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A nano-silicate material with exceptional capacity for CO₂ capture and storage at room temperature

Leide P. Cavalcanti¹, Georgios N. Kalantzopoulos², Juergen Eckert³, Kenneth D. Knudsen^{1,4} & Jon Otto Fossum⁴

In order to mitigate climate change driven by the observed high levels of carbon dioxide (CO₂) in the atmosphere, many micro and nano-porous materials are being investigated for CO₂ selectivity, capture and storage (CCS) purposes, including zeolites, metal organic frameworks (MOFs), functionalized polymers, activated carbons and nano-silicate clay minerals. Key properties include availability, non-toxicity, low cost, stability, energy of adsorption/desorption, sorbent regeneration, sorption kinetics and CO₂ storage capacity. Here, we address the crucial point of the volumetric capture and storage capacity for CO₂ in a low cost material which is natural, non-toxic, and stable. We show that the nano-silicate Nickel Fluorohectorite is able to capture 0.79 metric tons of CO₂ per m³ of host material - one of the highest capacities ever achieved - and we compare volumetric and gravimetric capacity of the best CO₂ sorbent materials reported to date. Our results suggest that the high capture capacity of this fluorohectorite clay is strongly coupled to the type and valence of the interlayer cation (here Ni²⁺) and the high charge density, which is almost twice that of montmorillonite, resulting in the highest reported CO₂ uptake among clay minerals.

A current major challenge in science and technology is the development of low cost materials with large CO₂ capture and storage (CCS)¹ capacity, retention ability and sorption selectivity². Important factors for the choice of material in this context include its availability, environmental friendliness, non-toxicity, a low level of greenhouse gas emission during processing, material stability, production cost, CO₂ storage capacity, energy of adsorption/desorption, sorbent regeneration, sorption kinetics and capacity per volume or per mass of host material. Many materials are being investigated including zeolites³, metal organic frameworks (MOFs)⁴, functionalized polymers^{5,6}, activated carbons⁷ and nano-silicate clay minerals^{8–10}. Also hybrid solutions using the best characteristics among all these absorbents are much investigated¹¹. This work presents a quantitative study of the capture of CO₂ by Fluorohectorite clay - a stable and low cost material - with different interlayer cations. Fluorohectorite clay is a modified hectorite clay, which is a species belonging to the smectite group¹², classified as a 2:1 layered silicates, with layer periodicity of approximately 1 nm. The periodic structure includes an interlayer space where a cation is lodged, bonding the structure and balancing the overall charges. The group of smectites, commonly addressed in short as clays, also comprise more popular species like montmorillonite clays. The synthetic fluorohectorite, studied in the present work, has been demonstrated, in several publications by our group, to be a representative and clean model system of nano-silicate smectite clay minerals¹³. Synthetic nano-silicate clays contain significantly fewer impurities (e.g. carbonates, (hydr)oxides, silica, and organic matter) than natural clays and show a more homogenous charge distribution than their natural counterparts¹⁴, leading to well-defined intercalation states^{15,16}. Intercalation of water in nano-silicate smectite clays occurs naturally and has been extensively studied with a wide range of techniques, among them neutron^{17,18} and X-ray scattering^{13,19}. Recent experiments and simulations have shown that also CO₂ can intercalate in smectite clays, both in supercritical²⁰, and in gaseous/liquid form²¹. We have previously demonstrated²² that under certain conditions of pressure and temperature, fluorohectorite clays

¹Institute for Energy Technology (IFE), Kjeller, Norway. ²Centre for Materials Science and Nanotechnology (SMN), Department of Chemistry, University of Oslo, Oslo, Norway. ³University of South Florida (USF), Tampa, USA. ⁴Norwegian University of Science and Technology (NTNU), Trondheim, Norway. Correspondence and requests for materials should be addressed to L.P.C. (email: leide.cavalcanti@gmail.com) or J.O.F. (email: jon.fossum@ntnu.no)

Material	Gravimetric capacity		Molar Uptake	(d) Density (g/cm ³)	Volumetric capacity	Final Pressure (bar)	Data
	Ratio (G) CO ₂ (g)/Material(g)	Fraction CO ₂ (g)/[CO ₂ (g) + Material(g)]	(G*m) CO ₂ (mmol)/Material(g)		(G*d) CO ₂ (ton)/Material(m ³)		
Clay NiFh (this work)	0.28	0.22	6.4	2.8	0.79 ± 0.02 [†]	55	exp
Clay NaFh (this work)	0.21	0.17	4.7	2.8	0.58 ± 0.02 [†]	53	exp
Clay LiFh (this work)	0.16	0.14	3.7	2.8	0.46 ± 0.02 [†]	53	exp
Montmorillonite CTAB N2 (Stevens, 2013)	<i>0.11</i>	<i>0.10</i>	2.42	2.8	<i>0.31</i>	1	exp
Zeolite 13X (Cavenati, 2004)	<i>0.32</i>	<i>0.24</i>	7.372	1.130	<i>0.35</i>	32	exp
co-IonomIM-17% (Mg ²⁺) (Rukmani, 2018)	<i>0.20</i>	0.17	4.5	0.89	<i>0.18</i>	2	S
MOF-aminoclay CuBTC@AC-2 (Chakraborty, 2016)	<i>0.24</i>	<i>0.19</i>	5.4	—	—	1	exp
mesoporous carbon MPPY4800 (Cox, 2017)	2.42	<i>0.71</i>	54	<i>0.38</i>	0.93	50	exp
MOF-210 (Furukawa, 2010; Sumida, 2012)	2.87	0.74	65	0.25	<i>0.72</i>	50	exp

Table 1. CO₂ intercalation values and clay parameters. **m** = 1000/Mw(CO₂); [†]Error propagation considering ± 2% uncertainty in mass of clay sample and ± 10% in volume; **exp** = experimental result; **S** = simulation; The values in **bold** are from the cited references; the values in *italic* were determined for the sake of comparison in this table.

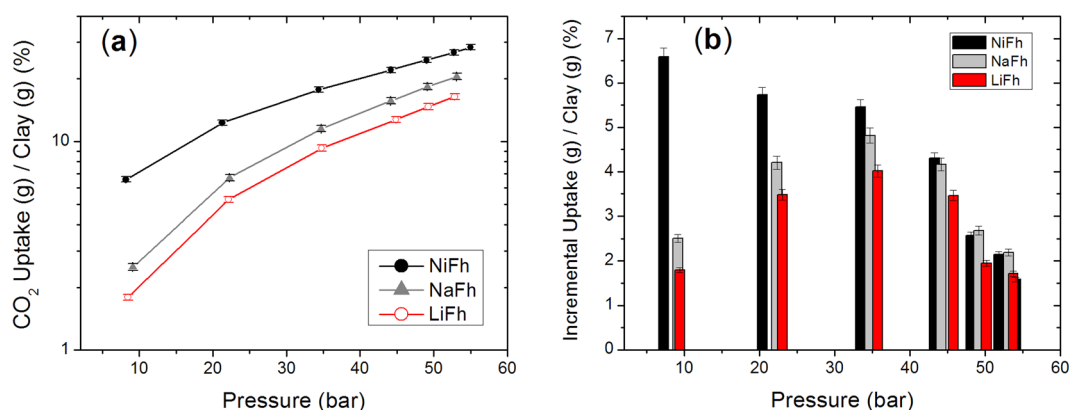


Figure 1. (a) Total uptake of CO₂ into Fluorohectorite nano-silicate clay minerals determined for each pressure step at room temperature; (b) Incremental uptake of CO₂ into Fluorohectorite clays for each pressure step.

can capture a large amount of CO₂ depending on the type of interlayer cation, and that Nickel-fluorohectorite clay (NiFh), in particular, will retain CO₂ up to a temperature of 35 °C at ambient pressure²³. The captured CO₂ can subsequently be released by heating above this temperature. These conditions are highly relevant for mapping out and understanding the mechanisms involved in CO₂ capture and retention by nano-silicates, either in geological formations, or in technological CO₂ absorbent materials.

Results and Discussion

We have utilized an accurately calibrated custom-made Sieverts apparatus for the quantification of CO₂ storage capacity of the nano-silicate clay minerals. The setup is described in detail in the Methods section. The high-pressure CO₂ uptake at room temperature (Fig. 1a) shows a maximum CO₂ intercalation of 28% in weight for NiFh clay at the final pressure of 55 bar. This value is equivalent to 6.45 mmol of CO₂ per gram of NiFh, which corresponds to 0.795 ton of CO₂ per m³ of clay at 55 bar and room temperature, given the crystallographic density of the clay (2.8 g/ml). This result demonstrates that NiFh is able to intercalate one of the largest amounts of CO₂ per volume of material of all porous materials reported in literature. Commercially available zeolite³ 13X can adsorb 0.35 ton/m³, the mesoporous carbon⁷ MPPY-4800 has been reported to uptake 0.93 ton/m³, whereas MOF-210⁴ exhibits a volumetric capacity of 0.72 ton/m³ of CO₂ per volume of host material. Nevertheless, MOFs report the highest gravimetric capacity records because of their low density. Table 1 includes a comparison of exceptional results on CO₂ uptake - showing both volumetric and gravimetric values - and specifically our results on high volumetric capacity clays, calling the attention to the diversity of characteristics among all materials that could be combined for a viable carbon capture and storage solution.

Material	Mw	Cation	N**	N/cation ***	d ₀₀₁ * not loaded	d ₀₀₁ * loaded, 1st peak	d ₀₀₁ * loaded, 2nd peak
Clay NiFh	791	Ni ²⁺	5.1	8.5	10.9	12.1	13.1
Clay NaFh	773	Na ⁺	3.6	3.0	9.6	12.3	—
Clay LiFh	754	Li ⁺	2.8	2.3	10.3	11.9	—

Table 2. Fluorohectorite clay parameters. *XRD data from previous work (Michels 2015) measured on samples of the same batch as in the present work; **Number of CO₂ molecules captured per unit cell, $N = (G/[Mw(CO_2)]/Mw(\text{clay}))$; ***Number of CO₂ molecules captured per cation, $N/\text{cation} = (N/x)$; $x = 0.6$ for Ni²⁺; $x = 1.2$ for Li⁺ and Na⁺.

The other clay types investigated here, NaFh and LiFh, are also found to be high capacity storage materials, with intercalation capacity of 21 wt % (corresponding to 0.58 ton/m³ or 4.7 mmol/g) and 16 wt % (corresponding to 0.46 ton/m³ or 3.7 mmol/g), both at a final pressure of 53 bar respectively. These numbers are higher than those found in a theoretical study on other clays⁹, for example, Na-Montmorillonite with a capacity of 1.5 mmol/g for a basal interlayer distance of 12 Å, which is comparable with the interlayer distance of our loaded samples as shown in Table 2. The volumetric capacity of LiFh was already studied by us and published elsewhere²³. Here we report new results on LiFh for a comparison using the same experimental protocol (dehydration, incubation time and incremental steps in pressure) as used for NiFh. The results for NiFh are original and demonstrate a significant development forward regarding CO₂ capture by a nano-silicate material.

NaFh and LiFh present very similar behavior in terms of the intercalation of CO₂, as shown in Fig. 1. This suggests a similar interaction between the CO₂ molecule and the Na⁺ and Li⁺ cations. They are both alkali metals of group 1 A with comparable ionic distribution in the nano-silicate clay interlayers. Previous results showed that after the intercalation into Fluorohectorites, CO₂ is stable inside the nano-silicate clay material and can be released upon heating²³, which indicates the formation of stable cation-CO₂ complexes or cation solvation into a CO₂ gas phase²⁴. The size and structure of the complex might favor the stability and can be probed by X-ray diffraction (XRD). The XRD results from our previous work²³, transcribed in Table 2, show that the interlayer separation occupied by CO₂ for NaFh and LiFh increases with the ionic radius of the cation. Na⁺ has a larger ionic radius than Li⁺, and the loaded NaFh is found to have a larger interlayer separation than LiFh, which means additional room to accommodate a larger complex or higher coordination number. This could explain our finding that NaFh intercalates more CO₂ than LiFh at the investigated pressures.

The total CO₂ intercalated ($\sum U_i$) as a function of pressure is shown in Fig. 1a, while Fig. 1b shows the incremental amount (U_i) of CO₂ intercalated at each step in pressure. The latter indicates that the process is driven towards a saturation limit, after which no additional intercalation will be possible. Since the incremental values have not reached zero at the maximum pressure used in this study, it is possible that CO₂ intercalation is not yet at the full potential for this material. At this stage, despite presenting already a high uptake of CO₂, further investigations into optimization of the CCS capacity of these materials may thus benefit from an extended pressure/temperature protocol as well as exploring the use of functionalized clays such as those prepared according to Breu's group²⁵. Reuse of the CO₂-loaded clay materials is possible after releasing the CO₂ by a combination of moderate heating and evacuation. This has been tested for NiFh, NaFh and LiFh (data not shown), with no sign of degradation of the material.

Table 1 shows the results for the CO₂ gravimetric and volumetric capacity for the clays studied in the present work, compared with Montmorillonite²⁶, Zeolite 13X³, functionalized polymers⁵, activated carbons⁷, MOF-aminoclay composites¹¹ and MOF-210⁴ data from the literature. The final pressure varies according to the characteristics of the material. Some materials, like the fluorohectorite clays, have low uptake for flue gas but are not saturated at low pressure, allowing storage at high pressure. Table 2 shows the molar weight, number of CO₂ molecules per unit cell (N) and the basal interlayer distance (d_{001}) for each clay type.

The molecular formula per unit cell for NiFh, NaFh and LiFh is expressed by



where $x = 1.2$ for LiFh ($M = \text{Li}$) and NaFh ($M = \text{Na}$) and $x = 0.6$ for NiFh ($M = \text{Ni}$)²⁷. The number N is found to be 5 in the case of NiFh. This means more than 8 molecules of CO₂ per Ni²⁺ cation, since NiFh has approximately 0.6 Ni²⁺ cations per unit cell²⁸. The two other clays, LiFh and NaFh, contain 1.2 cation per unit cell, which gives a value for the ratio N/cation between 2 and 3.

The Fig. 2 shows possible structures of CO₂-cation complexes assembled into NaFh and NiFh clay materials, respectively. These structures use as a starting point the crystal structure of water-containing clay, with cell parameters $a = 5.2432$ Å and $b = 9.0870$ Å, as published by Kalo *et al.*⁸, but here with the water molecules removed and substituted by another set of three atoms in the form of CO₂. Our sketch of the CO₂ intercalated fluorohectorite is intended to give a plausible picture of how the CO₂ molecules could be arranged between the layers upon removal of water molecules. These hypothetical structures were derived by iterative process taking into account the nature of CO₂-CO₂, and CO₂-host intercalations in a most qualitative way, while keeping interatomic distances from becoming too short. This was done without expanding the layer spacing from what it was for water. The three shortest CO₂ oxygen-to-host-oxygen distances were 2.31, 2.53 and 2.607 Å, but these can, of course, be readily increased by increasing the layer spacing. We have started with an interlayer distance of 10 Å, yielding a layer periodicity of 15 Å (as in Kalo *et al.*⁸ for 2 water layers), which is close to the XRD results in the work of Michels *et al.*²³ and the simulations in the work of Kadoura *et al.* (2012)⁹. The configuration of the intercalated

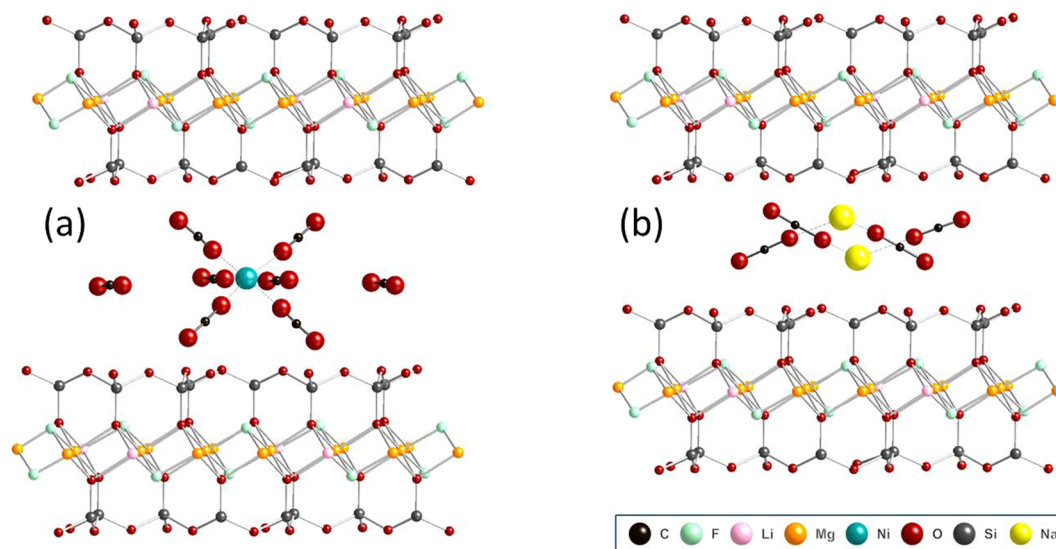


Figure 2. Suggested configuration for CO₂-cation complexation inside Fluorohectorite clay interlayer: (a) 8 molecules of CO₂ for each Ni²⁺ cation and (b) 2 molecules of CO₂ for each Na⁺ cation. (The structures were built using the software CrystalMaker[®]).

complex is expected to be rather dynamic and the number of CO₂ molecules around each cation is here estimated to be 2 for NaFh and 8 for NiFh based on the amount of material intercalated. For free Ni²⁺, the coordination number²⁹ with CO₂ can be as high as 6, and in Fig. 2(a) we assume this to be the case for intercalated Ni²⁺ as well. The binding of the two additional satellite molecules of CO₂ could come from interaction with the clay layers.

In conclusion, we have in this work compared alternative materials with exceptional gravimetric or volumetric capacity for CO₂ capture and storage. We have demonstrated that NiFh is able to capture 0.79 ton of CO₂ per m³ of clay at 55 bar and ambient temperature. This is one of the highest volumetric capacities of all CO₂ sorbent material reported to date. This result, combined with the diversity of characteristics of other high performance materials, could lead to new technological solutions for Carbon Capture and Storage (CCS). The storage capacity for fluorohectorite clays may well be further enhanced beyond the present results by utilizing functionalized clay minerals⁸. Moreover, it has also been suggested that clay materials can be used in gas separation, in particular, those of greenhouse gases such as methane⁹ from CO₂.

Clay materials such as the synthetic Fluorohectorites investigated here are harmless³⁰ and in addition, their production is expected to be substantially less expensive than other high performance porous synthetic materials considered for CO₂ capture, such as MOFs whose upscaling is particularly challenging. Furthermore, clays are also proven to be highly stable when exposed to external mechanical stress or humidity on geological time scales.

Our results show that the type of clay-interlayer cation is critical for CO₂ capture, whereas the clay nanolayers provide the large effective surface area responsible for the exceptional storage capacity. The remarkable capture capacity of NiFh is also related to (a) a high charge density, about twice that of Montmorillonite²⁸, and (b) the presence of divalent Ni²⁺ that frees up additional space for CO₂ intercalation, which results in a higher uptake per cation compared with the usual monovalent ions such as Na⁺. The internal surface area for fluorohectorite and montmorillonite was found to be 3 m²/g and 80 m²/g respectively in the work of Kaviratna *et al.*²⁸ (using the fluorohectorite sample bought from the same batch as in the present work), which could be an indication that the CO₂ uptake, in these two clays, is more dependent on the interlayer separation and interlayer cation than on the internal surface area. We believe that the main interaction mechanism responsible for the high CO₂ affinity is direct dipolar electronic interaction with the interlayer cation. The physisorption is probably also, to some degree, influenced by the charge distribution of the clay layered structure.

Other aspects of sorption kinetics are under evaluation and DFT calculations of the intercalate CO₂-cation structures are in progress using the initial model presented in Fig. 2 as starting point. This study will be combined with *in situ* spectroscopic characterization. Experiments using higher pressure, including liquid and supercritical CO₂, are also planned. Our Sieverts apparatus allows for temperature measurements which will be important for future determination of heats of adsorption and comparisons with DFT calculations. The present work has been conducted on dehydrated clays; however it is of considerable interest to evaluate the sorption performance in the presence of water and selectivity for CO₂ in the presence of CH₄ and N₂. The current results already make these materials highly interesting candidates for CO₂ capture from dried industrial combustion gases.

Methods

We have utilized a custom-made Sieverts apparatus for the quantification of CO₂ storage capacity of the clay materials. The instrument has been designed and constructed for minimizing the experimental error and has been accurately calibrated according to procedures described in the literature³¹. CO₂ gas was introduced to the reservoir and equilibrated for one hour, prior to allowing the expansion into the sample chamber and intercalation into the clay powder material. The number of CO₂ gas molecules initially in the reservoir, $n_i = P_i V_i / (Z_i R T_i)$, gas molecules was calculated using the compressibility of a real gas, $Z(p, T)$, as a function of pressure and

temperature with parameters from NIST tables as reported elsewhere³¹. For each pressure increment, the gas uptake was calculated from the difference $n_f - n_i$, where n_f is the final number of gas molecules expanded to the total volume, V_t (sample chamber + reservoir): $n_f = P_f(V_t - V_s)/(Z_fRT_f)$, where V_s , sample volume, is the mass of sample per its bulk density. Prior to the gas sorption the clay powder was degassed for 20 hours at 120 °C under dynamic vacuum (down to 10⁻⁷ mbar), and the subsequent experiments were performed at 25 °C. The synthetic clays Nickel Fluorohectorite (NiFh), Sodium Fluorohectorite (NaFh) and Lithium Fluorohectorite (LiFh) and CO₂ gas with purity >99.999% was used. LiFh was purchased from Corning Inc. NiFh and NaFh powder samples were obtained from the LiFh clay following a standard dialysis cation exchange protocol³² with no further analysis. Water intercalation in NaFh and NiFh samples, originated from the same LiFh batch that we have studied here, have been investigated by NMR spectroscopy (NaFh²⁹), and TGA (NiFh¹⁹). The cation coordination numbers proposed from these results are in full accordance with the clay layer charge reported by Kaviratna *et al.*²⁸.

The Sieverts apparatus had a reservoir volume of 16 ml and sample chamber of 13 ml. We have determined the number of CO₂ molecules at the reservoir before and after expansion of the reservoir into the sample chamber. The whole process consisted of three stages: (A) degassing of sample and chambers, (B) accumulation of CO₂ into the reservoir at a certain incremental step in pressure and, finally, (C) expansion of CO₂ into the sample chamber. The total CO₂ intercalation was determined as a sum of the intercalation amounts due to each incremental step in pressure. The CO₂ intercalation was replicated for testing reproducibility. The amount of powder sample inside the chamber was around 2 g and the bulk density around 0.7 g/ml. The total intercalation period, steps 1 to 3, was uniform around 4 days for all samples. Previous experiments²² showed that the kinetics of intercalation is slower for NaFh compared to NiFh and LiFh, so we chose to expose all samples to the longest period. We expect that the intercalation time might reduce under different conditions, for example with supercritical CO₂.

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Author Contributions

J.O.F. initiated and planned the work together with K.D.K. G.N.K. aided L.P.C. in the initial phase of the experiments and analysis. J.E. constructed the numerical CO₂-cation complexation representations. L.P.C. performed the experiments, analysis and wrote the first draft of the manuscript. All authors took active part in revisions and discussions towards the final manuscript.

Additional Information

Competing Interests: The authors declare no competing interests.

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