3M Novec fluids as alternative to perfluorocarbons for detector cooling at CERN

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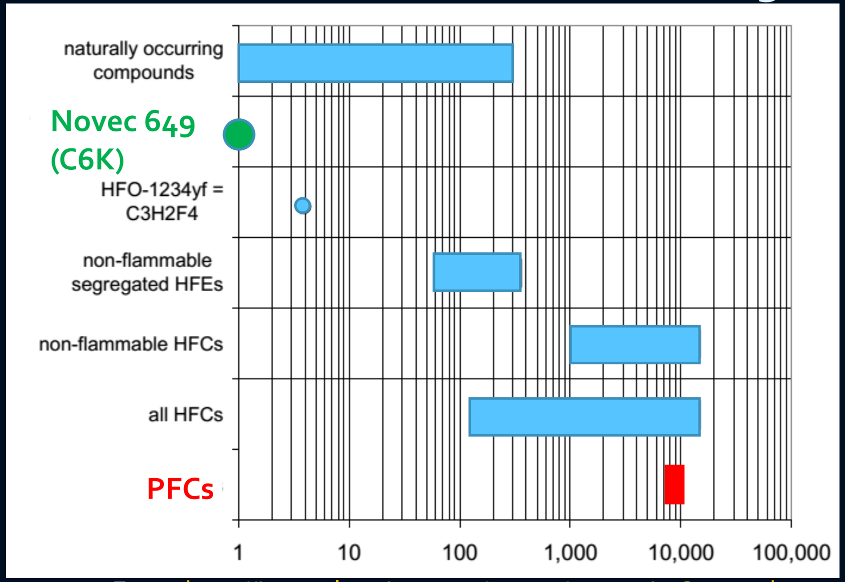
- Why seeking alternative coolants?
- Why 3M Novec fluids? (Novec 649, 7100 …)
- Why does they need to be validated?
- Novec project at CERN
- Radiation resistance
- Compatibility with materials
- Irradiation tests, specifications, goals

Why seeking alternatives to PFCs?

- Perfluorocarbons (PFCs) have unique properties: inertness, non-flammability, low pour point, quartz-like electrical resistivity, water-like pumpability at low temperatures, volatility and cleanness, relatively high radiation resistance.
- As coolants, widely used in ATLAS, CMS, LHCb
- However, they are strong greenhouse gases
- KYOTO Protocol, in force since 2005, commits its Parties to reduce GHG emissions

GWP: PFC vs other commercial refrigerants



From http://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=04509386

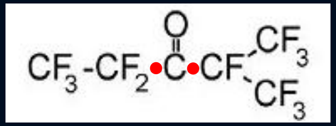
- CERN: the program to monitor and reduce the emissions of PFCs, sustainable alternative technologies for new developments are encouraged. C6F14 is deprecated for new projects
- LHCb SciFi photodetector cooling (-40°C): alternative baseline coolant, 3M Novec fluids

Why 3M Novec 649 (fluoroketone C6K)?

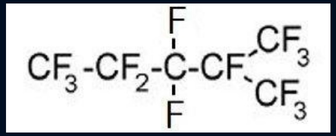
- Only fluorinated fluids match the low-temperature single-phase DC requirements [6]
- Apart from PFC, only 3M Novec fluids – FKs (C6K and C7K) and segregated HFE – are commercially available. HFEs: contain H and have GWP of ~300; FKs: no H, *GWP=1*
  FK: Novec 649/1230 and 774, HFE: Novec 7100, 7200
- C6K was in use since long time as a "clean fire suppressing agent", very well studied and covered by extensive literature (atmospheric fate, safety)
- C6K and HFEs are also promoted by 3M as a HTF intended, for example, for immersion cooling of data centers
- Thermo-physical properties: C6K is very similar to C6F14 (drop-in replacement?)
  - Slighty lower boiling point (49°C vs 56°C)
  - Lower electrical resistivity (10^4 GOhm-cm, like dry air, vs 10^6 GOhm-cm)
  - Thermally and hydraulically – better at low temperatures

Novec 649/1230 facts

- Known as "waterless water" or "dry water"
- Non-toxic, NOAEL > 10% v/v, US and EU certified for use in occupied areas
- The low GWP is due to the photolysis under UVB at ~305 nm (4.04 eV) causing the C6K molecule scissions into short-lived compounds and radicals
- Price ≈ C6F14 (Q2 2015 quotation)

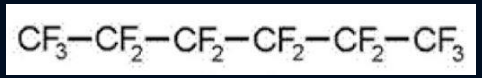


C6K
(3M "Novec 649")



iso-C6F14
(F2 "Flutec PP1")

- Chemically not as inert, as PFCs:
  it's a *ketone* (contains carbonyl C=O group)



n-C6F14
(3M "PF-5060")

Why do we need to validate Novec 649 for DC?

- Weakly reactive with
  - liquid water, producing an organic acid PFPrA and HFC-227ea (~ neutral gas).
  - alumina and alumino-silicates (used in filters for C6F14)
- Nothing is known about radiolytical properties of C6K (“radiation resistance”)
- Limited published data on the compatibility of C6K with materials (mostly 3M)
- Requires new methods of fluid purification (drying, acid removal) and monitoring – need to know the detrimental compounds produced by radyolysis
- Novec 649 is proposed as the baseline coolant in LHCb SciFi Tracker [1] and in the BGV project of BE/BI [2]. It will be also evaluated by the ATLAS DC group [3]
- Of potential interest to other CERN projects?

Novec validation project at CERN (I)

- Actual work started in ~ November 2014, after the thermal validation of N649 as a HTF for the SciFi
- Due to limited availability of the CERN chemical lab, the validation work will be outsourced to external labs
  - Chemical and radiolytical characterization
  - Material compatibility
  - Evaluate other alternative liquids (Novec 7100)
  - Coolant composition monitoring (online and offline)
  - Methods of initial and online cleaning

Radiation resistance (I)

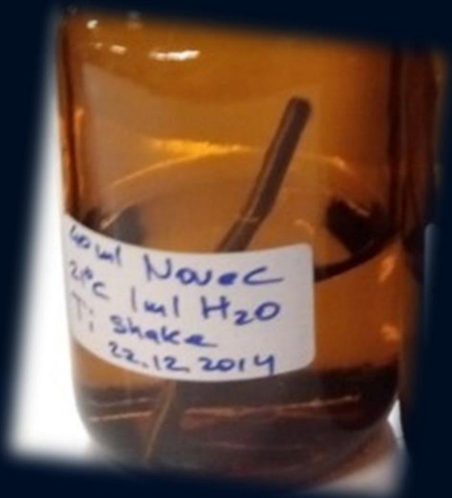
- Radiation damage for fluids is limited to radiolysis
- Irradiation tests at ~~O(10²)~~, O(10^3), O(10^4),), O(10^5) Gy, to assess the radiation damage to selected Novec fluids, are required (initially with γ-source, later with hadrons)
- Radiation resistance of a coolant can be characterized by the appearance rate of various detrimental contaminants or, globally, by the destruction rate per unit dose (or G-values per 100 eV of absorbed energy)
- Detrimental radiolysis products: acids (primarily HF), (pre-)polymers, toxic gases (eg COF2). Moisture, HCs and oxygen are main enemies!
- No important structural effects are expected for intended Novec fluids applications, so the focus must be on cleaning (initial and online)
- Need to find efficient cleaning agents alternative to zeolites and alumina

Radiation resistance (II): expectations for Novec

- Fluoroketones and ethers can be expected to be less “radiation hard” than C6F14 because of the lower energy of the weakest C-C bond: ~4 eV   (~8 eV in C6F14). Moreover, the presence of oxygen in the molecule might favor the COF_2 formation.
- For moderate total doses the expected effect is microscopic [5].
- Stricter requirements on the initial coolant purity!   Commercial Novec purity is 99.8-99.9%. It can be further improved either by initial purification

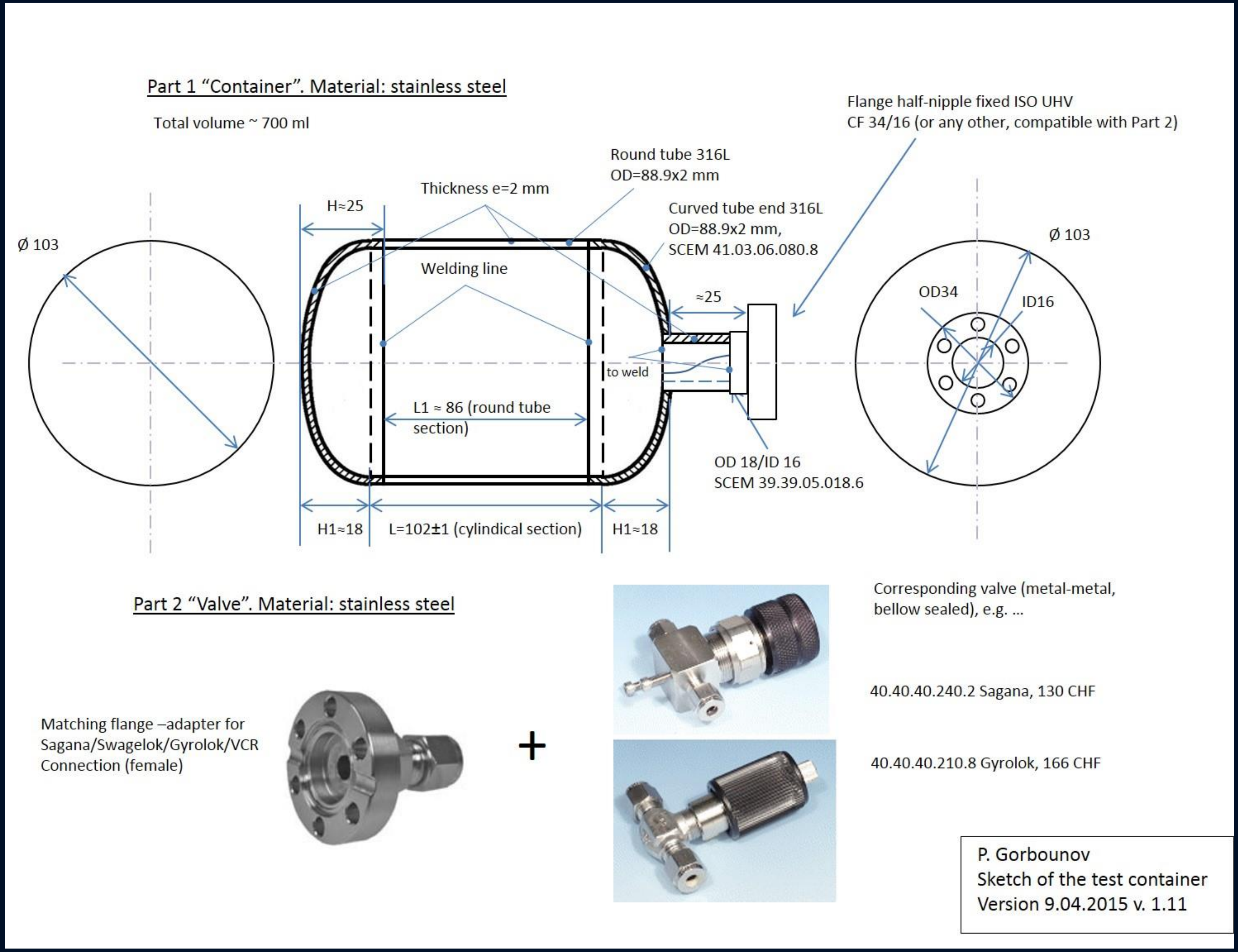
Compatibility with materials

- 3M: Novec and PFC fluids have similar compatibility with metals, hard plastics and elastomers. De facto proof: pool boiling and ORC applications
- An independent long-term (or accelerated) compatibility test with typical materials is desirable
- Radiation-assisted degradation of materials in contact with coolants – also to be addressed



Irradiation tests (I)

- 12 hermetic stainless steel containers (700 ml), certified for high pressure, with valves
- Liquid samples: 350 g per container
- (N649 + N7100) * 2 (redundancy) * (1 kGy + 10 kGy + 100 kGy)
- Initially, gamma source, to avoid container activation
- Special condition: low temperature, in the 0…-50°C range (to be specified)
- Preliminary agreement with manufacturer (3M, USA): they are willing to analyze irradiated samples… but this will involve sending them to the US… may involve insurmountable difficulties
- Analysis goal: to measure G_M-values and partial yields of all identifiable components in the gas and liquid phases after irradiation (IR and or UV spectrometry, chromatography, NMR… - whatever methods are available). A similar study was performed in 2006-2007 at CERN for C6F14 [10] and can be used as guidelines.



- **2 mm wall thickness will result in ~10% dose non-uniformity**
- **Combined with the natural 10% 1/r divergence non-uniformity, this will result in ~5% less average dose**

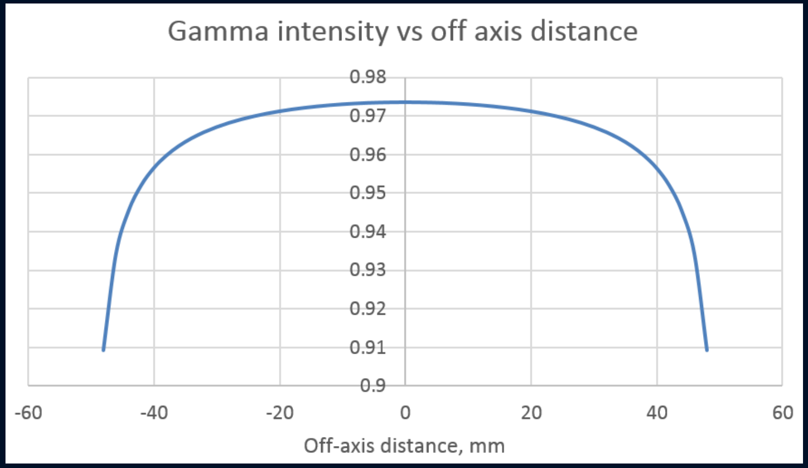


Table 5 - Experimental evaluation of various radioinduced products in PP1-56 (dose: 56kGy; fluid mass = 803 g)

Components identified in the gas phase					
Component	Peak (%)	Method	mass (g)	mol 10^{-4}	Δ radiation induced (mol 10^{-4})
CO_2	-	-	-	-	-
CF_4	3.24	GC-MSD	0.060	3.45	3.45
C_2F_6	1.024	"	0.0095	0.68	0.68
C_3F_8	0.661	"	0.0062	0.33	0.33
C_4F_{10}	0.286	"	0.0027	0.11	0.11
cyclo-C_5F_{10}	0.007	"	0.00006	0.028	0
$CF_3CF{=}CFCF_3$	0.002	"	0.19×10^{-4}	negligible	negligible
$(CF_3)_2C{=}CF_2$	0.001	"	0.09×10^{-4}	negligible	negligible
C_5F_{12}	1.024	"	0.0096	0.34	0.11
iso-C_6F_{14}	93.55	"	0.8853	26.14	- 1.78
n-C_6F_{14}	0.089	"	0.0008	0.025	0.01
n-C_7F_{16}	0.011	"	0.0001	0.0023	~0
PFC + O	0.022	"	0.0002	0.06	0.06
Total mol of radiolysis products appeared in gas phase					4.75 (all are PFCs)
Components identified in the liquid phase					
Component	(%)	Method	weight (g)	mol 10^{-4}	Δ radiation induced (mol 10^{-4})
C_3F_8	0.004	"	0.032	1.7	1.7
C_4F_{10}	0.016	"	0.128	5.4	5.4
cyclo-C_5F_{10}	0.002	"	0.0161	0.5	0
C_5F_{12}	0.271	"	2.18	75.6	0
cyclo-C_6F_{12}	0.009	"	0.0723	2.2	1.96
iso-C_6F_{14}	98.90	"	794.2	23496	- 100
n-C_6F_{14}	0.314	"	2.52	64.95	13.64
C_7F_{16}	0.113	"	0.907	23.39	14.08
other molecules (r.t. < 30 min)	0.345	"	2.77	82	38.8
pre-polymer	0.007	gravimetric	0.35	10.4	10.4
polymer	n.a.	-	-	0	0
HF	6.3×10^{-5}	potentiometric	0.0005	0.25	0.25
F^-	2.0×10^{-4}	"	0.0016	0.84	0.84
Total mol of radiolysis products in the liquid phase					87.07
Total mol of radiolysis products					91.82

The degradation ratio is expressed as numbers of mol of the radiolytical induced products or as C_6F_{14} number of mol consumed in the radiolytical process.

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CERN - TS Department

EDMS Nr: 842110 TS-Note-2007-005

Chemical and radiolytical characterization of perfluorocarbon fluids used as coolants for LHC experiments

Radiolysis effects in perfluorohexane fluids

S. Ilie, R. Setnescu, B. Teissandier

The C6F14 validation project for LHC

Irradiation tests (II)

- A concept of radiolysis-induced corrosion/erosion tests
- A number of small non-hermetic PE bottles with 30-40 ml of liquid samples and coupons of different typical metals/alloys used in cooling systems.
- Irradiated to (1 kGy + 10 kGy + 100 kGy), initially to gammas, to avoid sample activation, later – to mixed and/or neutrons
- After irradiation can be inspected at CERN EN-MME-MM, to identify radiolysis-specific surface effects (polymerization, oxidation....)

Specs for the irradiations at Fraunhofer Institute

Liquid samples

- **Contact at CERN**: P. Gorbounov (PH/LBO) and M.Battistin (EN/CV/PJ**)**
- **Irradiation type:** Co-60 gamma (TK 100/1000?)
- **Samples**: 3M Novec 649 and 3M Novec 7100 fluids in 700 ml SS containers
- **Target dose**: 0.6, 6, 60 kGy (H_2O) ≈ 1, 10 and 100 kGy at 25°C. Total dose accuracy: <10%
- **Target dose rate**: corresponding to ~10% dose uniformity at ±5 cm container (presumably, 0.1 Gy/s for TK1000 and 1 mGy/s for TK100)
- **Temperature**: if possible, below freezing (0…-40°C)
- **Component/System**: liquid fluorinated coolants/LHC detector cooling systems
- **Urgency**: quite urgent
- **Earliest start/latest end**: October 2015/end of 2015
- **Pictures**: test containers
- **CERN documentation**: this presentation, irradiation specs memo, analysis specs memo

Liquid + metal samples

- **Contact at CERN**: P. Gorbounov (PH/LBO) and M.Battistin (EN/CV/PJ**)**
- **Irradiation type:** Co-60 gamma (TK 100/1000?)
- **Samples**: 3M Novec 649 and 3M Novec 7100 fluids in soft 80-100 ml PE containers
- **Target dose**: 0.6, 6, 60 kGy (H_2O) ≈ 1, 10 and 100 kGy at 25°C. Total dose accuracy: <10% -- to be confirmed
- **Target dose rate**: corresponding to ~10% dose uniformity at ±1.5 cm container
- **Temperature**: to be specified
- **Component/System**: liquid fluorinated coolants/LHC detector cooling systems
- **Urgency**: not urgent
- **Earliest start/latest end**: November 2015/ May 2016
- **Pictures**: test containers
- **CERN documentation**: this presentation, irradiation specs memo

Summary

- CERN is seeking sustainable alternatives to C6F14, the popular coolant used in many experiments at the LHC
- 3M Novec fluids are promising candidates
- A project to validate 3M Novec 649 has been initiated by LH-LBO (for SciFi Tracker upgrade)
- Work has started, we are getting ready for the irradiation tests
- A very attractive option would be to perform the composition analysis of the irradiated samples at the Fraunhofer or a partner lab
- The Project TWIKI page: https://twiki.cern.ch/twiki/bin/view/LHCb/C6K

Thank you!

Nomenclature

3M	3M Company
C6F14	perfluorohexane, popular DC fluid
C6K	short for “6-carbon FK”
DC	detector cooling
FK	fluoroketone
FOM	figure of merit
GHG	greenhouse gas
GWP	global warming potential
HFE	hydrofluoroether(s)
HC	hydrocarbon(s)

HTF	heat transfer fluid
IER	ion-exchange resen(s)
MS	molecular sieve(s)
ORC	Organic Rangine Cycle
PFC	perfluorocarbons
SS	stanless steel
WP	work package

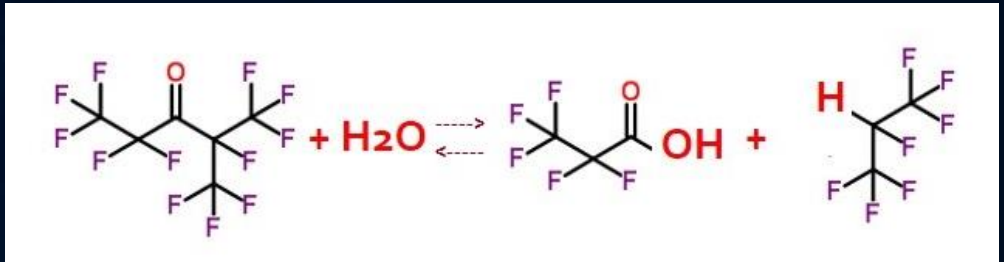
References

1. P.G., “Cooling for the LHCb Upgrade SciFi Tracker”, presented at TIPP’14
2. “Detector Cooling for the BGV Demonstrator in the LHC”, EDMS 1439028
3. PH/DT ATLAS_NOVEC Project
4. P.G., “Project: 3M Novec 649 as a replacement of C6F14 in liquid cooling systems” (Note 1) – literature survey
5. P.G.,“Assessment of the radiation damage to the coolant in SCiFi tracker” (Note 2)
6. P.G., M.Battistin, E.Thomas, “Comparison of liquid coolants for single-phase detector cooling” (Note 3)
7. P.G., M.Battistin., E.Thomas, “Alternative to liquid PFC C6F14 for mono-phase detector cooling applications at CERN” – the Work Package , EDMS 1489771 v 0.2
8. Annex 1 for the Work Package, “Commentaries to C6K validation tasks”
9. Annex 2 for the Work Package, “Questions to Novec 649 manufacturer”
10. S.Ilie et al., “ Chemical and radiolytical characterization of PFC liquids…”, EDMS 804849 and 842110

Backup slides

Chemical reactivity of N649 with water

- Most significant hazard for low-dose applications



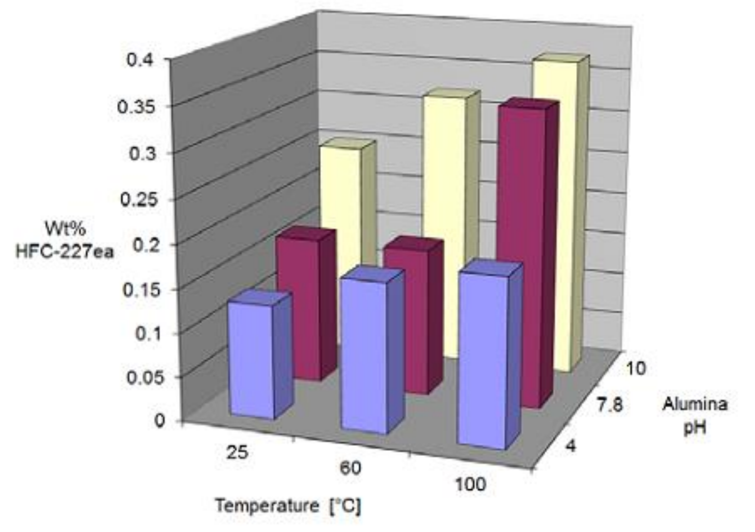
- Liquid water is required for the hydrolysis to proceed
- Won't react with water dissolved in the fluid
- PFPA will be accumulating in the aqueous phase
- Little, if any, reactivity with moist air

- Expected problems: if liquid water gets inside the cooling circuit or leaks outside and gets in a prolonged contact with condensation water.   NB: SS 316 is safe!
- Like with any chemical reaction, the hydrolysis rate will drop at low temperatures
- Initial concentration of PFPA in Novec 649 is < 5 ppm (3M)
- Water solubility in N649 is small: 20 ppm at 25°C (rapidly decreases at low T)
- Both moisture and acid levels in the coolant have to be monitored during the service

Corrosion of Ni-plated brass drain valve of the chiller

Chemical reactivity of N649: alumina, zeolytes

- 3M reported a weak reactivity of N649 with alumina and zeolytes (tested down to 25°C). Quite cursory study!
- The most important consequence, which will be central to the validation study, is that the MS- and alumina-based filters currently found in the C6F14 cooling systems will be not usable with N649, at least at moderate temperatures
- 3M recommends to use alternative desiccants, like silicagel (or metal sulfites for deep drying to < 1 ppm)
- Promising alternative: ion-exchange resins



Reactivity of N649 with Alumina of different acidity, quantified by HFC-227ea evolution

"Radiation hardness" (III) : a word on C6F14

2002 simplified tests by M.Atac et al. indicated that C6F14 resisted well the 20 kGy γ-dose.

Further comprehensive study of radiolytical properties of C6F14 was made in 2006-2007 at CERN by S.Ilie et al. [10], provide guidelines for N649 validation!

> "The induced acidity and the fluorine ion content, the presence of polymers or prepolymers, the appearance of new chemical species were the main radiation induced effects and these parameters were used to characterize the radiation hardness of the fluids..."

- Air, moisture and other H-containing contaminants caused "detrimental effects" like CF2O formation, corrosion (mainly for Al) and the appearance of polymeric deposits
- Branched iso-C6F14 was found to be more radiation-resistant than n-C6F14 (NB: C6K is branched!)
- The higher the liquid purity, the better its radiation resistance
- The detrimental radiolysis products could be effectively removed by inline cleaning. The cleaning agents , as well as the filter composition, were recommended (activated charcoal, alumina and MSs)
- Initial deoxygenation and dehydration is recommended

Purification for N649

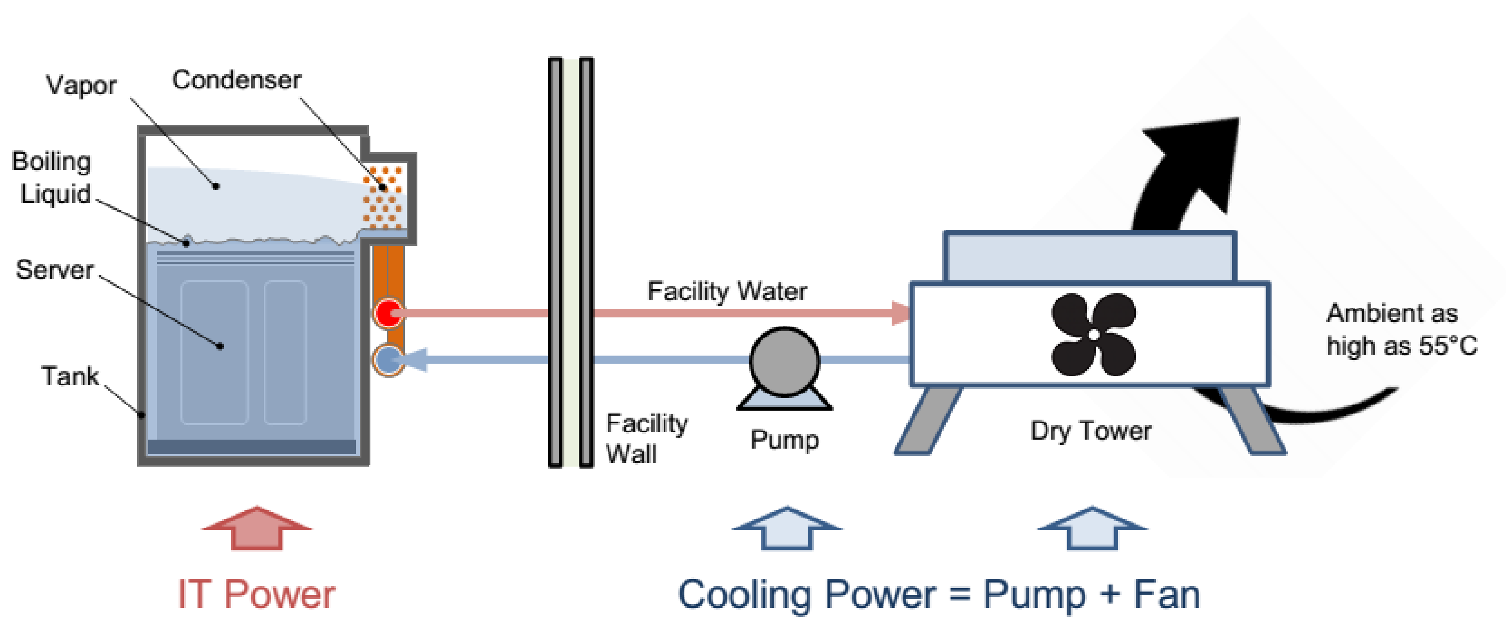
- Desiccants (regenerable)
  - $CaSO_4$ ("Drierite")
  - Silicagel (used in pool boiling)
  - Ion-exchange resins (acid, Na+ form)
- Acid removal
  - IER (eg Dowex M-43), non-regenerable
- General (HCs, pre-polymers, low-mol-w)
  - Activated carbon (acid washed!)

Suggested by 3M, shown to be efficient above water freezing

- Low temperatures? (online cleaning)
  - Practically no information
  - IER ?? (a good task to outsource!)
  - MS might be usable at ≤ -40°C !
- Hybrid filters:
  - Warm service (silicagel, IER, Drierite, activated carbon)
  - Cold service (activated carbon + MS)

Open bath liquid immersion cooling with Novec

Data centers of the future (from tens of teraflops to tens of petaflops) -- link



Navy research Lab
DC Washington

- Extremely energy efficient (up to 100 kW/m², vs ~10 kW/m² in air-cooled systems)
- NB: serious players are involved!
- No material compatibility concerns, even at >50°C!

Refrigerant

- **Baseline choice:** 3M™ NOVEC 649 thermal management fluid
  - fluoroketone, $C_6F_{12}O$
  - thermophysical properties similar to C_6F_{14}
  - volatile, dielectric, low viscosity
  - inflammable
  - low toxicity (widely used as a clean fire extinguishing agent in occupied spaces, e.g. data centers)
  - GWP=1
  - Reactive with liquid water (not important for our application)
  - 3M positions Novec fluids as a replacement for PFCs

Backup: C_6F_{14} (3M™ FC-72, F2™ PP1)

- very well studied, used in 13 LHC systems
- deprecated, GWP=7400