



CERN
CH1211 Geneva 23
Switzerland

EN Engineering Department

EDMS NO.
1489771

REV.
0.2

VALIDITY
draft

REFERENCE
WP-C6K-2015

Date: 2015-02-25

WORK PACKAGE

Alternatives to liquid fluorocarbons for detector cooling applications at CERN

Abstract

Many mono-phase convective detector cooling applications at CERN use perfluorohexane C6F14, a greenhouse gas with the GWP of 9300. The purpose of the proposed work package is to identify and conduct initial validation tests of other fluids as sustainable environment-friendly alternatives to C6F14. This activity, initiated by the CERN LHCb group (PH-LBO) and further endorsed by the CERN Detector Cooling Project, requires participation of chemists (inside or outside CERN) to perform chemical and radiolytical characterization. An example of a possible drop-in replacement of C6F14 is the fluoroketone C6K with GWP of ≈ 1 , recently proposed as a coolant for the SciFi Tracker upgrade in LHCb. The time frame of this project is about one year starting from February 2015. An early work is already ongoing.

DOCUMENT PREPARED BY:
Petr Gorbounov (PH-LBO)

DOCUMENT TO BE CHECKED BY:
Michele Battistin (EN-CV-PJ)
Eric Thomas (PH-LBO-DO)
Olivier Crespo (EN-CV-DC)

DOCUMENT TO BE APPROVED BY:
S. Bertolucci (DG-DI-DRC)
... (EN)
... (TE)
Mauro Nonis (EN-CV)
Rolf Lindner (PH-LBO-DO)

DISTRIBUTION LIST:

M.Taborelli, B.Teissandier, R.Setnescu, P.Gorbounov, M.Battistin, E.Thomas, O.Crespo, L.Zwalinski, P.Tropea, J.Gulley, S.Kleiner, E.Cennini



HISTORY OF CHANGES

| REV. NO. | DATE | PAGES | DESCRIPTIONS OF THE CHANGES |
|----------|------------|-------|---|
| 0.1 | 2015-02-25 | 8 | Draft |
| 0.2 | 2015-05-03 | 10 | Draft, with the style updated, Michele's corrections, deliverables updated (with more stress on purification), the active role of TE-VSC-SCC reduced to a "limited participation", following M.Taborelli's objections |



TABLE OF CONTENTS

| | | |
|--|---------------------------------------|---|
| Alternatives to liquid fluorocarbons for | detector cooling applications at CERN | |
| | | 1 |
| 1. INTRODUCTION..... | | 4 |
| 2. PURPOSE..... | | 4 |
| 3. DELIVERABLES..... | | 5 |
| 4. PLANNING | | 6 |
| 5. BUDGET AND REQUIRED RESOURCES | | 7 |
| 6. REFERENCES..... | | 7 |
| APPENDICES | | 9 |



1. INTRODUCTION

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 PFCs¹, potent green-house gases (GHG) covered by the Kyoto Protocol to the UN Framework Convention on Climate Changes, which are still being released by CERN in significant quantities. A sizable fraction of these emissions falls to C6F14 used in many detector cooling systems as a heat transfer fluid. For example, in LHCb C6F14 accounts for ~5 ktCO₂e, 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 run, 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 649² [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.

2. PURPOSE

The present work package (WP), earlier discussed at the PH management level [9], 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 chemical and radiolytical characterization of C6K, relevant for the intended application. CERN has already an experience of the C6F14 validation for cooling applications [10]. Depending on the availability of CERN chemists (TE-VSC-SCC section), the new study can be performed either at CERN or be outsourced to an external laboratory.
- finding and evaluation of other prospective environment-friendly alternatives to C6F14 which appeared on the market during the last decade.

¹ The acronyms used in the text are explained in Appendix A.1

² C₆F₁₂O, further referred to as C6K for brevity.



- designing and testing methods of in-line drying and purification of C6K and other prospective new liquid coolants from undesired by-products resulting from interactions within the cooling system and/or exposure to radiation³.

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 [12])⁴. 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 for mono-phase liquid cooling applications at CERN.
- In-depth analysis of the published data about prospective fluids, taking into account their core properties as coolants (thermal conductivity, viscosity etc) and secondary aspects important for the intended application in detector cooling systems (possibility of drop-in replacement of existing GHG coolants, electrical insulation properties, radiation resistance, potential long-term chemical effects etc).

The following information about C6K should be acquired as a result of experimental tests within the framework of the present package⁵:

- Reactivity with water:
 - the hydrolysis reaction kinetics at different temperatures and water concentrations;
 - reactivity with water vapour and solid phase (frost, ice);
- appropriate methods of in-line rectification (removal of moisture and the corrosive hydrolysis and radiolysis products from the circulating coolant);
- methods of early detection of corrosive and/or hazardous 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 metals of interest (in the order of decreasing relevance) are: titanium "grade 5" alloy, stainless steel, aluminium and copper;
- radiolysis effects under integral ionizing doses of 10, 100, 1000 Gy and neutron fluence of 10^{12} neq/cm², with the stress on formation of hazardous or undesirable compounds and methods of their real-time removal from the circulating fluid.

³ Because of greater chemical reactivity of new fluids, compared to C6F14 and other PFCs, the desiccants and acid absorbers currently used for C6F14 can be incompatible with these fluids.

⁴ The cooling system design has to take into account potential secondary corrosive properties of the coolant under anomalous circumstances, e.g upon an accidental water intake in the event of breaking the cooling circuit hermeticity.

⁵ 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 this WP.

The “radiation resistance” should be evaluated according to the intended use as liquid heat transfer agent for particle detector cooling. The relevant characteristics are viscosity, freezing and boiling points, density, development of solid and gaseous fractions, as well as undesirable (reactive, hazardous) liquid impurities that cannot be removed from cooling circuits by filtering.

Contributions are required from different groups involved in this WP, as listed in the table Table 1.

| Group | Contribution/interaction |
|--|--|
| PH-LBO | <ul style="list-style-type: none"> - coordination (till December 2015), preparatory work, market survey - procurement of sample fluids (together with EN-CV) - irradiation of the samples at CERN and off-CERN centres - physical laboratory tests (heat transfer properties, viscosity etc), together with EN-CV |
| EN-CV | <ul style="list-style-type: none"> - construction, certification and cleaning of test vessels for sample irradiation (Appendix A.1) - interaction with interested CERN groups, via the CERN-wide “Detector Cooling Project” (DCP) - follow-up, coordination as of December 2015 |
| Chemical laboratory (TE-VSC-SCC or external) | <ul style="list-style-type: none"> - pre-irradiation tests of (reactivity of C6K with water, assessment of material compatibility tests performed earlier at PH-LBO, evaluation of the initial sample purity); - study of water and acids removal methods compatible with the coolants under study (with possible outsourcing of this task); - study of radiolysis effects in irradiated samples, effects of impurities; - assessment of “radiation resistance” of tested fluid(s) with regards to the intended detector cooling application (together with PH-LBO and EN-CV). |

Table 1 – Task sharing between the participating groups.

4. PLANNING

The first round of studies, focused on C6K, has to be completed by the end of 2015. It will be coordinated by P. Gorbounov of PH-LBO (SciFi Tracker group). The follow-up studies (as of December 2015) will be coordinated by EN-CV. It is foreseen to perform at least two irradiations of the fluid samples (with charged particles and neutrons at the CHARM facility at CERN). The C6K validation report will be prepared by January 2016. The tentative planning is presented in the table Table 2. A more detailed planning taking into account the availability of TE-VSC-SCC resources and the results of pre-irradiation studies will be available as a separate file in the same EDMS page.

| Action | Planning |
|--------|----------|
|--------|----------|



| | |
|---|-------------------------------|
| Work package approval | March 2015 |
| Early material compatibility tests | Ongoing (since December 2014) |
| Market survey | January–March 2015 (ongoing) |
| Design and production of test vessels | March-May 2015 |
| Procurement of fluids for pre-irradiation tests | February 2015 |
| Pre-irradiation studies | March-December 2015 |
| First irradiation campaign at CERN | May 2015 |
| Second irradiation campaign | September 2015 |
| Post-irradiation studies | May-December 2015 |
| Physical tests (cooling) | April-November 2015 |
| Summary report | December 2015-January 2015 |

Table 2 — Proposed planning of the WP.

5. BUDGET AND REQUIRED RESOURCES

The CERN LHCb group (PH-LBO) has already allocated ½ FTE·year to this work (P. Gorbounov, PJAS). The additional required manpower is ~1.5 FTE·year, including

- ½ FTE chemist in TS-VSC-SCC,
- ½ FTE PJAS at PH-LBO (P. Gorbounov, June-November 2015)
- 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. Should outsourcing of some or all analytical and irradiation tasks be required, an additional funding will be needed (no cost estimate is available, yet). Indirect expenses include the use of CERN irradiation facilities (CHARM, GIF++) and technical services (cleaning etc). Indirect contributions to the WP expenses are also expected from large users of PFCs at CERN, like ATLAS, CMS etc.

6. REFERENCES

1. HSE safety objectives for 2014, CERN Bulletin, Issue 18-19/2014 April 2014, <https://cds.cern.ch/journal/CERNBulletin/2014/18/Announcements/1694520?ln=en>; CERN and Environment, <http://environmental-impact.web.cern.ch/environmental-impact/>
2. ILK review for PFC (2005) [EDMS 634952](#), M.Battistin (2006) [EDMS 774749](#); PFC monitoring and register management procedure, [EDMS 774749 v2](#), M.Battistin (2006) ; 2013 LHCb register of PFCs, E. Thomas (2013) [EDMS 1311056](#) ; all other CERN registers of PFC: EDMS search (greenhouse)



3. Chapter 3 "SciFi Tracker" of LHCb Tracker Upgrade Technical Design Report CERN-LHCC-2014-001; LHCb-TDR-015
<https://cds.cern.ch/record/1647400/files/LHCb-TDR-015.pdf>
4. a) Joint project "SiPM Cooling" LHCb/EN-CV
<https://edms.cern.ch/document/1271014/, Issue 181;>
b) SiPM Cooling Workshop, 17 October 2013 <https://indico.cern.ch/event/273434/>
5. a) 3M Novec 649 Engineered Fluid, [Product information;](#)
b) P. Gorbounov "3M Novec 649 as a replacement of C₆F₁₄ in liquid cooling systems", [EDMS 1421023](#) and https://twiki.cern.ch/twiki/pub/LHCb/C6K/NOvec_Memo_2.pdf
6. Detector Cooling for the BGV Demonstrator in the LHC , [EDMS 1439028](#)
7. a) P. Gorbounov, E. Thomas, "Thermal measurements with the SciFi read-out box mockups", LHCb Internal Note [LHCb-INT-2014-048](#) , in preparation;
b) P. Gorbounov, Summary Report on SiPM cooling at the 73rd LHCb week, September 2014,
<https://indico.cern.ch/event/335518/contribution/7/material/slides/1.pdf>
8. CERN Detector Cooling Project, <http://project-detector-cooling.web.cern.ch/project-detector-cooling/>
9. E. Thomas, presentation "GHG: alternative fluid workpackage", [EDMS 1479814 v.1](#)
10. M.Battistin, S.Ilie, R.Setnescu, B. Teissandier "Chemical and radiolytical characterization of some perfluorocarbon fluids used as coolants for LHC experiments", TS-Note-2006-010, [EDMS 804849](#)
11. P.Gorbounov, Assessment of the radiation damage to the coolant in SciFi tracker, November 2014, [EDMS 1421023](#) and
https://twiki.cern.ch/twiki/pub/LHCb/C6K/Memo_on_irradiation_damage_for_C6K.pdf
12. 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."

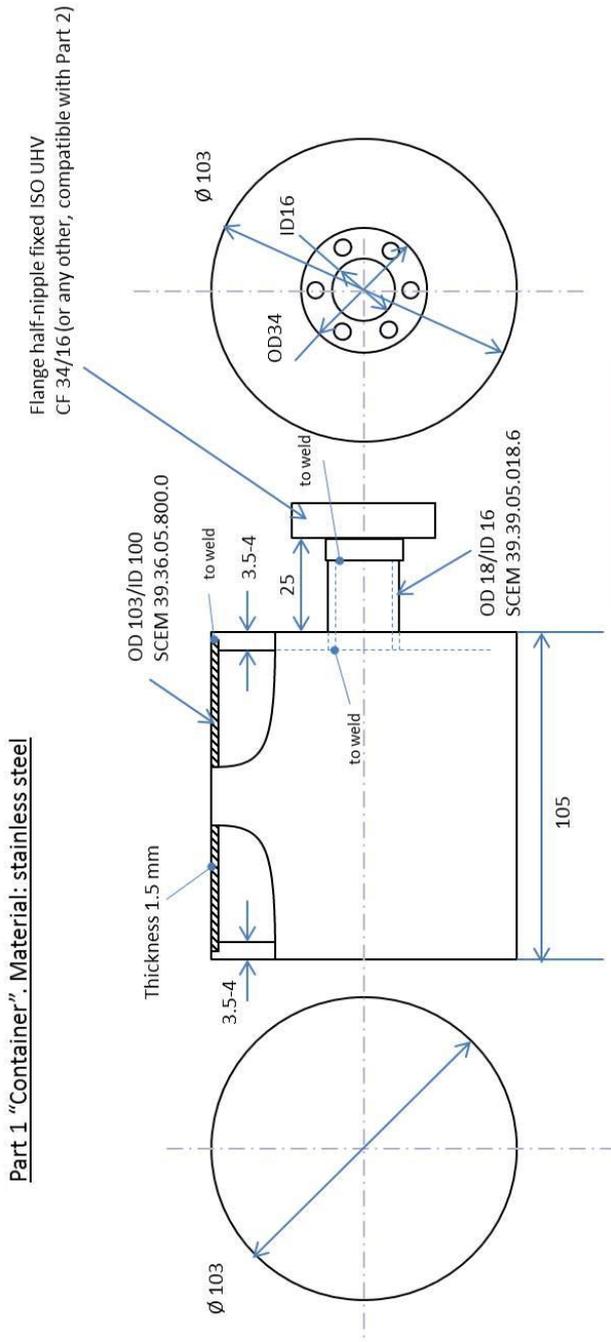


APPENDICES

A.1 Acronyms and explanation of terms

- 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 quantitative study under the typical detector cooling conditions.
- GHG** greenhouse gas
- GHP** global warming potential, measured in CO₂ equivalent my mass
- HF** fluoric acid (hydrogen fluoride)
- HSE** Occupational Health & Safety and Environmental Protection [Unit](#) of CERN, formerly the Safety Commission
- PFC** Perfluorocarbon(s)
- PFPA** [pentafluoropropyonic acid](#), a perfluorinated carboxil acid, the analog of propionic acid. A relatively strong organic acid (but considerably weaker than strong inorganic acids).
- SciFi** scintillating fibres, the technology chosen for the LHCb outer tracker upgrade
- WP** work package

A.2 Test vessels for irradiation of the fluid samples



Matching flange –adapter for
Sagana/Swagelok/Gyrolok/VCR
Connection (female)

P. Gorbounov
Sketch of the test container
Version 7.11.2014 v. 1.0

Part 2 "Valve". Material: stainless steel!