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

Qingdan Huang, Yong Wang, Jing Liu *, Yaru Zhang and Lian Zeng

Electric Power Test and Research Institute, Guangzhou Power Supply Co. Ltd., Guangzhou 510410, China; cloveryours@hotmail.com (Q.H.); wangy@guangzhou.csg.cn (Y.W.); zhangyaru1989@163.com (Y.Z.); whu282070193@live.com (L.Z.)
* Correspondence: greengasguangzhou@163.com; Tel.: +86-20-87125506

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 (C₄F₇N) 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 (GWP, 100, 2210 for C₄F₇N) is clearly lower than that of SF₆ (GWP, 100, 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, C₄F₇N 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, SF₆ could be decomposed into HF, H₂S, SO₂, SF₂, etc. with a trace amount of H₂O [5–7]. These products are highly toxic, and the acidic gases, such as HF,
H$_2$S and SO$_2$, 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 SF$_6$ 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 C$_4$F$_7$N can be thermally decomposed into CO, COF$_2$, CF$_3$CN, C$_2$F$_3$CN, etc. [8]. The theoretical study results indicate that HF, HCN could be generated by a discharge in the presence of trace H$_2$O [9]. Therefore, it is significant to control the moisture level of C$_4$F$_7$N 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 SF$_6$, 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$_4$F$_7$N 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$_4$F$_7$N, but also evaluate the compatibility of the adsorbents with the buffering gases. As we know, 5A molecular sieve is a good adsorbent for CO$_2$ and H$_2$O adsorption [10,11], therefore, its compatibility with C$_4$F$_7$N/CO$_2$ is suspected and needs to be confirmed. It is also reported that $\gamma$-Al$_2$O$_3$ is highly effective at adsorbing C$_4$F$_7$N [12]. However, the information about adsorbents that could be used for C$_4$F$_7$N/CO$_2$ is quite limited.

In this work, in order to study the compatibility of commonly used adsorbents with the new insulating gas C$_4$F$_7$N/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 toward C$_4$F$_7$N and CO$_2$. The chemical reagents used in this study, including Al(OH)$_3$, CaCl$_2$, MgSO$_4$, Na$_2$SO$_4$, NaF, 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 $^\circ$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$_4$F$_7$N was purchased from a commercial market with a purity of 99%. The chemical composition of the zeolite molecular sieves are listed in Table 1.

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

| Molecular Sieve | Chemical Composition | Pore Size/ nm |
|-----------------|----------------------|--------------|
| 3A              | Na$_{6.6}$K$_{3.4}$·[(AlO$_2$)$_{12}$(SiO$_2$)$_{12}$] | 0.3          |
| 4A              | Na$_{12}$·[(AlO$_2$)$_{12}$(SiO$_2$)$_{12}$] | 0.4          |
| 5A              | Ca$_6$·[(AlO$_2$)$_{12}$(SiO$_2$)$_{12}$] | 0.5          |
| F-03            | Na$_{12}$·[(AlO$_2$)$_{12}$(SiO$_2$)$_{15}$] | 1.0          |

### 2. Materials and Methods

#### 2.1. Chemical Reagents

The chemical reagents used in this study, including Al(OH)$_3$, CaCl$_2$, MgSO$_4$, Na$_2$SO$_4$, NaF, 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 $^\circ$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$_4$F$_7$N was purchased from a commercial market with a purity of 99%. The chemical composition of the zeolite molecular sieves are listed in Table 1.

#### 2.2. Adsorption Characterization

To study the adsorption performance of the selected chemicals and adsorbents toward C$_4$F$_7$N 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
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.

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

\[ I_c = \frac{A_b}{V} \]  
\[ V_{ad} = \sum_{i=1}^{n} \frac{(A_b - A_i)}{(m I_c)} \]

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 valve, 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).

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

\[ I_c = \frac{A_b}{V} \]  
\[ V_{ad} = \sum_{i=1}^{n} \frac{(A_b - A_i)}{(m I_c)} \]

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 valve, 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).
3. Results and Discussion

3.1. Compatibility of Samples with C₄F₇N

Due to its relatively high boiling point, the content of C₄F₇N 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 C₄F₇N should not be able to adsorb C₄F₇N. Some of the moisture adsorbents, including 3A, 4A, 5A and F-03 molecular sieves, the desiccants including Na₂SO₄, CaCl₂, and the HF adsorbents, including NaF, MgF₂, Al(OH)₃ and CaF₂, were tested for their adsorption capacities on C₄F₇N 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 C₄F₇N (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 H₂O molecules, however, it is calculated that the dynamic diameter for C₄F₇N 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, C₄F₇N molecules are only able to adsorb on the surface of the 3A and 4A molecular sieves, which led to low adsorption capacity.

| Items        | Average Peak Area Aₚ/mV·s | Iₛ/mV·s/mL | Sample Mass/g | Vₛad/mL/g |
|--------------|---------------------------|-------------|---------------|-----------|
| Blank control| 1059 ± 13                 | 3530        | -             | -         |
| 3A           | 1047 ± 3                  | 3490        | 0.1437        | 0.39      |
| 4A           | 1045 ± 8                  | 3485        | 0.0463        | 1.44      |
| 5A           | 741                       | 2470        | 0.0658        | 22.82     |
| F-03         | 1055 ± 10                 | 3516        | 0.1028        | 0.19      |
| CaCl₂        | 1060 ± 9                  | 3533        | 0.1236        | -         |
| MgSO₄        | 1055 ± 3                  | 3516        | 0.1327        | 0.15      |
| Na₂SO₄       | 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      |
| CaF₂         | 1058 ± 5                  | 3526        | 0.1042        | 0.05      |
| MgF₂         | 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 CF₃ group is smaller than 0.5 nm (0.4896 nm) [24], and therefore more surface area could be reachable for C₄F₇N adsorption on 5A molecular sieve. As shown in Figure 2D, C₄F₇N 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 C₄F₇N are strong. The adsorption capacity for C₄F₇N 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 C₄F₇N as shown in Figure 2E, in which the intensity of the signal peaks is slightly lower than that of the blank control.
3. Results and Discussion

3.1. Compatibility of Samples with C4F7N

Due to its relatively high boiling point, the content of C4F7N 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 C4F7N should not be able to adsorb C4F7N. Some of the moisture adsorbents, including 3A, 4A, 5A and F-03 molecular sieves, the desiccants including Na2SO4, CaCl2, and the HF adsorbents, including NaF, MgF2, Al(OH)3 and CaF2, were tested for their adsorption capacities on C4F7N 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 C4F7N (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 H2O molecules, however, it is calculated that the dynamic diameter for C4F7N 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, C4F7N molecules are only able to adsorb on the surface of the 3A and 4A molecular sieves, which led to low adsorption capacity.

Since the 5A molecular sieves could adsorb C4F7N, it is not suitable to use these materials to eliminate the moisture from C4F7N gas. One alternative strategy could be using the common desiccants, such as CaCl2, MgSO4, Na2SO4. These chemicals implement dewatering efficiently by forming crystal water. Since these chemicals possess low surface area, they should show negligible adsorption capacity of C4F7N. As shown in Figure 3, three desiccants, including CaCl2, MgSO4 and Na2SO4, show negligible adsorption with C4F7N. The adsorption capacity data listed in Table 2 also show that these chemicals do not intend to adsorb C4F7N. Therefore, these three desiccants could be used for dewatering of C4F7N gas.

Figure 2. Adsorption performance of adsorbent materials with C4F7N tested with pulse adsorption, (A) Blank control, (B) 3A, (C) 4A, (D) 5A molecular sieve, (E) F-03.
Some fluorides are good HF adsorbents, including NaF [17,25], MgF$_2$ and CaF$_2$ [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$_4$F$_7$N gas. Therefore, the adsorption performances of these chemicals on C$_4$F$_7$N 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, CaF$_2$ and Al(OH)$_3$ show negligible adsorption of C$_4$F$_7$N, while MgF$_2$ shows clear interaction with C$_4$F$_7$N. The adsorption capacity data listed in Table 2 also support the conclusion. These data suggest that NaF, CaF$_2$ and Al(OH)$_3$ are compatible with C$_4$F$_7$N when used as a HF remover.
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 C₄F₇N 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 C₄F₇N. 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 4.** Adsorption performance of HF adsorbents on C₄F₇N, (A) NaF, (B) CaF₂, (C) MgF₂, (D) Al(OH)₃.

A mixture of desiccant (CaCl₂) and HF remover (Al(OH)₃) was also tested for its compatibility with C₄F₇N 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 C₄F₇N. 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 C₄F₇N/CO₂, the ratio of CO₂ could be more than 90% (v/v), therefore, to remove moisture and HF, the compatibility of the adsorbents with CO₂ is significant. Both of CO₂ and HF are acidic gases, and the reactivity of the adsorbents with CO₂ 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,
such as CaCl$_2$, MgSO$_4$, Na$_2$SO$_4$, and HF remover, NaF, MgF$_2$, CaF$_2$ and Al(OH)$_3$ were tested with pulse adsorption procedures to determine their adsorption performance or interaction with CO$_2$.

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$_4$F$_7$N/CO$_2$ insulating gas.

![Figure 6](image-url)  
**Figure 6.** Adsorption performance of adsorbent materials with CO$_2$ tested with pulse adsorption, (A) Blank control, (B) 3A, (C) 4A, (D) 5A molecular sieve, (E) F-03.
would not react with CO2. Since no clear adsorption with C4F7N was observed, they could be used for removing the moisture in the insulating gas C4F7N/CO2. The pulse adsorption data presented in Figure 8 suggest that the four chemicals show adsorption with CO2, logically, the mixture of a desiccant and HF remover should also not adsorb or react with CO2. The data also suggest the three chemicals are compatible in CO2, which is the same result as tested in C4F7N. Therefore, the mixture of desiccants with HF remover could be used in C4F7N/CO2.

Similar with the results tested in C4F7N, the three desiccants did not show clear adsorption with CO2, as shown in Figure 7, and the data listed in Table 3. The data also suggest the three chemicals would not react with CO2. Since no clear adsorption with C4F7N was observed, they could be used for removing the moisture in the insulating gas C4F7N/CO2.

Table 3. Adsorption performance of the materials on CO2 based on the integrated area of pulse peaks.

| Items                      | Average Peak Area $A_p$/mV·s | $I_C$/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         |
| CaCl2                     | 524 ± 6                      | 1747          | 0.0506        | 0             |
| MgSO4                     | 525 ± 3                      | 1750          | 0.0682        | 0             |
| Na2SO4                    | 528 ± 5                      | 1760          | 0.1317        | 0             |
| Al(OH)3                   | 522 ± 2                      | 1740          | 0.1285        | 0.07          |
| NaF                       | 520 ± 4                      | 1733          | 0.1328        | 0.21          |
| CaF2                      | 518 ± 7                      | 1727          | 0.1233        | 0.38          |
| MgF2                      | 518 ± 6                      | 1727          | 0.1428        | 0.33          |
| m(CaCl2):m(Al(OH)3) = 1:1 | 519 ± 3                      | 1730          | 0.1235        | 0.30          |
| m(CaCl2):m(Al(OH)3) = 2:1 | 512 ± 3                      | 1707          | 0.1326        | 0.79          |

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

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 CO2. The pulse adsorption data presented in Figure 8 suggest that the four chemicals show negligible adsorption of CO2, and the adsorption capacity data listed in Table 3 are all below 0.5 mL/g. These data suggest that CO2 would not react with the four HF removers. The pKb of HF is 3.18, and
the pK\textsubscript{a1} of H\textsubscript{2}CO\textsubscript{3} is 6.38, therefore, the fluoride salts are stable in CO\textsubscript{2} gas. Al(OH)\textsubscript{3} is a weak alkali, and it is also stable in CO\textsubscript{2} gas.

Figure 8. Adsorption performance of HF adsorbents on CO\textsubscript{2}, (A) NaF, (B) CaF\textsubscript{2}, (C) MgF\textsubscript{2}, (D) Al(OH)\textsubscript{3}.

Since both the desiccants and HF remover studied in this work did not show clear reaction or adsorption with CO\textsubscript{2}, logically, the mixture of a desiccant and HF remover should also not adsorb or react with CO\textsubscript{2}. The data shown in Figure 9 and Table 3 prove that the mixture of CaCl\textsubscript{2} and Al(OH)\textsubscript{3} are compatible in CO\textsubscript{2}, which is the same result as tested in C\textsubscript{4}F\textsubscript{7}N. Therefore, the mixture of desiccants with HF remover could be used in C\textsubscript{4}F\textsubscript{7}N/CO\textsubscript{2}.

Figure 9. Adsorption performance of a mixture of desiccant and HF adsorbent on CO\textsubscript{2}, with a mass ratio of CaCl\textsubscript{2} to Al(OH)\textsubscript{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\textsubscript{4}F\textsubscript{7}N/CO\textsubscript{2}, due to the severe adsorption of the mixed gas on these molecular sieves. The 3A and 4A molecular sieves adsorb C\textsubscript{4}F\textsubscript{7}N and CO\textsubscript{2} slightly, and might be
used as adsorbents for \( \text{C}_4\text{F}_2\text{N}/\text{CO}_2 \). Desiccants, including \( \text{Na}_2\text{SO}_4 \), \( \text{CaCl}_2 \) and \( \text{MgSO}_4 \) show negligible adsorption with \( \text{C}_4\text{F}_2\text{N} \) and \( \text{CO}_2 \). Some HF removers, such as \( \text{NaF}, \text{CaF}_2 \), \( \text{Al(OH)}_3 \) 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 \( \text{C}_4\text{F}_2\text{N}/\text{CO}_2 \) insulated equipment.

**Author Contributions:** Investigation, Q.H.; funding acquisition Y.W.; methodology, J.L.; Investigation Y.Z.; Processes 2019 7. Zhang, X.; Chen, D.; Cui, H.; Dong, X.; Xiao, S.; Tang, J. Understanding of \( \text{SF}_6 \). Ind. Eng. Chem. Res. 2018, 57, 5173–5182. [CrossRef]

**Funding:** This research was funded by the project ‘Study on Physical, Chemical and Insulation Properties, and Engineering Demonstration of Environmental Insulating gas (I)-Project 3-Applied Feasibility Study of New Insulating Gas in Guangzhou Power Grid’, numbered as GZJKJXM20170730.

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

**References**

1. Wang, Y.; Huang, D.; Liu, J.; Zhang, Y.; Zeng, L. Alternative Environmentally Friendly Insulating Gases for \( \text{SF}_6 \). Processes 2019, 7, 216. [CrossRef]
2. Li, Y.; Zhang, X.; Xiao, S.; Chen, Q.; Tang, J.; Chen, D.; Wang, D. Decomposition Properties of \( \text{C}_4\text{F}_2\text{N}/\text{N}_2 \) Gas Mixture: An Environmentally Friendly Gas to Replace \( \text{SF}_6 \). Ind. Eng. Chem. Res. 2018, 57, 5173–5182. [CrossRef]
3. Li, Y.; Zhang, X.; Zhang, J.; Xiao, S.; Xie, B.; Chen, D.; Gao, Y.; Tang, J. Assessment on the toxicity and application risk of \( \text{C}_4\text{F}_7\text{N} \): A new \( \text{SF}_6 \) alternative gas. J. Hazard. Mater. 2019, 368, 653–660. [CrossRef] [PubMed]
4. Li, Y.; Zhang, X.; Zhang, J.; Fu, M.; Zhuo, R.; Luo, Y.; Chen, D.; Xiao, S. Experimental study on the partial discharge and AC breakdown properties of \( \text{C}_4\text{F}_2\text{N}/\text{CO}_2 \) mixture. High Voltage 2019, 4, 12–17. [CrossRef]
5. Zhong, L.; Ji, S.; Wang, F.; Sun, Q.; Chen, S.; Liu, J.; Hai, B.; Tang, L. Theoretical study of the chemical decomposition mechanism and model of Sulfur hexafluorid (\( \text{SF}_6 \)) under corona discharge. J. Fluorine Chem. 2019, 220, 61–68. [CrossRef]
6. Park, J.-H.; Shin, I.H.; Seo, S.H.; Choi, C.Y.; Son, Y-S. The optimization of \( \text{SF}_6 \) decomposition process using an electron beam. Radiat. Phys. Chem. 2018, 151, 192–197. [CrossRef]
7. Zhang, X.; Chen, D.; Cui, H.; Dong, X.; Xiao, S.; Tang, J. Understanding of \( \text{SF}_6 \) decompositions adsorbed on cobalt-doped SWCNT: A DFT study. Appl. Surf. Sci. 2017, 384, 371–382. [CrossRef]
8. Kieffer, Y. Characteristics of g3- an alternative to \( \text{SF}_6 \). In Proceedings of the 2016 IEEE International Conference on Dielectrics (ICD), Montpellier, France, 3–7 July 2016; p. 880.
9. Zhang, X.; Li, Y.; Xiao, S.; Tian, S.; Deng, Z.; Tang, J. Theoretical study of the decomposition mechanism of environmentally friendly insulating medium \( \text{C}_4\text{F}_2\text{N} \) in the presence of \( \text{H}_2\text{O} \) in a discharge. J. Phys. D Appl. Phys. 2017, 50, 325201. [CrossRef]
10. Pakseresht, S.; Kazemein, M.; Akbarnejad, M.M. Equilibrium isotherms for \( \text{CO}, \text{CO}_2, \text{CH}_4 \) and \( \text{C}_2\text{H}_4 \) on the 5A molecular sieve by a simple volumetric apparatus. Sep. Purif. Technol. 2002, 28, 53–60. [CrossRef]
11. AbdulKareem, F.A.; Mohd Shariff, A.; Ullah, S.; See, T.L.; Keong, L.K.; Mellon, N. Adsorption performance of 5A molecular sieve zeolite in water vapor–binary gas environment: Experimental and modeling evaluation. J. Ind. Eng. Chem. 2018, 64, 173–187. [CrossRef]
12. Xiao, S.; Zhang, X.X.; Chen, D.; Fu, M.L.; Tang, J.; Li, Y. Adsorption Characteristics of \( \gamma\text{-Al}_2\text{O}_3 \) for the Environment-friendly Insulating Medium \( \text{C}_4\text{F}_2\text{N}/\text{N}_2 \) and Its Decomposition Products. High Voltage Eng. 2018, 44, 3135–3140. [CrossRef]
13. Lin, R.; Ladshaw, A.; Nan, Y.; Liu, J.; Yiacoumi, S.; Tsouris, C.; DePaoli, D.W.; Tavlarides, L.L. Isotherms for Water Adsorption on Molecular Sieve 3A: Influence of Cation Composition. Ind. Eng. Chem. Res. 2015, 54, 10442–10448. [CrossRef]
14. Liu, X.; Wang, R. Effective removal of hydrogen sulfide using 4A molecular sieve zeolite synthesized from attapulgite. J. Hazard. Mater. 2017, 326, 157–164. [CrossRef] [PubMed]
15. Gabrus, E.; Witskievicz, K.; Nastaj, J. Modeling of regeneration stage of 3A and 4A zeolite molecular sieves in TSA process used for dewatering of aliphatic alcohols. Chem. Eng. J. 2018, 337, 416–427. [CrossRef]
16. Hussein, M.S.; Ahmed, M.J. Fixed bed and batch adsorption of benzene and toluene from aromatic hydrocarbons on 5A molecular sieve zeolite. *Mater. Chem. Phys.* 2016, 181, 512–517. [CrossRef]

17. Afzal, S.; Rahimi, A.; Elsani, M.R.; Tavakoli, H. Experimental study of hydrogen fluoride adsorption on sodium fluoride. *J. Ind. Eng. Chem.* 2010, 16, 147–151. [CrossRef]

18. Kaawar, Z.; Paulus, B. Adsorption of hydrogen fluoride on alkaline earth fluoride surfaces: A first-principles study. *J. Fluorine Chem.* 2019, 224, 67–72. [CrossRef]

19. Ju, J.; Liu, R.; He, Z.; Liu, H.; Zhang, X.; Qu, J. Utilization of aluminum hydroxide waste generated in fluoride adsorption and coagulation processes for adsorptive removal of cadmium ion. *Front. Environ. Sci. Eng.* 2016, 10, 467–476. [CrossRef]

20. Hiremath, C.R.; Kadoli, R.; Katti, V.V. Experimental and theoretical study on dehumidification potential of clay-additives based CaCl₂ composite desiccants. *Appl. Therm. Eng.* 2018, 129, 70–83. [CrossRef]

21. Fergus, J.W.; Hsu, T. Integrating humidity sensor based on a polybutadiene—MgSO₄ composite. *Meas. Sci. Technol.* 2005, 16, 1255–1260. [CrossRef]

22. Zhang, X.X.; Zhang, Q.C.; Zhang, J.; Li, Y.; Xiao, S.; Zhuo, R.; Tang, J. Experimental study on power frequency breakdown characteristics of C₄F₇N/CO₂ gas mixture under quasi-homogeneous electric field. *IEEE Access.* 2019, 7, 19100–19108. [CrossRef]

23. Li, Z.; Ding, W.; Liu, Y.; Li, Y.; Zheng, Z.; Liu, W.; Gao, K. Surface flashover characteristics of epoxy insulator in C₄F₇N/CO₂ mixtures in a uniform field under AC voltage. *IEEE Trans. Dielectr. Electr Insul.* 2019, 26, 1065–1072. [CrossRef]

24. Saheb, V.; Javanmardi, M. Theoretical studies on the mechanism and kinetics of the reaction of CF₃ radical with oxygen molecule. *J. Fluorine Chem.* 2018, 211, 154–158. [CrossRef]

25. Tavakoli, H.; Ghasemi, M.R. Equilibrium, kinetics and breakthrough studies for adsorption of hydrogen fluoride on sodium fluoride. *Chem. Eng. Process: Process Intensif.* 2010, 49, 435–440. [CrossRef]

26. Li, C.X.; He, S.J.; Jiang, D.Y.; Li, Q. Hydrogen Fluoride Adsorption Ability of some Inorganic Compounds. *Adv. Mater. Res.* 2012, 412, 1–4. [CrossRef]

27. McIntosh, G.J.; Agbenyegah, G.E.; Hyland, M.M.; Metson, J.B. Adsorptive capacity and evolution of the pore structure of alumina on reaction with gaseous hydrogen fluoride. *Langmuir* 2015, 31, 5387–5397. [CrossRef] [PubMed]

28. Chang, H.; Wu, Z.-X. Experimental Study on Adsorption of Carbon Dioxide by 5A Molecular Sieve for Helium Purification of High-Temperature Gas-Cooled Reactor. *Ind. Eng. Chem. Res.* 2009, 48, 4466–4473. [CrossRef]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).