C6K and Water

P. Gorbounov, 18/06/2015, Novec General Meeting

- Why water is undesirable and what do we know about C6K?
- Issues to be studied or considered
  - Moisture detection in C6K
  - Applicable desiccants
  - What to do in case of accidents
  - R&D issues

Why water in undesirable? (I)

- Water is undesirable even in C6F14
  - Hydrodynamic effects
  - Icing
  - Radyolisis
- Water in C6K is even more detrimental:
  - Liquid water reacts with C6K giving PFPA which is accumulation in the aqueous phase
  - Turbulent flow intensifies this process (liquid water emulsifies and the contact area increases)
- What do we know about C6K hydrolysis:
  - No hydrolysis occurs in contact with humid air
  - Water dissolved in C6K (up to 20 ppm at 25°C) does not react. Only liquid phase is reactive.
  - Essentially, a surface chemistry effect
  - The acidity of the aqueous phase can grow very high (earlier, 3M: only to pH=3; recent tests at Dynalene: pH down to ≈1 was observed after a prolonged stirring with the excess of water
  - Observation (to be verified!): no traces of water or acid have been detected in the bulk C6K
  - This was a big surprise, both to me and to 3M – we expected C6K to saturate with dissolved water to the "data sheet" level
  - The hydrolysis rate, like with any other chemical reaction, depends on the temperature.
  - 3M believes that the solid water should be also weakly reactive (TBC)

Why water in undesirable? (II)

Given all that, even for low-dose applications it becomes imperative to control and monitor moisture level in C6K

- Ideally, the moisture should stay at < 1 ppm level (dry coolant is safe!)
- This implies the need for highly efficient desiccant(s) to be incorporated in the cooling loop
- Real-time monitoring of the moisture level!
- Unstable or rising moisture level = trouble requiring intervention!
- Moisture level at saturation (for the given T) = water might stay in a supersaturated dissolve state, but eventually will precipitate (as droplets in laminar or static flow state, or as emulsion in turbulent flow state)

Issues to be studied or considered

- Moisture detection in C6K
- Applicable desiccants
- What to do in case of accidents
    - bad accidents with prompt liquid water penetration into the cirquit
    - minor external leaks
    - major leaks
- R&D issues, plans
    - At CERN
    - At external labs (Dynalene etc)

Moisture detection (I)

- Traditional method of measuring absolute water content in solver
  the Karl Fischer titration:
  - Sampling + chemical analysis using modern semi- or fully automatic laboratory instruments
  - Accuracy: down to 1 ppm (1 µg/1 g sample) for coulometric K
  - Essentially off-line = not good for monitoring
  - Expensive (reagents + laboratory work)
  - Ketons require special (even more expensive) reagents
- Spectrometric methods , e.g. NIR spectroscopy
  - At CERN
  - At external labs (Dynalene etc)

Moisture detection (II)

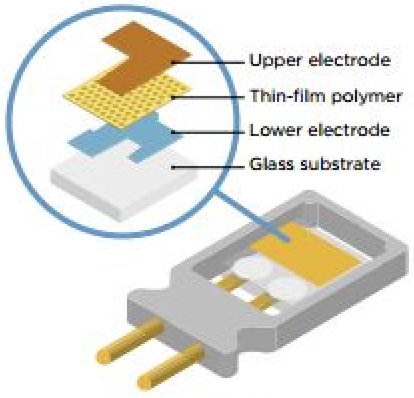
- Modern industrial approach to continuous moisture measurement, massively used to monitor the quality of transformer, combustion, lubricating and other (e.g. silicone) oils is based on thin-film capacitive sensors
  - They measure “relative saturation” = “water activity”

$$aw = {}^{M(T)}/_{S(T)}\,;\ 0 \le aw \le 1\ \text{, where}$$

M(T) = absolute water content; S(T) = saturation content

$$S(T) = S_{\infty} s \ / \ E/kT$$

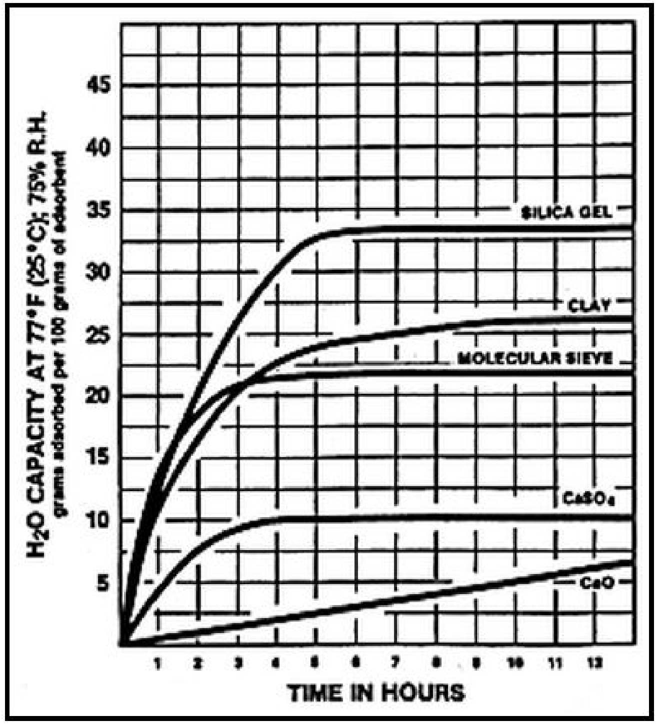
  - Relative saturation sensor can be calibrated by measuring M(T) at several S(T) different points. Here, KF titration is unavoidable!



Structure of the HUMICAP sensor.

Desiccants (I)

- For C6F14, molecular sieves (MS) are universally used, for moisture and other contaminants (acids!). MS are adsorbents and are usable at low temperatures
- 3M shows that the MS (and alumina) are weakly reactive with C6K at room T and above (no data for low temperatures!)
- For C6K, 3M recommends silicagel and (routinely used in full immersion apps) and metal sufphates (e.g. $CaSO_4$ = Drierite)
    - Both are inexpensive
    - Silicagel is very good for large water concentrations (> 0.1 %) and gas a very high drying capacity
    - Drierite can dry down to < 1 ppm, but typically has only 10% capacity (by weight)
- Ion-exchange resins (IER) have been demonstrated to be compatible with C6K – they can replace MSs…
    - Pros: regenerable, available, efficient
    - Cons: require columns; low-temperature performance?
- My intent: to delegate this study to Dynalene



Desiccants (II)

- Hypothesis (TBV): MS can be stable with C6K at lowest service temperatures (≤ -40°C). “Hybrid” approach:
  - >0°C – silicagel + Drierite (or IER) _ activated carbon
  - ≤ -40°C – MS
- Additional methods
  - Continous washing of C6K with dry and purified N2, in the expansion or dedicated washing) vessel

Bad accident: (liquid water gets into cooling circuit)

- Possible at > 0°C (out of service!)
- Identify and fix the problem
- Emergency drying cycle (silicagel + Drierite) + <u>acid removal (IER)</u>

Leak accidents

- C6K does not get in contact with water --- OK, it evaporates and is removed by flushed dry gas
- C6K gets in contact with condensation water
  - <0°C – little or no effect, C6K evaporates
  - >0°C – local acid accumulation, no harm for SS, possible corrosion for Al and copper

R&D issues

- How to saturate C6K with moisture? 3M and the literature recommend bubbling of humid gas (air or N2), with simultaneous monitoring by a humidity sensor. --- Tests are foreseen at CERN and Dynalene
- Absolute moisture measurements to calibrate the humidity sensor(s):
  - KF titration, with special reagents for ketones:
    - Signa Aldrich HYDRANAL Coulomat AK and CG-K
    - J.T.Baker Hydra-Point for Ketones
    - Other?