Reduction of Greenhouse Gas Emissions and Consumption at the CMS Experiment

Internal
Technical Evaluation Report

A. Aleksandrov, A. Ball, A. Colaleo, R. Guida,
A. Hristov, S. T. Khan, A. Lanaro, B. Mandelli, G.
Pugliese, A. Zambotti, X. Yang

Background

Perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), sulphur hexafluoride (SF_6), and nitrogen trifluoride (NF_3), referred to as "fluorinated greenhouse gases (F-GHG)", have been identified as potential global-warming gases because of their characteristics of strong infrared (IR) absorption and very long atmospheric lifetimes.
In 2014, the European Commission adopted a new regulation [1] that defines a new roadmap aiming at a reduction of non-CO_2 emissions by at least 60% compared with those in 2005, by 2030. F-GHG emissions were estimated at 90 million tonnes (Mt) of CO_2 equivalent in 2005, and are expected to increase to 104 Mt by 2030. A 60% reduction would mean a reduction to approximately 35 Mt of CO_2 equivalent by 2030. Moreover, the new regulation limits the maximum quantity of F-gases that can be distributed in the EU-market to 21% of the 2015 sales by 2030. This reduction might lead to cost escalation and limited availability.

Following the February 2015 memo issued by the then Director of Research, CMS started to examine ways of reducing CO_2 equivalent emissions, with an aim of reducing by 80% (compared with 2011 emissions) for the start of Run 4 [2]. This target has provoked work in several areas, but is likely to prove overly-ambitious, as will be explained below.

1. Fluorinated greenhouse gases in use in CMS

Two of the four gas detectors systems constituting the CMS Muon system use fluorinated gases: the Cathode Strip Chamber (CSC) and the Resistive Plate Chamber (RPC) systems. The Drift Tube (DT) and Gas Electron Multiplier (GEM) systems use Ar+CO_2 gas mixtures.
The CSC system uses an Ar (40%) + CO_2 (50%) + CF_4 (10%) gas mixture. The RPC system uses a $C_2H_2F_4$ (95.2%) + iC_4H_{10} (4.5%) + SF_6 (0.3%) gas mixture.
The F-GHG used by CSCs and RPCs, and their global warming impact [3] are summarized in Table 1.1. The presence of these specific gases in the CSC and RPC gas mixtures ensures both operation stability and detector longevity. CF_4 has three properties of importance to detector operation: first, it prevents detector aging; second, it increases electron drift velocity (important for rapid and unambiguous tagging of the bunch crossing with which a muon track is associated); and third, as a quenching agent it improves the stability of CSC operation.

Species	Lifetime (years)	GWP 100y	Mass (g/mol)
CF_4	50,000	6,500	~88
$C_2H_2F_4$	10.6	1,300	~102
SF_6	3,200	23,900	~144

Table 1.1 Lifetime in atmosphere, Global Warming Potential (GWP) and Mass of GHG contained in CMS CSC and RPC detector gas mixtures. Source: [3]

In RPCs, $C_2H_2F_4$ operates as an efficient photon quencher, while SF_6 is a strongly electronegative gas; both components stabilize RPC operation during the avalanche process.

2. CSC and RPC gas system design, and gas consumption and emission in Run 1 and Run 2

Both CSC and RPC gas systems are closed-loop systems with recirculation and purification operating with a 10-12% fresh gas replenishment rate (Run 2 figures). **The gas recirculation reduces CMS GHG consumption by ~90% of that with an open gas system.**

The CSC total gas system volume is 70 m^3. The nominal gas mixture flow is $6m^3/h$ and the 10% replenishment flow is 650 l/h (2017-18). In the CSC gas system, the 10% extracted gas is sent through a CF_4 recovery and reinjection plant before it is vented to air. Including the CF_4 recovery system, which has operated since 2012 with an average efficiency of 50% during Run 2, the F-GHG total emission from CSCs is presently 5% of the initial (~600 l/h) CF_4 gas flow, namely ~30 l/h. For CSC, the gas recirculation and CF_4 recovery systems thus reduce system GHG consumption by an additional 50%. The fraction of gas mixture which escapes the system because of micro leaks in the chambers is rather small (<1%) and stable over time, since the CSC is a rather hermetic system, and is currently (end of Run 2) about 50 l/h of which only 5 l/h is CF_4.

The RPC total gas system volume is 13 m^3. The nominal gas mixture flow is 9 m^3/h and the 12% replenishment flow is ~1100 l/h (2017-18). The RPC gas system is not as hermetic as the CSC system. A few chambers, equivalent to ~6% of the total system, have developed leaks over time, most originating from the rupture of fragile polyethylene gas pipes and junctions, and possibly caused by pressure instabilities in the ventilation system of the CMS underground cavern. Because of the sizeable leak rate, which is presently (end of Run 2) ~1000 l/h and balances the 12% fraction of replenishment gas, there is no measurable gas flow at the system exhaust. A campaign of leak repairs, scheduled in LS2, should improve overall detector hermeticity and establish an exhaust stream.

Figure 2.1 shows a diagram of the CSC and RPC gas system specification and operation.

F-GHG emission in CMS is largely dominated by the RPC system. During Run 1 CSCs were responsible for ~65 l/h of CF_4 emission whereas RPCs emitted ~600 l/h of $C_2H_2F_4$ and SF_6. In Run 2, CSCs have reduced their CF_4 emission to ~35 l/h, thanks to the CF_4 recuperation, and RPCs have increased their GHG emission to ~1000 l/h, because of the increased mixture flow to cope with the increased instantaneous luminosity, and the increased number of leaky chambers. Table 2.1 summarizes the F-GHG emissions at the end of Run 2 (2018) and their CO_2 equivalent masses.
The average F-GHG emission at CMS, in one day of Run 2, is thus ~160 t of CO_2-eq. This is equivalent to the amount of CO_2 emitted by ~4,500 2-liter car engines constantly idling 24h a day.

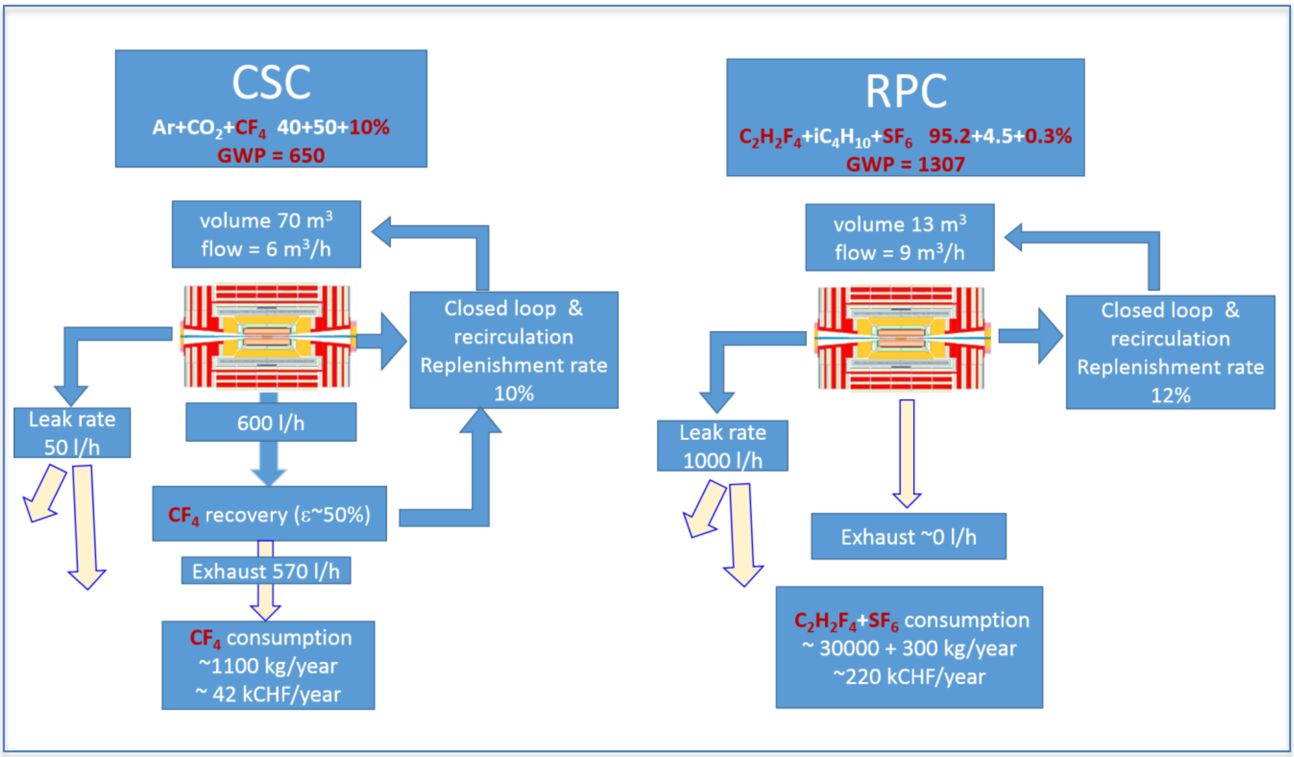


Fig. 2.1 Flow diagram of the CSC (left) and RPC (right) gas systems of CMS. Indicated flow rates and consumption figures are from the 2018 (Run 2) LHC running.

Gas consumption in Run 2 has increased compared to Run 1 because of the increased leak rate of RPCs but also because additional muon chambers were added during LS1 (2013-14) to the CSC system (ME4/2) leading to a 15% system volume increase, and to the RPC endcap (RE4/2) leading to a 5% system volume increase.

Gas	Volume (l/h)	CO_2-eq (kg/h)	Weight (kg/y)	CO_2-eq (t/y)
CF_4	35	817	1100	7,150
$C_2H_2F_4$	1000	5,410	30,000	39,000
SF_6	3.2	450	300	7,170
Total		6,677		53,320

Table 2.1 F-GHG emissions in CMS at the end of Run 2 (2018) and their CO_2 equivalent masses.

The F-gas consumption averaged over 9 months/year of LHC operation in Run 2 was ~115 kg/day of which 110 kg/day for the $C_2H_2F_4$ + SF_6 to the RPCs and ~4 kg/day for the CF_4 to the CSCs. Table 2.2 summarizes the annual consumptions since the start of Run 1.

Consumption/year	CF_4 (CSC)	$C_2H_2F_4$+SF_6 (RPC)
Run1 (2012)	2,800 Kg	29,000 + 250 Kg
2015	2,200 Kg	25,700 + 300 Kg
2016	2,000 Kg	38,500 + 240 Kg
2017	1,200 Kg	38,000 + 300 Kg
2018	1,300 Kg	30,400 + 0 Kg

Table 2.2 F-GHG average annual consumption in CMS in Run 1 and Run 2 estimated from supplier procurements. SF_6 in 2018 profited from previous year carry-over.

The average Run 2 annual emissions and consumptions, considering 9-months of LHC operation per year, are in reasonable agreement with each other (Tab. 2.3).

	Emission	Consumption	Cost/year
CF_4	3 kg/day	4 kg/day	46 kCHF
$C_2H_2F_4$ + SF_6	90 kg/day	110 kg/day	250 kCHF

Table 2.3. F-GHG emissions and consumptions averaged over 2017-2018. One must note that gas storage batteries are usually not completely emptied by the end of a given year of operation.

2.1 RPC leak history, leak repair and system consolidation plan

The RPC detector system equips both the barrel and the endcaps of CMS with a total of 1056 RPC detectors. In 2015 and 2016, a significant increase of the leak rate has been observed, from ~600 l/h (Run 1) to 1200 l/h (early Run 2). Most of the new leaks have developed in the barrel chambers. Specific interventions aimed at improving the operation of the underground ventilation system and the gas system controls have led to a constant improvement and, since 2017, the RPC leak rate has become more stable (Fig. 2.1.1).

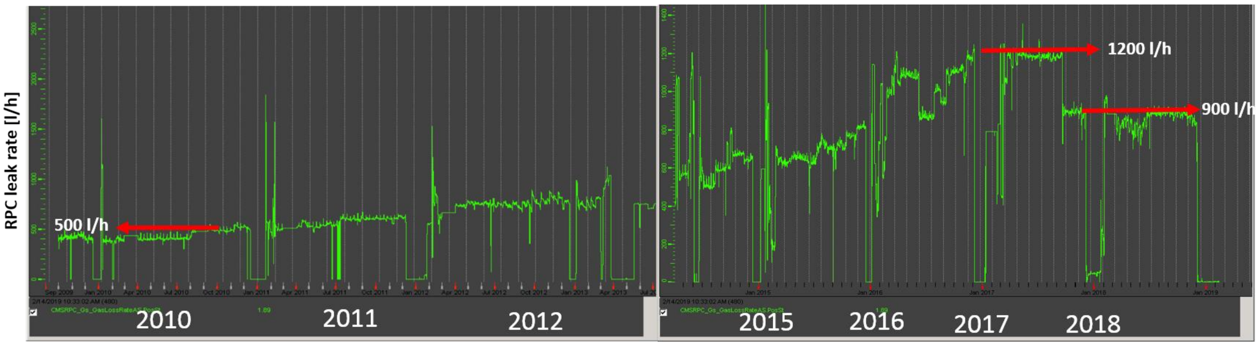


Fig. 2.1.1 Time evolution of the RPC system leak rate in Run 1 (2010-12) and Run 2 (2015-18).

At the start of 2018, the last year of Run 2, 26 leaky barrel RPC, constituting ~5% of the total number of barrel RPCs, were power disabled and their gas turned off, thus reducing the ~1200 l/h total leak rate to ~900 l/h. The disabled RPCs were a subset (26/63) of the leaky barrel chambers and were selected among those located in the outermost barrel stations RB3 and RB4 (Figure 2.1.2 left), to minimize the impact on muon trigger and tracking performance. Indeed this intervention caused no significant degradation to the overall L1 trigger performance during 2018 running, as shown in Figure 2.1.2 right.

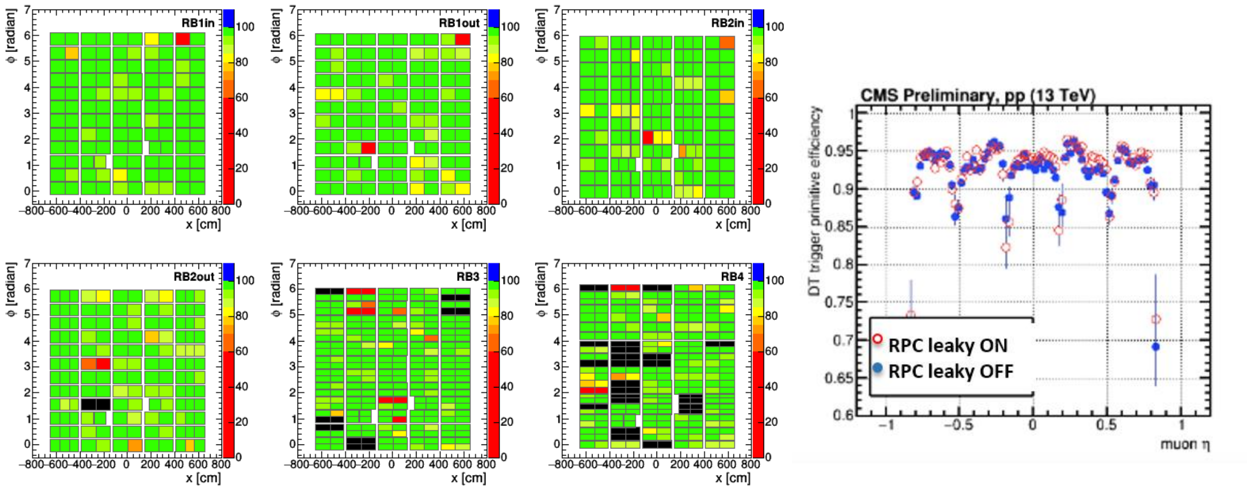


Fig. 2.1.2 Hit occupancy of RPCs in the barrel wheels of CMS (left). The black squares indicate the RPCs affected by gas leaks that were power disabled. CMS barrel trigger primitive efficiency in 2018 LHC running with a fraction of the RPCs disabled (blue dots) (right).

During LS2, the barrel RPCs will be accessible for about 4 month. An extensive leak repairs campaign is foreseen with the goal of repairing 50% of the leaky chambers. The detector repairs requires extended access to the CMS barrel wheels, the partial extraction of chambers and the use of specifically developed intervention techniques that minimize risks to nearby detectors.

To ensure operational stability, at increased gas flows, and to enhance protection against unexpected pressure differentials (from, e.g., abrupt ventilation changes, magnet quench, fire) CMS and PH-DT are implementing a series of gas system consolidation measures. The whole gas system turn-on procedure is being optimized to minimize pressure instabilities during re-filling after shutdown periods and when the gas mixture is changed. For example, at start-up the RPC detector system is typically exposed to over pressure conditions because of the loss of hydrostatic pressure caused by detector leaks. Additional pressure sensors, mounted on dummy chambers located at the same height as the real detectors, and regulation valves will be installed during LS2 to mitigate this effect. Moreover, new distribution modules will be equipped with automatic regulation valves in order to supply a smooth flow at the input of the system.

These measures together will allow recovery of some fraction of the leaky chambers, will halve the GHG emission in the underground cavern from 900 l/h to ~450 l/h, and will make the RPC systems less prone to the development of new leaks. Moreover, it is expected that between 500 l/h and 600 l/h of the 12% refreshed gas will flow to the system exhaust.

3. Estimated gas consumption and costs for Run 3 and beyond

The larger instantaneous and integrated luminosities expected at the LHC (Run 3) and HL-LHC (>Run 4) will necessarily require a revision of the gas systems operation. Detector gas flow and replenishment settings might need to be reconsidered because of higher currents drawn by the detectors and formation of new contaminants causing the pollution rate in the circulated mixture to increase faster. Irradiation tests simulating higher instantaneous luminosity indicate, for example, that the RPC gas mixture flow may need to be increased from 9 m^3/h to 15 m^3/h in 5 years of Run 4 to prevent development of uncontrollable ohmic-current discharges caused by the increased flux of particles. This would increase F-gas consumption (~220 t over 5 years) and operation costs.
CSCs, on the other end, operate in proportional mode and ionization currents remain manageable. The CSC gas flow should therefore remain unchanged provided the CF_4 fraction in the mixture is not significantly reduced from the present 10% (as mentioned earlier, CF_4 has beneficial anti-aging properties).

Concerning gas procurement, further EU legislation to reduce F-GHG emission could lead to cost increases and availability restrictions for F-gases. If consumption cannot be reduced, CMS could consider pre-purchasing and stockpiling the F-gases required to operate the CSC and RPC systems until the end of the LHC program. A provisional estimate of the gas volumes and cost required to operate for five consecutive years is shown in Table 3.1.

Detector	F-gas	Weight/5y (t)	Cost/5y (MCHF)
CSC	CF_4	5.5	0.2
RPC	$C_2H_2F_4$ + SF_6	220	1.8

Table 3.1 F-gas volumes and cost predictions for 5 years running at the LHC during Run 4. Volumes are calculated assuming a gas flow of 13 m^3/h (RPC), averaged over 5 years, and 6 m^3/h (CSC). Cost figures are based on 2019 gas prices.

If no reduction of F-GHG consumption is achieved, CMS will need ~ 2 MCHF to cover gas costs in order to operate CSCs and RPCs over a 5-year period. These measures are contingent on there not being a blanket ban on the use of F-GHG gases.

4. Technical solutions to decrease F-GHG gas consumption in CMS

Closed loop gas systems, like the CSC and RPC systems, limit gas consumption by ~90% provided detectors are sufficiently hermetic.

- ***It is mandatory to reduce the current gas leakage of the RPCs, thus restoring a gas stream at the exhaust, through a dedicated repair***

campaign and the implementation of long-term leak prevention measures (as described in sect. 2.1). In alternative, consider turning off progressively most-leaky chambers (after evaluation of impact on trigger and reconstruction).

Since its implementation, the CSC recuperation system has reduced the CF_4 consumption by ~50%, on average.

- ***Improve operation efficiency of CF_4 gas recovery system to ~70%.***

The implementation of a $C_2H_2F_4$+SF_6 recuperation system for RPC would reduce F-GHG gas consumption by a fraction equal to the efficiency of the recovery-reuse plant.

- ***Design and install a system for high efficiency (>90%) R134a and SF_6 recuperation and reinjection.***

The CSC group has conducted a series of tests on CSC detectors filled with an Ar+CO_2 gas mixture containing reduced percentages of CF_4 gas, namely 5% and 2%. Preliminary results from aging tests at GIF++ indicate CSCs survive the integrated luminosity expected at the HL-LHC with a safety factor 3, with a moderate degradation (<5%) of the performance (efficiency and spatial resolution)

- ***Operate the CSC system with a lower CF_4 fraction, from 10% to 5%, provided performance and longevity are maintained.***

If these actions were achieved in the next years, CMS would gradually reduce the F-GHG consumption and the total emission footprint. By Run 4 it is conceivable to assume a reduction of the F-GHG emissions by as much as ~60% with respect to the Run 1 emissions. The global CMS emission forecast is shown in Table 4.1.

CMS	Run 1 Emissions of GHG [l/h] - CO_2e [t/y]	Run 2 Emissions of GHG [l/h] - CO_2e [t/y]	Run 2 Notes	Run 3 Emissions of GHG [l/h] - CO_2e [t/y]	Run 3 Notes	Run 4 Emissions of GHG [l/h] - CO_2e [t/y]	Run 4 Notes
CSC	65 - 13,000	35 - 7,150	w/ 50% recup. eff.	35 - 7,150		18 - 3,680	reduce CF4 (10%→5%)
				23 - 4,700	w/ 70% recup. eff.	11 - 2,250	w/ 70% recup. eff.
RPC	900 - 41,550	1,000 - 46,170		1,200 - 55,400	Flow +10%	700 - 32,320	Flow +50% & recup.
				630 - 29,000	Disable half leaky RPCs & recup. (?)	430 - 19,860	& Disable half leaky RPCs
Total & vs Run 1	965 - 54,550	1,035 - 53,320 -2%		1,235 - 62,550 +15%	worst	718 - 36,000 -34%	worst
				653 - 33,700 -38%	best	441 - 22,110 -60%	best

Table 4.1 F-GHG global emission history (Run 1, Run 2) and forecast (Run 3, Run 4). The actions indicated in a given grey column are implemented in addition to those in the previous grey column.

A more direct way to reduce F-GHG consumption and emission would be to replace CF_4, R134a and SF_6 with eco-friendly gases. Besides being non-CO_2

emitting (according to the EPA definition), commercially available and affordable, the replacement gases must fulfill the following requirements:

- ensure operational stability of existing CSC and RPC detectors;
- ensure adequate performance for resolution, efficiency and timing;
- must have aging-preventing properties to ensure detector longevity throughout the entire LHC program.

A description of the ongoing R&D will be presented in the Appendix.

4.1 Design of a recuperation system for RPCs and optimization of the CF_4 recuperation system of CSCs.

F-GHG recovery systems have been developed in recent years at CERN for several gaseous detector systems at the LHC experiments: CMS-CSC (CF_4), ATLAS-TGC (nC_5H_{12}), LHCb-RICH1 (C_4F_{10}) and LHCb-RICH2 (CF_4).

The allocation of additional funding over the period 2019-2026, announced by the CERN Environmental Protection Steering board, offers the opportunity to design new generation gas recuperation systems and to consolidate the existing ones. R&D is ongoing for the design of an R134a ($C_2H_2F_4$) recuperation plant [4]. R134a is the most commonly used gas for particle detection at CERN, and thus is the major contributor to F-GHG emission. An early prototype system (Figure 4.1.1) has been tested with a real RPC detector: an R134a recuperation efficiency close to 100% was achieved [4], and the purity of the recuperated gas was comparable to the fresh gas. Further tests are ongoing to investigate the filtering capacity with respect to RPC-specific impurities. The next step will be the design and construction of a module allowing storage and re-use of the recuperated gas. Results with the prototype are encouraging and pave the way for the design of a full size recuperation system for Run 4.

Fig. 4.1.1 First prototype of the R134a recuperation plant successfully tested recently at CERN in the RPC detector system.

Fig. 4.1.2 Overview of the CF_4 recuperation plant installed in the surface gas building (SGX5) of the CMS experiment.

The second most commonly used F-GHG at CERN is CF_4. The CSC recuperation plant for CSC (Figure 4.1.2), which started operation in 2012, has already been mentioned. The concept of CF_4 warm separation by pressure swing on a molecular sieve was considered as a first option, and was preferred to a CF_4 liquefaction system for cost reasons. R&D studies are ongoing to improve the recuperation efficiency, which is presently ~50% on average. In the improved system, the CF_4 will be separated from the recuperated mixture by liquefaction, using N_2 or Argon [5].

5. Perspectives for achieving "zero" emissions: a point-of-use abatement system for PFC and CFC in exhaust streams

CMS has conducted a feasibility study for the implementation of an exhaust management system, so-called "abatement" system, capable of burning F-GHG into harmless compounds with high efficiency, before venting the exhaust stream into the atmosphere. The system operates with a 2-stage "burn-and-wash" method, which is the most commonly used abatement solution in the semiconductor industry. It consists in a thermal gas decomposition followed by wet scrubbing. Figure 5.1 shows a typical flow diagram of a commercial abatement unit. The F-GHG at the inlet are burned inside a controlled combustion chamber (reactor) at high temperatures (between 800-1800 ^oC, depending on the model). The combustion-decomposed gases flow through the cooling and cleaning unit, which also serves as a dust collector. A reservoir collects the circulated water from the wash process, which contains byproduct powder and soluble gases, while the abated gas stream, containing CO_2, water vapor and traces of HF, is vented. A scraper unit removes by-products (mainly SiO_2 powders) generated by the combustion process inside the reactor.

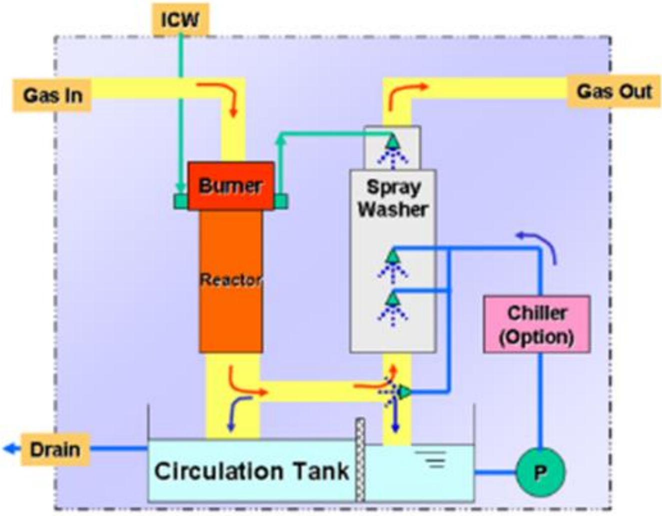


Fig. 5.1 Flow diagram of the abatement process

Two companies were contacted, EDWARDS (UK)[6] and EBARA (Japan) [7], and were provided with CSC and RPC requirements. System specifications included:
a 3-inlet system for

- a non-continuous ~570 l/h (10 SLM) gas mixture flow containing ~30 l/h of CF_4 at 3-300 mbar pressure (*inlet 1*);
- a continuous ~900 l/h (11.7 SLM) flow (RPC estimated exhaust rate in Run 4) containing ~850 l/h of R134a and ~3 l/h of SF_6 gases at 200 mbar pressure (*inlet 2*);
- spare (*inlet 3*).

Requirements are: continuous (24/7) system operation and high abatement efficiency. We have considered the worst-case scenario in which the RPC gas system does not integrate a R134a+SF_6 recuperation and re-use unit.

Ebara G5 system

Edwards ATLAS Etch system

Fig. 5.2 The EBARA G5 [8] and EDWARDS ATLAS [9] waste gas abatement units.

The proposed abatement units are based on the same operation mode and very similar technologies. The declared Destruction Rate Efficiencies are as follow: CF_4: ≥90%, 99% for EDWARDS and EBARA, respectively; SF_6 and R134a: ≥95% for both companies. Figure 5.2 shows the two units proposed, whereas Table 5.1 summarizes some of the system parameters.

	EBARA G5	**EDWARDS ATLAS Etch**
Size (w x d x h)	1200 x 650 x 1900 mm	1300 x 625 x 1870 mm
Weight	~750 kg	~800 kg
Burner (material/T)	Inox/1600 ^{O}C	Ceramic/800 ^{O}C
Consumption	1.7 kW	2.0 kW

Table 5.1 The EBARA G5 [8] and EDWARDS ATLAS [9] abatement unit specifications.

5.1 F-GHG emission reduction performance

Table 5.1.1 summarizes the chemical reactions occurring inside the abatement unit from the thermal decomposition by combustion of the F-GHG of the CSC and RPC detectors. Assuming a conservative abatement efficiency of 90%, the 900 l/h of F-GHG present in the 1470 l/h of gas streams sent to the abatement inlets will be reduced to 90 l/h of F-GHG, which are then vented into the atmosphere. The abatement process would reduce ~130 t of CO_2-eq emissions, equivalent to 30 l/h of CF_4 plus ~853 l/h of R134a+SF_6, to ~13 t per day of CMS operation during Run 4.

This emission reduction is equivalent to turning off ~3,300 of ~3,700 2-liter car engines idling 24h/day.

If the RPC R134a + SF_6 recovery system will operate in Run 4 with a recovery efficiency of 90%, then only ~100l/h, of which 90l/h are the F-GHG, will be sent from the RPC exhaust to the input of the abatement unit.
The overall ~90l/h (from RPC) plus ~30l/h (from CSC) will be abated to ~12l/h of F-GHG exhaust, which corresponds to ~2.9 t of CO_2-eq emitted per day.
This is the same emission as that from ~80 2-liter car engines idling 24h/day.

The abatement system cannot of course treat all gas from CSC and RPC because of the fraction that escapes from leaks in the RPC system and, to lesser extent, in the CSC system. Consequently, there remain a sizeable F-GHG emission due to detector leakage. The losses from the RPC system should however be considerably reduced by the leak repair program that is planned.
Considering the emission forecast shown on Table 4.1, one should expect that in Run 4 the abatement system would further reduce the global emissions to ~37% (worst) and to ~68% (best) of those in Run 1.

The abatement system produces ~15 m³ of wastewater per day containing by-products of the processed gases from the combustion and washing phases. During the CF_4 and $C_2H_2F_4$ combustion processes ~100 mol/h of F_2 are produced that, during the washing phase, will be converted into 109 mol/h, or ~52 kg/day, of HF. Therefore, the ~15 m³/day wastewater will have a ~0.35% HF concentration by volume and small amounts (~0.22 kg/day) of H_2SO_3-H_2SO_4 from the SF_6 combustion. The pH of the solution is ~2, neglecting the effect of S-compounds from SF_6. This wastewater, being highly acidic and toxic, of course cannot be disposed of directly into local watercourses or into the local sewage system. The two alternative options are:

- transfer off-site for treatment and disposal;
- on-site treatment and disposal.

The first option requires the storage of ~15 t of wastewater per day. Storage tanks for the wastewater must be able to hold the large volumes accumulated over several days, before periodic transportation to a disposal plant. A preliminary cost

abatement phase	Chemical reaction
Burning phase	$CF_4 + O_2 \rightarrow CO_2 + 2\ F_2$
	$SF_6 + O_2 \rightarrow SO_2 + 3\ F_2$
	$2\ C_2H_2F_4 + 5\ O_2 \rightarrow 4\ CO_2 + 2\ H_2O + 4\ F_2$
Washer phase	$2\ F_2 + 2\ H_2O \rightarrow 4\ HF + O_2$
	$SO_2 + H_2O \rightarrow H_2SO_3$
	$SO_3 + H_2O \rightarrow H_2SO_4$

Table 5.1.1 Most relevant chemical reactions occurring during the waste-gas abatement process.

estimate for transporting and disposing 500 kg of RPC waste gas, equivalent to ~1 week of operation, is ~17 kCHF. We discuss the second option in chapter 6.

5.2 Abatement system maintenance and operations costs

Some infrastructure (storage dewars and tanks, extraction pumps) is required, as well as auxiliary utilities and services for operation of the system, including fuel, soft water, cooling water (15 °C), O_2, N_2, dry air, service power. Table 5.2.1 provides a summary of the service requirements and an estimate of the monthly system operations cost for both the Ebara and Edwards systems.

With the adoption of an RPC recuperation system the running costs are expected to decrease by almost a factor of two because less O_2 is consumed during the combustion phase, since O_2 constitutes a substantial fraction to the operations cost.

Both companies have provided an estimation of the system yearly maintenance costs. EDWARDS has indicated in ~10 kCHF/year the maintenance cost for the ATLAS unit. EBARA has provided a somewhat lower maintenance cost ~2 kCHF/year for the G5 unit.

6. Prospects for achieving "zero" waste using a wastewater treatment plant

We have conducted a feasibility study for on-site treatment of the wastewater produced by the abatement system.

Three companies have been contacted and two, Enviro Chemie GmbH [10] and Sd Water Management [11], have responded positively. So far, more in-depth discussions has only been undertaken with Sd Water Management. The system requirements are as follows:

- the plant must be able to treat ~20 m^3 wastewater per day produced by the abatement system. The wastewater contains a maximum concentration of 0.4% HF and the pH is ~2.

Utilities & services	Consumption
Fuel (city gas)	40-130 m^3/day
Soft water	15 m^3/day
Chilled water	10-90 m^3/day
O_2 (combustion)	80 m^3/day
N_2 (purge)	200-350 m^3/day
Dry Air (purge)	200 m^3/day
Ventilation	1-3 m^3/min
Operation cost	9-16 kCHF/month

Table 5.2.1 Utilities and services required for the operation of the EDWARDS and EBARA abatement systems. Indicated ranges cover specifications of both models.

- The treatment process must ensure that HF residual levels are below limits imposed by French legislation on environmental protection for waste disposal in watercourses and public sewage systems.

French environmental protection regulations for wastewater disposal state the following [12]:

- the disposable wastewater pH must be within 5.5–8.5 for watercourses and 6.5–9 for sewage systems;
- The fluoride concentration cannot be above 15 mg/l for a maximum of 150 g/day of wastewater produced.

A schematic of a typical wastewater treatment plant is shown in Figure 6.1.

The treatment technique for achieving separation between waste and water consists in adding calcium hydroxide to the solution to reach a neutral pH value ~7 where hydrogen ions are bonded with hydroxide ions to form water while the fluorine ions are bonded with the calcium ions to form calcium fluoride waste.
The main treatment phases are as follows:

1) In the primary coagulant tank, lime is added to the 5-6% Calcium hydroxide $Ca(OH)_2$ aqueous solution to raise the pH to ~11-12 because calcium fluoride salt formation is favored in an alkaline environment. Processing time is ~30 min.

$$2\,HF + Ca(OH)_2 \rightarrow CaF_2 + 2\,H_2O$$
$$H_2SO_3 + Ca(OH)_2 \rightarrow CaSO_3 + 2\,H_2O$$
$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2\,H_2O$$

2) Neutralization to pH~8 with ~30% hydrochloric acid (HCl) aqueous solution. Processing time is ~40 min.

$$Ca(OH)_2 + 2\,HCl \rightarrow CaCl_2 + 2\,H_2O$$

3) Coagulation: addition of polyaluminum chloride (PAC) with pH=5 until pH of solution reaches 7. PAC is a coagulant and allows for better separation of the calcium fluoride salt from the liquid. Stirring time ~20 min.

4) Flocculation: in a separator vessel, addition of a flocculent that increases the sedimentation speed, and thus the separation of water from sludge.

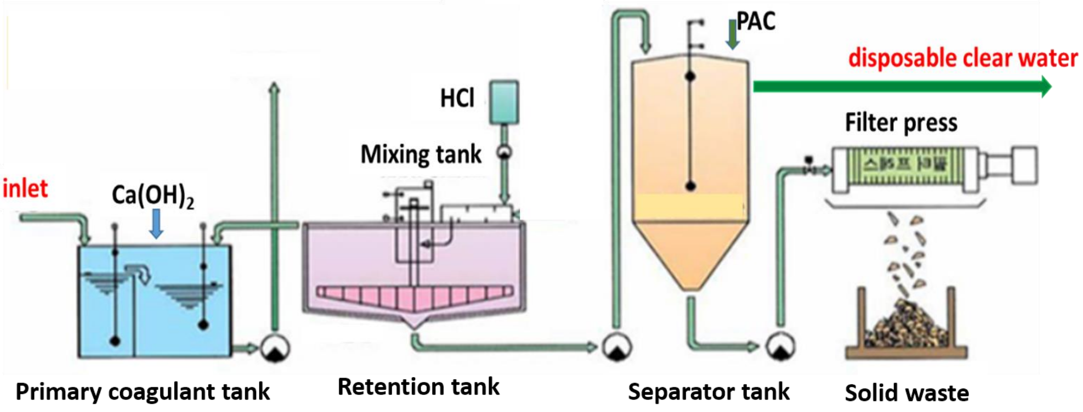


Fig. 6.1 Layout of a typical wastewater treatment plant. The schematic is for illustration purposes.

Semi-solid sludge (40% calcium fluoride salt, 60% water) settles into a deep cone tank. Clarified and neutral water is collected in a reservoir to be reused or for disposal into watercourses.

5) Solid waste: Sludge is transferred to a filter-press that removes water. The final result is cakes of calcium fluoride (CaF_2) so that F- has been transformed into an insoluble, water-stable compound. The estimated volume of solid waste produced by 20 m^3 wastewater is ~190 kg per day.

The treatment system, which has been proposed by Sd Water Management (Fig. 6.2), comprises 5 storage and operation tanks, each of footprint ~5 x 2 m^2. A surface area ~120 m^2, partially covered, is required for the installation of the complete plant. The clear water from the plant outlet is hard but could be softened and recycled to the abatement.

The expected system efficiency is ~98-99%. Therefore, for a processed wastewater volume of 15 m^3/day (CMS Run 3) the treated water at the outlet will contain 1-2% of the initial HF concentration, namely ~1 kg/day of the initial ~ 52 kg/day of HF. This quantity is still ~5 times higher than the limit imposed by French regulations of 15mg/l, or 0.225kg/day for the wastewater treated in a day, and thus the processed water cannot be disposed in watercourses or sewage systems.

There are two options:

- Reprocess the water a second time (feasible according to the vendor). This would lower the HF in solution to 0.02 kg/day from the original 50 kg/day, which is well below the ~0.3 kg/day limit.
- Decrease the input HF concentration in the wastewater by further decreasing the fraction of F-GHG in the input to the abatement system. This could be done by implementing an R134a+SF_6 recuperation system for RPC. With 90% recuperation efficiency, the HF in the input to the abatement is reduced from 109 mol/h to 17 mol/h (or from ~52 kg/day to 8 kg/day). After one cycle of water treatment, the final HF concentration is ~ 0.16 kg/day.

6.1 System maintenance cost and installation requirements

Preliminary and only indicative cost estimates for the procurement, installation and commissioning of a wastewater system which satisfies CMS requirements range between ~130 kCHF (Sd Water Management) and ~500 kCHF (EnviroChemie). The annual maintenance and operation costs are estimated at ~10 kCHF and 12 kCHF, respectively, by Sd Water Management. Some pictures of the EnviroChemie wastewater treatment plant in operation at CERN/B676 are shown in Figs. 6.3, 6.4, 6.5.

7. Conclusion

The proposed strategy for F-GHG emissions reduction and waste treatment using F-gas recuperation, abatement and wastewater systems can reduce to ~70% (optimistically) the environmental impact of F-GHG emitted from gaseous particle detectors, as well as their by-products, at CMS.

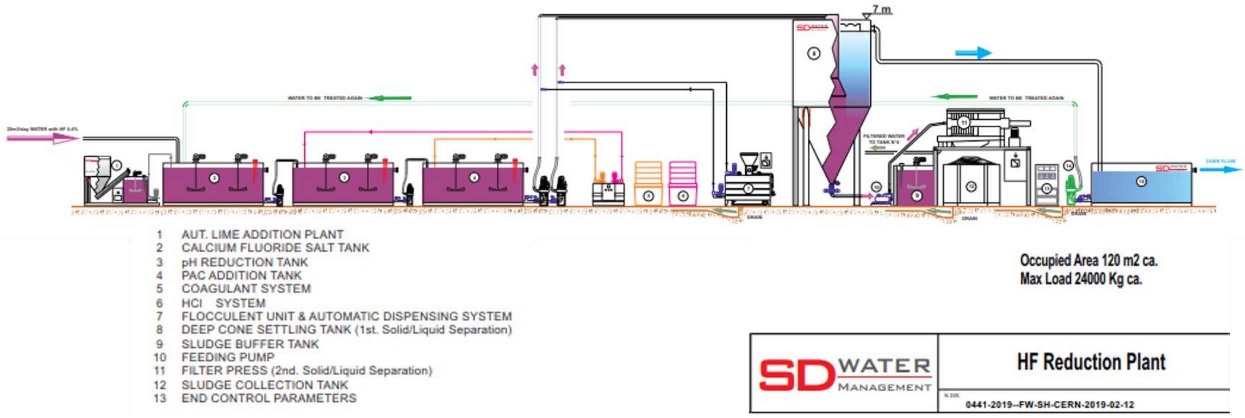


Fig. 6.2 The layout flow of the Sd Water Management plant

Fig. 6.3 The EnviroChemie "STEP" wastewater treatment plant in operation at CERN/ B676.

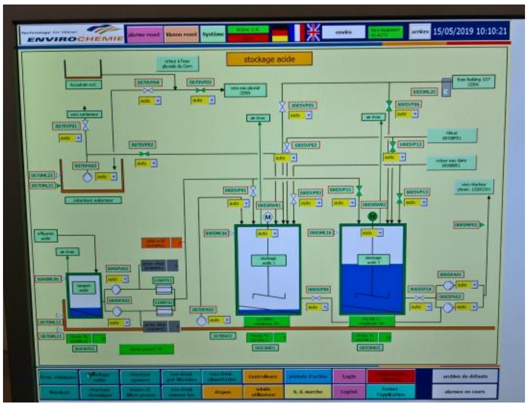


Fig. 6.4 The filter press of the CERN/B676 wastewater plant.

Fig. 6.5 The monitoring and control panel of the CERN/B676 wastewater plant.

Appendix

R&D on eco-friendly gases to replace F-GHG in RPC and CSC

The hunt for eco-friendly substitutes of F-GHG for employment in gaseous detectors for experimental physics is a multi-parameter problem that must take into account several aspects: compatibility with existing detector electronics, interaction with the detector constituent materials, aging properties, flammability, toxicity, hazards, costing, market availability, etc. Furthermore, properties of an eco-friendly alternative gas must be appropriate to the specific detector type and functionalities.

RPC detectors are operated in avalanche mode in order to maintain a reasonably low total collected charge, which extends longevity and enhances rate capability. The gas mixture of the CMS RPCs, consisting of 95.2% $C_2H_2F_4$, 4.5% iC_4H_{10}, 0.3% SF_6, prevents transitioning from avalanche to streamer amplification mode while keeping the detection efficiency above 95%.
Since 2015, the CMS RPC group in collaboration with CERN EP-DT, have started an extensive R&D program to replace the F-gases with eco-friendly alternatives. A promising candidate is one of the hydrofluoroolefin (HFO) family of industrial refrigerants, developed to replace refrigerants with high GWP values, specifically 1,3,3,3-tetrafluoropropene (HFO-1234ze), chemical formula $C_3H_2F_4$. This has a very low GWP (1-6) and a zero Ozone Depletion Potential (ODP).

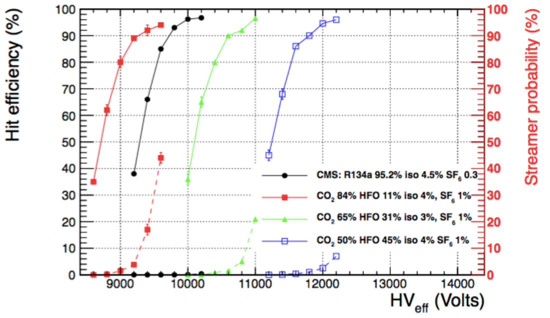


Fig. A.1 Single-gap RPC hit efficiency (continuous line) and streamer probability (dotted line) vs. HV for several standard and ecological gas mixtures.

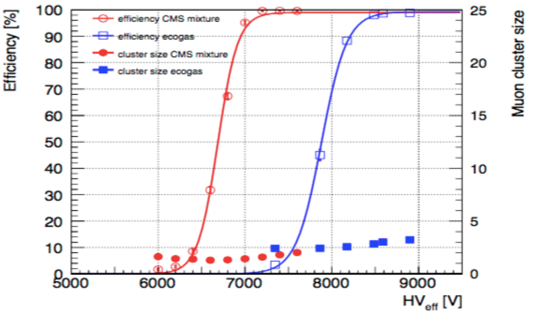


Fig. A.2 Double-gap RPC efficiency and cluster size vs. HV for the standard CMS gas mixture (red) and for the HFO-based gas mixture (blue).

In order to characterize its properties when used in RPC detectors, a 2 mm wide single-gap RPC and a 1.4 mm double-gap RPCs were operated with gas mixtures containing HFO-1234ze and CO_2, at both Ghent University and the LNF laboratory. The CO_2 is used to lower the HV working point without affecting the detector performance. Cosmic ray test results with the 2 mm single-gap RPC and different gas percentages are shown in Figure A.1. For a double-gap RPC, similar to those in use at CMS, the working point is expected to be about 200–300 V lower. With a 45% HFO-1234ze mixture the single-hit efficiency is above 95% and the streamer probability is below 10%, which is considered adequate for RPC operation. The operating voltage of 12 kV is however at the highest edge of what the present RPC HV power system can deliver. The 1.4 mm double-gap efficiency and cluster size results are shown in Figure A.2. The efficiencies, with and without the HFO, are comparable provided a shift of the HV working point of about 1.5 kV is applied.

CERN EP-DT gas group has performed several searches for eco-friendly gas mixtures, including HFO-1234ze, using 2 mm single-gap RPCs.
The use of HFO as primary gas requires operating at higher voltages than with $C_2H_2F_4$, and the gas amplification is lower, but the addition of an inert gas, like CO_2, allows the HV working point to be lowered. The addition of 10% CO_2 lowers the working point by ~800 V. About 40% to 50% of CO_2 is necessary to operate at a working point of ~9 kV. However, the streamer probability with HFO remains higher than with $C_2H_2F_4$ based mixtures, so that RPC operation can be unstable. Tests have shown (Fig. A.3) that some amount of $C_2H_2F_4$ and a higher SF_6 concentration added to the gas mixture can reduce the streamer probability. These HFO+$C_2H_2F_4$+SF_6+CO_2 gas mixtures have a GWP in the range of 500-600, which is about half that of mixtures without HFO.

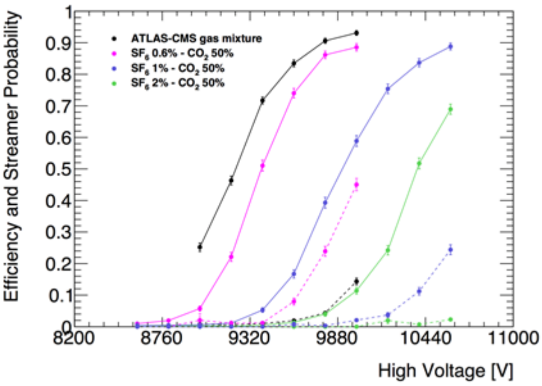


Fig. A.3 Efficiency (continuous lines) and streamer probability (dotted lines) as a function of the HV for gas mixtures with different concentrations of SF_6. CO_2 (50%), iC_4H_{10} (4.5%), while $C_2H_2F_4$ and HFO are kept at the same proportions.

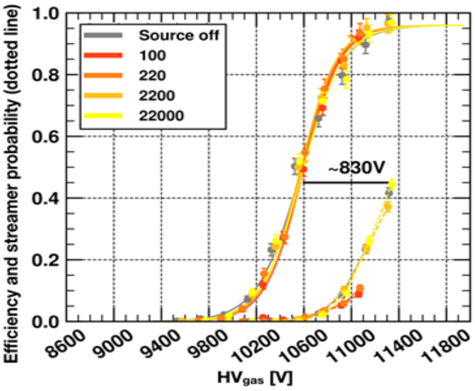


Fig. A.4 Efficiency (continuous lines) and streamer probability (dotted lines) as a function of the HV for the gas mixture $C_2H_2F_4$-HFO-CO_2-iC_4H_{10}-SF_6 (27.25/27.25/40/4.5/1). Colored lines correspond to increasing source intensities (from yellow to red).

The operation of RPC with two eco-friendly gas mixtures in a closed-loop gas system has been studied in LHC-like conditions, i.e. in the presence of high background radiation. The study was done at the CERN Gamma Irradiation Facility (GIF++), which provides a high-energy muon beam combined with an intense gamma source. An RPC filled with standard the gas mixture and with an HFO+CO_2 gas mixture has been irradiated at different dose rates, up to ~55 Hz/cm^2. With both mixtures, the measured detector current, streamer probability and avalanche charge are stable at different source intensities. However, these parameters with the HFO-based mixture are slightly higher than those with the standard gas mixture and compatible with the results obtained in laboratory [13]. Figure A.4 shows the efficiency and streamer probability for the HFO+$C_2H_2F_4$+CO_2 gas mixture. The efficiency curve is stable with increasing source intensity after correcting for the gas density and the electrode resistivity. This demonstrates that the muon detection efficiency is not dependent on the background rate. The

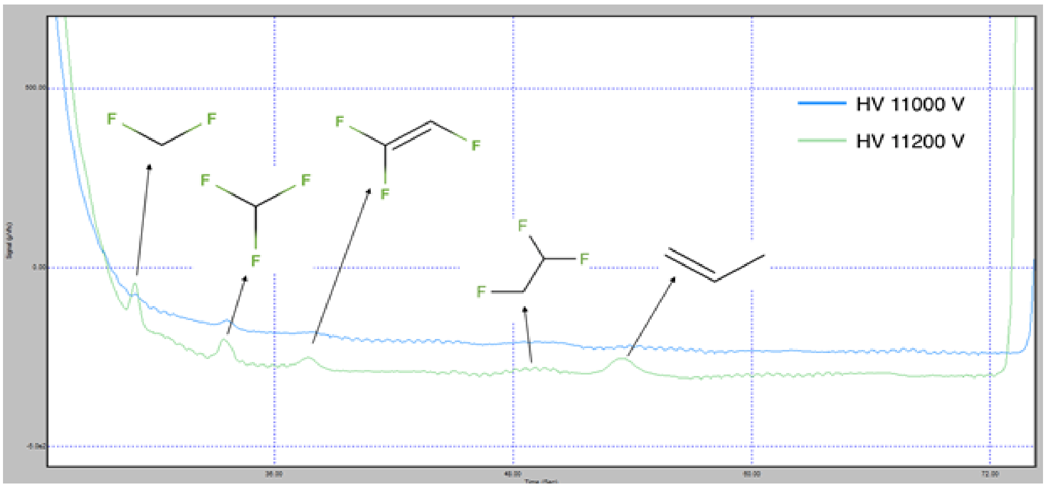


Fig. A.5 Gas chromatography spectrum of the analyzed return gas from an RPC filled with HFO and irradiated at a gamma rate of ~41.2 Hz/cm^2. Results are shown for two different operating voltages. Several impurities created under irradiation are visible and their concentration increases when the HV is increased by 200 V (green curve).

voltage difference between the points of 50% efficiency and 50% streamer probability is ~830 V. This is to be compared to ~1000 V for the standard gas mixture, i.e. the working plateau is slightly reduced with HFO-based gas mixtures. Preliminary studies on gas recirculation and formation of impurities under irradiation show that the HFO breaks down more easily than $C_2H_2F_4$, creating several impurities and hydrofluoric acid (Fig. A.5). The long-term operation of RPCs with HFO-based gas mixture with gas recirculation, and the long-term effects of these impurities, must be critically evaluated. A joint R&D project led by ALICE, ATLAS, CMS and EP-DT experts is ongoing to study the properties and performance of RPCs operated with HFO-1234ze based gas mixtures. Irradiation tests are being conducted at GIF++.

HFO-1234ze is also being considered as a candidate substitute for CF_4 in CSCs. An R&D devoted to the study of CSC operation and performance with an Ar+CO_2+HFO gas mixture just started at CERN and at PNPI (St-Petersburg). Small prototype CSCs, but of similar design and construction materials as the standard CSC in CMS, are being tested with HFO percentages of 2% 3% and 7.5% admixed with Ar (40%) and CO_2. The CSC gas gains from gas mixtures containing 2% HFO and 2% CF_4, shown in Figure A.6, indicates that a ~70 V increase of the HV working point of the CSC filled with 2% HFO provides the same gas gain of a CSC with 2% CF_4. The shift to higher voltage of the HV operating characteristic of the CSC with 2% HFO is also visible in the hit rate curve shown in Figure A.7. There are two important features: 1) the widths of the HV plateau, and 2) the hit rate responses are comparable. The second point suggests that the detection efficiency should also be comparable.
More performance studies and aging tests are planned to establish the working characteristics of CSCs operated with HFO instead on CF_4.

HFO-1234ze is an expensive gas, comparable in cost/kg to CF_4 and from 3 to 6 times more expensive than $C_2H_2F_4$.

Table A.1 summarizes the HFO-1234ze main parameters.

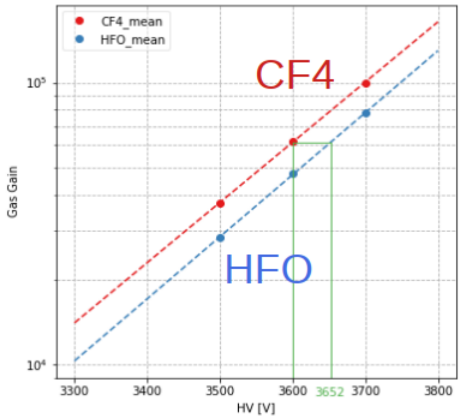


Fig. A.6 Absolute gas gain of a CSC prototype filled with Ar (40%)-CO_2 (58%) and CF_4 (2%) (red) and HFO-1234ze (blue). The vertical lines indicate the HV working points at the same gas gain of 6x10^4.

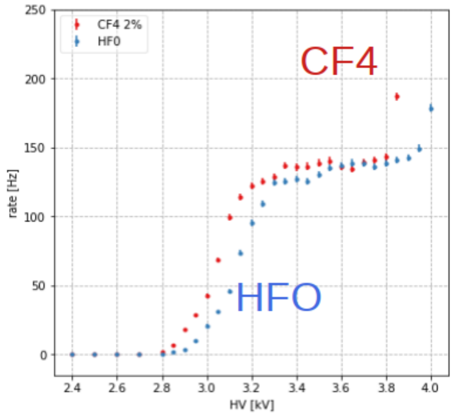
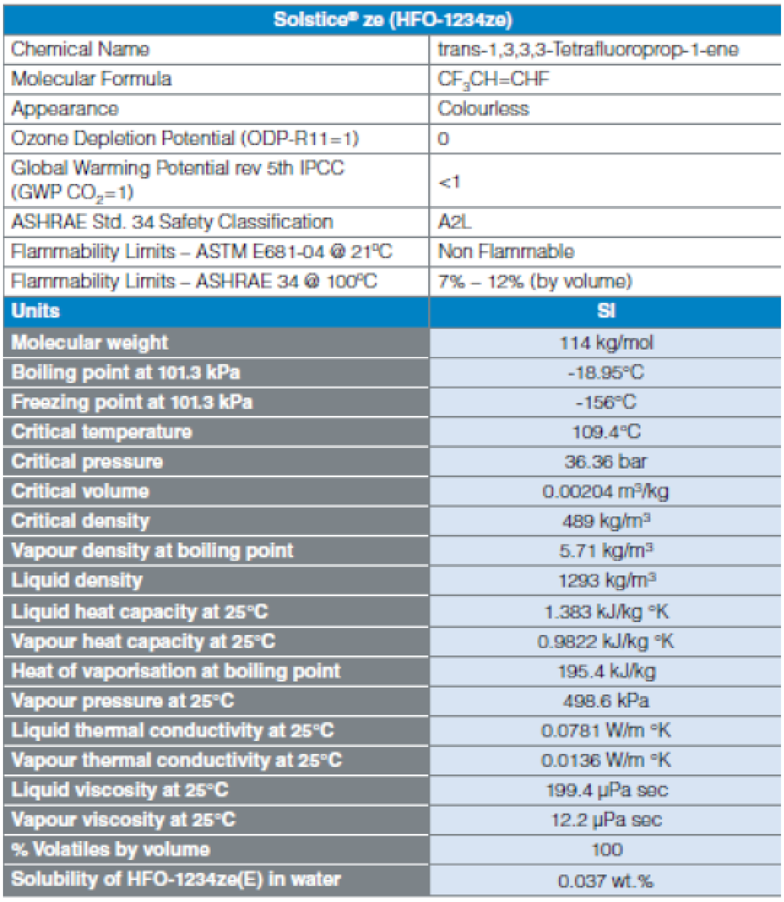


Fig. A.7 Single hit rate from a ^{108}Cd source measured at CERN with a CSC prototype equipped with standard CMS electronics. Test done with 2% CF_4 (red) and 2% HFO (blue) gas.



Solstice® ze (HFO-1234ze)	
Chemical Name	trans-1,3,3,3-Tetrafluoroprop-1-ene
Molecular Formula	$CF_3CH{=}CHF$
Appearance	Colourless
Ozone Depletion Potential (ODP-R11=1)	0
Global Warming Potential rev 5th IPCC (GWP CO_2=1)	<1
ASHRAE Std. 34 Safety Classification	A2L
Flammability Limits – ASTM E681-04 @ 21°C	Non Flammable
Flammability Limits – ASHRAE 34 @ 100°C	7% – 12% (by volume)
Units	**SI**
Molecular weight	114 kg/mol
Boiling point at 101.3 kPa	-18.95°C
Freezing point at 101.3 kPa	-156°C
Critical temperature	109.4°C
Critical pressure	36.36 bar
Critical volume	0.00204 m³/kg
Critical density	489 kg/m³
Vapour density at boiling point	5.71 kg/m³
Liquid density	1293 kg/m³
Liquid heat capacity at 25°C	1.383 kJ/kg °K
Vapour heat capacity at 25°C	0.9822 kJ/kg °K
Heat of vaporisation at boiling point	195.4 kJ/kg
Vapour pressure at 25°C	498.6 kPa
Liquid thermal conductivity at 25°C	0.0781 W/m °K
Vapour thermal conductivity at 25°C	0.0136 W/m °K
Liquid viscosity at 25°C	199.4 µPa sec
Vapour viscosity at 25°C	12.2 µPa sec
% Volatiles by volume	100
Solubility of HFO-1234ze(E) in water	0.037 wt.%

Table A.1 HFO-1234ze gas parameters.

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