Study on the Compatibility of Gas Adsorbents Used in a New Insulating Gas Mixture C4F7N/CO2

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Date Submitted: 2019-12-09

Keywords: insulating gas, HF removal, desiccants, adsorbents, perfluoroisobutyronitrile

Abstract:

An environment-friendly insulating gas, perfluoroisobutyronitrile (C4F7N), has been developed recent years. Due to its relatively high liquefaction temperature (around ?4.7 °C), buffer gases, such as CO2 and N2, are usually mixed with C4F7N to increase the pressure of the filled insulating medium. During these processes, the insulating gases may be contaminated with micro-water, and the mixture of H2O with C4F7N could produce HF under breakdown voltage condition, which is harmful to the gas insulated electricity transfer equipment. Therefore, removal of H2O and HF in situ from the gas insulated electricity transfer equipment is significant to its operation security. The adsorbents with the ability to remove H2O but without obvious C4F7N/CO2 adsorption capacity are essential to be used in this system. In this work, a series of industrial adsorbents and desiccants were tested for their compatibility with C4F7N/CO2. Pulse adsorption tests were conducted to evaluate the adsorption performance of these adsorbents and desiccants on C4F7N and CO2. The 5A molecular sieve showed high adsorption of C4F7N (22.82 mL/g) and CO2 (43.86 mL/g); F-03 did not show adsorption capacity with C4F7N, however, it adsorbed CO2 (26.2 mL/g) clearly. Some other HF adsorbents, including NaF, CaF2, MgF2, Al(OH)3, and some desiccants including CaCl2, Na2SO4, MgSO4 were tested for their compatibility with C4F7N and CO2, and they showed negligible adsorption capacity on C4F7N and CO2. The results suggested that these adsorbents used in the gas insulated electricity transfer equipment filled with SF6 (mainly 5A and F-03 molecular sieves) are not suitable anymore. The results of this work suggest that it is a good strategy to use a mixture of desiccants and HF adsorbents as new adsorbents in the equipment filled with C4F7N/CO2.

Record Type: Published Article

Submitted To: LAPSE (Living Archive for Process Systems Engineering)

Citation (overall record, always the latest version):LAPSE:2019.1289Citation (this specific file, latest version):LAPSE:2019.1289-1Citation (this specific file, this version):LAPSE:2019.1289-1v1

DOI of Published Version: https://doi.org/10.3390/pr7100698

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Article

Study on the Compatibility of Gas Adsorbents Used in a New Insulating Gas Mixture C₄F₇N/CO₂

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Received: 19 August 2019; Accepted: 26 September 2019; Published: 3 October 2019



Abstract: An environment-friendly insulating gas, perfluoroisobutyronitrile (C₄F₇N), has been developed recent years. Due to its relatively high liquefaction temperature (around -4.7 °C), buffer gases, such as CO₂ and N₂, are usually mixed with C₄F₇N to increase the pressure of the filled insulating medium. During these processes, the insulating gases may be contaminated with micro-water, and the mixture of H₂O with C₄F₇N could produce HF under breakdown voltage condition, which is harmful to the gas insulated electricity transfer equipment. Therefore, removal of H₂O and HF in situ from the gas insulated electricity transfer equipment is significant to its operation security. The adsorbents with the ability to remove H₂O but without obvious C₄F₇N/CO₂ adsorption capacity are essential to be used in this system. In this work, a series of industrial adsorbents and desiccants were tested for their compatibility with C₄F₇N/CO₂. Pulse adsorption tests were conducted to evaluate the adsorption performance of these adsorbents and desiccants on C₄F₇N and CO₂. The 5A molecular sieve showed high adsorption of C₄F₇N (22.82 mL/g) and CO₂ (43.86 mL/g); F-03 did not show adsorption capacity with C₄F₇N, however, it adsorbed CO₂ (26.2 mL/g) clearly. Some other HF adsorbents, including NaF, CaF₂, MgF₂, Al(OH)₃, and some desiccants including CaCl₂, Na₂SO₄, MgSO₄ were tested for their compatibility with C₄F₇N and CO₂, and they showed negligible adsorption capacity on C₄F₇N and CO₂. The results suggested that these adsorbents used in the gas insulated electricity transfer equipment filled with SF₆ (mainly 5A and F-03 molecular sieves) are not suitable anymore. The results of this work suggest that it is a good strategy to use a mixture of desiccants and HF adsorbents as new adsorbents in the equipment filled with C₄F₇N/CO₂.

Keywords: perfluoroisobutyronitrile; adsorbents; desiccants; HF removal; insulating gas

1. Introduction

Currently, SF₆ is the most widely used insulating gas in gas insulated electricity transfer equipment, such as gas insulated switchgear (GIS) and gas insulated line (GIL); however, due to its environmental issues, a new environmentally friendly insulating gas is urgently needed. Perfluoroisobutyronitrile (C_4F_7N) has been developed as a promising new insulating gas, which shows two times the dielectric strength compared with that of SF₆ at the same pressure [1]. Its global warming potential (GWP₁₀₀, 2210 for C_4F_7N) is clearly lower than that of SF₆ (GWP₁₀₀, 23,500), and its atmospheric lifetime is 35 years, which is much shorter than that of SF₆ with an atmospheric lifetime of 3200 years [2]. According to the above characteristics, C_4F_7N could be an alternative gas for SF₆ [3]. However, due to its high boiling point (-4.7 °C), buffering gas with low liquefaction temperature, such as N₂, CO₂, is needed to mix with it for electricity transfer applications [4].

As one of the most widely used insulating gas, SF_6 could be decomposed into HF, H_2S , SO_2 , SOF_2 , etc. with a trace amount of H_2O [5–7]. These products are highly toxic, and the acidic gases, such as HF,

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H₂S and SO₂, are corrosive to the gas insulated equipment, and therefore threaten the security of gas insulated electricity transfer equipment. Many of the regular adsorbents, such as 5A and F-03 molecular sieves, are commonly placed in the SF₆ gas insulated electricity transfer equipment to eliminate the moisture, and they are capable of adsorbing acidic gases once produced thermally or by discharge. The research results suggest that C₄F₇N could be thermally decomposed into CO, COF₂, CF₃CN, C_2F_5CN , etc. [8]. The theoretical study results indicate that HF, HCN could be generated by a discharge in the presence of trace H_2O [9]. Therefore, it is significant to control the moisture level of C_4F_7N gas by supplementing desiccants, and it is also beneficial to the security of the equipment to supplement HF adsorbents. As mentioned above, 5A molecular sieve is commonly used as an adsorbent to the decomposed products of SF₆, for the reason that it shows good moisture elimination efficiency and acidic gas adsorption capacity [10], and meanwhile, its adsorption capacity of SF_6 is quite low. Due to its high boiling point, C_4F_7N needs to mix with N_2 and CO_2 in application. One should not only evaluate the compatibility of the commonly used adsorbents with C_4F_7N , but also evaluate the compatibility of the adsorbents with the buffering gases. As we know, 5A molecular sieve is a good adsorbent for CO₂ and H₂O adsorption [10,11], therefore, its compatibility with C₄F₇N/CO₂ is suspected and needs to be confirmed. It is also reported that γ -Al₂O₃ is highly effective at adsorbing C₄F₇N [12]. However, the information about adsorbents that could be used for C₄F₇N/CO₂ is quite limited.

In this work, in order to study the compatibility of commonly used adsorbents with the new insulating gas C_4F_7N/CO_2 , a series of adsorbents, including 3A [13], 4A [14,15], 5A [10,16] zeolite molecular sieves, and an adsorbent commonly used in Chinese gas insulated electricity transfer equipment (GIS and GIL), F-03 zeolite molecular sieve, were tested for their adsorption performance with CO_2 and C_4F_7N . The adsorbents that are highly effective in the adsorption of HF, including NaF [17], CaF_2 [18], MgF_2 , Al(OH)₃ [19], and the desiccants, including Na₂SO₄, $CaCl_2$ [20], $MgSO_4$ [21] were investigated for their adsorption performance with CO_2 and C_4F_7N , respectively. The results suggested that the 5A and F-03 molecular sieve materials are highly effective in adsorption of CO_2 or C_4F_7N and are not suitable for using in C_4F_7N/CO_2 , while some of the HF adsorbents and desiccants showed good compatibility with C_4F_7N/CO_2 and could be screened as potential candidates.

2. Materials and Methods

2.1. Chemical Reagents

The chemical reagents used in this study, including $Al(OH)_3$, $CaCl_2$, $MgSO_4$, Na_2SO_4 , Na_F , MgF_2 , CaF_2 and the zeolite molecular sieve materials 3A, 4A were purchased from Sinopharm Co. Ltd. The adsorbents, 5A and F-03 zeolite molecular sieves, were offered by Shandong Taikai High Voltage Switchgear Co. Ltd. All of the chemicals with analytical grade or adsorbents were dried in an oven at 120 °C for 10 h to remove the moisture. Pure CO_2 (99.999%) used as a calibration gas was purchased from Xi'an Teda Cryogenic Equipment Co. Ltd.; and C_4F_7N was purchased from a commercial market with a purity of 99%. The chemical composition of the zeolite molecular sieves are listed in Table 1.

Molecular Sieve	Chemical Composition	Pore Size/nm
3A	Na _{6.6} K _{5.4} -[(AlO ₂) ₁₂ (SiO ₂) ₁₂]	0.3
4A	$Na_{12} \cdot [(AlO_2)_{12} \cdot (SiO_2)_{12}]$	0.4
5A	$Ca_6 \cdot [(AlO_2)_{12} \cdot (SiO_2)_{12}]$	0.5
F-03	$Na_{12} \cdot [(AlO_2)_{12} \cdot (SiO_2)_{15}]$	1.0

Table 1. Chemical composition and pore size of molecular sieves.

2.2. Adsorption Characterization

To study the adsorption performance of the selected chemicals and adsorbents toward C_4F_7N and CO_2 , pulse adsorption tests were conducted in chemical adsorption equipment (Builder PCA-1200, Beijing Builder Co. Ltd., Beijing, China). The schematic and picture of the pulse adsorption test is

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shown in Figure 1. When the pulse gas (tested gas) passed through the thermal conductivity detector (TCD), a pulse signal would show up, and the area of the signal peak is proportional to the amount of tested gas. Before testing the samples, the pulse adsorption procedure was run with an empty tube, and the obtained data were used as a blank control. To determine the adsorption performance of the samples, 0.05–0.20 g of each sample was filled in the sample tube, and the pulse adsorption procedures were conducted by turning a six-way valve to feed the calibration gas on a certain time interval. As shown in Figure 1A, for each test, in the first step, the quantitative loop was connected with the pulse gas line to fill with a fixed volume of pulse gas (0.30 mL), and in the six-way valve, gas passage 1 was connected with 6, while gas passage 4 was connected with 5. In the second step, the connection of the quantitative loop was switched to the sample tube, and in the six-way valve, gas passage 1 was connected with 2, and gas passage 4 was connected with 3. Then the carrier gas was purged and the pulse gas filled in the quantitative loop to pass through the sample and the TCD sequentially to record the pulse signal. Therefore, for each sample, 5-15 pulses were conducted depending on the adsorption performance of the testing sample, and the data obtained from the equipment were used to calibrate the adsorption capacity of the samples. For each sample, at least three tests were conducted, and the average data with less than 5% deviation were accepted.

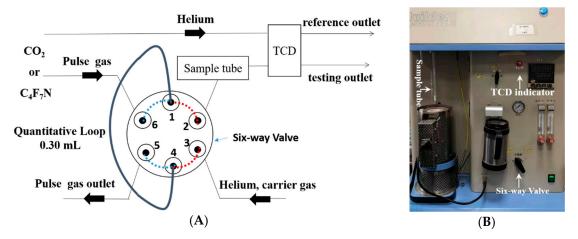


Figure 1. (**A**) Schematic and (**B**) picture of pulse adsorption test instrument (PCA-1200). TCD, thermal conductivity detector.

2.3. Data Analysis

The pulse signal data obtained were integrated to obtain the area of each peak. The area of each peak is proportional to the volume of calibration gas passed through the sample tube, and the difference of the area between the blank control was proportional to the amount of gas adsorbed by the samples. For each sample that adsorbed the target gas, several peaks with lower area than the control could be obtained, and the amount of gas adsorbed by the sample could be calculated according to the following equations

$$I_c = A_h/V \tag{1}$$

$$V_{ad} = \sum_{i=1}^{n} (A_b - A_i) / (m I_c)$$
 (2)

where A_b is the average area of peaks obtained with empty tubes for each tested calibrating gas in blank test; and V represents volume of the quantitative loop in the six-way vale, which is 0.30 mL in this work. The item I_c stands for the area of peaks for one milliliter calibrating gas; A_i is the peaks with lower area compared with the control, when pulsing calibrating gas through sample in the tube. The item n represents that the number of peaks showed lower integrated area than that of the control peaks and m was the mass of the testing samples that filled the tube (in the unit of g). V_{ad} represents the volume of calibrating gas adsorbed by the sample (mL/g).

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3. Results and Discussion

3.1. Compatibility of Samples with C_4F_7N

Due to its relatively high boiling point, the content of C_4F_7N used in the mixture gas is usually no more than 20% [22,23]. Therefore, the adsorbents or desiccants used to remove the moisture or acidic by-products from C_4F_7N should not be able to adsorb C_4F_7N . Some of the moisture adsorbents, including 3A, 4A, 5A and F-03 molecular sieves, the desiccants including Na_2SO_4 , $CaCl_2$, and the HF adsorbents, including Na_2F_2 , Na_2F_3 , were tested for their adsorption capacities on C_4F_7N gas.

As shown in Figure 2, comparing with the pulse adsorption spectra using an empty tube as a control (Figure 2A), the 3A and 4A molecular sieves show slight adsorption capacity of C_4F_7N (Figure 2B,C) with 0.39 and 1.44 mL/g, respectively as shown in Table 2. The 3A and 4A molecular sieves are usually used to dewater as they possess high surface areas and pore volumes [15], since the average pore sizes of 0.3 nm (for 3A molecular sieve) and 0.4 nm (for 4A molecular sieve) pore size are suitable to adsorb H_2O molecules, however, it is calculated that the dynamic diameter for C_4F_7N is around 0.7599 nm [12], which is significantly larger than the pore sizes of 3A and 4A molecular sieves. The surface area in micropores contributed most of the surface area, therefore, C_4F_7N molecules are only able to adsorb on the surface of the 3A and 4A molecular sieves, which led to low adsorption capacity.

Table 2. Adsorption performance of the materials with C_4F_7N based on the integrated area of pulse peaks.

Items	Average Peak Area $A_b/\text{mV}\cdot\text{s}$ $I_C/\text{mV}\cdot\text{s/mL}$	I /m N - /m I	Sample Mass/g	V _{ad} /mL/g
		$I_C/m v \cdot s/mL$		
Blank control	1059 ± 13	3530	-	-
3A	1047 ± 3	3490	0.1437	0.39
4A	1045 ± 8	3483	0.0463	1.44
5A	741	2470	0.0658	22.82
F-03	1055 ± 10	3516	0.1028	0.19
CaCl ₂	1060 ± 9	3533	0.1236	-
${ m MgSO_4}$	1055 ± 3	3516	0.1327	0.15
Na_2SO_4	1056 ± 6	3520	0.1636	0.09
$Al(OH)_3$	1056 ± 6	3520	0.1018	0.14
NaF	1057 ± 9	3523	0.1138	0.09
CaF ₂	1058 ± 5	3526	0.1042	0.05
MgF_2	1049 ± 19	3496	0.1445	0.33
m(CaCl2):m(Al(OH)3) = 1:1	1058 ± 10	3526	0.1426	0.04
m(CaCl2):m(Al(OH)3) = 2:1	1057 ± 8	3523	0.1329	0.07

With 5A molecular sieve, although its average pore diameter is 0.5 nm, there are significant pores with sizes larger than 0.5 nm, besides, on the axial direction of this molecule, the diameter of the CF_3 group is smaller than 0.5 nm (0.4896 nm) [24], and therefore more surface area could be reachable for C_4F_7N adsorption on 5A molecular sieve. As shown in Figure 2D, C_4F_7N shows significant adsorption on 5A molecular sieve. The pulse adsorption peaks shown in Figure 2D are trailing, which suggests that the interaction between 5A molecular sieve and C_4F_7N are strong. The adsorption capacity for C_4F_7N is 22.82 mL/g calculated according to Equations (1) and (2). As for the commonly used adsorbent F-03, it also shows slight adsorption of C_4F_7N as shown in Figure 2E, in which the intensity of the signal peaks is slightly lower than that of the blank control.

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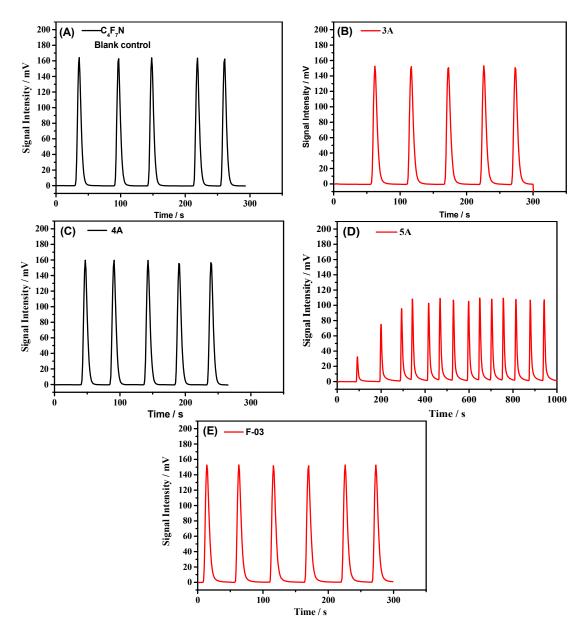


Figure 2. Adsorption performance of adsorbent materials with C_4F_7N tested with pulse adsorption, (**A**) Blank control, (**B**) 3A, (**C**) 4A, (**D**) 5A molecular sieve, (**E**) F-03.

Since the 5A molecular sieves could adsorb C_4F_7N , it is not suitable to use these materials to eliminate the moisture from C_4F_7N gas. One alternative strategy could be using the common desiccants, such as $CaCl_2$, $MgSO_4$, Na_2SO_4 . These chemicals implement dewatering efficiently by forming crystal water. Since these chemicals possess low surface area, they should show negligible adsorption capacity of C_4F_7N . As shown in Figure 3, three desiccants, including $CaCl_2$, $MgSO_4$ and Na_2SO_4 , show negligible adsorption with C_4F_7N . The adsorption capacity data listed in Table 2 also show that these chemicals do not intend to adsorb C_4F_7N . Therefore, these three desiccants could be used for dewatering of C_4F_7N gas.

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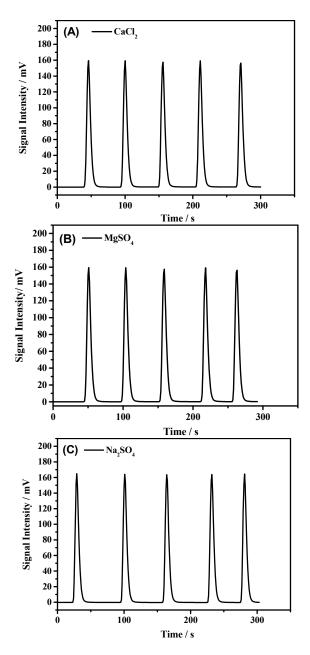


Figure 3. Adsorption performance of desiccants on C_4F_7N tested with pulse adsorption, (**A**) $CaCl_2$, (**B**) $MgSO_4$, (**C**) Na_2SO_4 .

Some fluorides are good HF adsorbents, including NaF [17,25], MgF₂ and CaF₂ [26]. Due to the reactivity with HF, Al(OH)₃ has also proved to be good HF remover [27]. These chemicals are potential HF removers that could be placed in the gas insulated electricity transfer equipment filled with C_4F_7N gas. Therefore, the adsorption performances of these chemicals on C_4F_7N are significant data. The ideal situation of negligible adsorption with this gas was expected to be observed. The pulse adsorption data are shown in Figure 4. As shown in these patterns, NaF, CaF₂ and Al(OH)₃ show negligible adsorption of C_4F_7N , while MgF₂ shows clear interaction with C_4F_7N . The adsorption capacity data listed in Table 2 also support the conclusion. These data suggest that NaF, CaF₂ and Al(OH)₃ are compatible with C_4F_7N when used as a HF remover.

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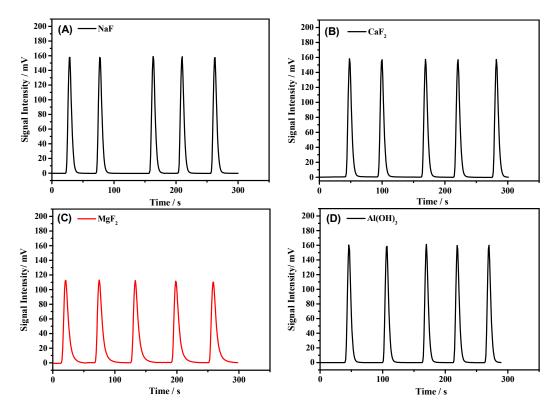


Figure 4. Adsorption performance of HF adsorbents on C_4F_7N , (**A**) NaF, (**B**) CaF_2 , (**C**) MgF_2 , (**D**) $Al(OH)_3$.

A mixture of desiccant ($CaCl_2$) and HF remover ($Al(OH)_3$) was also tested for its compatibility with C_4F_7N gas. As shown in Figure 5, regardless if the mass ratio of desiccant to HF remover was 1 or 2, the mixture did not show clear adsorption performance on C_4F_7N . These data suggest that using a mixture of desiccant and HF remover to eliminate the moisture and HF could be a promising way to substitute the 5A or F-03 adsorbents.

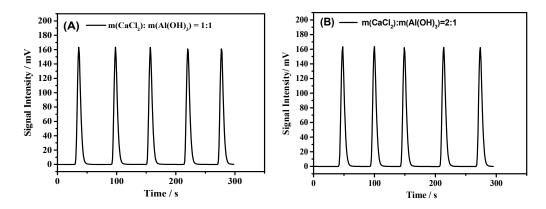


Figure 5. Adsorption performance of a mixture of desiccant and HF adsorbent, with a mass ratio of CaCl₂ to Al(OH)₃ equal to (**A**) 1:1, (**B**) 2:1.

3.2. Compatibility of Samples with CO₂

In C_4F_7N/CO_2 , the ratio of CO_2 could be more than 90% (v/v), therefore, to remove moisture and HF, the compatibility of the adsorbents with CO_2 is significant. Both of CO_2 and HF are acidic gases, and the reactivity of the adsorbents with CO_2 may compromise the efficiency for HF removal. In this work, the compatibility of the above tested molecular sieves, including 3A, 4A, 5A, F-03, the desiccants,

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such as CaCl₂, MgSO₄, Na₂SO₄, and HF remover, NaF, MgF₂, CaF₂ and Al(OH)₃ were tested with pulse adsorption procedures to determine their adsorption performance or interaction with CO₂.

As shown in Figure 6B,C, Figures 3A and 4A molecular sieves show slight adsorption of CO_2 compared with the blank control in Figure 6A, besides, the data listed in Table 3 show that the adsorption capacity is 0.8 mL/g and 3.13 mL/g, respectively. The 5A molecular sieve showed clear adsorption with CO_2 , as shown in Figure 6D, and this result is consistent with the previous study [28]. The peak intensity is lower than the blank control and they are trailing clearly, which suggests the CO_2 is strongly interacting with the 5A molecular sieve. The adsorption capacity listed in Table 3 is 43.66 mL/g. It is well known that 5A molecular sieve has high adsorption capacity of CO_2 [11,28]. The F-03 adsorbents also show a high CO_2 adsorption capacity, which is 26.2 mL/g as listed in Table 3. Therefore, 5A molecular sieve and F-03 are not compatible with C_4F_7N/CO_2 insulating gas.

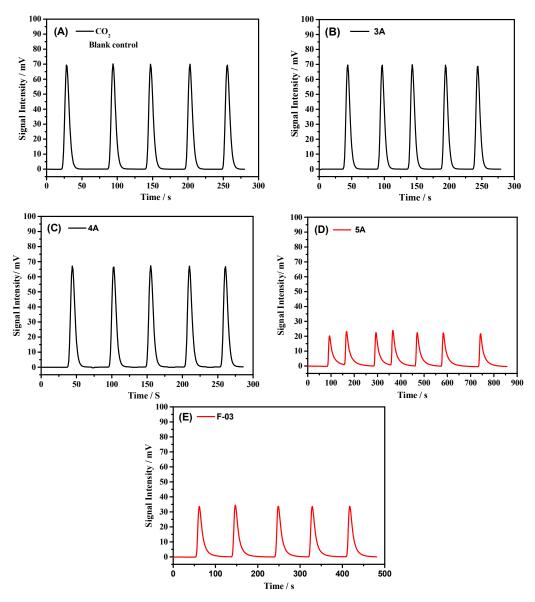


Figure 6. Adsorption performance of adsorbent materials with CO₂ tested with pulse adsorption, (**A**) Blank control, (**B**) 3A, (**C**) 4A, (**D**) 5A molecular sieve, (**E**) F-03.

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Items	Average Peak Area A _b /mV·s	<i>I_C</i> /mV·s/mL	Sample Mass/g	V _{ad} /mL/g	
Blank control	523 ± 4	1743	-	-	
3A	516 ± 4	1720	0.0824	0.80	
4A	499 ± 4	1663	0.073	3.13	
5A *	430	1433	0.0407	43.66	
F-03 *	427	1423	0.07	26.20	
CaCl ₂	524 ± 6	1747	0.0506	0	
$MgSO_4$	525 ± 3	1750	0.0682	0	
Na_2SO_4	528 ± 5	1760	0.1317	0	
$Al(OH)_3$	522 ± 2	1740	0.1285	0.07	
NaF	520 ± 4	1733	0.1328	0.21	
CaF ₂	518 ± 7	1727	0.1233	0.38	
MgF_2	518 ± 6	1727	0.1428	0.33	
$m(CaCl_2):m(Al(OH)_3) = 1:1$	519 ± 3	1730	0.1235	0.30	
$m(CaCl_0) \cdot m(Al(OH)_0) = 2.1$	512 + 3	1707	0.1326	0.79	

Table 3. Adsorption performance of the materials on CO_2 based on the integrated area of pulse peaks.

Similar with the results tested in C_4F_7N , the three desiccants did not show clear adsorption with CO_2 , as shown in Figure 7, and the data listed in Table 3. The data also suggest the three chemicals would not react with CO_2 . Since no clear adsorption with C_4F_7N was observed, they could be used for removing the moisture in the insulating gas C_4F_7N/CO_2 .

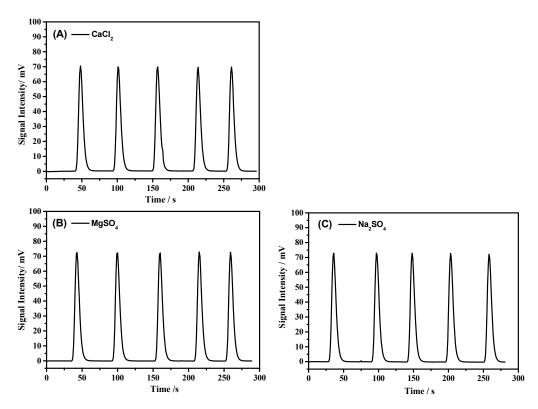


Figure 7. Adsorption performance of desiccants on CO₂ tested with pulse adsorption, (**A**) CaCl₂, (**B**) MgSO₄, (**C**) Na₂SO₄.

All of the four HF removers are alkaline chemicals, one would suspect that these chemicals may react with CO_2 . The pulse adsorption data presented in Figure 8 suggest that the four chemicals show negligible adsorption of CO_2 , and the adsorption capacity data listed in Table 3 are all below 0.5 mL/g. These data suggest that CO_2 would not react with the four HF removers. The p K_a of HF is 3.18, and

^{* 5}A molecular sieves and F-03 were tested for 10 cycles, and the others were tested for five cycles.

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the p K_{a1} of H_2CO_3 is 6.38, therefore, the fluoride salts are stable in CO_2 gas. Al(OH)₃ is a weak alkali, and it is also stable in CO_2 gas.

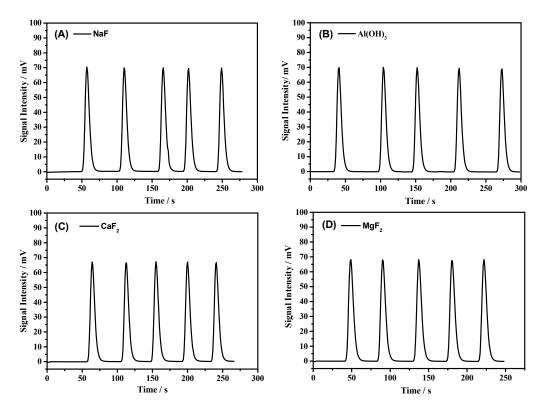


Figure 8. Adsorption performance of HF adsorbents on CO₂, (A) NaF, (B) CaF₂, (C) MgF₂, (D) Al(OH)₃.

Since both the desiccants and HF remover studied in this work did not show clear reaction or adsorption with CO_2 , logically, the mixture of a desiccant and HF remover should also not adsorb or react with CO_2 . The data shown in Figure 9 and Table 3 prove that the mixture of $CaCl_2$ and $CaCl_3$ are compatible in CO_3 , which is the same result as tested in $CaCl_3$. Therefore, the mixture of desiccants with HF remover could be used in $CaCl_3$.

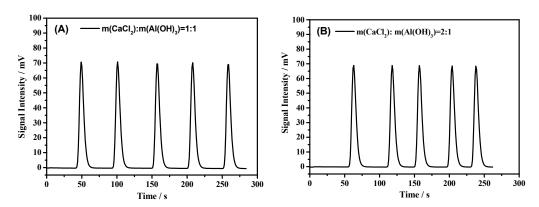


Figure 9. Adsorption performance of a mixture of desiccant and HF adsorbent on CO₂, with a mass ratio of CaCl₂ to Al(OH)₃ equal to (A) 1:1, (B) 2:1.

4. Conclusions

The pulse adsorption tests suggested that the commonly used adsorbents 5A and F-03 molecular sieves could not be used in C_4F_7N/CO_2 , due to the severe adsorption of the mixed gas on these molecular sieves. The 3A and 4A molecular sieves adsorb C_4F_7N and CO_2 slightly, and might be

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used as adsorbents for C_4F_7N/CO_2 . Desiccants, including Na_2SO_4 , $CaCl_2$ and $MgSO_4$ show negligible adsorption with C_4F_7N and CO_2 . Some HF removers, such as NaF, CaF_2 , $Al(OH)_3$ also show negligible adsorption with the two gases, and could be compatible with them sealed in related gas insulated electricity transfer equipment. Using a mixture of desiccant and HF remover could be a good strategy to remove the moisture and HF produced in the C_4F_7N/CO_2 insulated equipment.

Author Contributions: Investigation, Q.H.; funding acqusition Y.W.; methodology, J.L.; Investigation Y.Z.; Investigation L.Z.

Funding: This research was funded by the project 'Study on Physical, Chemical and Insulation Properties, and Engineering Demostration of Environmental Insulating gas (I)-Project 3-Applied Feasibility Study of New Insulating Gas in Guangzhou Power Grid', numbered as GZJKJXM20170330.

Conflicts of Interest: The authors declare no conflict of interest.

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