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Adsorption for CO₂ capture: experimental focus on the thermodynamic and kinetic role of water

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Abstract

A global energy transition based on low-carbon energy is urgently needed to limit greenhouse gas emissions and the resulting global warming in the next decades. To tackle greenhouse gas effects, particularly CO₂ contributing to 70% of the overall emissions, drastic changes must be made. TotalEnergies R&D is actively focusing efforts on different pieces of the CCUS (Carbon Capture Utilization and Storage) puzzle through different actions such as carbon capture using different technologies, geological sequestration, carbon conversion, *etc.*

Among existing post-combustion capture technologies, the most mature, absorption from amine solvent, still presents many important challenges such as high energy consumption, corrosion and emissions which makes it important to investigate alternative technologies. Adsorption on a porous media appears as a promising alternative and has become a very active domain with over 30 specific reviews in the last decade. Many solid porous sorbents have been developed and characterized such as amine-based silicas, Metal Organic Frameworks (MOF's), zeolites, Active Carbons (AC's), Covalent Organic Polymers (COP's), *etc.* Their characterization tends to focus specifically on CO₂ and nitrogen adsorption performances and less attention is paid to the effect water. Two main reasons are that experimental techniques are more complicated as water in vapour phase is difficult to handle and its modelling is complex. However not including water strongly limits the value of the results obtained for adsorption-based CO₂ capture as its impact on the sorbent and the process is vital to perform good technico-economical analysis in order to identify the most cost-effective combination of sorbent and process.

The aim of this work is thus to present an experimental study that allows to evaluate the global impact of the presence of different moisture relative levels in the flue gas on the thermodynamic and kinetic properties on small amounts of some reference samples by coupling various experimental qualitative and quantitative as well as static and dynamic methods. More precisely, the adsorption isotherms of pure gases measured by manometric and gravimetric devices are coupled with qualitative coadsorption experiments performed by means of a thermogravimetric (TGA) apparatus coupled with an humidity generator and quantitative dynamic experiments carried out with a breakthrough curves apparatus.

Keywords: CO₂ Capture, adsorption, water, adsorbent

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1. Introduction

The 2015 Paris agreement generated high awareness for the need for emergency action to tackle climate change. The target recommended by the experts is a carbon-neutral society by 2050 [17]. The production and use of energy is responsible for 70% of greenhouse gas emissions. While many Net Zero by 2050 scenarios anticipate that oil's share of the mix will fall significantly (at least two thirds) [6], they do not include the complete discontinuation of fossil energies. It is possible and necessary to limit the emissions caused by the use of oil and natural gas by blending them with biofuels and decarbonized gases, but this will require the "neutralization" of residual CO₂ emissions with nature-based solutions (carbon sinks) or storage in underground reservoirs. Albeit still an emerging market, CCS is bound to move from the industrial pilot stage to commercial development over the next decade. It represents a key tool in achieving carbon neutrality.

Nowadays, among the CCS chain, the capture step can represent two thirds of the total cost. In this frame, the most advanced technology for CO₂ capture is absorption. It is a well-known technology, commercially deployed for more than 60 years for diverse gas treatment applications, such as natural gas sweetening for example. For CO₂ capture from flue gas, the technology has already been commercially deployed using alkanolamine blends, for example at PetraNova plant [8]. However, it still holds important drawbacks, especially high energy demands for solvent regeneration (from ~3 to 5 GJ/t/CO₂ captured [1]), corrosivity of the amine solvent and emissions management, which altogether leads to a deterrent cost for massive commercial deployment with current carbon price.

Among potential alternative technological solutions, adsorption technologies are seen as promising candidates. Using a solid adsorbent removes the corrosion and emission issues and could hold the potential to decrease regeneration energy because of the lower heat capacity of solid sorbents as well as removing the need to heat and vaporize water as in aqueous solvent technology [3]. Heat integration on the other hand will be more complicated than with liquid sorbent media. Adsorption technologies for CO₂ capture consist usually of several steps: adsorption, regeneration, and potentially additional conditioning or cooling down steps. Those steps can be performed alternatively in fixed bed adsorbers for swing processes or in sequence for circulating mobile sorbent processes. Regeneration can use pressure, vacuum, temperature, steam, electricity or a combination of thereof. Main materials used are usually zeolites, amino-silicate, alkalized alumina and increasingly MOFs [4, 11, 15].

While the development of adsorption processes are moving quite fast up the TRL ladder [5, 7, 14, 16, 20, 21], they still have several challenges to overcome. Zanco et al [24] published a comparison of industry-ready processes for absorption, membrane and adsorption. For adsorption they chose a TSA and VSA type cycle, in a fixed bed configuration and the adsorbent being 13X zeolite. As 13X zeolite is sensible to water, they had to add a drying step to the process. The result of the process optimization and cost analysis showed that such an industry-ready adsorption process was not yet competitive compared to the absorption process it was compared to, and that the cost associated with the pre-drying step significantly contributed to the cost gap. This conclusion was equally reached by Joss et al. [9]. CO₂ adsorption in the presence of water is therefore one of the main issues that adsorption processes need to tackle and will be the main topic of this paper. However, one should not overlook other challenges including maximizing productivity, minimizing energy use, adsorbent stability, etc...

Nomenclature

TGA	Thermogravimetric Analysis
TSA	Temperature Swing Adsorption
VSA	Vacuum Swing Adsorption
DCB	Dynamic Breakthrough experiments
MOF	Metal Organic Framework

2. State of the art

Depending on combustion processes, flue gas is mainly composed of N₂ (60-75% vol), CO₂ (4-20% vol), O₂ (5-15%) and water. Traces of SO_x and NO_x and Argon can also be found [10]. Water content range from 6 to 20% vol, depending on fuel source with the highest content being found in incinerator flue gas and the lowest in pulverized coal application. Flue gas exits the burner at very high temperature and prior to reaching the main contactor (here the adsorber), is cooled down for example at 30°C [24] in a direct contact cooler (DCC). The flue gas exists the DCC at saturation level. Then upon entering the adsorber, the level of relative humidity will vary depending on the chosen adsorbing temperature. While for many processes, only the adsorption step involves dealing water, (some TSA processes uses direct steam as a heat media during the regeneration steps [4, 5, 14, 21]). The advantage of the direct contact is the improved heat exchange, the potential concentration swing and the exothermicity the adsorption of water may bring [19]. Moreover, water can be easily separated from CO₂ at the exit of the regenerator through condensation at however a significant energetic cost. For regeneration purposes, in general low pressure superheated steam is used. The process then requires some degree of sorbent drying before returning to the adsorption step the depth of which will be an optimum between the drying energy required, regeneration and adsorption performance. It is key for those three steps, desorption, regeneration, drying, (depending on the process chosen) to understand how water interacts with sorbents and to quantify the right performance parameters that will enable to select the best adsorbents.

Characterization performed in the literature for competitive adsorption usually include TGA (that can be coupled to MIS, IR or GC...) and dynamic breakthrough followed by different type of analyzer (MS, GC, IR). In general for TGA, samples are prehumidified [2, 10] which will give valuable information on the behavior in the presence of water but hardly mimics the process conditions of any steps in the process. Dynamic breakthrough experiments are very often stopped when CO₂ breaks through. As the water front usually moves much slower than the CO₂ front, this can mistakenly present the impact of water as much more limited than it is reality. To reach equilibrium may require very long time. Furthermore, how to extract the pertinent information to use in a model representative of what is really happening in the cycle steady state process is tricky [22, 23]

On the molecular point of view, CO₂ and water are both very small size molecules. CO₂ presents a significant quadrupole moment while H₂O has a high dipole moment. Kolle *et al.* [10] published an extensive review on the effect of water on solid sorbents for CO₂ adsorption. As seen in Table 1, as well in literature [3, 10, 11, 18] the main sorbents used or studied for post-combustion CO₂ adsorption are amine supported silicas (in general PEI/commercial silicas), zeolite (usually 13x) and MOFs and those three types of material exhibits different behaviours with regard to water. The most reported information is the impact of the presence of water on CO₂ capacity of the sorbent. Due to the very large number of sorbents existing, the impact of water on the adsorption of CO₂ range from negative to neutral to positive in some cases [13]. For CO₂ capacity, at the adsorption step operating conditions, in general studies show for 13X very negative impact (up to 99% capacity reduction at 80% RH), for PEI silicas neutral to positive and for MOF neutral to negative. Less information is available for impact on CO₂ desorption during desorption step or impact on diffusion/transfer if any. Competitive adsorption along the bed and difference in breakthrough front kinetics is rarely reported although in general water breakthrough front is much slower than the CO₂ one.

In this paper we will investigate different methodology to characterize the impact of the presence of different moisture relative levels in the flue gas on the thermodynamic and kinetic properties on small amounts of some reference samples by coupling different experimental qualitative and quantitative as well as static and dynamic methods.

3. Materials and Methods

3.1 Materials

Referent solids from each representative family of adsorbents (MOF's, zeolites and amine-based sorbents) were considered for this study. Samples used in this work are listed in Table 1.

Table 1 : Different samples used in this study.

Sample	Morphology	Pretreatment temperature (°C)	Provided by
13X zeolite	powder	300	Alfa Aesar
CALF-20	powder	120	Synthesized internally
KRICT F100	powder	120	KRICT
MOF-74(Mg)	powder	300	NOVOMOF
MiL – 96(Al)	powder	120	Synthesized internally

All the gases were provided by Linde Gas. Helium was purchased in 6.0 quality (purity $\geq 99.9999\%$) and carbon dioxide in 4.5 (purity $\geq 99.995\%$). Demineralized water was used both for water adsorption isotherms and coadsorption experiments.

3.2 Experimental methods

3.2.1 Pure gas adsorption equilibrium

3.2.1.1 CO₂ adsorption isotherms

All CO₂ adsorption isotherms were measured at 303K using around 100 mg of sample on an Autosorb iQ (Anton Paar, Austria) commercial volumetric apparatus. The system is fully automated and can operate in a wide range of temperature (from 253K to 393K). Temperature regulation in this work was implemented with a double jacket Dewar and a thermostatic bath respectively using water as thermal fluid. The samples were pretreated under secondary vacuum at their pretreatment temperature by means of electric heating.

3.2.1.2 Pure water vapor adsorption isotherms

Water vapor adsorption isotherms were performed at 303K by means of an IGA-sorp Dynamic Vapour Sorption commercial gravimetric analyzer (Hiden Isochema, UK) using around 30 mg of sample and over a total flow of 500 ml/min (water diluted in helium). The system is fully automated and can operate from 0% relative humidity (RH), up to 90% RH within a temperature range of 278K to 358K. The adsorption equilibrium tolerance for each relative humidity step is based on the variation of the sample mass and was set to $\pm 0.002\text{wt}/\text{min}$ within a time limit of 480 min. The samples were pretreated at their pretreatment temperature for 6 hours using integrated electrical heating system under a 500 ml/min helium flow at 1 bar.

3.2.2 CO₂/water coadsorption experiments

3.2.2.1 Ex-situ presaturation of the sample + thermogravimetric analysis

The apparatus used on this method is a commercial thermogravimetric analyzer TGA 2 from Mettler Toledo and the experimental procedure is the one described in the publication from Chanut et al [2]. In this protocol, few mg of sample (≈ 30 mg) are presaturated during two days at 100%RH and at room temperature in an airtight vessel containing liquid water. The sample is then loaded into the TGA and a several steps procedure according to the Figure 1 is applied with the aim to study CO₂ adsorption at 1 bar as a function of the amount of water remaining inside the pores of the solid. Firstly, the weakest adsorbed water molecules are desorbed at 303K by means of a 150 ml.min⁻¹ helium flow for several hours until the mass is stabilized (1). Then, a first step of pure CO₂ adsorption is performed (2) following by a desorption step with helium (3) in order to remove the CO₂ reversibly adsorbed. A heating step at 5 K.min⁻¹ at a desired temperature (4) is then applied in order to complete the desorption of CO₂ and to remove some water. After that, the sample is cooled down again under helium flow (5) and these steps are repeated by increasing the desorption

temperature up to the pretreatment temperature (2-5). The obtained results show CO₂ adsorption-desorption cycles as a function of different hydration states of the sample until it's completely dry.

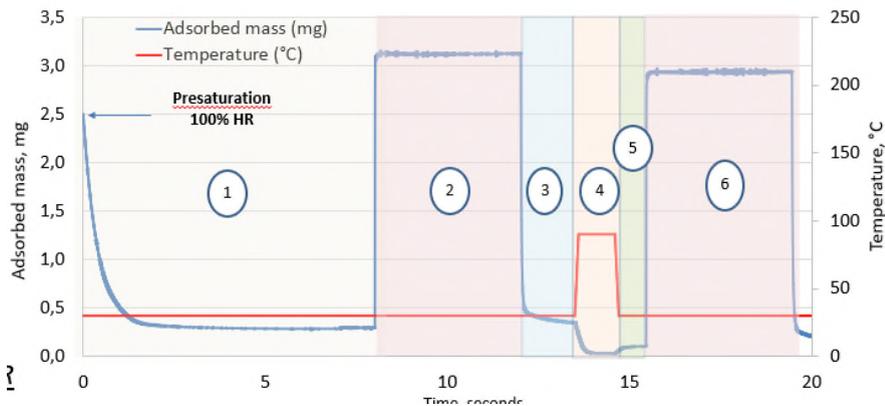


Figure 1. TGA procedure according to the publication of Chanut et al.

3.2.2.2 Humidity generator + Thermogravimetric Analysis

In this experimental protocol, the TGA 2 from Mettler Toledo was coupled with a WETSYS humidity generator from Setaram. This apparatus allows to generate 50 ml/min of a humid gas up to 90% HR and 70°C and to send it to the TGA through heated transfer line. The samples were submitted to two different methods. In the first one the sample is first pretreated under helium flow by increasing the temperature up to the pretreatment temperature according to a heating ramp of 5 K.min⁻¹. A first step of pure CO₂ adsorption at 303K and 1 bar is performed followed by a desorption under helium flow at the same temperature. After that, the regeneration of the adsorbent is completed by increasing the temperature up to the pretreatment temperature. In the next cycle, before the CO₂ adsorption step, the sample is equilibrated with a targeted relative humidity (RH) level with helium as carrier gas. The other steps are then repeated in the same order. Several cycles are performed by increasing the targeted RH level. In the second method, the sample is firstly pretreated in the same way as on the first method. The sample is then equilibrated with a targeted RH level with helium as career gas. Once the mass is stabilized, the sample is submitted to a CO₂ flow containing the same RH level. Different RH levels are performed independently.

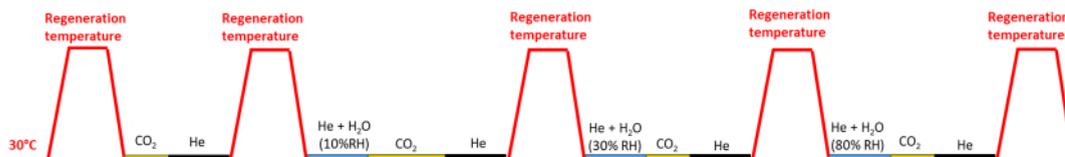


Figure 2. First method applied by coupling the TGA and the humidity generator.

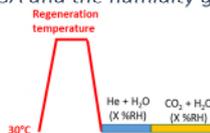


Figure 3. Second method applied by coupling the TGA and the humidity generator

3.2.2.3 Dynamic breakthrough curves

Breakthrough curves were obtained by means of a MixSorb S (3P Instruments, Germany). This apparatus allows to obtain dynamic data on hundreds mg of sorbent (depending on the adsorption capacities and the pressure drop, the amount of sorbent is adapted) and mixture several gases such as CO₂, O₂, He, N₂ and H₂O. The gases are humidified by passing through a bubbler. The bubbler is thermoregulated by Peltier effect and the temperature of the adsorption

column is controlled both with a jacket Dewar and a thermostatic bath or a heating mantle depending on the test purposes. The maximum flow of the apparatus is $300 \text{ ml}\cdot\text{min}^{-1}$. The samples are pretreated at the pretreatment temperature at 1 bar under $50 \text{ ml}\cdot\text{min}^{-1}$ of helium flow using the heating mantle.

4 Results and Discussion

4.1 Thermodynamics – adsorption capacities: Single components adsorption isotherms CO_2 and water

Figure 4a and 4b show respectively the CO_2 and water adsorption isotherms at 303 K for the 5 sorbents. CO_2 isotherms are all type-1-like isotherms and values found are in accordance to literature for each type or similar type of material [2, 10]. MOF74(Mg) and to a lesser extent, 13X zeolite, show much higher CO_2 loadings than the other materials especially between 0.05 and 0.2bars which is the range for flue gas adsorption processes, with the range of adsorption capacities going from ~ 1 to $\sim 7 \text{ mol/kg}$.

Regarding water, there is 3 types of isotherms, Type 1 for 13X zeolite and MOF74(Mg), S-shaped for MIL96(Al) and CALF-20 and Type-3 for KRICT-100. All sorbents adsorb significant quantities of water at 100%RH which is the RH expected at the outlet of the DCC ranging from 10 mol/kg for CALF20 to 40 mol/kg for MOF74(Mg).

At lower RH, KRICT100 and CALF20 show an interesting behavior, with especially low H_2O capacities (see also Lin et al [12]). While these RH are not reached at the inlet of the adsorber (unless drying is involved), it is very possible that they are reached within the adsorber itself (higher temperature). This is also indicative of a different behavior for competitive coadsorption with CO_2 as it seems water appears to adsorb difficulty at first before water-on-water adsorption starts taking over.

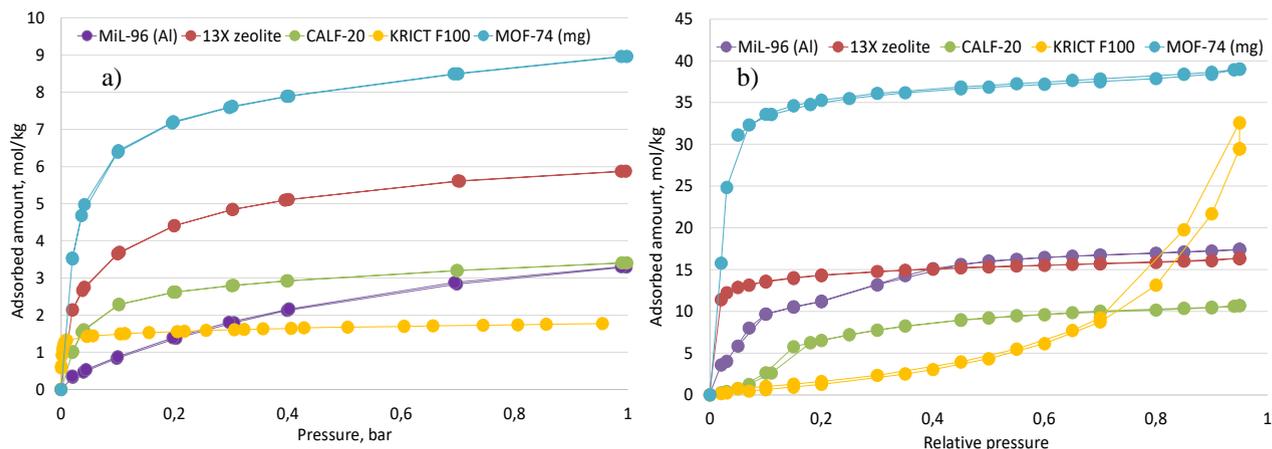


Figure 4. Adsorption isotherms of a) CO_2 on different samples at 303K; b) Water vapor on different samples at 303K.

4.2 $\text{CO}_2/\text{H}_2\text{O}$ coadsorption behavior: preadsorbed water and TGA

Figure 5a and 5b show detailed results obtained with the methodology described in 3.2.1 for 2 sorbents presenting 2 different water isotherms as 13X zeolite and CALF20. In blue (adsorbed mass), the first CO_2 adsorption step at ~ 5 minutes occurs on the prehumidified solid after a desorption step at room temperature (He sweeping at 30°C). The 3 other CO_2 adsorption steps at ~ 15 , 23 and 30 minutes occurs after progressive desorption of the water (and CO_2) at the 3 different temperatures (as described in 3.2.1). Results are not quantitative as we cannot know how much water and CO_2 has been desorbed in each step; however, the methodology shows drastic qualitative different behaviors for coadsorption with 13X's CO_2 capacity being drastically decreased by high levels of preadsorbed quantity of water (see steps at 5 min) in contrast with CALF20 which show no difference in the CO_2 adsorbed quantities and for which all the preadsorbed water appears to have been desorbed after the room temperature He sweep.

Figure 6 shows the CO₂ capacities for all the sorbents but only for the first (i.e low T°C desorption) and last step (high T°C desorption). This clearly shows that the CO₂ capacity for 13X zeolite and MOF74(Mg) are highly impacted by the preadsorbed water while MIL96(Al), CALF20 and KRICT100 are not. That confirms that 13X zeolite and MOF74(Mg) are highly hydrophilic, and water competes strongly with CO₂ for the adsorption sites.

This methodology, whilst bringing interesting insights, is not really representative of what is happening during the adsorption steps as there is no “first room temperature desorption step” since water flows together with the CO₂.

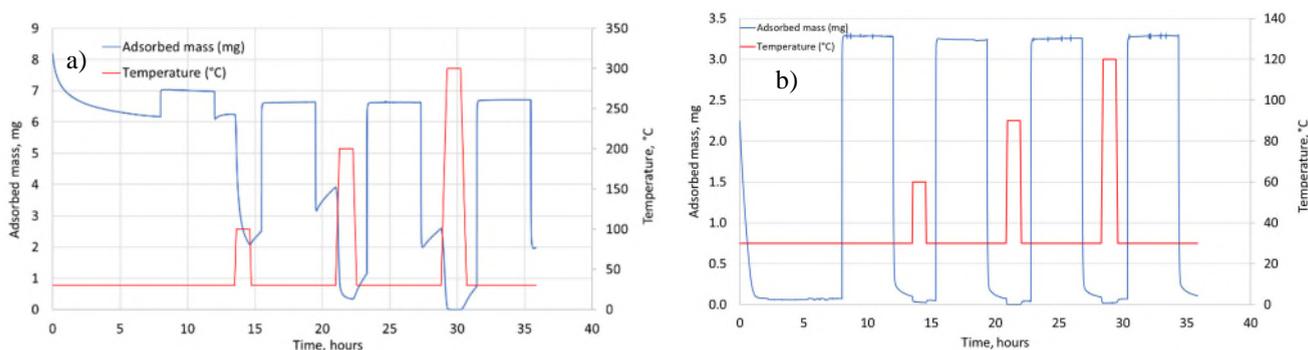


Figure 5. Adsorption – desorption curves of a) 13X Zeolite and b) CALF-20 according to the methods of Chanut et al [2].

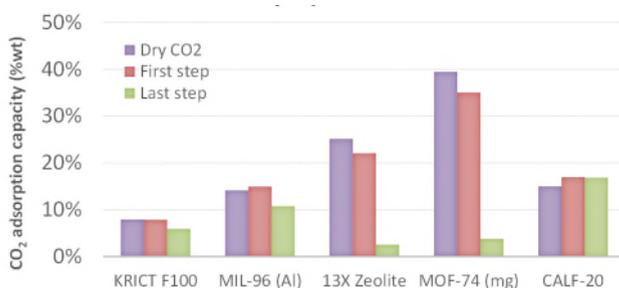


Figure 6. Impact of humidity on CO₂ adsorption on different samples according to the method from Chanut et al [2].

4.3 CO₂/H₂O coadsorption behavior: humidity generator + TGA

The method was therefore adapted by adding a humidity generator directly to the TGA apparatus (see 3.2.2.). In this methodology, in contrast with the previous one, the lightly adsorbed water was not removed before the CO₂ adsorption step (CO₂+ H₂O here) and the levels of humidity were increased progressively (from 10% RH to 80% RH).

Figure 7 shows the detailed results on highly hydrophilic adsorbents: 13X zeolite and MOF74(Mg). The water + He steps enable to see the much slower diffusion of water adsorption, with up to 5 hours of uptake time at 10% RH for MOF74(Mg) for example. The following coadsorption steps show that CO₂ capacity is close to 0 for all RH levels. This means that for those solids even small quantities of lightly adsorbed water (10% RH) are capable of preventing CO₂ adsorption somewhat in contrast with results from 4.1.2 that seemed to show that decreasing amounts of water was leading to higher CO₂ capacities (See Figure 5).

Figure 8 shows the results for CALF20, MIL96(Al) and KRICT F100. Here increasing levels of humidity saw decreasing amounts of CO₂ adsorbed meaning that the lightly adsorbed water (which is removed by He sweeping in the Chanut et al methodology see 3.2.1) can show high deterrent effect on CO₂ coadsorption. This could not be seen

in the 3.2.1 methodology. For these sorbents, at low saturated RH, there is still some CO₂ capacity. However as RH increases the CO₂ capacity decreases until it reaches 0. The CO₂ doesn't seem to be able to displace the water adsorbed.

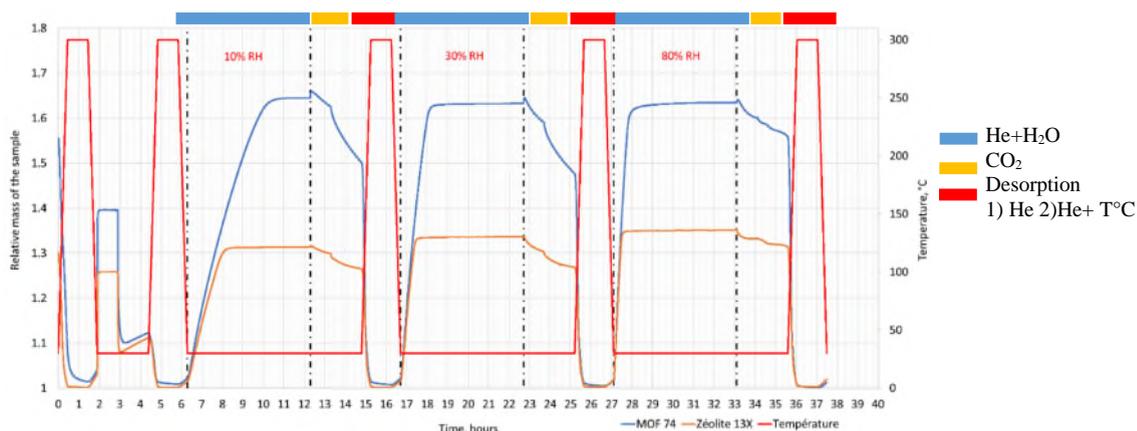


Figure 7. Obtained curves on MOF-74(Mg) and 13X zeolite by coupling humidity generator and TGA using the first method.

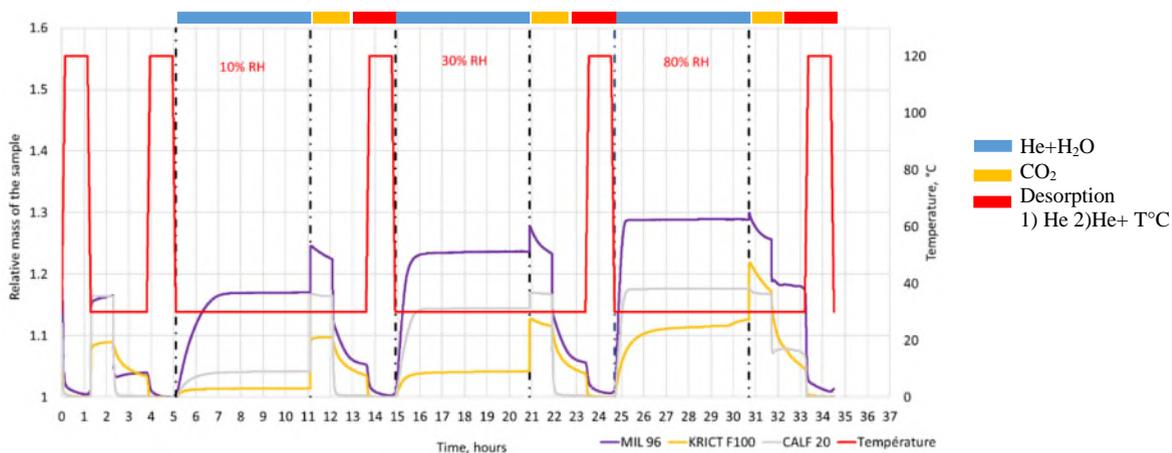


Figure 8. Obtained curves on MIL-96(Al), CALF-20 and KRICT F100 by coupling humidity generator and TGA using the second method.

CALF20 seems to be the adsorbent easiest to regenerate (almost all the adsorbed quantities are desorbed by He sweeping at adsorption temperature without increasing the temperature). Limit of this methodology is firstly that if the CO₂ displaces water from the solids, it will not be known without adding an analyzer at the outlet and secondly that this is not representative of a real adsorption step. Secondly, in reality the water coming with the CO₂ in the feed flow does not have time to saturate the sorbents before the CO₂ starts adsorbing especially as for highly hydrophilic sorbents (e.g. 13X zeolite and MOF74(Mg)), the water breakthrough front will move much slower than the CO₂ breakthrough front (due to higher water capacity and/or slower diffusion).

The value of those 2 methodologies is to help quickly observe qualitative different sorbent coadsorption behaviors and they could allow to rapidly pre-screen and eliminate uninteresting sorbents with very small quantities of material. Dynamic breakthrough will more realistically represent what is happening in the real adsorption bed.

4.4 Dynamic breakthrough curves

Dynamic breakthrough experiments were performed on 2 samples, i-e 13X zeolite and KRICT F100 at 10% CO₂ and 60% HR with Helium as balance gas at the same gas flow, pressure and temperature. These curves are presented in Figure 9.

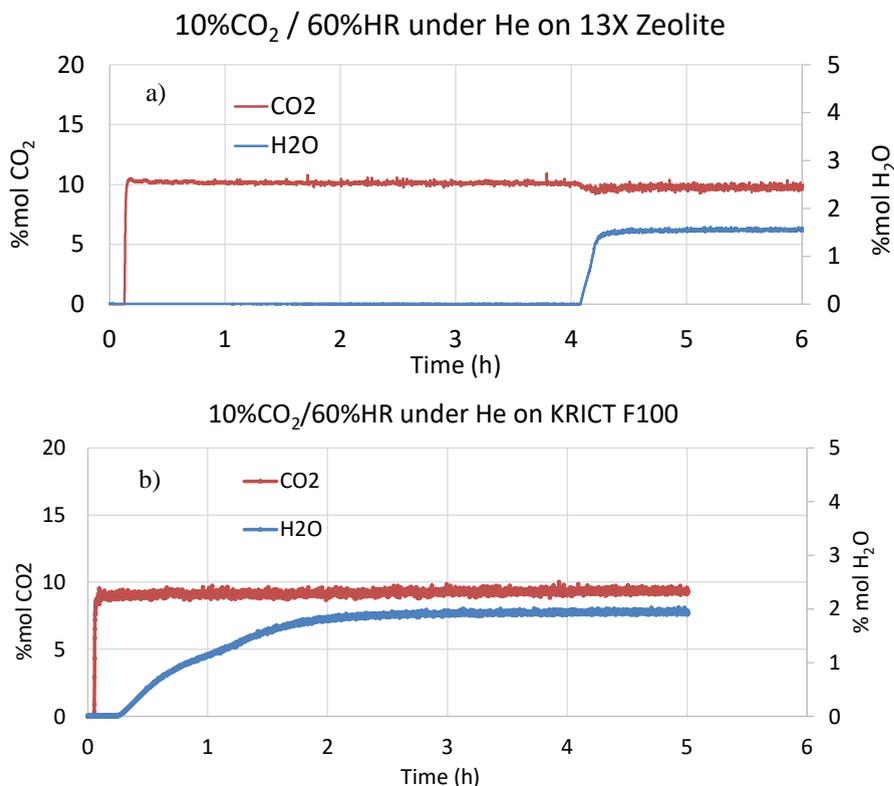


Figure 9: Example of breakthrough curves on a) 13X Zeolite and b) KRICT F100.

Concerning 13X zeolite, the CO₂ adsorption front saturates quite fast the adsorbent bed and breakthrough is observed after several minutes. The breakthrough curve shows a very steep profile showing fast kinetics [23]. However, the water adsorption front takes a lot of time to reach the outlet of the column (around four hours) and shows a steep shape as well. That means that the adsorption front velocity of each gas is quite different. Even if at equilibrium water displaces CO₂, it can be inferred that the progress rate of the adsorption fronts can be exploited in such a way that when the CO₂ has saturated all the adsorbent bed, the water adsorption front is barely at the beginning of the column, meaning that there is no competition between two components in most of the adsorption column length.

The case of KRICT F100 is different, the breakthrough time of each gas is more similar (few minutes for CO₂ and several minutes for water but less than half an hour). However, the shape of the adsorption fronts is quite different. While the CO₂ adsorption front is very steep (it takes some seconds to find the inlet concentration at the outlet), that of water is very spread and takes almost two hours to completely come out of the column meaning that the kinetics is slower. In this case, in addition to presenting less competition for the adsorption sites between the two molecules, the difference on kinetics could be used when working in dynamic adsorption.

5 Conclusion

Water adsorption and water/CO₂ coadsorption experimental data are key to design a good process for CO₂ capture. Coadsorption experiments have not been much performed. While breakthrough experiments and especially cycling

experiments remain the best way to study sorbent in almost real conditions, they are time consuming and require some quantities of material and ideally shaped material. This paper investigates experimental methods to study CO₂/water behavior using TGA and breakthrough apparatus on few mg of powder materials.

In conclusion, the **experimental methods used in this study allow to evaluate the impact of water qualitatively and quantitatively on CO₂ adsorption using some mg of sample. Studied materials can be classified in three groups from pure gas adsorption isotherms:** 13X zeolite and MOF-74(Mg) have high affinity towards CO₂ and H₂O with type I isotherms, CALF-20 and MIL-96(Al) have type I isotherms for CO₂ and S-type isotherm for water and KRICT F100 has type I isotherm for CO₂ and type III isotherm for water

Different qualitative behaviors of CO₂ adsorption for the sample in the presence of moisture can be observed from TGA methods. Water competes with CO₂ for adsorption sites in the case of 13X zeolite and MOF-74(Mg) while they do not compete for the same adsorption sites in the case of CALF-20, MIL-96(Al) and KRICT F100. At high relative humidities (>80 %RH) there is no CO₂ adsorbed in all cases and water and CO₂ adsorption are fully reversible in the case of CALF-20. CO₂ diffusion is much faster than water in all the cases.

Complementary breakthrough tests are necessary to have an idea of the dynamic behavior of the adsorbent and quantify the adsorbed amounts. Breakthrough tests ran on 13X zeolite and KRICT F100 shows that these kinds of tests are necessary to complete the evaluation of the sorbents regarding their behavior with moisture. It is difficult to extrapolate the behavior observed from TGA tests to that observed from breakthrough tests. In this way, TGA test should be used as a prescreening method.

As a follow-up, dynamic breakthrough experiments need to be performed on all samples to finish the comparison of the results with TGA methods. These results will be further used and analyzed using process modelling (mass transfer and thermodynamics). Data from TGA curves will be investigated for the possibility to be used to obtain diffusion parameters to integrate in the mass transfer model. These experimental methods will be also used to study the effect of material shaping (impact of binder, shaping). **Finally, regeneration studies will be performed using different regeneration methods (temperature, pressure, steam).**

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ADSORPTION FOR CO₂ CAPTURE : EXPERIMENTAL FOCUS ON THE THERMODYNAMIC AND KINETIC ROLE OF WATER

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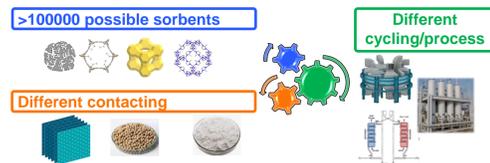
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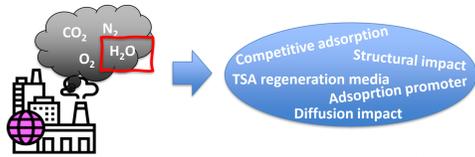
CONTEXT

- CCUS is part of the solutions to tackle climate change and according to IEA needs to reach of 7.65GtCO₂/year in 2050
- Deployment is still hindered by several factors including cost of capture especially for dilute sources
- Adsorption technologies could be an alternative to conventional absorption because of potential lower energy, emissions, corrosion and very large choice of sorbents, shaping and process combination

Net Zero by 2050, IEA



- However, many significant challenges for industrialization of adsorption remain, one of which is to efficiently deal with water



Chem. Rev. 2021, 121, 13, 7280-7345

OBJECTIVE: For the adsorption step:

- Investigate experimental methods to assess the role of water
- Understand & quantify the effect of water

ADSORBENTS SELECTION

From the literature, a series of 5 sorbents were selected for their expected different behaviours for water adsorption or coadsorption CO₂/H₂O

Sample	Type	Morphology	Pretreatment temperature (°C)	Provided by
13X zeolite	Zeolite	Powder	300	Alfa Aesar
KRICT F100	Amine/MOF	Powder	120	KRICT
MOF-74 (mg)	MOF	Powder	300	Novomof
MIL-96 (Al)	MOF	Powder	120	Synthesized internally
CALF-20	MOF	Powder	120	Synthesized internally

Joel M. Kollé, Mohammedreza Fayaz, and Abdelhamid Sayari. Understanding the Effect of Water on CO₂ Adsorption. Chemical Reviews 2021 121 (13), 7280-7345

PURE GAS ADSORPTION ISOTHERMS

EXPERIMENTAL METHODS

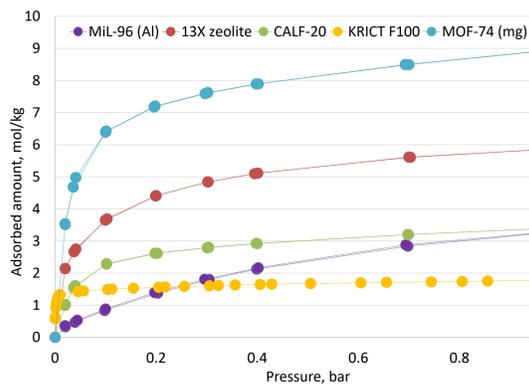
Low pressure high resolution isotherms (0 to 1 bar)

AUTOSORB iQ (Quantachrome®)

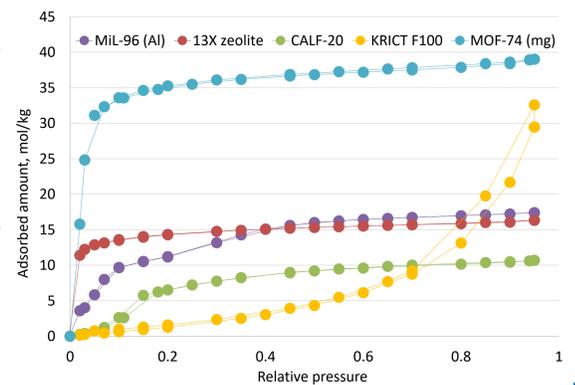
Vapor sorption isotherms

IGASorp Dynamic Vapor Sorption (DVS, Hiden Isochema®)

CO₂ adsorption isotherms – 30°C



Water adsorption isotherms – 30°C



CO₂/H₂O COADSORPTION BEHAVIOR

EXPERIMENTAL METHODS

Ex-situ presaturation up to 100% HR

Airtight vessel

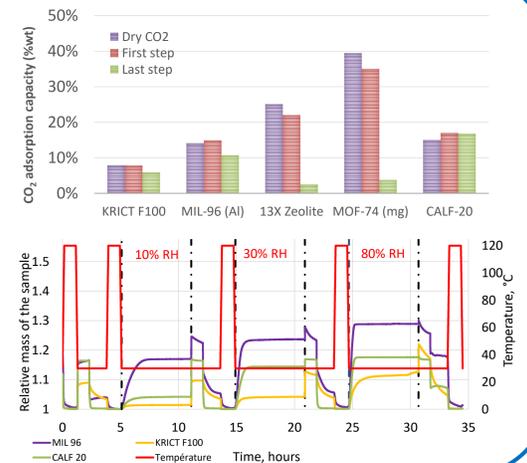
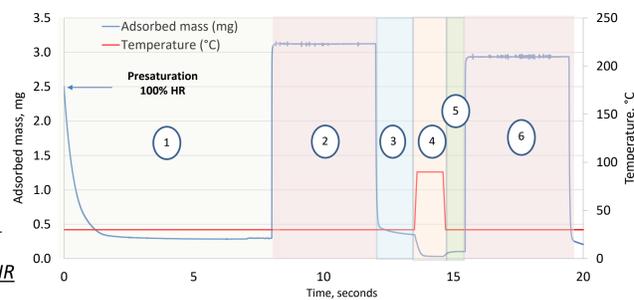
Thermogravimetric analysis (TGA)

TGA II (Mettler Toledo®)



In situ saturation with humidity generator at different %HR

Wetsys (Setaram®)



BREAKTHROUGH CURVES

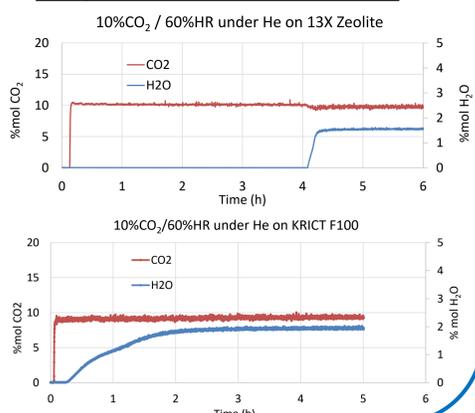
EXPERIMENTAL METHODS

Breakthrough curves on small amounts of samples

MixSorb S (3P Instruments®)



Exemple on 13X Zeolite and KRICT F100



CONCLUSIONS & PERSPECTIVES

- The experimental methods used in this study allow to evaluate the impact of water qualitatively and quantitatively on CO₂ adsorption using some mg of sample
- Studied materials can be classified in three groups from pure gas adsorption isotherms :
 - 13X zeolite and MOF-74 (mg) : high affinity towards CO₂ and H₂O with type I isotherms
 - CALF-20 and Mil-96 (Al) : type I isotherms for CO₂ and S-type isotherm for water
 - KRICT F100 : type I isotherm for CO₂ and type III isotherm for water
- Different qualitative behavior of CO₂ adsorption for the sample in the presence of moisture can be observed from TGA methods
 - Water competes with CO₂ for adsorption sites in the case of 13X zeolite and MOF-74 (mg)
 - Water and CO₂ do not compete for the same adsorption sites in the case of CALF-20, MIL-96 and KRICT F100
 - At high relative humidities (80 %HR) there is no CO₂ adsorbed in all cases
 - CO₂ diffusion is much faster than water in all the cases
 - Water and CO₂ adsorption are fully reversible in the case of CALF-20
- Perspective:
 - Results will be used in dynamic breakthrough modelling (mass transfer and thermodynamics)
 - Methods will be used to study shaped material (impact of binder, shaping)