

ORIGINAL RESEARCH PAPER

Gas decomposition and electrode degradation characteristics of a 20% C₃F₇CN and 80% CO₂ gas mixture for high voltage accelerators

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Abstract

Sulphur hexafluoride (SF₆) is a potent greenhouse gas used in high voltage accelerators. As a promising alternative to SF₆, the C₃F₇CN/CO₂ gas mixture and its by-products are of great interest to ensure the safe operation of accelerators that will adopt any SF₆-free solution. This work experimentally examines the electrical ageing characteristics of a 20% C₃F₇CN/80% CO₂ gas mixture tested using spark gaps under a pressure of 7.2 bar (abs.). Gas samples were collected after 1000 DC breakdowns and analysed using gas chromatography mass spectrometry (GC-MS) with an estimated toxicity value of 54,459 ppm_v, which indicates the aged mixture to be non-toxic. Subsequent investigation was conducted on the gas-solid interface after 500 breakdowns for both SF₆ and the 20% C₃F₇CN/80% CO₂ gas mixture. Aged electrodes were analysed using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) techniques. Electrode surface analysis revealed the formation of metal fluorides on the electrode surface tested using the 20% C₃F₇CN/80% CO₂ mixture, whereas metal fluorides and sulphides were detected for electrodes tested with SF₆. The findings provide a reference on the toxicity and gas-solid interaction of the electrically aged 20% C₃F₇CN/80% CO₂ gas mixture for potential retro-fill application in high voltage accelerators.

1 | INTRODUCTION

SF₆ gas has been used for high energy DC accelerators up to 20 MeV due to its excellent dielectric strength [1]. However, SF₆ has a high global warming potential (GWP), 23,500 times greater than that of CO₂ with a long atmospheric lifetime of 3200 years. The EU F-gas regulation aims to reduce the greenhouse gas emission level to two-thirds of 2014 by 2030 [2]. There are growing research activities worldwide aimed at finding an environmentally friendly alternative to SF₆ for use in high voltage equipment.

High voltage accelerators use a large volume of SF₆ (about 37,847 m³ for a 5 MeV Dynamitron® manufactured by IBA) under a high operating pressure to insulate the terminal column and the related sub-systems due to the high energy ratings. However, sparking is a common

failure mode in accelerators that leads to the destruction of components such as resistors, insulators and vaporisation of spark gap electrode materials. Switches are usually installed to protect and control the dissipation of rapid release of high electrostatic energy during breakdown [3–5]. The vaporised electrode materials during breakdown lead to solid by-products and their accumulation on insulator surfaces resulting in increased risk of insulator flashover [3].

Research on suitable SF₆ alternatives has led to the development of an insulating compound named heptafluoro-isobutyronitrile (C₃F₇CN), commercially known as 3M™ Novec™ 4710 [6]. C₃F₇CN is non-flammable and has demonstrated low toxicity in acute inhalation studies [6]. The 4 h lethal concentration at 50% mortality (LC_{50-4h}) is > 10,000 ppm and considered to be practically non-toxic [6].

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The GWP of C_3F_7CN is 2100 which reduces further when used in a low concentration as part of a mixture. For a 20% $C_3F_7CN/80\%$ CO_2 gas mixture, the calculated GWP is about 1100 and representing 95% reduction in GWP relative to SF_6 . Pure C_3F_7CN is an electronegative gas with excellent dielectric strength that is double that of SF_6 tested under a relatively uniform field [7]. The main disadvantage of C_3F_7CN is its high boiling point of $-4.7^\circ C$ and must be used as a mixture with a buffer gas such as CO_2 ($-78.5^\circ C$) to avoid liquefaction under higher pressures [8].

Any new alternative candidate should not pose adverse effects on maintenance personnel. Toxicity estimates using LC_{50-4h} on arced 10% $C_3F_7CN/90\%$ CO_2 mixture on male and female mice were found to be 100,000 and 95,500 ppm respectively [8]. After 2000 AC breakdowns using a 13.3% $C_3F_7CN/86.7\%$ CO_2 gas mixture [9], by-products such as CO , CF_4 , C_2F_4 , C_2F_6 , C_3F_6 , C_3F_8 , C_4F_6 , C_4F_{10} , C_2N_2 , CF_3CN , C_2F_3CN , C_2F_5CN , HCN and HF were detected.

Other studies examined electrode surface characterisation of electrically aged electrodes using different physico-chemical techniques. Solid by-products containing copper (Cu), nitrogen (N), fluoride (F), and silicon (Si) were found to be formed on the surface of brass electrodes after extensive AC breakdowns for a 13.3% $C_3F_7CN/86.7\%$ CO_2 mixture under 3 bar (abs.) [9]. For electrodes tested in a humid 20% $C_3F_7CN/80\%$ CO_2 gas mixture, the electrode surface was analysed by X-ray photoelectron spectroscopy (XPS) and by-products such as Fe-O, Fe-F, Cr-O, Cr-F, Ni-OH and metal carbonates were reported [10]. However, ageing study on stainless steel electrodes has not been reported. Replacing all SF_6 insulated accelerators globally is simply not economically viable. In the case of a retro-fill solution, SF_6 in the existing equipment could be replaced by an environmentally friendly alternative with minor modifications to achieve significant financial and environmental savings for the end users.

A 20% $C_3F_7CN/80\%$ CO_2 mixture was tested in this work due to its comparable breakdown performance as SF_6 reported in [7]. The performance of the 20% $C_3F_7CN/80\%$ CO_2 mixture over extensive number of DC breakdowns was experimentally assessed as a potential retro-fill solution. Toxicity estimates of the aged gas mixture and decomposed by-products were determined using the LC_{50-4h} values. Electrode surface analyses were conducted using XPS and X-ray diffraction (XRD) techniques to determine the elemental composition on the electrode surface after the experiment.

2 | EXPERIMENTAL SETUP

2.1 | Test vessel and gas handling procedure

As shown in Figure 1, a pressure vessel of 5 L volume made from stainless steel was fabricated and rated up to 10 bar (abs.). A small-scale vessel was used to ensure higher concentrations of decomposed by-products within the aged gas mixture. The vessel was fitted with a linear actuator that enables adjustment of test electrode gap under pressure. Spherical stainless steel

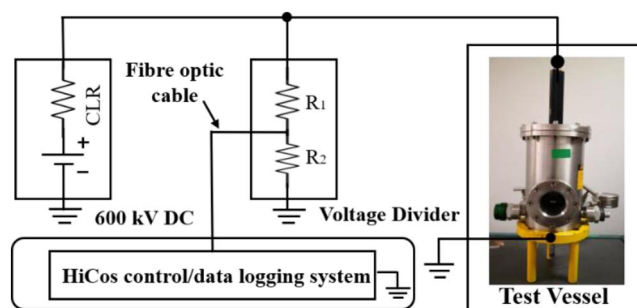


FIGURE 1 Experimental setup

electrodes of 5.8 mm diameters with a measured average surface roughness (R_a) of $\sim 0.2 \mu m$ were used for the experiments. A fixed gap of 1 mm and a representative pressure of 7.2 bar were adopted in this work to mimic the test conditions as found in accelerators for the spark gaps.

Prior to gas filling, the test electrodes and vessel were cleaned with acetone and the hoses were vacuumed below 1 mbar. The test vessel was first filled with dry CO_2 above atmospheric pressure and left for a period of time to absorb any residual moisture within the vessel. The vessel is then vacuumed again below 1 mbar before filling with the test candidate.

For SF_6 , the gas was filled directly from a commercial gas bottle with a gas purity of 100%. In the case of filling the 20% $C_3F_7CN/80\%$ CO_2 gas mixture, the manometric method was adopted [11]. C_3F_7CN gas was first filled to its partial pressure before slowly adding CO_2 gas to attain the desired test pressure for the mixture. A plug-in digital gauge was used to verify the analogue gauge reading at each filling stage.

The gas mixture was left to naturally become a homogeneously mix over a period of 36 h. A WIKA GA11 alternative gas analyser was used to measure and confirm the concentration of the gas mixture prior to testing. The analyser was calibrated to measure 15%–30% concentration of C_3F_7CN with a deviation of $\pm 0.3\%$ with functions of detecting humidity ($\pm 2^\circ C$) and oxygen contents ($\pm 0.3\%$). The liquefaction temperature of 20% $C_3F_7CN/80\%$ CO_2 mixture was calculated to be $1.8^\circ C$ under 7.2 bar (abs.), which is sufficient for retro-fill applications as accelerators typically operate under room temperature for indoor environments.

2.2 | Test circuit and experimental method

A high voltage DC generator rated at 600 kV/200 mA with a ripple factor of less than 3% was used for testing. A current limiting resistor rated at 800 kV/80 Ω was connected to the DC generator output to protect the equipment during breakdowns. The breakdown voltage was measured through a resistive voltage divider (GMR 1200 M Ω /600 kV) with a ratio of 1:1055. A HiCos control system was used to control the DC system via fibre optics and record the breakdown data for analysis after each test. A continuous rising voltage of 2 kV/s

TABLE 1 A summary of gas by-products and electrode surface analysis techniques

Electrodes	Sample	Technique
1000 breakdowns for 20% C ₃ F ₇ CN/80% CO ₂	Aged gas	GC-MS
	Electrode surface	XPS - THERMO
500 breakdowns for both 20% C ₃ F ₇ CN/80% CO ₂ and SF ₆	Electrode surface	XPS - Scienta Omicron
		XRD
		Surface roughness

ramp rate was used with a time interval of two minutes between consecutive breakdowns.

2.3 | Gas analysis and material characterisation

Table 1 summarises the gas by-products and electrode surface analyses conducted in this work.

2.3.1 | Gas chromatography mass spectrometry (GC-MS) analysis

Gas samples were collected 36 h after the final breakdown occurrence and analysed at LTM laboratory (ARC-GE) in Villeurbanne, France. Two gas samples were collected into two separate 1 kg storage cylinders. Each sample was analysed using Agilent GC 7890A coupled to a 5975 inert mass selective detector (MSD) spectrometer. The capillary separation column was Rtx-200 from Restek and helium was used as a carrier gas with positive electron ionisation. The toxicity of the aged 20% C₃F₇CN/80% CO₂ mixture was estimated according to T&D Europe technical guidance for validating the performance and safe use of SF₆ alternatives in electrical equipment [12]. For gas mixtures, the globally harmonised system (GHS) [13] introduced the following method for calculating the acute toxicity estimate (ATE):

$$\frac{100}{ATE_{mix}} = \sum_n \frac{C_i}{ATE_i} \quad (1)$$

where C_i is the mole fraction of gas component i ($i = 1, 2, n$ components), ATE_i is the acute toxicity estimate of ingredient i , ATE_{mix} is the acute toxicity of the gas mixture.

2.3.2 | XPS analysis

Electrodes after 1000 breakdowns using a 20% C₃F₇CN/80% CO₂ gas mixture were analysed using a THERMO K α XPS instrument, whilst the electrodes after 500 breakdowns for both SF₆ and 20% C₃F₇CN/80% CO₂ were analysed using Scienta Omicron ESCA2SR XPS. Both systems use an Al K-alpha monochromatic X-ray source with a characteristic energy of 1486.7 eV. CasaXPS software was used to analyse the data.

2.3.3 | XRD analysis

A 3 kW multi-purpose Rigaku SmartLab XRD system with Cu K-alpha radiation was used to identify the chemical composition of the compounds formed on the electrode surface that sustained 500 breakdowns. The scan speed of the system was 0.025° per second. MDI Jade software was subsequently used for the data analysis.

2.3.4 | Surface roughness

An Etamic W5 surface roughness tester was used to measure the electrodes before and after the experiment to determine the extent of the surface damage after extensive breakdowns tested for SF₆ and 20% C₃F₇CN/80% CO₂ gas mixture. The probe was set to measure 1.5 mm distance with 0.15 mm/s speed along the electrode surface. The average value from three sets of measurements was recorded for the clean and aged electrodes.

3 | RESULTS AND ANALYSIS

3.1 | Breakdown characteristics

Figure 2 shows the plot of 1000 DC breakdowns of the 20% C₃F₇CN/80% CO₂ mixture. A sharp decrease in breakdown voltage was observed within the first 200 breakdowns which stabilised for the remaining 800 breakdowns depicting a long L-shaped curve. The average breakdown voltage for groups of 20 data points in the first 200 breakdowns ranges from 35 kV down to 20 kV. Note that the 1000 breakdowns were carried out over 3 days with about 8–11 h stoppage at the end of each day. However, the breakdown characteristic of the gas mixture was consistent and did not demonstrate any sign of dielectric recovery. In Figure 3, the breakdown characteristic of SF₆ remained fairly consistent with an average breakdown voltage of 42 kV. In the case of the 20% C₃F₇CN/80% CO₂ mixture, a similar breakdown characteristic as shown in Figure 2 was observed with a sharp decrease in the breakdown performance after the first 100 breakdowns before it stabilised around 24 kV. The axial misalignment is inevitable due to multiple connecting components used within the pressure vessel to set up the test configuration. This is likely to have an effect on the breakdown voltage for a short 1 mm gap, which could have

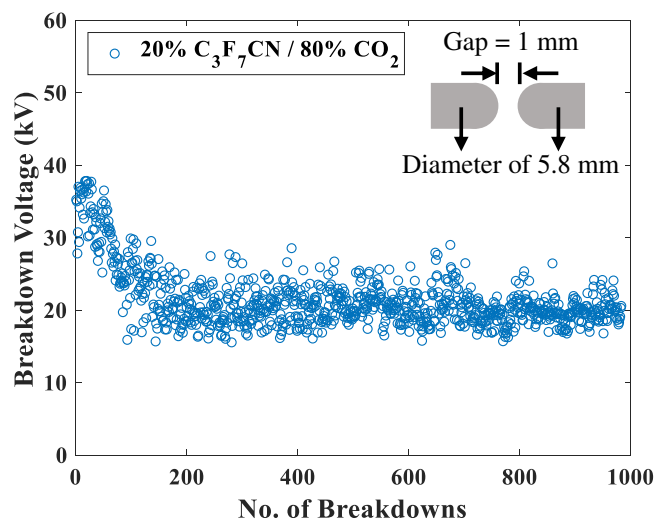


FIGURE 2 Negative DC breakdown characteristic of 20% C_3F_7CN /80% CO_2 gas mixture after 1000 breakdowns under 7.2 bar (abs.)

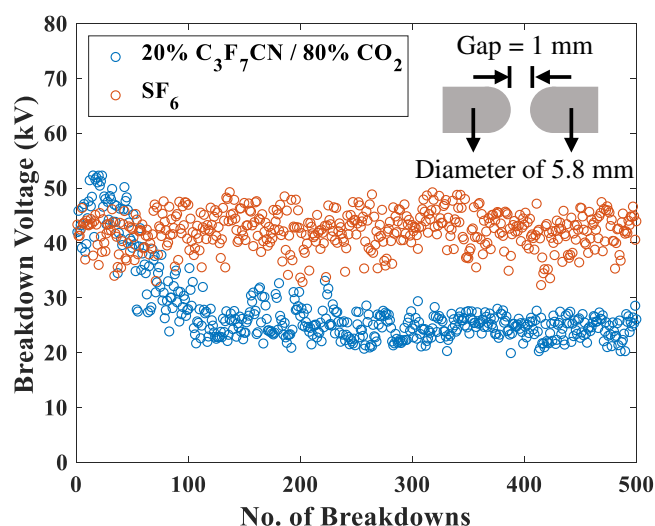


FIGURE 3 Comparison of negative DC breakdown characteristics for both 20% C_3F_7CN /80% CO_2 gas mixture and SF_6 gas after 500 breakdowns under 7.2 bar (abs.)

resulted in the difference between the initial breakdown voltages shown in Figures 2 and 3 for the 20% C_3F_7CN /80% CO_2 gas mixture.

It was clear that comparable breakdown trend could be obtained for the 20% C_3F_7CN /80% CO_2 mixture, whilst SF_6 did not demonstrate any sign of reduced breakdown performance. Table 2 shows two sets of decomposed gas mixtures after the ageing test. The total by-product detected after GC-MS analysis is around 0.017% and is not expected to impact the performance of the gas mixture. Thus, the reduced breakdown strength of the gas mixture is unlikely to be due to the degradation of the gas mixture. Experimental results indicate that the 20% C_3F_7CN /80% CO_2 mixture could be more sensitive to change in electrode surface roughness and field uniformity which will be discussed further in Sections 3.3.1–3.3.4.

3.2 | Gas decomposition analysis

3.2.1 | GC-MS analysis on 20% C_3F_7CN /80% CO_2

Table 2 shows the chemical compositions of by-products detected in the gas mixture from two separate gas samples collected after 1000 DC breakdowns for a 20% C_3F_7CN /80% CO_2 mixture. The overall composition of C_3F_7CN / CO_2 was approximately 99.7% for both samples. The total amount of by-products measured was less than 170 ppm (0.017%). CO was present in both collections with about 100 ppm concentration. Besides CO, the only detected compound with higher ppm (0.06%) is CF_3-CF_2-CN , which is a linear isomer that exists in the commercial C_3F_7CN gas supplied and not a by-product of C_3F_7CN gas degradation. An air impurity of 0.24% was detected and this could be due to accidental air ingress that could have occurred at either gas sample collection and handling or during the GC-MS analysis. Among the detected by-products, the concentration of CO is the highest as reported in [9] and CN-CN has the lowest ppm (0.26 ppm) detected.

3.2.2 | Toxicity estimation of 20% C_3F_7CN /80% CO_2 after 1000 breakdowns

Table 3 provides the known $LC_{50,4h}$ of gas components identified using GC-MS. The estimated $LC_{50,4h}$ values of the aged 20% C_3F_7CN /80% CO_2 mixture after 1000 breakdowns for the first and second sample collections were calculated to be 54,660 and 54,459 ppm respectively. These values are well above the inhalation hazard threshold for category 4 ($2500 < ATE \leq 20,000$) specified in [13]. Note that the cyanide groups of CF_3-CN , $CN-CN$ and $CF_2=CF-CN$ were identified with concentrations summing up to 0.08%. Despite the extremely low overall concentration of cyanide groups, personal protective equipments such as eye shield, face shield gloves, and the respirator are recommended for handling the electrically aged 20% C_3F_7CN /80% CO_2 mixture as specified in the material safety datasheet for C_3F_7CN [6].

3.3 | Electrode surface analysis

3.3.1 | XPS analysis of electrodes after 1000 breakdowns in 20% C_3F_7CN /80% CO_2

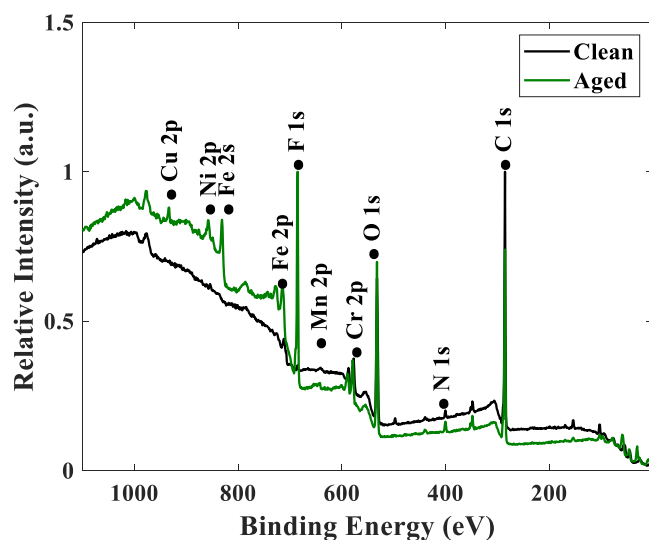
XPS analysis on the electrode surface was conducted to examine the chemical composition on the electrode surface. Table 3 shows the detected elements and chemical compositions (At. %) formed on the surface of the electrodes. Figure 4 shows the survey spectra of new and aged electrode areas after 1000 breakdowns. An increasing amount of Fe 2p and Ni 2p indicates the formation of metal compounds that are different from the clean electrode. The metallic ratio of Cr and Fe decreased from 1.25 to 0.6, which suggests the formation of Fe

TABLE 2 GC-MS results LC₅₀ of aged 20% C₃F₇CN/80% CO₂ after 1000 breakdowns [9, 14, 15]

Substances	1 st collection (ppm)	2 nd collection (ppm)	CAS no	LC ₅₀ (ppm)	Ref of LC ₅₀
CO ₂	800,300	799,400	124-38-9	470,000	[14]
C ₃ F ₇ CN	196,500	197,600	42532-60-5	12,000	[15]
CO	<100	<100	630-08-0	1807	[9]
CF ₄	6.89	6.22	75-73-0	-	-
C ₂ F ₆	10.73	11.19	76-16-4	>500,000	-
C ₃ F ₈	0.80	1.72	76-19-7	-	-
CF ₃ -CF ₂ -CF ₂ -CN	674.5	570	375-00-8	6000	-
CF ₃ -CF ₂ -CN	1.31	1.15	442-04-08	2730	[15]
CF ₂ =CF ₂	1.55	2.00	116-14-3	40,000	[9]
CF ₂ =CF-CF ₃	5.57	2.94	116-15-4	3060	[15]
CF ₃ -CN	5.44	4.44	353-85-5	250	[15]
CN-CN	0.26	0.38	460-19-5	175	[15]
CF ₂ =CF-CN	2.38	2.33	433-43-2	100	-

TABLE 3 The atomic percentage of the main elements identified on the clean electrode and aged electrode after 1000 breakdowns in the 20% C₃F₇CN/80% CO₂ gas mixture

Element	At. %	
	Clean electrode	Aged electrode
O 1s	15.9	19.7
C 1s	77.6	45.4
Fe 2p	0.8	4.3
Cr 2p	1.0	2.6
F 1s	0.2	21.8
Ni 2p	<0.1	1.0
N 1s	1.1	1.9

**FIGURE 4** Survey spectra of the clean electrode and aged electrode after 1000 breakdowns in the 20% C₃F₇CN/80% CO₂ mixture

compound on the surface of the electrode. Another observation is the large increase in the fluorine content found on the electrode surface before and after the test.

Figure 5 shows the high-resolution spectra of Fe 2p and F 1s identified on the electrode surface after 1000 breakdowns in 20% C₃F₇CN/80% CO₂. Doublet peaks at 711.4 and 714.7 eV indicate the formation of Fe-O and Fe-F, respectively [16]. Two peaks at 685.1 and 688.48 eV were identified from the F 1s spectra. The peak at 685.0 eV was reported to be F 1s in FeF₃ [16] and the 688.3 eV corresponds to the F 1s peak of SF₆ attached on the rubidium monolayer. The bonding energy of S-F in SF₆ is 3.432 eV/atom whereas the smallest bond energy of C₃F₇CN is 3.813 eV/atom [17]. Therefore, the lower energy peak in Figure 5b at 688.5 eV could be a similar bond as F in C₃F₇CN.

3.3.2 | XPS analysis on electrodes after 500 breakdowns

Figure 6 shows the survey spectra of the new and aged electrodes after 500 breakdowns conducted for SF₆ and 20% C₃F₇CN/80% CO₂ respectively. Table 4 shows the atomic percentage of the elements calculated from the survey spectra. The trend of element contents for the 20% C₃F₇CN/80% CO₂ gas mixture tested over 1000 and 500 breakdowns was comparable. Increased contents of O, C, Fe, Cr, N and F can be found on electrodes that sustained 1000 breakdowns. The higher content of by-products such as fluorides and oxides could be attributed to the higher number of breakdowns leading to further formation of deposition.

As shown in Table 4, the O 1s peaks were identified in all sample electrodes and the atomic percentage reduced slightly in both aged electrodes. In the case of Fe 2p, there was a much higher atomic percentage in the aged electrodes, which indicates that Fe on the electrode surface became part of the

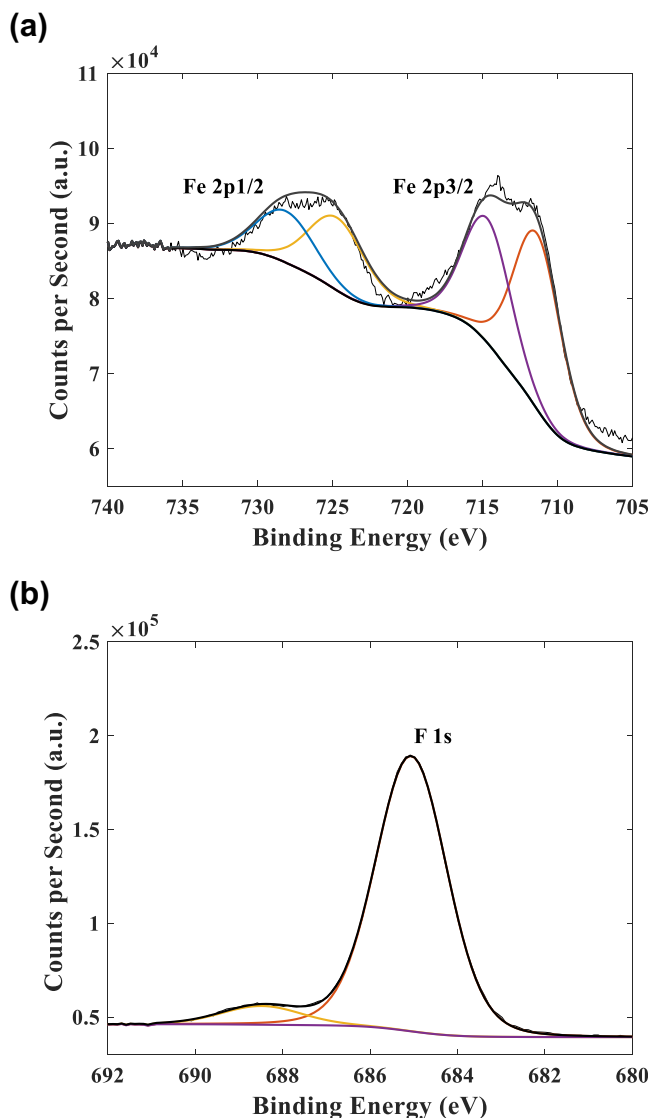


FIGURE 5 XPS analysis of (a) Fe 2p and (b) F 1s on the aged electrode after 1000 breakdowns tested with 20% $\text{C}_3\text{F}_7\text{CN}/80\%$ CO_2 gas mixture. XPS, X-ray photoelectron spectroscopy

solid precipitations. Similar behaviour was also observed for Cr and Ni.

Change in the relative percentage of alloying elements (Fe, Cr and Ni) in stainless steel indicates a characteristic change in the alloy's composition in the vicinity of the electrode surface. The increasing amount of Cr near the surface meant there is a depletion of Cr in the subsurface area, which leads to a loss of stainless steel characteristic. After the electrical ageing experiment using a 20% $\text{C}_3\text{F}_7\text{CN}/80\%$ CO_2 mixture, the metallic ratio of Cr to Fe increased from 0.16 to 0.36. However, for the SF_6 aged electrode, the ratio of Cr and Fe increased from 0.16 to 1.18. The change in the Cr/Fe ratio indicates that Cr has a higher reactivity towards SF_6 when compared to the $\text{C}_3\text{F}_7\text{CN}/\text{CO}_2$ mixture after extensive number of breakdowns. The increased concentration of F 1s was also found in the aged electrodes for SF_6 and $\text{C}_3\text{F}_7\text{CN}/\text{CO}_2$ ageing experiments. Evidence strongly

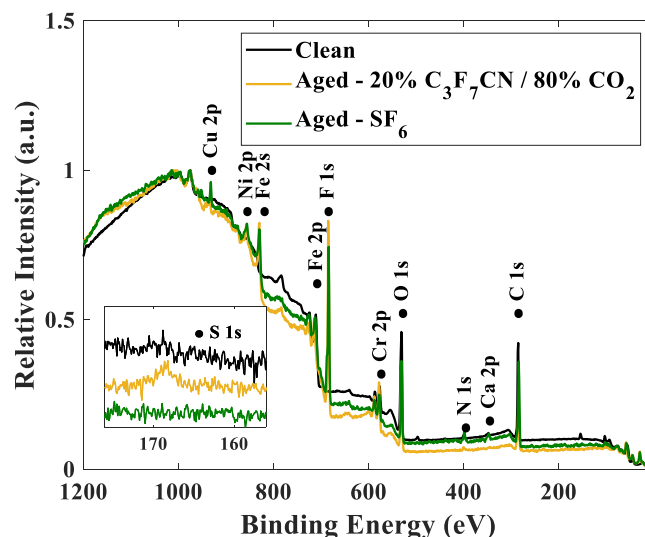


FIGURE 6 Survey spectra of the clean electrode and electrodes that sustained 500 breakdowns for SF_6 and 20% $\text{C}_3\text{F}_7\text{CN}/80\%$ CO_2 gas mixture

suggests that there is formation of fluoride during the repetitive breakdowns which was deposited on the aged electrode surface. The peak corresponding to sulphur in the SF_6 aged electrode indicates the formation of sulphide (see inset of Figure 6). A small percentage of N was identified in the $\text{C}_3\text{F}_7\text{CN}/\text{CO}_2$ aged electrode, which may be attributed to the reaction associated with the N element that is present in $\text{C}_3\text{F}_7\text{CN}$.

Figure 7a,b shows Fe 2p peaks of electrodes collected after ageing experiments with SF_6 and 20% $\text{C}_3\text{F}_7\text{CN}/80\%$ CO_2 respectively. The duplets in Figure 7a reveal three different states of Fe with the peak positions of Fe 2p_{2/3} being 710.81 eV, 713.61 and 715.20 eV respectively. The peak between 710.2 and 716.8 eV corresponds to Fe^{3+} [18]. The peak at 710.81 eV is identified as Fe_2O_3 which may be due to the pre-existing passivated layer on the surface of stainless steel electrodes [19]. Peaks at 713.61 and 715.2 eV indicate the bonding of Fe^{3+} with F or S [20, 21]. In Figure 7b, the peak positions of Fe 2p_{2/3} are at 710.42 and 713.69 eV. As $\text{C}_3\text{F}_7\text{CN}$ contains the F element, the peak at 713.69 eV indicates the presence of Fe-F bonding. A similar peak position (713.61 eV) in Figure 7a was also identified as the Fe-F bonding. However, the other peak at 715.2 eV is due to the Fe-S bonding. Figure 7c,d illustrate the F 1s peaks of both electrodes. The binding energy of metal fluorides lies between 684 and 685.5 eV. The peak at 684.85 eV in Figure 7c is associated with Fe-F bonding [22]. The peak at the lower binding energy (683.33 eV) could be the bonding of F with alloy elements such as Cr and Ni, which are naturally present in stainless steel materials. In Figure 7d, peaks at 684.27 and 683.36 eV are at similar positions as shown in Figure 7c, which could be Fe-F bonding and alloying element-F bonding. As shown in Figure 5, the F 1s peak of the electrode surface that

TABLE 4 The atomic percentage of the main elements in the clean electrode and aged electrodes after 500 breakdowns for both SF₆ and 20% C₃F₇CN/80% CO₂ gas mixture

Element	At. % of clean electrode	At. % of aged electrode by SF ₆	At. % of aged electrode by 20% C ₃ F ₇ CN/80% CO ₂
O 1s	22.50	8.85	6.75
C 1s	45.40	16.15	22.45
Fe 2p	7.67	19.28	33.25
Cr 2p	1.21	22.77	12.04
F 1s	-	9.73	8.04
Ni 2p	-	22.61	14.20
N 1s	0.95	0.62	3.27

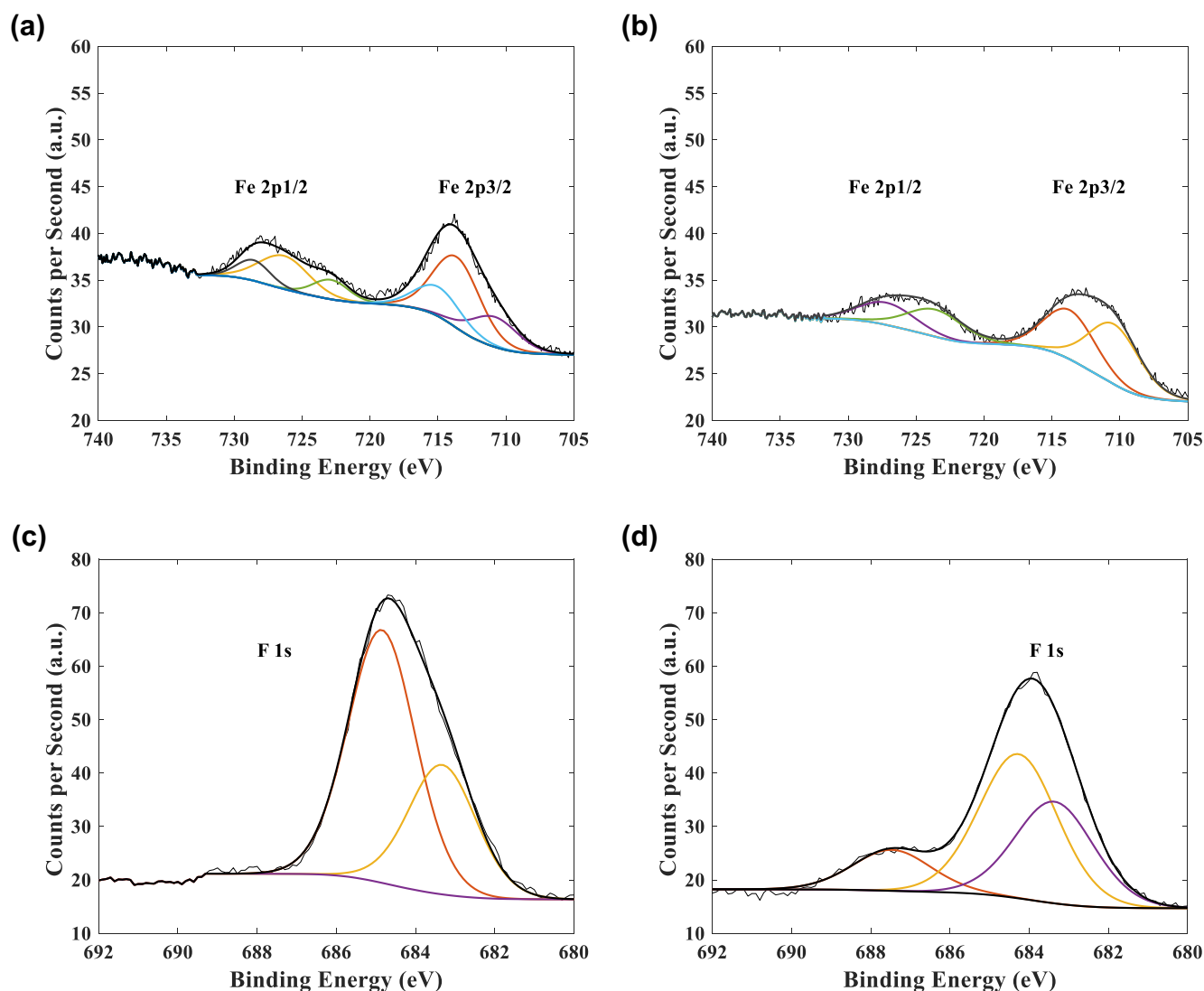


FIGURE 7 XPS analysis of electrode surface after 500 breakdowns for (a) Fe 2p spectra with SF₆; (b) Fe 2p spectra for 20% C₃F₇CN/80% CO₂; (c) F 1s spectra for SF₆; and (d) F 1s spectra for 20% C₃F₇CN/80% CO₂. XPS, X-ray photoelectron spectroscopy

sustained 1000 breakdowns only has one component in this major peak. The different number of components (chemical states) in composition is due to the incomplete fluorination during the experiment of 500 breakdowns. Furthermore,

the peak around 687 eV in Figure 7d cannot be identified in the NIST XPS database. This may be due to a similar bonding of F with other elements in C₃F₇CN as discussed in Section 3.3.1.

3.3.3 | XRD analysis of electrodes after 500 breakdowns

Figure 8 shows the X-ray diffraction patterns of the aged electrodes. The powder diffraction file (PDF) was used as the peak reference. The major peaks of FeF_3 (PDF #85-0481), C (PDF #50-1083), austenite (PDF#23-0298) and martensite (PDF# 44-1292) were identified from both gas media. A change in the relative intensity of austenite and martensite in these two cases indicates a varying characteristic phase change of stainless steel due to the test gas. This is in agreement with the discussion on the change in the composition of alloying elements as per XPS analysis (depicted in Table 4).

The surface of two aged electrodes for both SF_6 and $\text{C}_3\text{F}_7\text{CN}/\text{CO}_2$ contains FeF_3 (23.91° , 33.53° , 40.36° , 49.01° , 82.55° , 86.97°) as shown in Figure 8. This provides good correlation with XPS analysis of Fe-F bonding shown in Figure 7. The extra peak at 54.13° in the pattern of the SF_6 aged electrode shows the characteristic peak of FeS (PDF #76-0962) which agrees with the analysis of Fe-S bonding shown in Figure 7b. Further evidence can be seen in the additional peak of S (inset of Figure 6).

XRD and XPS analyses on the electrode surface tested for SF_6 show that sulphides and fluorides were formed on the stainless steel electrode surface after 500 breakdowns. For the electrode tested with the 20% $\text{C}_3\text{F}_7\text{CN}/80\% \text{CO}_2$ gas mixture, mainly fluorides were identified on the surface of the electrode. The content of alloy elements, Fe, Cr and Ni on the electrode surface also increased after the extensive number of breakdowns. Fe was found to be more reactive than Cr in the ageing test for $\text{C}_3\text{F}_7\text{CN}/\text{CO}_2$, whereas Cr was shown to be more reactive with SF_6 . This variation demonstrates that there will be a characteristic change in the electrode material depending on the test gas used.

3.3.4 | Surface roughness measurements

Table 5 gives the measurements of the electrode surface roughness before and after 500 breakdowns for both 20% $\text{C}_3\text{F}_7\text{CN}/80\% \text{CO}_2$ mixture and SF_6 . The maximum surface roughness (R_z) and R_a values [23] for both electrodes increased by about 10 times after the extensive number of DC breakdowns. The surface of the electrode tested with the 20% $\text{C}_3\text{F}_7\text{CN}/80\% \text{CO}_2$ gas mixture has comparatively higher R_a and R_z values than their SF_6 counterparts, which indicates that the electrode sustained more surface damage than the electrode tested with SF_6 despite the comparatively lower breakdown voltages for the last 400 breakdowns.

It appears that the 20% $\text{C}_3\text{F}_7\text{CN}/80\% \text{CO}_2$ mixture is more sensitive to the change in surface roughness due to accumulative breakdown damage on the electrodes. The swarm data of $\text{C}_3\text{F}_7\text{CN}$ have also shown that the effective ionisation coefficient increases much slower with increasing electric field than that of SF_6 . The slopes of $\text{C}_3\text{F}_7\text{CN}$ and SF_6 gases are 3.53×10^{-24} and $3.04 \times 10^{-23} \text{ m}^2/\text{Td}$, respectively [24, 25]. This means that less energy is required for to ionise $\text{C}_3\text{F}_7\text{CN}$ than SF_6 .

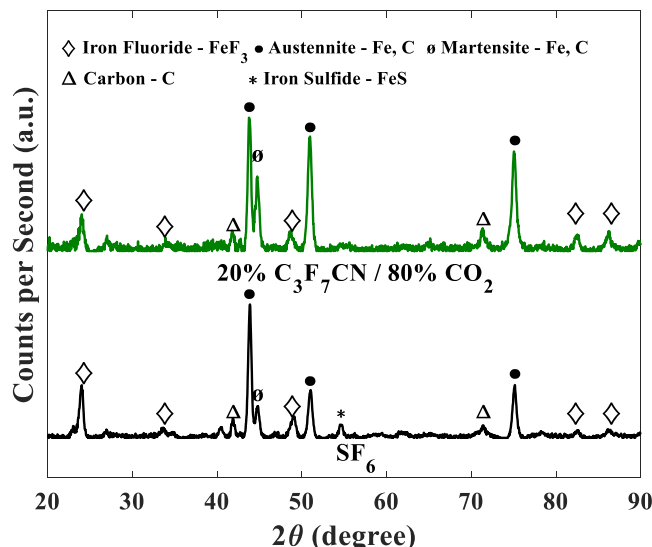


FIGURE 8 XRD analysis of electrode aged electrically for 20% $\text{C}_3\text{F}_7\text{CN}/80\% \text{CO}_2$ (green line) and SF_6 (black line). XRD, X-ray diffraction

TABLE 5 Surface roughness measurements of the electrode surface after 500 breakdowns for both 20% $\text{C}_3\text{F}_7\text{CN}/80\% \text{CO}_2$ gas mixture and SF_6

Gas	Measured electrode	R_a (μm)	R_z (μm)
20% $\text{C}_3\text{F}_7\text{CN}/80\% \text{CO}_2$	Aged	2.98	13.76
	Polished	0.24	1.49
SF_6	Aged	2.22	11.37
	Polished	0.23	1.32

4 | DISCUSSION

This work presents the technical viability of a 20% $\text{C}_3\text{F}_7\text{CN}/80\% \text{CO}_2$ gas mixture as a retro-fill solution for existing SF_6 -designed high voltage accelerators. The liquefaction temperature of the 20% $\text{C}_3\text{F}_7\text{CN}/80\% \text{CO}_2$ gas mixture is 1.8°C under 7.2 bar (abs.), which is acceptable for accelerators since they are used for indoor environments and under room temperature. To mitigate the liquefaction issue, the gas mixture must be pre-heated and re-circulated after each maintenance regime with appropriate temperature control measures in place. This will ensure that the gas mixture is homogeneously mixed prior to energisation.

The electrical ageing experiment shows a clear drop in breakdown performance within the initial 200 breakdowns. Figure 9 summarises the three potential interactions between the electrode and the gas medium investigated in this study. Chemical interaction includes the decomposition of the gas mixture and formation of metal fluorides and oxides under the negative DC field. GC-MS analysis reports the main gas by-products including CO , CF_4 , C_2F_6 , C_3F_8 and C_3F_6 . The concentration level of by-products will be dependent on the

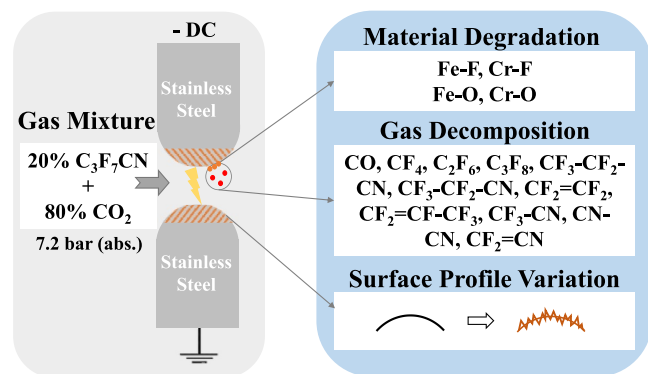


FIGURE 9 Ageing mechanism of 20% C₃F₇CN/80% CO₂ gas mixture

accumulative discharge energy of the entire test series. In this work and for accelerators, the discharge energy is significantly less than typical arc interruption applications. Several highly toxic gaseous by-products, such as CF₃-CN, CN-CN and CF₂=CF-CN, were identified with a total concentration of less than 10 ppm. For a 20% C₃F₇CN/80% CO₂ gas mixture, the toxicity of the two analysed gas samples was well above the inhalation hazard threshold for category 4 [13] and considered to be practically non-toxic. This strongly indicates that the proposed gas mixture can be adopted as a retro-fill solution from a safety aspect for high voltage accelerators.

Metal oxides and fluorides were identified on the surface of electrodes after electrical ageing through XPS and XRD analyses. There is a clear difference in the deposition contents identified on the stainless steel electrode surface between SF₆ and 20% C₃F₇CN/80% CO₂ gas mixture. Oxidation and fluorination of Fe and Cr on the surface during electrical ageing in 20% C₃F₇CN/80% CO₂ gas mixture can lead to the deterioration of mechanical properties and potential material compatibility issue.

For the tested spark gaps, the initial drop in the breakdown voltage of 20% C₃F₇CN/80% CO₂ mixture is mainly due to (i) change in surface roughness after an extensive number of breakdowns and (ii) gas dependent behaviour towards changing surface roughness. It has been reported that a 20% C₃F₇CN/80% CO₂ gas mixture possesses comparatively lower breakdown performance than SF₆ for a non-uniform field while exhibiting comparable performance for quasi and uniform fields [11]. This is further evidence that the gas mixture is more sensitive towards field inhomogeneity than SF₆, especially for highly divergent fields. This results in the initial drop in breakdown performance during transition from a polished surface (R_a of 0.2 μ m) to a rougher surface finish within the first 200 breakdowns. However, as the electrode surface becomes more rough, there is progressively less effect on the breakdown voltage for the final 800 breakdowns. The distance between spark gaps must be widened to account for the initial drop in breakdown performance for any retro-fill application utilising a 20% C₃F₇CN/80% CO₂ mixture.

5 | CONCLUSIONS

Negative DC breakdowns of 20% C₃F₇CN/80% CO₂ gas mixture showed that there is a significant drop in breakdown voltage. Chemical and solid by-product analyses of aged gas and electrode material have shown that a 20% C₃F₇CN/80% CO₂ mixture reacts differently to SF₆ when tested with a stainless steel electrode. The main conclusions of this work are as follows:

- Mixture of 20% C₃F₇CN/80% CO₂ is not as stable as SF₆ with a significant drop in breakdown performance observed within the first 200 breakdowns for the test configuration investigated in this study.
- The formation of solid by-products on the electrode surface leads to corrosion and could potentially cause material compatibility issue within the high voltage accelerator.
- The LC_{50_4h} of the electrically aged mixture is estimated to have an average LC₅₀ well above category 4 of 20,000 ppm specified in [12], indicating that the 20% C₃F₇CN/80% CO₂ mixture analysed is practically non-toxic despite sustaining 1000 DC breakdowns.
- Material characterisation techniques (XPS and XRD) revealed the oxidation and fluorination on the surface of electrodes that sustained breakdowns in the 20% C₃F₇CN/80% CO₂ mixture. The existence of metal sulphide was identified on the electrode tested with SF₆.
- The increase in the atomic percentage of Cr in SF₆ and Fe in 20% C₃F₇CN/80% CO₂ on the surface of the electrode indicates that the electrode surface underwent characteristic changes during the extensive breakdown process.

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