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Comparison of liquid coolants suitable for single-phase detector cooling

Abstract

Three different classes of commercial heat transfer fluids (PFCs, HFEs and FK) are selected as candidates for the single-phase liquid cooling system of the SciFi Tracker photodetectors. None of them is perfect, though. PFCs are strong greenhouse gases. C6F14, the popular PFCcoolant widely used at CERN because of its outstanding inertness and radiation resistance, has GWP of 9300. The heavier PFC fluid C7F16 with a wider liquid range has GWP of 7930. The 3M Novec fluids, designed as alternatives to PFCs and having sharply lower GWP, include a range of HFE liquids with GWP=60-300 and FK liquids, Novec 649 and 774, with GWP=1. These fluids are less inert and, arguably, less radiation resistant than PFCs. The 649, having the thermo-physical properties quite close to C6F14, had been tentatively selected as the baseline option for the SiPM cooling. HFE liquids Novec 7100 and 7200 can also be considered as alternatives. Environmental, safety and performance profiles of all above mentioned fluids are compared.

Abbreviations and acronyms

HTF	heat transfer fluid
HC	hydrocarbon(s)
HFC	hydrofluorocarbon(s)
PFC	perfluorocarbon(s)
GWP	global warming potential
C6F14	perfluorohexane C_6F_{14}
FK	fluoroketone(s)
C6K	C6-Fluoroketone, aka 3M Novec 649
HFE	hydrofluoroether(s)

1. Introduction

A single-phase liquid cooling for the SciFi tracker photodetectors [TDR 2014, TIPP 2014] was preferred to 2-phase cooling because of its lower cost, robustness, wider choice of coolants, more “off-the-shelf” cooling plant components (e.g., pumps). There were no compelling reasons to choose the more complex and demanding 2-phase technology, given the mostly passive thermal load of the SiPM read-out modules and the absence of severe material budget restrictions in this application. The freedom to choose the module connection topology[1] and reluctance to deal with high-pressure inside a fairly extensive system also favored the mono-phase choice. The environment-friendliness requirement alone was insufficient to opt, for example, for the “green” 2PACL CO2 cooling [Verlaat 2012].

The implicit idea was to use C6F14 as the coolant. This popular PFC fluid had been validated for the LHC [Battistin 2006] and used in many detector cooling systems at CERN. Its unique combination of properties (inertness, non-flammability, excellent dielectricity, safety, radiation resistance, water-like pumpability at low temperatures usually outweighs its main drawbacks:

[1] The more economical serial connection was assumed at the TDR time.

poor heat transfer characteristics, the relatively low boiling point (57°C) and, most importantly, a very high greenhouse potential (GWP = 9300 [Ivy 2012]), typical of all PFCs.

The environmental impact of C6F14 and other PFCs were tacitly disregarded compared to their obvious benefits for the design of the LHC detectors in early 2000. Now, ahead of the LHC detector upgrades, this situation has changed. With globally growing environmental awareness, the environmental impact aspects cannot be ignored anymore (at least at the official CERN level) and gradually become competitive with physics performance aspects. PFC emissions are now closely monitored at CERN []. There are two strategies to reduce them: by anticipating and preventing the losses and by replacing PFCs with "greener" fluids.

Given the big size of the SciFi Tracker and the complexity of manifolding, the inner cooling structures of ROBs and their interconnections[2], it will be difficult to make the SiPM cooling system totally "non-emissive" over the long term. Even in industrial applications [Tuma 2001], there are unavoidable operational losses related to the PFC's volatility and high thermal expansion (~ 1% per 10K). Thus, as long as we stay with liquid cooling, we have to count on a "green" solution as the baseline, while possibly keeping the cooling system (both detector and cooling plant sides) compatible with liquid PFCs, as a backup.

This memo summarizes our efforts to identify possible alternatives to C6F14 among modern commercially available fluids suitable for operation at -50C. Unfortunately, no perfect reconciliation of environment- and application-friendliness seems possible for the SciFi application, so some sort of compromise is unavoidable[3]. With C6F14 representing the extreme case of such a compromise, two other fluids have been shortlisted: the "TDR candidate" fluid 3M Novec 649, a FK with GWP=1, and the HFE fluid 3M Novec 7100.

For completeness, we also consider close alternatives to each of the candidate, within the same class: the FK Novec 774 and the HFE Novec 7200. Even the PFC class contains liquids that are somewhat superior to C6F14, e.g. 3M FC-84 (C7F16) which has a bit lower GWP and a bit better thermal properties, while having a higher boiling point (80C) and, hence, lower evaporation losses.

2. Alternative coolants

2.1 What do we want?

The requirements for the fluid in indirect cooling systems are nicely summarized in Refs [Cengel 2007] and [Mohapatra 2006]. In general, the best coolant is an inexpensive nontoxic liquid with excellent thermo-physical properties, a long service life and minimal regulatory constraints. It should be non-corrosive to the materials it comes in contact with. A high flash point and auto-ignition temperature are desired for safety reasons. Good thermo-physical properties (high thermal conductivity and specific heat; low viscosity) are required for the optimal heat transfer and low required pumping power.

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[2] Especially now that we are drifting to parallel, rather than serial, ROB connections and the 3D-printed cooling bars will be likely split into two halves.

[3] "The boundary conditions we have are contradictory, since a stable substance is by definition bad for the environment, since it remains long time in the atmosphere and something unstable is bad for the detectors. The only hope is … to find something which is not very stable to radiation, but non-corrosive. It will not be possible to apply it to the radiation area, but it will not be harmful for the atmosphere." [Taborelli 2014]

Water, one of the best HTFs available, is an obvious example of a good approximation to the ideal. However, liquids intended for electronics cooling are also required to be electrically non-conductive (“dielectric”) and clean.

Electrical conductivity becomes important if the coolant may leak out of a cooling loop or be spilled during maintenance and come in contact with sensitive electronics. By the “cleanness”, the ability to evaporate without leaving a residue that might attract dirt, deteriorate insulation or just irreversibly stain the setup is usually implied. DI water serves well for above-zero applications, though DI water based systems are usually quite expensive. DI water/glycol solutions are questionable because of their toxicity and “cleanness”. The best attainable volume resistivities for DI water and DI/glycol are about 10^7 and 10^8 ohm-cm, respectively [T&K 2003]. We shall mark this level as the reference.

To that we have to add the application-specific requirements. The required operating temperature range should be well within the total coolant’s liquid range[4]. For the SciFi cooling, the operating range is between -50C (the lowest foreseeable working SiPM temperature) and +40C (the SiPM annealing temperature).

The fluids for HEP detector cooling should be appropriate for working in the radiation environment specific to the application. This is not simply equivalent to requiring a superior radiation resistance for the coolant. In practice, it rather means that the radiolysis products appearing in the coolant should not adversely impact the cooling system integrity and efficiency over the project’s life time. When assessing this factor for indirect cooling, apart from the total dose and the radiation type, one has to take into account the pipe materials (metals, plastics, elastomers), their geometry (e.g., wall thickness), the presence and efficiency of the filtering elements in the cooling loop.

Traditionally, the radiation-related effects (especially for neutrons) were associated with the presence of hydrogen (H) in the coolant [Battistin 2010] – because of the combined effect of the high neutron cross-section of H and potential hazards of acids produced by the radiolysis. For example, in fluorinated liquids the radiolysis chain involving hydrogen will result in formation of fluor-containing acids, e.g. HF or PFPA, which might cause corrosion of the metallic cooling system elements. Hydrogen can be present either in the coolant’s molecule (like in HFEs), or in HC impurities, or in water dissolved in the coolant.

Obviously, the radiation-related requirements will be quite different for cooling of inner LHC detectors (with high radiation doses and thinnest possible heat exchanger walls) and for out-of-acceptance electronics (relatively thick-wall heat exchangers and low radiation doses, like in the SciFi tracker case). In [PG 2014 irrad memo] it is shown that, even under exaggerated pessimistic assumptions, the radiolysis effect for a fluoroketone fluid in SiPM cooling system will be microscopic – simply because of the low expected ionization dose and neutron fluence. The resulting concentration of acids will be low and the dominant radiation damage in this case will be associated with the impurities, rather than with the coolant itself. Similar arguments are applicable to any other fluid with no or low H content. Thus, the “no hydrogen” requirement can be tentatively lifted, as one of possible compromises.

[4] The range between the pour and boiling points at the operating pressure.

Our search for the SiPM coolant follows this hierarchy of criteria:

1. Commercial dielectric liquids
2. CERN regulations: non-flammable (no or high flash point[5]), non-toxic
3. Clean (no pollution of the workplace)
4. Operating temperature range: -50…40°C
5. Stable, non-corrosive (according to MSDN)

The shortlisted candidates are ranked according to their environmental, thermal transfer properties, pumpability, cost and safety, as well as material compatibility and reactivity.

2.2 What do we have?

A concise overview by S. Mohapatra (Mohapatra 2006) described the main classes of commercial liquids for electronics cooling. Current catalogues of leading coolant manufacturers, like 3M, DuPont, Solway Solexis, Exxon, indicate that the industry did not offer qualitatively new classes of fluids since the last major environmental policy shift which occurred after the Kyoto protocol entered into force in 2005. The industrial R&D efforts, quite expectedly, aimed at gaining the market for the mainstream applications, like air conditioning, power electronics and data center cooling, semiconductor manufacturing, home heating etc, which mostly belong to the above-zero °C and/or 2-phase cooling domains. A renaissance of interest to CO2 cooling is also observed, especially in the mobile air-conditioning sector [CO2-AC]. As to low-temperature single-phase applications, the only visible new "development" since mid-2000s was the addition of FK fluids, originally positioned as fire-fighting agents, to the HTF category, under new trade names (e.g. Novec 649, formerly known as Novec 1230).

Here are the main classes of stable dielectric coolants[6] that are liquids at a room temperature, with remarks on their safety, environmental and operational profiles:

- **Aromatics (HC):** Synthetic hydrocarbons of aromatic chemistry. These compounds are usually highly flammable and cannot be classified as non-toxic. Often they have strong odours, which can be irritating to the personnel. Temperature range: at or above room temperature, but some, like (diethylbenzene-based?) [Paratherm] CR, [Dynalene] MV, [Dowtherm] J, are good down to below -80C.
- **Silicate-ester (SE):** These synthetic liquids (i.e., [Coolanol] 20, 25R) were widely used as a dielectric coolant in military radar and missile systems. SEs have caused significant and sometimes catastrophic problems due to their hygroscopic nature and subsequent formation of flammable alcohols and silica gel. They are being replaced by aliphatic chemistry (polyalphaolefins or PAO).
- **Aliphatics (PAO):** Aliphatic hydrocarbons of paraffinic and iso-paraffinic type (including mineral oils) are petroleum-based fluids. They are non-toxic, have a non-discernible odour, and do not form hazardous degradation by-products. PAOs directly replaced the silicate-ester fluids in a variety of military and avionic applications. Example: Dynalene HF-LO (according to data sheet, is good down to -73C but combustible and toxic). Most PAO fluids have prohibitively high viscosity below 0C [Tuma 2009].

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[5] The temperature at which the vapors produced from a fluid will ignite (flash-off) with the presence of an ignition source (the fluid will not burn at this point).

[6] DI water and DI-glycol mixtures are excluded because of poor stability of their dielectric properties and limited usability below -25C.

- **Silicones:** A popular coolant chemistry is a liquid polymerized siloxane (e.g.,dimethyl(or ethyl, or phenyl) polysiloxane) commonly known as *silicone oil*. The molecular weight and the thermo-physical properties (freezing point and viscosity) of this synthetic polymer can be adjusted by varying the chain length and configuration. Silicone fluids are used, as lubricants and HTFs, at temperatures as low as -100°C and as high as 400°C. They are excellent dielectrics, have low odour, are nontoxic and stable within the design temperature range. Dimethylsiloxanes feature relatively good radiation resistance (up to ~10 kGy) and phenylsiloxanes withstand up to 1 MGy. Julabo recommends silicone oils as standard coolants [Julabo Fluids] for their open-bath chillers. However, low-temperature silicone oils are expensive, flammable and, because of low surface tension and low vapour pressure, very polluting liquids. Examples: Dow Syltherm XLT, Julabo Thermal HY, Gelest Silicone Fluids.
- **Fluorinated liquids[7] (PFC, PFE, HFE, FK)** have certain unique properties: first of all, unlike all other dielectric fluids, some of them are non-combustible, non-toxic and very inert. Secondly, some of these fluids have low freezing points and low viscosities at very low temperatures. In addition, unlike silicone oils, they are "clean" (in the sense discussed above). On the negative side, all these liquids are very expensive, have quite poor thermal properties as single-phase coolants. PFCs and PFEs are greenhouse gases. Due to the extremely low surface tension and incompatibility with fluoroplastics, floirinated liquids will easily develop leaks in the systems that are not specifically designed for their use. Their volatility may result in high operation costs.

The only truly non-flammable dielectric fluids are found among fluorinated compounds. Silicones could be considered, as well, because their flammability is quite low and the low flash point (e.g., 42C for Syltherm XLT) is offset by extremely poor volatility. However, silicon oils are famous for their property to badly pollute the workplace in case of unintended spill. This is the main reason that prohibits their use in large-scale systems. The aggregate heat transfer performance of silicone oils at low temperatures is not better that that of PFCs (see Section…), while the pumpability is by order of magnitude worse.

Thus, we are left with a handful of fluorinated heat transfer liquids suitable for operation at -50C. At first look, they are quite similar, all having zero ODP and being much heavier than water, stable, inert, very fluid and volatile. They all have rather poor heat transfer properties and do not differ much from each other in that respect (see Section …). The first and main difference between them is in their GWP:

- PFC: C6F14 and heavier linear or branched perfluoroalcanes (from 3M Company, F2 Chemicals, several other minor suppliers) are potent greenhouse gases with GWP of 8000…9300 (very bad);
- HFE: segregated HFE fluids produced exclusively by 3M Company as Novec 7000-series are environmentally safe with GWP from ~50 to ~330 (good);
- FK: C6- (3M Novec 649, Novec 1230) and C7- (3M Novec 774) fluoroketones both have GWP ≈ 1 (excellent).

The huge spread in GWP does not come for free: unlike really inert PFCs, both HFE and FK fluids have minor issues at the chemistry level. In addition, they have lower electrical resistivity compared to PFCs and, arguably, lower radiation resistance. However, these drawbacks are not dramatic and leave freedom for compromises, as will be discussed in the following Sections.

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[7] Commercial HFC (e.g. HFC-134a) and HFO (e.g. HFO-1234yf) fluids massively used in 2-phase A/C systems are gases at normal conditions.

All these fluids are available from the same supplier, 3M Company [3M HTF], and the rest of this memo is based on the 3M documentation (Product Information brochures, MSDSs, articles and reviews) available from open internet sources.

2.3 PFC fluids: C6F14 and C7F16

C6F14 and other PFC fluids are supplied by 3M under the brand name Fluoroinert Electronic Fluids. C6F14 comes as FC-72[8] [3M FC72]. Other Fluoroinerts suitable for SiPM cooling are FC-84 (C7F16 and isomers, [3M FC84]) and FC-770 [3M FC770]. We shall consider only FC-84 as an alternative to C6F14 in this class, as no sufficient amount of technical data is available for FC-770. PFC liquids, as a class, have extremely high electrical resistivity, $\sim 10^{15}$ Ohm·cm – better than air and comparable with FR4 ($<3.3\cdot 10^{14}$ and $\sim 10^{14}\ldots 10^{15}$ Ohm·cm, respectively).

2.4 Hydrofluoroether fluids

Segregated hydrofluoroethers (HFEs), supplied by the 3M Company [3M HTF] as Novec 7000-series fluids, have an excellent blend of thermal transport, safety, and environmental properties that make them good candidates for a secondary heat transfer system. They share many of the valuable performance properties of PFCs and are positioned by 3M as sustainable alternatives to PFCs, with much lower GWPs. Concise reviews of these fluids can be found in Refs [Tuma 2001] and [Tuma 2009].

For practical purposes relevant to heat transfer, Novec HFE fluids differ from Fluorinert fluids in their chemical structure, hydrocarbon solubility and electrical properties [3M FAQ]. Unlike PFC, the HFE molecules contain one oxygen and a few hydrogen atoms. In segregated HFEs, patented by the 3M, the perfluorinated portion of the molecule is “segregated” from a fully hydrogenated portion by oxigen atom (an ether linkage). The presence of hydrogen in the molecule makes this compound susceptible to OH radicals that break it in the troposphere, which predetermines their short atmospheric lifetime and the lower GWP. It also makes the molecule a good solvent for hydrogenated materials, in particular – for HC-based pasticizers in elastomers. Like PFCs, the HFE fluids can also dissolve other fluorochemicals, while featuring a good compatibility with metals, hard plastics and unplasticized elastomers.

Novec HFEs are good dielectrics but their resistivity (10^{8}-10^{9} Ohm·cm) may fall short in some HV applications with direct cooling, where PFCs would be eligible.

Finally, Novec HFEs are very stable, do not hydrolize, have no flash point and are non-toxic. No open information about radiation resistance of HFE is available.

We shall consider two Novec HFE liquids suitable for the operating temperature range between -100C and 50C: Novec 7100 [3M 7100] and Novec 7200 [3M 7200], having GWPs of ~300 and ~60 and boiling points of ……respectively.

2.5 Fluoroketone fluids

C6-fluoroketone (C6K) fluid 3M Novec 649, featuring a record low GWP=1 and the thermo-physical properties quite similar to C6F14, had been tentatively selected as the baseline solution for the SiPM cooling in SciFi. One known issue with this fluid is its weak reactivity with liquid water (i.e., a separate water phase): it hydrolizes producing an organic acid (PFPA). This is not the immediate issue for the intended application because of the sub-zero working temperature, the

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[8] It is also available as one of 3M Performance Fluids, the PF-5060; CERN purchases PF-5060, which is, essentially, identical to FC-72.

presence of moisture and acids filters and the use of corrosion-resistant materials (e.g. SS or titanium alloy) for tubing and cooling structures in the future system. The system design will also aim at avoiding water condensation or frost deposition on the inner and outer surfaces of the cooling system, thereby reducing the risks of direct contact with moisture in case of minor leaks. These risks are further reduced by a very high volatility of the C6K at above 0C. An in-depth study of C6K (as 3M Novec 649) at CERN is foreseen [CERN WP2015].

As a fire-suppressing agent 3M Novec 1230, C6K was present on the market long before joining the HFT category. The vast available literature about C6K is reviewed in Ref [PG 2014 C6K]. As a HTF, C6K is primarily recommended for immersion cooling (pool boiling) applications, because of its relatively low normal boiling point (49C). In about 2012, 3M introduced another FK fluid, Novec 774 [3M C7K], which is a mix of isomers with 7 carbons (C7K). It features a higher boilng point, 74C[9], and, otherwise, is quite similar to C6K (in particular, has GWP≈1). FKs are very good dielectrics (~10^{12} Ohm·cm).

Unfortunately, there is no published data about their radiation resistance. The low GWP is due to a photolysis at a near UV (with the absorption peak at 307 nm). The relatively weak O=C bond might cause a reduced resistance to ionizing radiation [Taborelli 2014], which, if confirmed, will limit the use of FKs to low-dose detector cooling applications.

3. Comparison of selected coolants

3.1 Heat transfer properties

3.2 Material compatibility

3.2 The summary

4. Conclusion

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