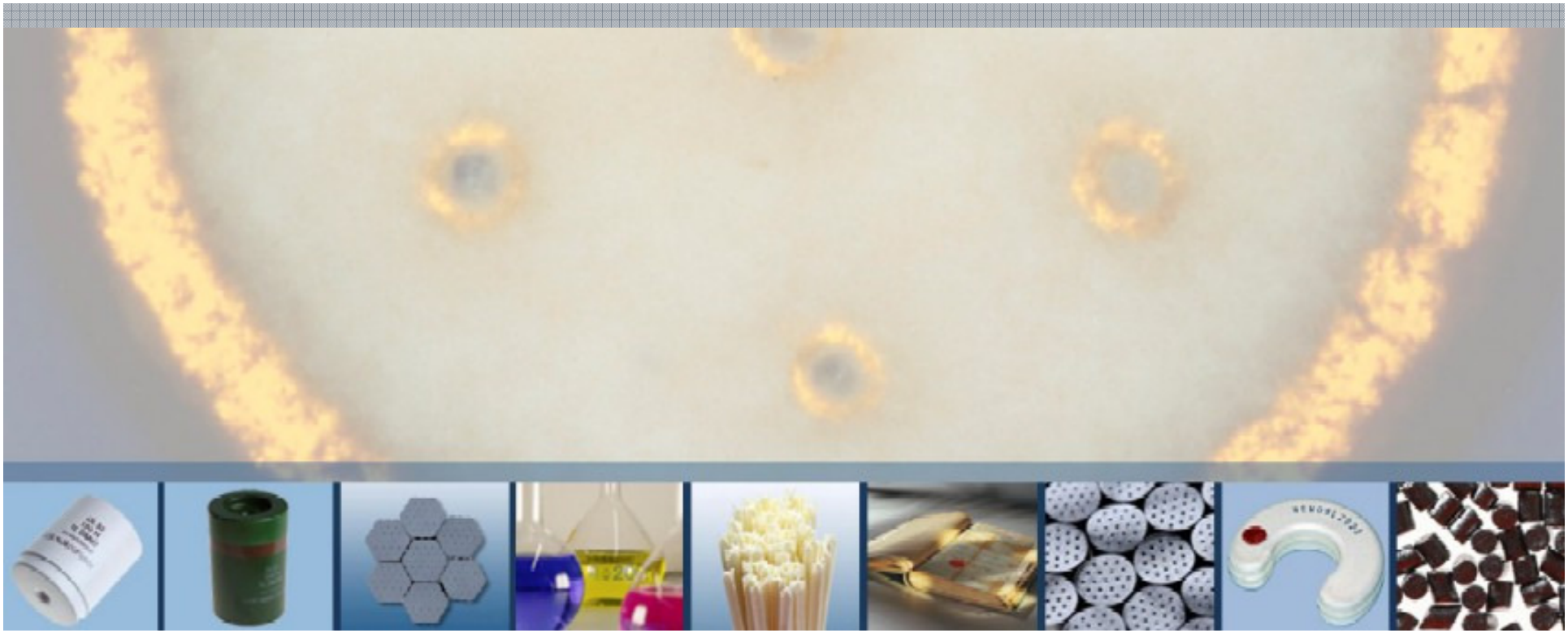
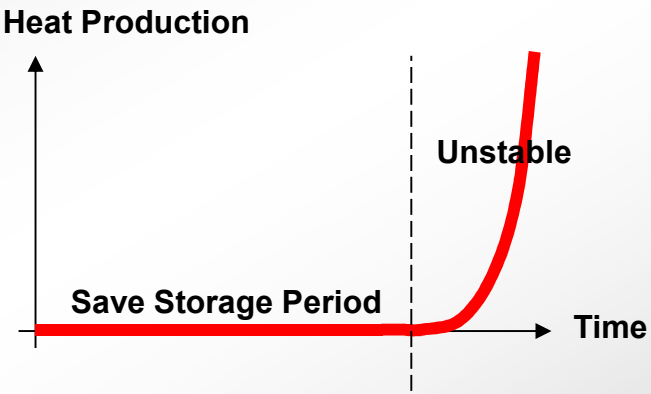


# A New and Cheap Method for the Evaluation of Shelf Life of Nitrocellulose

**Beat Vogelsanger, Ruth Sopranetti, Beate Pausch and Daniel Stegmaier**

# Introduction (1)

- Nitrate ester products without stabiliser (NC, NG, paste, premix) show a distinctive ageing behaviour:
  - First: Long storage period without visible ageing effects (in particular: no heat production)
  - For NC and paste, this safe period typically lasts for several years at ambient
  - During this period, perfectly stable propellants can be produced from theses materials
  - But: Nitrogen oxides ($NO_x$) are produced and accumulated during this period

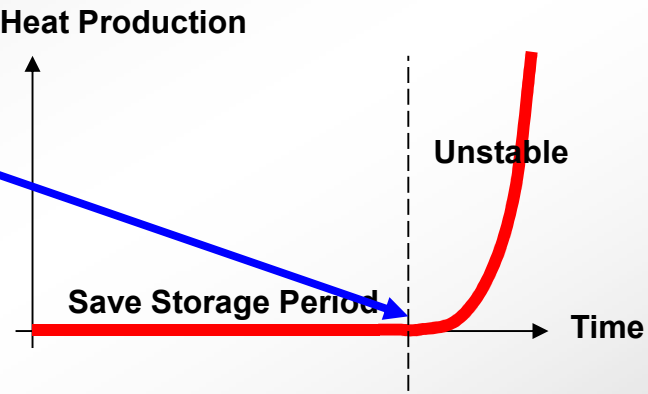



  - After end of safe storage period: Unstable condition; start of autocatalytic reaction with strong heat / $NO_x$ production → finally thermal explosion

- Conventional stability tests (such as Bergmann Junk Test / Methyl Violet Test) give only limited information regarding "real shelf life" of nitrate ester products because:
  - These tests are performed on dried samples, whereas NC and paste are always stored either water wet or alcohol wet
  - Conditions of these tests (e.g. temperature > 130°C) are too extreme to allow extrapolation to typical storage conditions

# Introduction (2)

- A good estimation of the "real shelf life" may be obtained by determining the start of the self-heating phase
- This can be done using suitable thermo-analytical instruments such as:
  - Acceleration Rate Calorimetry ARC (dynamic method)
  - Heat Flow Calorimetry (isothermal method)

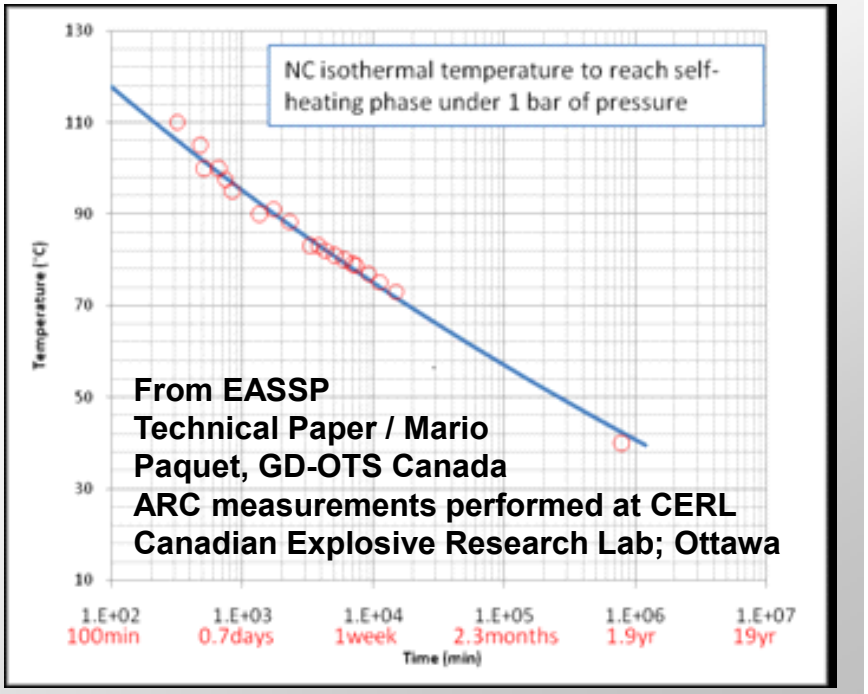



- An easy and cheap alternative would be to store the test samples in ovens at different temperatures with visual observation to detect start of self-heating phase

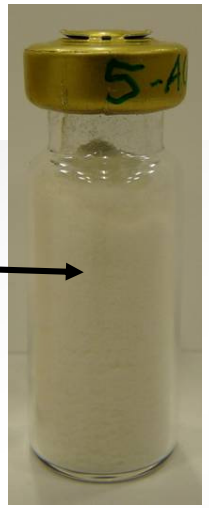
# Accelerating Rate Calorimetry ARC


- Operational Principle of dynamic ARC method:
  - NC sample is placed in sample bomb (= confined adiabatic environment)
  - Instrument determines the onset of exothermic reaction using an automatic heat-wait-search step scanning mode
  - Instrument then follows this exothermic reaction adiabatically
  - Time to reach self-heating phase under isothermal conditions is finally calculated from the recorded ARC temperature and pressure data using sophisticated thermo-kinetic simulation software
- Allows determination of shelf life values over a broad temperature range within a short period of time
- But: Instrument is expensive

  (we don't have it !) ☹



# Heat Flow Calorimetry HFC (1)

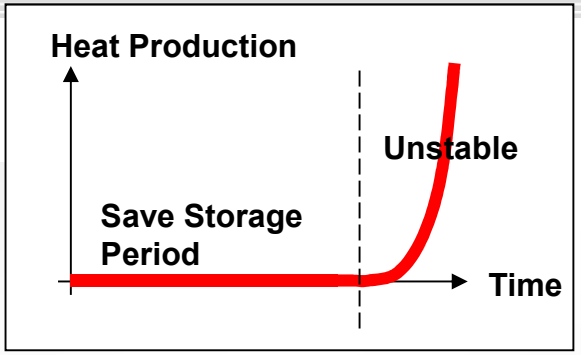



- **Operational Principle of HFC method:**
  - **NC sample is placed in hermetically sealed glass vial (= confined isothermal environment)**
  - **Instrument keeps sample at constant temperature and records any heat production or consumption**
  - **Start of self-heating phase is directly visible from obtained heat flow curves (= main advantage of this method; no calculations / model assumptions involved)**

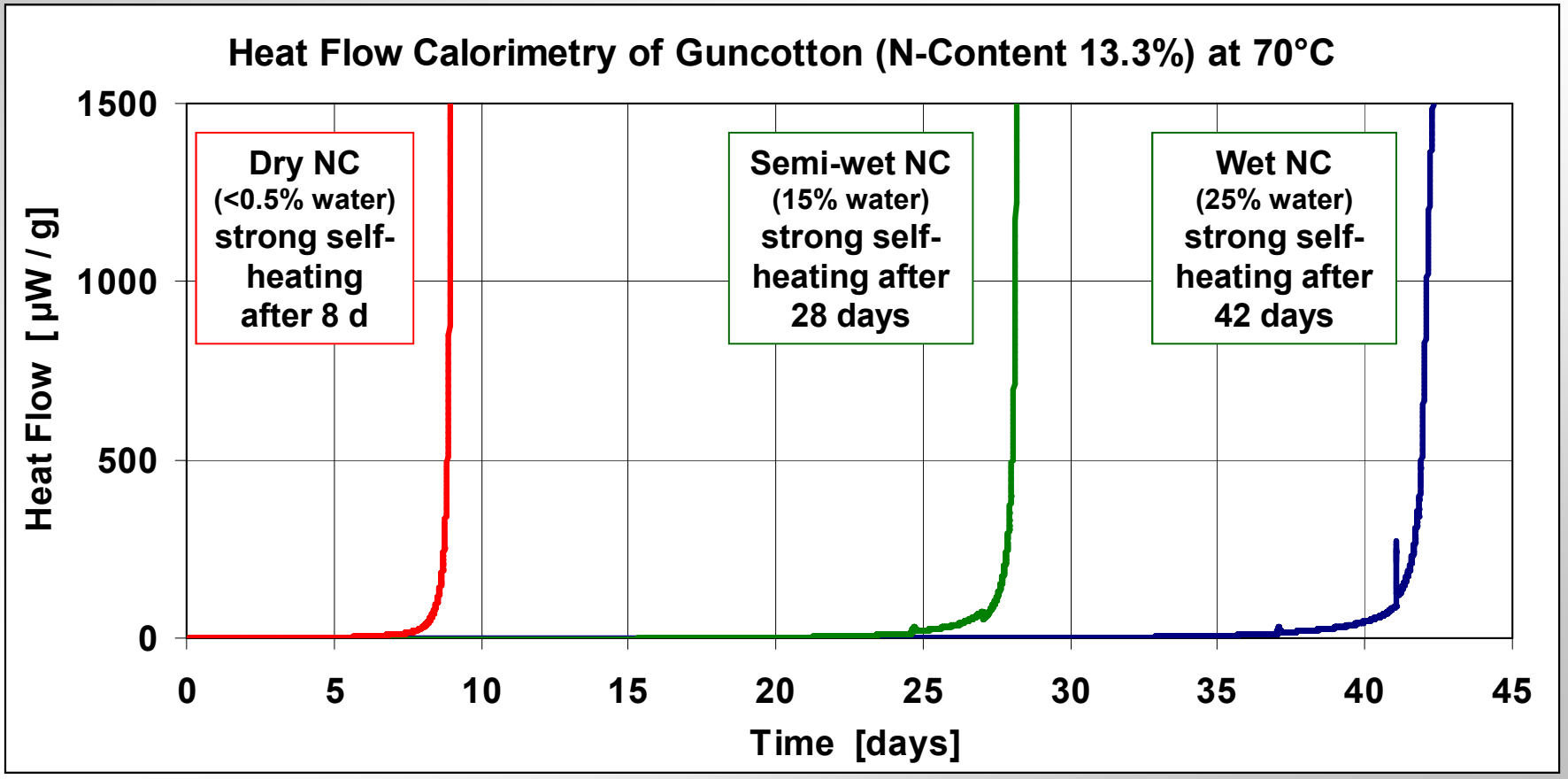
- **Disadvantages of HFC method:**
  - **Very costly (expensive instrument + very long testing time at lower temperatures (weeks at 80°C; 1-2 months at 70°C; 3-6 months at 60°C)**
  - **Repeatability of "time to autocatalysis" determination is poor → measurement of replicates necessary (→ multiplies cost)**
  - **Instruments may be damaged due to overpressure venting of the sample vial if the measurement is terminated too late (testing of 12 NC / paste samples destroyed 2 channels of the 1277 TAM !!)**


**HFC sample lifter separated from vial and ejected due to strong overpressure venting**

# Heat Flow Calorimetry HFC (2)

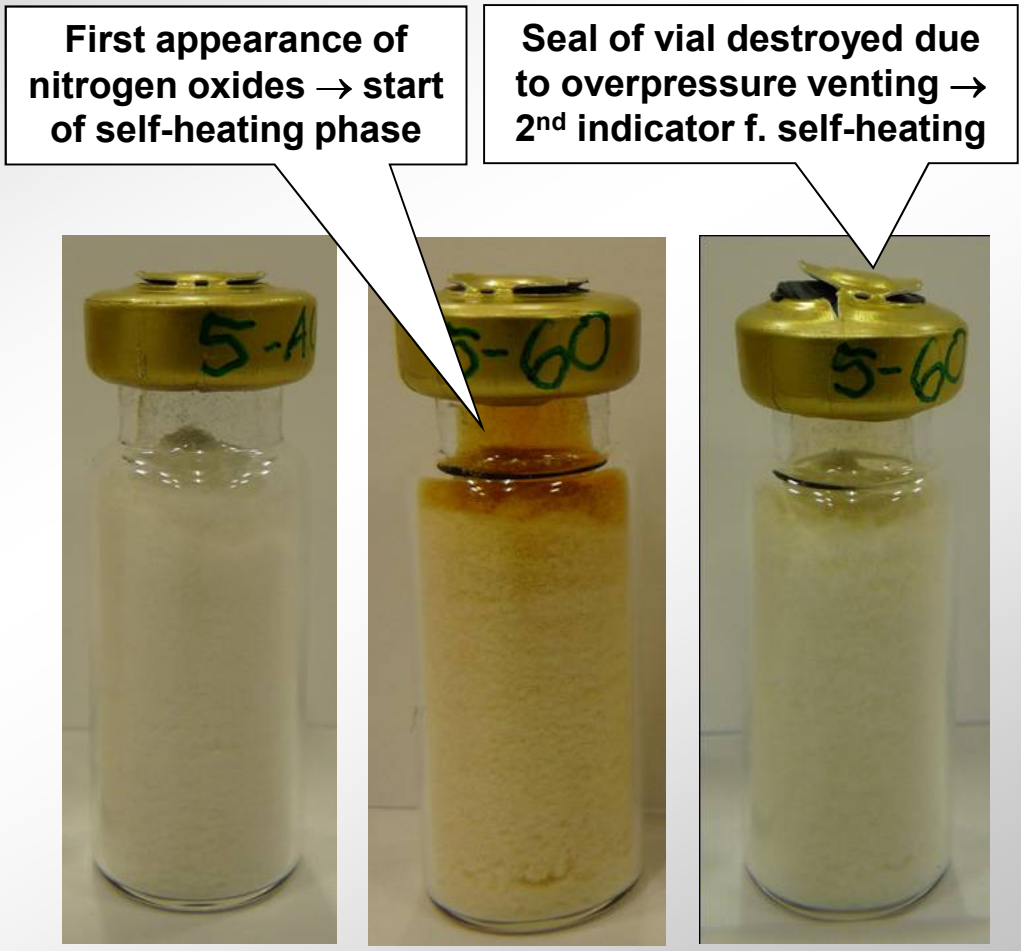



- Heat flow curves obtained were as expected from theory
- Strong influence of water content found



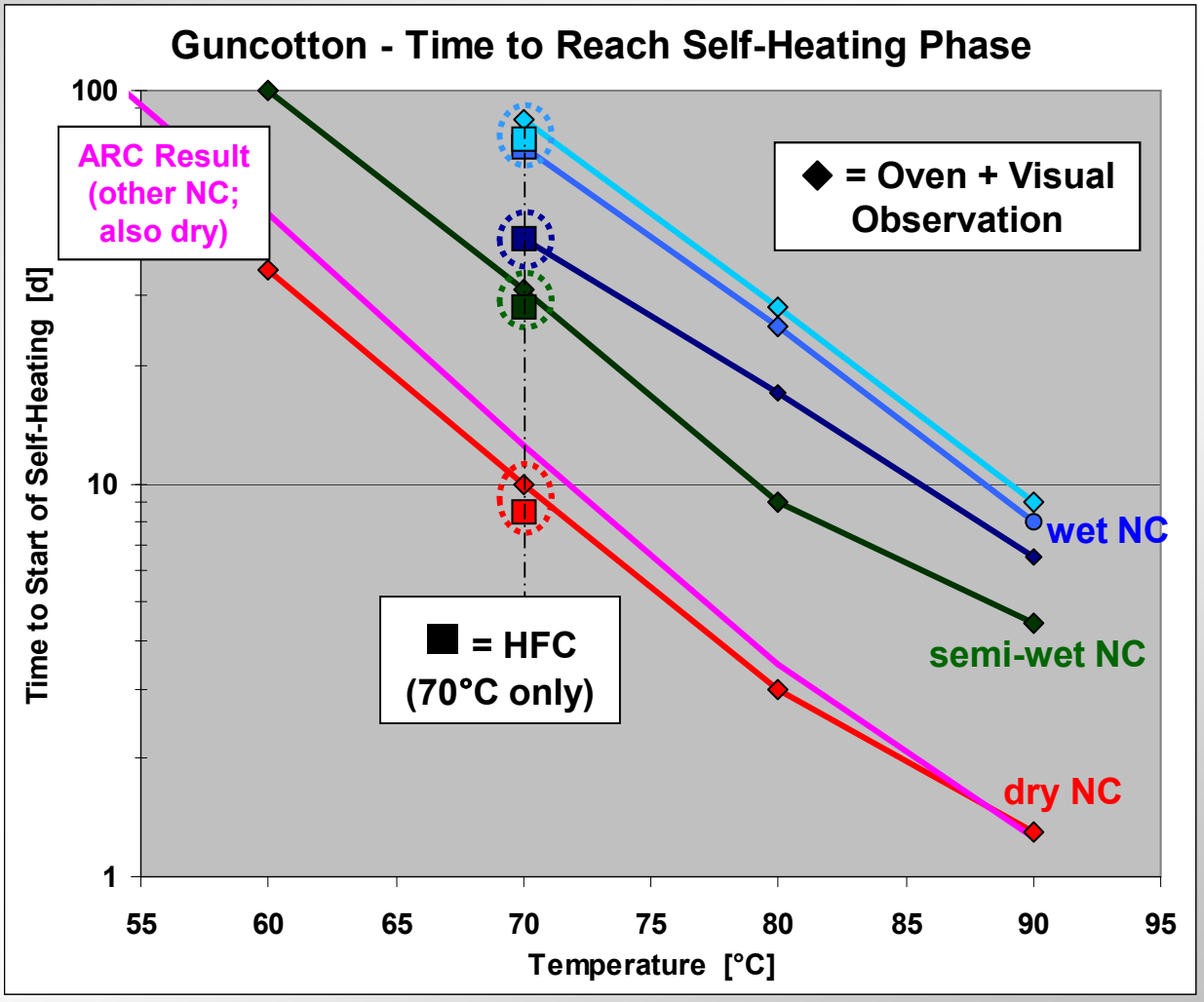
# Ageing in Oven + Visual Observation (1)

- **Principle of method:**
  - NC samples are placed in hermetically sealed glass vials
  - Sample vials are kept at a constant temperature in ovens
  - Start of self-heating phase is determined by visual observation (appearance of nitrogen oxides / "red fumes"; breaking of seal due to overpressure)
- **Advantages:**
  - Very cheap
  - Allows investigation of many different samples at different temperatures in parallel
- **Disadvantage:**
  - Start of self-heating phase is more difficult to detect



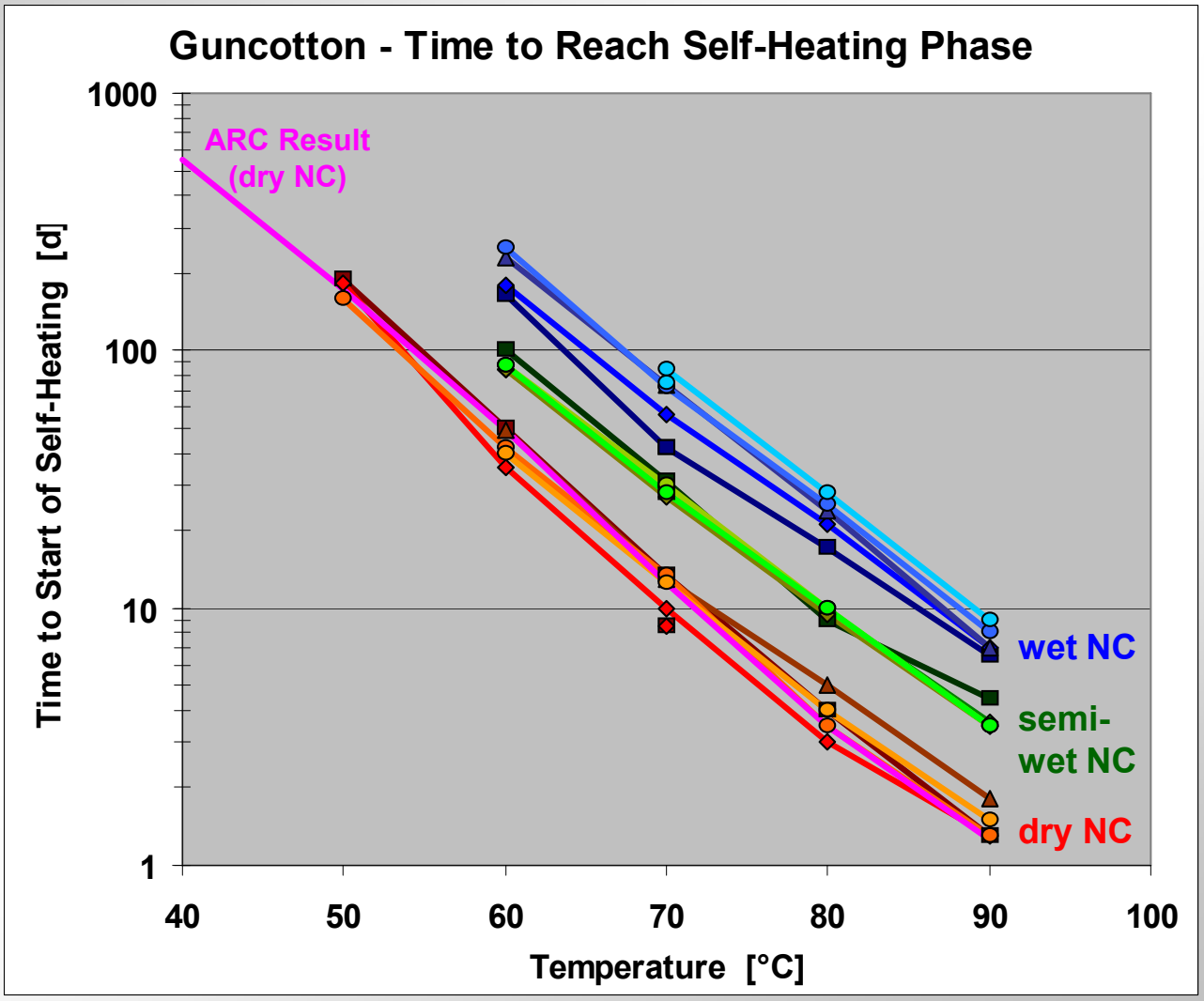
# Ageing in Oven + Visual Observation (2)

- Results of crude "Oven + Visual Observation" method coincide well with HFC results
- Results also coincide with ARC data as reported by Mario Paquet / CERL Ottawa



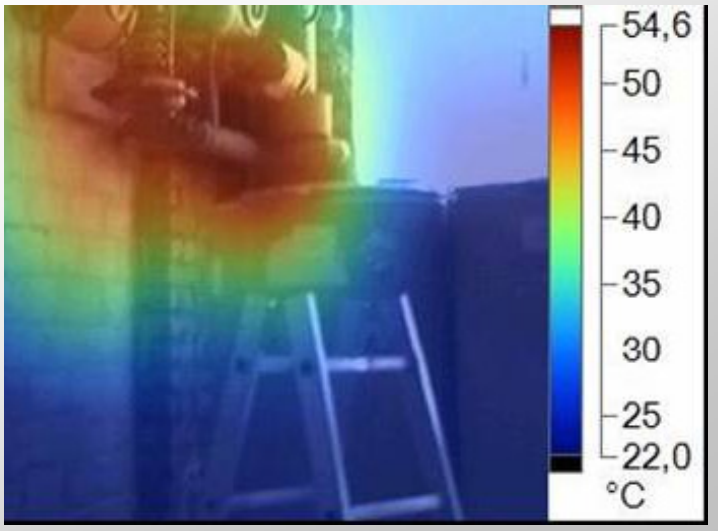
# Ageing in Oven + Visual Observation (3)

- Preliminary results of ongoing study (on 5 NC lots) already give a good overview regarding time to start of self-heating:
  - Influence of water content: wet / dry NC = factor 5
  - Influence of temperature: +10°C = factor 3



# Application: Investigation of Incidents with NC (1)

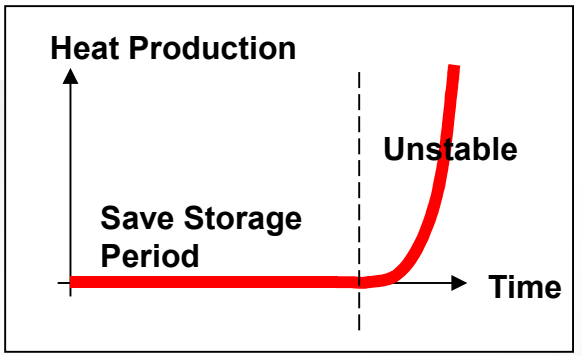
- Incident 1 during storage of NC:
  - Fire developed in NC storage building
  - Forensic investigation revealed that fire started in the region of NC drums which had been stored only 20 cm below an active steam station for 55 days
  - IR photographs taken after the incident showed that maximum temperature within steam station was 68°C, and that temperature at top of NC drums was up to 54°C
- Results of present study predict that start of self-heating is to be expected after storage for 55 days at approx. 56°C (dry NC), 64°C (semi-wet NC), and 70°C (wet NC)
- These results show that it is at least plausible that the fire was caused by the unsuitable storage conditions (NC drums in vicinity of steam station → accelerated ageing → start of self-heating)



# Application: Investigation of Incidents with NC (2)

- Incident 2 during storage of NC:
  - Fire developed in NC storage building
  - Storage building in tropic country, not air-conditioned, with outside temperatures between 23°C and 35°C all year round
  - Expected average temperature in storage building around 30°C
  - NC drums were stored for many years; only evaporated water was replenished
- Results of present study predict that start of self-heating is to be expected after storage at 30°C for approx. 3 years (dry NC), 7 years (semi-wet NC), and 14 years (wet NC)
- These results show that it is at least plausible that the fire was caused by the long storage under tropic conditions

# Summary and Conclusions




- The expected thermal ageing behaviour of NC was confirmed (fist a long safe period without heat production, followed by a rapid transition into the self-heating phase)
- An easy and cheap method to determine the "time to start of self-heating" was successfully introduced (storage of NC in ovens + visual detection)
- The thermal behaviour of different NC lots was investigated:
  - Influence of temperature was as expected (approx. factor 3 per 10°C)
  - Wet NC was found to have a considerably (up to factor 5) longer time to start of self-heating, despite moisture is expected to accelerate ageing
- Analysis of incidents which were caused by thermal (mis-)behaviour of NC showed that, in the real world, self-heating may occur somewhat earlier or already at slightly lower temp. than calculated from the obtained data
  - NC storage conditions should have a solid safety margin towards the calculated conditions for start of self-heating in order to avoid dangerous incidents

# Thanks very much for your attention !