Work package: **Alternatives to liquid fluorocarbons for detector cooling applications at CERN**

<u>Abstract:</u> Many mono-phase convective detector cooling applications at CERN use perfluorohexane C6F14, a green-house gas with the GWP of 9300. The purpose of the proposed work package is to identify and validate other fluids as sustainable environment-friendly alternatives to C6F14. This activity, initiated by the CERN LHCb group and endorsed by the CERN Detector Cooling Project, requires participation of the CERN radiochemistry group to perform chemical and radiolytical tests. Fluoroketone C6K, recently proposed as a coolant for the SciFi Tracker upgrade at the LHCb, is an example of a possible drop-in replacement of C6F14. Featuring the thermo-physical properties similar to C6F14 and a comparable cost, C6K has a dramatically smaller impact on the environment with its GWP of ≈1. The initial time frame of this work package is one year starting from January 2015.

1. Justification

As part of its general safety policy, CERN is committed to minimize the environmental impact of the research activities [1]. One of concerns in this domain is emissions of PFCs, potent green-house gases which are still being released by CERN in significant quantities. A sizable fraction of these emissions falls to C6F14 often used in detector cooling systems as a heat transfer fluid. For example, in LHCb C6F14 accounts for ~5 ktCO_2e, or one third of all GHG emissions by this experiment. A similar situation, even to a larger extent, is observed in other LHC experiments. The programme [2] to monitor and reduce PFC emissions at CERN is ongoing under the supervision of the CERN HSE Unit. In the long term, it implies promoting environment-friendly cooling technologies for new developments, in particular for LHC detectors upgrades, and search for drop-in alternatives to C6F14 for the existing systems with irreducible coolant losses.

These issues are addressed in the LS2 LHCb upgrade project which includes a replacement of the existing Outer Tracker with a new SciFi Tracker [3] requiring a large cooling system for its silicon photo-detectors, to operate them at down to -40°C. After evaluation [4] of several candidate options, a conventional mono-phase liquid cooling technology had been adopted, with the emphasis on using of a new thermal management fluid, fluoroketone 3M™ Novec 649[1] [5], having the GWP, essentially, identical to that of CO2 and, at the same time, the thermo-physical properties very similar to those of C6F14. This solution, reflected in the LHCb Tracker Upgrade TDR [1] and, recently, in the detector cooling proposal [6] for the emittance measurements at the LHC (BGV project), was supported by the thermal mock-up tests performed in 2014 by the CERN LHCb group [7]. As a coolant, C6K turned out to be quite similar to C6F14.

The idea of using C6K was endorsed by the CERN Detector Cooling Project [8] and has attracted attention of the CERN EN-CV group – in the broader context of finding alternative(s) to GHGs in cooling applications at CERN.

[1] $C_6F_{12}O$, further referred to as C6K for brevity.

2. The task

The present work package is aimed at

- validation of C6K for use in LHCb and other large LHC detectors, as a drop-on replacement of C6F14 in cooling applications at various temperature conditions and radiation environments. The work should include a detailed chemical and radiolytical characterization of C6K, like it was earlier done for C6F14 [9];
- finding and evaluation of other prospective environment-friendly alternatives to C6F14 which appeared on the market during the last decade.

The TS-VCS-SCC group [12] of CERN, which performed C6F14 validation in the past [9], has been contacted [10] to discuss a draft plan of a similar study for C6K. The intent of the present work package is to set up a joint task force with the Detector Cooling Project, LHCb SciFi project and TS-VSC-SCC group as participants.

Given the very small expected radiation damage to the coolant in the SciFi application [11], it is proposed to start with a pilot study of chemical properties of C6K, especially its reactivity with liquid water (reported by the manufacturer, 3M company [13])[2]. A full-scale radiological study of C6K and other prospective liquid coolants, with irradiations at CERN or external facilities, can be anticipated further on.

3. Deliverables

- An up-to-date market survey of different classes of commercial coolants suitable as sustainable alternatives to C6F14 and heavier fluorocarbons for mono-phase cooling applications at CERN.
- In-depth analysis of the published data about prospective fluids, taking into account their core properties as coolants and secondary aspects important for the intended application in detector cooling systems (possibility of drop-in replacement of existing GHG coolants, dielectricity, radiation resistance, potential long-term chemical effects etc).

In particular, the following information about C6K should be acquired:

- Reactivity with water[3]:
  - the hydrolysis reaction kinetics at different water concentrations;
  - its dependence on the fluid temperature;
  - reactivity with water vapour and solid phase (frost, ice)
- appropriate methods of in-line rectification (removal of moisture and the corrosive hydrolysis products from the circulating coolant);

[2] The cooling system design has to take the potential secondary corrosive properties of the coolant into account, like for other coolants exhibiting corrosive behaviour under certain anomalous circumstances, e.g. demineralized water.

[3] Studies of academic interest can be performed in parallel, for sake of a possible scientific publication, but their usefulness should be agreed upon within the framework of the proposed work package.

- methods of early detection of hydrolysis products in the coolant, to signal the problem in real time;
- compatibility with metals and their resistivity to the C6K hydrolysis products (PFPA, HF). The current alternatives, in the order of decreasing relevance), are: titanium "grade 5" alloy, stainless steel, aluminium and copper
- Radiolysis under integral ionizing doses of 10, 100, 1000 Gy and neutron fluence of 10^{12} neq/cm^2, with the stress on formation of hazardous compounds and methods of their real-time removal from the circulating fluid.

4. Time frame and required resources

The first round of studies has to be completed by the end of 2015. The estimated date of start is January 2015. The CERN LHCb group (PH-LBO) has already allocated ½ FTE·year (PJAS) to this work. The additional required manpower is ~1.5 FTE·year (including ½ FTE chemist in TS-VSC-SCC, ½ FTE PJAS at PH-LBO and ½ FTE Ph.D. student at EN-CV). The direct costs of 20-30 kCHF include purchasing of fluid samples and chemicals, manufacturing containers for irradiation tests and, optionally, outsourcing part of the analytical and irradiation tasks. Indirect expenses include the use of CERN irradiation facilities (CHARM, GIF++) and technical services (cleaning etc).

References

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13. From the 3M Product Bulletin "What you need to know about Novec…."
    - *"Novec 1230 reacts with moisture to form HFC-227ea and pentafluoropropionic acid (PFPA).*
    - *"Novec 1230 fluid **reacts with water only when dissolved in water and it is only minimally soluble in water**. Accordingly, only a very small amount of acid is formed when Novec 1230 fluid contacts liquid water and **no acid is formed when Novec 1230 fluid contacts water vapor.** This has been verified through numerous laboratory and full-scale tests in which Novec 1230 fluid was discharged into a humid atmosphere and monitored via methods such as FTIR. No formation of PFPA has been detected."*

Nomenclature

- **PFC** – perfluorocarbons
- **GWP** – global warming potential, measured in CO2 equivalent my mass
- **GHG** – greenhouse gas
- **HSE** – Occupational Health & Safety and Environmental Protection Unit of CERN, formerly the Safety Commission
- **SciFi** – scintillating fibres, the technology chosen for the LHCb outer tracker upgrade
- **C6F14** – liquid perfluorinated compound C_6F_{14} (CAS 355-42-0); the inert, dielectric and relatively radiation-resistant fluid widely used as a coolant at CERN.
- **C6K** – perfluoroketone $C_2F_5C(O)CF(CF_3)_2$ (CAS 756-13-8), the inert fluid historically used, as 3M Novec 1230, for clean fire suppression. Under the trade name Novec 649, it is also sold by 3M as a fluid for thermal applications, like 1- and 2- phase (full immersion) cooling. The radiation resistance of C6K has not been systematically studied, yet. Unlike C6F14, C6K is claimed to be weakly reactive with liquid water, producing an organic acid, but this property requires a quantative study under the typical detector cooling conditions.
- **PFPA** – pentafluoropropyonic acid
- **HF** – fluoric acid (hydrogen fluoride)