volume was calculated as the difference between the total pore volume and the micropore volume. The pore size distribution was determined using DFT models as described in Section 2.3.4. It is assumed that micropores with a width larger than 0.7 nm are accessible to  $N_2$  molecules [193].

Porosity in the range of ultramicropores was determined by  $CO_2$  adsorption at 273 K on a ASAP2020 sorption analyser (Micromeritics) at the Wrocław University of Science and Technology (Poland). Samples of about 100 mg were degassed under vacuum in the degas station at 473 K for 12 h. The Dubinin-Radushkevitch equation was applied to estimate the corresponding micropore volume ( $V_{DR,CO2}$ ) and the micropore surface area ( $S_0$ ) as described in Section 2.3.3.  $CO_2$  molecules are adsorbed in pores from 0.4 to approximately 1.5 nm in size [193].

## 2.5. Supplementary material

Table S 2-1. Experimental conditions for the uncertainty quantification of the experimental system with Nusorb® GXK. Experimental conditions (mass of adsorbent, flow rate, inlet pressure, Xe partial pressure and temperature) and results (Xe retention time at 10% and adsorption capacity, and Mass Transfer Zone) of the breakthrough experiments. The carrier gas was N<sub>2</sub>. The experiments were performed with column C3 and the Xe outlet concentration was measured with the mass spectrometer. From [181].

Run	М	F	Р	P <sub>Xe</sub>	Т	t <sub>10%</sub>	q <sub>Xe</sub>	MTZ
	(g)	(cm <sup>3</sup> min <sup>-1</sup> )	(kPa)	(Pa)	(K)	(min)	(mol kg <sup>-1</sup> )	(%)
1		400	130	32.6	293	39	1.3 10 <sup>-2</sup>	68
2		400	131	32.6	294	35	1.1 10-2	64
3		400	131	32.8	293	38	1.2 10-2	65
4		400	132	32.9	294	37	1.2 10-2	70
5	24.2	400	132	33.0	293	37	1.2 10-2	64
6	24.2	400	132	33.0	294	35	1.2 10-2	64
7		400	132	33.1	294	36	1.2 10 <sup>-2</sup>	64
8		400	132	32.9	292	37	1.2 10 <sup>-2</sup>	63
9		400	132	32.9	294	35	1.2 10 <sup>-2</sup>	64
10		400	133	33.1	294	35	1.1 10-2	70
Mean	-	400	132	32.9	294	36	1.2 10 <sup>-2</sup>	66

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# **Chapter 3**

Improving radioxenon monitoring systems

	Research objective	Main evaluation metrics
1	Investigate the potential of new porous materials for collecting and separating Xe directly from ambient air in the context of the international monitoring system	Xe collection and separation efficiency


# 3. Improving radioxenon monitoring systems

In this chapter addressing the first research objective, the use of silver-exchanged zeolites and alike (AgZs), and metal-organic frameworks (MOFs) for collecting and separating Xe directly from atmospheric air (*i.e.* without pre-purification) is investigated. The main objective is to determine if AgZs or MOFs can improve the Xe collection and separation efficiency (directly from atmospheric air) of radioxenon monitoring stations in the International Monitoring System (IMS). In addition, this study on Xe collection and separation from atmospheric air is also of particular relevance for the production of stable xenon.

This chapter is based on the following published paper:

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## Abstract

More efficient adsorbents for Xe collection and separation from air could provide new alternatives for cost-efficient production of stable Xe as well as for trace measurements of atmospheric radioxenon. AqZs have been reported to be more efficient than AC in collecting Xe at low pressures and Room Temperature (RT), but never for Xe collection from air. MOFs have been reported for high Xe/Kr selectivities in Xe and Kr enriched gas streams, but never for Xe collection from air either. Two AqZs (Aq-ETS-10 and Aq-ZSM-5), two MOFs (HKUST-1 and Ni-DOBDC) and one AC (Nusorb® GXK) are compared to determine their potential for collecting and separating Xe from air. The acquired adsorbent samples were characterized (by SEM, PXRD, TGA, N<sub>2</sub> adsorption at 77 K and CO<sub>2</sub> adsorption at 273 K) and the results are in agreement with observations made previously in the literature. Both AqZs show an unprecedented Xe adsorption capacity in  $N_2$  at 13.5 mPa (*i.e.* 100 ppb Xe, which is approximately the Xe partial pressure in air) and RT with 0.15 and 0.13 mmol kg<sup>-1</sup> for Ag-ETS-10 and Ag-ZSM-5, respectively. This high Xe adsorption capacity at low Xe concentration holds in dry air. Both AqZs have a high Xe selectivity over the major gas components in air at RT. They also show an unprecedented Xe selectivity over Kr of 1300 and 470 for Aq-ETS-10 and Ag-ZSM-5, respectively. Finally, it is possible to separate Xe from  $O_2$ , Ar,  $CO_2$ , Kr and Rn efficiently in both AqZs but it requires temperatures up to 521 K. The results clearly demonstrate that both AqZs investigated in this work are globally outperforming all other adsorbents for collecting and separating Xe from air. The only limitation found for the moment on these AgZs is the strong co-adsorption of moisture that significantly reduces the Xe collection at 50% Relative Humidity (RH).

# 3.1.Introduction

High purity Xe is necessary for applications such as nontoxic anaesthetic [194], propellant in ion thrusters for satellites and spacecrafts [195], and for UV light

sources used in the manufacture of semi-conductors [196]. By nature, Xe is found in the Earth's atmosphere at a trace level of 87 ppb. Commercial Xe is mainly produced by the energy-intensive cryogenic distillation of the Xe/Kr by-product obtained from cryogenic air distillation [197]. The global demand for high-purity Xe is increasing and resulted already in significant increases in its cost due to the limited production capacity [198]. A less energy demanding production route is being looked for to meet this increasing global demand.

One alternative route currently investigated is the separation of Xe from Kr in nuclear fuel reprocessing facilities due to the large quantities of Xe available during this process [175]. Over the last decade, researchers have been investigating the development and use of MOFs for Xe separation and storage in this context. These adsorbents are very promising as their adsorption and separation properties can be fine-tuned through the combination of metal clusters and organic linkers as well as with functionalization methods [149]. The main challenge is to recover stable Xe stripped from the remaining radioactive Kr, because of the long half-life of <sup>85</sup>Kr [199].

As presented in Section 1.3, the collection and separation of trace levels of radioxenon from atmospheric air is necessary for the verification of the Comprehensive Nuclear-Test-Ban Treaty (CTBT). The recent second generation of radioxenon monitoring systems (Section 1.3.3) for the IMS have improved detection capability, which could help to distinguish xenon background detections from nuclear weapon tests [92, 97, 98, 100]. One of the improvements in two of these new generation systems is the use of more efficient Xe adsorbents, namely AqZs, at different stages of the process depending on the system [98, 200]. In both cases, a pre-purification step is still performed to remove moisture and carbon dioxide before sending the air stream towards AgZs. According to the study of Topin et al. [200], Aq-ZSM-5 provided a similar Rn elimination factor as the initial AC in their Xe purification stage whilst reducing the volume of adsorbent required for this stage by a factor 10. Such an efficient Rn elimination is necessary to minimize the background component in the detector. The impact of moisture and carbon dioxide on the Xe collection and separation efficiency for these AgZs has not yet been reported. Monpezat et al. [141] showed that two AgZs, namely Ag-ETS-10 and Ag-ZSM-5, are much more efficient at RT than AC in collecting Xe from dry Xe-enriched air (*i.e.* 1 ppm Xe).

Both the production of high purity Xe and the measurement of trace levels of radioxenon would benefit from an efficient and selective adsorbent that could collect and separate Xe directly, *i.e.* without pre-purification, from atmospheric air as this would provide a simplified and less-energy demanding alternative. This alternative would require an adsorbent with a high Xe adsorption capacity and selectivity in air, ideally at RT, and a high Xe yield and Xe purity after desorption in temperature swing adsorption mode and/or (vacuum) pressure swing adsorption mode. To the best of our knowledge, MOFs and AgZs have not yet been investigated for this purpose. In this work, the authors fill this gap by investigating, for the first time, the use of AC, AgZ and MOF for the collection, at RT, and the separation of Xe directly from atmospheric air for the cost-efficient production of stable Xe and the measurement of trace levels of radioxenon.

## 3.2. Materials and methods

The morphology, composition, crystallinity, thermal stability and microporosity of the acquired adsorbents, in pelletized or granulized form, are characterized (Section 3.2.2 to 3.2.5) to ensure that the corresponding properties are in agreement with previous studies on the same adsorbents. The adsorbents used in the current study (one AC, two AgZs and two MOFs) are described in Section 3.2.1 Their potential for Xe collection, at RT, and separation directly from air is then investigated.

For the **Xe collection** part, three aspects are considered through Xe and air breakthrough measurements (Section 3.2.6). The **first** aspect is the Xe adsorption in  $N_2$  at RT to obtain a first insight on the differences in Xe adsorption in such relatively ideal conditions. The **second** aspect is to explore the effect of moisture on Xe adsorption in  $N_2$ . Finally the **third** one is the Xe adsorption capacity in air and Xe selectivity over the most relevant gas components in air.

For the **Xe separation** part, two aspects are considered. The **first** aspect is the separation of Xe from the most relevant gas components in air as detailed in Section 3.2.7. The **second** aspect (only relevant for radioxenon separation for IMS application) is the Xe/Rn separation potential of each adsorbent (Section 3.2.8).

The materials and methods that are common to multiple chapters (indicated in the yellow box in Figure 3-1) are described in full detail in Chapter 2, whereas materials and methods specific to the current chapter are detailed in the following sections.

C	Chapter 3 – Improving radioxenon
	monitoring systems
-	Adsorbents
	<ul> <li>1 activated carbon</li> </ul>
	<ul> <li>2 Ag-exchanged zeolites</li> </ul>
	- 2 metal-organic frameworks
-	Breakthrough measurements
-	N <sub>2</sub> and CO <sub>2</sub> adsorption
-	Powder X-ray diffraction and
	scanning electron microscopy
-	Thermogravimetric analysis
-	Xe/air separation
-	Xe/Rn separation

Figure 3-1. Materials and methods used in Chapter 3.

## 3.2.1. Adsorbents

The adsorbents used in the current study, *i.e.* Ag-ETS-10 (Ag-ETS-10\_2 silica bound sample), Ag-ZSM-5, Nusorb® GXK, Ni-DOBDC and HKUST-1, are described in Section 2.1.

## 3.2.2. Powder X-ray diffraction

The Powder X-Ray Diffraction (PXRD) measurements are described in Section 2.4.1.

## 3.2.3. Scanning electron microscopy

The acquisition of Scanning Electron Microscopy (SEM) images in combination with energy-dispersive X-ray spectra (EDX) are described in Section 2.4.2.

#### 3.2.4. Thermogravimetric analysis

ThermoGravimetric Analysis with Mass Spectrometry (TGA-MS) was performed at SCK CEN (Belgium). The analyses were conducted using a Setaram Setsys Evolution 16/18 coupled to a Pfeiffer Omnistar GSD320. The sample material (~200 mg) was transferred into an Al<sub>2</sub>O<sub>3</sub> crucible, suspended by a Pt/Rh wire in the furnace chamber. A Type S thermocouple located directly underneath the crucible was used to monitor and control the sample temperature. At the start of a measurement, the furnace chamber was first flushed with a constant flow of synthetic air (21 vol.% O<sub>2</sub>/N<sub>2</sub>, 160 cm<sup>3</sup> min<sup>-1</sup>) during 60 min. The remainder of the experiment was carried out using a flow rate of 60 cm<sup>3</sup> min<sup>-1</sup>. The temperature profile consisted in heating at a constant rate (5 K min<sup>-1</sup>) from 298 to 773 K (673 K for the Nusorb® GXK sample) with an isotherm of 60 min. Subsequently, cooling back to RT was performed at a constant rate (5 K min<sup>-1</sup>). During the experiment, the relative mass loss together with the intensity measured on mass 12, 14, 16, 17, 18 (specifically for H<sub>2</sub>O), 28, 32, 40, 44 (specifically for CO<sub>2</sub>) and 46 was recorded.

## 3.2.5. N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms

The collection of  $N_2$  isotherms at 77 K and  $CO_2$  adsorption isotherms at 273 K is described in Section 2.4.3.

## 3.2.6. Xe and air breakthrough measurements

Xe and air adsorption in the five adsorbents was evaluated using breakthrough experiments in column C3 as described in Section 2.2.

#### 3.2.7. Xe/air separation measurements

The potential for Xe separation from air on the adsorbents is investigated by adsorbing dry air for a limited time, to avoid any Xe breakthrough, followed by a thermal desorption to separate the different components. Column C3 was used for these experiments. A dry airflow is sent through the column during half of the time necessary to reach 10% of the Xe breakthrough on the adsorbent. The duration is based on an initial reference dry air breakthrough curve measurement (using the method described in Section 2.2). After the adsorption, a thermal desorption is directly started with a defined N<sub>2</sub> flow rate and temperature profile to separate Xe from  $O_2$ , Ar, Kr and  $CO_2$ . For each adsorbent, the flow rate and temperature profile were optimized as much as possible to minimize the content

of  $O_2$ , Ar, Kr and  $CO_2$  in the desorbed Xe peak. The temperature during the thermal separation ranged from 291 to 488 K, whereas the flow rate spanned from 50 to 400 cm<sup>3</sup> min<sup>-1</sup> depending on the adsorbent and the separation step. The desorbed Xe peak is delimited at 5 and 95% of the amount of desorbed Xe and is called the "90% Xe recovery peak" in the following.

#### 3.2.8. Xe/Rn separation measurements

A trap containing first a layer of 10 g of Nusorb® GXK, followed by 25 g of molecular sieve 4A, to capture any moisture, was charged with  $^{222}$ Rn in a dedicated laboratory at SCK CEN. The trap was charged with an activity, as measured in the dedicated laboratory, between 0.35 and 2.8 kBq of  $^{222}$ Rn under a N<sub>2</sub> gas stream following a procedure already described elsewhere [201]. This trap was connected to the Xe breakthrough measurement set-up in place of the humidifier. A radon detector (RAD7, Durridge Company) was placed at the outlet of the experimental set-up to monitor the outgoing  $^{222}$ Rn activity concentration. The  $^{222}$ Rn trap was flushed towards the adsorbent to be investigated, with a 250 ppm Xe in N<sub>2</sub> mixture to capture Xe and Rn on the adsorbent until full Xe breakthrough. Adsorption column C3 was used to contain the adsorbent. The trap was then disconnected from the experimental set-up and the investigated adsorbent was thermally desorbed under a N<sub>2</sub> flow to separate Xe from Rn. The temperature during the thermal desorption ranged from 203 to 523 K depending on the adsorbent, whereas the flow rate ranged from 20 to 400 cm<sup>3</sup> min<sup>-1</sup>.

## 3.3. Results and discussion

Samples of adsorbent pellets and granules acquired for this work were crushed to powders for their characterization with SEM/EDX, PXRD, TGA, N<sub>2</sub> adsorption at 77 K and CO<sub>2</sub> adsorption at 273 K to compare their morphology, composition, crystallinity, thermal stability and microporosity with literature data on the same adsorbents in fine powder form (Section 3.3.1). Adsorbent pellets or granules are necessary for industrial processes to avoid large pressure drops and dust contamination. It is thus necessary to verify that the production and pelletization process allowed maintaining the characteristics of the adsorbent.

Next, the Xe collection on each adsorbent is investigated through: Xe adsorption isotherms in  $N_2$  at RT, Xe adsorption measurements in a humid  $N_2$  gas stream, and dry air adsorption measurements (Sections 3.3.2 to 3.3.4). It allows to consider the adsorbents for Xe collection in relatively ideal conditions, in the presence of moisture and in atmospheric conditions. Finally, the Xe separation potential of each adsorbent is explored through Xe/air and Xe/Rn separation measurements (Sections 3.3.5 and 3.3.6). The Xe/Rn separation measurement is dedicated to the application of the adsorbents for trace level measurements of atmospheric radioxenon in the IMS.

#### 3.3.1. Adsorbent characterisations

The **morphology** of **Ag-ETS-10** (Figure 3-2a) corresponds very well to the truncated bi-pyramid crystals observed in previous works [163, 202]. Ag aggregates, as identified by EDX, in the range of tens to hundreds of nanometres were visible on the crystals in the SEM images (Figure 3-2 b-d). Ag nanoparticles in the range of a few tens of nanometres have been observed previously on TEM images of Ag-ETS-10 [138].



Figure 3-2. SEM characterization of Ag-ETS-10.



Figure 3-3. SEM characterization of Ag-ZSM-5.

The morphology of **Ag-ZSM-5** (Figure 3-3a) is also very similar to the flocculent structure observed in previous works [203, 204]. Very sparse Ag-aggregates, as identified by EDX, were observed and were in the range of a few hundreds of nanometres (Figure 3-3b). Previous studies have reported Ag nanoparticles in the nanometre range [205], which were not observed in the current work likely due to the limited resolution of the SEM that was used.

The diffractometer spectrum on Aq-ETS-10 obtained through **PXRD** confirmed the diffraction peaks for the ETS-10 framework as well as for silver oxide and metallic silver (Figure 3-4a) confirming the presence of silver nanoparticles. Not all diffraction peaks for the ETS-10 framework could be observed in the diffractometer spectrum of Ag-ETS-10, most likely due to site selectivity for Ag exchange in the ETS-10 framework, as reported by Tiscornia et al. [202]. As expected from the silver content reported by the producer of the Ag-ETS-10 sample used in this work, the relative intensity of the metallic silver peaks (38.2°) and silver oxide peaks (31.3° and 33.8°) measured on the Ag-ETS-10 sample is indicative of a high silver content as described in previous crystallography studies on Aq-ETS-10 with different silver contents [202]. A peak observed at 20.9° originated from the silica binder used to form the granules of Ag-ETS-10. The X-ray diffractometer spectrum of Aq-ZSM-5 corresponds very well to the ZSM-5 phase (Figure 3-4b). A relatively small diffraction peak is present at 38.2° and confirms the presence of some metallic silver in the sample, whereas no diffraction peak related to silver oxide could be observed. Such a metallic silver peak from silver nanoparticles has been observed in Aq-ZSM-5 in previous studies [143]. The absence of silver oxide peaks in Aq-ZSM-5 compared to Aq-ETS-10 could be due to the lower Ag content in the former.



Figure 3-4. X-ray diffractogram of a) Ag-ETS-10 and b) Ag-ZSM-5. The diffractogram of Ag-ETS-10 (top) is compared to the ones for crystals reported in the Crystallography Open Database [206] of ETS-10, Ag, Ag<sub>2</sub>O<sub>3</sub>, Ag<sub>2</sub>O and SiO<sub>2</sub>. The diffractogram of Ag-ZSM-5 (top) is compared to the one, reported in the Crystallography Open Database, of ZSM-5.

The TGA under air on Ag-ETS-10 (Figure 3-5a) showed a similar behaviour as previous TGA on Ag-ETS-10 [202]. The weight loss was 8.4% and mainly resulted from the desorption of water. **TGA** of Ag-ZSM-5 under air has never been reported. Like the Ag-ETS-10, the Ag-ZSM-5 maintained its integrity up to 773 K and lost 7.9% of its initial mass mainly through water desorption (Figure 3-5b).



Figure 3-5. Weight loss during the TGA of a) Ag-ETS-10 and b) Ag-ZSM-5 together with the relative outlet at mass 18 and 44.

The SEM image (Figure 3-6a) of **Nusorb® GXK** shows the typical pore morphology of AC. The pores visible on the SEM are in the range of 0.2 to 20 µm (Figure 3-6b). As expected with an amorphous material like AC, two broad peaks are observed on the PXRD spectra (Figure 3-7a) at the (002) and (100) planes of graphite. These are very similar to previous work on coconut shell-based steam activated carbon [207]. TGA of Nusorb® GXK, specifically under air, has never been reported. The TGA of Nusorb® GXK shows a loss of 11 % of the initial weight when reaching 673 K (Figure 3-7b). The weight loss below 673 K is driven by the desorption of both water and carbon dioxide. At 673 K, the AC starts to lose its integrity, with a loss of 17% of its weight during the 60-minute isotherm at 673 K, as expected according to the auto-ignition point at 723 K for this material.



Figure 3-6. SEM characterization of Nusorb® GXK.



Figure 3-7. a) X-ray diffractogram, and b) weight loss measured during the TGA on Nusorb® GXK together with the relative outlet at mass 18 and 44. Its diffractogram (a) is compared to the one of graphite as reported in the Crystallography Open Database [206].

The **morphology** of the **HKUST-1** sample (Figure 3-8a) is in agreement with the octahedral shape observed in previous studies [208] whereas the SEM images of the **Ni-DOBDC** sample (Figure 3-8b) shows a crystallite agglomerate similar to the ones observed in previous studies [209].



Figure 3-8. SEM image of a) HKUST-1 and b) Ni-DOBDC.

The **X-ray diffractogram** of the HKUST-1 sample (Figure 3-9a) corresponds very well to the ones observed in previous studies during which HKUST-1 was synthetized [210]. The same can be said for the PXRD spectra of the Ni-DOBDC sample (Figure 3-9b), which corresponds very well to previous studies during which Ni-DOBDC was synthetized [211].



Figure 3-9. X-ray diffractogram of a) HKUST-1 and b) Ni-DOBDC. Both diffractograms are compared to the one of a synthetized sample as reported in the Crystallography Open Database [206].

The TGA of HKUST-1 (Figure 3-10a) indicates that the sample first loses weight due to moisture desorption to about 86% of its initial mass below 458 K. Then the sample maintains a relatively stable mass until 543 K. At higher temperatures, the weight drops to only 35% of the initial mass following framework decomposition. This is in agreement with a TGA made under air in previous work on this adsorbent [212]. Similarly to HKUST-1, the TGA of Ni-DOBDC (Figure 3-10b) indicates that the sample first loses weight due to moisture desorption to about 70% of its initial mass until 548 K. At higher temperatures, the weight drops to only 38% of the initial mass following framework decomposition. This agrees well with a TGA made under N<sub>2</sub> in previous work [213].



Figure 3-10. Weight loss during the TGA of a) HKUST-1 and b) Ni-DOBDC together with the relative outlet at mass 18 and 44.

 $N_2$  adsorption isotherms at 77 K, complemented by  $CO_2$  adsorption isotherms at 273 K, were used to probe the mesopores and micropores of the five adsorbents (Figure 3-11). For the analysis of the pores present in the adsorbents,  $N_2$  adsorption isotherms at 77 K were used to allow a comparison with reported data in the literature. At present, the collection of a  $N_2$  adsorption isotherm at 77 K is the standard microporosity measurement in the literature for the adsorbents investigated in the current work. As explained in Section 1.6, Ar at 87 K is a less polarizable alternative probe for investigating micropores and mesopores in adsorbents with accessible metal sites, such as the AgZs and MOFs in this work, and could be considered for future studies on the microporous and mesoporous structure of these adsorbents.



N<sub>2</sub> uptake (cm<sup>3</sup> g<sup>-1</sup>)





Figure 3-12. Pore size distribution in each adsorbent obtained from the N<sub>2</sub> adsorption isotherm at 77 K. For Ag-ETS-10, Ag-ZSM-5 and HKUST-1, the Non-Local Density Functional Theory with cylindrical pores was used, whereas slit pores were used for Ni-DOBDC. For Nusorb® GXK, the Quenched-Solid Density Functional Theory with slit pores was used.

The pore size distributions, obtained from the N<sub>2</sub> adsorption isotherms at 77 K (Figure 3-12) indicate that the majority of the micropores are smaller than 1 nm, which highlights the need to specifically probe ultramicropores (diameter < 1 nm). The micropore analysis with CO<sub>2</sub> at 273 K is affected by the presence of accessible metal sites in the AgZs and MOFs investigated in this work but can still be useful for assessing the pore volume and porosity of ultramicropores in such materials [166].

The BET surface areas determined by N<sub>2</sub> adsorption isotherms at 77 K, using the Rouquerol BET consistency criteria (Figures S 3-1 to S 3-5), and the micropore surface areas (S<sub>0</sub>) determined through CO<sub>2</sub> adsorption isotherms at 273 K are in the following order: HKUST-1 > Nusorb® GXK > Ni-DOBDC > Ag-ZSM-5 > Ag-ETS-10. Together with the same order for the micropore volume determined by the Dubinin-Radushkevitch equation (Table 3-1), this shows that HKUST-1 has a higher microporosity than Nusorb® GXK and Ni-DOBDC, which all have a much higher microporosity than both AgZs.

Table 3-1. Surface area and pore volume determined from  $N_2$  and  $CO_2$ adsorption on the five adsorbents. BET surface area ( $S_{BET}$ ), micropore volume ( $V_{DR}$ ) and total pore volume ( $V_T$ ) from  $N_2$  adsorption. Micropore surface ( $S_0$ ) and volume ( $V_{DR,CO_2}$ ) from  $CO_2$  adsorption.

	N	CO2 at 273 K				
Adsorbent	S <sub>BET</sub> <sup>a</sup> (m² g⁻¹)	V <sub>DR</sub> <sup>b</sup> (cm³ g <sup>-1</sup> )	V <sub>T</sub> <sup>c</sup> (cm <sup>3</sup> g <sup>-1</sup> )	S0 <sup>b</sup> (m² g <sup>-1</sup> )	V <sub>DR, CO2</sub> <sup>b</sup> (cm <sup>3</sup> g <sup>-1</sup> )	
HKUST-1	1500 [3 10 <sup>-4</sup> -4 10 <sup>-2</sup> ]	0.57	0.67	1790	0.72	
Ni-DOBDC	795 [4 10 <sup>-3</sup> –6 10 <sup>-2</sup> ]	0.30	0.79	665	0.27	
Nusorb® GXK	1190 [1 10 <sup>-2</sup> -8 10 <sup>-2</sup> ]	0.43	0.50	803	0.32	
Ag-ZSM-5	302 [1 10 <sup>-4</sup> -6 10 <sup>-2</sup> ]	0.12	0.16	293	0.12	
Ag-ETS-10	206 [5 10 <sup>-5</sup> –6 10 <sup>-2</sup> ]	0.08	0.12	205	0.08	

<sup>a</sup> Calculated through the BET method in the relative pressure range indicated in brackets.

<sup>b</sup> Calculated through the Dubinin-Radushkevitch equation.

<sup>c</sup> Total pore volume determined at  $p/p_0 = 0.96$ .

The ratio of the micropore volume on the total pore volume is 85, 38, 86, 75 and 67% for HKUST-1, Ni-DOBDC, Nusorb® GXK, Ag-ZSM-5 and Ag-ETS-10 respectively. These values indicate that all adsorbents, except Ni-DOBDC, are dominated by micropores. The values for the MOFs and AgZs are in agreement with literature data [141, 211, 214, 215]. For Nusorb® GXK, the measured BET surface area is typical for steam activated carbon from coconut shells [207].

## 3.3.2. Xe adsorption isotherm in N<sub>2</sub>

Xe adsorption isotherms in N<sub>2</sub> at RT (Figure 3-13) were collected to investigate the Xe adsorption potential of each adsorbent in relatively ideal conditions and to allow a comparison with single-component Xe isotherms reported in the literature. To the best of our knowledge, Xe adsorption isotherm measurements in N<sub>2</sub> at RT have never been reported and compared for the five adsorbents.



Figure 3-13. Xe adsorption isotherms in  $N_2$  at room temperature. The measured Xe adsorption isotherms in  $N_2$  (filled symbols) are compared to reported single-component Xe adsorption isotherms measured at room temperature [141, 175, 181]. The experimental points measured in this work are fitted with Henry's law or Langmuir single- or dual-site relation depending on the adsorbent.

Both **AgZs** have a similar Xe adsorption isotherm in N<sub>2</sub> at RT for Xe partial pressures lower than 100 Pa (*i.e.* about 1000 ppm Xe). At higher pressures, Ag-ZSM-5 has a higher Xe adsorption capacity. The Xe adsorption isotherm in N<sub>2</sub> of Ag-ETS-10 and Ag-ZSM-5 follow a Langmuir single-site and dual-site isotherm, respectively (Table 3-2). One should remind here that Ag-ETS-10 has a packing density of 900 kg m<sup>-3</sup> compared to 590 kg m<sup>-3</sup> for the Ag-ZSM-5, which gives an advantage for Ag-ETS-10 in terms of Xe adsorption capacity by unit volume of adsorbent for Xe partial pressures lower than 100 Pa. The measurements on Ag-ZSM-5 are in agreement with the Ideal Absorbed Solution Theory (IAST) prediction performed in a previous study [140], which shows that IAST is well suited for estimating the binary mixture adsorption on Ag-ZSM-5. As shown in the work of Monpezat et al. [141], the Xe adsorption capacity at low Xe concentrations

in N<sub>2</sub>, between 1 and 100 ppm, is significantly lower, by up to two orders of magnitude, than the single-component Xe adsorption capacity due to the coadsorption of N<sub>2</sub> in AgZs. Surprisingly, the Xe adsorption capacity of 0.15 mmol kg<sup>-1</sup> in N<sub>2</sub> at 13.5 mPa measured in the current work on Ag-ETS-10 is more than one order of magnitude higher than the single-component Xe adsorption capacity of 7.5  $10^{-3}$  mmol kg<sup>-1</sup> reported in the study of Monpezat et al. [141] on the same adsorbent. More specifically, the Xe adsorption capacities at the two lowest pressures in the study of Monpezat et al. [141] are lower than the values measured in this work. There is no clear explanation for such a difference as: i) the sample used in the previous study was purchased from the same producer, ii) the BET surface area does not indicate any major difference in microporosity and iii) the silver content reported by the producer was similar. Further research would be necessary to fully compare both samples and measurement techniques to understand the reason for such a difference.

	Ag-ETS-10	Ag-ZSM-5	Nusorb® GXK	HKUST-1	Ni-DOBDC
Adsorption isotherm fit	Langmuir	Langmuir	Henry	Henry	Henry
K [m <sup>3</sup> kg <sup>-1</sup> ]	/	/	0.61	0.24	0.20
K [mol kg <sup>-1</sup> Pa <sup>-1</sup> ]	/	/	2.4 10-4	9.8 10 <sup>-5</sup>	8.0 10 <sup>-5</sup>
b₁ [Pa⁻¹]	1.4 10 <sup>-2</sup>	5.8 10 <sup>-3</sup>			
q <sub>s1</sub> [mol kg <sup>-1</sup> ]	0.63	0.56			
b₂ [Pa⁻¹]		3.0 10-4			
q <sub>s2</sub> [mol kg <sup>-1</sup> ]		1.6			
R <sup>2</sup> [-]	0.9993	0.9999	0.9957	0.9992	0.9999

Table 3-2. Fitted parameters for the Xe adsorption isotherms in N<sub>2</sub> at room temperature. The fitted parameters are for either the Langmuir isotherm (single-site or dual-site depending on the adsorbent) or Henry's isotherm.

Both AgZs have a Xe adsorption capacity in N<sub>2</sub> that is about 30 to 40 times higher than the one on **Nusorb® GXK** at Xe partial pressures lower than 10 Pa (*i.e.* about 100 ppm Xe). The Xe adsorption isotherm in N<sub>2</sub> on Nusorb® GXK is clearly linear over the full range of Xe partial pressures investigated. The Xe Henry's adsorption constant for Nusorb® GXK is 0.61 m<sup>3</sup> kg<sup>-1</sup>, which is in agreement with the value of 0.688 m<sup>3</sup> kg<sup>-1</sup> reported earlier for Xe in N<sub>2</sub> in a smaller Xe partial pressure range [181]. The Xe Henry's adsorption constant in N<sub>2</sub> was reported to be lower, by a factor 1.7, than the one in He, indicating an adsorption competition between Xe and N<sub>2</sub> in the Xe partial pressure range investigated previously [181]. At higher Xe partial pressures, the saturation capacity is being reached for both AgZs and the differences with Nusorb® GXK become smaller.

Both **MOFs** have a lower Xe adsorption capacity in N<sub>2</sub> than Nusorb® GXK by a factor between 3 and 7. The Xe adsorption isotherm in N<sub>2</sub> on both MOFs is clearly linear over the full range of Xe partial pressures investigated. One should remind here that the packing density of both MOFs is lower than for Nusorb® GXK, which further increases the difference in terms of amount of Xe retained per unit volume of adsorbent. The Xe Henry's adsorption constant for both MOFs, 0.24 and

0.20 m<sup>3</sup> kg<sup>-1</sup> for HKUST-1 and Ni-DOBDC, respectively, is similar to the values, 0.28 and 0.19 m<sup>3</sup> kg<sup>-1</sup> for HKUST-1 and Ni-DOBDC, respectively, reported previously for single-component Xe adsorption isotherms [175]. This would suggest that co-adsorption of N<sub>2</sub> does not significantly affect Xe adsorption at RT in the investigated range of partial pressure.

In terms of Xe adsorption capacity per unit of volume of adsorbent, the order is **Ag-ETS-10**  $\geq$  **Ag-ZSM-5** >> **Nusorb® GXK** > **HKUST-1** > **Ni-DOBDC** for Xe partial pressures lower than 1350 Pa (1000 ppm Xe) in N<sub>2</sub> at RT. For the lowest Xe partial pressure measured in this work (*i.e.* 13.5 mPa, corresponding to 100 ppb Xe), the ratio of the measured Xe adsorption capacity per unit volume of adsorbent is 96 for Ag-ETS-10/Nusorb® GXK and 260 for Ag-ETS-10/HKUST-1.

There are many other recent MOFs that have been reported in the literature for Xe/Kr separation, with higher Xe/Kr selectivity and Xe uptake values than HKUST-1 and Ni-DOBDC, as shown in Table S 3-1. However, these are not yet in a commercial stage (at least not available in hundreds of grams of pellets or granules) and, to the best of our knowledge, the highest estimated Xe adsorption capacity at 13.5 mPa, based on reported fits of single-component Xe adsorption isotherms at RT, is 2.6  $10^{-5}$  mol kg<sup>-1</sup> (Figure 3-14) on the "1a-Squarate" [216]. This is still 5.7 times lower than the value measured on the Aq-ETS-10 sample at 13.5 mPa Xe in  $N_2$  and at RT. In terms of adsorption capacity per unit of volume, the ratio Aq-ETS-10/1a-Squarate would most likely increase significantly due to a lower achievable density for pellets or granules of "1a-Squarate" compared to the granules of Ag-ETS-10. Further research in designing MOFs is ongoing to consider the thermodynamic-kinetic trade-off, which is critical at low pressure and has shown to significantly improve the Xe adsorption capacity at low Xe pressure [217]. Considering the existing data in the literature (Figure 3-14), both AgZs in this work are much more efficient for Xe collection at 13.5 mPa and RT than any other material currently reported. It is important to note that the adsorption capacities derived from literature data are based on Xe single-component fits, which might not be fully representative for the low Xe pressure region. In addition, the co-adsorption of  $N_2$  is not considered for the adsorption capacities derived from literature data.

It is known that the Xe adsorption capacity on Ag-ZSM-5 is a combination of two interactions, which have been proposed to be interactions in the zeolite microporous framework and interactions with Ag [143]. The literature reports are diverging on the nature of the Xe-Ag interaction in AgZs [143-146] and it is not yet clear if the interaction occurs with Ag<sup>0</sup> or Ag<sup>+</sup> clusters or with Ag<sup>+</sup> ions. However, it is clear that the interaction with Ag is the most important interaction at low Xe pressure. A similar strong Xe interaction on Ag-ETS-10 was observed through a high Xe adsorption capacity at low Xe partial pressure in single-component Xe adsorption isotherms [138, 141]. This strong Xe-Ag interaction at low Xe pressure is supported by the lower microporosity of both AgZs compared to Nusorb® GXK and both MOFs whilst the Xe adsorption capacity is much higher for AgZs than for the other adsorbents at low Xe pressures. Considering that the Xe adsorption at higher pressure in AgZs is mainly driven by the zeolite framework, the measured Xe adsorption isotherms in N<sub>2</sub> and reported single-

component Xe adsorption isotherms indicate that the ZSM-5 framework has a higher adsorption capacity than the ETS-10 framework, which is in agreement with the single-component Xe adsorption isotherms reported by Yu et al. [204] on ZSM-5 and ETS-10. For the low Xe pressure range, further research on the specific interaction with the Ag-related adsorption sites would be necessary to understand how the presence of N<sub>2</sub> in the gas stream affects the Xe adsorption.



Xe adsorption capacity (mol kg<sup>-1</sup>) at 13.5 mPa

Figure 3-14. Comparison of the Xe adsorption capacity at 13.5 mPa and room temperature. The measured Xe adsorption capacity in N<sub>2</sub> (black symbols) is compared with the 15 most promising Xe adsorption capacities on porous adsorbents (most promising adsorbent from each reference) estimated from reported Henry's adsorption constant or Langmuir / Langmuir-Freundlich parameters of single-component isotherms at RT in the literature (grey symbols) [133, 203, 216, 218-229].

## 3.3.3. Effect of moisture

Moisture uptake and its effect on Xe retention is explored by sending a humidified  $Xe/N_2$  gas stream, containing 250 ppm Xe, until full Xe breakthrough on each adsorbent. Two moisture contents were investigated: 5% and 50% RH. The results are compared with the same breakthrough experiment using a dry gas stream. For experiments with 50% RH, they are performed until both Xe and water have fully broken through the adsorbent.

The resulting Xe adsorption capacity is shown in Figure 3-15. The values for Nusorb® GXK and Ag-ETS-10 were reported in previous work [181]. Up until 50% RH, there is no significant effect of moisture on the Xe adsorption capacity for both MOFs. On the other hand, there is a clear decrease in Xe adsorption capacity in function of moisture content on Ag-ZSM-5. Similarly to the decrease by a factor 31 observed on Ag-ETS-10 in previous work [181], the Xe adsorption capacity on Ag-ZSM-5 decreases by a factor 34 when going from the dry gas mixture to the gas mixture with 50% RH.



Figure 3-15. Evolution of the Xe adsorption capacity as a function of the moisture content in the gas stream. The adsorption capacity is for a mixture of 250 ppm Xe in N<sub>2</sub> at RT. The results for Nusorb® GXK and Ag-ETS-10 are retrieved from a previous study [181].

The Xe breakthrough curves, obtained with the different moisture contents on Ag-ZSM-5, as shown in Figure 3-16, indicate a strong roll-up effect at 50% RH, as Xe is displaced from adsorption sites by water molecules. This is due to the preferential adsorption of water, shown by a later breakthrough than Xe in Figure 3-16. At 50% RH, the temperature clearly increased by almost 5 K showing the strong exothermic adsorption of moisture. As water molecules are preferentially adsorbed, they are competing with Xe downstream on the adsorption sites and are displacing Xe along the water uptake progression in the column. During the Xe roll-up, 90% of the adsorbed Xe is released from the adsorbent. The Xe retention time at 10% breakthrough decreases by a factor 4.4 when going from dry conditions to 50% RH. This is very similar to the previous observation on Aq-ETS-10 where 92% of the adsorbed Xe was released during the roll-up and where a decrease by a factor 2.3 in Xe retention time at 10% was observed [181]. According to these explorative measurements, there is a clear effect of moisture on Xe collection in both AgZs, but the most important aspect for Xe collection is the impact on the retention time, which is more limited than the impact on the Xe adsorption capacity itself.



Figure 3-16. Comparison of the Xe (bottom) and moisture (middle) breakthrough curves, and temperature of the column (top) on Ag-ZSM-5 in dry conditions, and at 5% and 50% RH.

The water uptake at RT, after full water breakthrough at 50% RH in the 250 ppm Xe in  $N_2$  gas stream, was determined for each adsorbent. The value measured on the Ag-ETS-10 is 14 wt.%. To the best of our knowledge, this is the first measurement of the water uptake in these conditions on Aq-ETS-10. An adsorption capacity for water of 4.5 and 7.6 wt.% at 50% RH has been reported in previous work for Na-ETS-10 and Ca-ETS-10, respectively [230]. The water uptake on Aq-ZSM-5 is known to vary with the Si/Al ratio, more specifically with the number of Brønsted acid sites. Values in the range of 1 to 10 wt.%, reported in previous studies [231], are in agreement with the value of 11 wt.% at 50% RH measured in this work. The producer of Nusorb® GXK reports a water uptake at 50% RH of 10 wt.% [172], which is clearly higher than the measured value of 2.8 wt.%. The water uptake on Ni-DOBDC of 48 wt.% is in agreement with reported values in the literature [232]. The measured water uptake on HKUST-1 of 68 wt.% is significantly higher than the values reported in the literature, which are in the range of 30 to 45 wt.% for pellets [232]. It has been reported that adsorption characteristics of HKUST-1 can vary significantly depending on the synthesis procedure [233], which could explain such a difference.

## 3.3.4. Adsorption of dry air

Dry air breakthrough measurements were performed at RT to study the applicability of each adsorbent for collecting Xe directly from dry air and to investigate how the presence of  $O_2$ , Ar,  $CO_2$  and Kr affects the Xe adsorption in the five adsorbents. For this purpose, the adsorption column was filled with 50 cm<sup>3</sup> of adsorbent and the breakthrough of N<sub>2</sub>, O<sub>2</sub>, Ar, Kr, CO<sub>2</sub> and Xe at RT was measured (Figures S 3-6 to S 3-8) after a thermal desorption with He. The O<sub>2</sub> and Ar outlet showed a clear roll-up due to the adsorption competition with N<sub>2</sub> on both

AgZs (Figure S 3-6), whereas such a competition is not observed on Nusorb® GXK and both MOFs (Figures S 3-7 and S 3-8). As expected from the previous Xe adsorption isotherms in N<sub>2</sub>, the AgZs provide a much longer Xe retention, as shown in Figure 3-17a), than the two other types of adsorbents. Nusorb® GXK gives also a longer Xe retention than the two MOFs. Looking at the gas processed to reach 50% of the Xe breakthrough, the values are 1.7, 0.67, 2.2  $10^{-2}$ , 4.8  $10^{-3}$  and 3.7  $10^{-3}$  m<sup>3</sup> for Ag-ETS-10, Ag-ZSM-5, Nusorb® GXK, HKUST-1 and Ni-DOBDC, respectively. The Xe adsorption capacity in air of each adsorbent is very similar to the one measured in N<sub>2</sub>, which indicates that there is no other major competition effect than the one with N<sub>2</sub>.



a) Normalized outlet (-)

Figure 3-17. a) Xe (logarithmic x-axis) and b) Kr (linear x-axis) normalized breakthrough curves in dry air at RT.

In contrast to Xe, the Kr retention at 50% breakthrough is in the same range, *i.e.* 0.5 to 2 dm<sup>3</sup> of air processed, for all five adsorbents (Figure 3-17b). This gives rise to a  $S_{Xe/Kr}$  in air at RT of 1300 for Ag-ETS-10 (Table 3-3), which, to the best of our knowledge, is the highest Xe/Kr selectivity in air at RT ever reported for an adsorbent as shown in Table S 3-1. The difference in behaviour of Xe in AgZs compared to the AC and both MOFs, together with the similar behaviour of Kr in all five adsorbents suggests that Kr does not interact in the same way in AgZs as Xe. The  $S_{Xe/Kr}$  measured in this work is much higher than the value of 246 reported during a breakthrough measurement on Ag-ETS-10 with 1 ppm Xe and 1 ppm Kr in dry air at RT [141]. This is likely explained by the lower Xe adsorption capacity at low Xe partial pressure measured in the previous work and the difference in the composition of the gas mixture. The Xe/Kr selectivity of 470, measured on the Aq-ZSM-5, is higher than the measured Xe/Kr selectivity of 318 reported previously during air breakthrough measurements with 1 ppm Xe and 1 ppm Kr in dry air at RT [141]. Again, the difference in composition of the gas mixture could explain the difference as the adsorption isotherm for Xe is likely not fully linear in this range. In addition, Monpezat et al. [141] calculated, based on singlecomponent isotherms and using IAST, a selectivity of 469, which is in very good agreement with the value measured in this work. Xe/Kr selectivities in air at RT have never been reported for Nusorb® GXK, HKUST-1 and Ni-DOBDC. However, the reported Xe/Kr selectivity at RT from single-component Henry's adsorption constant of 8.5 and 5.8 for HKUST-1 and Ni-DOBDC, respectively [175], are in very good agreement with the measured values of 9.3 and 5.8 (Table 3-3) in the current work. This indicates that these two MOFs show a negligible adsorption competition in the presence of the other gaseous components in air.

Adsorbent	S <sub>Xe/N2</sub>	S <sub>Xe/02</sub>	Xe/O <sub>2</sub> S <sub>Xe/Ar</sub>		S <sub>Xe/Kr</sub>	S <sub>Xe/air</sub>
Ag-ETS-10	3.8 10 <sup>3</sup>	1.2 10 <sup>4</sup>	1.5 10 <sup>4</sup>	86	1.3 10 <sup>3</sup>	4.3 10 <sup>3</sup>
Ag-ZSM-5	1.8 10 <sup>3</sup>	3.2 10 <sup>3</sup>	3.2 10 <sup>3</sup>	19	4.7 10 <sup>2</sup>	1.9 10 <sup>3</sup>
Nusorb GXK	74	75	76	0.94	18	72
HKUST-1	22	22	21	1.5	9.3	22
Ni-DOBDC	13	16	18	0.17	5.8	13

Table 3-3. Xe selectivity over  $N_2$ ,  $O_2$ , Ar,  $CO_2$ , Kr and air, in dry air conditions and at room temperature.



Figure 3-18. Comparison of the selectivity of Xe over Kr in dry air at RT. The measured S<sub>Xe/Kr</sub> (black symbols) is compared to the 15 most promising values on porous adsorbents (most promising adsorbent from each reference) estimated from reported Henry's adsorption constant or Langmuir / Langmuir-Freundlich single-component parameters at RT in the literature (grey symbols) [133, 175, 203, 216-222, 224-229, 234-241].

To the best of our knowledge, the highest Xe/Kr selectivity currently reported is 51, from Langmuir-Freundlich single-component adsorption isotherms at RT with the natural Xe and Kr concentration in air, for the 1a-Squarate MOF [216]. This is 29 times lower than the one measured at RT on Ag-ETS-10. Numerical studies of Lin et al. [242] have shown that a Xe/Kr selectivity of 129 could theoretically be achievable at RT within the currently investigated MOFs. The AgZs clearly outperform any other adsorbent, reported in the literature so far, in selectively retaining Xe compared to Kr at RT (Figure 3-18). It is also important to note that

the selectivities from literature data are derived, based on single-component fits, which might not be fully representative for the low pressure region and are not considering co-adsorption effects. Depending on the material, these effects could affect the Xe and Kr adsorption capacity in dry air at RT and thus yield a different selectivity.



Figure 3-19. Comparison of the selectivity of Xe over  $N_2$  in dry air at RT. The measured  $S_{Xe/N_2}$  (black symbols) is compared to the 15 most promising values on porous adsorbents (most promising adsorbent from each reference) estimated from reported Henry's adsorption constant or Langmuir / Langmuir-Freundlich single-component parameters at RT in the literature (grey symbols) [133, 175, 203, 216-222, 224-229, 234-241].

In addition, the Xe selectivity on the other gaseous components in air at RT on Ag-ETS-10 is 3.8  $10^3$ , 1.2  $10^4$ , 1.5  $10^4$  and 86 for N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>, respectively. To the best of our knowledge, these are the highest values ever reported for the Xe selectivity over the other gaseous components in air at RT as shown with the literature review in Table S 3-1. For the other adsorbents investigated, the order based on S<sub>Xe/air</sub> (Table 3-3) is **Ag-ETS-10 > Ag-ZSM-5 >> Nusorb® GXK > HKUST-1 > Ni-DOBDC**. The highest value previously reported for S<sub>Xe/N2</sub>, using dual-site Langmuir-Freundlich single-component isotherms, at RT is 763 on the ZJU-74a-Pb MOF [224], which is about a factor 5 lower than for Ag-ETS-10 (Figure 3-19).

The silver-exchange on the two zeolites increases the Xe selectivity over N<sub>2</sub>, O<sub>2</sub>, Ar and Kr at RT by one to two orders of magnitude compared to the Xe selectivity reported on the base zeolites in previous work [204]. This again supports the theory of the strong interaction of, specifically, Xe with silver at low Xe partial pressures.

These results at RT clearly show that both AgZs are currently providing the highest Xe adsorption capacity as well as the highest Xe selectivity over N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> and Kr, allowing to obtain the highest amount of Xe with the lowest relative impurity content by unit volume of material. Thus, AgZs are currently unprecedented candidates to collect Xe directly from dry air at RT.

#### 3.3.5. Xe/air separation

Following the adsorption of Xe from air in these adsorbents, the next critical step is to separate the collected Xe from the other air components for the production of Xe or for the measurement of atmospheric radioxenon in IMS systems. To investigate the potential for separating the collected Xe from the other gas components in air, dry air was adsorbed up to half of the Xe retention time at 10% breakthrough followed by a thermal desorption to separate the different components. The thermal desorption profiles together with the Xe, Kr, CO<sub>2</sub>, Ar and O<sub>2</sub> outlet profiles are shown in Figure 3-20. The flow rate used during these thermal desorption experiments (Figure S 3-9) was optimized for each material to obtain the best possible separation.



*Figure 3-20. Desorption curves and temperature profiles after dry air adsorption. The dashed lines marks 5% and 95% of the desorbed Xe peak (i.e. the 90% Xe recovery peak).* 

Both **AgZs** show a very promising Xe separation potential as the desorbed gas in the 90% Xe recovery peak from Ag-ETS-10 and Ag-ZSM-5 contained, gas carrier not included, at least 13 and 1.2 vol.% Xe, respectively, and the major impurity remaining was CO<sub>2</sub> with 70 and 91 vol. %, respectively (Table 3-4). This is also directly observed in Figure 3-20 with a further desorption of CO<sub>2</sub> during the second heating stage, from about 360 to 490 K, dedicated to the Xe recovery. The 90% Xe recovery peak required 5.0 and 2.6 dm<sup>3</sup> of N<sub>2</sub> for Ag-ETS-10 and Ag-ZSM-5, respectively. To separate Xe on these AgZs, a temperature around 486 – 491 K was used.

Table 3-4. Comparison of the recovered Xe amount and purity. The adsorbed amount (nads) is given together with the amount desorbed (ndes) during the 90% Xe recovery peak. The composition of the desorbed gas (Cdes.), carrier gas excluded, is given in vol. % at STP together with the volume of carrier gas (N2) used during the 90% Xe recovery peak.

		Ag-ETS-10	Ag-ZSM-5	Nusorb	HKUST-1	Ni-DOBDC
	O <sub>2</sub>	1.7 10 <sup>-3</sup>	1.4 10-3	2.8 10 <sup>-3</sup>	1.9 10 <sup>-3</sup>	2.5 10 <sup>-3</sup>
	Ar	6.5 10 <sup>-5</sup>	6.5 10 <sup>-5</sup>	1.2 10-4	9.3 10 <sup>-5</sup>	1.0 10-4
n <sub>ads</sub> (mol)	CO <sub>2</sub>	5.0 10 <sup>-4</sup>	4.9 10 <sup>-4</sup>	1.6 10-4	5.7 10 <sup>-5</sup>	3.0 10 <sup>-5</sup>
	Kr	8.7 10 <sup>-8</sup>	5.4 10 <sup>-8</sup>	6.3 10 <sup>-8</sup>	2.5 10 <sup>-8</sup>	3.7 10 <sup>-8</sup>
	Xe	3.0 10 <sup>-6</sup>	3.7 10 <sup>-7</sup>	3.4 10 <sup>-8</sup>	7.5 10 <sup>-9</sup>	6.4 10 <sup>-9</sup>
	O <sub>2</sub>	3.5 10 <sup>-6</sup>	1.4 10 <sup>-5</sup>	2.8 10 <sup>-5</sup>	7.7 10 <sup>-6</sup>	3.8 10 <sup>-5</sup>
	Ar	4.6 10 <sup>-7</sup>	5.8 10 <sup>-7</sup>	2.1 10 <sup>-6</sup>	1.9 10 <sup>-7</sup>	8.0 10-7
n <sub>des</sub> (mol)	CO <sub>2</sub>	1.6 10 <sup>-5</sup>	2.2 10 <sup>-5</sup>	1.0 10 <sup>-5</sup>	4.7 10 <sup>-5</sup>	1.3 10 <sup>-6</sup>
(110)	Kr	8.7 10-11	5.4 10 <sup>-11</sup>	1.1 10 <sup>-9</sup>	5.0 10 <sup>-11</sup>	2.2 10 <sup>-10</sup>
	Xe	2.9 10 <sup>-6</sup>	3.0 10 <sup>-7</sup>	3.3 10 <sup>-8</sup>	6.9 10 <sup>-9</sup>	5.6 10 <sup>-9</sup>
	Xe	13	1.2	8.2 10 <sup>-2</sup>	1.2 10 <sup>-2</sup>	1.4 10 <sup>-2</sup>
~	O <sub>2</sub>	15	5.9	69	14	95
C <sub>des</sub> . (vol %)	Ar	2.0	2.4	5.2	0.34	2.0
	CO <sub>2</sub>	70	91	26	86	3.2
	Kr	3.8 10 <sup>-3</sup>	2.2 10-4	2.6 10 <sup>-3</sup>	9.1 10 <sup>-5</sup>	5.5 10 <sup>-4</sup>
V (dm <sup>3</sup> )	N <sub>2</sub>	5.0	2.6	26	0.81	1.9

During the desorption on **Nusorb® GXK**, the 90% Xe recovery peak provided 820 ppm Xe in the desorbed gas, whereas the major impurity was  $O_2$  with 69 vol.%. The Xe recovery peak required 26 dm<sup>3</sup> of  $N_2$ . The desorption of Xe was achieved at RT on Nusorb® GXK. However, Nusorb® GXK was heated to 467 K to completely desorb  $CO_2$  from the adsorbent, whereas  $CO_2$  was desorbed before Xe in both AgZs. This shows that both AgZs can provide a higher Xe purity whilst requiring only a slightly higher temperature to fully desorb the adsorbent. In addition, a lower volume of  $N_2$  was required on both AgZs compared to Nusorb® GXK.

The thermal desorption of **Ni-DOBDC** allowed to recover 140 ppm Xe during the 90% Xe recovery peak. The main impurity remaining was  $O_2$  with 95 vol.% and 1.9 dm<sup>3</sup> of  $N_2$  were required for the recovery peak. A temperature of 355 K was necessary to fully desorb the adsorbent. This is obviously much lower than for both AgZs and Nusorb® GXK but the Xe purity is also drastically lower. Finally, the separation on **HKUST-1** gave 120 ppm Xe from the desorbed gas in the 90% Xe recovery peak. The main impurity was  $CO_2$  with 86 vol.%. 0.81 dm<sup>3</sup> of  $N_2$  were required for the recovery peak. HKUST-1 could be fully desorbed at 360 K.

It is clear that the choice of one adsorbent over another depends on the application, the required purity and allowed energy consumption. Both AgZs showed the highest Xe purity by at least one order of magnitude but they also demand the highest energy for the separation, whereas both MOFs were the lowest energy demanding for the separation whilst providing lower Xe purities. However, the combination of high Xe adsorption capacity in air, the high Xe selectivity over the other major gaseous components in air and the higher Xe purity during separation on both AgZs are placing them as outstanding candidates for direct Xe production from atmospheric air and for radioxenon collection and separation in IMS systems.

## 3.3.6. Xe/Rn separation

For IMS application, interferences from Rn daughters on the Xe peaks in the radiation detector should be minimized. It is thus necessary to minimize the presence of Rn in the purified Xe gas to be measured. Accordingly, the Xe/Rn separation capability of the adsorbents was investigated with dedicated experiments. After full breakthrough of Xe together with a pulse of 0.35 to 2.8 kBq of <sup>222</sup>Rn, depending on the experiment, the adsorbent was thermally desorbed progressively, with an optimized flow rate (Figure S 3-10), to separate the adsorbed Xe from Rn. During the Xe breakthrough, no <sup>222</sup>Rn breakthrough was observed on all five adsorbents. Resulting thermal desorption profiles for Xe and Rn on each adsorbent are shown in Figure 3-21.



Figure 3-21. Thermal desorption profiles of Xe and Rn.

The maximum temperature used for Nusorb® GXK, HKUST-1 and Ni-DOBDC was well below temperatures for which a degradation of the sample was observed from TGA. Xe and <sup>222</sup>Rn yields from these thermal desorption experiments ranged from 92% to 114% for all adsorbents, which is within the uncertainties of the experimental set-up. It is clear that a high Xe/Rn separation can be achieved on both AgZs with very sharp release profiles. The downfall is that high temperatures are required to reach this separation. On both AqZs, Xe is desorbed at around 470 K whereas Rn is desorbed at around 520 K. A fairly good separation can also be achieved on HKUST-1 at temperatures below 446 K with some overlap between the Xe and Rn peaks. Depending on the decontamination factor that has to be achieved, such an overlap could be acceptable. For Nusorb® GXK and Ni-DOBDC, there is a much larger overlap between the desorbed Xe and Rn peaks, which does not allow to obtain a good Xe/Rn separation. For both MOFs and the AC, the Xe and Rn release peaks are much wider in terms of temperature range, which shows that both Xe and Rn can easily be displaced by the  $N_2$  carrier gas, whereas for both AqZs, the driving force for the desorption of Xe and Rn is the temperature itself.

## 3.4.Conclusions

Two AgZs, one AC and two MOFs were investigated for the collection at RT and the separation of Xe from air. The pellets and granules, acquired in this work, are in agreement with the corresponding powders described in previous work based on SEM/EDX, PXRD and TGA as well as on N<sub>2</sub> adsorption at 77 K and on CO<sub>2</sub> adsorption at 273 K. The AgZs provide a much higher Xe adsorption capacity in N<sub>2</sub> at RT and at low Xe partial pressures. This can go up to a factor 40 compared to the AC and a factor 90 compared to the best of the two MOFs. In comparison with fitted single-component isotherms in the literature, Ag-ETS-10 is providing a Xe adsorption capacity in N<sub>2</sub> at 13.5 mPa and at RT that is at least 5.7 times higher than the highest estimated value from the literature.

The high Xe adsorption capacity at RT on both AgZs is confirmed in dry air, as they provide a Xe retention time at 50% breakthrough that is one to two orders of magnitude higher than the AC, and two to three orders of magnitude higher than the two MOFs. The AgZs have a Xe/Kr selectivity in air at RT of 1300 and 470 for Ag-ETS-10 and Ag-ZSM-5, respectively. This is much higher than the AC and the two MOFs but also at least a factor 29 higher, specifically for Ag-ETS-10, than the highest Xe/Kr selectivity at RT reported in the literature for a synthetized adsorbent. Moreover, both AgZs provide a high Xe selectivity over N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub> at RT, demonstrating their high potential for collecting large amounts of Xe with relatively limited amounts of the other major gaseous components in air.

Following Xe collection from air at RT, Xe can be recovered with limited  $O_2$ , Ar,  $CO_2$  and Kr impurities on both AgZs. This recovery requires temperatures up to 491 K on AgZs. The Xe purity obtained on AgZs is at least one order of magnitude higher than for the AC and at least two orders of magnitude higher than for both MOFs, when excluding the carrier gas. More importantly for IMS application, both AgZs show the highest Xe/Rn separation of the five adsorbents. The temperature required to fully desorb Rn on AgZs was about 520 K.

At RT, the combination of the high Xe adsorption capacity in air, a high Xe selectivity over the main gaseous components in air and the low impurities (from stable air components but also from Rn) in the recovered Xe peak on both AgZs place them as polyvalent adsorbents that could be used as a single filter for the collection at RT and the separation of Xe from air. The only downfalls currently observed are: i) the relatively higher energy consumption for separating Xe during the thermal desorption compared to both MOFs and ii) the strong co-adsorption of moisture, observed in the current explorative measurements, that can decrease the Xe retention time, as shown for 250 ppm Xe in  $N_2$  at RT, by a factor ranging from 2 to 4 for both AgZs, whereas no decrease was observed on the three other adsorbents.

Future work is necessary on the potential Xe separation properties of the investigated adsorbents as well as on the effect of moisture on Xe collection in AgZs. Work on Xe separation would need to look further into the quantification of the purified Xe gas, produced over multiple purification stages, from dry and humid air, through either Temperature Swing Adsorption or Pressure Swing Adsorption as well as the durability of the adsorbent. In addition, other, currently non-commercial, promising adsorbents could be considered for similar future investigations.

# 3.5.Acknowledgments

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## 3.6. Supplementary material



#### 3.6.1. Adsorbent characterisations

Figure S 3-1. a) Selected points for the BET isotherm fit and b) selected points based on the Rouquerol plot for HKUST-1.



Figure S 3-2. a) Selected points for the BET isotherm fit and b) selected points based on the Rouquerol plot for Ni-DOBDC.



Figure S 3-3. a) Selected points for the BET isotherm fit and b) selected points based on the Rouquerol plot for Nusorb® GXK.



Figure S 3-4. a) Selected points for the BET isotherm fit and b) selected points based on the Rouquerol plot for Ag-ZSM-5.



Figure S 3-5. a) Selected points for the BET isotherm fit and b) selected points based on the Rouquerol plot for Ag-ETS-10.

#### 3.6.2. Xenon collection at room temperature

Table S 3-1. Estimated Xe adsorption capacity at 13.5 mPa and Xe selectivities over other components in air for reported adsorbents. The values are based on Henry's adsorption constant, single-site or dual-site Langmuir or Langmuir-Freundlich parameters from single-component isotherms on porous adsorbents. When different functionalized versions of the same initial porous material or when adsorbents in the same family are reported: the most promising adsorbents for  $q_{Xe}$  at 13.5 mPa,  $S_{Xe/N_2}$  and  $S_{Xe/Kr}$  are listed. For each adsorbent, the type of adsorbent and the corresponding temperature for the fitted parameters are given. The values measured on Ag-ETS-10, Ag-ZSM-5, Nusorb® GXK, HKUST-1 and Ni-DOBDC in this work are contained at the end of the table as well for comparison.

Adsorbent	Туре	q‰ at 13.5 mPa (µmol kg⁻¹)	Sxe/N2 (-)	Sxe/0 <sub>2</sub> (-)	Sxe/Ar (-)	Sxe/co <sub>2</sub> (-)	Sхе/кг (-)	т (К)	Ref.
Nusorb GXK	Activated Carbon	8.3 <sup>e</sup>	-	-	-	-	23 <sup>e</sup>	293	[172]
Koestrolith 13X-K2	Zeolite	1.2 <sup>b</sup>	-	91 <sup>b</sup>	100 <sup>b</sup>	-	12 <sup>b</sup>	303	[243]
Kroestrolith 4AK	Zeolite	8.7 10 <sup>-2b</sup>	-	6.4 <sup>b</sup>	6.9 <sup>b</sup>	-	1.8 <sup>b</sup>	303	[243]
KS05	Activated Carbon	5.3ª	-	-	-	-	-	298	[182]
SorboNorit B3	Activated Carbon	0.97 <sup>b</sup>	-	28 <sup>b</sup>	29 <sup>b</sup>	-	7.7 <sup>b</sup>	303	[243]
Co3(HCOO)6	Metal-Organic Framework	1.4ª	-	-	-	-	12ª	298	[244]
MOF-74-Co	Metal-Organic Framework	1.8ª	18ª	-	45ª	-	10ª	292	[245]
NOTT-100	Metal-Organic Framework	1.4ª	21ª	-	23ª	-	6.9ª	292	[245]
PCN-14	Metal-Organic Framework	1.3ª	25ª	-	2.2ª	-	6.5ª	292	[245]
ССЗ	Porous Organic Cage	2.1ª	-	-	-	-	13ª	298	[175]
CROFOUR-1-Ni	Metal-Organic Framework	1.1 <sup>d</sup>	-	-	-	-	10 <sup>d</sup>	298	[246]
FMOF-Cu	Metal-Organic Framework	7.8 10 <sup>-2a</sup>	-	-	-	-	1.3ª	298	[175]
HKUST-1	Metal-Organic Framework	1.6ª	-	-	-	-	8.5ª	298	[175]
IRMOF-1	Metal-Organic Framework	0.23ª	-	-	-	-	3.3ª	292	[175]
MIL-100(Fe)	Metal-Organic Framework	0.17ª	-	-	-	-	5.7ª	303	[247]
MIL-101(Cr)	Metal-Organic Framework	0.31ª	-	-	-	-	5.3ª	303	[247]
Ni-MOF-74	Metal-Organic Framework	1.1ª	-	-	-	-	5.8ª	298	[175]
Noria	Porous organic material	1.2ª	-	-	-	-	9.4ª	298	[248]
SBMOF-1	Metal-Organic Framework	5.2ª	-	-	-	-	16ª	298	[175]
Zinc Tetrazolate	Metal-Organic Framework	0.20ª	-	-	-	-	3.8ª	298	[175]
Co <sup>2+</sup> -CPM-6	Metal-Organic Framework	0.85ª	-	-	-	-	7.8ª	298	[249]
Y-csq-MOF-1	Metal-Organic Framework	1.4ª	-	-	-	-	13ª	298	[250]
ZIF-8	Metal-Organic Framework	7.2 10 <sup>-2</sup> c	-	-	-	-	2.3 <sup>c</sup>	298	[251]
H-SAPO-34	Zeolite	0.27 <sup>b</sup>	-	-	-	-	3.4 <sup>b</sup>	298	[252]

K-SAPO-34	Zaalita	0.22h					a ob	200	[252]
	Zeolite	0.22	-	-	-	-	3.8°	298	[252]
MOF-Cu-H	Framework	5.4ª	57 <sup>a,d</sup>	-	-	-	16ª	298	[238]
PAF-45S	Porous Organic Framework	1.5ª	-	-	-	-	17ª	298	[253]
SCU-11-A	Metal-Organic Framework	0.65ª	-	-	-	-	5.7ª	298	[254]
UiO-66-NH2	Metal-Organic Framework	1.3ª	-	-	-	-	11 <sup>a</sup>	283	[255]
UiO-66- NH2(OMe)2	Metal-Organic Framework	0.60ª	-	-	-	-	14ª	283	[255]
ZIF-11	Metal-Organic Framework	0.69ª	-	-	-	-	10ª	298	[219]
Z11CBF-1000- 2	Metal-Organic Framework derived carbon	11ª	-	-	-	-	20ª	298	[219]
1a-Squarate	Metal-Organic Framework	26 <sup>b</sup>	340 <sup>b, d</sup>	220 <sup>b, c</sup>	740 <sup>b</sup>	-	51 <sup>b</sup>	298	[216]
Ag-ETS-10	Silver- exchanged zeolite	130ª	-	-	-	-	140ª	298	[141]
Ag-ZSM-5	Silver- exchanged zeolite	3300ª	-	-	-	-	300ª	298	[141]
DD3R	Zeolite	0.60 <sup>b</sup>	-	-	-	1.9 <sup>b</sup>	-	298	[256]
HOF-BTB	Hydrogen- bonded frameworks	0.27 <sup>c</sup>	-	-	-	-	4.6 <sup>c</sup>	295	[257]
Zn(ox)0.5(trz)	Metal-Organic Framework	2.1ª	-	-	-	-	13ª	298	[258]
Al-Fum-Me	Metal-Organic Framework	2.4ª	-	-	-	-	10 <sup>a</sup>	298	[259]
CTF-0	Porous Organic Framework	0.27ª	-	-	-	-	5.2ª	298	[260]
CTF-1	Porous Organic Framework	1.1ª	-	-	-	-	4.6ª	298	[260]
IISERP-MOF-2	Metal-Organic Framework	9.2ª	-	-	-	-	19ª	298	[218]
MIL-120-Al	Metal-Organic Framework	3.0ª	48 <sup>a, c</sup>	36 <sup>a, c</sup>	1.1 <sup>a, c</sup>	-	11ª	298	[240]
NKMOF-1-Ni	Metal-Organic Framework	4.5 10 <sup>-2 d</sup>	0.85 <sup>d</sup>	-	0.88 <sup>d</sup>	-	5.1 <sup>d</sup>	298	[261]
PAF-45	Porous Organic Framework	1.4ª	-	-	-	-	8.1ª	298	[260]
UiO-66	Metal-Organic Framework	0.57ª	-	-	-	-	6.8ª	298	[262]
UTSA-74	Metal-Organic Framework	0.75 <sup>b</sup>	-	-	-	-	8.7 <sup>b</sup>	298	[263]
ZIF-69	Metal-Organic Framework	0.80ª	-	-	-	-	8.4ª	298	[264]
Zr-Fum-Me	Metal-Organic Framework	2.4ª	-	-	-	-	15ª	298	[262]
Ag-MOF-303	Metal-Organic Framework	1.8 <sup>c</sup>	-	-	-	-	10 <sup>c</sup>	298	[265]
AI-CDC	Metal-Organic Framework	4.4 <sup>b</sup>	250 <sup>b, c</sup>	15 <sup>b, c</sup>	63 <sup>b, c</sup>	-	10 <sup>b</sup>	298	[237]
ATFG	Covalent Organic Framework	0.59ª	-	-	-	-	6.1ª	298	[266]
Ca-SINAP-1A	Metal-Organic Framework	3.1ª	-	-	43ª	-	10ª	293	[267]
Ce-SINAP-1	Metal-Organic Framework	0.91ª	-	-	30ª	-	8.2ª	293	[268]
ECUT-51	Metal-Organic Framework	1.1ª	-	-	-	-	8.7ª	298	[269]
ECUT-60	Metal-Organic Framework	3.0ª	-	-	-	-	12ª	298	[270]

HCP-Ni	Hyper- crosslinked polymer	1.0ª	-	-	-	-	8.9ª	298	[271]
Ni@C-800	Metal-Organic Framework derived carbon	3.1 <sup>b</sup>	-	-	-	-	15 <sup>b</sup>	298	[235]
NiCo@C-700	Metal-Organic Framework derived carbon	2.6 <sup>b</sup>	140 <sup>b</sup>	170 <sup>b</sup>	170 <sup>b</sup>	-	25⁵	298	[235]
TFP-TAPA	Covalent Organic Framework	0.91ª	-	-	-	-	10ª	298	[272]
TFP-TAPA-Bu	Covalent Organic Framework	1.8ª	-	-	-	-	10ª	298	[272]
ТрВD	Covalent Organic Framework	0.18ª	-	-	-	-	6.7ª	298	[266]
ТрРа	Covalent Organic Framework	0.37ª	-	-	-	-	6.2ª	298	[266]
Ag-SSZ-13	Silver- exchanged zeolite	19ª	120ª	-	-	-	50ª	298	[203]
CALF-20	Metal-Organic Framework	2.9ª	53 <sup>a, c</sup>	-	-	-	13ª	298	[239]
CopzNi	Metal-Organic Framework	10 <sup>d</sup>	330 <sup>d</sup>	190 <sup>d</sup>	210 <sup>d</sup>	-	25 <sup>d</sup>	298	[220]
ETS-10	Zeolite	1.6ª	-	-	-	-	13ª	298	[204]
FJU-55	Metal-Organic Framework	1.5ª	-	-	-	-	11ª	298	[234]
GBC-900	Granular Carbon	11ª	210 <sup>a, c</sup>	180 <sup>a, c</sup>	36 <sup>a, c</sup>	-	24ª	298	[133]
HOF-40	Hydrogen- bonded frameworks	0.71ª	230 <sup>a, c</sup>	36 <sup>a, c</sup>	-	-	11ª	298	[236]
HOF-ZJU-201a	Hydrogen- bonded frameworks	10 <sup>b</sup>	110 <sup>b</sup>	160 <sup>b</sup>	130 <sup>b</sup>	-	22 <sup>b</sup>	298	[222]
HOF-ZJU-202a	Hydrogen- bonded frameworks	9.4 <sup>b</sup>	130 <sup>b</sup>	130 <sup>b</sup>	120 <sup>b</sup>	-	18 <sup>b</sup>	298	[222]
JXNU-13-F	Metal-Organic Framework	0.62ª	-	-	-	-	5.5ª	298	[273]
LPC-MOF	Metal-Organic Framework	1.4ª	-	-	-	-	13ª	298	[274]
Ni(4- DPDS)2CrO4	Metal-Organic Framework	7.2ª	111ª	-	-	-	22ª	298	[227]
Ni(4- DPDS)2WO4	Metal-Organic Framework	5.3ª	240ª	-	-	-	26ª	298	[227]
Ni(AIN)2	Metal-Organic Framework	15ª	-	-	-	-	23ª	298	[221]
NU-200	Metal-Organic Framework	5.9°	-	4100 <sup>c</sup>	-	-	26 <sup>c</sup>	298	[229]
AG-3	Activated	2.9ª	-	-	97ª	-	16ª	293	[226]
VSK-5	Activated	7.4ª	-	-	110ª	-	16ª	293	[226]
SKT-3	Activated Carbon	6.9ª	-	-	100ª	-	17ª	293	[226]
NWC 12x40	Activated Carbon	7.3ª	-	-	120ª	-	17ª	293	[226]
SMOF-AsFSIX- 1a	Metal-Organic Framework	1.9 <sup>b</sup>	-	-	-	-	5.1 <sup>b</sup>	298	[275]
SMOF-PFSIX- 1a	Metal-Organic Framework	1.9 <sup>b</sup>	-	-	-	-	4.1 <sup>b</sup>	298	[275]
SSZ-13	Zeolite	0.81ª	-	-	-	-	10ª	298	[204]

ZUL-C2	Metal-Organic Framework	5.4 <sup>d</sup>	-	-	-	-	14 <sup>d</sup>	298	[276]
ZSM-5	Zeolite	2.3ª	-	-	-	-	15ª	298	[204]
ZJU-74a-Pb	Metal-Organic Framework	9.9 <sup>d</sup>	760 <sup>d</sup>	240 <sup>d</sup>	200 <sup>d</sup>	-	46 <sup>d</sup>	296	[224]
ZIF-7-lm	Metal-Organic Framework	1.7ª	80ª	-	-	-	-	298	[217]
AI-SBD	Metal-Organic Framework	1.6ª	-	-	-	-	13ª	298	[277]
Na-SDB	Metal-Organic Framework	1.7ª	-	-	-	-	10 <sup>a</sup>	298	[277]
CAU-10-H-CH3- 0.21-0.79	Metal-Organic Framework	2.0ª	-	-	-	-	15ª	298	[278]
СК-700-1	Activated Carbon	2.8ª	-	-	-	-	16 <sup>a</sup>	298	[279]
CMP-PY-TBTP	Conjugated Micropore Polymer	0.89ª	-	-	-	-	9.3ª	298	[280]
CoNi-DAB	Metal-Organic Framework	5.8 10 <sup>-3 d</sup>	-	-	-	-	17 <sup>d</sup>	298	[241]
MOF-11	Metal-Organic Framework	9.4ª	-	-	-	-	16ª	298	[223]
NU-1107-Ag(I)	Metal-Organic Framework	1.4ª	-	-	-	-	9.2ª	298	[281]
C-PVDC-600	Carbon Molecular Sieve	9.2ª	-	-	-	-	14ª	298	[225]
C-PVDC-700	Carbon Molecular Sieve	7.7ª	150 <sup>a, b</sup>	150 <sup>a, b</sup>	140 <sup>a, b</sup>	-	15ª	298	[225]
NU-1801	Metal-Organic Framework	0.82ª	-	-	-	-	7.2ª	298	[282]
QS-PAF-3	Porous Organic Polymer	0.94ª	-	-	-	-	11ª	298	[283]
TIFSIX-Cu-TPA	Metal-Organic Framework	0.58 <sup>b</sup>	-	-	-	-	5.4ª	298	[284]
Ni-DOBDC	Metal-Organic Framework	1.0 <sup>e</sup>	13 <sup>e</sup>	16 <sup>e</sup>	18 <sup>e</sup>	0.17 <sup>e</sup>	5.8 <sup>e</sup>	296	This work
HKUST-1	Metal-Organic Framework	2.1 <sup>e</sup>	22 <sup>e</sup>	22 <sup>e</sup>	21 <sup>e</sup>	1.5 <sup>e</sup>	9.3 <sup>e</sup>	296	This work
Nusorb GXK	Activated Carbon	3.3 <sup>e</sup>	74 <sup>e</sup>	75 <sup>e</sup>	76 <sup>e</sup>	0.94 <sup>e</sup>	18 <sup>e</sup>	296	This work
Ag-ZSM-5	Silver- exchanged zeolite	130 <sup>e</sup>	1800 <sup>e</sup>	3200 <sup>e</sup>	3200 <sup>e</sup>	19 <sup>e</sup>	470 <sup>e</sup>	296	This work
Ag-ETS-10	Silver- exchanged zeolite	150 <sup>e</sup>	3800 <sup>e</sup>	12000 <sup>e</sup>	15000 <sup>e</sup>	86 <sup>e</sup>	1300 <sup>e</sup>	296	This work

2 Zeolite
 2 Zeolite



Figure S 3-6. Air breakthrough curves on Ag-ETS-10 (left) and Ag-ZSM-5 (right). The breakthrough curves were obtained with 50 cm<sup>3</sup> of adsorbent at 294 K. For Ag-ETS-10, the flow rate was 30 cm<sup>3</sup> min<sup>-1</sup> until 1.25 10<sup>-3</sup> m<sup>3</sup>, then
200 cm<sup>3</sup> min<sup>-1</sup> until 8.19 10<sup>-2</sup> m<sup>3</sup> and 2000 cm<sup>3</sup> min<sup>-1</sup> until full Xe breakthrough. For Ag-ZSM-5, the flow rate was 30 cm<sup>3</sup> min<sup>-1</sup> until 2.97 10<sup>-3</sup> m<sup>3</sup> and then 400 cm<sup>3</sup> min<sup>-1</sup> until full Xe breakthrough.



Figure S 3-7. Air breakthrough curves on Nusorb® GXK. The breakthrough curves were obtained with 50 cm<sup>3</sup> of Nusorb® GXK at 294 K. The flow rate was 30 cm<sup>3</sup> min<sup>-1</sup> until 4.87 10<sup>-3</sup> m<sup>3</sup>, then 200 cm<sup>3</sup> min<sup>-1</sup> until 1.04 10<sup>-2</sup> m<sup>3</sup> and finally 400 cm<sup>3</sup> min<sup>-1</sup> until full Xe breakthrough.



Figure S 3-8. Air breakthrough curves on HKUST-1 (left) and Ni-DOBDC (right). The breakthrough curves were obtained with 50 cm<sup>3</sup> of adsorbent at 294 K. For HKUST-1, the flow rate was 30 cm<sup>3</sup> min<sup>-1</sup> until full Xe breakthrough. For Ni-DOBDC, the flow rate was 30 cm<sup>3</sup> min<sup>-1</sup> until 1.39 10<sup>-3</sup> m<sup>3</sup> and then 100 cm<sup>3</sup> min<sup>-1</sup> until full Xe breakthrough.


#### 3.6.3. Xe separation

Figure S 3-9. Temperature and flow rate profiles during the thermal separation of Xe from  $O_2$ , Ar,  $CO_2$  and Kr.



*Figure S 3-10. Temperature and flow rate profiles during the thermal separation of Xe from Rn.* 

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# **Chapter 4**

# Improving Ar-37 monitoring systems

	Research objective	Main evaluation metrics
2	Investigate the collection and separation of Ar using a single adsorbent operating at or close to ambient conditions for on-site inspections	Ar yield and relative enrichment





# 4. Improving <sup>37</sup>Ar monitoring systems

In this chapter covering the second research objective, the applicability of Ag-ETS-10 as a single filter medium for the collection and separation of Ar from subsoil gas and atmospheric air is investigated. The aim is to determine if Ag-ETS-10 can be used as a single filter medium at or close to Room Temperature (RT) in Ar sampling systems for On-Site Inspection (OSI) for a less energy demanding Ar separation process. The separation performance of Ag-ETS-10 for this application is evaluated through the Ar yield and enrichment.

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Gueibe C., Rutten, J., Camps, J., Riedmann, R., Moyaux, D., Schroeyers, W., Gryglewicz, G., Kuznicki, S., & Schreurs, S. (Submitted) Adsorptive Ar separation from air on self-bound Ag-ETS-10 granules. *Microporous and Mesoporous Materials*.

#### Abstract

Efficient Ar separation, from air and subsoil gas, on a single adsorbent, operating at or near RT, could provide an energy-efficient alternative for the detection of <sup>37</sup>Ar from underground nuclear weapon tests. Ag-ETS-10, a silver-exchanged titanosilicate, was reported to be very efficient to separate  $O_2$  from air due to its high  $N_2/O_2$  and  $Ar/O_2$  selectivities at RT. The Ar separation from air on Aq-ETS-10 has never been investigated. In this work, self-bound Ag-ETS-10 was investigated for this purpose. It has a higher microporosity by 20 to 30%, depending on the probing molecule, than silica-bound Ag-ETS-10. This increase is translated in 25% higher Ar in He adsorption capacities, yielding a heat of adsorption of 19.8 kJ mol<sup>-1</sup>. Air breakthrough measurements at RT demonstrate that an almost  $N_2$ -free mixture enriched in Ar, with 6.4% Ar and 93.3%  $O_2$ , can be recovered with a 10% Ar yield. Further Ar enrichment of the resulting  $Ar/O_2$  mixture is possible but becomes more difficult in Ar-rich mixtures. The Ar separation from air and subsoil gas is influenced by both the  $O_2$  and Ar concentration, whereas it is not influenced by a relative humidity of 50% in the inlet gas stream. A vacuum pressure swing adsorption-based separation was investigated and yielded a maximum Ar concentration, in an almost N<sub>2</sub>-free mixture, of 5.6% for a 10% Ar yield. Lastly, the Ar concentration can be increased to 8.2%, together with 89.7% O<sub>2</sub>, by lowering the temperature during the air adsorption from RT to 248 K.

#### 4.1.Introduction

By nature, Ar is the third most abundant gas in the Earth's atmosphere with a concentration of 0.93% by volume [47]. Natural Ar in the atmosphere is mainly composed of three stable isotopes: <sup>40</sup>Ar, <sup>38</sup>Ar and <sup>36</sup>Ar. The atmosphere contains also naturally traces of the following radioactive Ar isotopes: <sup>39</sup>Ar (T<sub>1/2</sub>: 268 years), <sup>37</sup>Ar ( $T_{1/2}$ : 35 days) and <sup>42</sup>Ar ( $T_{1/2}$ : 32.9 years). The production route of <sup>37</sup>Ar in the atmosphere is neutron activation through the  $^{40}$ Ar(n,4n)<sup>37</sup>Ar and  $^{36}$ Ar(n,y)<sup>37</sup>Ar reactions [110]. In the lithosphere,  $^{37}$ Ar is mainly produced by cosmogenic neutron activation of Ca through the  ${}^{40}Ca(n,\alpha){}^{37}Ar$  reaction [107].

As discussed in Section 1.3, the neutrons emitted by an underground nuclear explosion (UNE) are also producing <sup>37</sup>Ar, by neutron activation of <sup>40</sup>Ca in the surrounding soil, with a yield that can result in detectable levels of <sup>37</sup>Ar in subsurface soil gas even in geologic structures with a low Ca content [37]. Compared to other radioactive inert gases that are likely to escape from an UNE cavity, such as radioxenon, <sup>37</sup>Ar has a longer half-life and remains thus longer detectable. Following this demonstration, <sup>37</sup>Ar sampling and detection is considered as an important technique for OSI for the verification of the Comprehensive Nuclear-Test-Ban Treaty (CTBT) [285]. Research is currently ongoing on the following three themes for the use of <sup>37</sup>Ar as an OSI measurement technique for CTBT verification: i) determine the <sup>37</sup>Ar emanation fraction in different geological materials and understand the transport of <sup>37</sup>Ar towards the soil surface, ii) understand the <sup>37</sup>Ar background in the atmosphere and in soil gas, and iii) develop field deployable <sup>37</sup>Ar sampling and measuring systems.

Concerning the first research theme, it was shown that the <sup>37</sup>Ar emanation fraction from geological materials has a significant variability [286]. Several groups have investigated the detectability of <sup>37</sup>Ar produced by an UNE by modelling the <sup>37</sup>Ar transport towards the soil surface in combination with experiments [287-292]. The scientific community addressing the second theme is studying the <sup>37</sup>Ar background, through measurements and simulations, as this is crucial to discriminate a potentially UNE-related <sup>37</sup>Ar detection from the background [108, 109, 292-298]. Measured atmospheric <sup>37</sup>Ar concentrations are ranging from 0.5 to 3.8 mBq m<sup>-3</sup> [113, 299], whereas measured <sup>37</sup>Ar concentrations in soil air are up to about 100 mBq m<sup>-3</sup> at 1.5 – 2.5 m depth [107, 300]. Riedmann and Purtschert [107] calculated that the concentration could even be 10 times higher in soils at high altitude.

Finally for the last research theme, a few research groups have studied the separation and measurement of <sup>37</sup>Ar from atmospheric air and soil gas. Initially, <sup>37</sup>Ar measurements were done, using low-background gas proportional counters, in underground laboratories, but advances in active and passive shielding have allowed measurements in surface level laboratories [301]. Such <sup>37</sup>Ar measurements are very sensitive to ppm levels of other gaseous components in air (*e.g.* N<sub>2</sub> and O<sub>2</sub>) and require high-purity Ar [302].

Specifically for OSI, deployable sampling and measuring systems have been developed [105, 303] as briefly discussed in Section 1.3.4. The most recent one was developed by Pacific Northwest National Laboratory (PNNL, USA) using a Dual Reflux Pressure Swing Adsorption (DR-PSA) process on a Li-exchanged faujasite zeolite (Li-LSX) to remove  $N_2$  from air samples of about 0.4 m<sup>3</sup> [105]. The DR-PSA is followed by a cobalt oxide-based oxygen removal system operated at 973 K and regenerated at 1223 K under vacuum, and an electrochemical pump tube operated at 873 K to disassociate oxygen and conduct ionic oxygen out of the tube [105]. In this system, the remaining trace contaminants are removed by a Li-LSX purification trap operating between 173 and 153 K and the purified Ar, about

2 dm<sup>3</sup> in volume, is then collected on a large surface area trap held at 103 K [105]. A 50% Ar yield is thus obtained in such a system. However, as proposed by Aldener et al. [101], Ar separation and <sup>37</sup>Ar measurement could also be performed on the exhaust sample of the sampling trap used in a field-deployable radioxenon sampling and measuring system for OSI, which can handle gas samples up to 12 m<sup>3</sup>. The exhaust sample at this stage is mainly depleted in CO<sub>2</sub>, H<sub>2</sub>O, Xe and Rn [101]. Meaning that for retrieving 2 dm<sup>3</sup> of pure Ar (*i.e.* corresponding to the volume recovered in the system of PNNL), a lower Ar yield, as low as about 2%, could be acceptable when working on the exhaust of a radioxenon sampling and measurement system collecting up to 12 m<sup>3</sup> of air. Accordingly, a 2% Ar yield is considered as the lower limit in this work for evaluating the performance of an adsorbent for Ar separation.

Field-deployable systems, for the detection of <sup>37</sup>Ar during an OSI, could benefit from less energy demanding processes for the separation of Ar from atmospheric air and subsoil gas. The separation of  $O_2$  from  $N_2$  in air by  $O_2$  or  $N_2$  selective noncryogenic adsorption on various porous materials has been investigated in many papers which have been exhaustively reviewed over the years [304-308]. As discussed in Section 1.5, the separation of Ar and  $O_2$  by selective adsorption of one component over the other at RT has been investigated by different groups on a variety of adsorbents. In particular for zeolites, it was demonstrated that silverexchanging zeolites can significantly improve their affinity for  $N_2$  over Ar and  $O_2$ , and also their affinity for Ar over O<sub>2</sub> [161]. It was shown that Ag-ETS-10 combined both a particularly high  $N_2/O_2$  and  $Ar/O_2$  selectivity compared to other porous adsorbents [305]. These properties have been the basis for studies on the production of high purity  $O_2$  from atmospheric air in Ag-ETS-10 [156, 162-164, 309, 310]. There is currently no experimental investigation on the production of high purity Ar, from both atmospheric air and subsoil gas, using Ag-ETS-10 as a single separation medium operating at RT.

In this work, the use of Aq-ETS-10 for Ar separation from air is investigated. Ag-ETS-10 was selected due to its commercial availability and particularly high  $N_2/O_2$  and  $Ar/O_2$  selectivities amongst values of adsorbents reported in the literature. The textural properties of the acquired self-bound Ag-ETS-10 granules are compared to literature data. Then, the Ar adsorption properties of the Ag-ETS-10 sample are compared to published data through Ar adsorption isotherms, the Ar isosteric heat of adsorption, air breakthrough curves as well as 5% and 50% Ar in  $O_2$  breakthrough curves. Considering that various gas compositions can be encountered in OSI, the effect of varying moisture levels, and oxygen and argon concentrations on the Ar separation properties, as observed in breakthrough curves, is determined. Using these results, a single-bed Vacuum Pressure Swing Adsorption (VPSA) system is used to assess, for the first time, the potential of Ag-ETS-10 in such a configuration for Ar separation directly from dry air for OSI purposes. In addition, the potential for further enhancing the Ar separation capability from atmospheric air on Aq-ETS-10 at lower temperatures, down to 213 K, is investigated for the first time as well.

# 4.2. Materials and methods

A self-bound Ag-ETS-10 sample was used in this study. Its porous structure parameters were determined by  $N_2$  adsorption-desorption at 77 K and by  $CO_2$  adsorption at 273 K (Section 4.2.2). Ar adsorption and separation performances on this sample were investigated by breakthrough measurement in various conditions (Section 4.2.3). A VPSA-based Ar separation on self-bound Ag-ETS-10 was investigated to assess its potential for OSI and is described in Section 4.2.4. The analysis of the results obtained with the VPSA system is described in Section 4.2.5.

The materials and methods that are common to multiple chapters (indicated in the yellow box in Figure 4-1) are described in full details in Chapter 2, whereas materials and methods specific to the current chapter are detailed in the following sections.



Figure 4-1. Materials and methods used in Chapter 4.

Two stainless steel columns were used throughout this research. The first column, called C4, was filled with, depending on the experiments, 99.5 or 225.3 g of Ag-ETS-10. This column was used for measuring the Ar adsorption isotherm as well as the effect of temperature on the Ar separation. The second stainless steel column, called C5, was filled with 352.0 g of Ag-ETS-10.

# 4.2.1. Adsorbent

The self-bound Ag-ETS-10 used in this work is described in Section 2.1.

# 4.2.2. Characterization of the textural properties

The collection of  $N_2$  sorption isotherms at 77 K and  $\text{CO}_2$  adsorption isotherms at 273 K is described in Section 2.4.3.

# 4.2.3. Breakthrough measurements

Ar adsorption and Ar separation were evaluated using breakthrough experiments as described in Section 2.2.

#### 4.2.4. Vacuum pressure swing adsorption system

A VPSA system, based on the Aq-ETS-10 adsorbent in a single adsorption column (C5), was used to investigate the collection and separation of Ar from air as shown in Figure 4-2. Similar to the breakthrough measurements described in Section 2.2, the inlet mixture was obtained either by mixing high purity gases using a gas mixing unit or directly from the gas composition of the gas cylinder, feeding the appropriate mass flow controller. A differential pressure sensor (KELLER, PD-23 series) monitors the differential pressure on the adsorption column. The inlet pressure on the column was set at 300 to 340 kPa depending on the experiments. Gas, collected in the adsorption column, can be extracted in an expansion tank, via a metering valve (MV) (FITOK, MS Series) to limit the outlet flow rate and a mass flow-meter (Voëqtlin, red-y smart series), by first pulling a vacuum of about 7 kPa on the expansion tank, with a diaphragm vacuum pump (VACUUBRAND, MZ 2 NT). The outlet flow rate was limited to 200 cm<sup>3</sup> min<sup>-1</sup>. In between adsorption runs on the column, the adsorbent is regenerated by flushing with He and then pulling the above mentioned vacuum. The separation exhaust gas can be recovered in one of the two 8 L expansion tanks (elbi, HM8), with an EPDM rubber membrane separating each chamber, coupled with a pressure sensor (Druk, UNIK 5000) on the collected gas side. Collected separation exhaust gases can be processed again on the adsorption column using both expansion tanks and pressurized air to apply a pressure of about 340 kPa on the membrane of the expansion tank to displace the collected gas. A needle valve, NV, is also used to control the flow rate between the expansion tanks and the Mass Spectrometer (MS) when measuring the content of an expansion tank.



*Figure 4-2. Schematical representation of the vacuum pressure swing adsorption system.* 

The system was used to investigate the Ar separation from dry air. For these experiments, the column was regenerated, by a He flush followed by vacuum, and was then loaded with a certain volume of air as fed by one of the mass flow controllers. The content was then pulled towards an expansion tank in under-

pressure. The exhaust gas was continuously monitored by the MS. Different loadings, resulting in different pressure differentials along the column, were investigated using this method.

The solenoid valves, V1-V16, (Burkert, Type 6013) are operated in a LabVIEW application, which also records continuously the following parameters: temperature on the surface of the column, pressure differential on the column, vacuum pressure at the entry of the vacuum pump, dewpoint at the outlet of the system (not shown in the figure), flow rates of the three mass flow controllers, flow rate measured by the mass flow meter at the outlet of the column and pressures before both expansion tanks. The partial pressures measured by the MS were calibrated regularly with the necessary high purity gases.

#### 4.2.5. Ar yield and relative Ar enrichment

In this work, the Ar yield [-] is expressed by Equation 4-1, where  $n_{Ar,in}$  [mol] is the amount of Ar fed to the adsorption column and  $\dot{n}_{Ar,out}$  [mol s<sup>-1</sup>] is the outlet Ar molar flow rate.  $n_{Ar,in}$  is obtained from the inlet Ar concentration as fed by the mass flow controllers, and either from the volume loaded on the adsorption column itself or from the volume filled in the expansion tank, when the gas was first collected in an expansion tank. During the exhaust collection between  $t_1$  [s] and  $t_2$  [s],  $\dot{n}_{Ar,out}$  [mol s<sup>-1</sup>] is obtained from the flow rate exiting the column, measured by the mass flow meter, and the Ar concentration measured by the MS with the necessary calibrations. As multiple time windows can provide a similar yield, all combinations are calculated. When concentrations are described for a certain yield, they correspond to the maximum concentration in a range of  $\pm 1\%$ around the reported yield (*e.g.* 10%). For measurements with the smaller column, C1, the range is extended to  $\pm 2.5\%$  due to the lower amount of data points.

$$Yield = \frac{\int_{t_1}^{t_2} \dot{n}_{Ar,out} dt}{n_{Ar,in}}$$
 Equation 4-1

The relative Ar enrichment [%] (Equation 4-2) is defined as the difference between the Ar concentration in the exhaust gas ( $C_{Ar,out}$  [mol m<sup>-3</sup>]) and the one in the inlet gas ( $C_{Ar,in}$  [mol m<sup>-3</sup>]), divided by the Ar concentration in the inlet gas.

Relative Ar enrichment = 
$$\frac{C_{Ar,out} - C_{Ar,in}}{C_{Ar,in}} \cdot 100\%$$
 Equation 4-2

#### 4.3.Results and discussion

#### 4.3.1. Textural properties

In Figure 4-3a) and b), the N<sub>2</sub> adsorption-desorption isotherm at 77 K and the  $CO_2$  adsorption isotherm at 273 K, respectively, on the self-bound Ag-ETS-10 are compared to the ones on a silica-bound sample published previously [311]. The microporous properties (Table 4-1) indicate an increase in the BET surface area

 $(S_{BET})$ , using the Rouquerol BET consistency criteria (Figure S 4-1), and micropore volume ( $V_{DR}$ ), as determined from N<sub>2</sub> adsorption at 77 K, by about 30% compared to the sample with silica binder investigated previously. Similarly, an increase of about 20% is observed for the micropore surface (S<sub>0</sub>) and volume ( $V_{DR,CO_2}$ ), as determined from the CO<sub>2</sub> adsorption at 273 K. The self-bound Ag-ETS-10 has a 15% higher packing density compared to the silica-bound Ag-ETS-10 previously investigated [311], which can explain part of the increases observed. The remainder of the increase can be attributed to a better accessibility of micropores in the self-bound material compared to the silica-bound one, as the non-porous silica binder can block the access to micropores.



Figure 4-3. a)  $N_2$  adsorption and desorption isotherm at 77 K and b)  $CO_2$ adsorption isotherm at 273 K for self-bound Ag-ETS-10. The filled symbols are for the adsorption, whereas the non-filled symbols are for the desorption. The isotherms are compared to a silica-bound sample investigated previously [311].

Table 4-1.	Calculated sur	face area al	nd pore volume	of self-bo	und Ag-ET	S-10.
The values	are compared	to the silica	-bound sample	reported p	previously	[311].

		Silica-bound Ag-ETS-10 [311]	Self-bound Ag-ETS-10
	S <sub>BET</sub> (m² g <sup>-1</sup> )ª	206 [5 10 <sup>-5</sup> - 6 10 <sup>-2</sup> ]	263 [2.2 10 <sup>-5</sup> - 6 10 <sup>-2</sup> ]
$N_2$ at 77 K	V <sub>DR</sub> (cm³ g <sup>-1</sup> ) <sup>b</sup>	0.08	0.10
	V <sub>T</sub> (cm³ g⁻¹)°	0.12	0.12
CO at 272 K	S₀ (m² g⁻¹) <sup>b</sup>	205	246
CU <sub>2</sub> at 273 K	V <sub>DR,CO2</sub> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	0.08	0.10

<sup>a</sup> Calculated through the BET method in the relative pressure range indicated in brackets.

<sup>b</sup> Calculated through the Dubinin-Radushkevitch equation.

<sup>c</sup> Total pore volume determined at  $p/p_0 = 0.96$ 

As can be seen from Figure 4-3a), the total micro and mesopore volume determined from the  $N_2$  adsorption at  $p/p_0 = 0.96$  is very similar and indicates

that the mesopore volume is reduced in self-bound Ag-ETS-10. This can be explained by a decrease in the intra-crystalline mesopore volume in self-bound Ag-ETS-10 as no binder is used.

The observed increases in the microporosity development in self-bound Aq-ETS-10 are also translated to a higher adsorption capacity for  $N_2$ ,  $CO_2$ , Kr and Xe by 31, 28, 36 and 11%, respectively, from dry atmospheric air (Figure S 4-2) compared to the silica-bound Aq-ETS-10 sample investigated previously [311]. For  $N_2$  and  $CO_2$ , the results are clearly in line with the measurements at 77 K for  $N_2$  and 273 K for CO<sub>2</sub>. As demonstrated in Chapter 2, the typical uncertainties on adsorption capacities measured by the breakthrough measurement set-up are about 10%. The increase for Kr is similar to the one for  $N_2$  and  $CO_2$ . Interestingly, the increase in adsorption capacity for Xe is more limited and could, next to the uncertainties, be due to different preferential adsorption sites, as it is known that silver in Aq-ETS-10 is a particularly strong adsorption site for Xe at low partial pressures [138, 311]. Such a strong interaction in Ag-ETS-10 was also observed for Rn [201, 312] but was not observed for Kr as demonstrated by the very high Xe/Kr selectivity on silica-bound Aq-ETS-10 in previous research [311]. It should be noted that the binding process (with or without silica binder) is done before the Ag-exchange. It is clear that the increase for Xe is related to the 15% increase in packing density and thus in available adsorption sites. The adsorption of Ar and  $O_2$  are discussed more in detail for the Ar separation from air in the following sections.

# 4.3.2. Ar adsorption and separation at room temperature

Ar adsorption isotherms in He and  $N_2$  at 294 and 248 K on self-bound Ag-ETS-10 are shown in Figure 4-4. The fitted values for the temperature dependent Langmuir isotherm based on the Ar in He adsorption isotherms are reported in the figure.

The obtained heat of adsorption, 19.8 kJ mol<sup>-1</sup>, is very similar to the values, in the range of 15.2 to 21.3 kJ mol<sup>-1</sup>, reported on a silver-exchanged hierarchical ETS-10 [313]. Similar values are also observed on carbon molecular sieves, unexchanged zeolites and other silver-exchanged zeolites (AqZs) [161, 314]. The Henry's constant at 303 K, based on the fitted temperature-dependent Langmuir isotherm, is 7.3  $10^{-5}$  cm<sup>3</sup> g<sup>-1</sup> Pa<sup>-1</sup>, which is in the upper range of values reported by Sebastian and Jasra [161] for other AqZs. The Ar in He adsorption isotherm at 294 K is higher by a factor 1.5 than the one reported previously at 303 K by Hejazi et al. [164], which is shown in Figure 4-4 as comparison. The calculated adsorption isotherm at 303 K, based on the temperature dependent Langmuir isotherm fit, yields adsorption capacities higher by a factor of 1.25 compared to the values reported by Hejazi et al. [164]. This difference is due to a difference in sample as Hejazi et al. [164] used a silica-bound sample, whereas a self-bound sample was used in the current work. As discussed for the microporous and mesopore properties, an increase by 15% was expected based on the difference in packing density of self-bound and silica-bound Aq-ETS-10, whereas the remaining difference can be due to a combination of pore accessibility and measurement uncertainties.



*Figure 4-4. Ar adsorption isotherms on self-bound Ag-ETS-10. In comparison, a single component Ar adsorption isotherm measured at 303 K in the literature is plotted as well [164].* 

Looking at the linear range of the Ar in He adsorption isotherms (*i.e.* up to 13 kPa), the measured Ar adsorption capacity increases by a factor 2.1 to 5.1, depending on the partial pressure, when going from 294 to 248 K. When going from He to  $N_2$  as carrier gas, the measured Ar adsorption capacity at 294 K decreases, due to the increased co-adsorption, by a factor from 2.5 to 4.5, depending on the partial pressure. Whereas it decreases by a factor from 3.8 to 8.8 at 248 K.



Figure 4-5. N<sub>2</sub>, O<sub>2</sub> and Ar breakthrough curves from dry air. The breakthrough curves were measured at 200 cm<sup>3</sup> min<sup>-1</sup> and RT.

The capability of self-bound Ag-ETS-10 to separate Ar from air was assessed by an air breakthrough measurement. The resulting breakthrough curves are shown in Figure 4-5. The  $N_2/Ar$  and  $N_2/O_2$  selectivities are 5.7 and 9.5, respectively,

whereas the  $Ar/O_2$  selectivity is 1.7. The  $N_2/O_2$  and  $Ar/O_2$  selectivities are different than the ones reported previously, on a silica-bound Ag-ETS-10, in air, *i.e.* 12.88 and 1.41, respectively, from inverse-phase gas chromatography [38]. Next to the difference in the sample itself (*i.e.* self-bound compared to silica-bound), the differences in selectivities could also partly be due to the difference in measurement methodology, in particular due to kinetic effects, as much larger quantities of Aq-ETS-10 were used in this work. The air breakthrough measurement was repeated three times to get insight in the variability from run to run in the adsorption capacity, the selectivities and the retrieved concentrations. The relative deviation of the adsorption capacity and selectivity against the average value was within 5% for values related to  $N_2$  and Ar, whereas it was within 15% for values related to  $O_2$ . For the retrieved Ar concentrations in the range of 10 to 70% Ar yield, the variability is much more limited as the Ar concentrations are within a relative deviation of 3.5% compared to the average value. The Ar concentration in function of the Ar yield in the exhaust gas, during the air breakthrough measurement, is shown in Figure 4-6. As an example, exhaust samples with 10% and 60% Ar yield, with the corresponding  $N_2$ ,  $O_2$  and Ar concentrations, are highlighted in the figure. The sample with a 10% Ar yield results in an Ar concentration of  $6.4 \pm 0.2\%$  in almost exclusively O<sub>2</sub>. The one with a 60% Ar yield provides an Ar concentration of  $5.2 \pm 0.2\%$  together with 91.9% O<sub>2</sub>. One should note that the removal of  $N_2$  from air leaves a composition of 4.3% Ar and 95.7% O<sub>2</sub>. Despite the 10% Ar yield, the first sample clearly shows that a significant, direct, Ar separation from  $O_2$  is achieved in addition to removing N<sub>2</sub>.



*Figure 4-6. Ar concentration in exhaust samples from dry air as a function of Ar yield.* 

Next, the Ar separation from a 5% Ar / 95%  $O_2$  mixture, mimicking the composition after a first air separation stage, was investigated with a dedicated breakthrough measurement. This measurement was complemented by a breakthrough measurement of a 50% Ar / 50%  $O_2$  mixture to investigate the potential for further Ar separation from  $O_2$  in increasingly Ar-rich mixtures. The difference between the inlet and outlet concentration, indicative of the adsorbed gas, in function of the volume processed for both mixtures is shown in Figure 4-7a). Based on the adsorption capacities, the Ar/O<sub>2</sub> selectivity is about

1.4 in both mixtures. It is clear that the selectivity in a binary mixture is much closer, compared to the one obtained in air, to the value of 1.49 reported previously, based on single-component adsorption isotherms [162]. At full breakthrough equilibrium, the selectivity of 1.44 and 1.38 for 5% and 50% Ar in  $O_2$ , respectively, seem to indicate that it becomes more difficult to separate both components in Ar-rich mixtures. According to the preferential adsorption of Ar on Ag-ETS-10, the separation is here investigated by looking at the Ar concentration and yield in the adsorbed phase as shown in Figure 4-7b). The mixture can clearly be enriched in Ar using self-bound Ag-ETS-10 at RT. As expected however, the separation becomes more and more difficult as the Ar concentration increases in the mixture. For instance, the relative enrichment, for a 80% Ar yield, is 37% for a 5% Ar in  $O_2$  mixture, whereas it decreases to 15% for a 50% Ar in  $O_2$  mixture.



Figure 4-7. Ar and O<sub>2</sub> adsorbed concentration in Ar/O<sub>2</sub> mixtures together with the obtained relative Ar enrichment. a) Relative adsorbed concentration from 5% Ar in O<sub>2</sub> (bottom) and 50% Ar in O<sub>2</sub> (top) mixtures at 200 cm<sup>3</sup> min<sup>-1</sup> and RT.
b) Relative Ar enrichment in function of the Ar yield, in the adsorbed phase, for both mixtures. A 80% Ar yield is shown with the magenta boxes and ellipses.

Considering a 10% Ar yield from dry atmospheric air, a mixture of 6.4% Ar in, mainly,  $O_2$  can be recovered on self-bound Ag-ETS-10 at RT. Assuming a selectivity of 1.34 for all Ar concentrations in  $O_2$ , corresponding to the value observed at 80% Ar yield for 50% Ar in  $O_2$ , then a 99+% Ar sample can be obtained with an Ar yield of about 0.04%. On the other side the mixture with 5.2% Ar in, mainly,  $O_2$  obtained with a 60% Ar yield, would, using the same assumptions, provide a 99+% Ar sample with an Ar yield of about 0.23%. It is clear that Ar separation from dry atmospheric air on self-bound Ag-ETS-10 is possible at RT, but a large part of the Ar gas is lost in the process, resulting in yields lower than what would currently be acceptable for OSI, *i.e.* 2%. However, it has to be noted that part of the lost Ar gas could be recovered for further Ar enrichment on self-bound Ag-ETS-10 to increase the total Ar yield.

#### 4.3.3. Effect of moisture, Ar and O<sub>2</sub> concentrations

It is known that Ag-ETS-10 has a high affinity for moisture [181, 201]. To investigate the potential effect of moisture on the Ar separation from air, air breakthrough measurements were performed with 5% and 50% RH. The corresponding breakthrough curves are compared to a dry air breakthrough measurement in Figure 4-8. The positions of the breakthrough curves are slightly different from run to run due to the uncertainties on the measurement and on the start of the experiment. However, there is clearly no significant difference in the Ar separation capability in these three conditions, as the breakthrough curves are equivalent. In all conditions, about 6% Ar was recovered in, mainly,  $O_2$  in a 10% Ar yield exhaust sample. It has to be noted that between each run, the adsorbent was regenerated at 473 K so that moisture did not accumulate in the adsorbent. In a VPSA-based process, moisture might accumulate over time and influence the Ar separation properties.



*Figure 4-8. Breakthrough curves from air with different moisture levels (from top to bottom: dry, 5% RH and 50% RH). The breakthrough curves were measured at 200 cm<sup>3</sup> min<sup>-1</sup> and RT. 10% Ar yield exhaust samples are highlighted (magenta dashed boxes) and the corresponding gas compositions are given.* 

An Ar separation system operating for OSI should be able to handle efficiently large volumes of gases with a variable composition and Ar concentration [104]. As the  $O_2$  composition in subsoil air decreases with increasing depths, the effect of the  $O_2$  concentration in the Ar separation from subsoil gas needs to be assessed. To investigate this aspect, 1% Ar in  $N_2$  was mixed with 0.25, 1 and 21%  $O_2$ . The resulting breakthrough curves (except for 0.25%  $O_2$ ) are compared to the ones measured with the anaerobic mixture (*i.e.* 1% Ar in  $N_2$ ) in Figure 4-9. The first clear observation from these breakthrough curves is the much sharper and more intense Ar roll-up with increasing  $N_2$  concentration in the inlet gas stream. In addition, the  $N_2$  breakthrough is faster with higher  $N_2$  concentrations in the inlet

gas as could be expected, as the  $N_2$  partial pressure, about 130 kPa, is in the saturation region of previously published  $N_2$  adsorption isotherms [156, 162, 310]. Next to these direct observations, the highest Ar concentration in the exhaust gas, obtained for Ar yields between 5 and 10%, decreases with increasing  $O_2$ concentration in the inlet gas. The Ar concentration goes from 31% to about 6% when going from an anaerobic inlet mixture to 21% O<sub>2</sub> in the inlet gas. It is clear that  $O_2$  in the inlet gas strongly competes, together with  $N_2$ , with Ar in Ag-ETS-10. The best Ar separation capability is thus obtained in an anaerobic gas mixture. However, the picture is different when looking at a 50% Ar yield, as the ratio of the recovered Ar concentration on the Ar inlet concentration is 1.3, 1.8 and 6.0 for the gas mixture without  $O_2$ , and with 1% and 21%  $O_2$ , respectively. It is clear that when  $O_2$  is present only in smaller amounts, the achieved enrichment at 50% Ar yield is much lower than when 21% O<sub>2</sub> is present. Larger Ar yields, with reasonable Ar enrichment, can thus be achieved in atmospheric air compared to mixtures with lower  $O_2$  contents. This is due to the combination of a lower  $N_2$ partial pressure and a stronger O<sub>2</sub> competition with Ar in atmospheric air.



Figure 4-9. Ternary breakthrough curves with different  $O_2$  contents. The measurements were performed at 200 cm<sup>3</sup> min<sup>-1</sup> and RT. The exhaust sample with the highest purity for an Ar yield of 5 to 10% is highlighted (magenta dashed boxes) and the corresponding gas composition is given.



Figure 4-10. Breakthrough curves of N<sub>2</sub> and Ar from 1% Ar in N<sub>2</sub> in dry conditions (top), with 5% RH (middle), and 50% RH (bottom). They were obtained at 200 cm<sup>3</sup> min<sup>-1</sup> and RT. The gas composition of exhaust samples with the highest purity for an Ar yield higher than 5% (shown in magenta) are given.

The effect of moisture on the Ar separation from an anaerobic gas stream (1% Ar in N<sub>2</sub>) was also explored (Figure 4-10). Slight differences were observed in the highest Ar concentration that could be achieved (for an Ar yield of about 5%) depending on the moisture levels, but these differences are attributed to the larger uncertainties in the quantification due to the sharp Ar roll-up peaks. It should again be noted here that moisture is not accumulated, as the adsorbent is thermally regenerated at 473 K between each breakthrough measurement, and that the potential accumulation of moisture in a VPSA system might further influence the Ar separation in consecutive cycles.



Figure 4-11. Ternary breakthrough curves with different Ar contents. The measurements were performed at 200 cm<sup>3</sup> min<sup>-1</sup> and RT. The gas composition of the exhaust sample with the highest purity for an Ar yield of 10% (magenta dashed boxes) is given.

The Ar concentration can also vary, to a smaller extent than for  $O_2$ , in gas samples to be processed for OSI. To investigate the influence of the Ar concentration on the Ar separation in relevant gas compositions, breakthrough curves were collected from gas mixtures with 0.08 and 0.8% Ar together with 21%  $O_2$  in  $N_2$ (Figure 4-11). In these conditions, the Ar separation is improved at lower Ar concentration, as the relative enrichment for a 10% Ar yield sample is 71 and 44% for 0.08 and 0.8% Ar, respectively.

It is clear that the  $O_2$  and Ar concentrations in the samples to be processed for OSI will have a major influence on the Ar separation performance of Ag-ETS-10 operating at RT, whereas the presence of humidity in the gas stream will not directly affect the separation performance.

#### 4.3.4. Vacuum pressure swing Ar separation from dry air

Following the potential for Ar separation from dry atmospheric air demonstrated with the breakthrough measurements, the VPSA system was used to investigate the potential for Ar separation in self-bound Ag-ETS-10 in such conditions. The effect of the pressure differential on the column, as measured by the corresponding sensor, on the Ar separation from dry atmospheric air was investigated. This was performed by setting the pressure differential to 240, 150 and 120 kPa. The resulting exhaust gases are shown in Figure 4-12a). Compared to the breakthrough curve shown in Figure 4-5, the Ar peak obtained by VPSA in the investigated conditions is less intense, which results in lower achievable Ar concentrations (*i.e.*  $5.6 \pm 0.2\%$  Ar at maximum in VPSA mode compared to  $6.4 \pm 0.2\%$  Ar at maximum in breakthrough mode) as observed in Figure 4-12b).



*Figure 4-12. a) Exhaust gas composition and b) obtained Ar concentrations from the vacuum pressure swing separation at varying pressure differentials. The magenta dashed boxes and ellipses are exhaust samples with 10% Ar yield.* 

The maximum Ar yield obtained in VPSA-mode with an inlet pressure of 240 kPa is 54% compared to 85% with the breakthrough measurement. The Ar yield decreases with decreasing pressure differentials as it becomes more difficult to

extract the adsorbed gas. Next to the difficulty to extract the gas, it is likely that part of the Ar exhaust gas is lost in the gas lines and valves of the used VPSA system. This could be improved in future studies.

It is clear that the Ar enrichment increases with decreasing pressure differential. Looking at a 10% Ar yield, the Ar concentration goes from  $5.0 \pm 0.2$  to  $5.6 \pm 0.2\%$  when going from 240 to 120 kPa for the pressure differential, as shown in Table 4-2. For such an Ar yield, the gas is clearly purified from  $N_2$  and enriched in Ar. It has to be noted that in the current configuration of the system, a fraction of the measured traces of  $N_2$  in the exhaust gas at the beginning of the gas extraction is actually not from the exhaust gas itself but rather from the suction, due to the vacuum of the MS, of ambient air in the measurement gas line, as it is not pressurized before the measurement. Looking at the  $Ar/O_2$  mixture only, a relative enrichment of 26%, compared to  $N_2$ -free air, is obtained at 120 kPa, which is about half the relative enrichment that was obtained from the breakthrough measurement. Similarly at a 45% Ar yield, the Ar concentration ages from  $3.0 \pm 0.1$  to  $4.1 \pm 0.1\%$  when decreasing the pressure differential. It is clear that further improvements are necessary on the developed VPSA system to reach the enrichment values obtained by breakthrough measurements. Next to further investigations on the pressure differential, improvements on the VPSA system can be investigated by working on the absolute inlet pressure and the maximum outlet flow rate.

Ar yield (%)	Pressure differential (kPa)	Ar (%)	02 (%)	N <sub>2</sub> (%)
	240	5.0 ± 0.2	91.0	4.1
10	150	5.3 ± 0.2	92.2	2.5
	120	5.6 ± 0.2	91.7	2.7
	240	$3.0 \pm 0.1$	66.1	30.9
45	150	3.7 ± 0.1	81.4	14.9
	120	$4.1 \pm 0.1$	88.4	7.6

Table 4-2. Gas composition in vacuum pressure swing adsorption gas exhaust samples for a 10% and 45% Ar yield obtained from three pressure differentials.

#### 4.3.5. Ar separation at lower temperatures

Next to the previously described possible improvements in the VPSA system, the Ar separation could also be improved by operating the Ag-ETS-10 at lower temperatures during the adsorption. This was investigated by measuring air breakthrough curves on about 100 cm<sup>3</sup> self-bound Ag-ETS-10 at RT, 248, 233 and 213 K. The resulting breakthrough curves (except for 233 K) are shown in Figure 4-13a), whereas the resulting Ar concentration in function of Ar yield is shown in Figure 4-13b).

As can be observed by the difference in the shape of the breakthrough curves and the roll-up of Ar and  $O_2$ , the importance of the competition between the three components varies significantly with the temperature. The frost point of the air used in these experiments was about 223 K. Accordingly, it is not expected that the moisture content can influence notably the Ar separation in these single run

experiments. The highest Ar concentrations for Ar yields below 60% are obtained at 248 K. Further decreasing the temperature, decreases the Ar concentration in the exhaust samples. For Ar yields higher than 60%, higher Ar concentrations are obtained at RT. Looking at Ar yields of about 10%, the relative enrichment for N<sub>2</sub>free gas is 58, 98, 83, and 54% at 294, 248, 233 and 213 K, respectively. This demonstrates that an optimization is possible for the Ar separation from atmospheric air, with Ar yields below 60%, based on the operating temperature in a range from RT to 233 K. Further investigations on the adsorption of each gas component, by adsorption isotherm measurements at the corresponding temperature, could be performed in the future to better understand the observed competition between the three components. Next to the Ar separation from air, further Ar enrichment from the obtained  $Ar/O_2$  mixture could be optimized in function of the temperature as well.



Figure 4-13. N<sub>2</sub>, O<sub>2</sub> and Ar breakthrough curves and achieved Ar concentrations from dry air at room temperature and lower temperatures. a) Breakthrough curves were collected at 136 cm<sup>3</sup> min<sup>-1</sup> and at 294 K (top), 248 K (middle) and 213 K (bottom). The x-axis is shifted to the maximum of the Ar roll-up of each breakthrough. b) Ar concentration in function of Ar yield in exhaust samples.

# 4.4.Conclusions

In conclusion, Ag-ETS-10 was investigated for the first time specifically for the separation of Ar from air and subsoil gas. Self-bound Ag-ETS-10 was used and provides a higher microporosity, by 20 to 30%, than silica-bound Ag-ETS-10. Air breakthrough measurements demonstrate that self-bound Ag-ETS-10 can be used at RT to obtain an almost N<sub>2</sub>-free mixture enriched in Ar, with a relative Ar enrichment of 25%, for a 60% Ar yield. The obtained gas mixture can be further enriched in Ar but the enrichment becomes more difficult in Ar-rich mixtures. It is estimated that 99+% Ar could be reached with a maximum Ar yield of 0.23%.

It was found that the Ar separation performance depends on the Ar and  $O_2$  concentration in the gas to be purified, whereas it is not impacted by a relative humidity of up to 50% in the inlet gas. An almost N<sub>2</sub>-free mixture enriched in Ar, with a relative Ar enrichment of 26%, could be obtained by vacuum pressure swing adsorption but only with a 10% Ar yield. Finally, lowering the temperature during the adsorption from RT to 248 K allows to increase the relative Ar enrichment from 60 to 97% for a 10% Ar yield.

Higher Ar yields, meeting the requirements for OSI (*i.e.* > 2% for 99+% Ar), could be achieved by further improvements. In particular operation at lower temperature, but well above cryogenic temperature to minimize the energy consumption, is a potential way forward to reach the requirements.

#### 4.5. Supplementary material



Figure S 4-1. a) Selected points for the BET isotherm fit and b) selected points based on the Rouquerol plot for self-bound Ag-ETS-10.



Figure S 4-2. Breakthrough curves for a)  $N_2$ , b) Kr, c)  $CO_2$  and d) Xe from dry atmospheric air on self-bound Ag-ETS-10. The breakthrough curves (blue lines) are compared to the ones measured previously on silica-bound Aq-ETS-10 (black

lines) [311]. For the previous study, a smaller column having an internal diameter of 2 cm was filled with silica-bound Ag-ETS-10 whereas in the current work, 100 cm<sup>3</sup> of self-bound Ag-ETS-10 was used in a column with an internal diameter of 2.8 cm.

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# **Chapter 5**

Reducing radioxenon emissions through more efficient adsorbents

	Research objective	Main evaluation metrics
3	Examine the potential of silver-exchanged zeolites for trapping radioactive Xe more efficiently at fission-based medical isotope production facilities to reduce radioxenon emissions	Xe adsorption capacity and regeneration conditions



## **Graphical abstract**

# 5. Reducing radioxenon emissions

In this chapter dealing with the third research objective, the use of silverexchanged zeolites (AgZs) for mitigating radioxenon emissions at civilian nuclear installations is investigated. The objective is to determine if AgZs are more efficient than Activated Carbon (AC) in conditions relevant for fission-based Medical Isotope Production Facilities (MIPFs). Should this be the case, AgZs could further minimize radioxenon emissions from these facilities and improve the detection capability of the International Monitoring System (IMS) for nuclear weapon tests. The potential of AgZs compared to AC is evaluated through Xe adsorption and desorption measurements in relevant conditions.

This chapter is based on the following published paper:

Gueibe, C., Rutten, J., Camps, J., Moyaux, D., Schroeyers, W., Auer, M., & Schreurs, S. (2022). Application of silver-exchanged zeolite for radioxenon mitigation at fission-based medical isotope production facilities. *Process Safety and Environmental Protection*, *158*, *576-588*. DOI: <u>10.1016/j.psep.2021.12.031</u>

## Abstract

Atmospheric radioxenon releases from fission-based MIPFs are the main contributors to the radioxenon background being observed in the IMS for the verification of the Comprehensive Nuclear-Test-Ban Treaty (CTBT). This background is impacting the detection capability of the IMS network for potential nuclear explosions. Reducing the radioxenon emissions from these facilities requires the optimization of the deployed filtration process. The investigation of more efficient Xe adsorption materials than AC, which is currently used for this application, can play an important role for such an optimization. In this work, the Xe adsorption capacity of AqZs is compared to the one of ACs in relevant conditions for fission-based MIPFs. The most promising AgZ candidate, a silverexchanged titanosilicate (Ag-ETS-10), is investigated in more detail for its application to further reduce radioxenon releases. As operational conditions depend on the production and off-gas treatment processes, the effect of Xe concentration, flow rate, temperature and moisture on the Xe adsorption in Aq-ETS-10 is reported. Furthermore, since AqZs are far more expensive than ACs, it is crucial to be able to regenerate the material, whilst maintaining its full Xe adsorption properties for successive reuse. Accordingly, the durability of Ag-ETS-10 is investigated with regard to desorption and adsorption cycles, but also with regard to gamma irradiation.

## 5.1.Introduction

As discussed in Section 1.3.2, the Noble Gas (NG) component of the IMS is observing a worldwide radioxenon background coming from civilian sources [57, 59, 60, 62, 83]. The researchers in this field have collected a large amount of data on the inventory of radioxenon released to the atmosphere by different civilian nuclear installations and their impact on the IMS [36, 64, 69, 70, 315, 316]. The main sources of radioxenon releases to the atmosphere were determined to be a

limited number of MIPFs around the globe. Even though these radioxenon releases are well below national regulations for the protection of the public and environment, they are still high enough to be detected by the very sensitive IMS NG stations [114].

As explained in Section 1.3.2, the current knowledge on civilian radioxenon releases is not sufficient to understand all observations in the IMS NG network. which would be required to be able to confidently discriminate between possible detections from a nuclear explosion and the normal background observations [90, 317]. In order to minimize the impact of the main civilian sources on the IMS NG network, Bowyer et al. [119] proposed an upper level of  $5 \ 10^9$  Bg day<sup>-1</sup> for radioxenon releases from MIPFs. The worldwide radioxenon background is expected to become even more complex in the near future due to new emerging MIPFs [318]. It will thus be increasingly critical to reduce the radioxenon releases from these facilities [319]. As described in Section 1.3.2, the <sup>133</sup>Xe releases from the largest MIPFs are estimated to be on average in a range from  $10^{12}$  to  $10^{13}$  Bg per day [36], which would thus need an additional decay period of 40 to 57 days to reach the proposed upper level. MIPFs are producing radionuclides, mainly <sup>99</sup>Mo and its daughter product <sup>99m</sup>Tc, for medical applications through the dissolution of irradiated uranium targets. The main Xe release, in the ventilation system, is directly the result of the target dissolution, where the off-gases are driven out of the dissolver by a He or  $N_2$  flow for their subsequent treatment [320]. The typical flow rate used is in the order of 1000 cm<sup>3</sup> min<sup>-1</sup> for a duration of about one hour for the dissolution [321-323]. Each facility has its own production process with its own off-gas treatment. For alkaline dissolution of uranium targets, a particular attention is needed for hydrogen removal in the off-gas treatment [320]. In case an acidic solution is used for target dissolution, a particular attention is needed for iodine trapping in the off-gas treatment, as well as nitrogen oxide if activated carbon filters are used [320]. After pre-treatment (including moisture removal), the off-gas can be further processed to mitigate radioxenon releases.

As briefly described in Section 1.4, the most common method used for mitigating radioxenon releases in MIPFs, and in nuclear installations in general, is through the adsorption of Xe on ACs, possibly with the combination of gas storage tanks, as this is a well-proven technique and is the most convenient method for such applications [114, 182, 324-327]. Cryo-trapping can also be used to retain the released radioxenon, but requires extensive gas pre-treatment and is more expensive than the adsorption-based method [114]. For the adsorption method, the adsorbed Xe is trapped in AC for a certain period of time to allow sufficient decay before being released to the atmosphere. The Xe adsorption on AC requires either a large volume of AC or a cooling system to operate the AC at low temperatures for an efficient Xe adsorption [121]. Next to this drawback, ACs pose an increased risk of fire [114]. Furthermore, there is a preference for passive systems that do not require an active cooling system as this could lead to uncontrolled radioxenon releases in case of failure. Existing facilities have an additional challenge to further decrease their radioxenon emissions as they have limited space/footprint available to implement a more efficient radioxenon mitigation system.

Due to the ignition risk with AC, researchers have been investigating the use of zeolites, as they are non-combustible. As discussed in Section 1.5.3, several studies demonstrated that zeolites had a lower Xe adsorption capacity than AC at Room Temperature (RT) [136, 324, 328]. However, it has been demonstrated that silver-exchanged zeolites (AgZs) offer a significantly higher Xe adsorption capacity at RT and low Xe partial pressures compared to AC [137, 140, 141, 329]. To the best of our knowledge, the application of AgZs for radioxenon mitigation at MIPFs has not yet been specifically reported in the literature. As mentioned in Section 1.5.1, a new class of porous materials, called metal-organic frameworks, have been investigated for Xe/Kr separation and showed promising results for this specific separation [149]. However, these materials have currently a Xe adsorption capacity at RT that is in the same range as the one from AC [149]. They would thus currently not improve the efficiency of radioxenon mitigation with regard to the volume and footprint required.

In this work, the authors investigated the use of AgZs for the capture of radioxenon releases from the dissolution process of MIPFs to provide a potential solution to further reduce the emissions while maintaining the same volume and footprint for the system. First, different AgZs are compared to typical ACs used in the nuclear industry. Based on this comparison, the most promising AgZ, a silver-exchanged titanosilicate (Ag-ETS-10), is further investigated for its use and durability in this specific context. Ag-ETS-10 is here classified as zeolite due to its similarity.

# 5.2. Materials and methods

Two types of Xe adsorbents were selected for this study, namely: ACs (as reference adsorbent) and AgZs (Section 5.2.1). In order to investigate the Xe adsorption properties of the different adsorbents, a Xe breakthrough measurement system was used (section 5.2.2). Finally, the durability of one of the AgZs against gamma irradiation was investigated in a gamma irradiation facility at the Belgian Nuclear Research Centre (section 5.2.3).

The materials and methods that are common to multiple chapters (indicated in the yellow box in Figure 5-1) are described in full details in Chapter 2, whereas materials and methods specific to the current chapter are detailed in the following sections.



Figure 5-1. Materials and methods used in Chapter 5.

## 5.2.1. Adsorbents

The chosen activated carbons were: Norit RKJ 1, Nusorb® GXK and Nuclearcarb® 203C. The following silver-exchanged zeolites (or alike) were investigated: Ag-Mordenite, Ag-ETS-10\_1 (silica-bound), Ag-ETS-10\_2 (silica-bound), Ag-Chabazite\_1 and Ag-Chabazite\_2. Ag-ETS-10\_1 corresponds to a sample produced with the synthesis method reported in Kuznicki et al. [138]. The synthesis method of the Ag-ETS-10 was further developed to improve its adsorption properties, as reported by Shi et al. [163], leading to the development of the denser Ag-ETS-10\_2 sample, which is also investigated. More information on the adsorbents can be found in section 2.1.

## 5.2.2. Xe breakthrough measurements

The breakthrough experimental system was designed, as discussed in Section 2.2, to perform Xe breakthrough measurements in varying conditions of Xe concentration, flow rate, temperature and moisture content. For the Ag-Chabazite\_2 sample specifically, a temperature of 433 K was used during the desorption, as a decrease in Xe adsorption capacity during successive adsorption/desorption cycles was observed at the standard regeneration temperature of 473 K. Depending on the breakthrough measurement, columns C1 to C3 were used.

## 5.2.3. Gamma irradiation

A sample of Ag-ETS-10\_2 was irradiated in the BRIGITTE (Big Radius Installation under Gamma Irradiation for Tailoring and Testing Experiments) gamma irradiation facility at SCK CEN. The BRIGITTE irradiation facility is described in Fernandez et al. [330]. The sample, with a mass of 22 g, was irradiated for 50 hours in this facility under a constant and homogeneous gamma absorbed dose rate of 20 kGy h<sup>-1</sup>, resulting in a total gamma absorbed dose of 1 MGy.

## 5.3.Results and discussion

The comparison of the Xe adsorption capacity of the studied adsorbents is presented and discussed in subsection 5.3.1. In the same subsection, the effect of moisture on the Xe adsorption capacity and a specific comparison of the two Ag-ETS-10 samples is given as well. In subsections 5.3.2 to 5.3.8, the applicability of Ag-ETS-10 in conditions relevant for radioxenon mitigation in MIPFs is discussed.

## 5.3.1. Comparison of Xe adsorption properties

Xe adsorption capacities at about 6.5, 13, 65 and 130 Pa at RT, in Xe/He and Xe/N<sub>2</sub> mixtures (*i.e.* 50, 100, 500 and 1000 ppm Xe), were measured on the **different AC and AgZ adsorbents**, except on the Ag-ETS-10\_1 that is discussed separately hereafter. The detailed experimental conditions can be found in Supplementary material Table S 5-1A for He and in Table S 5-1B for N<sub>2</sub>. The resulting Xe adsorption capacities are presented in Figure 5-2a) for ACs and in Figure 5-2b) for AgZs.



Figure 5-2. Xe adsorption isotherms at room temperature. Overview of the measured Xe adsorption capacity in He and  $N_2$  on a) ACs and b) AgZs.

Assuming a linear adsorption isotherm for the three ACs, the Xe Henry's adsorption constant is 1.15, 0.947 and 0.725  $m^3 kq^{-1}$  in He, and 0.688, 0.635 and 0.781 m<sup>3</sup> kg<sup>-1</sup> in N<sub>2</sub> for Nusorb® GXK, Nuclearcarb® 203C and Norit RKJ1, respectively. For Nusorb® GXK and Nuclearcarb® 203C, there is a clear decrease in Xe adsorption when going from He to  $N_2$ , whereas for Norit RKJ1 the difference is within the measurement uncertainties. These results indicate that there is no significant  $Xe/N_2$  adsorption competition at RT in the range of partial pressures investigated for Norit RKJ1, whereas there is a significant Xe/N<sub>2</sub> adsorption competition in the two other ACs. When He is used as carrier gas, Nusorb® GXK clearly offers the highest Xe adsorption capacity, whereas when  $N_2$  is used as carrier gas, the three ACs offer a similar Xe adsorption capacity. The highest Xe Henry's adsorption constant for Nusorb® GXK is about 17% lower than the one reported at RT by Nucon International Inc. [172] for which the carrier gas and Xe partial pressure were not reported. The highest Xe Henry's adsorption constant for Nuclearcarb® 203C is about 20% lower than the one reported at STP by the producer with, again, an unknown gas composition and Xe partial pressure [173]. For this AC, the difference in temperature (RT compared to 273 K) could explain the lower Xe Henry's adsorption constant.

For all AgZs, there is a significant Xe/N<sub>2</sub> adsorption competition as all Xe adsorption capacities measured in N<sub>2</sub> were lower than the ones measured with He. The order, with regard to the highest Xe adsorption capacity, for AgZs is Ag-ETS-10\_2 > Ag-Chabazite\_2 > Ag-Chabazite\_1 > Ag-Mordenite. The Xe adsorption capacity at about 65 Pa on the Ag-ETS-10\_2 sample is 0.48 mol kg<sup>-1</sup> at RT, which is very similar to the 0.46 mol kg<sup>-1</sup> reported by Kuznicki et al. [138] in the same conditions on an Ag-ETS-10 sample. However, as shown in the

following paragraphs, the Ag-ETS-10 2 sample has a higher Xe adsorption capacity, by about 20%, than the Aq-ETS-10 1 sample. The latter corresponds to a similar sample as the one reported in Kuznicki et al. [138]. The highest Xe adsorption capacity measured on the Ag-Chabazite samples was 0.24 mol kg<sup>-1</sup> at about 130 Pa on the Aq-Chabazite 2 sample. Assuming a Langmuir type adsorption isotherm, the extrapolated Xe adsorption capacity at 1 kPa on this sample would be 0.53 mol kg<sup>-1</sup>, which is lower than the reported values of 0.79 to 0.88 mol kg<sup>-1</sup> at 1 kPa by Hirano et al. [179]. Differences in the isotypic chabazite structure, the activation temperature and silver exchange likely explain the difference [331, 332]. The ratio of the Xe adsorption capacity of Aq-Chabazite 2 to Aq-Chabazite 1 ranged from 1.5 to 2.0 for Xe/He mixtures and from 2.0 to 2.4 for  $Xe/N_2$  mixtures. The results on both Aq-Chabazite samples clearly indicate that the Xe adsorption capacity is a function of silver loading. This is in agreement with the observations made by Daniel et al. [142] on Pentasiltype zeolites. Finally, the Aq-Mordenite had the lowest Xe adsorption capacity of all adsorbents investigated. The Xe adsorption capacity in He at about 130 Pa and RT was 4.3 10<sup>-3</sup> mol kg<sup>-1</sup> for this sample, which is well below the Xe adsorption capacity measured by Munakata et al. [137] of about 0.3 mol kg<sup>-1</sup> at about 100 Pa and 273 K on a Ag-Mordenite. The difference in temperature is clearly part of the explanation for this difference. However, it is unlikely that the Xe adsorption capacity would increase by about two orders of magnitude when going from RT to 273 K. Bever and Jacobs [333] showed that silver nanoparticles are only formed on Aq-Mordenites under an external reducing agent and at a sufficiently high temperature. As no information on the synthesis process of the Aq-Mordenite, studied in this work, is available, it is possible that the used synthesis process did not efficiently result in silver nanoparticles, which could be part of the cause for the observed difference.

The benefit of using the Aq-ETS-10 2 sample over a nuclear grade AC, such as Nusorb<sup>®</sup> GXK, for Xe adsorption, both in He and  $N_2$ , is clear from Figure 5-2. The Xe adsorption capacity at 6.5 and 130 Pa in Xe/He (*i.e.* 50 and 1000 ppm Xe) increases by a factor 81 and 8.5, respectively, whereas in  $Xe/N_2$  it increases by a factor 31 and 10 at 6.5 and 130 Pa, respectively. As the available space for a Xe trapping system in an existing facility could be limited, the Xe adsorption capacity per unit of volume is in this case a more crucial factor. As shown in Table 2-1 in Chapter 2, the density of the Aq-ETS-10 2 sample is about twice the density of Nusorb® GXK, which, in terms of volume, further increases the adsorbed amount of Xe by a factor two. The comparison in terms of volume on the amount of Xe retained in the material, the Xe retention time at 10 and 90% breakthrough, and the Mass Transfer Zone (MTZ) percentage is given by the ratio of these quantities in Table 5-1 for two Xe concentrations in both Xe/He and Xe/N<sub>2</sub> mixtures. The detailed experimental conditions for the underlying breakthrough curves can be found in Supplementary material Table S 5-3. As can be seen in Table 5-1, the ratio for the adsorbed amount of Xe ranges from 17.9 up to 185 depending on the Xe concentration and carrier gas. More importantly, the ratio for the retention time at 10% breakthrough is even higher with values ranging from 20.2 up to 211. In practice at 50 ppm Xe in He, the same volume of adsorbent can be used for a time period that is 211 times longer. The lower MTZ ratio in the Ag-ETS-10 2 sample compared to Nusorb® GXK indicates a faster overall mass transfer kinetic and thus a sharper breakthrough. The smaller MTZ ratio at 1000 ppm Xe in N<sub>2</sub> is the result of a decrease of the MTZ on Ag-ETS-10\_2 when going from 100 to 1000 ppm Xe in N<sub>2</sub>, whereas the MTZ remained unchanged on Nusorb® GXK. The decrease on Ag-ETS-10\_2 is due to the weaker N<sub>2</sub> competition effect at 1000 ppm, as indicated by the small difference in Xe adsorption capacity in He and N<sub>2</sub> at 1000 ppm (Figure 5-2).

	Comion and	Ratio	Ratio Ag-ETS-10_2/Nusorb® GXK					
Xe con. (ppm)	Carrier gas	n <sub>Xe</sub>	<b>t</b> 10%	MTZ ratio (-)				
50	Не	185	211	155	0.6			
1000	Не	18.2	20.2	15.8	0.6			
100	N <sub>2</sub>	43.4	49.9	39.4	0.7			
1000	N <sub>2</sub>	17.9	23.7	14.0	0.2			

Table 5-1. Comparison of the Xe adsorption performances of Ag-ETS-10\_2 and<br/>Nusorb® GXK for two Xe concentrations in He and in N2.

The Xe breakthrough curves of Ag-ETS-10 1 and Ag-ETS-10 2 were compared, with a gas mixture of 1000 ppm Xe/He at RT, to determine the improvement in Xe adsorption of the new sample, produced with a **new synthesis method**. The detailed experimental conditions can be found in Supplementary material Table S 5-4. The resulting average Xe adsorption capacity was 0.61 mol kg<sup>-1</sup> for the Ag-ETS-10\_1 sample and 0.72 mol kg<sup>-1</sup> for the Ag-ETS-10\_2 sample, corresponding to a relative increase of 18%. In addition, it has to be noted that the density of the Ag-ETS-10\_2 sample increased by 22.2% compared to the Ag-ETS-10\_1 sample, which further increases the Xe adsorption capacity per unit volume of adsorbent. The resulting average Xe retention time at 10% breakthrough per unit mass of adsorbent was 21 min  $q^{-1}$  for the Aq-ETS-10 1 sample and 26 min  $g^{-1}$  for the Ag-ETS-10\_2 sample, corresponding to a relative increase of 24%. These increases are significant compared to the 10% measurement uncertainty. Shi et al. [163] reported a relative increased retention time per unit mass of material of 28 % for Ar for a high density Ag-ETS-10 compared to the regular Aq-ETS-10. This is in agreement with the results obtained in the current work for Xe.

Normalized Xe outlet (-)



Figure 5-3. Xe breakthrough curves obtained on the Ag-ETS-10\_1 and Ag-ETS-10\_2 samples.

In Figure 5-3, for each sample, one of the obtained breakthrough curves is presented, normalized with regard to the Xe inlet concentration. For this comparison, the x-axis is rescaled by dividing the time by the mass of each sample, as the masses were not exactly the same (25.9 and 26.8 g for Aq-ETS-10 1 and Aq-ETS-10 2, respectively). The average MTZ percentage corresponded to 38% and 20% of the bed length for the Ag-ETS-10 1 and Ag-ETS-10\_2 samples, respectively, indicating a significantly smaller MTZ percentage in the Ag-ETS-10 2 sample. The Xe breakthrough curve on the Aq-ETS-10 2 sample follows a logistic function ('S' shape profile) around the retention time at 50% breakthrough as expected for ideal breakthrough curves, whereas the breakthrough curve on the Aq-ETS-10 1 sample does clearly not follow a logistic function. The lower slope at the beginning of the breakthrough curve on the Ag-ETS-10\_1 sample is due to a slower overall mass transfer kinetic, which is likely the result of a difference in binder. Even more interesting is the sharper breakthrough at the end of the curve for the Ag-ETS-10 1 sample, which would indicate a preferential channel with less adsorbent encountered by the gas at the end of the adsorbent bed. This could be due to an imperfect packing of the Aq-ETS-10 1 sample, with an inhomogeneous packing density along the adsorbent bed, as highlighted during other experiments and discussed in Section 5.3.8. The higher Xe adsorption capacity and retention time at 10% breakthrough clearly demonstrate that it is still possible to further optimize the adsorption materials for the capture of xenon and thus decrease the volume of material required for a defined amount of xenon to be captured.

As moisture can still be present in the gas stream going from the production process to a potential radioxenon mitigation system, **the effect of moisture** on the Xe adsorption capacity for the different materials was investigated. The

adverse impact of moisture on iodine adsorption in AqZs has been shown in the past [334]. However, the effect of moisture content in the gas stream on the Xe adsorption in AgZs, has to the best of our knowledge, not yet been reported. For this purpose, two moisture contents were investigated: 5% and 50% Relative Humidity (RH). These are compared with a run in dry conditions. Before the experiment, the sample was fully regenerated and then the chosen moisture content was maintained until the full Xe breakthrough was observed. For a mixture of 250 ppm Xe/N<sub>2</sub> at RT, with these three moisture levels in the inlet gas stream, the obtained Xe adsorption capacity is shown in Figure 5-4 for all adsorbents, except for Aq-ETS-10 1. The detailed experimental conditions can be found in Supplementary material Table S 5-5. As can be seen in Figure 5-4, a significant decrease in Xe adsorption capacity was observed for the Ag-ETS-10 2 and Aq-Chabazite 2 samples at 50% RH. The Xe adsorption capacity decreased by a factor 31 when going from dry conditions to 50% RH on Ag-ETS-10 2, whereas it decreased by a factor 6.6 on Ag-Chabazite\_2. A decrease in Xe adsorption coefficient on coconut-based AC was demonstrated by Underhill et al. [335] when the AC was equilibrated with the moisture content in advance. This is clearly different from the methodology used in the current work, as it is here considered that the adsorbent is fully desorbed before each use. In this case, the water uptake is clearly not sufficient to decrease the Xe adsorption capacity on the ACs investigated.



Figure 5-4. Effect of moisture on the Xe adsorption capacity. Evolution of the Xe adsorption capacity as a function of the moisture content in the gas stream (250 ppm Xe in  $N_2$  at RT).

The effect on the Xe retention time at 10% breakthrough, for the Ag-ETS-10\_2 sample, was much more limited than on the Xe adsorption capacity as it decreased only by a factor 2.3. This is highlighted in Figure 5-5, where the normalized Xe breakthrough is shown for the three moisture contents on the Ag-ETS-10\_2 sample. As can be seen in the figure, the Xe breakthrough at 10% is occurring significantly faster at 50% RH but the main loss in Xe adsorption capacity is in fact due to the strong roll-up of Xe, as Xe is displaced from the adsorption sites by water molecules [336]. During the roll-up, 92% of the adsorbed Xe is released from the material. Such a roll-up of Xe was also observed on the Ag-Chabazite\_2 sample at 50% RH, for which the retention time decreased by a factor 1.3. A Xe roll-up is critical for radioxenon mitigation systems, as this would lead to a large Xe release. The moisture content, when using these AgZs, should thus be well controlled to avoid this situation.



Figure 5-5. Comparison of the normalized Xe breakthrough curves obtained on the Ag-ETS-10\_2 sample in dry conditions, and at 5% and 50% RH.

As shown in the previous paragraphs, Ag-ETS-10 is a promising adsorbent to support the reduction of radioxenon emissions of MIPFs by providing a more efficient Xe adsorption per unit of volume of adsorbent compared to all ACs and all other AgZs considered in this work. The applicability of Ag-ETS-10 for this specific industrial setting is further considered in the following sections. The effect of inlet concentration, column geometry, flow rate and temperature on the Xe breakthrough curves was investigated. In addition, the durability of Ag-ETS-10\_2 against gamma irradiation was explored. Finally, the regeneration of the material and its durability against desorption/adsorption cycles were investigated.

## 5.3.2. Effect of inlet concentration

The effect of the inlet concentration on the Xe adsorption capacity of Ag-ETS-10\_2 was shown in Section 5.3.1. The Xe adsorption isotherm of this sample (Figure 5-2) clearly indicated a Langmuir type adsorption isotherm, as the material started to get saturated with Xe at the highest Xe partial pressures. In comparison, Nusorb® GXK had a linear adsorption isotherm in the Xe partial pressure range investigated. In Figure 5-6a) for Ag-ETS-10\_2 and in Figure 5-6b)

for Nusorb® GXK, one of the measured Xe breakthrough curves after desorption, resulting in Figure 5-2, is shown for both 100 and 1000 ppm Xe in N<sub>2</sub> at RT. The detailed experimental conditions for these breakthrough curves can be found in Supplementary material Table S 5-6. For Nusorb® GXK, both breakthrough curves (Figure 5-6b) are overlapping each other within the 10% measurement uncertainty as expected from the linear adsorption isotherm.



Figure 5-6. Comparison of the breakthrough curves at room temperature from *a*) Ag-ETS-10\_2 and *b*) Nusorb® GXK.

For the Aq-ETS-10 2 sample however, the Xe adsorption capacity increased by a factor 3.5 when going from 100 to 1000 ppm Xe in N<sub>2</sub> at RT. From Figure 5-6a), it can clearly be observed that the slope of the curve is very different depending on the Xe concentration. On average, the MTZ percentage represented 50 and 16% of the bed length at 100 and 1000 ppm Xe, respectively. The Xe breakthrough at 1000 ppm Xe has a very sharp breakthrough profile, which indicates a very fast overall mass transfer kinetic. Whereas the Xe breakthrough at 100 ppm Xe has a significantly flatter slope compared to the one at 1000 ppm Xe, which in turn indicates a slower overall mass transfer kinetic. As the breakthrough curves were obtained on the same amount of material, geometry, flow rate and other experimental conditions, it can only be concluded that the overall mass transfer kinetic has a concentration dependency in this material. Such an observation was also made by Puertolas et al. [337] with propene breakthrough curves on a ZSM-5 zeolite, having a Langmuir type adsorption isotherm, where the slope increased with increasing concentrations. The "trough" in the Xe breakthrough curve at 100 ppm could be due to some imperfections in the packing of the adsorbent in the test bed. Such imperfections are discussed further in Section 5.3.8. The results are clearly highlighting that the design of a Xe adsorbent bed, with adsorbents having a Langmuir adsorption isotherm, should take into consideration the specific Xe concentration of the process to assess the dimensions of the adsorbent bed correctly.

#### 5.3.3. Effect of column geometry

The effect of the Length to Diameter ratio (L/D) of the adsorption column on Xe adsorption was investigated by measuring Xe breakthrough curves for two different ratios, 1.1 and 3.8, in a mixture of 1000 ppm Xe in He at RT and for the same mass of adsorbent. In practice, the same Ag-ETS-10\_2 sample was used in adsorption columns C1 (L/D 1.1) and C2 (L/D 3.8). Detailed experimental conditions can be found in Supplementary material Table S 5-7. The resulting Xe breakthrough curves are shown in Figure 5-7.

#### Normalized Xe outlet (-)



Figure 5-7. Xe breakthrough curves, with 1000 ppm Xe in He at room temperature, obtained with column C1 and C2 filled with the same Ag-ETS-10\_2 sample.

The Xe adsorption capacity obtained with C1 was 0.69 mol kg<sup>-1</sup> and with C2 it was  $0.72 \text{ mol } \text{kg}^{-1}$ . These values are within the measurement uncertainties and are in agreement with the expectations. As the adsorption capacity is measured at equilibrium, the geometry of the adsorption column should not affect the adsorption capacity. The difference between both breakthrough curves is thus on the Xe adsorption kinetic which is, as can be seen in the figure, significantly different. The MTZ percentage represented 90 and 27% of the bed length for C1 and C2, respectively. The retention time at 10% breakthrough went from 5.4 hours in C1 to 9.4 hours in C2. The increase due to the larger L/D ratio is thus 72% and provides a significant difference in volume required for a certain retention time. The smaller slope for the smaller L/D ratio indicates a slower overall mass transfer kinetic, whereas the steeper slope for the higher L/D ratio indicates in turn a faster overall mass transfer kinetic. The decrease in bed diameter going from C1 to C2 gives a higher superficial velocity, and thus a shorter contact time with the adsorbent. The MTZ percentage is expected to increase with increasing superficial velocity as will be discussed in Section 5.3.4. The current results indicate however an opposite trend; this is likely due to a better flow distribution in C2 compared to C1. This is explained by the use of the same inletpipe diameter for both columns, which gives rise to a smaller velocity gradient in the transverse direction in C2 compared to C1 due to the smaller diameter of C2. The earlier breakthrough in C1 is due to a smaller volume of adsorbent in the

region where the velocity is the highest (*i.e.* along the axis) due to the shorter length of C1, whereas the longer time required to reach equilibrium is due to the lower velocity in the region along the column wall. The flow distribution in the adsorbent is an aspect that should be considered with care in the design of Xe trapping systems. The effect of flow rate in a fixed column geometry is further discussed in the following section. The steeper slope at the end of the Xe breakthrough curve in C1 could be due to some imperfections in the packing of the material in the adsorption column as discussed further in Section 5.3.8.

## 5.3.4. Effect of flow rate

The effect of the flow rate on Xe adsorption in the Ag-ETS-10\_2 sample was investigated by measuring the Xe breakthrough at four flow rates, *i.e.* 280, 400, 1400 and 2800 cm<sup>3</sup> min<sup>-1</sup>, in the same column. All other conditions were kept constant. The detailed experimental conditions can be found in Supplementary material Table S 5-8. The Xe breakthrough curves obtained at these flow rates are shown in Figure 5-8, where the x-axis has been rescaled with the flow rate for visualisation purposes and is thus representing the volume of gas processed in the adsorbent bed.



Normalized Xe outlet (-)

Figure 5-8. Normalized Xe breakthrough curves obtained on the Ag-ETS-10\_2 sample with different flow rates.

The Xe adsorption capacity varied between 0.46 and 0.55 mol kg<sup>-1</sup>, which is perfectly within the 10% measurement uncertainty on the average value obtained in Figure 5-2 for this Xe partial pressure. There is thus no significant effect on the Xe adsorption capacity, indicating that equilibrium was reached within the material for all flow rates. The retention volume at 10% breakthrough was 0.190, 0.183, 0.165 and 0.161 m<sup>3</sup> for 280, 400, 1400 and 2800 cm<sup>3</sup> min<sup>-1</sup>, respectively, which indicates a slower overall mass transfer kinetic when the flow rate increases.

For this aspect, the superficial velocity of the gas inside the adsorption column is a critical factor. The superficial velocity was 1.5, 2.1, 7.4 and 15 cm s<sup>-1</sup> for a flow of 280, 400, 1400 and 2800 cm<sup>3</sup> min<sup>-1</sup>, respectively. As the adsorbent filling in the column was kept constant, this increased velocity resulted in a shorter contact time with the adsorbent inside the column. The results clearly show that the

adsorption sites are much more difficult to reach at a high superficial velocity resulting in a longer time duration, and a larger MTZ percentage, to reach equilibrium. The MTZ percentage of the bed length as a function of superficial velocity is shown in Figure 5-9. In this figure, a linear equation was fitted. The resulting R-squared is 0.85 indicating indeed a linear correlation in this range of superficial velocity. Such a linear relationship was shown numerically by Rezaei and Webley [338] for  $CO_2/N_2$  separation on different adsorbent structures. More surprising is the change of slope in each breakthrough curve occurring at about 40-50% breakthrough. This could again be due to an inhomogeneous packing of the material in the adsorption test bed as will be discussed in Section 5.3.8. Another possible cause for this change in slope could be related to the two distinct adsorption sites in these AgZs, one adsorption site for the zeolite and a second one for the silver nanoparticles [143], which could have different mass transfer properties.



Figure 5-9. Mass Transfer Zone percentage as a function of superficial velocity fitted by a linear relation.

## 5.3.5. Durability against gamma irradiation

Xe adsorption capacity, retention time at 10% breakthrough, and MTZ percentage, were measured during a 1000 ppm Xe in He adsorption run at RT before and after a gamma irradiation of 1 MGy on the Ag-ETS-10\_2 sample. Xe breakthrough curves before and after irradiation are compared in Figure 5-10. The detailed experimental conditions can be found in Supplementary material Table S 5-9. The average Xe adsorption capacity, measured after irradiation, was 0.63 mol kg<sup>-1</sup>, which is 6% lower than the average Xe adsorption capacity before irradiation. The average Xe retention time at 10% breakthrough measured after irradiation was 8.8 h, which is 6% higher than before irradiation. The values are thus clearly within the measurement uncertainties and no significant effect on Xe adsorption was observed. On the other hand, the MTZ percentage represented 27% of the adsorbent after irradiation, whereas it represented 39% before irradiation. The decrease in MTZ percentage is clearly significant. However, as will be discussed in Section 5.3.8, this is likely related to an inhomogeneous packing of the material

inside the adsorption column, which was observed before irradiation as well. Accordingly, no effect on the Xe adsorption properties could be observed after a 1 MGy gamma irradiation. To the best of our knowledge, this study is the first investigation on the durability of this AgZ against gamma irradiation.

As shown by Saey et al. [84] and Lee et al. [121], the major contributor to the radioxenon releases from MIPFs is  $^{133}$ Xe and the typical  $^{133}$ Xe activity released after the dissolution of irradiated targets is in the range of  $10^{14}$  Bq. By considering the isotopic power of 2.14  $10^{-14}$  W Bq<sup>-1</sup> from beta decay and 7.39  $10^{-15}$  W Bq<sup>-1</sup> from gamma decay for  $^{133}$ Xe (JEFF-3.1 Nuclear Data Library), this would yield a power of 2.14 and 0.739 J s<sup>-1</sup> from beta and gamma decay, respectively. The exploration of the durability of the Ag-ETS-10\_2 sample was performed on a sample of 21.6 g. Considering this mass and that all beta and gamma radiation would be absorbed in the material, this would yield in turn an absorbed dose of 0.36 and 0.12 MGy/h or about 1 MGy for 3 and 8 hours of operation for beta and gamma radiation, respectively. This means that the current exploration of the durability of the extended in the future, not only to consider beta radiation but also to explore a higher absorbed dose, in order to ensure its durability to radiation in realistic operational conditions at MIPFs.





## 5.3.6. Xe adsorption at 333 K

Radioactive decay of the different Xe isotopes could result in a heat build-up in the material. If not sufficiently dissipated, this could decrease the adsorption capacity as adsorption is an exothermal process where the adsorption capacity decreases with increasing temperature following a van 't Hoff equation [187]. In order to assess this potential decrease, Xe breakthrough curves with 1000 ppm Xe in He at 333 K were evaluated and compared to these obtained at RT. 333 K is considered as the upper level for operation without dedicated cooling during adsorption. The detailed experimental conditions can be found in Supplementary material Table S 5-10.

The obtained average Xe adsorption capacity, retention time at 10% breakthrough and MTZ percentage are shown in Table 5-2. The Xe adsorption capacity decreased by a factor 2.5 from RT to 333 K, whereas the Xe retention time decreased by a factor 1.3. The MTZ percentage did not change between the different experiments, which were performed with the same filling and thus the same packing. The reduction in adsorption capacity and retention time could thus have a significant effect and could potentially cause an earlier breakthrough if the radioactive decay would result in an increase in temperature during operation.

Table 5-2. Comparison of Xe adsorption properties on the Ag-ETS-10\_2 sampleat RT and at 333 K for the experiments with 1000 ppm Xe in He.

T(K) P(kPa)		q <sub>Xe</sub> (mol kg <sup>-1</sup> )	t <sub>10%</sub> (h)	MTZ (%)		
296	174	0.61	9.1	20		
333	173	0.25	7.1	20		

#### 5.3.7. Regeneration conditions

The regeneration of AgZs without any loss of Xe adsorption capacity is crucial, as these materials are far more expensive than typical ACs. In addition, an efficient regeneration process is needed to minimize the operational cost of a Xe trapping system. Accordingly, the regeneration of the Ag-ETS-10\_2 sample was investigated at three desorption temperature set points, *i.e.* 423 K (internal temperature: 409 K), 473 K (internal temperature: 444 K) and 523 K (internal temperature: 494 K), under a continuous He flow. The detailed experimental conditions of these desorption runs, together with their subsequent adsorptions, are given in Supplementary material Table S 5-11. The desorption curves, normalized to the maximum Xe concentration obtained at 523 K, for these experiments are shown in Figure 5-11.



Figure 5-11. Desorption curves (left axis -  $C_{Xe}$  - lines) and temperature profiles (right axis – T - symbols) for different temperature set points on Ag-ETS-10\_2.

A heating ramp of 2 K min<sup>-1</sup> was used and once the temperature set point was reached, it was maintained for 3 hours before shutting down the heating element. As can be seen in the figure for the desorption run at 523 K, the maximum of the desorption was reached before getting at 523 K (at about 473 K) and a back-fall to 1% of the maximum was obtained 0.6 hours after reaching the temperature plateau. For the run at 473 K, the maximum was reached at the set point, as could have been expected from the run at 523 K, the desorption peak is however broader and falls back to 1% of the maximum only after 2.3 hours. Finally, for the run at 423 K, the maximum is reached at the set point temperature. It would most likely have increased further if the temperature set point was higher as shown in the previous runs. The peak is again broader and does not fall back to 1% of its maximum before the end of the temperature plateau. This could, of course, be improved by a longer heating duration or eventually a higher flow rate.

The Xe adsorption capacities during the subsequent adsorptions with 1000 ppm Xe in He at RT were 0.73, 0.73 and 0.70 mol kg<sup>-1</sup> after the desorption at 523, 473 and 423 K, respectively. The Xe retention time at 10% breakthrough during these adsorptions was 9.4, 9.5 and 9.2 hours in the same order. Finally, the MTZ percentage represented 29, 27 and 24% of the bed length, again in the same order. According to the measurement uncertainties, there are no significant variations in these parameters. This is indicating that, even though the desorption at 423 K did not fall back to 1% of its maximum during the temperature plateau, the desorption was still sufficient to recover the Xe adsorption capacity.

The choice on the temperature, duration and flow rate will depend on the particular conditions at a facility and can be optimised. The use of a higher temperature allows to limit the amount of gas to be used for the desorption and could be an important aspect in the operation of such a system. In addition, a desorption with  $N_2$  was also investigated at 523 K (internal temperature of 485 K) and indicated that the subsequent adsorption with 1000 ppm Xe in He at RT remained within the measurement uncertainties of previous adsorption runs. The detailed experimental conditions for these experiments can be found in Supplementary material Table S 5-12. This is highlighted in Table 5-3 where the Xe adsorption capacity, retention time at 10% breakthrough, and MTZ percentage during a subsequent adsorption run after a desorption with He and  $N_2$  are given. As can be seen in the table, the results obtained during the subsequent adsorption of Xe in He are very similar and within the measurement uncertainties. This indicates that in this desorption configuration, He can be replaced by  $N_2$  and still provides the same adsorption properties.

	Desor	ption	Subsequent adsorption				
Carrier gas	T <sub>set point</sub> (K)	T <sub>internal</sub> (K)	t <sub>set point</sub> (h)	q <sub>xe</sub> (mol kg⁻¹)	t <sub>10%</sub> (h)	MTZ (%)	
Не	523	484	3	0.59	8.4	20%	
N <sub>2</sub>	523	485	3	0.61	8.9	15%	

Table 5-3. Desorption conditions for the runs with He and  $N_2$  and the results obtained during the subsequent adsorption.

## 5.3.8. Durability against desorption/adsorption cycles

Another key aspect for the cost of such a xenon trapping system for fission-based MIPFs is the durability of the adsorption material against desorption/adsorption cycles. In total, 20 desorption/adsorption cycles were performed on the same Ag-ETS-10\_2 sample, the detailed experimental conditions can be found in the Supplementary material Table S 5-13. During these cycles, the Xe adsorption capacity, retention time at 10% breakthrough, and MTZ percentage during adsorptions at 1000 ppm Xe in He at RT were compared. These parameters are compared in Figure 5-12 for the relevant cycles.



**Relative deviation (%)** 

Figure 5-12. Evaluation of the durability of the Ag-ETS-10\_2 sample through Xe adsorption properties. Top: Relative deviation of the Xe adsorption capacity (□) and retention time at 10% breakthrough (•). Bottom: MTZ percentage during the 20 desorption/adsorption cycles. The green vertical lines indicate the moment the sample was removed from the adsorption test bed and was, after a certain time, poured back in the test bed. The dotted line corresponds to the average value for each period without consideration of the points indicated in red.

Cycles 9, 10 and 17 corresponded to pulsed experiments and could thus not be compared based on the previous indicators. Also, cycles 18 and 19, corresponding to adsorption experiments at 333 K, could not be compared. Furthermore, cycles 5 and 6, highlighted in red in the figure, corresponded to adsorption runs that occurred after desorption under N<sub>2</sub> at a temperature of about 403 K, which was clearly not enough to fully desorb xenon with the defined flow rate and duration as can be seen in the figure with the significantly lower adsorption indicators. For the remaining cycles, *i.e.* 1 - 4, 7 - 8, 11 - 16 and 20, called hereafter 'relevant cycles', the above mentioned indicators were compared to investigate the durability of the material. It has to be noted that the gamma irradiation mentioned

in Section 5.3.5 was done in-between cycle 12 and 13, as indicated by the blue line in Figure 5-12. In this figure, the relative deviation of these indicators from the average obtained on the relevant cycles is shown. As can be seen in the figure, the Xe adsorption capacity and retention time at 10% breakthrough are remaining within the 10% measurement uncertainty. Accordingly, no significant effect on Xe adsorption was observed. The average Xe adsorption capacity and retention time at 10% breakthrough of these relevant cycles was 0.67 mol kg<sup>-1</sup> and 9.0 hours, respectively, for an average Xe partial pressure of 180 Pa and a temperature of 291 K. On the other hand, as can be seen in Figure 5-12, the MTZ percentage is varying much more compared to the two previous indicators, with values ranging from 15 up to 40%. Interestingly, there are regular steps in the MTZ percentage, occurring between cycle 10 and 11, 12 and 13, 14 and 15, and, 17 and 18, which are corresponding to moments where the adsorbent was removed from the adsorption column, stored for a certain time and then poured back in the column. This is thus likely a consequence of a different packing in the adsorbent test bed and not of a degradation of the material itself as the equilibrium adsorption capacity is still reached.



Figure 5-13. Evolution of the Xe breakthrough curves just after a filling of the adsorption test bed with the Ag-ETS-10\_2 sample.

This is highlighted in Figure 5-13, where one breakthrough curve after each filling of the adsorption test bed, i.e. cycle 1, 11, 13, 15 and 20, is shown. As could be expected from the MTZ percentages, the shape and slope of the breakthrough curves are very different. This could be explained by a difference in packing after the different fillings, which gave rise to preferential channels for xenon where it encountered less adsorbent material at some locations within the adsorbent bed. This difference in packing was not observed on the measured pressure drop, as the pressure drop along the column, about 100 hPa, was driven by the stainless steel sintered wire mesh and remained at this value for all experiments with the Aq-ETS-10 2 sample. This could potentially be improved by using a less restrictive wire mesh or a more sensitive pressure drop sensor than the ones used in this work. The uniformity of the packing density could also potentially be improved by using different Ag-ETS-10\_2 particle sizes, which could better fill-in the gaps in the test bed. Shi et al. [163] demonstrated that by using two different Ag-ETS-10 2 particle sizes within the same adsorbent bed, a significant increase in packing density could be achieved.



*Figure 5-14. Evolution of the Xe breakthrough curves during the first filling of the adsorption test bed with the Ag-ETS-10\_2 sample.* 

In comparison, breakthrough curves measured during the first filling of the column, except for cycles 5 and 6 for the previously mentioned reasons, are shown in Figure 5-14. It is clear from the figure that the shape is very similar for all these breakthrough curves and the differences are within the measurement uncertainties.

In view of reducing the operational cost, the reuse of Ag-ETS-10 for successive adsorptions is a key aspect. As it was shown in the previous figures, Ag-ETS-10 can be reused for at least 20 times without a significant effect on the Xe adsorption properties. According to the obtained results, the packing of the material inside the adsorption column should be carefully executed and controlled in order to eliminate void spaces in between the adsorbent particles, which could cause a faster Xe breakthrough.

# 5.4.Conclusions

In this work, Xe adsorption capacities of five AgZs and three ACs were compared at RT. A silver-exchanged titanosilicate, Ag-ETS-10, showed a much higher Xe adsorption capacity than all other materials investigated in a range of Xe partial pressures relevant for MIPFs. The Xe adsorption capacity and Xe retention time at 10% breakthrough of this AgZ were demonstrated to be a factor 18 to 210 higher than these of a typical nuclear grade AC, depending on the Xe partial pressure and carrier gas. However, a decrease of Xe adsorption capacity was observed at 50% RH for this specific AgZ as well as for a Ag-Chabazite sample. Accordingly, the moisture content of the gas stream is a critical aspect for their use for radioxenon mitigation. For all other adsorbents, no significant effect of moisture could be observed on the Xe adsorption properties.

It was shown that the Xe adsorption kinetics in Ag-ETS-10 could be optimized by optimizing the column geometry and the flow rate of the inlet gas stream. This AgZ was shown to be resistant to a 1 MGy gamma irradiation as well as to 20 desorption/adsorption cycles, allowing the material to be reused for several successive Xe adsorptions. Furthermore, the Xe adsorption properties of Ag-ETS-10 were recovered after a desorption at a temperature as low as 423 K under a He flow.

Such an efficient Xe adsorption material could be used to further decrease radioxenon emissions from these MIPFs, which in turn would decrease their impact on the IMS network for the CTBT verification.

# 5.5.Acknowledgments

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# 5.6.Supplementary material

## 5.6.1. Comparison of Xe adsorption isotherms

Table S 5-1A. Experimental conditions and results for the Xe/He adsorption isotherms. The experiments were performed with column C3 and the Xe outlet concentration was measured with the mass spectrometer.

Adsorbent	Mass (g)	Xe conc. (ppm)	P (kPa)	Pxe (Pa)	Т (К)	qxe (mol kg⁻¹)
Ag-ETS-10_2	23.1	50	133	6.64	294	0.31
Ag-ETS-10_2	23.1	100	136	13.6	295	0.39
Ag-ETS-10_2	23.1	500	137	68.4	295	0.47
Ag-ETS-10_2	23.1	1000	134	134	295	0.49
Ag-ETS-10_2	23.1	50	135	6.74	293	0.33
Ag-ETS-10_2	23.1	100	135	13.5	293	0.41
Ag-ETS-10_2	23.1	500	131	65.3	293	0.49
Ag-ETS-10_2	23.1	1000	130	130	293	0.51
Ag_Chabazite_1	12.4	50	130	6.48	294	9.3 10 <sup>-3</sup>
Ag_Chabazite_1	12.4	100	128	12.8	294	1.9 10 <sup>-2</sup>
Ag_Chabazite_1	12.4	500	125	62.3	294	8.3 10-2
Ag_Chabazite_1	12.4	1000	126	126	294	0.14
Ag_Chabazite_1	12.4	50	126	6.29	295	1.0 10-2
Ag_Chabazite_1	12.4	100	129	12.9	294	2.1 10-2
Ag_Chabazite_1	12.4	500	129	64.6	294	9.1 10 <sup>-2</sup>
Ag_Chabazite_1	12.4	1000	127	127	294	0.15
Ag_Chabazite_2	18.4	50	127	6.35	300	1.8 10-2
Ag_Chabazite_2	18.4	100	125	12.5	300	3.6 10 <sup>-2</sup>
Ag_Chabazite_2	18.4	500	125	62.4	299	0.14
Ag_Chabazite_2	18.4	1000	125	125	299	0.21
Ag_Chabazite_2	18.4	50	124	6.21	300	2.0 10-2
Ag_Chabazite_2	18.4	100	124	12.4	299	4.3 10 <sup>-2</sup>
Ag_Chabazite_2	18.4	500	124	62.1	299	0.14
Ag_Chabazite_2	18.4	1000	125	125	299	0.24
Ag_Mordenite	59.6	50	125	6.26	298	3.8 10 <sup>-4</sup>
Ag_Mordenite	59.6	100	125	12.5	298	9.0 10 <sup>-4</sup>
Ag_Mordenite	59.6	500	125	62.3	298	3.0 10 <sup>-3</sup>
Ag_Mordenite	59.6	1000	125	125	298	4.7 10-3
Ag_Mordenite	59.6	50	125	6.23	300	4.7 10-4
Ag_Mordenite	59.6	100	127	12.7	299	7.9 10 <sup>-4</sup>
Ag_Mordenite	59.6	500	127	63.6	299	2.4 10 <sup>-3</sup>

			1			1
Ag_Mordenite	59.6	1000	127	127	299	3.9 10 <sup>-3</sup>
Norit RKJ 1	11.3	50	125	6.23	300	2.7 10 <sup>-3</sup>
Norit RKJ 1	11.3	100	124	12.4	300	5.2 10 <sup>-3</sup>
Norit RKJ 1	11.3	500	125	62.6	300	1.9 10 <sup>-2</sup>
Norit RKJ 1	11.3	1000	125	125	300	3.6 10 <sup>-2</sup>
Norit RKJ 1	11.3	50	125	6.23	298	2.2 10 <sup>-3</sup>
Norit RKJ 1	11.3	100	125	12.5	297	4.6 10 <sup>-3</sup>
Norit RKJ 1	11.3	500	125	62.4	296	1.8 10-2
Norit RKJ 1	11.3	1000	125	125	296	3.6 10 <sup>-2</sup>
Nusorb® GXK	11.3	50	128	6.41	294	4.4 10-3
Nusorb® GXK	11.3	100	128	12.8	294	7.9 10 <sup>-3</sup>
Nusorb® GXK	11.3	500	128	64.1	294	3.2 10 <sup>-2</sup>
Nusorb® GXK	11.3	1000	128	128	294	5.9 10 <sup>-2</sup>
Nusorb® GXK	11.3	50	129	6.43	295	3.4 10 <sup>-3</sup>
Nusorb® GXK	11.3	100	129	12.9	294	6.8 10 <sup>-3</sup>
Nusorb® GXK	11.3	500	129	64.3	294	3.1 10-2
Nusorb® GXK	11.3	1000	129	129	294	5.8 10 <sup>-2</sup>
Nuclearcarb® 203C	12.7	50	127	6.33	296	2.1 10-3
Nuclearcarb® 203C	12.7	100	127	12.7	295	3.9 10 <sup>-3</sup>
Nuclearcarb® 203C	12.7	500	127	63.4	295	2.3 10-2
Nuclearcarb® 203C	12.7	1000	127	127	294	4.7 10 <sup>-2</sup>
Nuclearcarb® 203C	12.7	50	127	6.34	296	2.0 10-3
Nuclearcarb® 203C	12.7	100	127	12.7	295	4.4 10 <sup>-3</sup>
Nuclearcarb® 203C	12.7	500	126	62.8	294	2.6 10 <sup>-2</sup>
Nuclearcarb® 203C	12.7	1000	127	127	294	5.0 10 <sup>-2</sup>

Adapathant	Mass	Xe conc.	Р	Рхе	т	qxe
Adsorbent	(g)	(ppm)	(kPa)	(Pa)	(K)	(mol kg <sup>-1</sup> )
Ag-ETS-10_2	45.0	50	137	6.87	296	5.9 10 <sup>-2</sup>
Ag-ETS-10_2	45.0	100	136	13.6	295	0.10
Ag-ETS-10_2	45.0	500	134	67.0	295	0.27
Ag-ETS-10_2	45.0	1000	134	134	296	0.34
Ag-ETS-10_2	45.0	50	138	6.89	294	5.6 10 <sup>-2</sup>
Ag-ETS-10_2	45.0	100	134	13.4	296	0.13
Ag-ETS-10_2	45.0	500	134	64.4	296	0.32
Ag-ETS-10_2	45.0	1000	134	134	296	0.41
Ag_Chabazite_1	12.4	50	130	6.48	295	6.2 10 <sup>-3</sup>
Ag_Chabazite_1	12.4	100	130	13.0	294	1.2 10 <sup>-2</sup>
Ag_Chabazite_1	12.4	500	126	62.7	294	5.6 10 <sup>-2</sup>
Ag_Chabazite_1	12.4	1000	127	127	294	0.10
Ag_Chabazite_1	12.4	50	130	6.48	295	6.1 10 <sup>-3</sup>
Ag_Chabazite_1	12.4	100	130	13.0	294	1.2 10 <sup>-2</sup>
Ag_Chabazite_1	12.4	500	130	64.8	294	5.4 10 <sup>-2</sup>
Ag_Chabazite_1	12.4	1000	130	130	294	9.9 10 <sup>-2</sup>
Ag_Chabazite_2	18.4	50	124	6.21	298	1.6 10-2
Ag_Chabazite_2	18.4	100	124	12.4	298	2.9 10 <sup>-2</sup>
Ag_Chabazite_2	18.4	500	124	61.7	298	0.12
Ag_Chabazite_2	18.4	1000	123	122	298	0.20
Ag_Chabazite_2	18.4	50	124	6.21	298	1.3 10-2
Ag_Chabazite_2	18.4	100	125	12.4	297	2.8 10 <sup>-2</sup>
Ag_Chabazite_2	18.4	500	125	62.2	297	0.11
Ag_Chabazite_2	18.4	1000	123	123	296	0.20
Ag_Mordenite	59.6	50	125	6.23	298	2.1 10 <sup>-4</sup>
Ag_Mordenite	59.6	100	126	12.6	298	3.9 10 <sup>-4</sup>
Ag_Mordenite	59.6	500	126	63.0	298	1.5 10-3
Ag_Mordenite	59.6	1000	125	125	298	2.6 10 <sup>-3</sup>
Ag_Mordenite	59.6	50	126	6.31	298	1.8 10-4
Ag_Mordenite	59.6	100	126	12.6	298	3.5 10-4
Ag_Mordenite	59.6	500	126	63.1	298	1.4 10-3
Ag_Mordenite	59.6	1000	125	125	298	2.3 10-3
Norit RKJ 1	11.3	50	126	6.30	295	2.1 10-3
Norit RKJ 1	11.3	100	126	12.6	295	4.2 10 <sup>-3</sup>

Table S 5-2. Experimental conditions and results for the Xe/N<sub>2</sub> adsorption isotherms. The experiments were performed with column C3 and the Xe outlet concentration was measured with the mass spectrometer.

11.3	500	126	63.0	295	2.0 10-2
11.3	1000	125	125	295	3.9 10 <sup>-2</sup>
11.3	50	126	6.31	294	2.3 10 <sup>-3</sup>
11.3	100	126	12.6	294	4.5 10 <sup>-3</sup>
11.3	500	126	63.1	294	2.1 10-2
11.3	1000	125	125	294	4.0 10-2
24.2	50	134	6.68	300	1.9 10 <sup>-3</sup>
24.2	100	130	13.0	294	4.4 10 <sup>-3</sup>
24.2	500	134	66.7	298	2.0 10-2
24.2	1000	134	133	299	3.6 10-2
24.2	50	134	6.69	301	1.8 10-3
24.2	100	131	13.1	294	4.6 10 <sup>-3</sup>
24.2	500	133	66.3	298	1.9 10 <sup>-2</sup>
24.2	1000	133	133	298	3.7 10 <sup>-2</sup>
12.7	50	125	6.25	294	2.1 10 <sup>-3</sup>
12.7	100	127	12.7	294	4.0 10-3
12.7	500	127	63.3	294	1.7 10-2
12.7	1000	126	126	294	3.2 10-2
12.7	50	127	6.33	295	1.8 10-3
12.7	100	127	12.7	295	3.5 10 <sup>-3</sup>
12.7	500	125	62.4	294	1.6 10-2
12.7	1000	126	125	294	3.2 10-2
	11.3      11.3      11.3      11.3      11.3      24.2      24.2      24.2      24.2      24.2      24.2      24.2      24.2      24.2      24.2      24.2      24.2      24.2      12.7      12.7      12.7      12.7      12.7      12.7      12.7      12.7      12.7      12.7      12.7      12.7      12.7      12.7      12.7	11.3      500        11.3      1000        11.3      50        11.3      100        11.3      500        11.3      500        11.3      500        11.3      500        24.2      500        24.2      500        24.2      500        24.2      500        24.2      500        24.2      500        24.2      500        24.2      500        24.2      500        24.2      500        24.2      500        12.7      50        12.7      100        12.7      500        12.7      50        12.7      1000        12.7      500        12.7      500        12.7      500        12.7      500        12.7      500        12.7      100        12.7      100	11.3      500      126        11.3      1000      125        11.3      50      126        11.3      100      126        11.3      500      126        11.3      500      126        11.3      500      126        11.3      500      126        11.3      1000      125        24.2      50      134        24.2      100      131        24.2      500      134        24.2      500      134        24.2      500      133        24.2      500      133        24.2      500      133        24.2      1000      133        24.2      1000      125        12.7      500      127        12.7      500      127        12.7      500      127        12.7      500      127        12.7      100      127        12.7      500      127        12.7      500 <th>11.350012663.011.3100012512511.3501266.3111.31001266.3111.350012663.111.350012663.111.3100012512524.25001346.6824.210013466.724.25001346.6924.25001346.6924.25001346.6924.25001336.3124.25001336.3124.25001336.2524.2100013313324.25001336.2512.75001276.2512.75001276.3312.75001276.3312.75001276.3312.75001276.3412.75001276.3412.75001276.3412.75001276.3412.75001276.3412.750012562.412.750012562.412.750012562.412.750012562.412.750012562.412.750012562.412.750012562.412.750012562.412.75001</th> <th>11.350012663.029511.3100012512529511.3501266.3129411.31001266.3129411.350012663.129411.350012663.129411.350012663.129411.350012663.129411.3100012512529424.25001346.6830024.250013466.729824.25001346.6930124.25001346.6930124.25001346.6930124.25001336.3329824.2100013313329812.75001256.2529412.750012712.729412.75001276.3329512.7100012712.729512.75001276.3329512.75001276.3329512.75001276.3329512.75001276.3329512.750012562.429412.750012562.429412.750012562.429412.750012562.429412.750012562.4<!--</th--></th>	11.350012663.011.3100012512511.3501266.3111.31001266.3111.350012663.111.350012663.111.3100012512524.25001346.6824.210013466.724.25001346.6924.25001346.6924.25001346.6924.25001336.3124.25001336.3124.25001336.2524.2100013313324.25001336.2512.75001276.2512.75001276.3312.75001276.3312.75001276.3312.75001276.3412.75001276.3412.75001276.3412.75001276.3412.75001276.3412.750012562.412.750012562.412.750012562.412.750012562.412.750012562.412.750012562.412.750012562.412.750012562.412.75001	11.350012663.029511.3100012512529511.3501266.3129411.31001266.3129411.350012663.129411.350012663.129411.350012663.129411.350012663.129411.3100012512529424.25001346.6830024.250013466.729824.25001346.6930124.25001346.6930124.25001346.6930124.25001336.3329824.2100013313329812.75001256.2529412.750012712.729412.75001276.3329512.7100012712.729512.75001276.3329512.75001276.3329512.75001276.3329512.75001276.3329512.750012562.429412.750012562.429412.750012562.429412.750012562.429412.750012562.4 </th

Table S 5-3. Experimental conditions and results for the comparison of Ag-ETS-10\_2 and Nusorb® GXK. The experiments were performed with column C3. The Xe detection instrument, either a Mass Spectrometer (MS) or a Thermal Conductivity Detector (TCD), used for each experiment is indicated in the last column.

Adsorbent	Gas	Mass (g)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	Pxe (Pa)	Т (К)	<b>t</b> 10%	q <sub>xe</sub> (mol kg <sup>-1</sup> )	MTZ (%)	Det.
Ag-ETS-10_2	He	23.1	400	133	6.64	294	92 h	0.31	39	MS
Ag-ETS-10_2	He	23.1	400	131	131	294	7.6 h	0.49	32	MS
Nusorb® GXK	He	11.3	400	129	6.43	295	26 min	3.4 10 <sup>-3</sup>	68	MS
Nusorb® GXK	He	11.3	400	129	129	295	23 min	5.4 10 <sup>-2</sup>	55	MS
Ag-ETS-10_2	N2	45.0	400	136	13.6	295	29 h	0.10	50	MS
Ag-ETS-10_2	N2	45.0	400	136	136	292	15 h	0.45	15	TCD
Nusorb® GXK	N2	24.2	400	130	13.0	294	35 min	4.4 10 <sup>-3</sup>	71	MS
Nusorb® GXK	N2	24.2	400	132	132	292	37 min	4.7 10 <sup>-2</sup>	65	TCD

Table S 5-4. Experimental conditions and results for the comparison of the Aq-ETS-10 1 and Aq-ETS-10 2 samples. The carrier gas was He. The experiments were performed with column C1 and the Xe outlet concentration was measured with the thermal conductivity detector.

Sample	Mass (g)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	Pxe (Pa)	Т (К)	t10% (h)	q <sub>xe</sub> (mol kg <sup>-1</sup> )	MTZ (%)
Ag-ETS-10_1	25.9	319	173	173	296	9.0	0.60	37
Ag-ETS-10_1	25.9	322	175	175	296	9.1	0.62	38
Ag-ETS-10_2	26.8	334	185	185	290	11	0.71	19
Ag-ETS-10_2	26.8	334	185	185	294	12	0.73	22

Adsorbent	Mass (g)	Dewpoint (K)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	Pxe (Pa)	Т (К)	<b>t</b> 10%	q <sub>xe</sub> (mol kg <sup>-1</sup> )
Ag-ETS-10_2	45.0	221	800	136	34.1	293	18 h	0.29
Ag-ETS-10_2	45.0	255	800	137	34.4	294	15 h	0.24
Ag-ETS-10_2	45.0	282	800	138	34.5	296	7.5 h	9.1 10 <sup>-3</sup>
Ag-Chabazite_1	12.4	228	400	128	32.0	295	59 min	3.1 10-2
Ag-Chabazite_1	12.4	256	400	127	31.8	294	58 min	2.9 10 <sup>-2</sup>
Ag-Chabazite_1	12.4	283	400	127	31.7	296	52 min	2.8 10 <sup>-2</sup>
Ag-Chabazite_2	16.0	222	400	124	31.0	299	2.8 h	6.7 10 <sup>-2</sup>
Ag-Chabazite_2	16.0	256	400	124	31.0	299	2.8 h	7.0 10 <sup>-2</sup>
Ag-Chabazite_2	16.0	286	400	124	30.9	301	2.2 h	1.1 10-2
Ag-Mordenite	59.6	225	400	126	31.5	299	4.0 min	7.9 10 <sup>-4</sup>
Ag-Mordenite	59.6	254	400	125	31.1	301	3.8 min	8.6 10 <sup>-4</sup>
Ag-Mordenite	59.6	263	400	125	31.1	299	4.1 min	9.3 10-4
Norit RKJ 1	11.3	228	400	126	31.5	295	16 min	1.1 10-2
Norit RKJ 1	11.3	255	400	126	31.5	297	15 min	1.1 10-2
Norit RKJ 1	11.3	284	400	126	31.6	297	16 min	1.1 10-2
Nusorb® GXK	24.2	226	400	133	33.1	294	34 min	1.1 10-2
Nusorb® GXK	24.2	252	400	131	32.8	293	37 min	1.5 10-2
Nusorb® GXK	24.2	282	400	132	32.9	294	35 min	1.2 10-2
Nuclearcarb® 203C	12.7	227	400	126	31.6	294	15 min	8.7 10 <sup>-3</sup>
Nuclearcarb® 203C	12.7	255	400	126	31.4	295	15 min	8.5 10-3
Nuclearcarb® 203C	12.7	283	400	126	31.5	296	15 min	9.1 10 <sup>-3</sup>

Table S 5-5. Experimental conditions and results for investigating the effect of moisture. The carrier gas was  $N_2$ . The experiments were performed with column C3 and the Xe outlet concentration was measured with the mass spectrometer.

## 5.6.2. Applicability of Ag-ETS-10 for radioxenon mitigation

Table S 5-6. Experimental conditions and results for investigating the effect of inlet concentration on the Ag-ETS-10\_2 sample. The Xe detection instrument, either a Mass Spectrometer (MS) or a Thermal Conductivity Detector (TCD), used for each experiment is indicated in the last column. The carrier gas was N<sub>2</sub> and the experiments were performed with column C2.

Adsorbent	Mass (g)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	Pxe (Pa)	Т (К)	<b>t</b> 10%	qxe (mol kg⁻¹)	MTZ (%)	Det.
Nusorb GXK	24.2	400	130	13.0	294	35 min	4.4 10 <sup>-3</sup>	71	MS
Nusorb GXK	24.2	400	131	13.1	294	37 min	4.6 10 <sup>-3</sup>	67	MS
Nusorb GXK	24.2	400	132	132	292	37 min	4.7 10 <sup>-2</sup>	62	TCD
Nusorb GXK	24.2	400	132	132	294	35 min	4.4 10 <sup>-2</sup>	69	TCD
Ag-ETS-10_2	45.0	400	136	13.6	295	29 h	0.11	50	MS
Ag-ETS-10_2	45.0	400	134	13.4	296	36 h	0.13	49	MS
Ag-ETS-10_2	45.0	400	136	136	292	15 h	0.45	15	TCD
Ag-ETS-10_2	45.0	400	136	136	293	15 h	0.45	16	TCD

Table S 5-7. Experimental conditions and results for investigating the effect of column geometry on the Ag-ETS-10\_2 sample. The carrier gas was He and the Xe outlet concentration was measured with the thermal conductivity detector.

Column	Mass (g)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	Pxe (Pa)	Т (К)	t10% (h)	q <sub>Xe</sub> (mol kg-1)	MTZ (%)
C1	21.6	334	185	185	294	5.4	0.69	90
C2	21.6	329	181	181	289	9.4	0.72	27

Table S 5-8. Experimental conditions and results for investigating the effect of flow rate on the Ag-ETS-10\_2 sample. The experiments were performed with column C2 and the carrier gas was He. The Xe outlet concentration was measured with the mass spectrometer.

Mass (g)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	P <sub>Xe</sub> (Pa)	Т (К)	t10% (h)	qxe (mol kg⁻¹)	MTZ (%)
23.1	280	130	130	294	11	0.46	24
23.1	400	131	131	294	7.6	0.49	32
23.1	1400	138	138	295	2.0	0.50	55
23.1	2800	148	148	295	1.0	0.55	62

Table S 5-9. Experimental conditions and results before and after irradiation of the Ag-ETS-10\_2 sample. The experiments were performed with column C2 and the carrier gas was He. The Xe outlet concentration was measured with the thermal conductivity detector.

	Mass (g)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	Pxe (Pa)	Т (К)	t10% (h)	q <sub>xe</sub> (mol kg <sup>-1</sup> )	MTZ (%)
Defens invediation	21.6	325	178	178	289	8.2	0.67	40
Before irradiation	21.6	326	178	178	290	8.4	0.68	38
	21.6	325	177	177	289	8.8	0.64	28
After irradiation	21.6	326	178	178	290	8.8	0.63	26

Table S 5-10. Experimental conditions and results for the comparison between adsorption at room temperature and at 333 K on the Ag-ETS-10\_2 sample. The experiments were performed with column C2 and the carrier gas was He. The Xe outlet concentration was measured with the thermal conductivity detector.

Mass (g)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	Pxe (Pa)	Т (К)	t10% (h)	qxe (mol kg⁻¹)	MTZ (%)
21.6	320	173	173	294	9.2	0.62	20
21.6	319	174	174	297	9.0	0.59	20
21.6	320	173	173	333	7.0	0.22	21
21.6	319	172	172	333	7.1	0.28	19

Table S 5-11. Experimental conditions and results during the investigation of the desorption temperature on the Ag-ETS-10\_2 sample. The experiments were performed with column C2 and the carrier gas was He. The Xe outlet concentration was measured with the thermal conductivity detector. During the desorption, the set point was maintained for 3 hours.

	D	esorption	n		Adsorption						
M (g)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	Tset (K)	Tint (K)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	P <sub>Xe</sub> (Pa)	Т (К)	t10% (h)	qxe (mol kg⁻¹)	MTZ (%)
21.6	69	135	423	409	328	180	180	289	9.2	0.70	24
21.6	69	135	473	444	328	180	180	289	9.5	0.73	27
21.6	69	136	523	494	329	180	180	289	9.4	0.73	29

Table S 5-12. Experimental conditions and results during the investigation of the desorption gas on the Ag-ETS-10\_2 sample. The experiments were performed with column C2. He was used as carrier gas for the adsorption. The Xe outlet concentration was measured with the thermal conductivity detector. During the desorption, the set point was maintained for 3 hours. The mass of Ag-ETS-10\_2 was 21.6 g.

D	esorpti	on		Adsorption							
F (cm <sup>3</sup> min <sup>-1</sup> )	Gas	P (kPa)	Tint. (K)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	P <sub>Xe</sub> (Pa)	т (К)	t10% (h)	qxe (mol kg⁻¹)	MTZ (%)	
67	He	129	484	321	174	174	297	8.4	0.59	20	
62	N2	110	485	320	173	173	296	8.9	0.61	15	

Table S 5-13. Experimental conditions and results during the 20 adsorption/desorption cycles on the Ag-ETS-10\_2 sample. The experiments were performed with column C2. He was used as carrier gas for the adsorption. The Xe outlet concentration was measured with the thermal conductivity detector. During the desorption, the set point was maintained for 3 hours. The mass of Ag-ETS-10\_2 was 21.6 g.

	D	esorpti	on	Adsorption							
#	F (cm <sup>3</sup> min <sup>-1</sup> )	Gas	P (kPa)	Tint. (K)	F (cm <sup>3</sup> min <sup>-1</sup> )	P (kPa)	Pxe (Pa)	т (К)	t10% (h)	qxe (mol kg⁻¹)	MTZ (%)
1	69	He	136	488	329	181	181	289	9.4	0.72	27
2	69	He	136	494	329	180	180	289	9.4	0.73	29
3	69	He	136	505	329	181	181	288	9.4	0.74	29
4	69	He	135	409	328	180	180	289	9.2	0.70	24
5	64	N2	118	408	328	180	180	288	7.1	0.52	19
6	64	N2	117	400	328	180	180	290	6.4	0.45	19
7	69	He	135	444	328	180	180	289	9.3	0.73	27
8	69	He	134	448	327	179	179	288	9.2	0.67	32
9	68	He	133	450		Puls	ed adsor	ption ex	perimer	nt	
10	69	He	134	455		Puls	ed adsor	ption e>	perimer	nt	
	Adsor	rbent w	as remov	ved fro	m the test bed	and refill	ed after	r 21 da	ys of st	orage	
11	69	He	136	495	325	178	178	289	8.2	0.67	40
12	68	He	133	499	326	178	178	290	8.4	0.68	38
	Adsorbent	was rer	noved fro	om the	test bed for ga	mma irra	diation	and re	filled at	fter 13 days	
13	67	He	130	506	325	177	177	289	8.8	0.64	28
14	68	He	133	506	326	178	178	290	8.8	0.63	26
	Adsor	rbent w	as remov	ved fro	m the test bed	and refill	ed after	r 74 da	ys of st	orage	
15	67	He	129	484	321	174	174	297	8.4	0.59	20
16	62	N2	110	485	320	173	173	296	8.9	0.61	15
17	66	He	127	499		Puls	ed adsor	ption e>	kperimer	nt	
	Adso	rbent w	as remov	ved fro	m the test bed	and refill	ed after	r 19 da	ys of st	orage	
18	66	He	127	496	320	173	173	333	7.0	0.22	21
19	66	He	126	489	319	172	172	333	7.1	0.28	18
20	66	He	126	499	318	172	172	294	9.2	0.62	20

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# **Chapter 6**

# Durability of silverexhanged zeolites

	Research objective	Main evaluation metrics
4	Assess the durability of Ag-ETS-10 and Ag-ZSM-5 after multiple thermal regeneration cycles as well as after irradiation	Xe adsorption capacity and structural characterization

#### **Graphical abstract**



# 6. Durability of silver-exchanged zeolites

In this chapter addressing the fourth research objective, the durability of Ag-ZSM-5, a silver-exchanged zeolite (AgZ), and Ag-ETS-10, a silver-exchanged titanosilicate, against radiation and thermal regeneration cycles is investigated. Ag-ETS-10 will be classified as AgZ in the following due to the strong similarity with zeolites. From Chapters 3 and 5, it is clear that Ag-ETS-10 and Ag-ZSM-5 are promising candidates for a more efficient radioxenon trapping at fission-based Medical Isotope Production Facilities (MIPFs) as well as for a more efficient Xe collection and separation from dry air. For their use in radioxenon mitigation, their radiation resistance, in conditions similar to the ones encountered in MIPFs, needs to be verified. Similarly, for the use in Xe collection and Xe separation, their durability against successive thermal regeneration cycles needs to be confirmed. For this investigation, the durability is assessed by Xe adsorption measurements as well as complementary structural characterization techniques.

This chapter is based on the following published paper:

Gueibe, C., Rutten, J., Moyaux, D., Camps, J., Schroeyers, W., Gryglewicz, G., Derveaux, E., Hasan, MD. M., & Schreurs, S. (2024). Radiation resistance and durability against thermal regeneration cycles of Ag-ETS-10 and Ag-ZSM-5 for collecting radioxenon. *Process Safety and Environmental Protection, 188, 1423-1436*. DOI: <u>10.1016/j.psep.2024.06.057</u>

#### Abstract

Efficient porous adsorbents are crucial for: the mitigation of radioxenon emissions from nuclear installations, the production of Xe and for the detection of clandestine nuclear weapon tests. AgZs, specifically Ag-ZSM-5 and Ag-ETS-10, are promising candidates for these applications. However, knowledge on their radiation resistance is lacking and further research is necessary on their durability against thermal regeneration cycles. The radiation resistance was investigated for the first time by in situ irradiation with <sup>133</sup>Xe up to about 100 MGy on Ag-ETS-10 and Aq-ZSM-5. In parallel, the durability of non-irradiated samples against at least 43 thermal regeneration cycles was investigated on both adsorbents. Fresh, irradiated and thermally regenerated samples were analysed using different characterization techniques. The characterizations, and more specifically Xe adsorption at 296 K, did not show particular alterations due to the irradiation and thermal regeneration cycles. This is a major step forward for more efficient radioxenon trapping as it proves that both adsorbents can be used up to these irradiation levels and withstand 43 thermal regeneration cycles without any significant loss of Xe adsorption performance. Noteworthy, peak shifting and broadening were observed in the <sup>29</sup>Si Nuclear Magnetic Resonance (NMR) signals of irradiated Aq-ETS-10 due to the paramagnetic <sup>133</sup>Cs decay product.

### 6.1.Introduction

AgZs or silver-exchanged zeolite-like frameworks are known to have a particularly strong adsorption affinity for Xe below a certain pressure [138, 142, 144, 145], as confirmed in Chapters 3 and 5. Due to the strong affinity, these adsorbents are promising candidates for a more efficient: i) radioxenon trapping or separation in nuclear installations [181, 339], and ii) separation of trace levels of stable or radioactive Xe from air [98, 200, 311]. An even stronger adsorption affinity was observed for Rn on AgZs with also a promising potential for trapping the Rn decay product of <sup>226</sup>Ra [201, 312, 340]. Using these AgZs for such applications requires a thorough investigation of their durability, amongst others against thermal regeneration cycles. Trapping radioactive noble gases in nuclear installations additionally requires the assessment of their radiation resistance.

During the fission of uranium, a spectrum of fission fragments is produced as shown in Figure 1-4 in Chapter 1. Some of these fission products can be used in radioactive pharmaceuticals for medical applications [341]. This is the case for <sup>99</sup>Mo (half-life of 66 hours), which is used as a generator for its shorter lived decay product <sup>99m</sup>Tc (half-life of 6 hours). <sup>99m</sup>Tc is used as a radioactive tracer for medical diagnostic imaging and represents about 80% of all nuclear medicine procedures [116]. Most of the <sup>99</sup>Mo, used as generator of <sup>99m</sup>Tc, is produced by fission of uranium targets [116]. The remainder of <sup>99</sup>Mo is produced by alternative routes such as neutron activation of <sup>98</sup>Mo targets and high energy gamma irradiation of <sup>100</sup>Mo [342].

The uranium targets are irradiated in research reactors to fission the uranium and produce, amongst others, <sup>99</sup>Mo as a fission fragment. The <sup>99</sup>Mo contained in the irradiated uranium targets needs to be recovered by a separation and purification process. This is done in dedicated facilities, hereafter called MIPFs, by dissolving the uranium targets, in an alkaline or acidic solution, followed by multiple steps to gradually separate <sup>99</sup>Mo from other fission products and reach the necessary purity [342]. During the dissolution and separation processes, other fission products are separated from the uranium targets. The presence of volatile radioelements poses particular challenges as they need to be safely controlled to ensure the protection of workers, the public, and the environment [121]. In particular, radioiodine and radioxenon isotopes need to be trapped for a sufficient time before being released to the atmosphere to minimize the impact on the public and environment. Retention systems are used to allow these isotopes to decay to the activity levels, authorized by national regulations, that can be released.

As briefly discussed in Section 1.4, different methods, sometimes used in combination, are currently used to retain the radioxenon isotopes: i) adsorption on activated carbon (AC) beds, ii) cryo-trapping and iii) holding tanks [114]. The Xe adsorption capacity of AC is very low at room temperature (RT), but it increases with decreasing temperatures [124]. More efficient and non-combustible adsorbents (as AC poses a risk of fire [114]) for radioxenon could reduce the footprint of the adsorption columns and simplify the retention process whilst improving the safety.

As shown in Section 1.3.2, the regulated radioxenon releases from MIPFs are still high enough to be observed in the ultra-sensitive worldwide monitoring network, the International Monitoring System (IMS), operated for the verification of the Comprehensive Nuclear-Test-Ban Treaty (CTBT) [77, 90, 343]. Bowyer et al. [119] concluded that an emission of 5  $10^9$  Bq day<sup>-1</sup> for <sup>133</sup>Xe from a MIPF is an acceptable upper bounding target from the perspective of minimal impact to nuclear explosion monitoring stations. As discussed in Chapter 5, this would require the largest radioxenon emitting MIPF to increase their current <sup>133</sup>Xe retention time by 40 to 57 days [181]. This can only be achieved by finding more efficient adsorbents to keep the volume of adsorbent small enough which allows an application close to the source.

In Chapter 5, our research demonstrated that the volume of adsorbent (at RT) to retain a certain amount of Xe, in conditions relevant for a MIPF, could be reduced by a factor 18 to 185, depending on the carrier gas ( $N_2$  or He) and Xe concentration (50 to 1000 ppm), by using Ag-ETS-10 instead of a typical nuclear grade AC (Nusorb® GXK) [181]. Similarly, Monpezat et al. [141] showed that the Xe adsorption capacity, for a mixture of 400 ppm Xe and 40 ppm Kr in air, is increased by a factor of about 20 when going from an AC to Ag-ZSM-5. Both Ag-ETS-10 and Ag-ZSM-5 are clearly promising materials for reducing the radioxenon emissions from MIPFs by retaining radioxenon more efficiently at RT.

The radiation resistance and durability against thermal regeneration cycles is a crucial aspect to be investigated for operational use of AgZs to further reduce radioxenon emissions from nuclear installations. In Chapter 5, it has already been shown that Aq-ETS-10 can withstand a homogeneous 1 MGy gamma irradiation without losing its Xe adsorption capacity [181]. However, Ag-ETS-10 can retain Xe so efficiently that 1 MGy would represent only a few hours of operation in a MIPF [181]. Accordingly, further investigations on the radiation resistance of Ag-ETS-10 at higher absorbed doses are needed. To the best of our knowledge, there have been no reports on the radiation resistance of Aq-ZSM-5. In Chapter 5, the durability of Ag-ETS-10 against 20 thermal regeneration cycles, performed at temperatures between 443 and 503 K under a He flow, was investigated and demonstrated no degradation on the Xe adsorption performance [181]. Similarly, it was shown that Ag-ZSM-5 could withstand 25 thermal regeneration cycles, performed at 573 K under  $N_2$ , without significant degradation of the Xe adsorption performance as long as no chlorine-containing volatile organic compounds were present during the adsorption part of the cycles [171]. Further studies on a higher number of thermal regeneration cycles, and performing cycles in different conditions, would support the operational use of these adsorbents in MIPFs.

On another relevant topic, we demonstrated in Chapter 3 that Xe can be efficiently collected and separated directly from dry atmospheric air on Ag-ETS-10 and Ag-ZSM-5. Both adsorbents could be used to perform a more energy-efficient collection and separation of Xe from air for the production of stable Xe and for the low-level detection of atmospheric radioxenon in the IMS. The durability against thermal regeneration cycles is of relevance in this context as well.

In this work, the authors first compared the Xe adsorption performance of Ag-ETS-10 and Ag-ZSM-5, together with the best-reported adsorbents, in conditions relevant for radioxenon trapping at MIPFs. For the first time, the radiation resistance of Ag-ETS-10 and Ag-ZSM-5 was investigated under extreme irradiation conditions as would be encountered in MIPFs. In addition, the durability against thermal regeneration cycles for both AgZs was investigated further than the currently reported durability studies.

# 6.2. Materials and methods

Two promising AgZs (*i.e.* Ag-ETS-10 and Ag-ZSM-5) were selected for this study (Section 6.2.1). The Xe adsorption properties were determined by breakthrough measurements (Section 6.2.2). Two aging processes were investigated: thermal regeneration cycles (Section 6.2.3) and irradiation (Section 6.2.4). A convection-diffusion-adsorption model, detailed in Section 6.2.5, was used to simulate the activity distribution during the irradiation. As explained in Section 6.2.6, the activity distribution was then used in a Monte Carlo code (PENELOPE) to estimate the absorbed dose in the irradiated samples by simulating the coupled electron-photon transport. Both fresh and aged samples were characterized by SEM/EDX, PXRD, by N<sub>2</sub> adsorption-desorption at 77 K and by CO<sub>2</sub> adsorption at 273 K (Sections 6.2.7 to 6.2.9). In addition, the samples were characterized by  $^{27}$ Al- and  $^{29}$ Si solid-state NMR spectroscopy as detailed in Section 6.2.10. The decay product, *i.e.*  $^{133}$ Cs, content in irradiated samples was determined by X-Ray Fluorescence (XRF) (Section 6.2.11).

The materials and methods that are common to multiple chapters (indicated in the yellow box in Figure 6-1) are described in full details in Chapter 2, whereas materials and methods specific to the current chapter are detailed in the following sections.



Figure 6-1. Materials and methods used in Chapter 6.

#### 6.2.1. Adsorbents

The samples, Ag-ETS-10\_2 (silica bound) and Ag-ZSM-5, used in this work are described in Section 2.1.

#### 6.2.2. Xe breakthrough experiments

The Xe adsorption properties were determined by Xe breakthrough measurements with the methodology described in Section 2.2.

#### 6.2.3. Thermal regeneration cycles

In total, 44 and 43 thermal regeneration cycles were executed on Ag-ETS-10 and Ag-ZSM-5, respectively. The thermal regeneration cycles were performed on column C3 (Section 2.2.1) filled with 13.1 and 13.6 g of Ag-ETS-10 and Ag-ZSM-5, respectively. The regeneration conditions for each cycle are summarized in Table 6-1.

Table 6-1. Regeneration conditions (duration,	temperature and gas) used on
both adsorbents during the thermal	l regeneration cycles.

Cycles Adsorbent		Gas	t (h)	Т (К)	
1-41	Ag-ETS-10 & Ag-ZSM-5	N <sub>2</sub>	0.8 - 14.5		
42	Ag-ETS-10	Air/N <sub>2</sub>	7.8/2.4	105	
42	Ag-ZSM-5	Air/N <sub>2</sub>	7.8/1.3	405	
43	Ag-ETS-10	N <sub>2</sub>	6.4		
43	Ag-ZSM-5	N <sub>2</sub>	3.3	EDE	
44	Ag-ETS-10	N <sub>2</sub>	7.7	535	

The regeneration duration varied from 0.8 to 14.5 hours depending on two aspects: i) when the Xe partial pressure reached the background level of  $10^{-13}$  mbar, which depends on the Xe concentration used during the breakthrough measurement, and ii) when there was an opportunity to stop the regeneration after reaching the background level as it was performed manually. Up to and including the  $41^{st}$  cycle, all regenerations were performed on both adsorbents with the same gas and temperature. A  $42^{nd}$  cycle was performed to check potential degradations of the AgZs with a thermal regeneration under air followed by N<sub>2</sub> to desorb potential air components. The  $43^{rd}$  cycle for Ag-ETS-10 was done with the same gas and temperature as for cycles 1 to 41. The last cycle on each adsorbent, *i.e.*  $44^{th}$  for Ag-ETS-10 and  $43^{rd}$  for Ag-ZSM-5, focused on the effect of a higher thermal regeneration temperature (*i.e.* 535 K). Samples of about 1 g were taken from the column for further characterizations at cycle 20 for both adsorbents, at cycle 43 for Ag-ZSM-5 and at cycle 44 for Ag-ETS-10. After each regeneration, a Xe breakthrough measurement was performed under different conditions.

The Xe concentration in air and the flow rate used for the breakthrough measurement after each cycle are shown in Figure 6-2 for both adsorbents. The detailed experimental conditions for each cycle can be found in Supplementary material Table S 6-1 and Table S 6-2.



Figure 6-2. Xe concentration in air and flow rate used during the breakthrough measurements after each thermal regeneration cycle for a) Ag-ETS-10 and b) Ag-ZSM-5.

The relative variation of the Xe adsorption capacity and retention volume at 50% breakthrough was used as a metric for all cycles to investigate the durability of the adsorbents. Finally, the Mass Transfer Zone (MTZ), as given in Equation 2-2 in Chapter 2, was used as a metric for comparing Xe breakthrough curves performed with the same Xe concentration and flow rate.

#### 6.2.4. In situ irradiation: experimental set-up

For the in situ irradiation, purified <sup>133</sup>Xe from the production process at the Institute of RadioElements (IRE), Belgium, was used. The <sup>133</sup>Xe vials contained 53 and 48 TBq for the irradiation experiment on Ag-ETS-10 and Ag-ZSM-5, respectively. These vials contained in total, *i.e.* including the stable Xe isotopes, 114 and 113 mg of Xe for Ag-ETS-10 and Ag-ZSM-5, respectively.

Masses of 30.5 and 26.6 g of Ag-ETS-10 and Ag-ZSM-5, respectively, were packed in C6 columns, positioned vertically in the system, as depicted in Figure 6-3a). For a 1000 ppm Xe in N<sub>2</sub> mixture, these masses of Ag-ETS-10 and Ag-ZSM-5 can retain 1650 mg of Xe [311]. These masses are clearly large enough, even when considering deviations from the assumed mixture and the kinetics of the adsorption, to retain the total amount of Xe contained in the <sup>133</sup>Xe vials, which ensured that all the irradiation would occur in the adsorbent. For radiation safety purposes during the irradiation, the columns were fitted in a system with 1 cm lead shielding all around as shown in Figure 6-3b). Thermal regeneration of the adsorbent was possible with two nozzle band heaters (International Heating Products), covering each a 6 cm length of the column, on both columns. The regeneration was controlled by a temperature controller (TC Direct, 304-200) in combination with a thermocouple (type K) on the external surface of the column.



Figure 6-3. Pictures of the irradiation system. a) Side view of the irradiation system containing two stainless steel columns, one filled with Ag-ETS-10 and the other with Ag-ZSM-5. b) Top view of the irradiation system with the 1 cm lead shielding installed.

Before the irradiation experiment, a reference Xe breakthrough measurement, with 10 ppm Xe in N<sub>2</sub> at 500 cm<sup>3</sup> min<sup>-1</sup>, was performed twice on the regenerated adsorbents to check the initial Xe adsorption properties. These initial measurements were finalized by a regeneration at 483 K under a N<sub>2</sub> flow at 400 cm<sup>3</sup> min<sup>-1</sup> on both adsorbents prior to transporting the system to IRE for the irradiation.



Figure 6-4. Schematic representation of the irradiation experiment. The collimated Geiger-Müller 1 (GM1) tube is monitoring the inlet of the column, whereas GM2 is monitoring the outlet.

The system was then installed at IRE with, as depicted in Figure 6-4, the inlet of the relevant column connected to the vial containing the purified <sup>133</sup>Xe. The other side of the vial was connected to a high purity N<sub>2</sub> cylinder to displace the <sup>133</sup>Xe gas, at a flow rate of about 400 cm<sup>3</sup> min<sup>-1</sup>, towards the adsorption column. The radioactive content of the gas line in between the <sup>133</sup>Xe vial and the adsorption column was monitored with a collimated Geiger-Müller tube (GM1). In a similar fashion, the gas line at the outlet of the column was also measured with a GM tube (GM2) to ensure that no <sup>133</sup>Xe was leaving the adsorption column during its adsorption. Once the <sup>133</sup>Xe was completely transferred to the adsorption column as observed from GM1 and GM2, the column was isolated for 8 days by manual valves just before and after the column. The temperature of the external surface of the stainless steel column was monitored during the adsorption of <sup>133</sup>Xe. The

After 8 days of irradiation, the adsorbents were regenerated at IRE at 483 K under a He flow at about 400 cm<sup>3</sup> min<sup>-1</sup> to remove the remaining  $^{133}$ Xe. The residual radioxenon activity in each column was characterized by collimated in situ High Purity Ge (HPGe) gamma spectrometry after the regeneration. As the residual activity (6 orders of magnitude lower than the initial activity), from <sup>133</sup>Xe together with some <sup>131m</sup>Xe, in the column with Aq-ETS-10 was still higher than the exemption level, this column was regenerated for longer periods of time and up to 523 K. The system was transported back to the SCK CEN laboratory for further characterization once the residual activity was below the exemption level. At the SCK CEN laboratory, the column containing Ag-ETS-10 was regenerated under a  $N_2$  flow at 200 cm<sup>3</sup> min<sup>-1</sup> up to 543 K in an attempt to reduce the residual activity. No noticeable reduction was observed in the counts of the 164 keV peak of  $^{131m}Xe$ as measured with a HPGe gamma spectrometer (Mirion, Aegis<sup>TM</sup>). As the residual activity in the column containing Ag-ZSM-5 was low enough, the regeneration was performed under the standard regeneration conditions used for this research, *i.e.* at 493 K under a N<sub>2</sub> flow at 200 cm<sup>3</sup> min<sup>-1</sup>. After the regeneration, a Xe breakthrough measurement, with 10 ppm Xe in  $N_2$  at 500 cm<sup>3</sup> min<sup>-1</sup>, was again performed twice on the regenerated adsorbents to assess the Xe adsorption properties after irradiation. The columns were then emptied by taking subsamples of 1 cm height starting from the material at the inlet-side of the column.

#### 6.2.5. In situ irradiation: modelling

To determine the activity distribution during the irradiation experiment, the mass transport phenomena in the adsorption column were modelled with the COMSOL Multiphysics® software using a similar approach as Ladshaw et al. [344]. The geometry of the adsorption column is depicted in Figure 6-5.

First the stationary gas flow in the adsorption column was modelled using the continuity equation and by considering a laminar flow (as the Reynolds number was 30 at the maximum, *i.e.* in the inlet tube, at 400 cm<sup>3</sup> min<sup>-1</sup>) of an incompressible fluid and by using Darcy's Law, as shown in Equation 6-1, for the velocity field in the porous materials.

$$\vec{u} = -\frac{\kappa}{\varepsilon \, \mu} \vec{\nabla} P$$
 Equation 6-1

In Equation 6-1,  $\vec{u}$  [m s<sup>-1</sup>] is the velocity field,  $\kappa$  [m<sup>2</sup>] and  $\epsilon$  [-] are the permeability and porosity of the porous media, respectively, and  $\mu$  [Pa s] and P [Pa] are the viscosity and pressure of the gas, respectively.



Figure 6-5. Adsorption column geometry used in COMSOL Multiphysics® and in the PENELOPE code. The axis corresponds to the vertical direction. The adsorbent volume in this figure is for Ag-ETS-10, the volume was higher for Ag-ZSM-5 due to its lower packing density.

At the inlet boundary, the normal inflow velocity was set as the fluid volumetric flow rate (F [m<sup>3</sup> s<sup>-1</sup>]) through the inlet tube cross section (A<sub>inlet</sub> [m<sup>2</sup>]). At the outlet boundary, the pressure (P<sub>out</sub> [Pa]) was fixed to the pressure measured at the inlet (P<sub>in</sub> [Pa]), by the corresponding sensor, from which the pressure drop ( $\Delta$ P [Pa]), as measured with the necessary sensor, on the column was subtracted. The permeability is optimized to reach the inlet pressure in the simulations. The porosity  $\epsilon$  of the adsorbent (0.11 for Ag-ETS-10 and 0.09 for Ag-ZSM-5) is obtained from the reported total pore volume measured by N<sub>2</sub> adsorption-desorption at 77 K and the packing density [311]. As the fluid restriction was mostly induced by the AgZs, the borosilicate glass fibre filter was neglected in the mass transport simulation. The viscosity of the fluid (air or N<sub>2</sub>) is obtained from literature data [345].

The mass transport in the gas phase during the experiments is then modelled using a convection-diffusion equation including an adsorption term as shown in Equation 6-2. In this equation,  $\rho$  [kg m<sup>-3</sup>] is the density of the adsorbent, c [mol m<sup>-3</sup>] is the concentration in the gas phase, t [s] is the time and D [m<sup>2</sup> s<sup>-1</sup>] is the effective diffusion coefficient. Assuming negligible mass transfer resistance, the adsorption coefficient K, in Equation 6-3, is the derivative of the single-site and dual-site Langmuir isotherm for Ag-ETS-10 and Ag-ZSM-5, respectively. The parameters for the Langmuir adsorption isotherm on these adsorbents was retrieved from data collected in Chapter 3.

$$(\varepsilon + \rho K) \frac{\partial c}{\partial t} + \vec{\nabla} \cdot (-D \vec{\nabla} c + \vec{u} c) = 0$$
 Equation 6-2  
$$K = \frac{\partial q}{\partial c}$$
 Equation 6-3

At the inlet boundary of the adsorbent, the Xe concentration (as provided by the experimental conditions) is defined with a Dirichlet boundary condition. The flux at the outlet of the adsorbent is limited to the advective flux with the necessary boundary condition.

The diffusion coefficient for a specific combination of temperature, flow rate and adsorbent is obtained by fitting the outlet Xe concentration profile, obtained by Equation 6-2, with a dedicated Xe breakthrough measurement. The mass transport was assumed to occur in isothermal conditions, as the variations in temperature during the adsorption were limited to maximum 15 K. This model, with the optimized permeability and diffusion coefficient in the relevant conditions, allowed to determine the Xe concentration in the adsorbent. Using the known amount of activity loaded on the adsorbent during the irradiation, the activity distribution could also be determined using the model.

#### 6.2.6. In situ irradiation: Monte Carlo simulations

To determine the absorbed dose in the irradiated adsorbents, the Monte Carlo simulation of particles was performed with the PENELOPE version-2018 software [346], which employs FORTRAN-based subroutines. Specifically, the Penmain.f subroutine within PENELOPE was employed for the simulation process. The simulation of radionuclide decay in PENELOPE involved the utilization of the Fortran subroutine package PenNuc [347]. This particular subroutine furnishes a set of state variables for particles (photons, electrons, positrons, and alphas) emitted in a randomly simulated decay path of the targeted radionuclide, leading to either a metastable level or the ground state of the daughter nucleus.

The geometry depicted in Figure 6-5 for Ag-ETS-10 was used in the PENELOPE geometry composition code and the adsorbent was meshed with sub-cylinders of 5 mm height. A similar geometry was used for Ag-ZSM-5 with the only difference that it took more space in the column due to its lower packing density. The material density and composition used in PENELOPE are detailed in Table S 6-3 in Supplementary material. Based on the activity distribution, the dose deposited in

each sub-cylinder of adsorbent was determined using energy deposition tally. The primary source used in the simulations was the radionuclide  $^{133}$ Xe.

#### 6.2.7. Powder X-ray diffraction

The Powder X-Ray Diffraction (PXRD) measurements are described in Section 2.4.1.

#### 6.2.8. Scanning electron microscopy

The acquisition of Scanning Electron Microscopy (SEM) images in combination with Energy-Dispersive X-ray spectra (EDX) are described in Section 2.4.2.

#### 6.2.9. N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms

The collection of  $N_2$  isotherms at 77 K and  $CO_2$  adsorption isotherms at 273 K is described in Section 2.4.3.

#### 6.2.10. Solid-state nuclear magnetic resonance spectroscopy

Solid-state <sup>29</sup>Si MAS (Magic Angle Spinning) NMR spectroscopy was performed at the Hasselt University, Belgium. The spectra were acquired on an Agilent VNMRS DirectDrive 400 MHz spectrometer (9.4 T wide bore magnet) equipped with a T3HX 3.2 mm probe. Magic angle spinning was performed at 6.5 kHz. The signal of talc ( $H_2Mg_3O_{12}Si_4$ ) was used to calibrate the chemical shift scale (- 98 ppm). Acquisition parameters were set as follows: a spectral width of 300 ppm, a 90° pulse length of 4.5 µs, an acquisition time of 15 ms, a recycle delay time of 60 s and about 4000 accumulations. High power proton dipolar decoupling during the acquisition time was set to 80 kHz.

Solid-state <sup>27</sup>Al MAS NMR spectra were acquired at the Hasselt University, Belgium. The spectra were acquired on the same spectrometer. Magic angle spinning was performed at 20 kHz. AlCl<sub>3</sub> was used to calibrate the chemical shift scale (0 ppm). Acquisition parameters were set as follows: a spectral width of 4000 ppm, a 90° pulse length of 1  $\mu$ s, an acquisition time of 11 ms, a recycle delay time of 2 s and about 20000 accumulations. High power proton dipolar decoupling during the acquisition time was set to 80 kHz.

#### 6.2.11.X-Ray fluorescence

Irradiated samples were analysed for Cs using a high performance Energy Dispersive XRF (EDXRF) spectrometer (XEPOS HE, Spectro Analytical Systems) at VITO, Belgium. The 50 W / 60 kV X-ray tube consists of a binary alloy of cobalt and palladium, which allows sensitive analysis of elements from K to Mn. The 60 kV provides extra power for analysing elements from Z = 45 to Z = 58. The instrument is provided with a silicon drift detector. The analyser is configured to produce the best excitation conditions for a specified group of elements, using bandpass filter excitation, or combined polarized/direct excitation. An XRF sampling cup, provided with a 4 µm prolene foil (Chemplex), was filled with the sample and subsequently, placed in the autosampler of the EDXRF system. The

quantification was performed using a TurboQuant II software package for screening unknown samples.

# 6.3.Results and discussion

#### 6.3.1. Reference Xe breakthrough measurements

To compare the Xe adsorption, in conditions relevant for MIPFs, a reference Xe breakthrough measurement, with 1000 ppm Xe in  $N_2$  at RT and a flow rate of  $600 \text{ cm}^3 \text{ min}^{-1}$ , was performed on a regenerated fresh sample of 50 cm<sup>3</sup> of both Aq-ETS-10 and Aq-ZSM-5 (Figure 6-6a). The time to reach 10% of the breakthrough curve was 5.5 and 8.7 h for Ag-ZSM-5 and Ag-ETS-10, respectively. The resulting adsorption capacity was 0.43 and 0.39 mol kg<sup>-1</sup> for Ag-ZSM-5 and Aq-ETS-10, respectively. The reader should be reminded here that Aq-ETS-10 has a higher packing density than Aq-ZSM-5. Previous studies have shown that the size of the silver nanoparticles in the zeolite plays a significant role in the adsorption of Xe [143, 348]. We showed in previous research that a substantial number of large Ag particles, in the range of tens to hundreds of nanometres, were visible by SEM on the ETS-10 crystals [311]. On the other hand, almost no Ag particles could be observed by SEM on the ZSM-5 crystals likely due to smaller Ag particles, which could not be observed with the limited resolution of the SEM that was used [311]. Such differences in the silver particle size can explain a similar adsorption capacity on both AgZs despite their significantly different silver content.

These Xe adsorption capacities in  $N_2$  agree with previous measurements [311]. They are compared, in Figure 6-6b), to the 15 most promising Xe adsorption capacities at 130 Pa (1000 ppm at 130 kPa) and RT, as estimated from reported single-component isotherm fits in the literature [133, 203, 216, 218-223, 225, 226, 246, 276, 339]. Only a silver-exchanged mordenite was reported to have a significantly higher Xe adsorption capacity in these conditions [339]. Courtney et al. [339] also measured a silver-exchanged beta zeolite with a similar Xe adsorption capacity, as for Aq-ETS-10 and Aq-ZSM-5, in these conditions. Compared to the breakthrough measurements in this work, the single-component fits in the literature, determined for other applications, do not consider the competition of N<sub>2</sub> with Xe and kinetic effects during column adsorption. All other reported adsorbents provide a lower Xe adsorption capacity by at least a factor two in single-component adsorption. In Chapter 3, our research showed that the difference in Xe adsorption capacity, in N2 and at RT, between on one side Ag-ETS-10 and Ag-ZSM-5, and on the other side two MOFs and an AC, is increasing with decreasing partial pressures in the range from 1000 to 10 Pa owing to the non-linear adsorption isotherm of AqZs in this partial pressure range [311].

From the 15 adsorbents compared in Figure 6-6b), only the VSK-5 AC was a commercial product, whereas all others were laboratory made samples. Ag-ZSM-5 is also commercially available. However, the noble gas adsorption properties of commercial Ag-ZSM-5 might differ from the ones observed on the laboratory sample used in this work. For instance, the Rn adsorption equilibrium constant on a commercial Ag-ZSM-5 sample was 500 times lower than the one measured on

the laboratory sample, which is likely partially due to differences in the silver exchange procedure and differences in the synthetized ZSM-5 itself [201, 312]. However, Ag-ZSM-5 can be produced on a commercial scale and is thus a potential candidate for mitigating radioxenon releases in the near future.



Figure 6-6. a) Xe breakthrough curves on Ag-ZSM-5 and Ag-ETS-10 and b) comparison of the Xe adsorption capacity with reported adsorbents. The comparison is performed with the 15 most promising Xe adsorption capacities at 130 Pa and RT estimated from reported Henry's adsorption constant or Langmuir / Langmuir-Freundlich or Sips parameters of single-component isotherms at RT in the literature [133, 203, 216, 218-223, 225, 226, 246, 276, 339].

#### 6.3.2. Durability against thermal regeneration cycles

The durability against 43 and 44 thermal regeneration cycles was investigated for Ag-ZSM-5 and Ag-ETS-10, respectively. After each regeneration, a Xe breakthrough measurement was performed. The relative deviation of the Xe adsorption capacity ( $q_{Xe}$ ) and retention volume at 50% breakthrough ( $V_{50\%}$ ), compared to the average value for the relevant Xe concentration, was quantified for both adsorbents. An uncertainty of about 10% was determined in Chapter 2 for the adsorption capacity and retention volume based on successive adsorption runs in the same conditions with the experimental set-up.



Figure 6-7. Evolution of the Xe adsorption properties, compared to the average value (black line), in function of thermal regeneration cycle for a) Ag-ETS-10 and b) Ag-ZSM-5. The typical 10% measurement uncertainty is shown with the dashed line.

As shown in Figure 6-7a), no degradation is observed from the Xe adsorption capacity on Ag-ETS-10 as the 5<sup>th</sup> and 95<sup>th</sup> percentiles are within 8.7% from the average value. The retention volume at 50% breakthrough fluctuates slightly more, as the 5<sup>th</sup> and 95<sup>th</sup> percentiles are within 15% of the average. Part of the reason for these higher fluctuations are the differences in time resolution in function of flow rate and Xe concentration, which have a higher impact on this parameter. Consequently, no clear degradation trend can be observed on this parameter neither. The regeneration under air (cycle 42) and the one at 535 K under N<sub>2</sub> (cycle 44) did not significantly affect both metrics.

Concerning Ag-ZSM-5, the variations are much more pronounced as can be seen in Figure 6-7b). The 5<sup>th</sup> and 95<sup>th</sup> percentiles of the relative deviation on the Xe adsorption capacity are within 35%, whereas the percentiles of the relative deviation on the retention volume at 50% are within 30%. The distribution is however evenly spread around the average value all along the 43 cycles and does not indicate a degradation trend as a function of thermal regeneration cycles. The regeneration under air (cycle 42) did not significantly affect both metrics. The highest Xe adsorption capacity was obtained at cycle 43, which was performed after the regeneration at 535 K under N<sub>2</sub>. Therefore, one potential reason for such higher variations on Ag-ZSM-5 is a higher sensitivity to the regeneration duration at 485 K, which varied from 0.8 to 14.5 hours depending on the cycle. This is also supported by the smaller variations observed by Monpezat et al. [171] on the Xe adsorption capacity of the same Ag-ZSM-5 sample, after regeneration cycles performed at 573 K for 2 hours, when no Cl-containing VOCs were present. The regeneration conditions for Ag-ZSM-5 should thus be further investigated to find the optimal regeneration conditions in N<sub>2</sub> (*i.e.* temperature, duration and flow rate).



*Figure 6-8. Mass transfer zone and Xe breakthrough curves during the thermal regeneration cycles. MTZ measured on a) Ag-ETS-10 and c) Ag-ZSM-5. Individual Xe breakthrough curves on b) Ag-ETS-10 and d) Ag-ZSM-5.* 

The MTZ and the corresponding breakthrough curves, for the 10 ppm Xe in air breakthrough measurements at 500 cm<sup>3</sup> min<sup>-1</sup>, are shown in Figure 6-8 for both adsorbents. It is clear that the MTZ, as indicator of the shape of the breakthrough curves, changed significantly after emptying and refilling the column with Ag-ETS-10 between cycle 20 and 21 to take the necessary subsample for further characterizations. The retention time at 10% breakthrough in these conditions went from an average value of 13.9 to 8.77 hours when emptying and refilling the column after cycle 20. Similar variations in the MTZ on Ag-ETS-10 were observed after emptying and refilling an adsorption column in Chapter 5. This indicates that the initial packing was not fully reproduced and that some preferential channels, with less adsorbent, were present in the column. The measured pressure drop on the column did not indicate a major change between cycle 20 and 25. A

sensitive pressure drop measurement might directly provide an indication that the packing of the adsorbent differs from one filling to the other. No differences in the MTZ were observed when emptying and refilling the column with Ag-ZSM-5.

Further characterizations were performed on a subsample after 20 cycles for both adsorbents, after 43 cycles for Ag-ZSM-5 and after 44 cycles for Ag-ETS-10. The morphology, the size of Ag nanoparticles, visible with the SEM, and the elemental composition observed with SEM/EDX on all thermally regenerated AgZs (figures S 6-1 to S 6-2 and figures S 6.4 to S 6.5 in the Supplementary material) were not different than for the fresh sample previously reported [311]. No changes were observed in the X-ray diffraction peaks (Figure S 6-7 in the Supplementary material) that were reported in the same study. Metallic silver and silver oxide were again observed in the thermally regenerated Ag-ETS-10 samples (after 20 and 44 cycles), whereas only the same small peak for metallic silver was visible in the thermally regenerated Ag-ZSM-5 samples (after 20 and 43 cycles).

Table 6-2. Calculated surface area and pore volume of aged samples. BET surface area ( $S_{BET}$  in  $m^2 g^{-1}$ ), micropore volume ( $V_{DR}$  in  $cm^3 g^{-1}$ ) and total pore volume ( $V_T$  in  $cm^3 g^{-1}$ ) from  $N_2$  adsorption. Micropore surface ( $S_0$  in  $m^2 g^{-1}$ ) and volume ( $V_{DR,CO_2}$  in  $cm^3 g^{-1}$ ) from CO<sub>2</sub> adsorption. The values are compared to the ones measured on fresh samples reported previously [311].

Adaauhaut	Commis	N <sub>2</sub> at 77 K				CO <sub>2</sub> at 273 K	
Adsorbent	Sample	<b>S</b> <sub>BET</sub> <sup>a</sup>	V <sub>DR</sub> <sup>b</sup>	V <sub>T</sub> c	<b>S</b> 0 <sup>b</sup>	$V_{DR, CO_2}^{b}$	
	Fresh	206 [5 10 <sup>-5</sup> -6 10 <sup>-2</sup> ]	0.08	0.12	205	0.08	
Ag_ETS_10	20 cycles	201 [1.5 10 <sup>-5</sup> -5 10 <sup>-2</sup> ]	0.08	0.12	220	0.09	
Ag-215-10	44 cycles	211 [2 10 <sup>-5</sup> -6 10 <sup>-2</sup> ]	0.08	0.12	216	0.09	
	Irradiated 1 <sup>st</sup> layer	195 [5 10 <sup>-5</sup> -6 10 <sup>-2</sup> ]	0.07	0.12	231	0.09	
	Fresh	302 [1 10 <sup>-4</sup> -6 10 <sup>-2</sup> ]	0.12	0.16	293	0.12	
4a-76M-6	20 cycles	256 [5 10 <sup>-5</sup> -7 10 <sup>-2</sup> ]	0.10	0.14	265	0.11	
Ay-23M-3	43 cycles	308 [2 10 <sup>-5</sup> –6 10 <sup>-2</sup> ]	0.12	0.16	306	0.12	
	Irradiated 2 <sup>nd</sup> layer	277 [1 10 <sup>-4</sup> -6 10 <sup>-2</sup> ]	0.11	0.15	278	0.11	

<sup>a</sup> Calculated through the BET method in the relative pressure range indicated in brackets.

<sup>b</sup> Calculated through the Dubinin-Radushkevitch equation.

<sup>c</sup> Total pore volume determined at  $p/p_0 = 0.96$ .

The meso and microporous properties, derived from  $N_2$  adsorption-desorption at 77 K and from  $CO_2$  adsorption at 273 K (figures S 6-8 to S 6.10 in the Supplementary material), of the thermally regenerated samples are summarized in Table 6-2. All calculated properties on Ag-ETS-10 samples after 20 and 44 cycles were within the typical measurement uncertainties (about 5 %) compared to the properties of the fresh sample previously measured [311]. The picture is slightly

different for Aq-ZSM-5, as all calculated meso and microporous properties for the sample after 20 cycles were, depending on the property, 10 to 15% lower than the ones for the fresh sample measured in the same previous study. However, all calculated properties for the sample after 43 cycles are within the typical uncertainties compared to the ones of the fresh sample. Consequently, there is no degradation of the meso and microporous properties due to the thermal regeneration cycles. Similar to the variations observed in the Xe breakthrough measurements, the higher variations in meso and microporous properties on Aq-ZSM-5 are likely due to the adsorption and subsequent non-optimal regeneration conditions, before the  $N_2$  and  $CO_2$  adsorption measurement, which did not allow the removal of all adsorbates in Aq-ZSM-5. After cycle 20, the adsorption column was not regenerated before taking the necessary subsample. This subsample was only regenerated just before the  $N_2/CO_2$  adsorption, which was likely not enough to fully desorb all adsorbates. Whereas the subsample after 43 cycles was taken after a regeneration in the adsorption column, which was then further regenerated just before the  $N_2/CO_2$  adsorption.



Figure 6-9. Solid-state <sup>29</sup>Si MAS NMR spectra of the fresh and thermally regenerated Ag-ETS-10 samples.

The solid-state <sup>29</sup>Si NMR spectra of the fresh and cycled Ag-ETS-10 samples are shown in Figure 6-9. Five distinct signals can be identified in the spectrum of the fresh Ag-ETS-10 sample. The first three signals at -95.9 ppm, -97.9 ppm and -98.7 ppm are all assigned to Si(3Si,1Ti), which are crystallographically inequivalent Si atoms linked to three other Si atoms and one Ti atom through oxygen bridges [349]. A fourth signal, corresponding to the upfield shoulder on the peak at -95.9 ppm, was also reported previously as a Si(3Si,1Ti) site on a similar Ag-ETS-10 sample [349]. The fifth signal at -107.4 ppm is assigned to Si(4Si,0Ti). Some slight peak broadening is observed on the cycled samples, and, in general, the <sup>29</sup>Si NMR peaks in silver-exchanged ETS-10 show somewhat more broadening and an upfield shift, up to 4.1 ppm for the Si(4Si,0Ti) site, compared to reported <sup>29</sup>Si NMR peaks in the unexchanged ETS-10 framework [350]. The peak broadening in cycled samples can be caused by an increase in the local

structural disorder from dehydration during the regeneration at elevated temperature as shown in previous studies on Ag-ETS-10 [349].



Figure 6-10. Solid-state a) <sup>29</sup>Si and b) <sup>27</sup>Al MAS NMR spectra of the fresh and thermally regenerated Ag-ZSM-5 samples.

The solid-state <sup>29</sup>Si and <sup>27</sup>Al NMR spectra of the fresh and cycled Ag-ZSM-5 samples are shown in Figure 6-10 a) and b), respectively. The signal at 56.1 ppm in the <sup>27</sup>Al spectrum is assigned to Al(4Al,0Si). The first signal at -107.0 ppm in the <sup>29</sup>Si spectrum is assigned to Si(3Si,1Al), whereas the second signal at -112.7 ppm is assigned to Si(4Si,0Al). These NMR spectra are very similar to other NMR observations made on an unexchanged ZSM-5 zeolite with a similar Si/Al ratio [351]. The <sup>27</sup>Al and the <sup>29</sup>Si NMR spectra after 20 and 43 cycles are identical to the spectra of the fresh sample, indicating that no change in the local environment of Si and Al could be observed.

Accordingly, no degradation due to the thermal regeneration cycles could be observed for both adsorbents based on Xe adsorption at RT, SEM/EDX, PXRD, N<sub>2</sub> adsorption-desorption at 77 K, CO<sub>2</sub> adsorption at 273 K and solid-state <sup>27</sup>Al and <sup>29</sup>Si NMR spectroscopy.

#### 6.3.3. Radiation resistance

Breakthrough measurements with 10 ppm Xe in N<sub>2</sub>, at 500 cm<sup>3</sup> min<sup>-1</sup> and RT, were performed before and after in situ <sup>133</sup>Xe irradiation. For Ag-ETS-10, the first part of the breakthrough curves is different as shown in Figure 6-11a) and as indicated by an average retention time at 10% breakthrough of 24 and 18 hours before and after irradiation, respectively. As seen in the previous section, such variations in the shape of the breakthrough curves have been observed when emptying and refilling the adsorption column due to differences in the adsorbent packing. After the irradiation and before the breakthrough measurement, the column was put on its side for the collimated in situ gamma spectrometry at IRE, which likely disturbed the original adsorbent packing inside the column. The variation on the Xe adsorption capacity itself was more limited as the average capacity was  $1.6 \ 10^{-2}$  and  $1.4 \ 10^{-2}$  mol kg<sup>-1</sup> before and after irradiation, respectively. Such a limited variation is typical for breakthrough measurements in these conditions. Accordingly, no significant degradation on the Xe adsorption performances of Ag-ETS-10 is attributed to the irradiation. For Ag-ZSM-5, the two initial breakthrough curves are different (Figure 6-11b), which was likely caused by the difference in the duration of the thermal regeneration (*i.e.* 5.2 and 9.9 hours for run 1 and run 2, respectively) before the breakthrough measurement, as similar variations were seen during the thermal regeneration cycles (also likely due to differences in regeneration duration). The average retention time at 10% breakthrough was 18 and 19 hours before and after irradiation, respectively. The Xe adsorption capacity in turn was  $1.5 \ 10^{-2}$  and  $1.4 \ 10^{-2}$  mol kg<sup>-1</sup> before and after irradiation on the Xe adsorption performances was observed on Ag-ZSM-5 after the irradiation.



Figure 6-11. 10 ppm Xe in  $N_2$  breakthrough curves before and after irradiation on a) Ag-ETS-10 and b) Ag-ZSM-5.

During the adsorption of  $^{133}$ Xe on both AgZs, the inlet  $^{133}$ Xe profile was measured with GM1 and could be used to determine the total Xe concentration profile at the

inlet using the total amount of Xe, *i.e.* including the stable Xe isotopes, contained in the <sup>133</sup>Xe vial (Figure 6-12). The adsorption process during the irradiation is mainly driven by stable Xe as most of the Xe contained in the <sup>133</sup>Xe vial was stable. The determination of the inlet Xe concentration profile allowed to calculate the activity distribution in the column at the start of the irradiation (*i.e.* once the columns were isolated after the full adsorption). This was done by: i) replicating, twice, the adsorption with the same stable Xe concentration profile on the sample after irradiation and flushing the adsorbed Xe with N<sub>2</sub> at the same flow rate until full Xe breakthrough, and ii) fitting the experimental breakthrough curve with the simulated outlet Xe concentration profile, obtained by Equation 6-2, to determine the effective diffusion coefficient in the conditions of the irradiation experiment. As the overall Xe adsorption properties were maintained after the irradiation, the replication is considered representative for the irradiation experiment itself.



Figure 6-12. Replication of the Xe inlet profile at IRE together with the measured and simulated outlet curve. Inlet Xe molar flow rate as derived from GM1 and as replicated at SCK CEN with stable Xe for a) Ag-ETS-10 and b) Ag-ZSM-5. Relative Xe outlet profile compared to the simulation with the corresponding optimized diffusion coefficient (D) for c) Ag-ETS-10 and d) Ag-ZSM-5.

The effective diffusion coefficient was obtained by fitting the modelled and replicated breakthrough curves. A deviation on the adsorption coefficient K of 10% and 25% was allowed for Ag-ETS-10 and Ag-ZSM-5, respectively, to account for the uncertainties on the adsorption capacity as observed from the thermal regeneration cycles. For Ag-ETS-10, the optimized value for D and the variation

on K were  $1.5 \ 10^{-4} \ m^2 \ s^{-1}$  and +5%, respectively. The values were  $6.0 \ 10^{-5} \ m^2 \ s^{-1}$  and -13% for Ag-ZSM-5. As expected, the wider Ag-ETS-10 outlet peak is fitted with a higher diffusion coefficient. The difference in effective diffusion coefficient between adsorbents can originate from multiple factors: adsorbent particle size and shape, pore network, adsorbate-adsorbent interaction properties and column packing [352].

Knowing the diffusion coefficient, the Xe concentration in each adsorbent after the adsorption of the content of the  $^{133}$ Xe vial could be calculated in COMSOL Multiphysics®. It took 1.9 and 1.7 hours to adsorb the content of the  $^{133}$ Xe vial for Ag-ETS-10 and Ag-ZSM-5, respectively. The Xe concentration at the beginning of the irradiation (*i.e.* once the adsorption of the vial was completed and the columns were isolated) is shown in Figure 6-13 a) and b) for Ag-ETS-10 and Ag-ZSM-5, respectively. The resulting  $^{133}$ Xe activity and absorbed dose, as calculated with the PENELOPE code per 1 cm layer sample, is shown in Figure 6-13 c) and d) for Ag-ETS-10 and Ag-ZSM-5, respectively. The highest dose per 1 cm layer was 110 and 160 MGy for Ag-ETS-10 and Ag-ZSM-5, respectively. The absorbed dose, integrated on the full sample, was 21 and 20 MGy for Ag-ETS-10 and Ag-ZSM-5, respectively.



Figure 6-13. Simulated <sup>133</sup>Xe activity distribution and corresponding absorbed dose. Simulated Xe concentration at the beginning of the irradiation at IRE for a) Ag-ETS-10 and b) Ag-ZSM-5. Calculated <sup>133</sup>Xe activity and resulting absorbed dose in each 1 cm sample in the adsorption column for c) Ag-ETS-10 and d) Ag-ZSM-5. The sample selected for further characterizations is highlighted in green.

Further characterizations were performed on the first layer of Ag-ETS-10 with an estimated absorbed dose of 73 MGy, as preliminary calculations indicated (incorrectly) that this sample would receive the highest dose. For Ag-ZSM-5, the

second layer with an estimated dose of 160 MGy was used for the characterizations. The morphology, size of Ag nanoparticles and elemental composition observed with SEM/EDX on both irradiated AqZs (Figure S 6-3 and Figure S 6-6 in the Supplementary material) did not change compared to the fresh sample previously reported [311]. Similarly, no changes were observed in the X-ray diffraction peaks (Figure S 6-7 in the Supplementary material) compared to the ones reported in the previous study on the fresh samples. Concerning silver, metallic silver and silver oxide peaks were again present in the irradiated Aq-ETS-10 sample, whereas only the same small peak for metallic silver was visible in the irradiated Ag-ZSM-5 sample. As shown in Table 6-2 in the previous section, the meso and microporous properties of both AqZs, derived from  $N_2$ adsorption-desorption at 77 K and from CO<sub>2</sub> adsorption at 273 K (figures S 6.8 to S 6.10 in the Supplementary material), of both AgZs were also conserved after the irradiation. As shown in Figure 6-14 a) and b), both the <sup>27</sup>Al and <sup>29</sup>Si NMR spectra of the irradiated Aq-ZSM-5 sample were unchanged compared to the spectra of the fresh sample.



Figure 6-14. Solid-state <sup>29</sup>Si and <sup>27</sup>Al MAS NMR spectra of the irradiated samples. a) Solid-state <sup>29</sup>Si MAS NMR spectra of the fresh Ag-ETS-10 sample and the 1<sup>st</sup>, 2<sup>nd</sup>, and last layer of the irradiated sample. Solid-state b) <sup>29</sup>Si and c) <sup>27</sup>Al MAS NMR spectra of the fresh Ag-ZSM-5 sample and the 2<sup>nd</sup> layer of the irradiated sample.

For Ag-ETS-10, the situation is quite different in the <sup>29</sup>Si NMR spectrum after irradiation, as shown in Figure 6-14c). In the spectrum of the first layer of the irradiated Ag-ETS-10 sample, the signals corresponding to both the Si(4Si, 0Ti) site and Si(3Si, 1Ti) sites, are broadened and upfield shifted compared to the fresh sample. The peak broadening is partly caused again by dehydration at elevated temperatures. The maximum temperature reached during the regeneration runs

after the irradiation was 540 K. This temperature is similar to the one used during cycle 44 of the thermal regeneration cycles. The duration of the regeneration at these temperatures, under a  $N_2$  flow, was 10 and 7.7 hours for the irradiation and the thermal regeneration cycles, respectively. As only a limited peak broadening was observed after the thermal regeneration cycles, it is unlikely that the regeneration of the irradiated sample has caused the altered local <sup>29</sup>Si environment. It is interesting to note that the first peak at -95.9 ppm of the Si(3Si,1Ti) sites is not significantly shifted, whereas the two peaks at -97.9 and -98.7 ppm are shifted upfield by about 1.5 ppm compared to the fresh sample. The same shift is observed for the signal of the Si(4Si,0Ti) site. It is clear that the irradiation experiment did alter the local environment of the different Si sites, except the first group of cristallographycally inequivalent Si(3Si,1Ti) sites. Following, these observations, a <sup>29</sup>Si NMR spectrum was acquired on the last layer as well as on the second layer of the irradiation column to better understand the origin of the peak shift and broadening. As a similar shift and peak broadening is observed in Figure 6-14c) on the three layers of Ag-ETS-10 in the irradiation column, it is unlikely that the origin of the shift is the irradiation itself, as negligeable irradiation is expected in the last layer. There is no indication that <sup>133</sup>Xe reached the last layer of adsorbent based on: i) the GM2 measurements during the irradiation experiment, ii) the conserved Xe adsorption properties (with a much higher amount of Xe that can be retained than the actual Xe amount during the irradiation), and iii) the simulation of the activity distribution. The origin for this peak broadening can be found in the decay of adsorbed  $^{133}Xe$  to stable  $^{133}$ Cs in the zeolite during the irradiation experiment. The presence of  $^{133}$ Cs in some irradiated samples, both in Aq-ZSM-5 and Aq-ETS-10, was also confirmed by XRF (Table S 6-4 in the Supplementary material). The detection of  $^{133}$ Cs by XRF is explained by the very high Xe adsorption capacity of both AqZs. The  $^{133}$ Cs content in the second and last layer of the irradiated Ag-ETS-10 is 240 and 100  $\mu$ g cm<sup>-3</sup>, respectively. The <sup>133</sup>Cs content in the first layer was not measured but this layer is also likely to contain some <sup>133</sup>Cs as well. The presence of the paramagnetic <sup>133</sup>Cs in the zeolite can cause peak shifting and broadening, which are reported to occur when paramagnetic elements are close to probed atoms [353, 354]. These effects are due to the dipolar interaction between the electron spin magnetic moment of the paramagnetic centre and the magnetic moment of the probed nucleus. This peak shifting and broadening can be used in the future, in conjunction with other techniques like X-ray photoelectron spectroscopy or atomic emission spectroscopy and coupled with ab initio modelling, to perform a detailed investigation of the location of the <sup>133</sup>Cs decay product in Ag-ETS-10. Nonetheless, these alterations in the <sup>29</sup>Si NMR signal of Aq-ETS-10 did not impact the Xe adsorption performance of the whole irradiated sample.

No alterations were observed on the irradiated Ag-ZSM-5 sample, suggesting that <sup>133</sup>Cs in Ag-ZSM-5 is not close enough to the <sup>29</sup>Si and <sup>27</sup>Al atoms to have a sufficiently strong dipolar interaction. In addition, <sup>29</sup>Si and <sup>27</sup>Al peaks of Ag-ZSM-5 are not altered by the silver exchange. The ZSM-5 structure observed by NMR spectroscopy appears to be less sensitive to the presence of silver and thus potentially also to the <sup>133</sup>Cs in the vicinity.

Accordingly, it is clear that no degradation due to the irradiation itself could be observed for both adsorbents based on Xe adsorption at RT, SEM/EDX, PXRD, N<sub>2</sub> adsorption-desorption at 77 K, CO<sub>2</sub> adsorption at 273 K and solid-state <sup>27</sup>Al and <sup>29</sup>Si NMR spectroscopy.

# 6.4.Conclusions

AgZs or silver-exchanged zeolite-like frameworks are promising candidates for a more efficient radioxenon emission abatement in nuclear installations, which in turn can reduce the impact of nuclear installations on nuclear weapon test monitoring. More specifically Ag-ETS-10 and Ag-ZSM-5 have a Xe adsorption capacity at RT, in typical conditions for radioxenon trapping at MIPFs, about a factor two higher than any non-silver-exchanged zeolite-like framework reported so far. Ag-ETS-10 and Ag-ZSM-5 are thus clear candidates for a more efficient radioxenon trapping at RT in a near future, provided that they are durable in these conditions.

Firstly, the durability of Ag-ETS-10 and Ag-ZSM-5 against thermal regeneration cycles was investigated. These adsorbents have proven to withstand 44 and 43 thermal regeneration cycles, for Ag-ETS-10 and Ag-ZSM-5, respectively, at 485 K under  $N_2$  without any loss of Xe adsorption performance. In addition, no alteration in their structural properties was observed through SEM/EDX, PXRD, <sup>27</sup>AI- and <sup>29</sup>Si solid-state NMR spectroscopy,  $N_2$  adsorption-desorption at 77 K and  $CO_2$ adsorption at 273 K. The effect of air during the regeneration was investigated in one cycle and did not result in any alteration on the Xe adsorption properties of both adsorbents. Similarly, no notable change on the Xe adsorption was observed when increasing the temperature to 535 K under  $N_2$  in one cycle on both adsorbents. However, the shape of the breakthrough curves of Aq-ETS-10 is sensitive to the packing of the material inside the adsorption column when emptying and refilling the column. This is not the case for Ag-ZSM-5 for which the shape of the breakthrough curves remained the same when emptying and refilling the column. For Ag-ZSM-5, the regeneration conditions used in this work were not optimal to sufficiently remove the adsorbates and recover the Xe adsorption properties. The suboptimal regeneration conditions resulted in variations of up to 40% on these properties along the cycles due to differences in regeneration duration. Further investigations on the regeneration conditions would be necessary for its optimal use in radioxenon trapping.

Secondly, the radiation resistance of Ag-ETS-10 and Ag-ZSM-5 was investigated for the first time by in situ irradiation, for about 8 days, through the adsorption of about 50 TBq of <sup>133</sup>Xe on both adsorbents. This irradiation resulted in about 20 MGy when integrating the dose over the whole material. Looking at 1 cm height subsamples, the highest dose was 110 and 160 MGy for Ag-ETS-10 and Ag-ZSM-5, respectively. Aside from the variations already observed during the thermal regeneration cycles (*i.e.* sensitivity to packing for Ag-ETS-10 and suboptimal regeneration conditions for Ag-ZSM-5), no significant loss of performance on the Xe adsorption properties could be observed after irradiation. Further characterizations were performed on a 1 cm height sample that received 160 MGy for Ag-ZSM-5 and 73 MGy for Ag-ETS-10. The structural properties observed by SEM/EDX, PXRD,  $^{27}\text{Al}$  solid-state NMR spectroscopy,  $N_2$  adsorption-desorption at 77 K and CO\_2 adsorption at 273 K were unchanged.

The signals in the solid-state <sup>29</sup>Si NMR spectra of irradiated Ag-ETS-10 samples show upfield shifting and peak broadening compared to the signals in the spectrum of the fresh sample. This effect is caused by the dipolar interaction between the paramagnetic <sup>133</sup>Cs decay product of <sup>133</sup>Xe in the zeolite and the observed <sup>29</sup>Si nucleus. These observations could be used in the future to locate the <sup>133</sup>Cs decay product and investigate its potential impact on the long term durability of Ag-ETS-10 and on the long term availability of Xe adsorption sites. Although the presence of <sup>133</sup>Cs in both zeolites was confirmed by XRF, no changes were observed in the <sup>29</sup>Si NMR peaks of Ag-ZSM-5. This can be explained by the characteristic broader peaks in this zeolite and a tendency to be less sensitive to the extra-framework cations.

The demonstration of the durability of both AgZs against radiation and thermal regeneration cycles is a major step forward towards their application for volume-efficient radioxenon trapping. Future work is necessary on the effect of potential contaminants that can be present in the gas stream at nuclear installations. The long-term behaviour of the silver-exchanged zeolites, when gradually loaded with the <sup>133</sup>Cs decay product, would need further investigation. Other promising adsorbents could be considered in the future, using a similar approach to ensure their durability in these conditions.

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#### 6.6.Supplementary material

#### 6.6.1. Materials and methods

Table S 6-1. Experimental conditions during the 44 thermal regeneration cycles on Ag-ETS-10. t is the duration of the regeneration, T is the temperature during the regeneration or adsorption, F is the flow rate during the regeneration or adsorption, P is the pressure during the regeneration or adsorption and  $C_{Xe}$  is the Xe concentration in air during the adsorption.

	Desorption			Adsorption					
Cycle	<b>C</b>	t	Т	F	Р	C <sub>Xe</sub>	F	Р	Т
	Gas	(h)	(K)	(cm³ min⁻¹)	(kPa)	(ppm)	(cm <sup>3</sup> min <sup>-1</sup> )	(kPa)	(K)
1	N <sub>2</sub>	3.5	481	400	130	10	500	129	294
2	N <sub>2</sub>	2.1	483	200	127	0.087	2000	142	295
3	N <sub>2</sub>	2.2	483	200	126	0.087	2000	141	295
4	N <sub>2</sub>	1.6	483	200	127	0.087	2000	142	295
5	N <sub>2</sub>	1.5	483	200	128	10	500	130	294
6	N <sub>2</sub>	2.2	483	200	129	0.087	2000	144	295
7	N <sub>2</sub>	2.0	483	200	128	0.087	2000	144	295
8	N <sub>2</sub>	2.0	483	200	128	0.087	2000	143	295
9	N <sub>2</sub>	1.8	483	200	128	0.087	2000	143	295
10	N <sub>2</sub>	2.0	483	200	128	10	500	130	294
11	N <sub>2</sub>	2.1	483	200	129	0.087	2000	143	295
12	N <sub>2</sub>	2.4	483	200	127	0.087	2000	142	295
13	N <sub>2</sub>	2.3	483	200	128	0.087	2000	143	295
14	N2	2.8	483	200	128	0.087	2000	143	295
15	N2	2.1	483	200	128	10	500	130	295
16	N2	2.3	483	200	128	0.087	2000	143	295
17	N <sub>2</sub>	2.3	483	200	128	0.087	2000	143	295
18	N <sub>2</sub>	2.5	483	200	128	0.087	2000	142	295
19	N <sub>2</sub>	2.3	483	200	126	0.087	2000	141	295
20	N2	2.8	483	200	127	10	500	129	295
21	N <sub>2</sub>	8.7	486	200	128	100	1000	135	296
22	N <sub>2</sub>	3.6	486	200	130	100	1000	136	296
23	N <sub>2</sub>	6./	487	200	130	100	1000	136	296
24	N <sub>2</sub>	7.0	487	200	129	100	1000	136	296
25	N <sub>2</sub>	6.6	487	200	130	10	500	131	295
26	IN <sub>2</sub>	2.6	487	200	130	10	1000	137	296
27	IN2	9.8	488	200	130	10	500	132	296
28	IN2	2.0	489	200	128	10	1000	138	296
29	IN2	5.4	489	200	131	10	500	138	296
30	N <sub>2</sub>	73	409	200	128	10	1000	133	290
32	N <sub>2</sub>	6.1	409	200	120	10	1000	137	295
32	N <sub>2</sub>	2.8	409	200	127	10	1000	138	290
34	N <sub>2</sub>	6.2	489	200	130	10	1000	137	295
35	N <sub>2</sub>	3.0	400	200	130	10	500	137	295
36	N <sub>2</sub>	23	486	200	130	10	1000	138	295
37	N2	7.4	486	200	131	10	1000	137	295
38	No.	6.3	486	200	130	10	1000	137	295
39	N2	13.8	486	200	130	10	1000	137	295
40	N2	7.4	486	200	130	10	500	133	295
41	N2	3.4	486	200	131	10	1000	137	295
42	Air/N <sub>2</sub>	7.8/2.4	485	400	134	10	1000	137	295
43	N2	6.4	485	400	134	10	1000	136	295
44	N2	7.7	535	200	130	10	1000	136	295

Table S 6-2. Experimental conditions during the 43 thermal regeneration cycles on Ag-ZSM-5. t is the duration of the regeneration, T is the temperature during the regeneration or adsorption, F is the flow rate during the regeneration or adsorption, P is the pressure during the regeneration or adsorption and  $C_{Xe}$  is the Xe concentration in air during the adsorption.

	Desorption			Adsorption					
Cycle	Cas	t	Т	F	Р	Cxe	F	Р	Т
	Gas	(h)	(K)	(cm <sup>3</sup> min <sup>-1</sup> )	(kPa)	(ppm)	(cm <sup>3</sup> min <sup>-1</sup> )	(kPa)	(K)
1	N <sub>2</sub>	3.8	481	400	132	10	500	131	295
2	N <sub>2</sub>	3.9	482	200	129	0.087	1500	142	295
3	N <sub>2</sub>	1.4	482	200	129	0.087	1500	142	295
4	N <sub>2</sub>	1.1	482	200	130	0.087	1500	143	295
5	N <sub>2</sub>	1.1	482	200	130	10	500	131	295
6	N <sub>2</sub>	1.3	482	200	129	0.087	1500	142	295
7	N <sub>2</sub>	0.9	482	200	129	0.087	1500	142	295
8	N <sub>2</sub>	0.8	482	200	129	0.087	1500	142	295
9	N <sub>2</sub>	3.2	482	200	129	0.087	1500	143	295
10	N <sub>2</sub>	0.8	482	200	130	10	500	132	295
11	N <sub>2</sub>	0.9	482	200	130	0.087	1500	144	295
12	N <sub>2</sub>	1.1	482	200	130	0.087	1500	144	295
13	N <sub>2</sub>	1.0	490	200	130	0.087	1500	143	306
14	N <sub>2</sub>	1.4	494	200	130	0.087	1500	144	306
15	N <sub>2</sub>	1.6	484	200	130	10	500	132	297
16	N <sub>2</sub>	1.0	483	200	130	0.087	1500	143	296
17	N <sub>2</sub>	1.0	482	200	130	0.087	1500	143	296
18	N <sub>2</sub>	0.9	490	200	130	0.087	1500	143	297
19	N <sub>2</sub>	1.0	486	200	130	0.087	1500	144	299
20	N <sub>2</sub>	1.1	490	200	130	10	500	133	295
21	N <sub>2</sub>	11.0	486	200	131	10	1000	140	294
22	N <sub>2</sub>	6.0	486	200	131	10	1000	140	294
23	N <sub>2</sub>	4.8	486	200	131	10	1000	141	294
24	N <sub>2</sub>	4.8	486	200	132	10	1000	141	294
25	N <sub>2</sub>	14.5	486	200	134	10	500	135	294
26	N <sub>2</sub>	6.8	486	200	133	10	1000	143	294
27	N <sub>2</sub>	3.9	471	200	134	10	1000	144	295
28	N <sub>2</sub>	2.0	487	200	134	10	1000	143	295
29	N <sub>2</sub>	3.4	487	200	133	10	1000	143	294
30	N <sub>2</sub>	4.5	486	200	134	10	500	135	294
31	N <sub>2</sub>	3.7	486	200	133	10	1000	143	294
32	N <sub>2</sub>	4.2	487	200	134	10	1000	144	295
33	N <sub>2</sub>	4.4	487	200	134	10	1000	143	295
34	N <sub>2</sub>	3.4	487	200	133	10	1000	143	295
35	N <sub>2</sub>	2.5	487	200	133	10	500	135	294
36	N <sub>2</sub>	8.3	486	200	132	10	1000	143	295
37	N <sub>2</sub>	5.9	486	200	133	10	1000	143	295
38	N <sub>2</sub>	4.3	486	200	134	10	1000	143	295
39	N <sub>2</sub>	2.6	487	200	134	10	1000	144	295
40	N <sub>2</sub>	6.3	487	200	134	10	500	135	295
41	N <sub>2</sub>	1.9	487	200	134	10	1000	142	295
42	Air/N <sub>2</sub>	7.8/1.3	486	400	138	10	1000	141	295
43	N <sub>2</sub>	3.3	534	400	139	10	1000	142	295

Material	Composition (wt.%)	Density (g cm <sup>-3</sup> )
TP316L	Cr: 18 / Ni: 14 / Mo: 3 / Mg: 2 / Fe: 63	7.9
TP304L	Cr: 20 / Ni: 12 / Mg: 2 / Fe: 66	7.9
Ag-ETS-10	Ag: 30 / Ti: 7 / Si: 26 / O: 37	0.90
Ag-ZSM-5	Ag: 11 / Si: 38 / O: 48 / Al: 3	0.59
Air	N <sub>2</sub> : 76 / O <sub>2</sub> : 23 / Ar: 1	0.0012
Borosilicate glass fibre filter	O: 54 / Si: 38 / B: 4 / Na: 3 / Al: 1	0.18

Table S 6-3. Material composition and density used in the PENELOPE code.

SEM/EDX



Figure S 6-1. SEM characterization of Ag-ETS-10 after 20 thermal regeneration cycles. SEM image showing (a) the typical truncated bi-pyramid crystals, (b) Ag aggregates (in red) on the Ag-ETS-10 crystal and (c) the Ag composition in one aggregate compared to a location on the crystal without an aggregate. The aggregate size, based on the major axe considering elliptical aggregates, is in the range of tens to hundreds of nm (d).



Figure S 6-2. SEM characterization of Ag-ETS-10 after 44 thermal regeneration cycles. SEM image showing (a) the typical truncated bi-pyramid crystals, (b) Ag aggregates (in red) on the Ag-ETS-10 crystal and (c) the Ag composition in one aggregate compared to a location on the crystal without an aggregate. The aggregate size, based on the major axe considering elliptical aggregates, is in the range of tens to hundreds of nm (d).


Figure S 6-3. SEM characterisation of the irradiated Ag-ETS-10 sample. SEM image showing (a) typical truncated bi-pyramid crystals, (b) Ag aggregates (in red) on the Ag-ETS-10 crystal and (c) the Ag composition in one aggregate compared to a location on the crystal without an aggregate. The aggregate size, based on the major axe considering elliptical aggregates, is in the range of tens to hundreds of nm (d).



Figure S 6-4. SEM characterisation of the Ag-ZSM-5 sample after 20 thermal regeneration cycles. SEM image showing (a) the typical flocculent structure and (b) sparse Ag aggregates of a few hundreds of nanometres on Ag-ZMS-5 together with the Ag composition in one aggregate compared to a location on the crystal without an aggregate.



Figure S 6-5. SEM characterisation of the Ag-ZSM-5 sample after 43 thermal regeneration cycles. SEM image showing (a) the typical flocculent structure and (b) sparse Ag aggregates of a few hundreds of nanometres on Ag-ZMS-5 together with the Ag composition in one aggregate compared to a location on the crystal without an aggregate.



Figure S 6-6. SEM characterisation of the irradiated Ag-ZSM-5 sample. SEM image showing (a) typical flocculent structure and (b) sparse Ag aggregates of a few hundreds of nanometres on Ag-ZMS-5 together with the Ag composition in one aggregate compared to a location on the crystal without an aggregate.



Figure S 6-7. X-ray diffractogram of aged samples of a) Ag-ETS-10 and b) Ag-ZSM-5.The X-ray diffractograms are equivalent to the ones of the fresh samples studied previously [311].





Figure S 6-8. N<sub>2</sub> adsorption and desorption isotherms at 77 K (left) and CO<sub>2</sub> adsorption isotherms at 273 K (right) for aged samples of Ag-ETS-10 (top) and Ag-ZSM-5 (bottom).The filled symbols are for the adsorption whereas the nonfilled symbols are for the desorption. The isotherms are compared to the results for a fresh sample reported previously [311].





*Figure S 6-9. Selected points for the BET isotherm fit (a, c and e) and selected points based on the Rouquerol plot (b, d and f) for the aged Ag-ETS-10 samples. From top to bottom: sample after 20 cycles, after 44 cycles and after irradiation.* 





Ag-ZSM-5-43 cycles



Figure S 6-10 Selected points for the BET isotherm fit (a, c and e) and selected points based on the Rouquerol plot (b, d and f) for the aged Ag-ZSM-5 samples. From top to bottom: sample after 20 cycles, after 43 cycles and after irradiation.

#### • XRF analysis of irradiated samples

Table S 6-4. Cs content in irradiated subsamples as measured by XRF. The layers that were not measured are indicated by "-". For Ag-ETS-10, the column length was much shorter due to its higher density and contained only 8 layers.

d (cm)	Cs (g m <sup>-3</sup> )	
- ()	Ag-ETS-10	Ag-ZSM-5
0	-	140
1	240	-
2	180	390
3	120	350
4	150	260
5	-	-
6	-	-
7	100	-
8		-
9		-
10		-
11		-
12	NA	-
13		-
14		-
15		-
16		< 3

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# **Chapter 7**

# Summary, conclusions and outlook

# 7. Summary, conclusions and outlook

#### 7.1.Summary and conclusions

Weapons of mass destruction have a devastating power and are a global concern. The atomic bombings of Hiroshima and Nagasaki at the end of World War II are regrettable examples of this devastating power. Despite these devastating consequences, more than 2000 nuclear weapon tests were performed by eight countries throughout the world after WWII to develop nuclear weapons or to verify the aging behaviour of previously developed nuclear weapons. Over time, international efforts have taken place to ban nuclear weapon testing and prevent the spread of nuclear weapons. One of the resulting international treaties is the Comprehensive Nuclear-Test-Ban Treaty (CTBT), which bans all nuclear weapon tests on Earth. Next to its comprehensive nature, the Treaty foresees a verification regime to detect any nuclear explosion.

For the verification of the CTBT, the nuclear nature of an explosion can only be proven by the measurement of radioactive matter that has been generated. Radioactive noble gases are the most likely to escape from an underground nuclear weapon test due to their inert nature compared to other radioactive matter produced. Accordingly, the worldwide monitoring of atmospheric traces of radioactive noble gases, especially xenon, released by a clandestine nuclear weapon test is important for the verification of the CTBT. A comprehensive description of the context is given in Chapter 1. When describing the state of the art on the radioxenon component of the International Monitoring System (IMS), the need for further improving the efficiency of the Xe collection and separation process was highlighted. Such an improvement could be used to further increase the detection capability, for traces from nuclear weapon tests, of radioxenon monitoring stations, which is corresponding to the **first** research objective of this PhD. Besides radioxenon, <sup>37</sup>Ar is a key tracer for an underground nuclear weapon test in case of an On-Site Inspection (OSI) of a suspected test location. The collection and separation of Ar from subsoil gas and from atmospheric air in sampling and measuring systems currently developed for OSI is an energyintensive process. The need for less energy demanding processes for Ar separation was identified as the **second** research objective.

Moreover, radioxenon monitoring in the atmosphere for CTBT verification is challenged by the presence of a complex worldwide radioxenon background. This challenging radioxenon background is detailed in Chapter 1. Research on the reduction of radioxenon emissions from civilian sources can alleviate this issue. The most important sources are a few fission-based Medical Isotope Production Facilities (MIPFs) operating around the world. Their radioxenon emissions are well below the regulatory limits to protect the population and the environment. Still, they are high enough to influence the ultrasensitive radioxenon monitoring component of the IMS. The radioxenon emissions could be reduced by developing more efficient adsorbents allowing to trap radioxenon for a longer time in the facility before being released to the atmosphere, which corresponds to the **third** research objective. Once efficient adsorbents are found, both for the collection and separation of noble gases for CTBT sampling and measuring systems, and for trapping radioxenon in civilian facilities, their durability in the relevant conditions needs to be confirmed. The relevant conditions are described in Chapter 1. The **fourth** research objective aimed at investigating the durability of two promising adsorbents (a silver-exchanged zeolite and a silver-exchanged titanosilicate) against the radiation levels that are encountered in civilian nuclear facilities and against successive thermal regeneration cycles as would be encountered in both civilian nuclear facilities and IMS monitoring stations.

In Chapter 2, the materials and methods that were used for multiple research objectives are detailed. Three types of adsorbents were investigated: Activated Carbon (AC), Silver-exchanged Zeolite or alike (AgZ), and Metal-Organic Framework (MOF). AC was used as reference material to compare the potential of new adsorbents, *i.e.* AgZs or MOFs, for the relevant applications. An experimental set-up was developed to measure the breakthrough of gas species in the investigated adsorbents. The experimental set-up allows for measurements in a large variety of conditions with regard to: gas mixture (air, Xe or Ar mixed in He or N<sub>2</sub>, and Ar, O<sub>2</sub> and N<sub>2</sub> ternary mixtures), temperature (213 to 543 K), humidity levels (up to 50% RH), flow rate (30 to 2000 cm<sup>3</sup> min<sup>-1</sup>) and column geometry. Next to the measurement of the adsorption capacity at equilibrium, the set-up allows to obtain information on the kinetic of the adsorption process (*e.g.* mass transfer zone and retention times at certain outlet concentrations).

As detailed in Chapter 2, gas adsorption was used throughout the research and gas adsorption isotherms were collected with different probing molecules. The adsorption isotherms for Xe and Ar in a carrier gas were fitted with the Langmuir isotherm equation. The N<sub>2</sub> adsorption isotherms collected at 77 K were fitted with the Brunauer-Emmett-Teller equation to determine the monolayer surface area of the adsorbent occupied by N<sub>2</sub> molecules. The Dubinin-Radushkevitch equation was used for fitting both N<sub>2</sub> isotherms at 77 K and CO<sub>2</sub> isotherms at 273 K to determine the microporous volume of the adsorbents. The pore size distribution in the adsorbents was evaluated using density functional theories to analyse the N<sub>2</sub> adsorption-desorption isotherms at 77 K.

Furthermore, Powder X-Ray Diffraction (PXRD), and Scanning Electron Microscopy (SEM), coupled with Energy Dispersive X-ray (EDX) spectroscopy, were used to characterize the crystallinity, morphology and composition of the adsorbents. These methods, used for multiple research objectives, were described in Chapter 2. They were used to compare the properties of the adsorbent samples that were investigated to the properties of similar adsorbents reported in the literature. These characterisation techniques were also used to investigate the durability of AgZs against irradiation and thermal regeneration cycles.

Chapters 3 to 6 each deal with one of the four research objectives of the PhD.

Chapter 3: Improving radioxenon monitoring systems

	Research objective	Main evaluation metrics
1	Investigate the potential of new porous materials for collecting and separating Xe directly from ambient air in the context of the international monitoring system	Xe collection and separation efficiency

In Chapter 3, the use of new types of adsorbents for a more efficient Xe collection and separation from atmospheric air is investigated. An enhanced efficiency would support further improvements of the radioxenon monitoring stations in the IMS, which would help to cope with the radioxenon background. For this purpose, the Xe collection and separation performance of two AgZs and two MOFs are compared to the performance of a reference AC. The acquired samples were characterized by SEM/EDX, PXRD, N<sub>2</sub> adsorption isotherms at 77 K and CO<sub>2</sub> adsorption isotherms at 273 K. As the separation of Xe from other gas components in air is performed by thermal desorption, a thermogravimetric analysis was performed on each sample to determine their thermal stability. The separation itself was investigated using the developed experimental breakthrough set-up.

It was shown that the morphology, composition, crystallinity, and thermal stability of the acquired samples are in good agreement with published data on similar adsorbents. Both AgZs (Ag-ETS-10 and Ag-ZSM-5) are thermally stable up to 773 K. The AC (Nusorb® GXK) has an auto-ignition point at 723 K and integrity loss started to be observed at 673 K. Concerning the two MOFs (HKUST-1 and Ni-DOBDC), the frameworks began to decompose at about 545 K. Next, the microporosity of the five adsorbents, as determined from  $N_2$  adsorption at 777 K and  $CO_2$  adsorption at 273 K, was comparable to published data. The surface area and micropore volume was the highest for HKUST-1 followed by Nusorb® GXK and then Ni-DOBDC. Both AgZs have a much lower surface area and micropore volume.

Despite their lower surface area and micropore volume, AgZs have a much higher Xe adsorption capacity both in N<sub>2</sub> and in air. Compared to AC, they can **collect Xe** from about 30 to 40 times more air for the same mass. The Xe adsorption capacity in air was 210 and 140 µmol kg<sup>-1</sup> for Ag-ETS-10 and Ag-ZSM-5, respectively. Even when considering reported data on non-commercial adsorbents, the Xe adsorption capacity of both AgZs is about one order of magnitude higher for the lowest investigated Xe concentration in N<sub>2</sub> (*i.e.* 100 ppb Xe). Both AgZs have unprecedented selectivities for Xe adsorption compared to the other gas components in air (up to 4300, compared to 72 for the AC). They are however sensitive to the presence of moisture in the gas stream as shown by a decrease in Xe adsorption capacity by a factor 30 to 35 when going from dry conditions to 50% RH. Concerning **Xe separation** from air, both AgZs allowed to reach a much higher Xe concentration (up to 13% vol., which is a factor 160 higher compared to AC) after a single thermal separation cycle. They only require a slightly higher temperature (487 K) to be fully regenerated compared to AC (467 K). Similarly,

the AgZs are very efficient in separating Xe from Rn, as needed for the activity measurement in radioxenon monitoring systems, during thermal desorption with very sharp and non-overlapping desorption peaks. They require a higher temperature (up to 520 K) compared to AC (about 425 K) to desorb radon.

In conclusion, both AgZs are significantly more performant, for **Xe collection and separation** from dry atmospheric air, than the AC and the two MOFs considered in this investigation. This is also true when compared to literature data on noncommercial adsorbents. However, the gas stream needs to be dried before being used and AgZs need higher temperatures for separating Xe from air and Rn. For their application as a single adsorbent to collect and separate Xe from dry atmospheric air, further investigations would be needed on the quantification of the purified Xe gas, the purification over multiple stages (in temperature or pressure swing adsorption mode) and their durability (as addressed in Chapters 5 and 6).

	Research objective	Main evaluation metrics
2	Investigate the collection and separation of Ar using a single adsorbent operating at or close to ambient conditions for on-site inspections	Ar yield and relative enrichment

• Chapter 4: Improving <sup>37</sup>Ar monitoring systems

In Chapter 4, the use of self-bound Ag-ETS-10 as a single adsorbent, operating at or close to Room Temperature (RT), for collecting and separating Ar from subsoil gas and from atmospheric air for OSI is investigated. This would provide a much more simplified and less energy demanding Ar separation process. The microporosity of self-bound Ag-ETS-10 was investigated by N<sub>2</sub> adsorption at 77 K and by CO<sub>2</sub> adsorption at 273 K. The Ar adsorption and separation properties were investigated with the experimental breakthrough set-up. A Vacuum Pressure Swing Adsorption (VPSA) system was developed specifically for this study, allowing to investigate the Ar separation potential of the adsorbent in such an operating mode. The VPSA results were quantified using the **Ar yield** and the **relative Ar enrichment**.

It was shown that the surface area and micropore volume, both determined by  $N_2$  adsorption at 77 K and by  $CO_2$  adsorption at 273 K, of self-bound Ag-ETS-10 was higher by 20 to 30% than the silica-bound version due to the higher density of the material (15%) and an improved pore accessibility. This increase is also observed in the Ar in He adsorption isotherm at RT when compared to published data on silica-bound Ag-ETS-10.

Air breakthrough measurements confirmed the strong preferential adsorption of  $N_2$  over  $O_2$  and Ar (selectivity of 5.7 and 9.7, respectively) as well as the preferential adsorption of Ar over  $O_2$  (selectivity of 1.7) already observed in silicabound Ag-ETS-10. By selecting part of the outlet gas, a significant Ar enrichment can be obtained (up to 6.4% Ar) in a single adsorption stage, by stripping the

collected gas from N<sub>2</sub> but also by separating Ar from O<sub>2</sub>. The gas mixture stripped from N<sub>2</sub> can also be further enriched in Ar by separating Ar from O<sub>2</sub> over successive adsorption-desorption steps on the same adsorbent. For OSI purposes, varying Ar, O<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O compositions will be encountered and it was demonstrated that: i) moisture levels below 50% RH would not impact the Ar separation performance on a single separation run, ii) the lack of O<sub>2</sub> in the gas stream decreases the achievable Ar yield for a collected gas with a composition enriched in Ar, iii) the Ar separation is slightly improved in gas mixtures with a lower Ar concentration than in air.

The investigation on the VPSA-based Ar collection and separation showed that pressurizing the gas feed during the adsorption (Pressure part of the VPSA process) decreases the Ar separation performance. The exploration with lower temperatures, between 213 and 294 K, used during the adsorption demonstrated that the optimal temperature for an efficient Ar separation, for Ar yields up to 50%, can be found around 248 K.

In conclusion, self-bound Ag-ETS-10 has a high potential for Ar separation from air for OSI purposes. The adsorption part could be operated at about 248 K to maximize the Ar separation, whereas the desorption could either be performed by vacuum or by thermal desorption (VSA and/or TSA). Further research is needed on the cyclic process of a V/TSA system to ensure that the necessary Ar yield and enrichment can be achieved for OSI.

	Research objective	Main evaluation metrics
3	Examine the potential of silver-exchanged zeolites for trapping radioactive Xe more efficiently at fission-based medical isotope production facilities to reduce radioxenon emissions	Xe adsorption capacity and regeneration conditions

• Chapter 5: Reducing radioxenon emissions

In Chapter 5, the potential of AgZs for trapping radioactive Xe at MIPFs, more efficiently compared to AC, is investigated. More efficient radioxenon trapping at these facilities would allow a lower radioxenon background in the atmosphere. Three nuclear grade ACs were used as reference adsorbents and were compared to five AgZs. The investigation was performed by comparing the Xe adsorption properties for relevant concentrations, as obtained from breakthrough experiments. The best AgZ was then further investigated for its application in such facilities.

The comparison of the **Xe adsorption capacity** in a dry gas stream showed that the Ag-ETS-10 had a much higher adsorption capacity (490 mmol kg<sup>-1</sup> for a 1000 ppm Xe in He mixture) than any other adsorbent. Compared to a typical nuclear grade AC (Nusorb® GXK), the amount of Xe adsorbed per unit volume in Ag-ETS-10 is about 20 to 180 times higher. However, the two most promising AgZs (Ag-ETS-10 followed by a silver-exchanged Chabazite) were significantly

impacted when moisture was added to the gas stream. The Xe adsorption capacity for a gas stream with 50% RH decreased by a factor 7 to 30 compared to dry conditions on these two adsorbents.

As the gas stream in MIPFs can be dehumidified before radioxenon trapping, Ag-ETS-10 was selected for further investigation on its applicability in MIPFs. It was demonstrated that breakthrough experiments were particularly well suited for optimizing the design of radioxenon trapping systems, as they allow to investigate the shape of the breakthrough curve under different conditions (in particular inlet concentration, column geometry and flow rate). The durability of Ag-ETS-10 against irradiation and thermal regeneration cycles was explored for the first time. It was shown that it can withstand a 1 MGy gamma irradiation (corresponding to a few hours of operation in a MIPF) and 20 thermal regeneration cycles under He and N<sub>2</sub>. The high radioxenon activity that would be retained in the adsorbent in a MIPF could increase its temperature due to decay. An increase from 296 to 333 K would only decrease the retention time by a factor 1.3. The Xe adsorption capacity of Ag-ETS-10 can be recovered by **thermal regeneration** at or even below 483 K under He or N<sub>2</sub>.

In conclusion, Ag-ETS-10 is a strong candidate to trap radioxenon more efficiently at MIPFs. The volume of adsorbent required can be decreased by one to two orders of magnitude, in function of the conditions, compared to actual ACs. For its use in MIPFs, further research is needed on its durability against a higher irradiation dose and even more thermal regeneration cycles (as addressed in Chapter 6).

	Research objective	Main evaluation metrics
4	Assess the durability of Ag-ETS-10 and Ag-ZSM-5 after multiple thermal regeneration cycles as well as after irradiation	Xe adsorption capacity and structural characterization

• Chapter 6: Durability of silver-exchanged zeolites

In Chapter 6, the durability against radiation (with higher doses) and thermal regeneration cycles (with more cycles) of both Ag-ETS-10 and Ag-ZSM-5 is investigated to further assess their potential both for radioxenon trapping at MIPFs and Xe collection and separation for radioxenon monitoring systems. The experimental breakthrough set-up was used to assess the evolution of the **Xe adsorption properties** after the aging processes. About 40 thermal regeneration cycles were performed, in air and N<sub>2</sub>, on both adsorbents. Both adsorbents were irradiated in situ by adsorbing <sup>133</sup>Xe at the Institute for RadioElements (IRE, Fleurus, Belgium). Finite element modelling of the gas transport and adsorbent during the irradiation experiment. Monte Carlo simulations were then executed to estimate the distribution of the absorbed dose from the irradiation in the adsorbents. Fresh and aged samples were **characterized** by SEM/EDX, PXRD, N<sub>2</sub> adsorption isotherms at 77 K and CO<sub>2</sub> adsorption isotherms at 273 K. Solid-state

NMR spectroscopy was also used to investigate changes, from both aging processes, in the local environment of  $^{29}\rm{Si}$  in both adsorbents and of  $^{27}\rm{Al}$  for Ag-ZSM-5.

No degradation of Xe adsorption properties could be observed due to the thermal regeneration cycles nor the irradiation on both adsorbents. The morphology, composition, and crystallinity of the samples were maintained on cycled and irradiated samples (73 MGy for Ag-ETS-10 and 160 MGy for Ag-ZSM-5). Similarly, the microporous properties, as determined from N<sub>2</sub> adsorption at 77 K and CO<sub>2</sub> adsorption at 273 K, were not degraded due to the thermal regeneration cycles nor the irradiation. The <sup>29</sup>Si and <sup>27</sup>Al local environments were not altered after the thermal regeneration cycles on both adsorbents and after the irradiation on Ag-ZSM-5. For Ag-ETS-10, the <sup>29</sup>Si signals were broadened and upfield shifted after the irradiation. This peak broadening and shifting is due to the presence of the paramagnetic decay product (<sup>133</sup>Cs) of <sup>133</sup>Xe and is visible in Ag-ETS-10 as its <sup>29</sup>Si sites seem to be closer to <sup>133</sup>Cs (up to 390 g m<sup>-3</sup>) in the irradiated samples of both adsorbents.

In conclusion, both adsorbents conserved their Xe adsorption performance and no alteration in their morphology, composition, crystallinity, microporosity and the local environment of <sup>29</sup>Si and <sup>27</sup>Al, could be observed after at least 43 thermal regeneration cycles, and a 73 and 160 MGy irradiation for Ag-ETS-10 and Ag-ZSM-5, respectively. The range of irradiation used in this work corresponds to hundreds of hours of operation in MIPFs and is a major step forward for their application in MIPFs. In addition, their durability against thermal regeneration cycles will also support their further use in radioxenon monitoring systems.

# 7.2.Outlook

The results show that Ag-ETS-10 and Ag-ZSM-5 could be used for **collecting and** separating Xe directly from dry air. Both AgZs could be used for a simplified gas processing, with less pre-treatment of the gas, in next generation radioxenon monitoring systems. A pre-purification step will be necessary as these adsorbents are very sensitive to moisture. But a two-stage separation process would be possible with first a dehumidification on a dedicated adsorbent (or any other method) and then the Xe collection and separation on one of the two AqZs. The second stage could be repeated multiple times to further purify the recovered Xe gas. Care should be taken with other contaminants, such as CI-containing volatile organic compounds, that have been shown in the literature to degrade the Aq-ZSM-5 and might be enriched during the dehumidification process. Further studies should focus on such a two-stage process and investigate the much longerterm stability of both adsorbents when used with dry air. From the durability study, they can withstand at least 43 cycles, but this only corresponds to 10 days of operation (when considering one thermal regeneration cycle per collected sample) for the most demanding second generation radioxenon monitoring system. Using a system with only two stages could further decrease the processing time (allowing to decrease the detection limit for the short-lived <sup>135</sup>Xe) and maximize the Xe recovery, allowing also to reduce the detection limits for the four isotopes.

Such simplified processes would increase the detection capability of these systems for nuclear weapon tests as well as increase the discrimination capability due to a higher likelihood to detect multiple isotopes. Such a simplified process, with Ag-ETS-10 or Ag-ZSM-5 working directly on dry air, is also of relevance for radioxenon sampling and measuring systems for OSI and could provide similar improvements.

In another context, a similar process could also be used to produce stable xenon and provide an **energy-efficient alternative** to the current cryogenic distillation of the Xe/Kr by-product obtained from cryogenic air distillation. The global demand for high-purity Xe is increasing and such an alternative will become more and more critical in the future. Similarly, the results could be used for collecting atmospheric radioxenon on AgZs during **nuclear emergencies** to detect its presence in the atmosphere. This is particularly relevant as noble gases are the first radionuclides to be released during nuclear accidents due to their inert nature. Similarly, AgZs could be used to collect radioxenon in nuclear facilities for **stack monitoring** in routine and emergency conditions.

The research on Ag-ETS-10 as single filter material, operating at or close to ambient conditions, for Ar collection and separation could support the development of more efficient OSI <sup>37</sup>Ar sampling and measuring systems. In this case, the process is not impacted, at least during a single cycle, by the presence of moisture so that Aq-ETS-10 can be used as a single filter material. The recovered gas can be efficiently stripped from  $N_2$  as well as enriched in Ar with a first separation stage on Aq-ETS-10 operating at 248 K. The regeneration of the adsorbent after this first adsorption stage would need further investigation to find the most optimal regeneration process (heating and/or vacuum). After this first stage, further Ar enrichment in the obtained  $Ar/O_2$  mixture would be necessary. Such an enrichment is possible by multiple cycles over Ag-ETS-10 at RT. However, the obtained Ar yield would not be sufficient so that this part of the process needs further investigations. Such further investigations could focus on the  $Ar/O_2$  separation on Aq-ETS-10 operating **at a lower temperature** (*e.g.* also at 248 K). If such a lower temperature would significantly improve the  $Ar/O_2$ separation, then further research would be needed to investigate the actual Ar yield and enrichment over multiple cycles of a system operating in these conditions. In addition, a similar approach, as the one used in this work, could be used to investigate other promising adsorbents (e.g. Ba-RPZ) for Ar collection and separation for OSI. More efficient systems would reinforce their use as a crucial measurement technique for CTBT verification during OSI, which is the ultimate verification measure under the Treaty that can provide unequivocal evidence of a suspected nuclear weapon test. In addition, there are currently discussions within the CTBT community to evaluate the use of <sup>37</sup>Ar as a complementary measurement for **IMS noble gas monitoring stations**. Further developments on Ar collection and separation could also support its use for IMS.

The research on AgZs (in particular Ag-ETS-10 and Ag-ZSM-5), including their durability, for the **mitigation of radioxenon** releases provides a solution for Xe mitigation at civilian facilities, especially facilities that have a large contribution to the IMS noble gas component, to minimize their impact on CTBT verification. From

the research performed, it is clear that both AqZs can much more efficiently trap radioxenon and they can be reused at least 43 times by thermal regeneration. The demonstration of their radiation resistance up to about 100 MGy is a significant step forward for their application across the major radioxenon emitting MIPFs. Further investigations on the durability against higher irradiation doses can be performed gradually by using them in the production process of MIPFs itself and checking their adsorption properties over time. This is being done at the Institute of RadioElements (IRE, Fleurus), where Ag-ETS-10 is used to collect radioxenon from their dissolution process. The evaluation of the adsorption performance of the Aq-ETS-10 samples, used at IRE, in function of time can further provide insight in its radiation resistance and in the behaviour of the decay products. With regard to their durability against thermal regeneration cycles, 43 cycles would be achieved in several months and here also a verification of their adsorption properties over time would be needed to ensure their durability. The decrease of the radioxenon emissions of MIPFs would clearly improve the detection capability of the radioxenon component of the IMS as the background level will be lowered.

One major issue for CTBT verification that could be encountered in the future is the deployment of a large number of small modular reactors at many more locations than the current NPPs. They will all emit some radioxenon in the atmosphere, potentially altering the observations from other sources, such as a clandestine nuclear weapon test. This would further complicate the CTBT verification by radioxenon observations. Their emissions might be lower but the probability of a source close to an IMS location will certainly increase. Accordingly, their emissions will most likely be picked-up by the IMS and mixed with other sources. Here also the research performed on more efficient adsorbents for radioxenon mitigation is particularly relevant. There are many designs being investigated: from the well-known pressurized or boiling water reactors to new designs such as molten-salt reactors or lead-cooled fast reactors. Since the development is at very different design stages of their conception, it is currently difficult to estimate their Xe releases. However, once this information becomes available, together with the details of the gas streams, studies can be performed to determine the need for Xe mitigation and the potential of AqZs in this context, based on the current work.

# Samenvatting, conclusies en vooruitzichten

#### 7.3.Samenvatting en conclusies

Massavernietigingswapens hebben een enorm verwoestende kracht en vormen een wereldwijde bezorgdheid. De atoombomaanvallen op Hiroshima en Nagasaki aan het einde van de Tweede Wereldoorlog toonden de betreurenswaardige resultaten van hun destructieve capaciteit. Ondanks de verwoestende gevolgen werden na de Tweede Wereldoorlog meer dan 2000 kernwapenproeven uitgevoerd door acht landen over de hele wereld om nieuwe kernwapens te ontwikkelen of om het verouderingsgedrag van ontwikkelde kernwapens te verifiëren. In de loop der tijd zijn er internationale inspanningen geleverd om kernwapenproeven te verbieden en de verspreiding van kernwapens te voorkomen. Een van de resulterende internationale verdragen is het alomvattend kernstopverdrag (Comprehensive Nuclear-Test-Ban Treaty in het Engels, afgekort CTBT), dat alle kernwapenproeven op aarde verbiedt. Naast zijn alomvattende aard voorziet het verdrag ook in een verificatieregime om elke nucleaire explosie te detecteren.

Voor de verificatie van het CTBT kan de nucleaire aard van een explosie alleen worden bewezen door de meting van radioactieve stoffen die geproduceerd zijn. Radioactieve edelgassen hebben de grootste kans om te ontsnappen uit een ondergrondse kernwapenproef vanwege hun inerte aard in vergelijking met andere geproduceerde radioactieve stoffen. De wereldwijde monitoring van sporen van radioactieve edelgassen in de atmosfeer, vooral xenon, die vrijkomen bij een clandestiene kernwapenproef is bijgevolg belangrijk voor de verificatie van het CTBT. Een uitgebreide beschrijving van de context wordt gegeven in Hoofdstuk 1. Bij het beschrijven van de stand van zaken met betrekking tot de radioactieve xenon component van het "International Monitoring System" (IMS), werd de noodzaak benadrukt om de efficiëntie van het bemonsterings- en scheidingsproces van Xe verder te verbeteren. Een dergelijke verbetering zou kunnen worden gebruikt om het detectie vermogen voor sporen van kernwapenproeven in monitoringstations voor radioactief xenon verder te vergroten, hetgeen met het **eerste** onderzoeksdoel van dit doctoraatsproefschrift. Naast radioactief xenon is <sup>37</sup>Ar een belangrijke tracer voor een ondergrondse kernwapenproef in het geval van een "On-Site Inspection" (OSI) van een vermoedelijke proeflocatie. Het bemonsteren en scheiden van Ar uit ondergrondse gassen en uit atmosferische lucht in bemonsterings- en meetsystemen die momenteel zijn ontwikkeld voor OSI is een energie-intensief proces. De behoefte aan minder energie-intensieve processen voor Ar-scheiding werd geïdentificeerd als het tweede onderzoeksdoel.

Een bijkomende vaststelling is dat de monitoring van radioactief xenon in de atmosfeer voor de verificatie van het CTBT bemoeilijkt wordt door de aanwezigheid van een complexe wereldwijde achtergrond van radioactief xenon ook wel radioxenon genoemd. Deze uitdagende radioxenon achtergrond wordt gedetailleerd beschreven in Hoofdstuk 1. Onderzoek naar de vermindering van radioxenon uitstoten van civiele bronnen kan dit probleem helpen verlichten. De belangrijkste bronnen van civiele uitstoten zijn enkele splijting-gebaseerde productiefaciliteiten voor medische isotopen (MIPF's) die wereldwijd verspreid zijn. Hun radioxenon uitstoten liggen ruim onder de wettelijke limieten om de bevolking en het milieu te beschermen. Toch zijn ze hoog genoeg om de ultrasensitieve radioxenon monitoringsystemen van het IMS te beïnvloeden. De radioxenon uitstoten zouden kunnen worden verminderd door efficiëntere adsorptiematerialen te ontwikkelen die radioactief xenon langer in de faciliteit kunnen tegenhouden voordat het in de atmosfeer wordt vrijgegeven, wat overeenkomt met het **derde** onderzoeksdoel.

Zodra efficiënte adsorptiematerialen zijn gevonden, zowel voor de bemonstering en scheiding van edelgassen ten behoeve van CTBT-bemonsterings- en meetsystemen, als voor het tegenhouden van radioactief xenon in civiele faciliteiten, moet hun duurzaamheid onder de relevante omstandigheden worden aangetoond. De relevante omstandigheden worden beschreven in Hoofdstuk 1. Het **vierde** onderzoeksdoel was gericht op het onderzoeken van de duurzaamheid van twee veelbelovende adsorptiematerialen (een zilver-uitgewisseld zeoliet en een zilver-uitgewisseld titanosilicaat) tegen de stralingsniveaus die worden aangetroffen in civiele nucleaire faciliteiten en tegen opeenvolgende thermische regeneratiecycli zoals die zouden worden gebruikt in zowel civiele nucleaire faciliteiten als in IMS-monitoringstations.

In Hoofdstuk 2 worden de materialen en methoden die voor meerdere onderzoeksdoelen zijn gebruikt, gedetailleerd beschreven. Drie soorten adsorptiematerialen werden onderzocht: Actieve Kool (AC, vanuit het Engels), Zilver-uitgewisseld Zeoliet of soortgelijke materialen (AqZ), en Metaal-Organisch Raamwerk (MOF, vanuit het Engels). AC werd gebruikt als referentiemateriaal om het potentieel van nieuwe adsorptiematerialen, namelijk AgZ's of MOF's, voor de relevante toepassingen te vergelijken. Een experimentele opstelling werd ontwikkeld om de doorbraak van gassen in de onderzochte adsorptiematerialen te meten. De experimentele opstelling maakt metingen mogelijk in een grote verscheidenheid aan omstandigheden met betrekking tot: gasmengsel (lucht, Xe of Ar gemengd in He of N<sub>2</sub>, en Ar, O<sub>2</sub> en N<sub>2</sub> in tertiaire mengsels), temperatuur (213 tot 543 K), vochtigheidsniveaus (tot 50% relatieve vochtigheid), debiet (30 2000 cm<sup>3</sup> min<sup>-1</sup>) en kolomgeometrie. Naast tot de meting van de adsorptiecapaciteit in evenwicht, maakt de opstelling het mogelijk om informatie te verkrijgen over de kinetiek van het adsorptieproces (bijv. massatransferzone en retentietijden bij bepaalde uitgangsconcentraties).

Zoals gedetailleerd in Hoofdstuk 2, werd gasadsorptie gedurende het hele onderzoek gebruikt en werden gasadsorptie-isothermen verzameld met verschillende proefmoleculen. De adsorptie-isothermen voor Xe en Ar in een draaggas werden gefit met de Langmuir-isothermvergelijking. De N<sub>2</sub> adsorptieisothermen verzameld bij 77 K werden gefit met de Brunauer-Emmett-Tellervergelijking om het monolaagoppervlak van het adsorptiemateriaal, bezet door N<sub>2</sub> moleculen, te bepalen. De Dubinin-Radushkevitch-vergelijking werd gebruikt voor het fitten van zowel N<sub>2</sub> isothermen bij 77 K als CO<sub>2</sub> isothermen bij 273 K om het volume aan microporiën van de adsorptiematerialen te bepalen. De poriegrootteverdeling in de adsorptiematerialen werd geëvalueerd met behulp van dichtheidsfunctionaaltheorieën om de  $N_2$  adsorptie-desorptie-isothermen bij 77 K te analyseren.

Bovendien werden poeder röntgendiffractie (PXRD, vanuit het Engels) en rasterelektronenmicroscopie (SEM, vanuit het Engels), gekoppeld aan "Energy Dispersive X-ray" (EDX) spectroscopie, gebruikt om de kristalliniteit, morfologie en samenstelling van de adsorptiematerialen te karakteriseren. Deze methoden, die voor meerdere onderzoeksdoelen werden gebruikt, worden beschreven in Hoofdstuk 2. Ze werden gebruikt om de eigenschappen van de onderzochte stalen van adsorptiematerialen te vergelijken met de eigenschappen van gelijkaardige adsorptiematerialen die in de literatuur worden gerapporteerd. Deze karakterisatietechnieken werden ook gebruikt om de duurzaamheid van AgZ's tegen bestraling en tegen thermische regeneratiecycli te onderzoeken.

Hoofdstukken 3 tot 6 behandelen elk een van de vier onderzoeksdoelen van het doctoraatsproefschrift.

	Onderzoeksdoel	Belangrijkste evaluatiemetingen
1	Onderzoek het potentieel van nieuwe poreuze materialen voor het bemonsteren en scheiden van Xe direct uit omgevingslucht in de context van het IMS.	Xe bemonsterings- en scheidingsefficiëntie

• Hoofdstuk 3: Verbetering van radioactief xenon monitoringsystemen

In Hoofdstuk 3 wordt het gebruik van nieuwe soorten adsorptiematerialen voor een efficiëntere bemonstering en voor de scheiding van Xe uit atmosferische lucht onderzocht. Een verbeterde efficiëntie zou verdere verbeteringen van de radioxenon monitoringstations in het IMS ondersteunen, wat zou helpen om de radioxenon achtergrond aan te pakken. Voor dit doel worden de prestaties van twee AgZ's en twee MOF's voor de bemonstering en scheiding van Xe vergeleken met de prestaties van een referentie-AC. De bestudeerde stalen van adsorptiematerialen werden gekarakteriseerd door SEM/EDX, PXRD, N<sub>2</sub> adsorptieisothermen bij 77 K en CO<sub>2</sub> adsorptie-isothermen bij 273 K. Aangezien de scheiding van Xe van andere gascomponenten in lucht door thermische desorptie wordt uitgevoerd, werd een thermogravimetrische analyse uitgevoerd op elk staal om hun thermische stabiliteit te bepalen. De scheiding zelf werd onderzocht met behulp van de ontwikkelde experimentele doorbraak-opstelling.

De morfologie, samenstelling, kristalliniteit en thermische stabiliteit van de bestudeerde stalen komen goed overeen met gepubliceerde gegevens voor vergelijkbare adsorptiematerialen. Beide AqZ's (Aq-ETS-10 en Aq-ZSM-5) zijn thermisch stabiel tot 773 K. AC (Nusorb® De GXK) heeft een zelfontbrandingstemperatuur van 723 K en integriteitsverlies wordt waargenomen vanaf 673 K. Wat betreft de twee MOF's (HKUST-1 en Ni DOBDC), deze structuren begonnen hun integriteit te verliezen bij ongeveer 545 K. Vervolgens was de microporositeit van de vijf adsorptiematerialen, zoals bepaald uit N<sub>2</sub> adsorptie bij 77 K en  $CO_2$  adsorptie bij 273 K, vergelijkbaar met gepubliceerde gegevens. De oppervlakte en het volume aan microporiën waren het hoogst voor HKUST-1, gevolgd door Nusorb® GXK en vervolgens Ni-DOBDC. Beide AgZ's hebben een veel lagere oppervlakte en een veel kleiner volume aan microporiën.

Ondanks hun lagere oppervlakte en kleiner volume aan microporiën hebben AgZ's een veel hogere Xe adsorptiecapaciteit, zowel in  $N_2$  als in lucht. Vergeleken met AC kunnen ze Xe bemonsteren uit ongeveer 30 tot 40 keer meer lucht voor dezelfde massa. De Xe adsorptiecapaciteit in lucht was 210 en 140 µmol kg<sup>-1</sup> voor respectievelijk Aq-ETS-10 en Aq-ZSM-5. Zelfs wanneer rekening wordt gehouden met gerapporteerde gegevens over niet-commerciële adsorptiematerialen, is de Xe adsorptiecapaciteit van beide AqZ's ongeveer een grootteorde hoger voor de laagste onderzochte Xe concentratie in N<sub>2</sub> (d.w.z. 100 ppb Xe). Beide AgZ's hebben ongekende selectiviteiten voor Xe vergeleken met de andere gascomponenten in lucht (tot 4300, vergeleken met 72 voor de AC). Ze zijn echter gevoelig voor de aanwezigheid van vocht in de gasstroom, zoals blijkt uit een afname van de Xe adsorptiecapaciteit met een factor 30 tot 35 bij het overgaan van droge omstandigheden naar 50% relatieve vochtigheid. Wat betreft de scheiding van Xe uit lucht, beide AgZ's maakten het mogelijk om een veel hogere Xe concentratie te bereiken na één thermische scheidingscyclus (tot 13% vol., wat een factor 160 hoger is vergeleken met AC). Ze vereisen slechts een iets hogere temperatuur (487 K) om volledig te worden geregenereerd in vergelijking met AC (467 K). De AgZ's zijn ook zeer efficiënt in het scheiden van Xe van Rn, zoals nodig is voor de activiteitsmeting in radioxenon monitoringsystemen, tijdens thermische desorptie met zeer scherpe en nietoverlappende desorptiepieken. Ze vereisen wel een hogere temperatuur (tot 520 K) om radon te desorberen in vergelijking met AC (ongeveer 425 K).

In conclusie, beide AgZ's zijn aanzienlijk performanter voor de **bemonstering en scheiding van Xe** uit droge atmosferische lucht dan de AC en de twee MOF's die in dit onderzoek zijn bestudeerd. Dit geldt ook voor de vergelijking met literatuurgegevens over niet-commerciële adsorptiematerialen. De gasstroom moet echter worden gedroogd voordat deze materialen worden gebruikt en AgZ's hebben hogere temperaturen nodig voor het scheiden van Xe uit lucht en Rn. Voor hun toepassing als enig adsorptiemateriaal om Xe uit droge atmosferische lucht te bemonsteren en te scheiden, zou verder onderzoek nodig zijn naar de kwantificatie van het gezuiverde Xe gas, de zuivering over meerdere cycli (in temperatuur- of drukwissel-adsorptiemodus) en hun duurzaamheid (zoals behandeld in Hoofdstukken 5 en 6).

	Onderzoeksdoel	Belangrijkste evaluatiemetingen
2	Onderzoek de bemonstering en scheiding van Ar met behulp van één adsorptiemateriaal dat werkt bij of nabij omgevingsomstandigheden voor "on-site inspections".	Ar opbrengst en relatieve verrijking

• Hoofdstuk 4: Verbetering van <sup>37</sup>Ar monitoringsystemen

In Hoofdstuk 4 wordt het gebruik van zelfgebonden Ag-ETS-10 als enig adsorptiemateriaal, werkend bij of nabij kamertemperatuur (RT, vanuit het Engels), voor het bemonsteren en scheiden van Ar uit ondergrond gassen en uit atmosferische lucht voor OSI onderzocht. Dit zou een veel eenvoudiger en minder energie-intensief Ar scheidingsproces opleveren. De microporositeit van zelfgebonden Ag-ETS-10 werd onderzocht door N<sub>2</sub> adsorptie bij 77 K en door CO<sub>2</sub> adsorptie bij 273 K. De Ar adsorptie- en scheidingseigenschappen werden onderzocht met de experimentele opstelling om doorbraak metingen uit te voeren. Een "Vacuum Pressure Swing Adsorption" (VPSA) systeem werd specifiek voor deze studie ontwikkeld om het Ar scheidingspotentieel van het adsorptiemateriaal in een dergelijke bedrijfsmodus te onderzoeken. De VPSA-resultaten werden gekwantificeerd met behulp van de **Ar opbrengst** en de **relatieve Ar verrijking**.

Het bleek dat het oppervlak en het volume aan microporiën, beide bepaald door  $N_2$  adsorptie bij 77 K en door  $CO_2$  adsorptie bij 273 K, van zelfgebonden Ag-ETS-10, 20 tot 30% hoger waren dan de silica-gebonden versie vanwege de hogere dichtheid van het materiaal (15%) en een verbeterde porie toegankelijkheid. Deze toename wordt ook waargenomen in de Ar in He adsorptie-isotherm bij RT in vergelijking met gepubliceerde gegevens over silica-gebonden Ag-ETS-10.

Luchtdoorbraakmetingen bevestigden de sterke voorkeuradsorptie van  $N_2$  over  $O_2$ en Ar (selectiviteit van respectievelijk 5,7 en 9,7) evenals de voorkeuradsorptie van Ar over  $O_2$  (selectiviteit van 1,7) die al werd waargenomen in silica-gebonden Ag-ETS-10. Door een deel van het uitlaatgas te selecteren, kan een significante Ar-verrijking worden verkregen (tot 6,4% Ar) in één adsorptiecyclus, door het verzamelde gas van  $N_2$  te ontdoen maar ook door Ar van  $O_2$  te scheiden. Het gasmengsel dat van  $N_2$  is ontdaan, kan ook verder worden verrijkt in Ar door Ar van  $O_2$  te scheiden over opeenvolgende adsorptie-desorptie stappen op hetzelfde adsorptiemateriaal. Voor OSI-doeleinden zullen variërende Ar,  $O_2$ ,  $N_2$  en  $H_2O$ samenstellingen worden aangetroffen en het werd aangetoond dat: i) vochtigheidsniveaus onder 50% relatieve vochtigheid de Ar scheidingsprestaties bij een enkele scheidingsrun niet zouden beïnvloeden, ii) het ontbreken van  $O_2$  in de gasstroom de haalbare Ar opbrengst vermindert (voor een verzameld gas met een samenstelling verrijkt in Ar), iii) de Ar scheiding enigszins wordt verbeterd in gasmengsels met een lagere Ar concentratie dan deze in lucht.

Het onderzoek naar de op VPSA gebaseerde Ar bemonstering en scheiding toonde aan dat het onder druk zetten van de gasinvoer tijdens de adsorptie (drukgedeelte van het VPSA-proces) de Ar scheidingsprestaties vermindert. De verkenning met lagere temperaturen, tussen 213 en 294 K, gebruikt tijdens de adsorptie, toonde aan dat de optimale temperatuur voor een efficiënte Ar scheiding, voor Ar opbrengsten tot 50%, rond 248 K kan worden gevonden.

In conclusie, zelfgebonden Ag-ETS-10 heeft een hoog potentieel voor Ar scheiding uit lucht voor OSI-doeleinden. Het adsorptiegedeelte zou kunnen worden uitgevoerd bij ongeveer 248 K om de Ar scheiding te maximaliseren, terwijl de desorptie ofwel door vacuüm of door thermische desorptie (VSA en/of TSA) zou kunnen worden uitgevoerd. Verder onderzoek is nodig naar het cyclische proces van een V/TSA-systeem om ervoor te zorgen dat de benodigde Ar opbrengst en verrijking voor OSI toepassingen kunnen worden bereikt.

• Hoofdstuk 5: Vermindering van de radioactief xenon uitstoten

	Onderzoeksdoel	Belangrijkste evaluatiemetingen
3	Onderzoek het potentieel van zilver- uitgewisselde zeolieten voor het efficiënter opvangen van radioactief Xe bij splijting- gebaseerde productiefaciliteiten voor medische isotopen om radioxenon uitstoten te verminderen	Xe adsorptiecapaciteit en regeneratieomstandigheden

In Hoofdstuk 5 wordt het potentieel van AgZ's voor het opvangen van radioactief Xe bij MIPF's, op een efficiënter manier dan AC, onderzocht. Efficiënter opvangen van radioxenon bij deze faciliteiten zou een lagere radioactief xenon achtergrond in de atmosfeer mogelijk maken. Drie AC's, voor nucleaire toepassingen, werden gebruikt als referentie adsorptiematerialen en werden vergeleken met vijf AgZ's. Het onderzoek werd uitgevoerd door de Xe adsorptie-eigenschappen voor relevante concentraties te vergelijken, zoals verkregen uit doorbraakexperimenten. De beste AgZ werd vervolgens verder onderzocht voor zijn toepassing in dergelijke faciliteiten.

De vergelijking van de **Xe adsorptiecapaciteit** in een droge gasstroom toonde aan dat de Ag-ETS-10 een veel hogere adsorptiecapaciteit had (490 mmol kg<sup>-1</sup> voor een 1000 ppm Xe in He mengsel) dan de andere adsorptiematerialen. Vergeleken met een typische AC voor nucleaire toepassingen (Nusorb® GXK) is de hoeveelheid Xe die per volume-eenheid in Ag-ETS-10 wordt geadsorbeerd ongeveer 20 tot 180 keer hoger. De eigenschappen van de twee meest veelbelovende AgZ's (Ag-ETS-10 gevolgd door een zilver-uitgewisselde chabaziet) werden echter aanzienlijk negatief beïnvloed wanneer vocht aan de gasstroom werd toegevoegd. De Xe adsorptiecapaciteit voor een gasstroom met 50% relatieve vochtigheid nam met een factor 7 tot 30 af in vergelijking met droge omstandigheden op deze twee adsorptiematerialen.

Aangezien de gasstroom in MIPF's kan worden ontvochtigd voordat radioactief xenon wordt opgevangen, werd Ag ETS 10 geselecteerd voor verder onderzoek naar zijn toepasbaarheid in MIPF's. Er werd aangetoond dat doorbraak experimenten bijzonder geschikt waren voor het optimaliseren van het ontwerp van radioxenon opvangsystemen, omdat ze het mogelijk maken om de vorm van de doorbraakcurve onder verschillende omstandigheden te onderzoeken (bijvoorbeeld inlaatconcentratie, kolomgeometrie en debiet). De duurzaamheid van Ag-ETS-10 tegen bestraling en thermische regeneratiecycli werd voor het eerst onderzocht. Ag-ETS-10 kan een geabsorbeerde dosis van 1 MGy aan gamma-bestraling (overeenkomend met enkele uren werking in een MIPF) en 20 thermische regeneratiecycli onder He en N<sub>2</sub> weerstaan. De hoge radioactief xenon activiteit die in het adsorptiemateriaal in een MIPF zou worden vastgehouden, zou de temperatuur kunnen verhogen door verval. Een stijging van 296 naar 333 K

zou de retentietijd slechts met een factor 1,3 verminderen. De Xe adsorptiecapaciteit van Ag-ETS-10 kan worden hersteld door **thermische regeneratie** bij of zelfs onder 483 K, onder een He of  $N_2$  gasstroom.

In conclusie, Ag-ETS-10 is een sterke kandidaat om radioactief xenon efficiënter op te vangen bij MIPF's. Het benodigde volume adsorptiemateriaal kan met een tot twee grootteordes worden verminderd, afhankelijk van de omstandigheden, vergeleken met de huidige AC's. Voor gebruik in MIPF's is verder onderzoek nodig naar de duurzaamheid tegen een hogere stralingsdosis en nog meer thermische regeneratiecycli (zoals behandeld in Hoofdstuk 6).

- OnderzoeksdoelBelangrijkste<br/>evaluatiemetingen4Beoordeel de duurzaamheid van<br/>Ag-ETS-10 en Ag-ZSM-5 na meerdere<br/>thermische regeneratiecycli en na<br/>bestralingXe adsorptiecapaciteit en<br/>structurele karakterisering
- Hoofdstuk 6: Duurzaamheid van zilver-uitgewisselde zeolieten

In Hoofdstuk 6 wordt de duurzaamheid tegen straling (met een hogere stralingdosis) en thermische regeneratiecycli (met meer cycli) van zowel Ag-ETS-10 als Ag-ZSM-5 onderzocht om hun potentieel verder te beoordelen, zowel voor het opvangen van radioactief xenon bij MIPF's als voor het bemonsteren en scheiden van Xe voor radioxenon monitoringsystemen. De experimentele opstelling voor doorbraak metingen werd gebruikt om de evolutie van de Xe adsorptie eigenschappen na de verouderingsprocessen te beoordelen. Ongeveer 40 thermische regeneratiecycli werden uitgevoerd in lucht en N<sub>2</sub> op beide adsorptiematerialen. Beide adsorptiematerialen werden in situ bestraald door <sup>133</sup>Xe te adsorberen bij het "Institute for RadioElements" (IRE, Fleurus, België). Eindige-elementen modellering van het gastransport en het adsorptieproces werden uitgevoerd om de activiteitsverdeling in het adsorptiemateriaal tijdens het bestralingsexperiment te bepalen. Monte Carlo simulaties werden vervolgens uitgevoerd om de verdeling van de geabsorbeerde dosis van de bestraling in de adsorptiematerialen te schatten. Verse en verouderde stalen werden gekarakteriseerd door SEM/EDX, PXRD, N<sub>2</sub> adsorptie-isothermen bij 77 K en CO<sub>2</sub> adsorptie-isothermen bij 273 K. Vaste stof NMR spectroscopie werd ook gebruikt om verandering, ten gevolge van beide verouderingsprocessen, in de lokale omgeving van <sup>29</sup>Si in beide adsorptiematerialen en van <sup>27</sup>Al in Aq-ZSM-5 te onderzoeken.

Er kon geen degradatie van de Xe adsorptie-eigenschappen worden waargenomen noch als gevolg van de thermische regeneratiecycli noch ten gevolge van de bestraling op beide adsorptiematerialen. De morfologie, samenstelling en kristalliniteit van de stalen werden behouden op geregenereerde en bestraalde stalen (73 MGy voor Ag-ETS-10 en 160 MGy voor Ag ZSM 5). Evenzo werden de microporeuze eigenschappen, zoals bepaald door N<sub>2</sub> adsorptie bij 77 K en CO<sub>2</sub> adsorptie bij 273 K, niet gewijzigd door de thermische regeneratiecycli noch door de bestraling. De <sup>29</sup>Si- en <sup>27</sup>Al-lokale omgevingen waren niet veranderd na de thermische regeneratiecycli op beide adsorptiematerialen en na de bestraling op Ag-ZSM-5. Voor Ag-ETS-10 waren de <sup>29</sup>Si-signalen verbreed en verschoven na de bestraling. Deze piekverbreding en - verschuiving is te wijten aan de aanwezigheid van het paramagnetische vervalproduct (<sup>133</sup>Cs) van <sup>133</sup>Xe en is zichtbaar in Ag-ETS-10 omdat de <sup>29</sup>Si-atomen dichter bij <sup>133</sup>Cs lijken te liggen dan in Ag-ZSM-5. Röntgenfluorescentiemetingen bevestigden de aanwezigheid van <sup>133</sup>Cs (tot 390 g m<sup>-3</sup>) in de bestraalde stalen van beide adsorptiematerialen.

In conclusie, beide adsorptiematerialen behielden hun Xe adsorptie prestaties en er kon geen verandering in hun morfologie, samenstelling, kristalliniteit en microporositeit, en in de lokale omgeving van <sup>29</sup>Si en <sup>27</sup>Al worden waargenomen na ten minste 43 thermische regeneratiecycli en een bestraling van 73 en 160 MGy voor respectievelijk Ag-ETS-10 en Ag-ZSM-5. De geabsorbeerde dosis die in dit werk werd gebruikt, komt overeen met honderden uren werking in MIPF's en is een grote stap voorwaarts voor hun toepassing in MIPF's. Bovendien zal hun duurzaamheid tegen thermische regeneratiecycli ook hun verdere gebruik in radioxenon monitoringssystemen ondersteunen.

### 7.4. Vooruitzichten

De resultaten tonen aan dat Ag-ETS-10 en Ag-ZSM-5 kunnen worden gebruikt voor het bemonsteren en scheiden van Xe direct uit droge lucht. Beide AgZ's kunnen worden gebruikt voor een vereenvoudigde gasverwerking, met minder voorbehandeling van het gas, in de volgende generatie radioxenon monitoringsystemen. Een voorafgaande zuiveringsstap zal nodig zijn omdat deze adsorptiematerialen zeer gevoelig zijn voor vocht. Maar een tweestaps scheidingsproces zou mogelijk zijn met eerst een ontvochtiging op een speciaal adsorptiemateriaal (of een andere methode) en vervolgens de Xe bemonstering en scheiding op een van de twee AgZ's. De tweede stap kan meerdere keren worden herhaald om het teruggewonnen Xe gas verder te zuiveren. Er moet voorzichtig worden omgegaan met andere verontreinigingen, zoals CI-bevattende Vluchtige Organische Stoffen. Er werd in de literatuur aangetoond dat Clbevattende VOS de Aq-ZSM-5 kunnen degraderen. Verdere studies moeten zich richten op een dergelijk tweestaps proces en op de veel langere termijn stabiliteit van beide adsorptiematerialen wanneer ze met droge lucht worden gebruikt. Uit de duurzaamheidstudie blijkt dat ze minstens 43 cycli kunnen doorstaan, maar dit komt slechts overeen met 10 dagen werking (rekening houdend met één thermische regeneratiecyclus per bemonstering) voor het meest veeleisende tweede-generatie radioxenon monitoringsysteem. Het gebruik van een systeem met slechts twee stappen zou de verwerkingstijd verder kunnen verkorten (waardoor de detectielimiet voor de kortlevende <sup>135</sup>Xe kan worden verlaagd) en het procesverlies van Xe kunnen verminderen, waardoor ook de detectielimieten voor de vier isotopen kunnen worden verlaagd. Dergelijke vereenvoudigde processen zouden de detectiecapaciteit van deze systemen voor kernwapenproeven vergroten en de discriminatiecapaciteit verhogen vanwege een grotere kans om meerdere isotopen te detecteren. Een dergelijk vereenvoudigd proces, met Aq-ETS-10 of Aq-ZSM-5, dat direct op droge lucht werkt, is ook relevant voor radioxenon bemonsterings- en meetsystemen voor OSI en zou vergelijkbare verbeteringen kunnen bieden.

In een andere context zou een aanverwant proces ook kunnen worden gebruikt om stabiel xenon te produceren en een **energie-efficiënt alternatief** te bieden voor de huidige cryogene destillatie van het Xe/Kr bijproduct verkregen uit cryogene luchtscheidingsinstallaties. De wereldwijde vraag naar hoogzuiver Xe neemt toe en een dergelijk alternatief zal in de toekomst steeds crucialer worden. De resultaten kunnen ook gebruikt worden voor het bemonsteren van atmosferisch radioactief xenon op AgZ's tijdens nucleaire noodsituaties om de aanwezigheid ervan in de atmosfeer te detecteren. Deze detecties zijn bijzonder relevant omdat edelgassen de eerste radionucliden zijn die vrijkomen tijdens **nucleaire ongevallen** vanwege hun inerte aard. Bovendien kunnen AgZ's gebruikt worden om radioactief xenon te bemonsteren in nucleaire faciliteiten voor het bepalen van **schoorsteen emissies** onder routine- en noodomstandigheden.

Het onderzoek naar Aq-ETS-10 als enkelvoudig filtermateriaal, werkend bij of nabij omgevingsomstandigheden, voor Ar bemonstering en scheiding zou de ontwikkeling van efficiëntere OSI 37Ar bemonsterings- en meetsystemen kunnen ondersteunen. In dit geval wordt het proces niet beïnvloed, althans niet tijdens een enkele cyclus, door de aanwezigheid van vocht, zodat Ag-ETS-10 kan worden gebruikt als enig filtermateriaal. Lucht kan efficiënt worden ontdaan van  $N_2$  en verrijkt in Ar met een eerste scheidingsfase op Ag-ETS-10 werkend bij 248 K. De regeneratie van het adsorptiemateriaal na deze eerste adsorptiefase zou verder onderzoek vergen om het meest optimale regeneratieproces te vinden (verwarming en/of vacuüm). Na deze eerste fase zou verdere Ar verrijking in het verkregen Ar/O<sub>2</sub> mengsel nodig zijn. Dit is mogelijk door meerdere cycli over Ag-ETS-10 bij RT uit te voeren. De finale Ar opbrengst zou echter onvoldoende zijn, zodat dit deel van het proces verder onderzoek vereist. Dergelijk verder onderzoek zou zich kunnen richten op de  $Ar/O_2$  scheiding op Ag-ETS-10 werkend bij een lagere temperatuur (bijv. 248 K). Als een dermate lagere temperatuur de Ar/O<sub>2</sub> scheiding aanzienlijk zou verbeteren, zou verder onderzoek nodig zijn om de uiteindelijke Ar opbrengst en verrijking over meerdere cycli van een systeem, dat onder deze omstandigheden werkt, te onderzoeken. Bovendien zou een soortgelijke benadering, zoals in dit werk werd toegepast, kunnen worden aangewend om andere veelbelovende adsorptiematerialen (bijv. Ba-RPZ) te onderzoeken voor Ar bemonstering en scheiding voor OSI. Efficiëntere systemen zouden het gebruik van <sup>37</sup>Ar metingen, als cruciale meettechniek voor CTBTverificatie tijdens OSI, versterken, wat de ultieme verificatiemaatregel is onder het Verdrag dat ondubbelzinnig bewijs kan leveren van een vermoedelijke kernwapenproef. Bovendien zijn er momenteel discussies binnen de CTBTgemeenschap om het gebruik van <sup>37</sup>Ar als aanvullende meting voor IMSedelgasmonitoringstations te evalueren. Verdere ontwikkelingen op het gebied van Ar bemonstering en scheiding zouden ook het gebruik ervan voor IMS kunnen ondersteunen.

Het onderzoek naar AgZ's (in het bijzonder Ag-ETS-10 en Ag-ZSM-5), inclusief onderzoek van hun duurzaamheid, voor de **vermindering van radioxenon uitstoten** biedt een oplossing voor Xe-mitigatie voor civiele faciliteiten, met name

faciliteiten die een grote invloed hebben op de IMS-edelgascomponent, om hun impact op CTBT-verificatie te minimaliseren. Uit het uitgevoerde onderzoek blijkt duidelijk dat beide AqZ's radioactief xenon veel efficiënter kunnen opvangen en dat ze minstens 43 keer kunnen worden hergebruikt door thermische regeneratie. De demonstratie van hun stralingsbestendigheid tot ongeveer 100 MGy is een belangrijke stap voorwaarts voor hun toepassing in de belangrijkste radioxenon uitstotende MIPF's. Verder onderzoek naar de duurzaamheid tegen een hogere stralingsdosis kan geleidelijk worden uitgevoerd door ze te gebruiken in het productieproces van MIPF's zelf en hun adsorptie-eigenschappen in de loop van de tijd te controleren. Dit wordt gedaan bij het Institute for RadioElements (IRE, Fleurus), waar Aq-ETS-10 wordt gebruikt om radioactief xenon op te vangen uit hun oplossingsproces. De evaluatie van de adsorptieprestaties van het bij IRE aebruikte Ag-ETS-10 staal in functie van de tijd kan verder inzicht geven in de stralingsbestendigheid en het gedrag van de vervalproducten. Met betrekking tot hun duurzaamheid tegen thermische regeneratiecycli zouden 43 cycli in enkele maanden worden bereikt en hier zou ook een verificatie van hun adsorptieeigenschappen in de loop van de tijd nodig zijn om hun duurzaamheid vast te stellen. De vermindering van de radioxenon uitstoten van MIPF's zou duidelijk de detectiecapaciteit van de radioxenon component van het IMS verbeteren, aangezien het achtergrondniveau verlaagd zal worden.

Een belangrijk probleem voor CTBT-verificatie dat in de toekomst zou kunnen optreden, is de inzet van een groot aantal kleine modulaire kernreactoren op veel meer locaties dan de huidige kerncentrales. Ze zullen allemaal wat radioxenon in de atmosfeer uitstoten, wat de waarnemingen van andere bronnen, zoals een clandestiene kernwapenproef, zou kunnen beinvloeden. Dit zou de CTBTverificatie door radioxenon monitoring verder compliceren. Hun uitstoot-niveaus kunnen lager zijn, maar de kans op een nabijgelegen bron bij een IMS-locatie zal zeker toenemen. Hun uitstoten zullen dus waarschijnlijk in het IMS worden opgepikt en vermengd met andere bronnen. Ook hier is het onderzoek naar efficiëntere adsorptiematerialen voor radioactief xenon mitigatie bijzonder relevant. Er worden veel ontwerpen onderzocht: van de bekende druk- of kokendwaterreactoren tot nieuwe ontwerpen zoals gesmoltenzoutreactoren of met loodgekoelde snelle reactoren. Aangezien de ontwikkeling zich in zeer verschillende ontwerpfasen bevindt, is het momenteel moeilijk om hun Xe uitstoten in te schatten. Zodra deze informatie echter bekend zal zijn, samen met de details van de gasstromen, kunnen studies worden uitgevoerd om de behoefte aan Xe mitigatie en het potentieel van AgZ's in deze context te bepalen, gebaseerd op het huidige werk.
# Scientific output & Curriculum Vitae

## Scientific output

## 2024

## Journal contribution

Gueibe, C., Rutten, J., Moyaux, D., Camps, J., Schroeyers, W., Gryglewicz, G., Derveaux, E., Hasan, MD. M., & Schreurs, S. (2024). Radiation resistance and durability against thermal regeneration cycles of Ag-ETS-10 and Ag-ZSM-5 for collecting radioxenon. *Process Safety and Environmental Protection, 188, 1423-1436*. DOI: <u>10.1016/j.psep.2024.06.057</u> [Article - cat: A1]

Gueibe C., Rutten, J., Camps, J., Riedmann, R., Moyaux, D., Schroeyers, W., Gryglewicz, G., Kuznicki, S., & Schreurs, S. (Submitted) Adsorptive Ar separation from air on self-bound Ag-ETS-10 granules. *Microporous and Mesoporous Materials*.

## Conference material

Gueibe, C., Rutten, J., Camps, J., Riedmann, R., Schroeyers, W., Moyaux, D., & Schreurs, S. (2024). Vacuum pressure swing adsorption-based Ar separation from air on a single adsorbent. INGE 2024, Vienna, Austria. [Presentation – cat: C2]

## 2023

## Journal contribution

Gueibe, C., Rutten, J., Camps, J., Moyaux, D., Schroeyers, W., Plenteda, R., Hermanspahn, N., Minta, D., & Schreurs, S. (2023). Silver-exchanged zeolites for collecting and separating xenon directly from atmospheric air. *Separation and Purification Technology, 323, Article 124433*. DOI: <u>10.1016/j.seppur.2023.124433</u> [Article - cat: A1]

## Conference material

Gueibe, C., Camps, J., Rutten, J., Moyaux, D., Schroeyers, W., Plenteda, R., Hermanspahn, N., Minta, D., & Schreurs, S. (2023). Unprecedented xenon collection and separation from air on silver-exchanged zeolites. ENVIRA 2023, Seville, Spain. [Presentation – cat: C2]

Gueibe, C., Rutten, J., Camps, J., Hermanspahn, N., Moyaux, D., Schroeyers, W., Minta, D., & Schreurs, S. (2023). Xe collection and purification from air in three types of porous materials. CTBT Science and Technology Conference 2023, Vienna, Austria. [Poster – cat: C2]

Gueibe, C., Rutten, J., Camps, J., Schroeyers, W., Gryglewicz, G., Derveaux, E., & Schreurs, S. (2023). On the radiation resistance and thermal durability of silverexchanged zeolites for trapping radioxenon. WOSMIP: Workshop on Signatures of Man-made Isotope Production IX, Santiago, Chile. [Presentation – cat: C2]

## 2022

## Journal contribution

Gueibe, C., Rutten, J., Camps, J., Moyaux, D., Schroeyers, W., Auer, M., & Schreurs, S. (2022). Application of silver-exchanged zeolite for radioxenon mitigation at fission-based medical isotope production facilities. *Process Safety and Environmental Protection*, *158*, *576-588*. DOI: <u>10.1016/j.psep.2021.12.031</u> [Article - cat: A1]

## Conference material

Gueibe, C., Rutten, J., Camps, J., Moyaux, D., Schroeyers, W., & Schreurs, S. (2022). Investigation of xenon adsorption in three types of porous materials. CRF-ChemCYS, Blankenberge, Belgium. [Poster – cat: C2]

Gueibe, C., Rutten, J., Camps, J., Moyaux, D., Schroeyers, W., Auer, M., & Schreurs, S. (2022). Application of silver-exchanged zeolite for the mitigation of civilian radioxenon releases. WOSMIP: Workshop on Signatures of Man-made Isotope Production VIII, Stockholm, Sweden. [Poster – cat: C2]

## 2021

## **Conference material**

Gueibe, C., Rutten, J., Camps, J., Dominique, M., Schroeyers, W., & Schreurs, S. (2021). Experimental investigation of adsorbent materials for the mitigation of civilian radioxenon releases. WOSMIP: Workshop on Signatures of Man-made Isotope Production Remote II, Online. [Presentation – cat: C2]

Gueibe, C., Rutten, J., Camps, J., Schroeyers, W., Hermanspahn, N., Moyaux, D., & Schreurs, S. (2021). Investigation of Xe adsorbents in conditions relevant for IMS noble gas systems. INGE - International Noble Gas Experiment 2021, Online. [Presentation – cat: C2]

## **Curriculum vitae**



## **Christophe Gueibe**

Nationality: Belgian Date of birth: 20/05/1988 Gender: Male

Email address: <a href="mailto:christophegueibe@gmail.com">christophegueibe@gmail.com</a>

**Home:** (Belgium)

#### WORK EXPERIENCE

#### Researcher and Research Project Leader, Crisis Management and Decision Support

Belgian Nuclear Research Centre (SCK CEN) [ 01/02/2013 - Current ]

City: Mol | Country: Belgium

- · Atmospheric dispersion modelling of radioactive material and radiological impact assessment.
- · Nuclear and radiological emergency preparedness and intervention.
- Radiological expert (Celeval) and local coordinator of measurement teams (Celmes) for the Belgian nuclear emergency plan.
- · Nuclear Security (Radioactive sources, nuclear material and vital equipment).
- Radionuclide expert in the Belgian National Data Centre (NDC.be) in the framework of the Comprehensive Nuclear-Test-Ban Treaty.
- Noble gas adsorption and desorption on porous materials.
- Project workpackage leader within SCK CEN.
- Teaching and leading table top and field exercises.

#### Researcher

Comprehensive Nuclear-Test-Ban Treaty Organization (CTBTO) [21/09/2015 - 18/12/2015]

City: Vienna | Country: Austria

Knowledge Exchange Program between the Belgian Nuclear Research Centre (SCK CEN) and the Comprehensive Nuclear-Test-Ban Treaty Organization (CTBTO) to:

- perform research on the radioxenon emissions from Nuclear Power Plants and Medical Isotope Production
- Facilities and their impact on the International Monitoring System (IMS) for the verification of the CTBT;
- contribute to the understanding of the radioxenon detections in the IMS.

#### **EDUCATION AND TRAINING**

Master in Science Physics with research focus (spec. Physics of Matter and Radiation) with honours *University of Namur, Belgium* [ 01/09/2006 – 30/06/2012 ]

Training on Preparedness and Response for Nuclear and Radiological Emergencies

Belgian Nuclear Research Centre (SCK CEN), Belgium [ 06/05/2013 - 10/05/2013 ]

Training on NDC Capacity Building: Access and Analysis of Radionuclide IMS Data and IDC Products Comprehensive Nuclear-Test-Ban Treaty Organization (CTBTO), Austria [07/09/2015 - 18/09/2015]

#### PRINCE2(R) Foundation level

Propellor, Belgium [ 16/03/2020 - 20/03/2020 ]

#### **PhD in Industrial Engineering**

University of Hasselt, Belgium [ 15/02/2021 - Current ]

#### LANGUAGE SKILLS

Mother tongue(s): French

#### Other language(s):

#### English

LISTENING C1 READING C1 WRITING C1 SPOKEN PRODUCTION C1 SPOKEN INTERACTION C1

Dutch

LISTENING C1 READING C1 WRITING B2 SPOKEN PRODUCTION B2 SPOKEN INTERACTION B2

Levels: A1 and A2: Basic user; B1 and B2: Independent user; C1 and C2: Proficient user

#### **DIGITAL SKILLS**

#### General

Microsoft Office / Windows / Linux / SQLMYSQL

#### Scientific programming

Fortran / Matlab / Python

#### Scientific software

COMSOL Multiphysics (Advanced) / Origin / VISIPLAN

#### **Decision support systems**

JRODOS / Hotspot

#### PUBLICATIONS

Xenon mitigation project - Phase I: adsorption materials

Gueibe et al., 2014, SCK CEN Open Reports BLG-1099.

Xenon mitigation project - Phase II: design study

Gueibe et al., 2015, SCK CEN Open Reports BLG-1100.

Xenon mitigation project - Phase III: prototype construction and testing

Gueibe et al., 2015, SCK CEN Open Reports BLG-1106.

#### Radioxenon Project - Task II/1: Conclusion Report

Gueibe et al., 2017, SCK CEN Open Reports BLG-1130.

Setting the baseline for estimated background observations at IMS systems of four radioxenon isotopes in 2014

Gueibe et al., 2017, Journal of Environmental Radioactivity, 178-179, 297-314.

OPERRA Deliverable D5.50: HARMONE Development of monitoring strategies using relevant scenarios from WP1

Gueibe et al., 2017, SCK CEN Open Reports BLG-1123 (OPERRA D5.50).

#### Radioxenon Project - Task II/2: Design Studies

Gueibe et al., 2018, SCK CEN Open Reports BLG-1140.

Study of materials for improved adsorption of xenon at IMS radionuclide stations - Task 1 / Selection of materials and initial comparison study

Gueibe et al., 2020, SCK CEN Open Reports BLG-1214.

Study of materials for improved adsorption of xenon at IMS radionuclide stations: Task 2 / In-depth studies of selected materials

Gueibe et al., 2020, SCK CEN Open Reports BLG-2923.

# Application of silver-exchanged zeolite for radioxenon mitigation at fission-based medical isotope production facilities

Gueibe et al., 2022, Process Safety and Environmental Protection, 158, 576-588.

Silver-exchanged zeolites for collecting and separating xenon directly from atmospheric air

Gueibe et al., 2023, Separation and Purification Technology, 323, Article 124433.

# Radiation resistance and durability against thermal regeneration cycles of Ag-ETS-10 and Ag-ZSM-5 for collecting radioxenon

Gueibe et al., 2024, Process Safety and Environmental Protection, 188, 1423-1436.

#### HONOURS AND AWARDS

[ 02/12/2016 ] Pacific Northwest National Laboratory Wozzie Award

Link: https://www.ctbto.org/press-centre/news-stories/2016/workshop-on-the-signatures-of-man-made-isotope-production-wosmip-vi/

[10/2021] European platform on preparedness for nuclear and radiological emergency response and recovery NERIS Young Scientist Award

[26/11/2024] Belgian Nuclear Society Young Generation Poster competition 2nd price

Link: https://bnsorg.be/event/nuclear-science-contest-2024/

#### COMMUNICATION AND INTERPERSONAL SKILLS

#### Good communication skills

Good communication skills gained through experience as speaker at various national and international conferences and international expert meetings, leader of work packages in internal and external projects and trainer for various national and international trainings

#### Good writing skills

Good writing skills in English gained through writing scientific publications.