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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 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 the 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.

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HISTORY OF CHANGES

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0.1	2015-02-25	8	Draft
0.2	2015-03-05	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/support"
0.3	2015-03-11/16	16	Appendix 3 is added, with a more detailed description of the work plan
0.4	2015-03-19		Minor corrections, EN-MME-MM is mentioned along with TE-VSC-DCC



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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/year, 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 GWP₁₀₀≈1 (i.e. similar 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 [3] 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 (DCP) [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 presented at the CERN 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 on-line drying, degassing 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, compatibility with materials, 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 package:

- Methods and techniques of *composition analysis* compatible with C6K;
- Reactivity with water*, as function of temperature and water phase; dynamics of water extraction in case of accidental direct contact of liquid water with C6K;
- appropriate methods of *on-line rectification* (removal of moisture and the corrosive hydrolysis and radiolysis products from the circulating coolant);
- methods of *early detection* of corrosive and hazardous products in the coolant, to signal the problem in real time;
- compatibility with metals*, resistivity of metals to the C6K hydrolysis products (mainly PFFA). The current metals of interest (in the order of decreasing relevance) are: titanium "grade 5" alloy, stainless steel, aluminium and copper;
- radiation resistance* of the fluid to the integral ionizing doses of 50 and 1000 Gy and neutron fluence of 10^{12} neq/cm², taking into account the intended use as liquid heat transfer agent. The stress should be on development of solid and gaseous fractions, undesirable (reactive, hazardous) liquid impurities, as well as changes in the relevant physical properties of the liquid fraction: viscosity and boiling point.

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.



Contributions are required from different groups involved in this WP, as listed in the table Table 1 (see more details in the Appendix A.3).

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, compatibility with materials, viscosity etc), together with EN-CV, the DCP
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 DCP - follow-up, coordination as of December 2015
Chemical laboratory (CERN in-house or external)	<ul style="list-style-type: none"> - consultancy and technical assistance (TE-VSC-SCC) - pre-irradiation tests (reactivity of C6K with water, assessment of material compatibility tests performed earlier at PH-LBO, evaluation of the initial sample purity), initial rectification; - study of water and acids removal methods compatible with the coolants under study; - study of radiolysis effects in irradiated samples, effects of impurities, corrosion; - general 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 and low-dose cooling applications, 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), dedicated to the broader implementation of the alternative coolants in the LS2 and LS3 LHC detector upgrades, will be coordinated by EN-CV. It is foreseen to perform three irradiations of the fluid samples (with charged particles and neutrons at the CHARM facility at CERN). Intermediate C6K validation report will be prepared by January 2016 and the summary report – in April 2016. The tentative planning is presented in the table Table 2. A more detailed planning taking into account the availability of in-house analytical resources at CERN 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
1 st irradiation campaign at CERN	May 2015
2 nd irradiation campaign	September 2015
Post-irradiation studies (external lab)	May-December 2015
Chemical studies (external lab)	March-November 2015
Intermediate report	December 2015-January 2016
Long-term materials compatibility study, test bench with circulation and filtration	January 2015 on
Preparation for high-dose irradiations	February 2016
3 rd irradiation campaign, analysis	March-April 2016
Summary report	April 2016

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 resources through April 2016 are as follows:

- 1 FTE-year at PH-LBO for P.Gorbounov (applied physicist) – PJAS contract extension from June through November 2015 and subsistence from December 2015 through April 2016;
- a budget of 50 kCHF for materials (fluid samples, special containers, test bench construction, chemicals) and chemical analysis outsourcing.

We also request to secure

- a limited consultancy and technical support team by the TE-VSC-SCC and EN-MME-MM teams, essential for interacting with the external labs and preparations for irradiations of the fluid samples.

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.



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Part 2: "Radiolysis effects in C₆F₁₄ fluids", TS-Note-2007-005, EDMS 642110 <https://edms.cern.ch/file/842110/1/TS-Note-2007-005.pdf>
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 PFFA has been detected.*"

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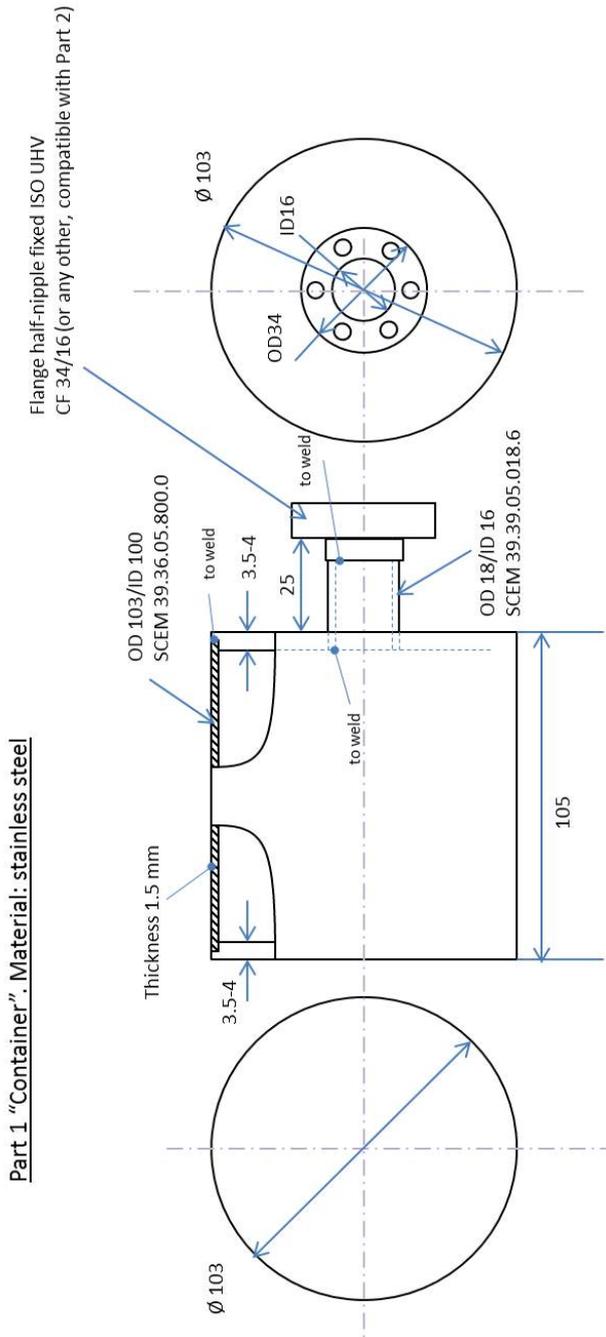


APPENDICES

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.
- DCP** Detector Cooling Project (CERN)
- GHG** greenhouse gas
- GWP** 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



A.3 Detailed work plan (draft to be discussed at TE-VSC-SEE)

The WP (Sections 2 and 3) highlights the directions for the investigation of the C6K properties relevant for cooling applications at CERN. The study of C6F14 performed earlier at CERN [10] provides useful guidelines for such a study and suggests the following points to focus on:

- Instrumentation: selection of the analysis methods and techniques. They can be similar or equivalent to those used for C6F14 study [10], like gas chromatography (GC), spectrophotometry (FT-IR, UV-Vis), ion-selective potentiometry, viscosimetry etc, but not limited to these. Additional analysis methods (NMR?) can be involved, if appropriate.
- Purification of as-provided fluids.
- On-line purification: finding efficient methods of on-line treatment of circulating coolant (fresh or irradiated), to remove detrimental products resulting from the fluid irradiation ("radiation-induced") and from the processes within the cooling system unrelated to radiation (intake of water and/or air, extraction of polluting impurities from the cooling system structures and so on). It is important to take into account the *typical working temperatures* of the coolant, which can be well below 0°C: -40°C... -70°C.
- Most important purification targets: water, air (oxygen), corrosive and toxic by-products (acids, gases...)
- Material compatibility.

One of the main messages of the C6F14 study was: the coolant should be kept as *pure*, as possible – from the moment of the system filling through the entire life cycle. The impurities will cause problems and eliminating the very cause of the threat is the best way to secure the coolant stability and the system safety and integrity. Therefore, to learn everything about *purification* (or "cleaning", or "filtering") of the coolant is the goal No. 1 of the validation studies.

The goal No. 2 is to acquire knowledge about all detrimental chemical and radiation-induced products that can develop in the coolant during its service and determine criteria to decide when the coolant should be recycled. This defines the choice of specific filters and the "quality control" used during the fluid service. The C6F14 study [10] recommends to monitor the acidity, the F-ion and the polymer contents; use UV-Vis spectrophotometry for the on-line control and activated carbon (AC), activated alumina (AA) and molecular sieves (MS) for on-line cleaning. The two principal impurities that were shown to impact the radiation resistance in the case of C6F14 were *water* and *oxygen*.

The goal No. 3 is the *material compatibility*. All available information on the compatibility of the coolant with organic and inorganic substances (metals, polymers, elastomers, typical filtering materials, other fluids) has to be collected and compared with the list of materials in the cooling system. Critical missing information has to be obtained experimentally.

In the case of C6K, the fact of its intrinsic chemical reactivity, caused by the presence of the carbonyl group in its molecule, prevents from copying the methods of the previous C6F14 study and adds more "dimensions" to the fluid validation. The factors to consider here are:



1. Reactivity with liquid phase water by hydrolysis giving PFPA and a HFC compound (HFC 227ea) with a lower molecular weight.
2. Reported reactivity with the AA which precludes their use as desiccants and fluoride adsorbers, recommended for C6F14. This requires a search for alternative methods of filtering of low-molecular-weight (LMW) impurities. In addition, this might also limit the use of the gas chromatography (tbc).
3. The carbonyl group in the molecule is not only the cause of (1) and (2), it facilitates the molecule scission by ionizing radiation and complicates the radiolytical reactions, serving as a direct precursor to formation of such compounds as aldehydes, carbonyl acids and the very toxic *carbonyl fluoride* CF₂O in the final state. CF₂O was also detected among radiolysis products of C6F14 – in presence of oxygen and water, but one can speculate that in C6K fluoroketone its yield might be higher. This is alarming because the water content (to hydrolyze CF₂O and remove it “naturally”) in C6K will be limited by the proper hydrolysis and the energetic online drying, while the use of conventional AA filters is precluded by the (2) above.
4. The carbonyl group in the C6K molecule will probably reduce the usefulness of the UV-Vis spectrometry for the online monitoring (tbc).

I propose the following draft plan. The study, by analogy with the C6F14 project [10], will be split in two major stages: the *chemical* and the *radiolytical* characterization. Given the higher priority of low radiation-dose applications (SciFi, BGV, ATLAS Thermo-syphon), the chemical characterization (the Stage 1) is more important at the moment. The main deliverables here are *dedicated methods of C6K drying, PFPA detection and removal at low temperatures*.

Preparation for the radiolytical study can begin in parallel or be delayed, depending on the availability of the corresponding laboratory resources. The instrumentation for the post-irradiation analysis can be prepared and calibrated with the original fluid by adding controlled amounts of contaminants to it. The same applies to a development of on-line degassing (O₂, CO₂) and removal/neutralization of LMW by-products (CF₂O, HF) at low temperatures.

Radiolytical characterization (the Stage 2) is of primary importance for the wider range of cooling applications, involving the service in “hotter” areas (inner detectors, cables cooling). It will also be complementary to the low-dose application study by providing a deeper understanding of C6K-specific radiolysis mechanisms, evaluation of G-factors and yields of acids. This study can also be staged, beginning with pilot tests with irradiation of a limited number of samples to two representative doses and further refined studies, e.g. with gamma and neutron irradiation and dedicated radiation-induced corrosion tests.

Stage 1 (chemical characterization)

- **C6K samples.** Start with available C6K sample (3M Novec 649, purity 99.8% [13]). Also obtain a sufficient quantity of ultra-pure sample – in the lab by additional cleaning (distillation, degassing, filtration with AC etc)⁵. Optionally, analyze the composition of the 0.2% impurities. Evaluate a possibility of the massive ultra-purification of the coolant prior to filling the cooling system with it.

⁵ As a last resort, the ultra-pure research-grade compound can be purchased, but the price can be astronomical.



- **C6K hydrolysis.** Acquire initial experience with C6K hydrolysis. The published data concerns mostly the hydrolysis of the gas phase in the atmosphere [14] or the uptake of a small amount of liquid C6K into water [15]. Our application deals with the bulk of C6K and a possible small intake of moisture. Questions to be addressed:
 - what is the dynamics of water extraction from the liquid phase in direct contact with C6K, as function of T (between +25C and, say, -40C);
 - is the water dissolved in C6K completely hydrolyzed, thereby prompting further extraction and posing no limit on the increase of acidity? Does it make sense to speak of the “water content” in the as-provided C6K⁶?
 - Will C6K interact with solid water (ice, frost)?
 - How the air (oxygen) dissolved in C6K affects the hydrolysis (if at all)?
- Test the efficiency, capacity and stability of different classes of desiccants suitable for C6K. Information from 3M about C6K drying is only qualitative and somewhat contradictory: Ref. [21] claims that molecular sieves (MS) and silica gel (SG) “appear useful” for removing water from C6K”, while [16] suggests using inorganic desiccants for C6K (anhydrous Ca and Mg sulphates... NaSO₄?) and avoiding MS and SG. In my opinion, one interesting and promising direction is to consider ion-exchange resins, e.g. DOWEX [17, p.7] for C6K drying. Activated Carbon??
- **Acids in C6K.**
 - Select (or develop) the baseline technique to detect acids and measure the acid concentration in C6K, primarily sensitive to PFFA, HF and, possibly, to a wider range of acids. Note that the method of [10] based on H₂O extraction is hardly usable with C6K. Given the particular importance of early detection of the acidity build-up (as an indicator of an accidental water intake somewhere in the circulation loop), the stress should be on the *on-line acid detection at a low temperature*, down to -70C.
 - Test the efficiency, capacity and stability of different classes of acid removal methods for C6K, for a wide range of acids that can be foreseen as hydrolysis and radiolysis products – HF, PFFA, TFA etc. Among other methods, consider AC, carbon molecular sieves (CMS), ion-exchange resins (e.g. DOWEX M-43 for non-polar fluids [18]).
- **Material compatibility.**
 - Help to interpret the outcome of the early tests (about 40 test vials) launched in December 2014 [19].
 - Evaluate the compatibility of C6F and other Novec fluids [20] with several elastomers that are potentially usable in detector cooling circuits, like ultra-pure plasticizer-free silicone rubbers (eg Tygon 2075, 2001) or PU rubbers (eg Tygotan C-555-A).
- **Chemical compatibility with PFCs.** Verify the expected miscibility and lack of chemical reactivity of C6K with PFCs, especially C3F8 (liquid phase) and C6F14.

⁶ The 3M Product Information [5a] quotes 20 ppm for water solubility in C6K. NB: the corresponding MSDS quotes “Nil” for C6K solubility in water.

This is of interest because of a theoretical possibility of a contact between these fluids in the existing cooling systems.

- **Activated carbon filter.** Test AC as a universal C6K purification filter (for the entire temperature range) and select the most appropriate AC grade.

Preparation for the Stage 2

- **Carbonyl Fluoride.** Propose and test a method of safe removal and neutralization of CF₂O evolved from C6K. It would be nice to combine CF₂O removal with extraction of other LMW impurities and gases (especially O₂). Example: closed circuit purging with N₂ inside the expansion tank, with on-line carbon molecular membrane to retain C6K and select CF₂O as permeate and hydrolyze or adsorb it (eg with AA). Check if inline AC filter will be effective for extracting CF₂O from the liquid phase (see below).
- **Gaseous impurities and evolutions.** Evaluate degassing techniques for C6K – to remove (O₂, CO₂, gaseous fluorides). Example: Ar or N₂ purging, CMS.
- **Other filtering methods.** This has been partly covered in Stage 1 (initial purification, drying, removal of acids). Questions to be addressed: a) whether the molecular sieves and membranes, in any possible form of this technique, are applicable to C6K cleaning; b) same for ion-exchange resins (take into account the low working temperatures).
- **Fluid Composition.** The activity to identify and test the instrumentation to measure the composition of the coolant and identify impurities (spectrometry, chromatography, NMR etc) can unfold in parallel to the Stage 1. Ideally, it should converge by the moment when the radiolytical characterization starts (see below).

Phase 2 (radiolytical characterization), pilot study

- Manufacture, clean and fill the SS containers under controlled conditions, according to the following scheme:
 - *Purified C6K* x 4 compositions (N,A,NW, AW) x 2 sets = 8 samples
 - N: argon (or N₂) at 0.5 barG
 - A: dry air at 4 barG
 - NW: argon (or N₂) at 0.5 barG + DI water (600 ppm)
 - AW: dry air at 0.5 barG + DI water (600 ppm)
 - NB: Flat test (SS and/or Ti Grade 5) strips (180x10x1 mm³) in all containers (tbc)
 - *As-received C6K* x 1 composition (AW) x 2 sets = 2 samples
- Irradiate all samples with fast charged hadrons (e.g., at the CERN CHARM facility) to 50 Gy and 1000 Gy doses representative for “low” and “medium” radiation environment application, taking into account the factor of “dilution” for the coolant [11] circulating between the irradiated and service zones.
- Analyze the compositions of the liquid and gas phases in all exposed samples and compare the results with the starting fluids compositions. Like in the C6F14 study [10], the contents of the following three classes of radiation-induced impurities have to be evaluated:



- High-molecular-weight pre-polymers soluble in C6K and insoluble polymers
 - Acids and F-ions
 - LMW products in gas and liquid phases: lower fluoroketones (including, and especially, CF₂O), other fluorinated compounds, CO₂. Also, for the gas phases: initial and final pressures; for the liquid phase: initial and final viscosities.
- Analyze the state of the test strip surfaces (etching, composition of deposits)
 - Estimate G(-M) and partial G-factors for C6K

The minimal analysis (in the case of limited analytical resources) should focus on global features important for cooling: overall yield of acids (especially HF) and CF₂O, the amount of residues in vacuum distillation of irradiated fluids, viscosity of irradiated fluids and their corrosiveness with different metals (SS titanium, aluminum, brass, bronze).

Acronyms used in this Appendix

SS – stainless steel

SG – silica gel

LMW – low-molecular-weight

AC – activated carbon

AA – activated alumina

MS – molecular sieve(s)

MM – molecular membrane(s)

CMS , CMM – carbon molecular Sieve, Membrane

TFA – trifluoroacetic acid

CF₂O – carbonyl fluoride, difluoroketone, fluorophosgene

HFC – hydrofluorocarbon

tbc – to be confirmed