



# Strategies for optimizing the usage of greenhouse gas in particle detection systems

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- Greenhouse gases (GHGs) for particle detection
- F-gas regulations
- Strategies for optimizing GHGs usage: results, new projects and plans
  - Recirculation systems
  - Recuperation systems
  - Ecofriendly gases
  - GHGs disposal
- Conclusions/**Lessons to remember**



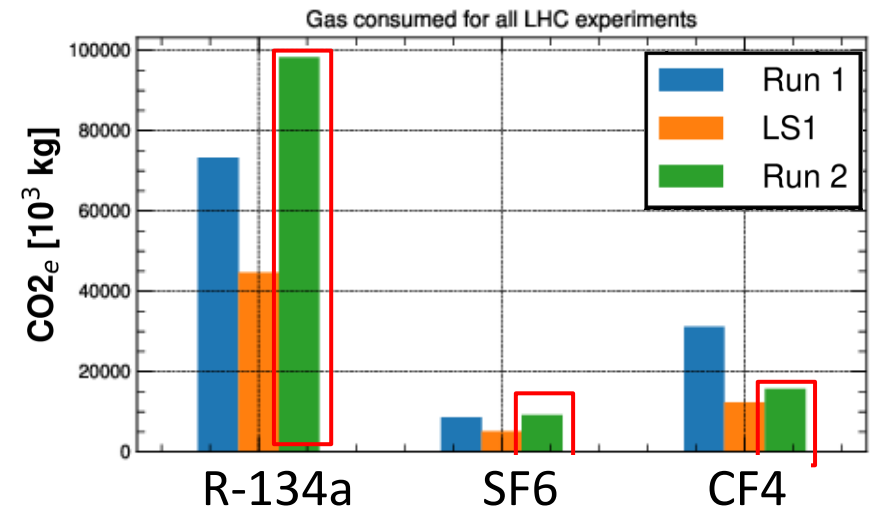
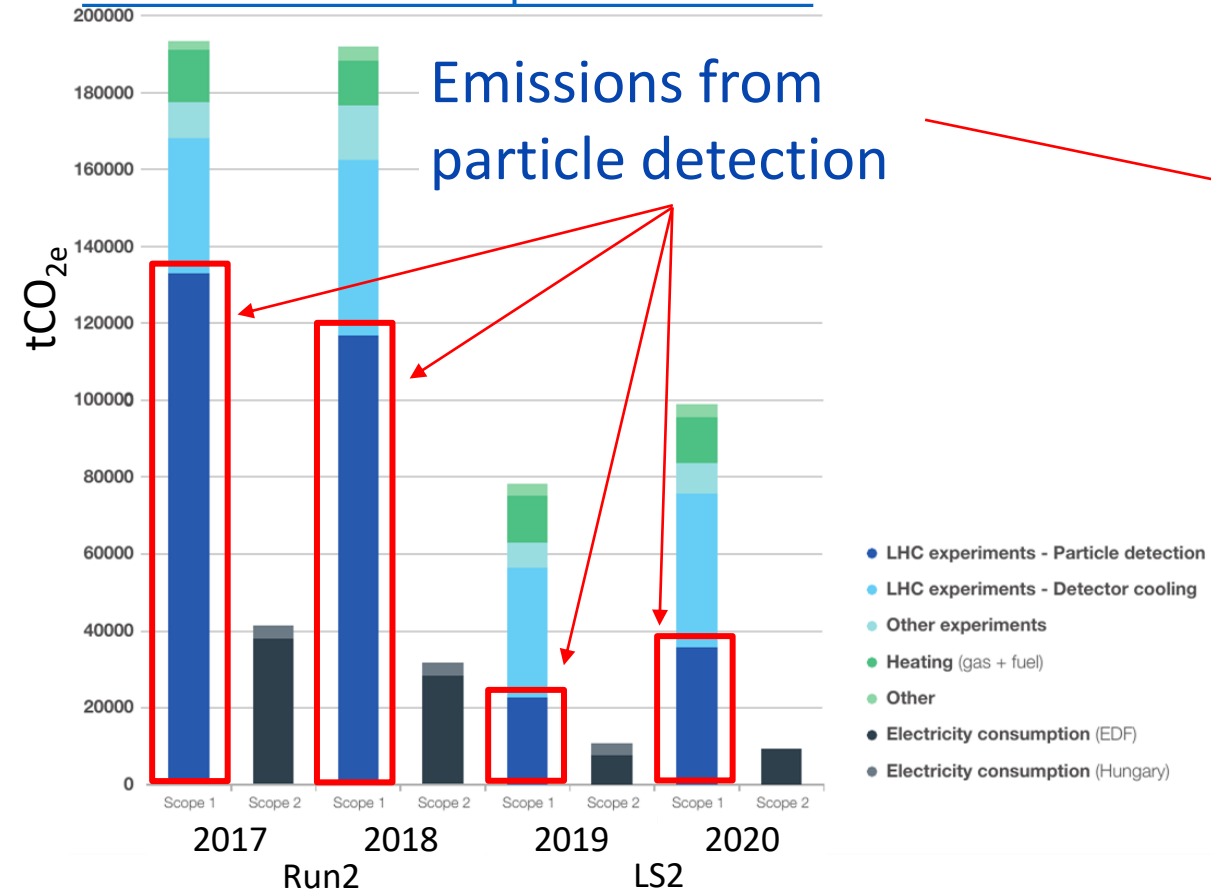
# Greenhouse gas usage

- [CERN Environment Report 2019-2020](#)
- [2021: CERN's Year of Environmental Awareness.](#)
- [CERN Environment workshop: 12 and 13 October 2022](#)
- [CERN Environment Report 2021-2022](#)

Total CERN emissions during 1 year of Run 2 ~ **200 000 tCO<sub>2</sub>e**

~ **50%** from particle detectors → mostly due to leaks and operation

- **C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>/R-134a** biggest contributor → leaks from RPC detector
- **CF<sub>4</sub>** → due to operation of CSC and RICH systems
- **SF<sub>6</sub>** → Related to RPCs as R-134a



-40% GHG emissions from Run1 to Run2 excluding ATLAS and CMS-RPCs  
 -25% GHG emissions from Run2 to Run3 excluding ATLAS and CMS-RPCs

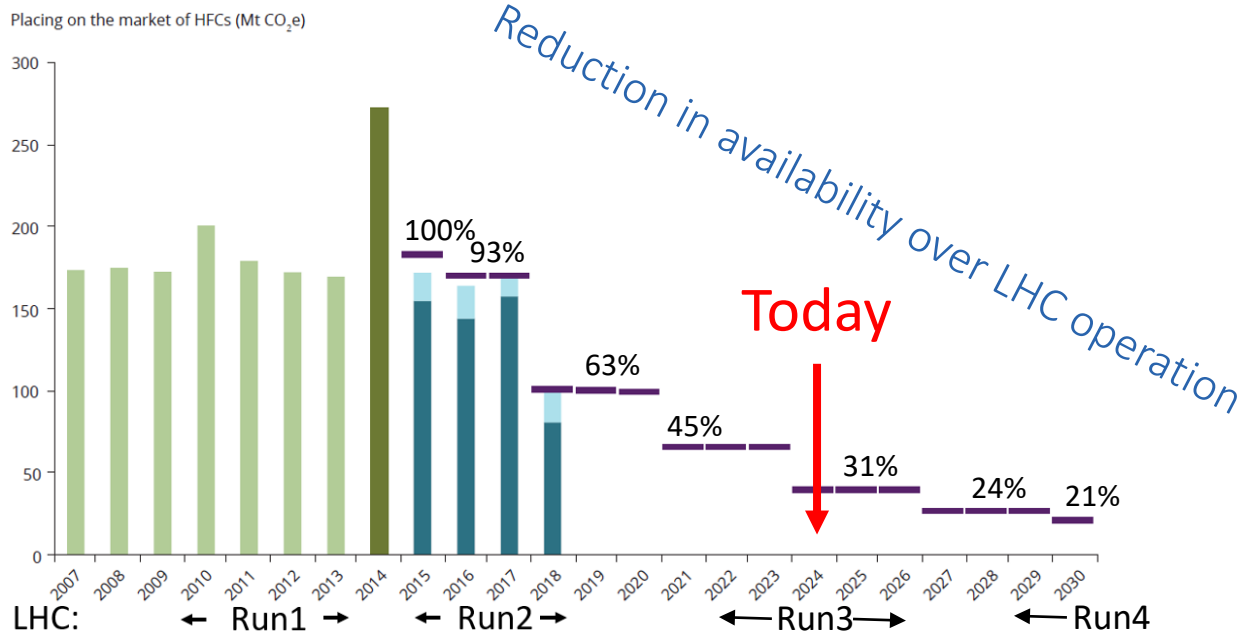
**New objective: -28% by 2024 wrt 2018 (Run2)**

# Greenhouse gas regulation

Due to the environmental risk, “**F-gas regulations**” started to appear. For example, the EU517/2014 is:

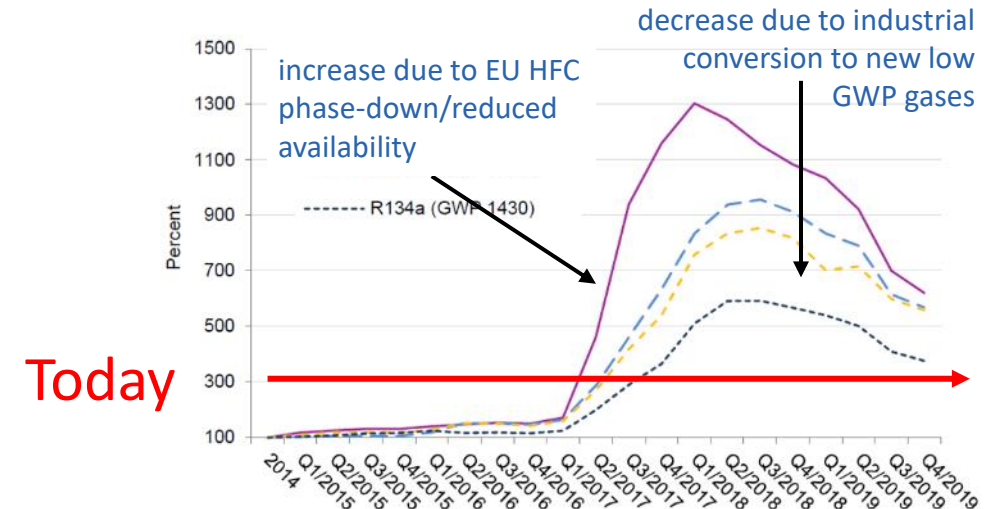
- **Limiting the total amount** of the most important F-gases that can be sold from 2015 onwards. By 2030, it limits the use to 1/5 of 2014 sales.
- **Banning the use of F-gases** in new equipment where less harmful alternatives are available.
- **Preventing emissions of F-gases** from existing equipment by requiring checks, **proper servicing and recovery of gases**.

Figure ES.1 Progress of the EU HFC phase-down



## HFC phase down: effects on HFC availability and prices

### Price fluctuations:



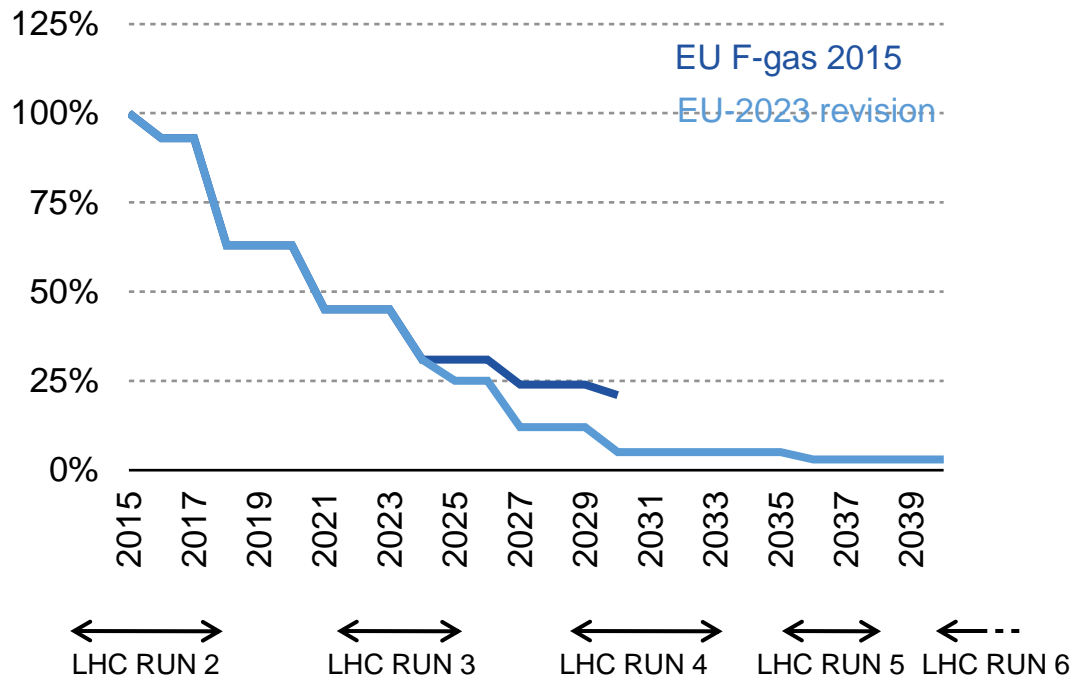
Sources: European Environment Agency, Fluorinated greenhouse gases 2019 report  
 Öko Recherche report, March 2020 J. Kleinschmidt et al.

**Goal: reduce F- gases consumption and emissions from particle detectors**

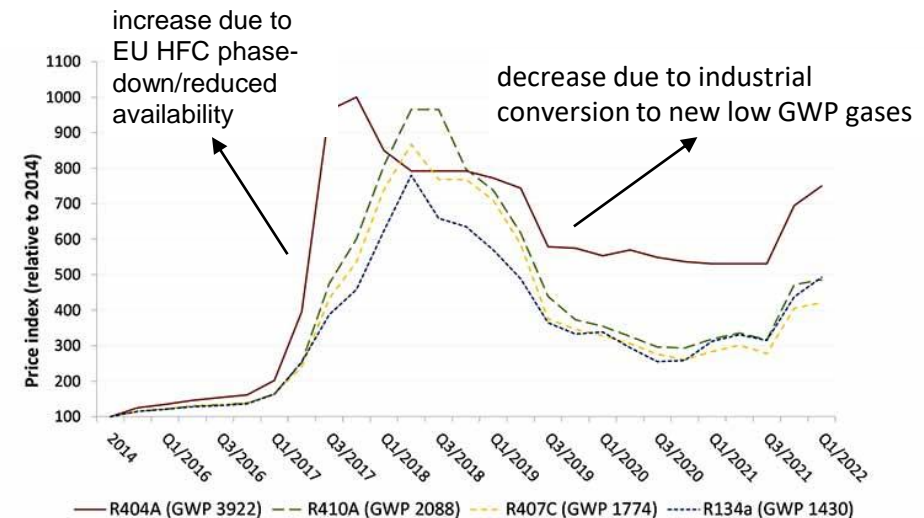
# New F-gas regulation: from phase down to phase out

The new Regulation establishes the **total elimination of HFCs by 2050**

- It is a major step towards climate neutrality
- First goal: reduction of 55% GHG emissions by the end of this decade compared to 1990 levels
- New restrictions also in the use of SF<sub>6</sub> and especially for high GWP gases
- It will result in a reduction in production and reduced quotas for F-Gas refrigerants, leading to an inevitable increase in prices for higher GWP refrigerants
- It will probably affect not-EU market
- Important also to consider possible new regulation for all PFAS



Average purchase prices of the most commonly used HFC refrigerants



# And now: PFAS - “forever chemicals”

PFASs: any chemical with at least a –CF<sub>3</sub> group or a–CF<sub>2</sub>– group (without any H/Cl/Br/I atom attached to it)

PFASs play a key economic role. In 2022, 3M announced that it will end PFAS production by 2025

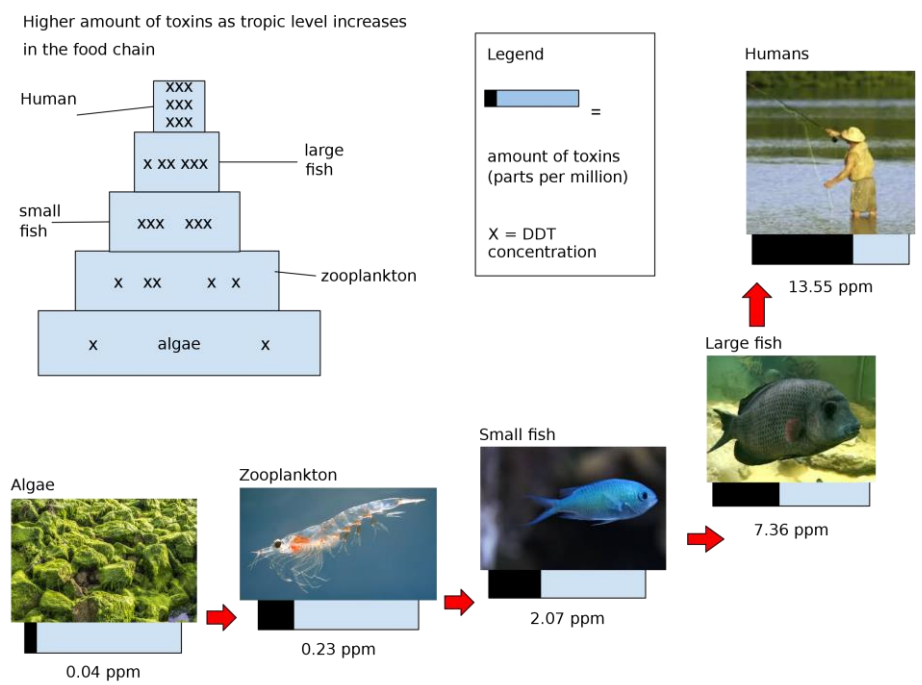
The restriction was proposed by Germany, Netherlands, Sweden, Denmark and Norway for EU

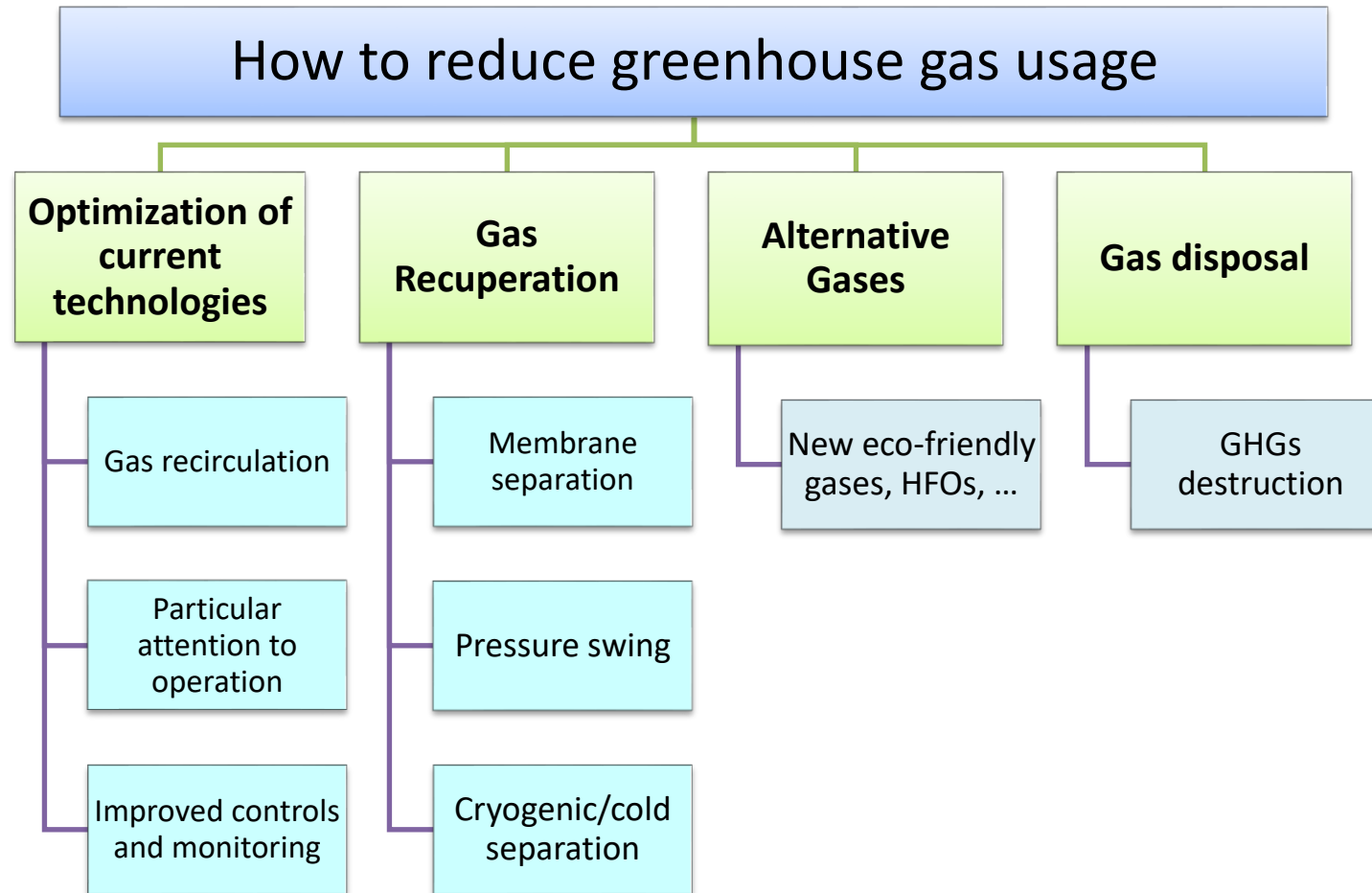
It aims to be the biggest chemical ban out of health considerations

Imports will be also considered in the restriction



## Bioaccumulation and biomagnification

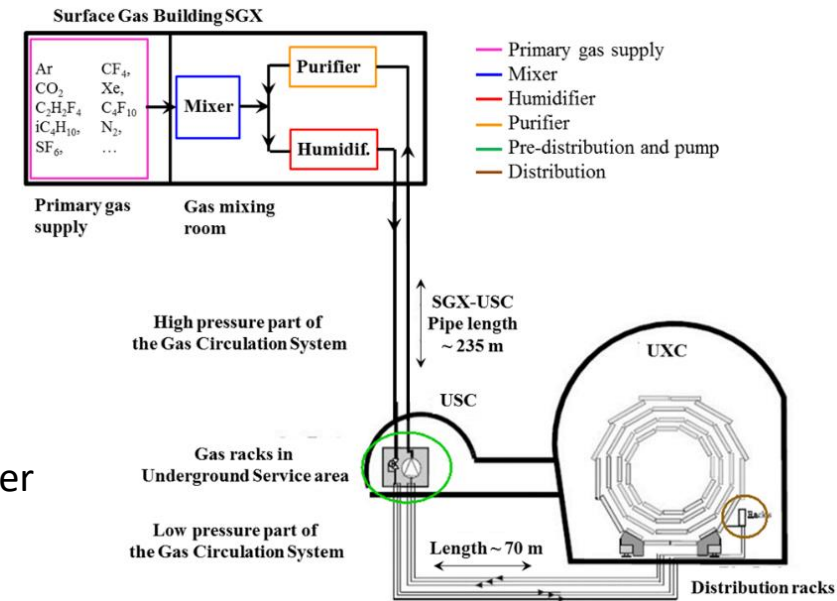




In collaboration with HSE/CEPS

Gas systems extend from the surface building to service balcony on the experiment following a route few hundred meters long.

- Primary gas supply point is located in surface building
- Gas system distributed in three levels:
  - Surface (SG)
  - Gas Service room (USC)
  - experimental cavern (UXC)
- The gas systems were built according to a common standard allowing minimization of manpower and costs for maintenance and operation.



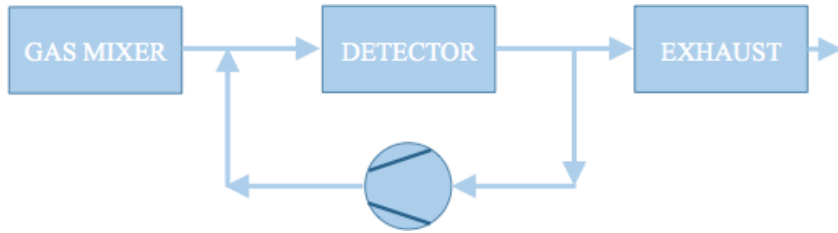
- Few numbers:
  - Construction started in 2000; Operational since 2005-2006
  - Need to validate the gas system components (ageing test setup)
  - 30 gas systems detectors at the LHC experiments
  - 300 Universal Euroracks → x2 height of Eiffel Tower
  - 60 PLCs
  - 150 MFCs
  - 4000 flow meters in distribution racks
  - ~ 70 gas analysers and 6 gas chromatographers
- The CERN gas service team (EP-DT-FS, BE-ICS)

- **Reliability**
  - LHC experiments are operational 24/24 7/7
  - Gas systems must be available all time
- **Automation**
  - Large and complex infrastructure
  - Resources for operation
  - Repeatability of conditions
- **Stability**
  - Detector performance are strictly related with stable conditions (mixture composition, pressures, flows, ...)



# Optimization of current technologies: gas recirculation

- All gas systems are designed to recirculate the gas mixture: average 90% **gas recirculation** → 90% reduction of consumption/emissions



## Advantages:

- Reduction of gas consumption

## Disadvantages:

- Complex systems
- Constant monitoring (hardware and mixture composition)
- Use of gas purifying techniques

- The remaining 10% is what we started to address from LS1. It is needed to compensate for:

- Leaks at detector: 85 % (mainly ATLAS and CMS RPC systems)
- 15% N<sub>2</sub> intake (CMS-CSC, LHCb-RICH1, LHCb-RICH2)

- Two remaining open mode systems upgraded to gas re-circulations from Run1 to Run2:

- ALICE-MTR: from Run1 to Run2: 75% GHG reduction
- LHCb-GEM: from Run1 to Run2: 90% GHG reduction

→ For both detector systems: **Original investment was totally paid back by gas cost saving during few years of operation**

- and laboratory setups:

- 2013: Development of ["A portable gas recirculation unit" JINST 12 T10002](#)
- 2020: Development of [Gas recirculation systems for RPC detectors: from LHC experiments to laboratory set-ups - RPC2022](#)

# Gas recirculation and “small” detector system: LHCb-GEM example

Mixture: **CF<sub>4</sub> 40%**, Ar 45%, CO<sub>2</sub> 15%

Detector volume: ~ 50 liters (but very high flow needed) → R&D for operation of GEM detector systems with gas recirculation

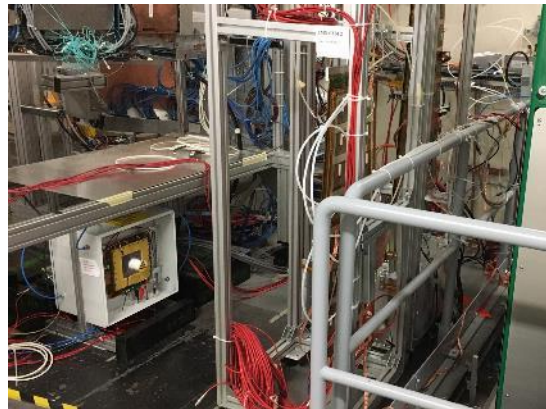
**2013:**

Development of small gas recirculation systems  
Started test in lab with radioactive source (GEM never operated in recirculation before)



**2016-...:**

Validation continued at CERN  
Gamma Irradiation Facility



Gas mixture purification studies

**2016-...:**

LHCb-GEM upgraded to gas  
recirculation



**From Run1 to Run2:  
90% GHG reduction**

**Original investment already largely paid back by gas cost saving during operation**

LHCb-GEM detector operation became more stable thanks to less frequent replacement of CF<sub>4</sub> cylinders

**Need to consider longer time scale:**

**as this example shows also for a small system there can be a positive balance on longer time**

Nowadays GHGs usage for particle detectors @ LHC is dominated by the large ATLAS and CMS RPC systems: mixture recirculation is already almost at design level (85-90%) and today it is limited by leaks at detector level

## Further optimization requires:

- **Fixing leaks at detector level**
  - Huge ongoing effort of RPC detector communities (ATLAS and CMS)
  - but critical/fragile gas connectors are extremely difficult to access
  - Good technical progress
- **Gas system upgrade to minimize any pressure/flow fluctuation**
  - Goal: new upgrades to cope with observed fragility of some detector components
  - Positive effects already visible at end of Run2:
    - . Reduced leak developments at start-up
    - . Pressure regulation improved by 70%
- **Minimize impact of cavern ventilation (tested in collaboration with EN-CV)**
- **Look for other external causes (vibrations, ...)**
- **Detector R&D to validate higher recirculation fraction**
- **Tools to check detector and gas system tightness**



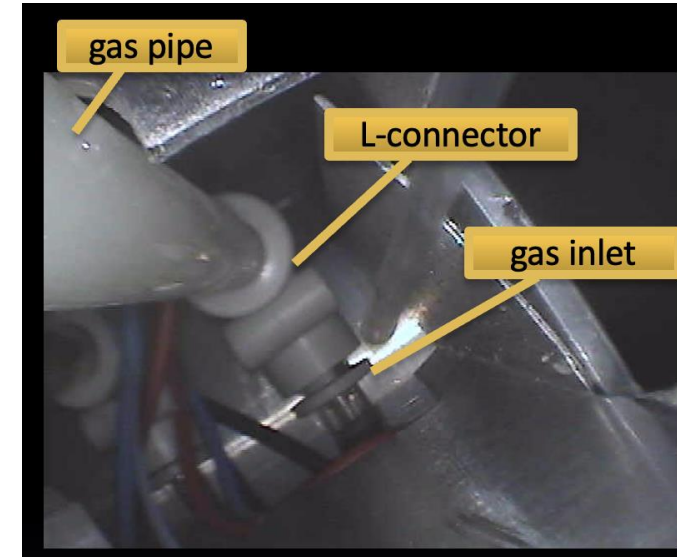
Since Run 1 the ATLAS and CMS RPC systems experience the development of leaks at the chambers level

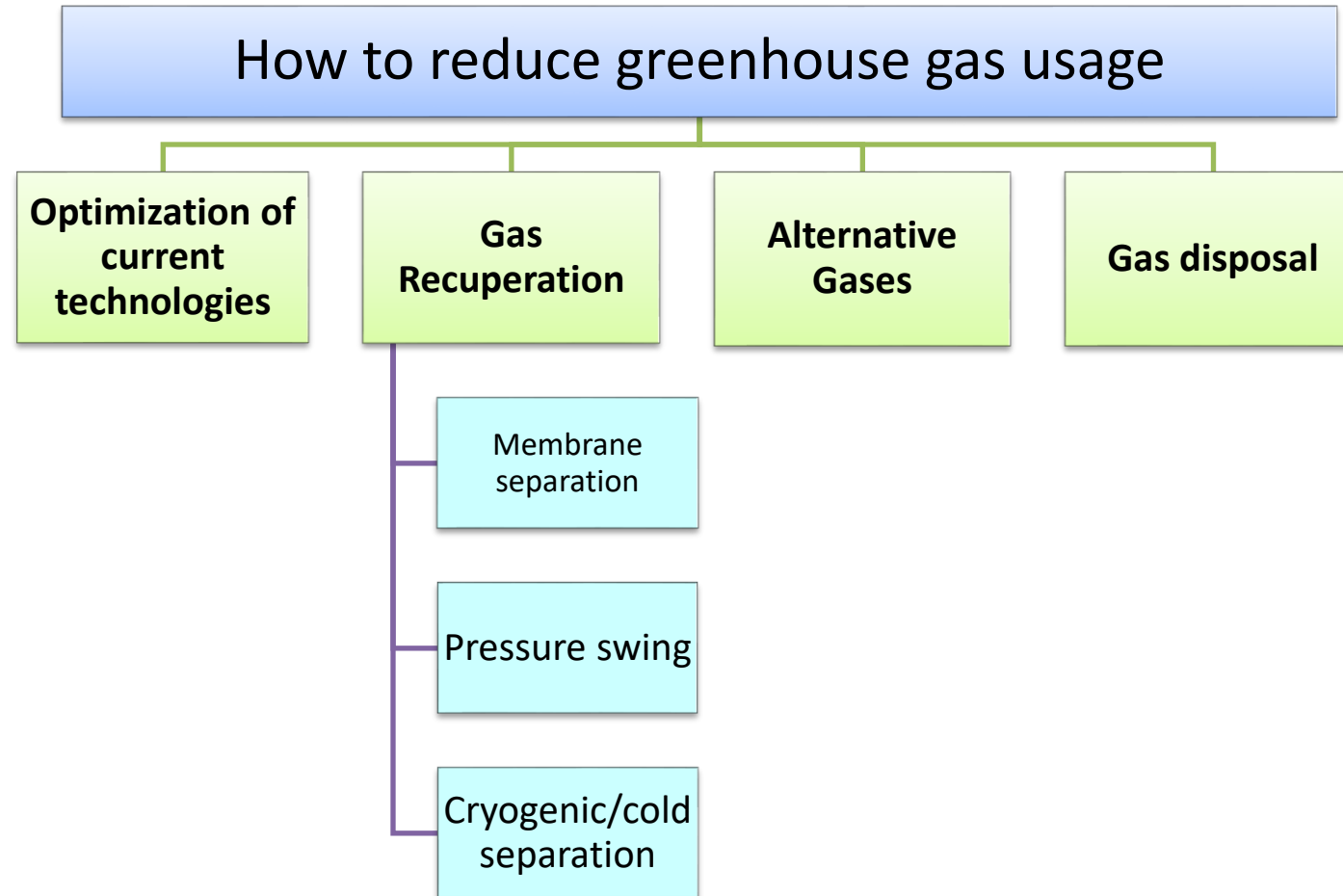
## ATLAS RPC case

- Leaks originate at the gas inlets which tend to crack due to inborn fragility
  - Aggravated by mechanical and chemical stress
  - Cracks develop slowly (over months) until reaching a breaking point
- 8000 inlets in total, located in couples in 4000 boxes on chamber corners, often with difficult access
- Difficult to localize some types of leaks
- Reparation campaign during EYETS and LS
- But new leaks keep developing

## CMS RPC case

- Two sources of gas leaks appeared at different time scale
  - T or L polycarbonate gas connectors break due to original construction fragility in few of them
  - Polyethylene LD pipes become brittle/deteriorated
  - Very difficult (*or sometimes impossible*) access to reach these connectors and pipes
  - Reparation campaign during LS
  - New policy of disconnecting chambers with big leaks (RPC system redundant for CMS trigger)
- **Avoid plastic pipes**
  - **More attention to mechanical coupling of pipes and detectors**

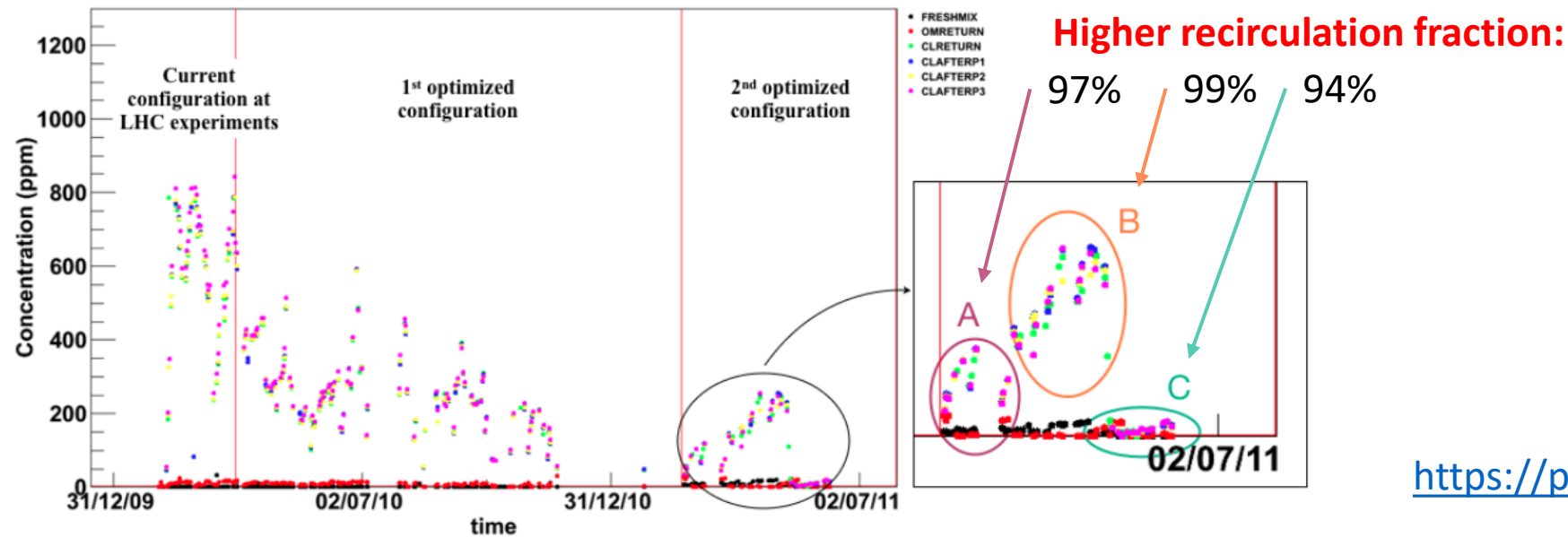




## Not always the recirculation fraction can be increased easily: two examples

- 1) Detector operation validated for ageing up to 90%
  - What about recirculating more? (example RPC: only short test performed in the past (2011) up to 97-99%)
- 2) N2 intake by diffusion (example: CMS-CSC detector)

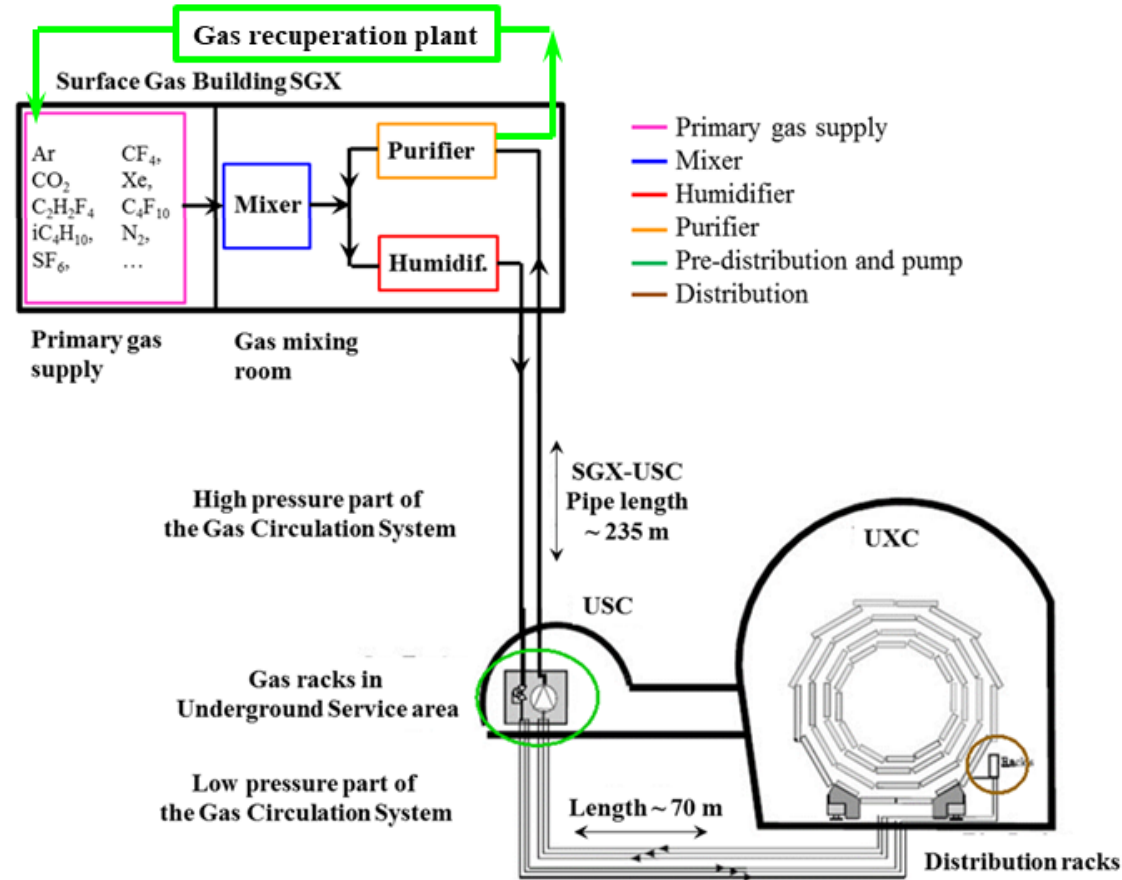
RPC: Gas recirculation and impurities in past test



<https://pos.sissa.it/159/029/pdf>

- Need to validate at max recirculation rate the detector operation since the beginning of the R&D phase
- Avoid materials permeable to air for the detector construction

Possibility to recuperate a single gas component from exhausted mixture



Many LHC gas systems already with gas recuperation

**Advantages:**

- Further reduction of gas consumption

**Disadvantages:**

- Higher level of complexity
- Dedicated R&D
- Gas mixture monitoring fundamental

■ **Ongoing R&D aims in testing the feasibility for new recuperation systems:**

- **R134a** for ALICE-RPC, ATLAS-RPC, CMS-RPC, ALICE-TOF

■ **and substantial improvements of existing systems:**

- **CF<sub>4</sub>** for CMS-CSC, LHCb-RICH2

- **C<sub>4</sub>F<sub>10</sub>** for LHCb-RICH1

- Recuperation is effective only if leaks at detector level will be reduced
- R134a recuperation can drastically decrease GHG consumption
- Costs for R134a recuperation system paid back in two years

## CMS-CSC CF<sub>4</sub> recuperation plant

### Problem:

Too high N<sub>2</sub> concentration for gas recirculation due to diffusion leak from detector components

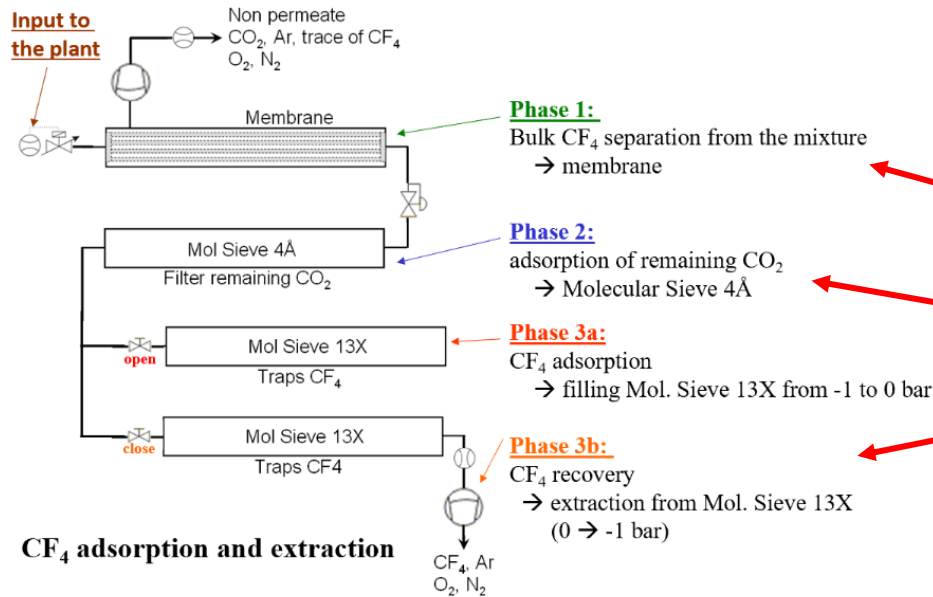
R&D started in 2009, Operation from 2012. Several technical and resource problems

Average efficiency 60-70% reached in 2021 (with additional resources)

### Technical challenge:

First plant built for CF<sub>4</sub> warm adsorption  
A completely non-standard system

From Run1 to Run2  
up to 44% GHG reduction



If gas recuperation system is needed: fundamental to invest in R&D and resources since the beginning



**Positive effects** – CF4 and R134a examples:

## CF4 recuperation for CMS-CSC

10% CF4 in gas mixture  $\sim$  70 l/h  $\sim$  2200 kg/year  $\sim$  100 kCHF/year (at current price)

With 65% or recuperation efficiency

→ 1400 kg/year CF4 saved  $\sim$  **-60 kCHF/year**  $\sim$  **-10500 tCO2e/year**

## R134a recuperation for CMS-RPC

95.2% R134a in gas mixture  $\sim$  700 l/h  $\sim$  12t/year  $\sim$  130 kCHF/year (at current price)

With 80% or recuperation efficiency

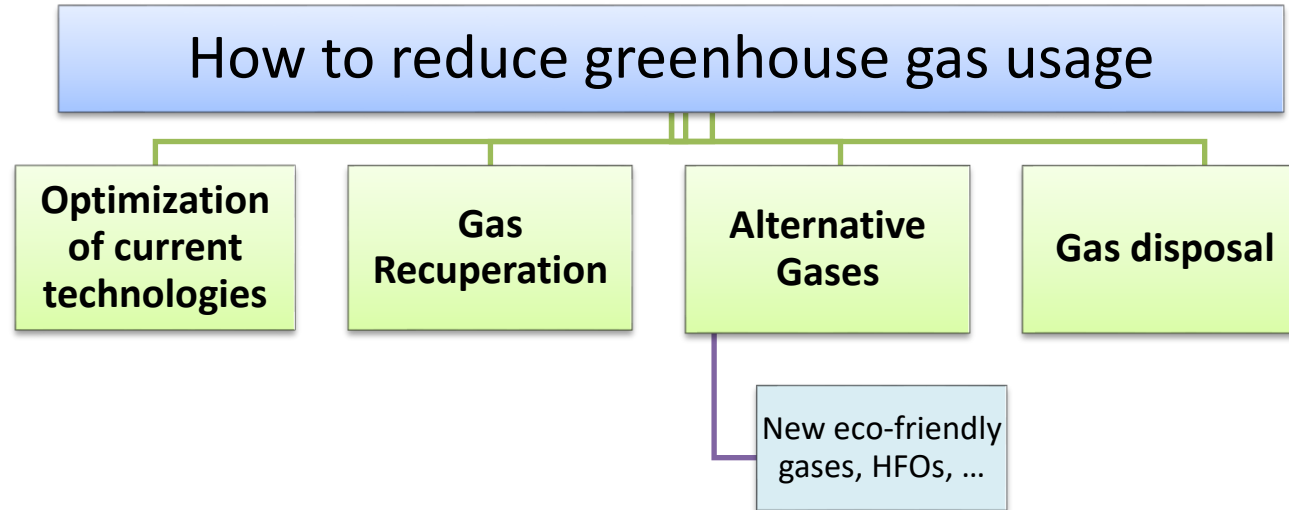
→ 12 t/year R134a saved  $\sim$  **-130 kCHF/year**  $\sim$  **-18000 tCO2e/year**

allowing to maintain constant operational cost and GHG emissions despite the increase in fresh flow required to cope with the increase of luminosity

**Detector operation is less subject to market crisis affecting price and availability.**

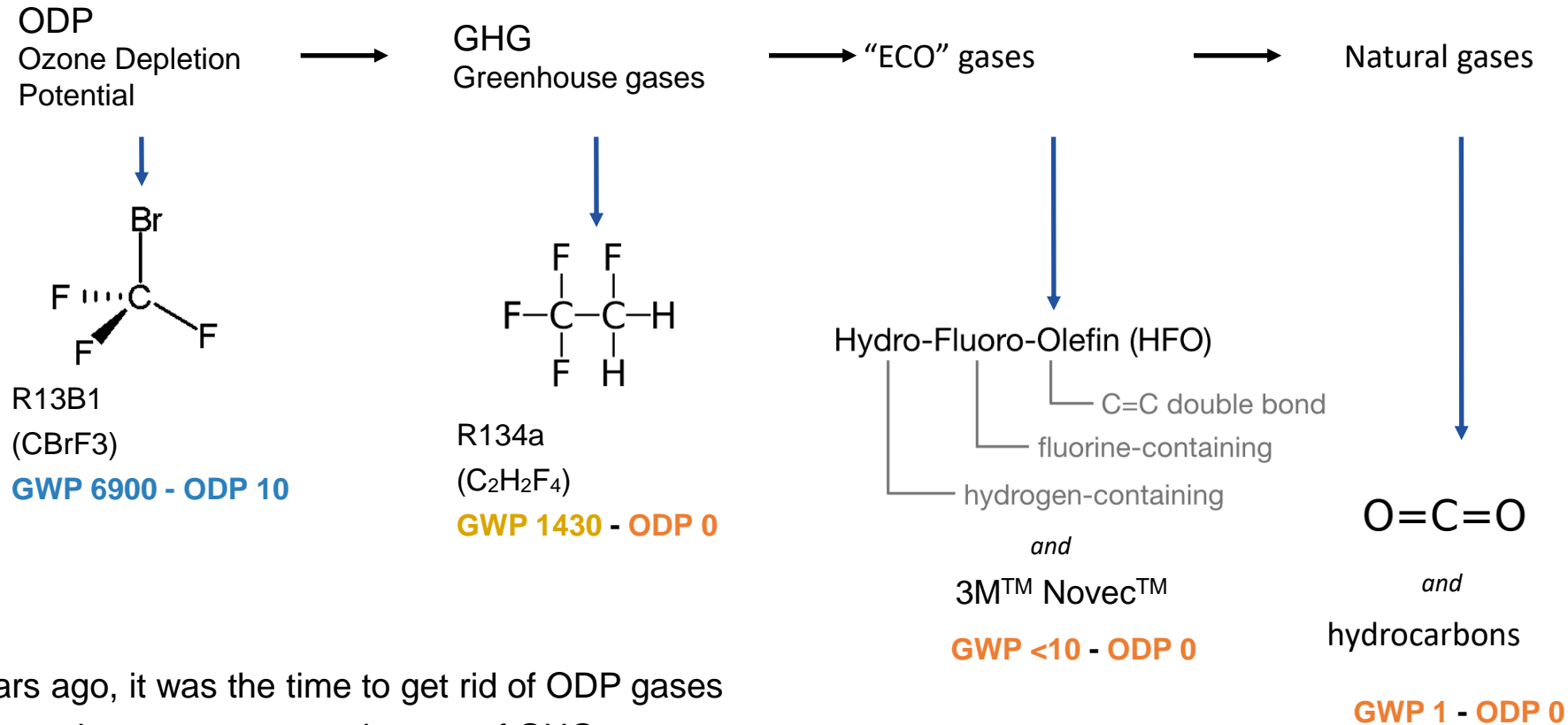
**Indeed, the availability of recuperated gases can mitigate difficult situations when there is a shortage of fresh gas.**

**In 2022 when there was a major disruption of CF4 availability in Europe: the CMS-CSC detectors could be operated and therefore participate to the CMS data taking only thanks to the usage of recuperated CF4.**



# Gases for particle detectors

It is not the first time we are looking for “new” ecofriendly gases...and, probably, not the last

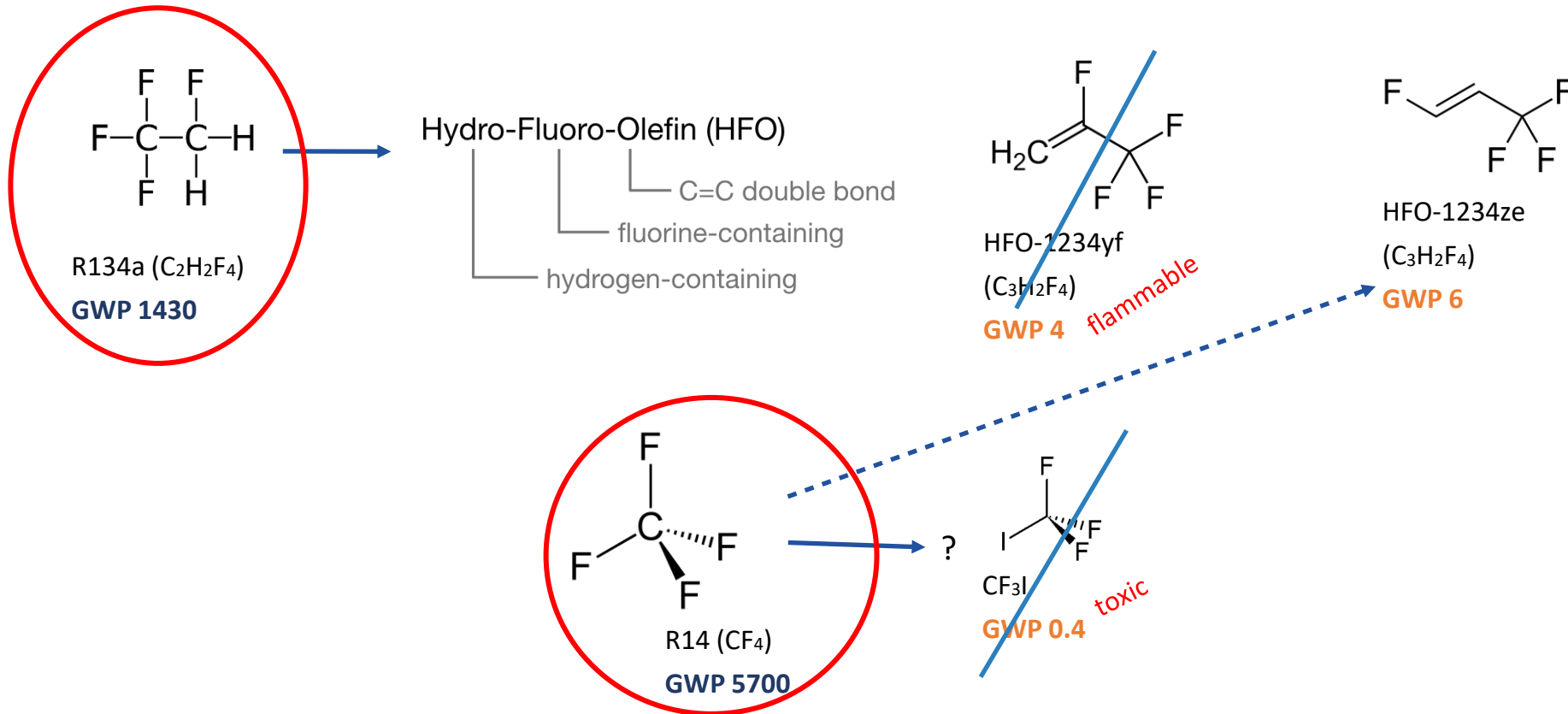


- ~20-30 years ago, it was the time to get rid of ODP gases
- There was not the awareness on the use of GHGs
- Many gaseous detectors were conceived with use of GHGs
- Now it is time to address the usage of GHG worldwide, including particle detectors
- New concerns are already raising for the use of new “eco-friendly” gases, most of which are PFAS

# Possible alternatives to GHG gases

New eco-friendly liquids/gases have been **developed for industrial applications as refrigerants** and HV insulating medium...

→ many gases tested, but not straightforward for detector operation. Best options:

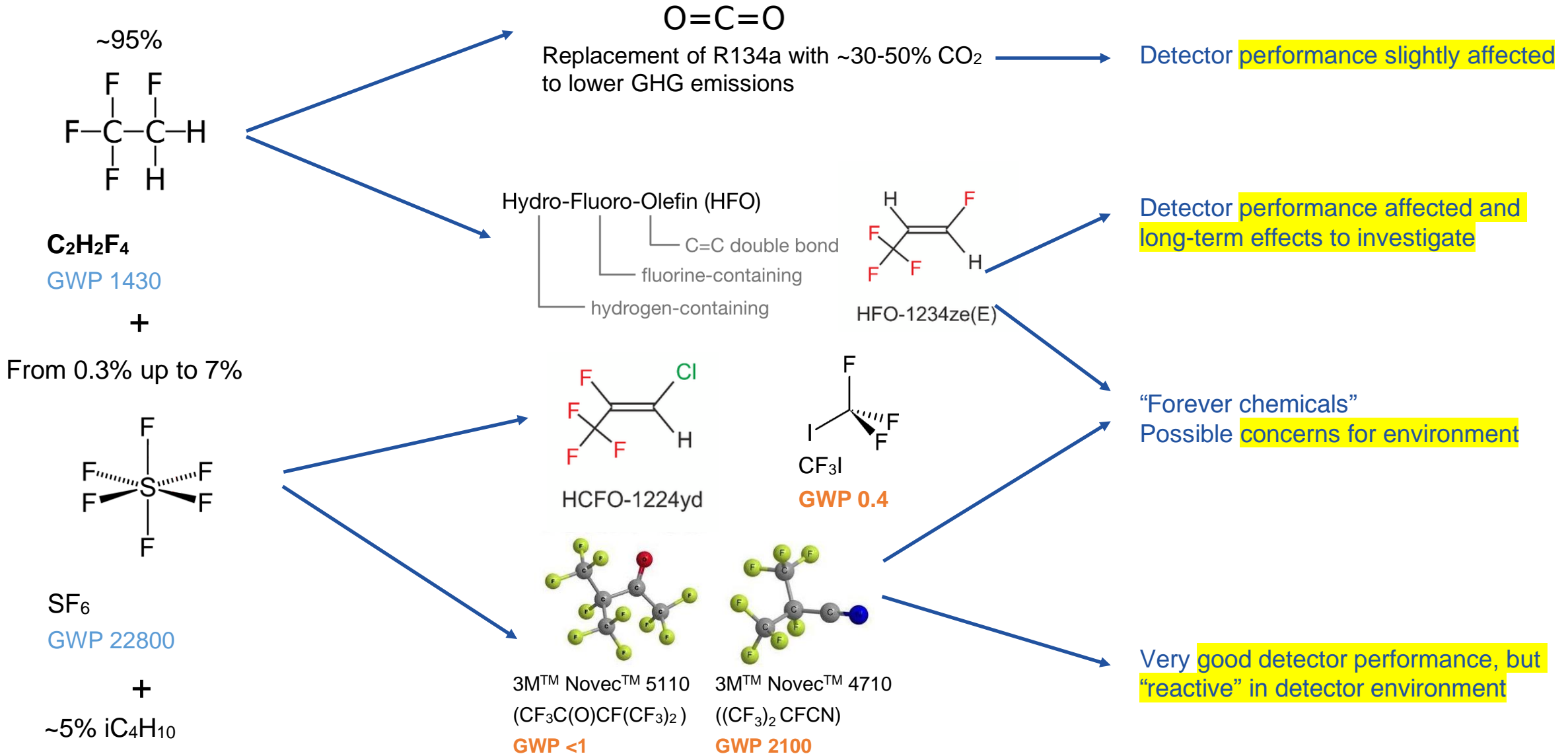


Very difficult challenge for already installed detectors where it is not possible to change of FEB electronics, HV system, etc

However, in any case to be considered

- Long-term operation (to evaluate possible aging issues)
- No flammability or toxicity of the gas mixture

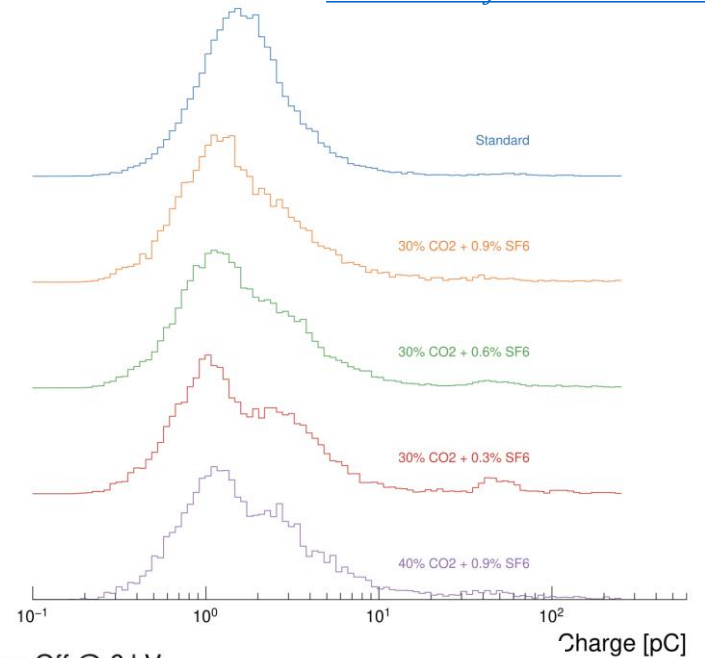
# Alternatives for RPC gas mixture: R134a and SF6



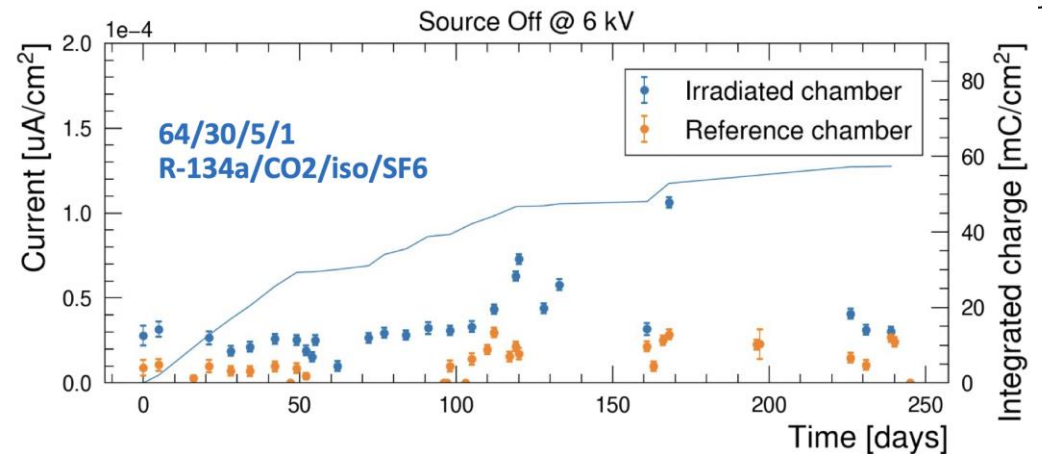
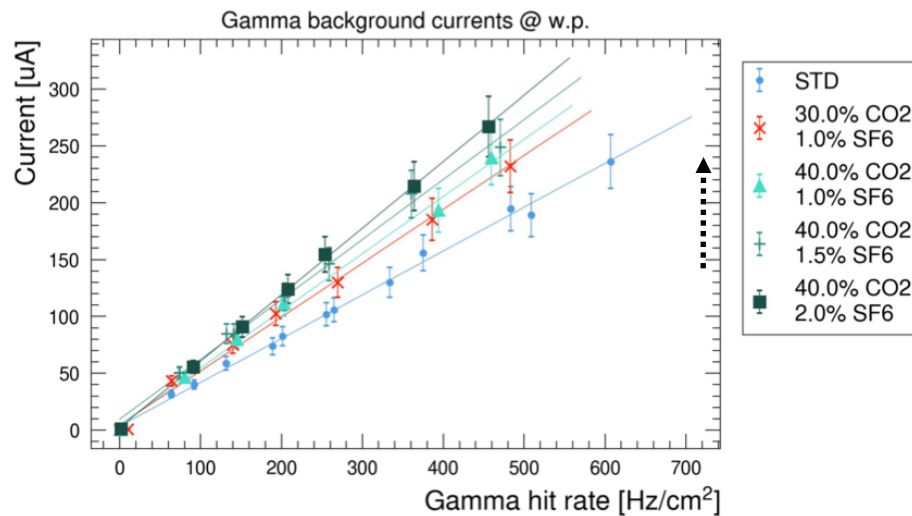
## CO<sub>2</sub> as mid-term solution for RPC to mitigate GHG emissions of LHC RPC systems

- CO<sub>2</sub> selected as best compromise
- He also good candidate but cannot use in experimental caverns
- The addition of CO<sub>2</sub> increases the streamer probability and broad the charge distribution
  - Necessary to increase the SF<sub>6</sub> concentration up to 1%
  - Increase of currents of >15% under irradiation
- Very good time resolution
  - The CO<sub>2</sub> reduce the mean free path
- Long-term performance studies under gamma irradiation
  - Up to now, no sign of performance degradation

[doi 10.1016/j.nima.2023.168088](https://doi.org/10.1016/j.nima.2023.168088)



Already in use in ATLAS RPC system since summer 2023





# Mid-term solution: addition of CO2 to std gas mix

## Positive effects:

Replacement of 30% R134a with CO2 brings a **reduction of 14% of the tCO2eq emitted per year**

mixture	GWP	tCO2e/year
R134a+iC4H10+SF6	1482	52373
CO2+R134a+iC4H10+SF6	1529	44784
		<b>-14%</b>

In addition, the **operational cost is lower**

mixture	R134a used (kg/m3 gas mix)	SF6 used (kg/m3 gas mix)	
R134a+iC4H10+SF6	4.3	0.02	
CO2+R134a+iC4H10+SF6	2.91	0.065	
	<b>-11 t/year</b>	<b>+356 kg/year</b>	
	<b>-115 kCHF</b>	<b>+13 kCHF</b>	<b>-102 kCHF/year</b> <b>-29%</b> <b>1 year with std+CO2 mix ~ 250 kCHF</b>

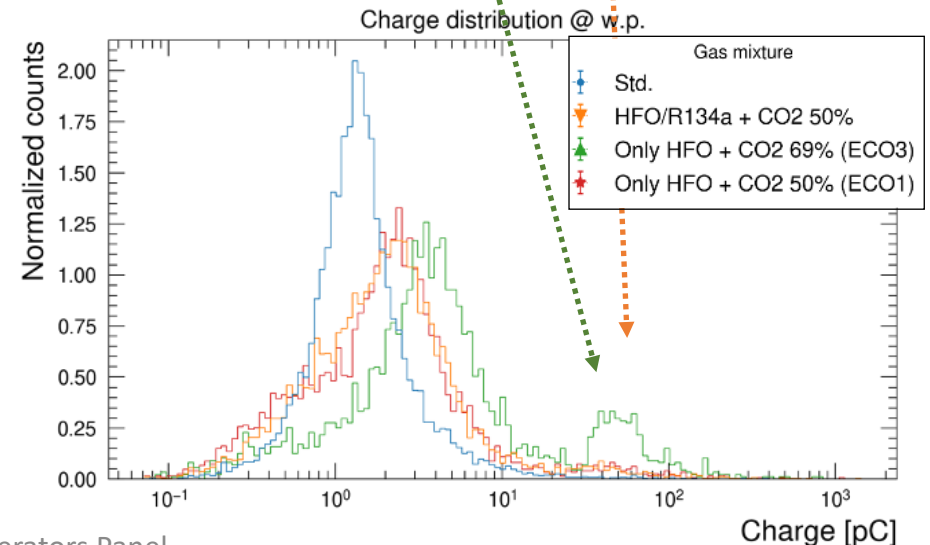
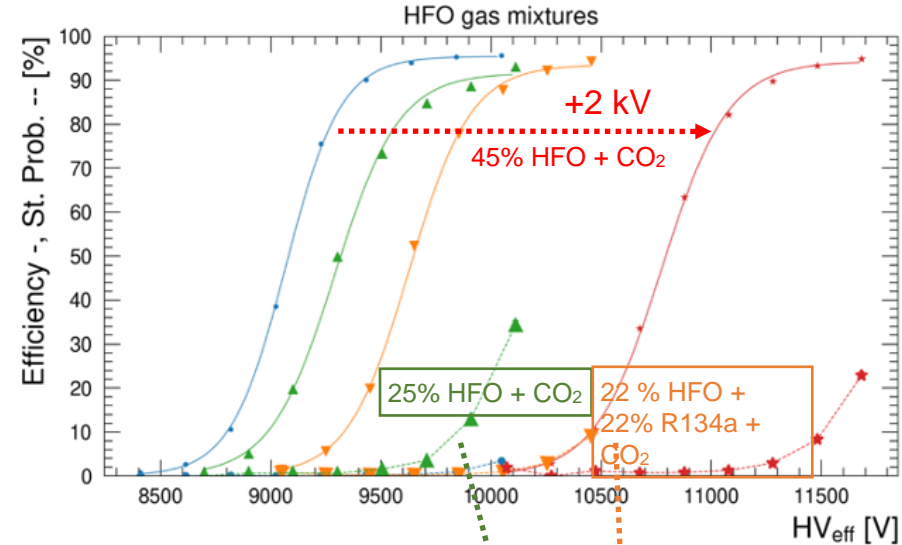
and detector **operation is less subject to market crisis** affecting price and availability

## HFO1234ze identified as possible replacement of R134a

- Cannot replace 1:1 the R134a
- Too high w.p.: add He or CO<sub>2</sub> to lower it
- The HFO and CO<sub>2</sub> move the charge distribution towards higher values
- Currents increase seems to be dominated by the CO<sub>2</sub>
- HFO brings a higher prompt charge content than R134a
- The addition R-134a helps lowering the background currents and prevent w.p. to be too high

## R-1234ze performance with CO<sub>2</sub> (+ R-134a) with cosmic muons

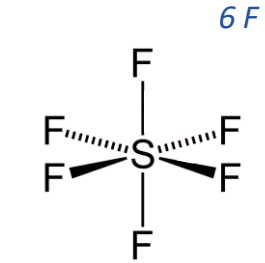
- **45% HFO + CO<sub>2</sub> (ECO1)**
- Too high w.p. and high charge
- **25% HFO + CO<sub>2</sub> (ECO3)**
- Low GWP
- High charge content and presence of streamers. Higher currents
- **22% HFO + 22% R134a + CO<sub>2</sub>**
- Higher GWP
- Lower charge content than HFO only
- **Possible compromise** between performance and environment





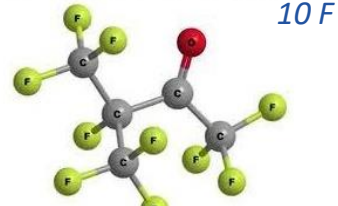
# Alternatives to SF<sub>6</sub>

Scrivi good/bad



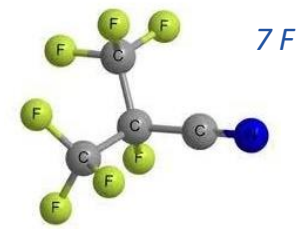
SF<sub>6</sub>  
GWP 23900

- Chemical inertness: extremely stable
- Exceptionally long lived in the atmosphere
- Excellent dielectric property
  - SF<sub>6</sub> x 2.5 than Air
- Non-flammable and toxic
- Gaseous form
- No major reactions
  - Ok with H<sub>2</sub>O, Cl and acids



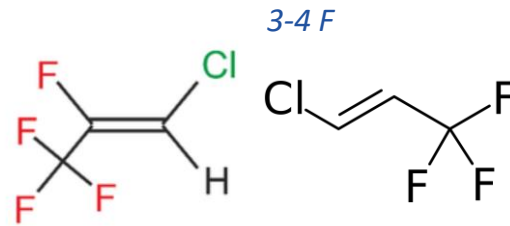
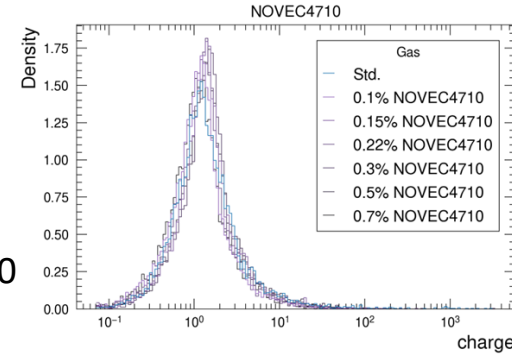
3M™ Novec™ 5110  
(CF<sub>3</sub>C(O)CF(CF<sub>3</sub>)<sub>2</sub>)

GWP <1 - Atm. lifetime 15 days  
High boiling point: 27 C  
Sensitive to UV radiation  
Higher HV working point  
Not very good performance



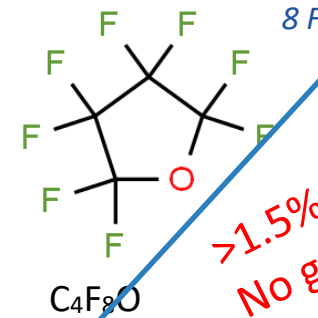
3M™ Novec™ 4710  
((CF<sub>3</sub>)<sub>2</sub>CFCN)

GWP 2100 - Atm. lifetime 30 years  
Good performance, but it may react with H<sub>2</sub>O



AMOLEA™ HFO-1224yd  
(CF<sub>3</sub>-CF=CHCl)

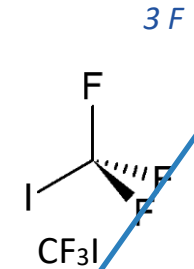
GWP <1 - Atm. lifetime 20 days  
Good performance.  
Presence of Cl (aging test mandatory)



C<sub>4</sub>F<sub>8</sub>O  
GWP 8700

Atm. lifetime >3000 years

>1.5% needed  
No gain in GWP



CF<sub>3</sub>I  
GWP 0.4

Atm. lifetime 6 days

toxic

# Not only detector performances....

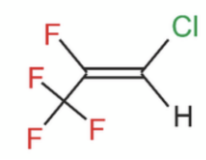
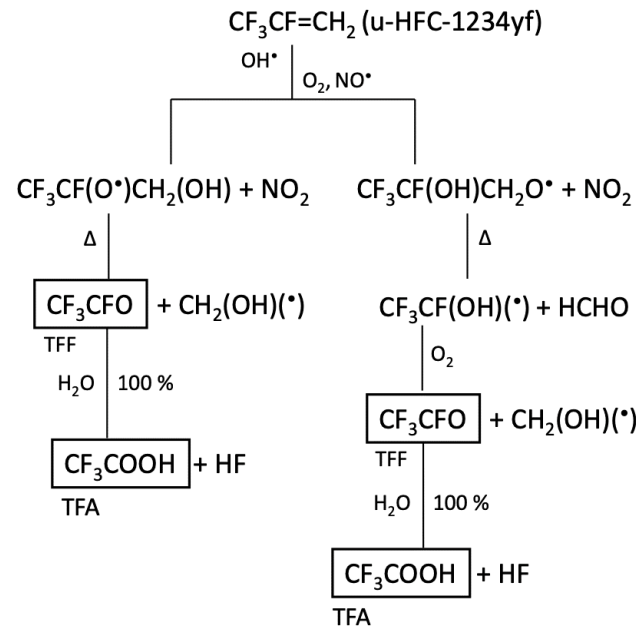
Two factors identify the greenhouse gases and their effects on climate: the radiative efficiency and lifetime in the atmosphere

*The lower are the GWP and the lifetime, the easier is the creation of sub-products*

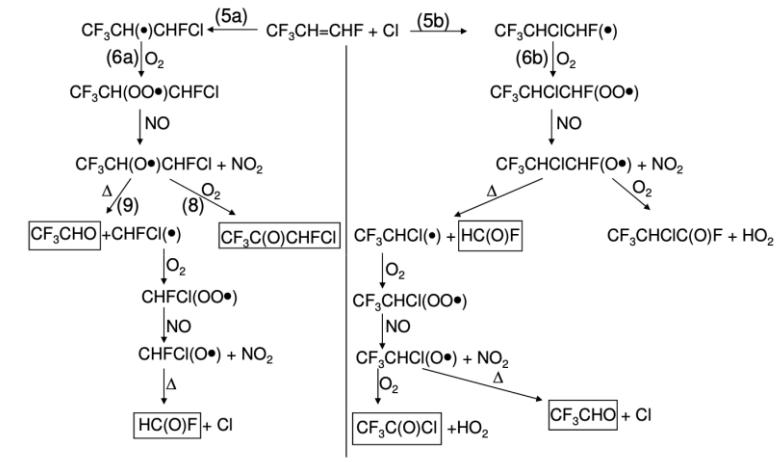
*Do these sub-products have an impact on detector lifetime?*

Three factors determine the atmospheric lifetime

- Rain out → Water solubility
- Oxidation → Reactivity with OH
- Photolysis → UV absorbance



HFO-1224yf  
 Degradation products:  
 TFA, CO<sub>2</sub>, HF, HCl



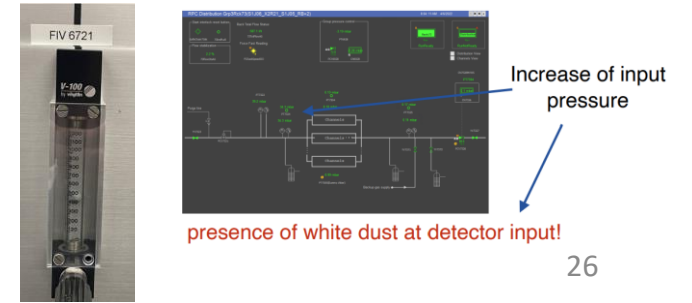
## Hydrofluoric Acid (HF)

HFO produces much more HF than R134a in RPC detectors

## Trifluoroacetic acid (TFA)

- HFO1234ze is estimated to break down into TFA at less than 10%, whereas R-1234yf will break down into TFA at 100% (R134a at 21%)
- TFA highly soluble: no formation of insoluble salts
- Phytotoxic

Observation with ppm of HCFC (importance of long-term validation tests):



## New detectors for upgrades (ATLAS-BIS/BI)

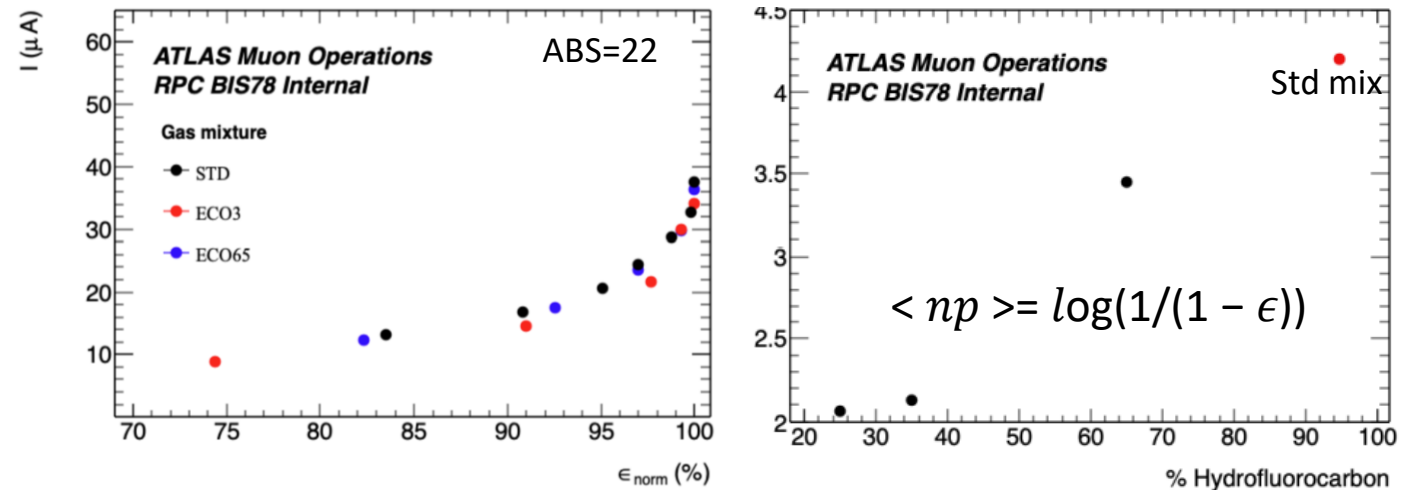
- Triplet (3 single gaps; 1 mm gas gap)
- **Very effective Faraday cage** allowing to operate with low noise and trigger on 2/3 coincidence
- **New FEB with new chip:**
  - . Low noise
  - . Allowing threshold as low as 1 fC
    - from 30 to 3 pC per photon count
    - **Increased rate capability (x10)**
    - **Low ageing (÷10)**
- 3 independent singlets providing 3D+time
- Combined  $\sigma_t$  160 ps

## New detectors for upgrades (CMS-iRPC)

- double gap (1.4 mm gas gap)
- new FEB:
  - . PETIROC2C re-designed
  - . Threshold < 50 fC
  - . TDC  $\sigma_t$  20 ps
  - . TDC and detector  $\sigma_t \sim 160$  ps
    - position resolution of  $\sim 1.6$  cm

Mixtures from ECOGAS@GIF

collaboration: ECO3 = 25%HFO/70%CO2/4%ISO/1%SF6  
 ECO2 = 35%HFO/60%CO2/4%ISO/1%SF6  
 ECO65 = 65%HFO/30%CO2/4%ISO/1%SF6



From:

[CERN EP Seminar: Summary of RPC workshop](#)

[RPC 2022 workshop: Overview:](#)

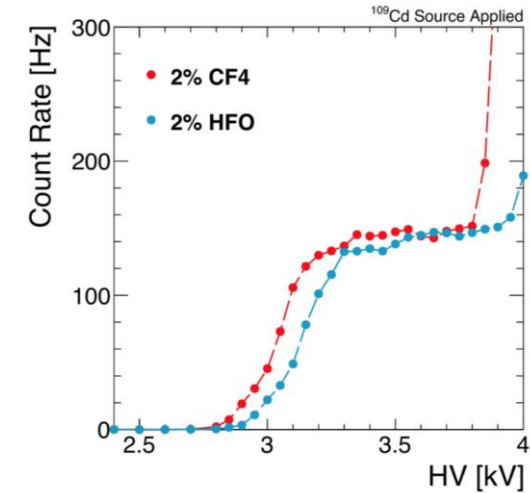
[Exploring the performance limits of the new generation of ATLAS RPCs](#)

[XVI Workshop on Resistive PlaCMS iRPC FEB development and validation](#)

*CF<sub>4</sub> is used in different types of particle detectors to prevent aging, to enhance time resolution or because of its scintillation photon emission*

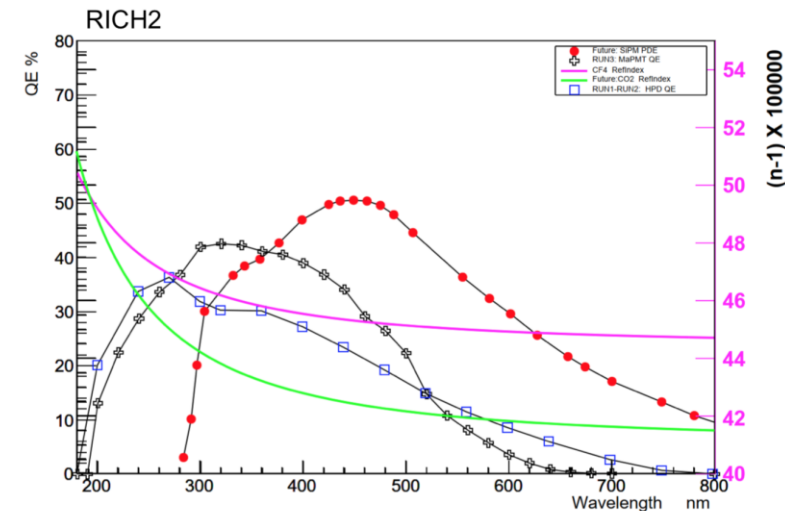
## CMS CSC studies (K. Kuznetsova)

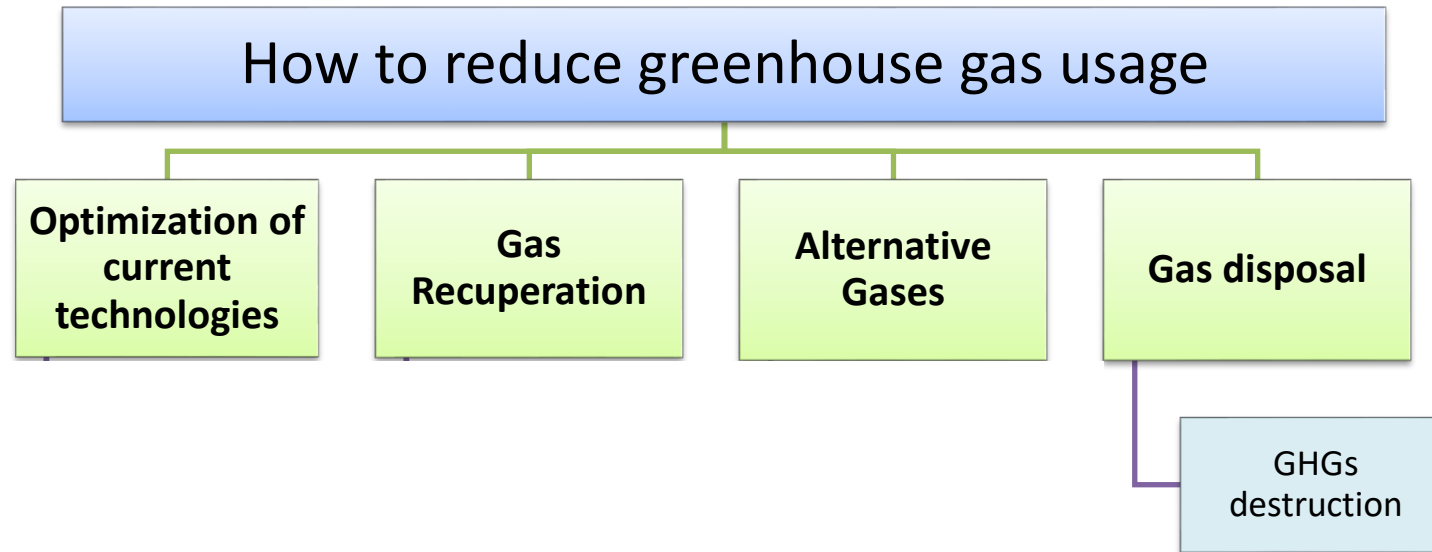
- CF<sub>4</sub> is a source of fluorine radicals to protect against anode ageing
  - Now 10% CF<sub>4</sub> in CSC gas mixture
- Two possible approaches to reduce GHG consumption (beyond the recirculation and recuperation systems)
  - **Decrease the CF<sub>4</sub> concentration**: preliminary results show that 5% could be safe for operation
  - **CF<sub>3</sub>I and HFO1234ze not best candidates**
  - Look for other alternatives to CF<sub>4</sub> on-going



## LHCb RICH studies (S. Easo and O. Ullaland)

- RICH detectors use either CF<sub>4</sub> or C<sub>4</sub>F<sub>10</sub>
  - Necessary for good refractive index
- Replacement of C<sub>4</sub>F<sub>10</sub> with **C<sub>4</sub>H<sub>10</sub>**
  - Refractive index matches very well
  - But C<sub>4</sub>H<sub>10</sub> flammable
- Replacement of CF<sub>4</sub> with **CO<sub>2</sub>**
  - Under investigation
- Use of SiPM to reduce the chromatic error and increase the yield





Industrial system able to destroy GHGs avoiding their emission into the atmosphere have been considered.

Abatement plants are employed when GHG are polluted and therefore not reusable.

Very high costs if compared with recirculation and recuperation plants.

Found also companies available to take PFC/HFC based mixture for disposal, but extremely expensive.

In addition, the **GHGs disposal is not helping in the current market situation where availability decreases and price increase.**

On the contrary, the advantages of gas recuperation plants are going beyond the reduction of GHG emissions and the economical aspects:

the availability of recuperated gases can mitigate difficult situations when there is a shortage of fresh gas.

In 2022 when there was a major disruption of CF<sub>4</sub> availability in Europe: the CMS-CSC detectors could be operated and therefore participate to the CMS data taking only thanks to the usage of recuperated CF<sub>4</sub>.

## GHGs usage in particle detectors

### F-gas regulation

- Due to the environmental risk, “F-gas regulations” started to **limit the GHGs usage and requiring recovery, proper servicing to prevent emission** (EU case)
- **availability and price are today critical** for old F-gases

### Detector design

- It is fundamental to look not only at detector performance but also at the **infrastructure**
- New generation detectors should **limit the risk of developing leaks**
- If detectors are tight, gas consumption can be limited thanks to **gas recirculation and recuperation plants** (useful not only for GHGs but also for any expensive gases)

## Strategies for GHG usage optimization

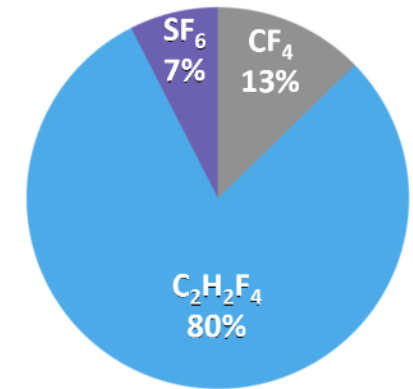
### Optimization of current technologies

- Particular attention to gas system and detector operation
- Gas systems upgrade beyond original design
- Improved/higher gas recirculation

## Gas recuperation plant

- **Gas recuperation will be effective only if leaks at detector level will be reduced**
- R&D costs for R134a recuperation system is well justified by running costs
- R134a recuperation prototype0 is more complicated than expected but showed good performance:
  - . ~ 80% recuperation efficiency and good gas quality
- Consolidation of existing plants (CF<sub>4</sub>, C<sub>4</sub>F<sub>10</sub>) ongoing:
  - . CMS-CSC-CF<sub>4</sub> recuperation efficiency increased to 70%
  - . LHCb-RICH2-CF<sub>4</sub> installed
  - . LHCb-RICH1-C<sub>4</sub>F<sub>10</sub> design ongoing

*Recuperation of R134a can drastically decrease GHG consumption*



## New eco-gases

- New low-GWP gases can easily break
  - **Sensitive to UV, humidity and oxidation**
  - HF, TFA sub-products are produced and their effects on long-term operation need to be evaluated
- **Missing cross-section to perform simulation studies**
  - Dedicated measurements needed
- R-1234ze, NOVEC, ... are currently the main fluorinated alternative but:
  - For 2 mm gas gap RPC, the addition of a 4th mixture components (CO<sub>2</sub>, ?) is needed to maintain reasonable HV working point
  - availability and price are still a matter of concern
  - long term operation in high radiation environment to be studied
- **New generation detectors and electronics seems to be more compatible with new eco-friendly gases** than old-generation 2 mm gas gap RPC
  - Upgrades for LHC experiments (ATLAS and CMS RPC Phase2 upgrades)



## GHGs abatement/disposal

- Commercial systems exist. Adopted when gases cannot be reused.
- Heavy infrastructures required (CH<sub>4</sub>+O<sub>2</sub> supply, Wastewater treatment)
- Since availability/price can become a real problem in the future it is better to optimize consumption
- Destruction in external companies: more expensive than Gas abatement system.

## Additional challenge: finding right profile for resources for R&D and new recuperation plants operation:

- Chemist, industrial chemistry engineer, engineer, physicist
- **Right level of resources** should be allocated to GHGs related activities since the beginning (detector and infrastructures design phase)

Industrial system able to destroy GHGs avoiding their emission into the atmosphere have been considered  
Abatement plants are employed when GHG are polluted and therefore not reusable.

However, PFCs are stable and difficult to abate

Carbon-fluorine bond is the fourth strongest single bond

- Multiple C-F bonds on the same carbon enhance stability
- C-C or C-H bonds are weaker and decrease stability
- S-F bond is strong too

Stability is reflected in atmospheric lifetimes

Stability is closely related to ease of abatement

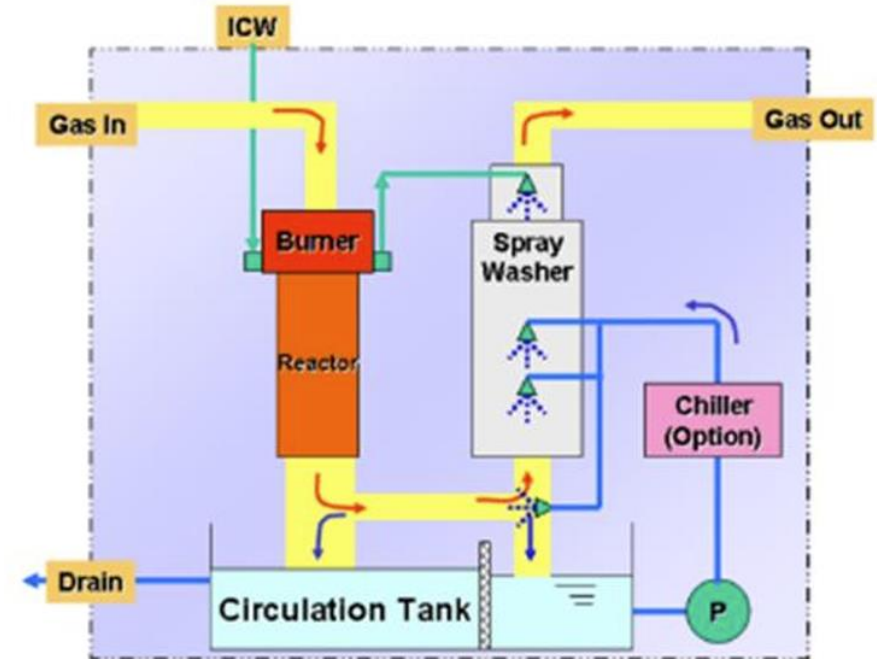
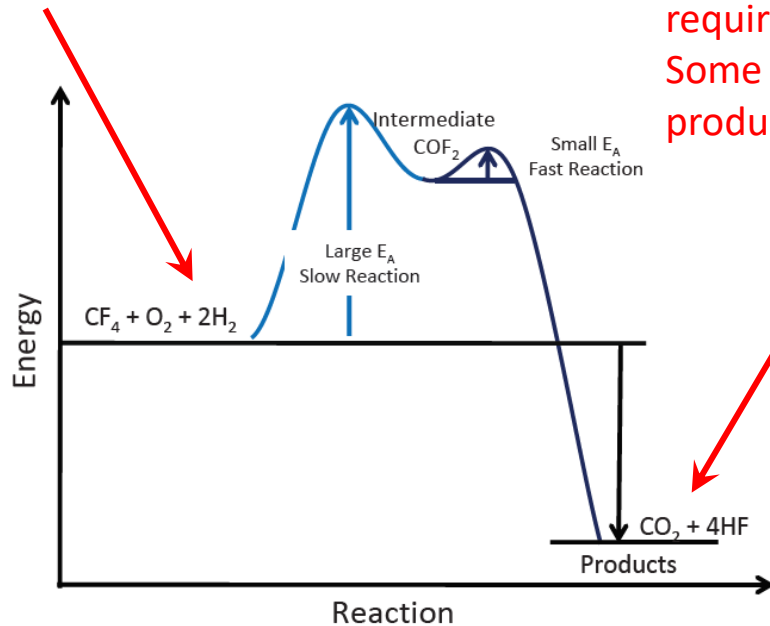
Fluorinated gas lifetime in atmosphere (years)	
<b>CF4</b>	<b>50000</b>
C2F6	10000
<b>SF6</b>	<b>3200</b>
C3F8	2600
c-C4F8	3200
NF3	740
CHF3	270
<b>C2H2F4</b>	<b>14</b>
CH2F2	5

Reaction of  $\text{CF}_4$  to  $\text{CO}_2$  and HF is very exothermic, but also requires a big push to break the very strong C-F bonds  
 -This is why  $\text{CF}_4$  abatement is so difficult  
 -Actual reaction is much more complicated than shown

Burn-wet is the primary POU (point of use) abatement technology

Huge quantities of  $\text{O}_2$  and  $\text{CH}_4$  needed to overcome  $E_A$   
 Some  $100 \text{ m}^3/\text{day}$  needed

Final product is HF!  
 One liter of  $\text{CF}_4$  generates 4 liters of HF  
 Water treatment plant required!  
 Some  $\text{m}^3/\text{day}$  wastewater produced



Small commercial systems for burn-wet exist but require heavy infrastructures:

- $\text{CH}_4 + \text{O}_2$  supply
- **Waste water treatment**

Industrial system able to destroy GHGs: two options considered



*Ebara G5 system*



*Edwards ATLAS Etch system*

Approximative cost of burner system: 130 kCHF

Utilities & services	Consumption
Fuel (city gas)	40-130 m <sup>3</sup> /day
Soft water	15 m <sup>3</sup> /day
Chilled water	10-90 m <sup>3</sup> /day
O <sub>2</sub> (combustion)	80 m <sup>3</sup> /day
N <sub>2</sub> (purge)	200-350 m <sup>3</sup> /day
Dry Air (purge)	200 m <sup>3</sup> /day
Ventilation	1-3 m <sup>3</sup> /min
Operation cost	9-16 kCHF/month

abatement phase	Chemical reaction
Burning phase	$\text{CF}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{F}_2$
	$\text{SF}_6 + \text{O}_2 \rightarrow \text{SO}_2 + 3 \text{F}_2$
	$2 \text{C}_2\text{H}_2\text{F}_4 + 5 \text{O}_2 \rightarrow 4 \text{CO}_2 + 2 \text{H}_2\text{O} + 4 \text{F}_2$

## Waste water treatment plant



abatement phase	Chemical reaction
Washer phase	$2 F_2 + 2 H_2O \rightarrow 4 HF + O_2$
	$SO_2 + H_2O \rightarrow H_2SO_3$
	$SO_3 + H_2O \rightarrow H_2SO_4$

Sewage resulting from operation are compressed for disposal

Approximative cost of wastewater treatment system:  
500 kCHF

The EnviroChemie “STEP” wastewater treatment plant  
One already in operation at CERN and similar to what we would need

	Recovery systems			Abatement systems		
gas potentially recovered (2012 -2025)	R134a (kg)	SF6 (kg)	CF4 (kg)	R134a (kg)	SF6 (kg)	CF4 (kg)
Beginning of operation	2023	~2025	2012			
	17200	96	6505	0	0	0
Money saved from gas recovered (kCHF) (2012 -2025)	~500			0		
Money spent for construction – CAPEX (kCHF)	525			617		
M&O (kCHF/year)	15			16		
Manpower (kCHF/year)	60			84		
Emissions (tCO2eq/year)	39114			2600		