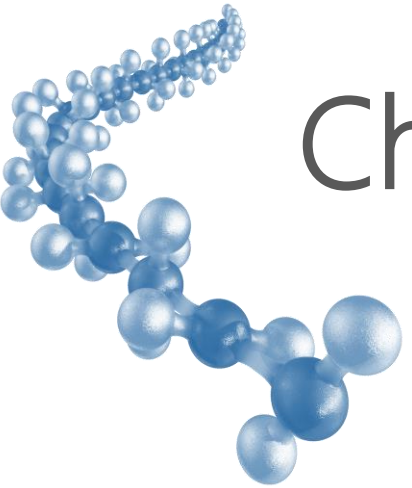
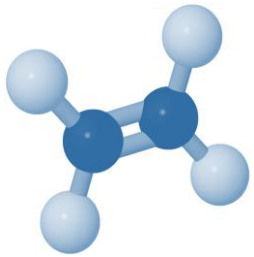


Chemical recycling of fluoropolymers

Closing the fluorine loop



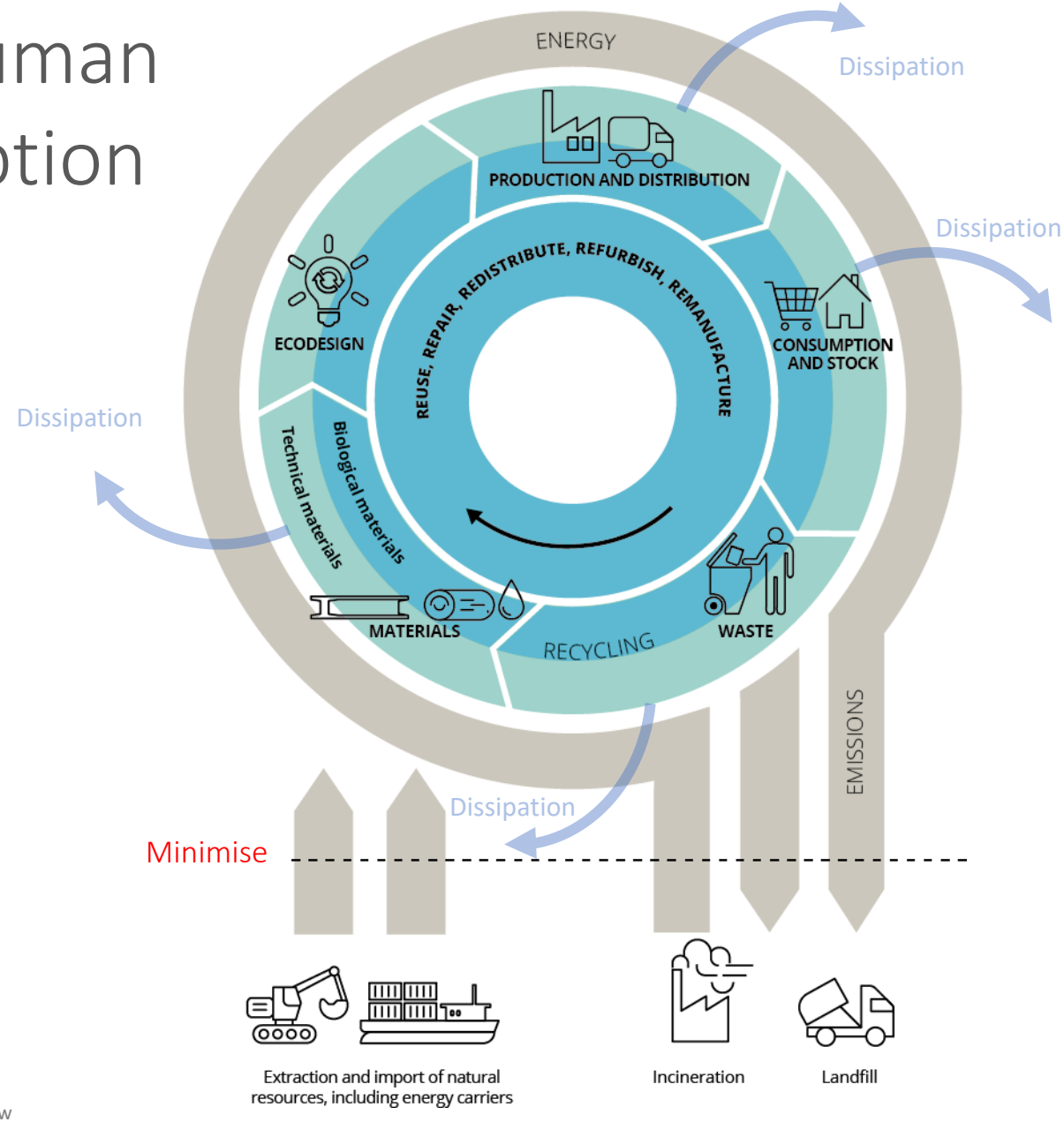
Thorsten Gerdes,
Achim Schmidt Rodenkirchen, Klaus Hintzer

SKZ - Innovations using Fluoropolymers
03.05. - 04.05.2023, Würzburg/Rottendorf

- Institute in cooperation with the University of Bayreuth
- Interdisciplinary applied research and development in the field of combined electrothermal processes and process intensification since 1997.
- Non-profit organization

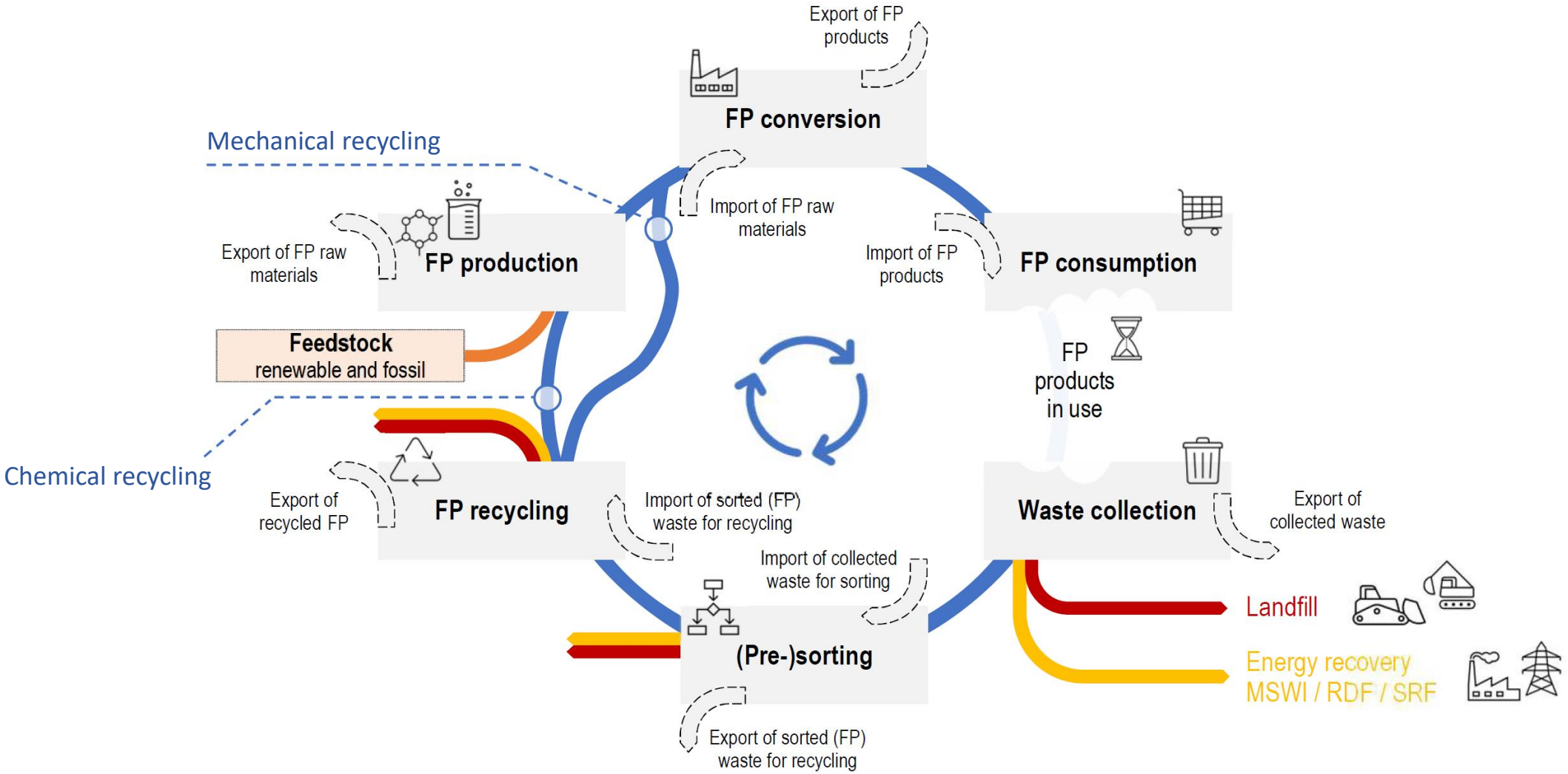
Decoupling of value creation & human wellbeing from resource consumption

Circular Economy as contribution to the EU target of net zero greenhouse gas emissions, allowing economic growth to be decoupled from resource consumption.



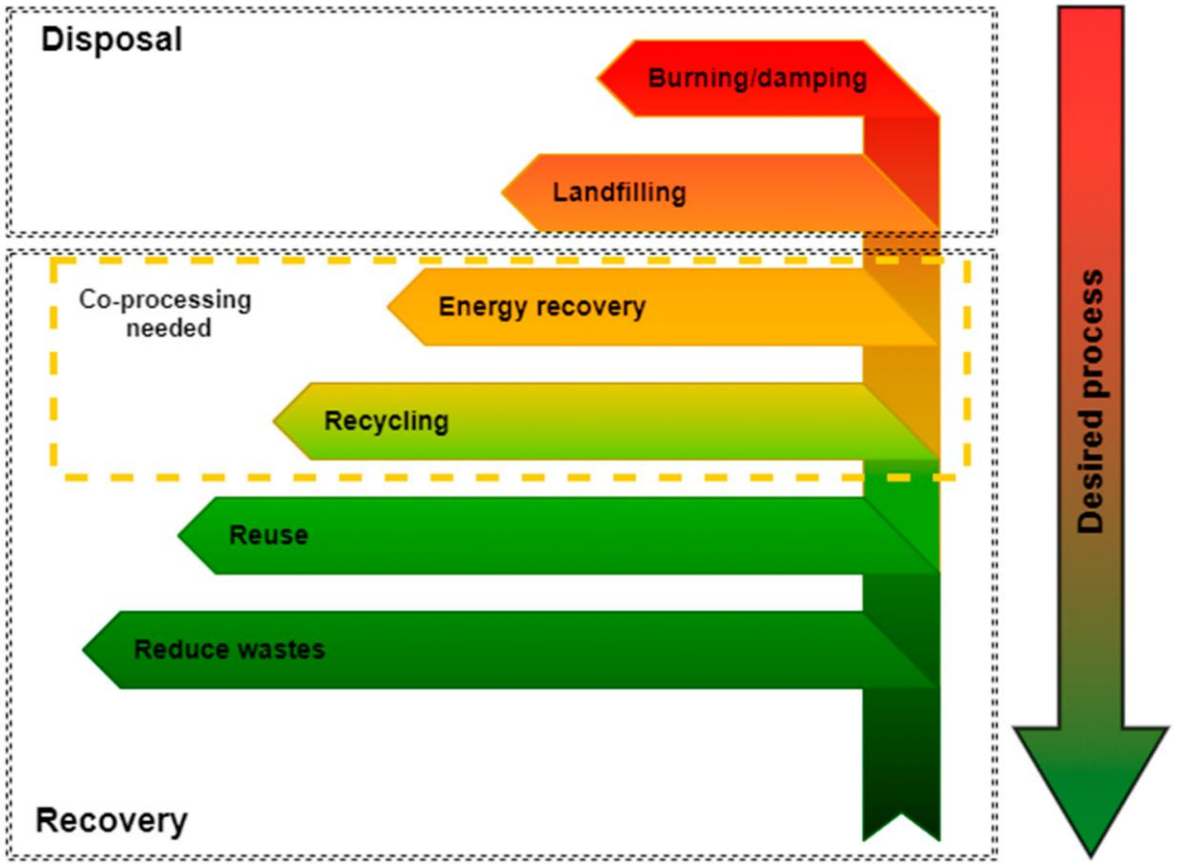
https://www.eea.europa.eu/soer/2020/soer-2020-visuals/circular-economy-system-diagram/view

Circular economy for fluoropolymers



C. Linder, H. Beylage und J. Hein, „Fluorpolymer waste in Europe 2020 - End-of-Life (EOL) analysis of fluoropolymer applications, products and associated waste streams," Conversio / proK Fachgruppe, 2022

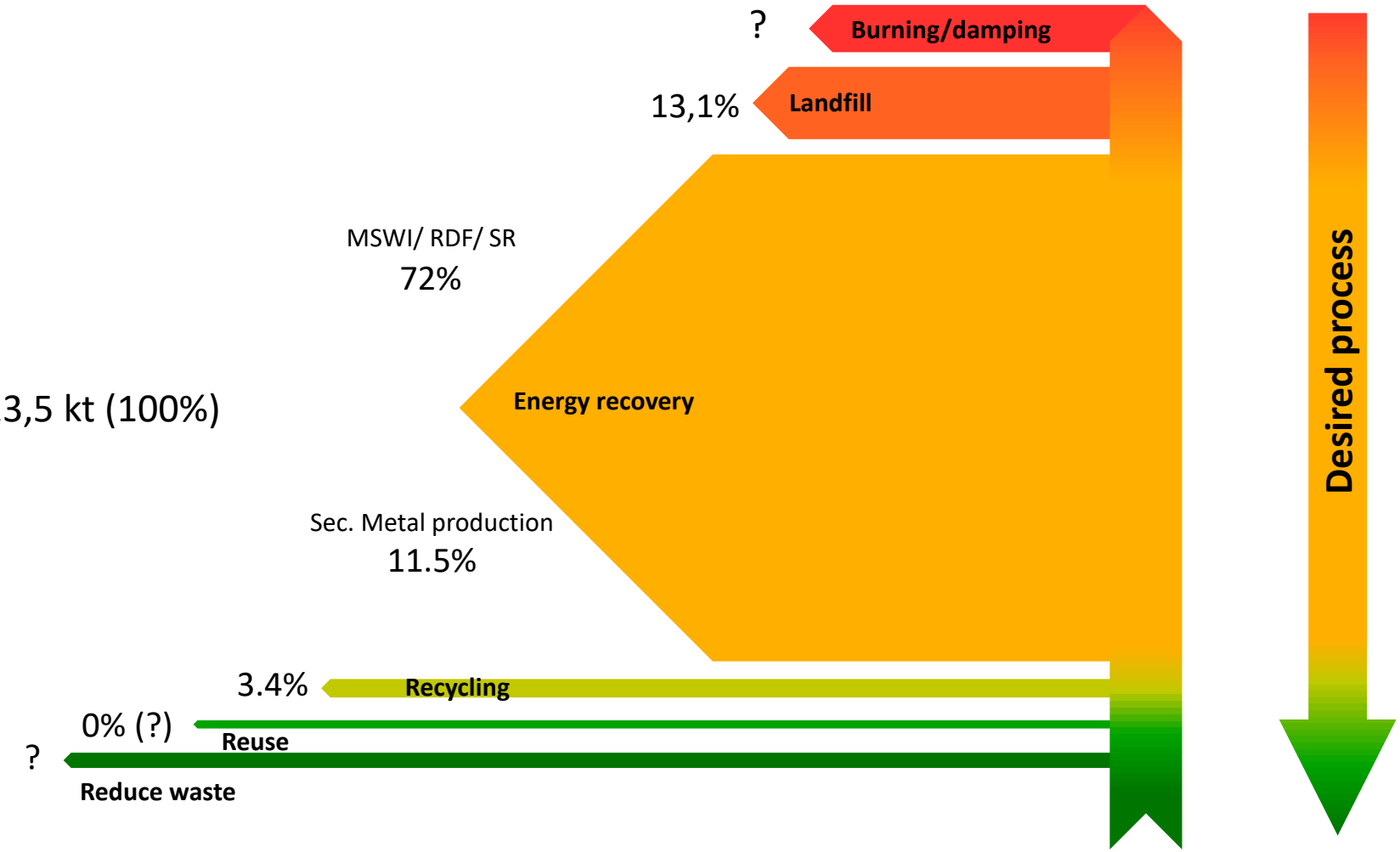
Polymers waste EoL options based on the EU Waste Framework Directive



https://www.mdpi.com/2073-4360/13/5/713

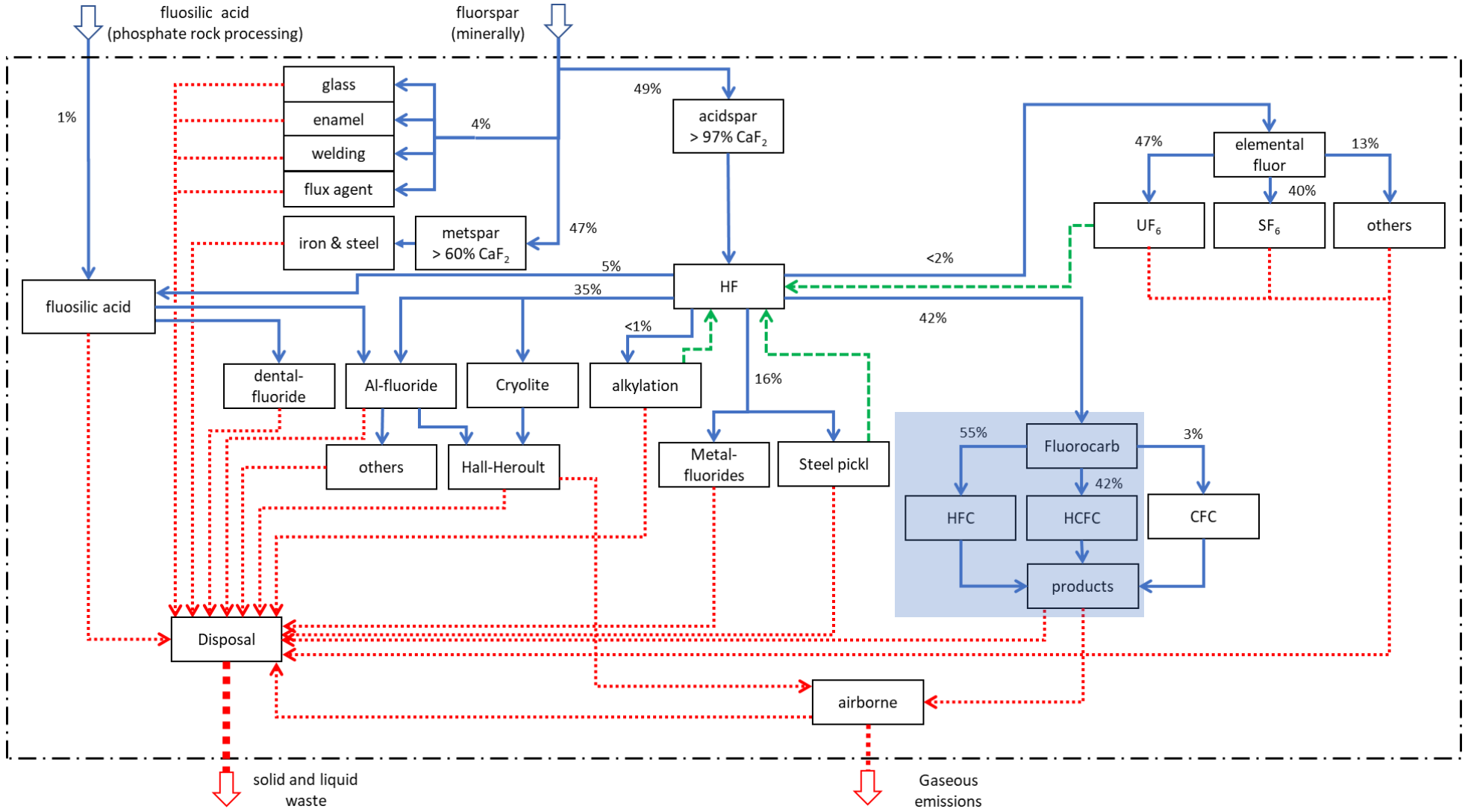
EoL fluorinated polymer material flows in Europe in 2020

EoL-waste collected 23,5 kt (100%)



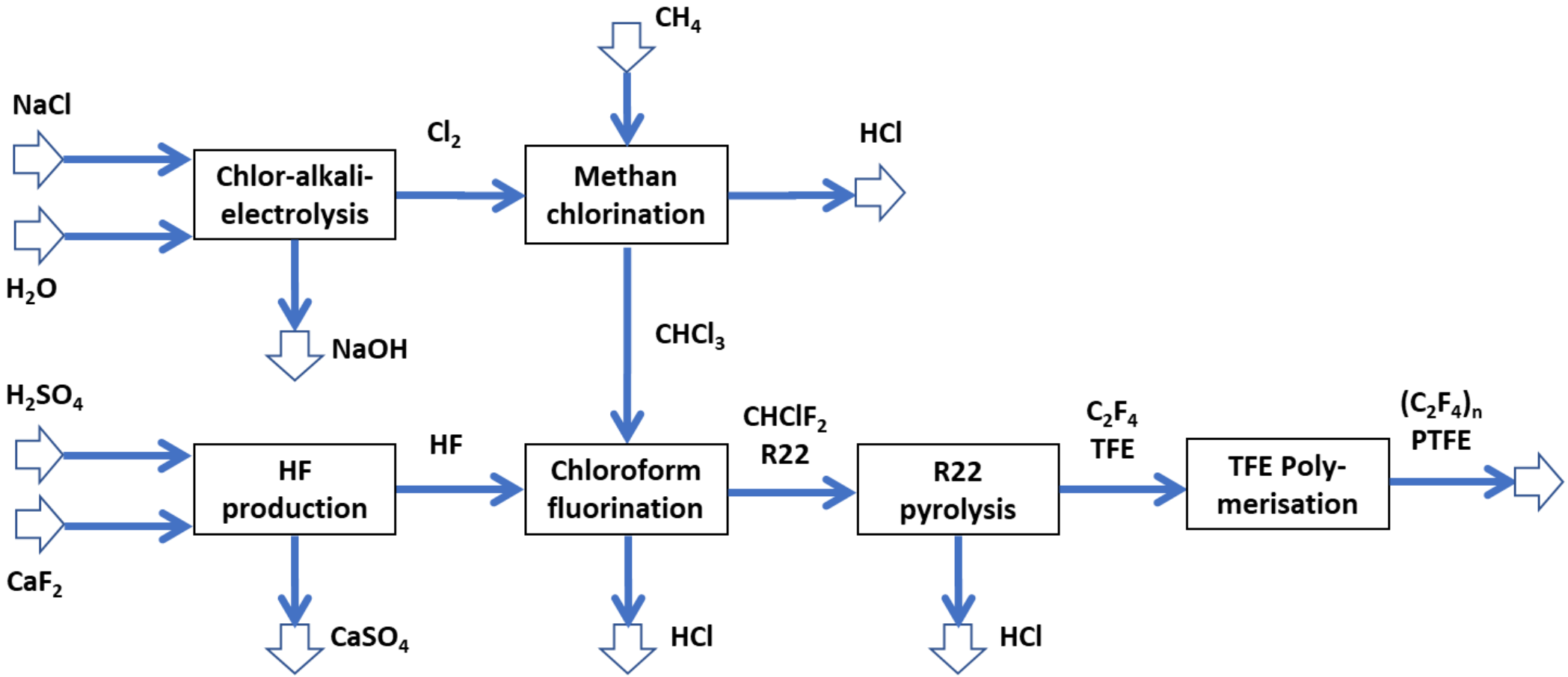
Data from: C. Linder, H. Beylage und J. Hein, „Fluorpolymer waste in Europe 2020 - End-of-Life (EOL) analysis of fluoropolymer applications, products and associated waste streams," Conversio / proK Fachgruppe, 2022

The world of fluorine

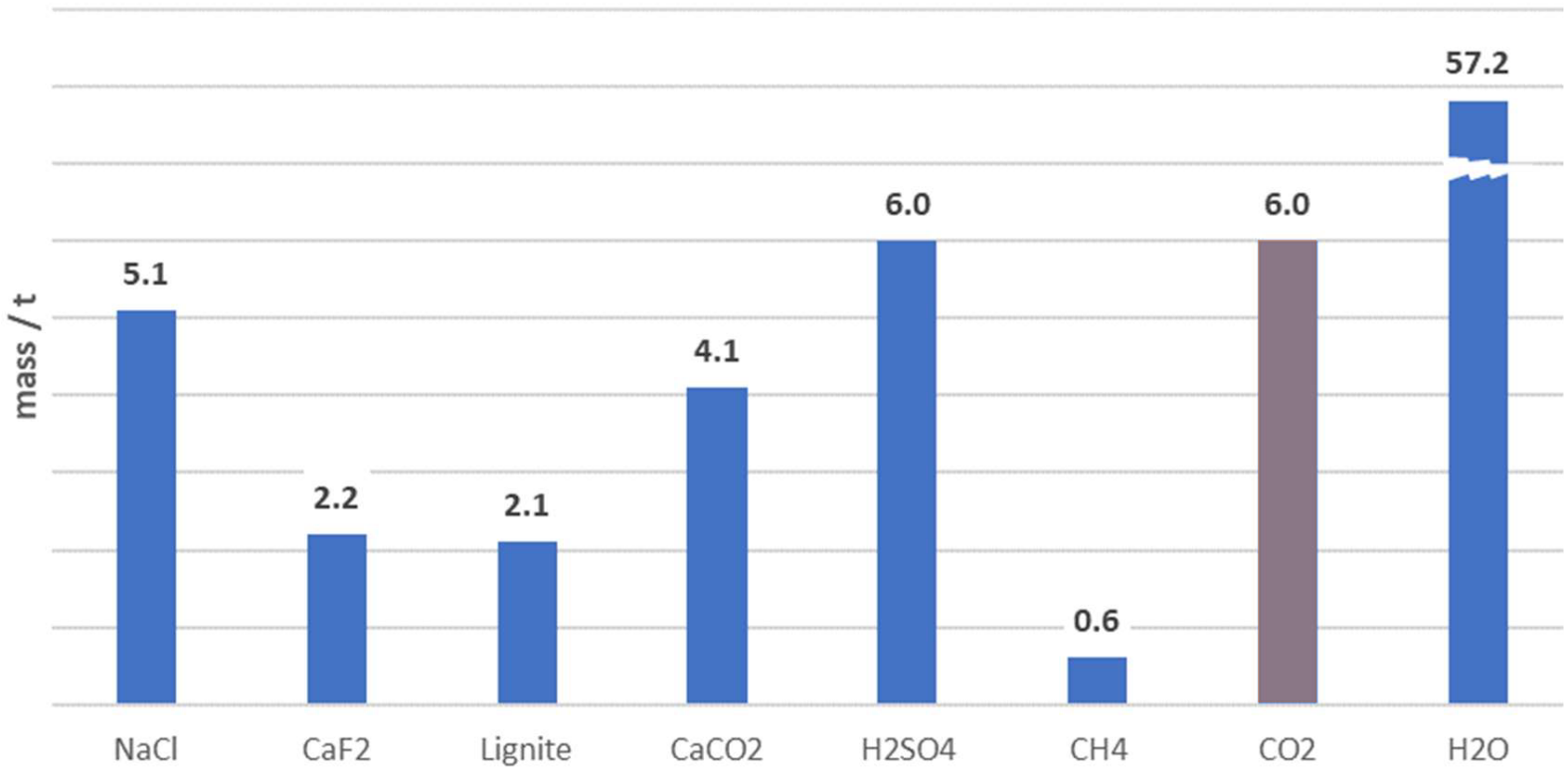


Villalba, Ayres und Schroder, „Accounting for fluorine: production use and loss," Journal of Industrial Ecology, 2008

Synthesis of fluoropolymers

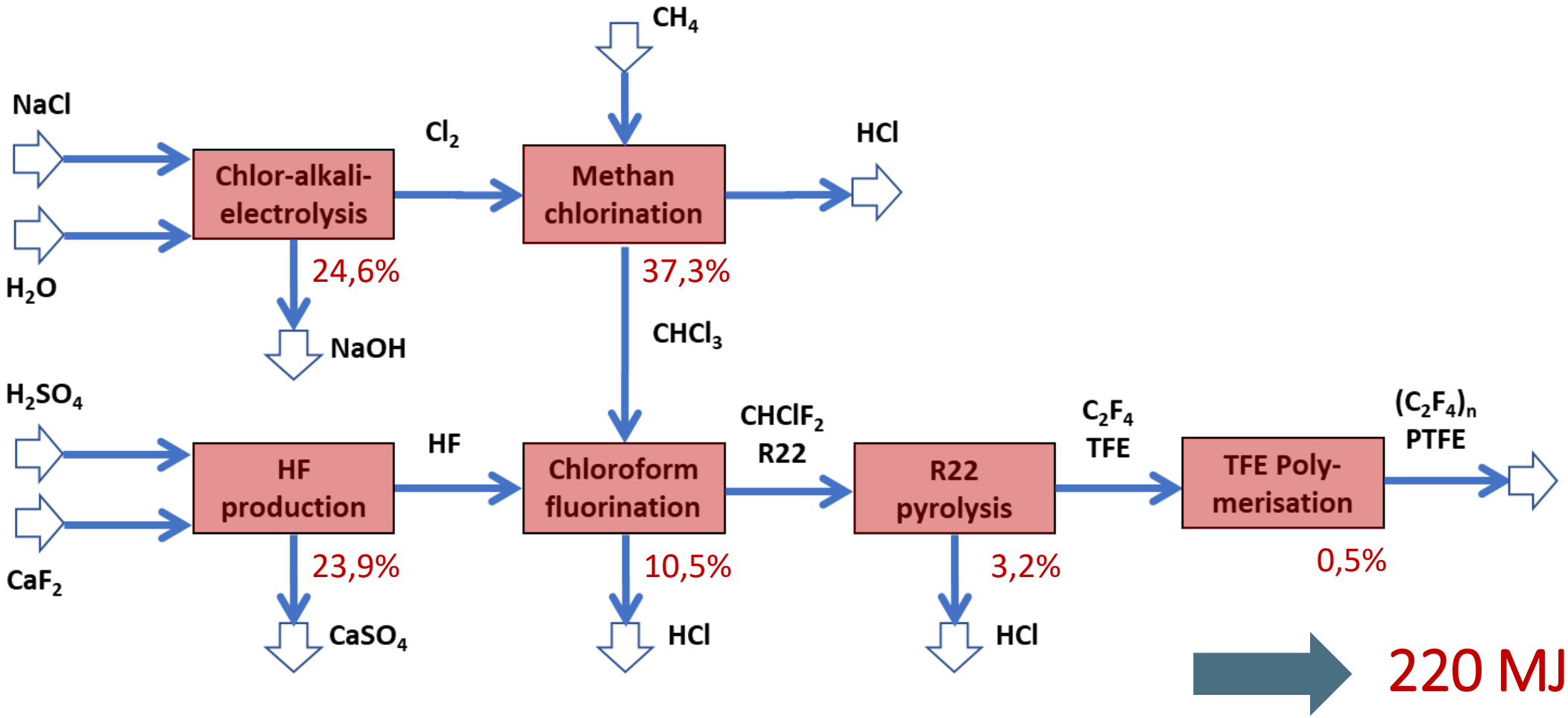


Fluoropolymer production: consumption of resources



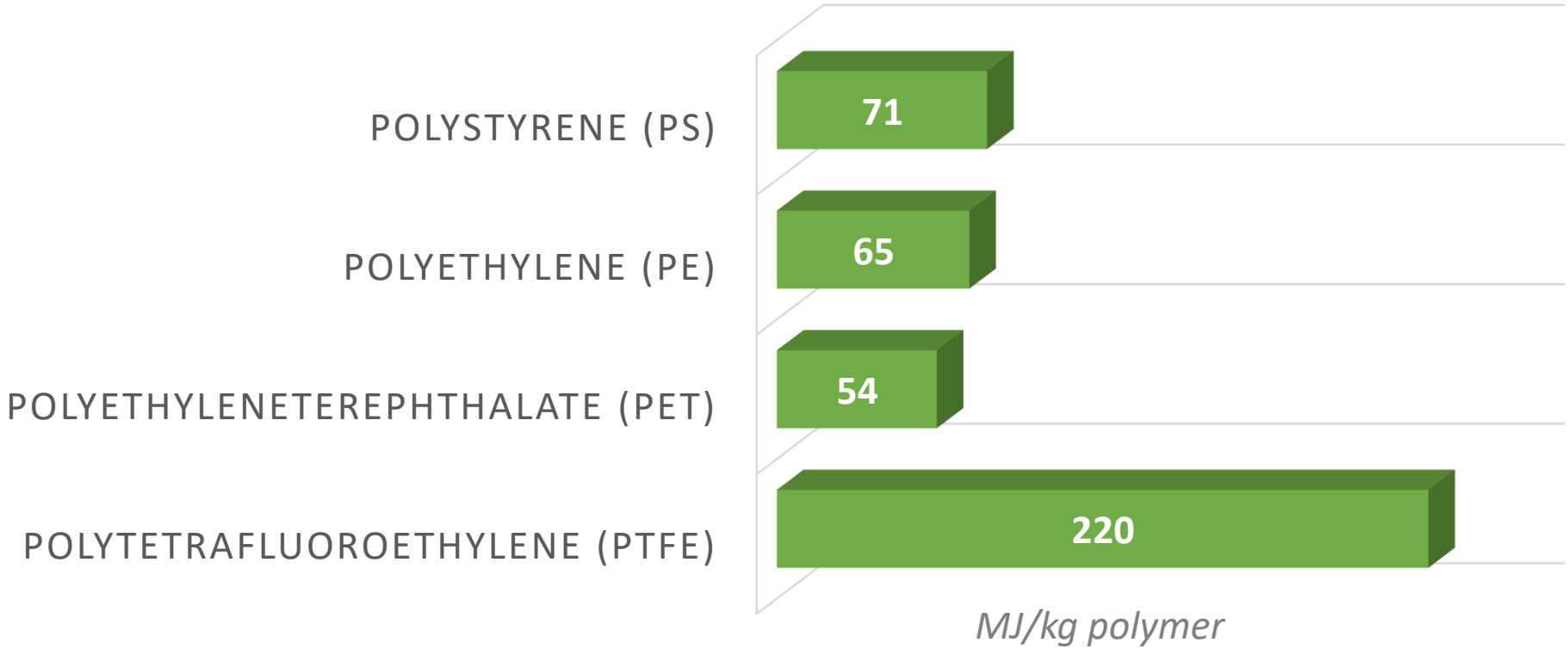
Based on the production of 1 t PTFE

Energy demand for PTFE-production



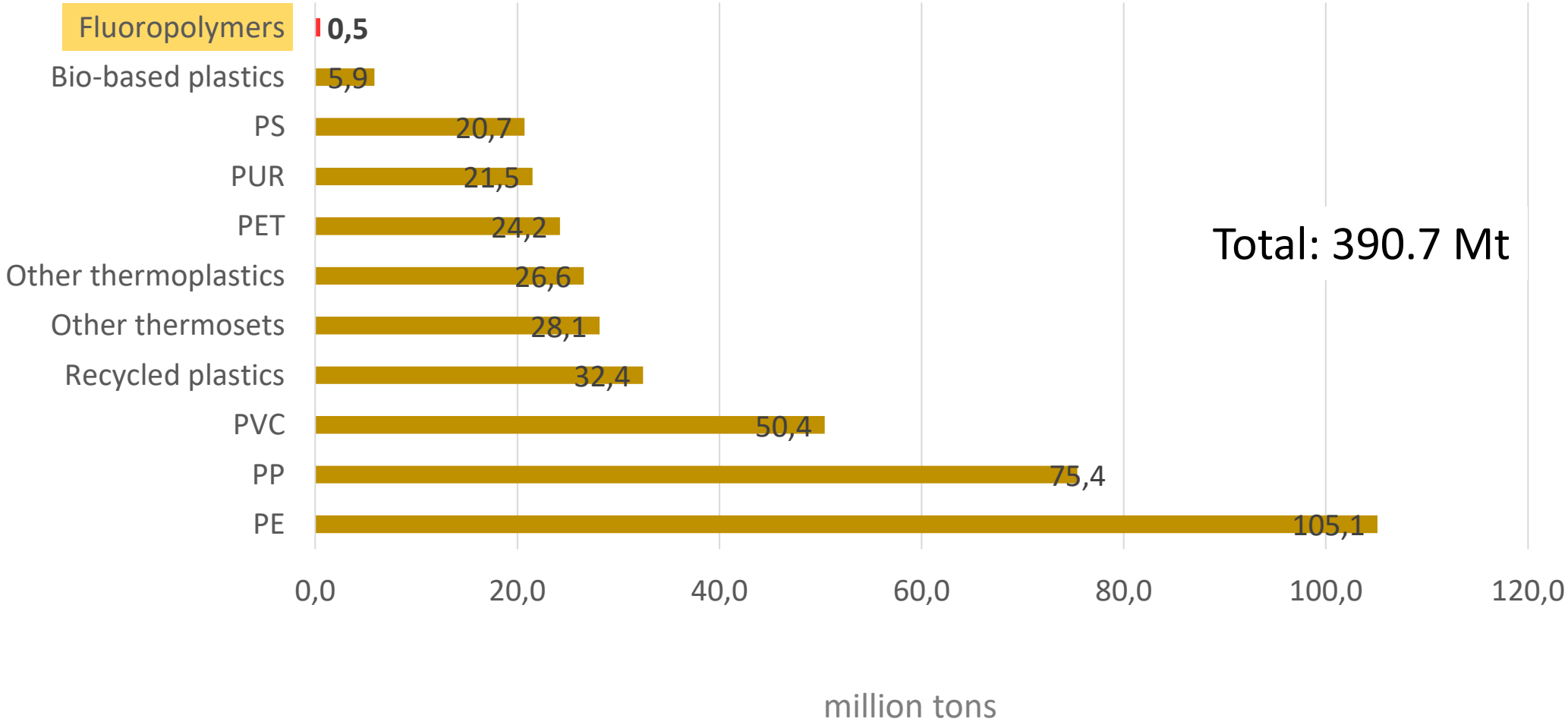
Abraham, V., Comparative life cycle assessment and environmental impacts of PTFE production and recycling, Master thesis, University Bayreuth, Germany 2013

Cumulative Energy Demand (CED) of bulk plastics



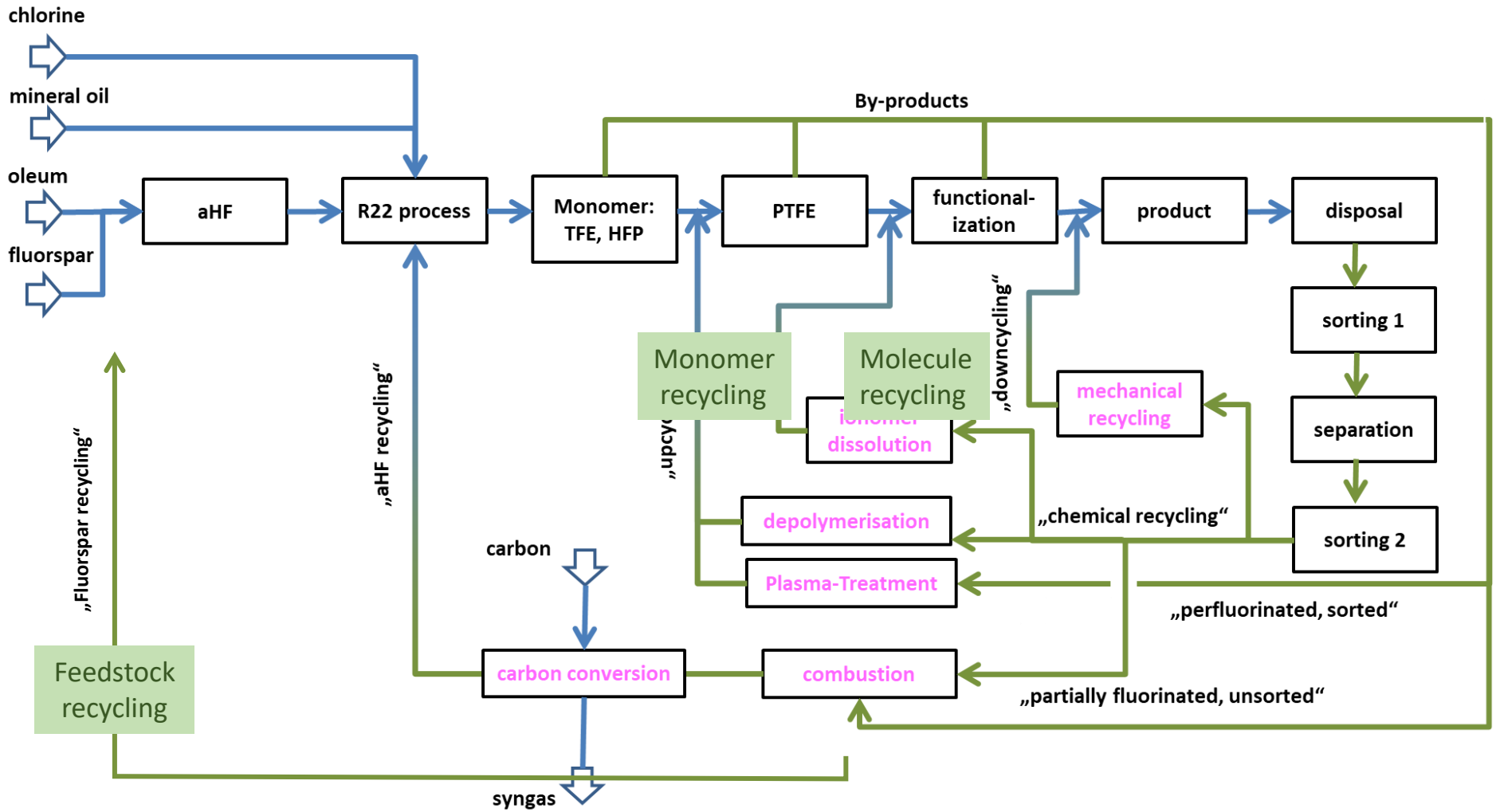
Shen, L., Nieuwlaar, E., Worrell, E., and Patel, M. K., Life cycle energy and GHG emissions of PET recycling: Change-oriented effects, International Journal of Life Cycle Assessment 16 (2011)
Patel, M., KEA (Cumulative Energy Demand) für Produkte der Organischen Chemie, Working paper of project no. 104 01 123 for the German Environment Agency (Bundesumweltamt)

Global polymer production 2021



https://plasticseurope.org/knowledge-hub/plastics-the-facts-2022/
https://en.kunststoffe.de/a/specialistarticle/fluoroplastics-245074

R&D in the field of FP-recycling

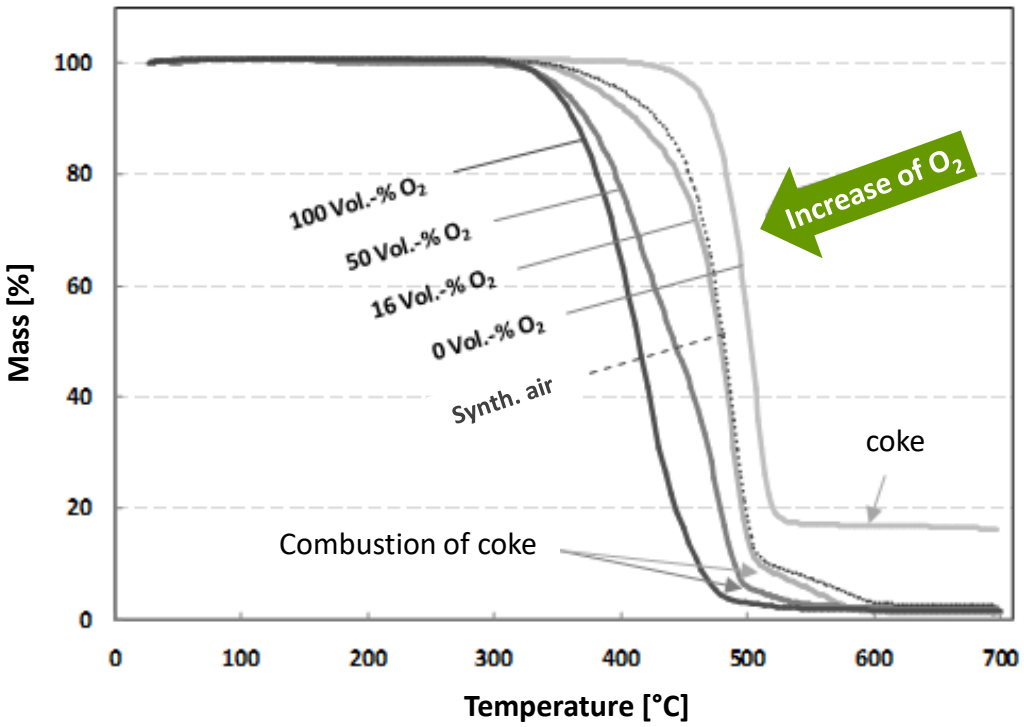


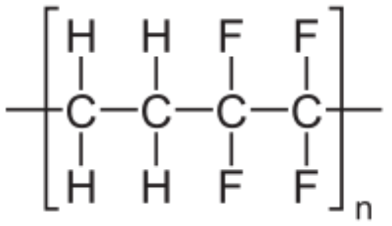
TRL of processes developed by InVerTec between 4 (plasma) and 8 (Depolymerization)

Feedstock recycling:

Combustion of partially fluorinated polymers

Ethylen – Tetrafluorethylen Copolymer (ETFE)

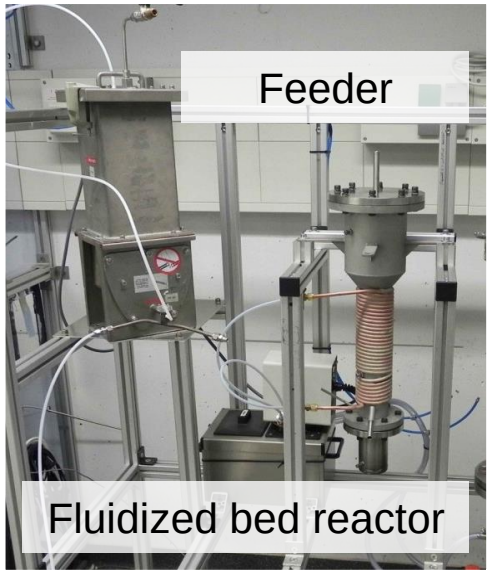




$$C_4H_4F_4\,(g) + 4O_2\,(g) + N_2(g) \xrightarrow{T}$$

$$4HF(g) + 4CO_2\,(g) + N_2(g)$$

$\Delta_R H$ = -2100 kJ/mol



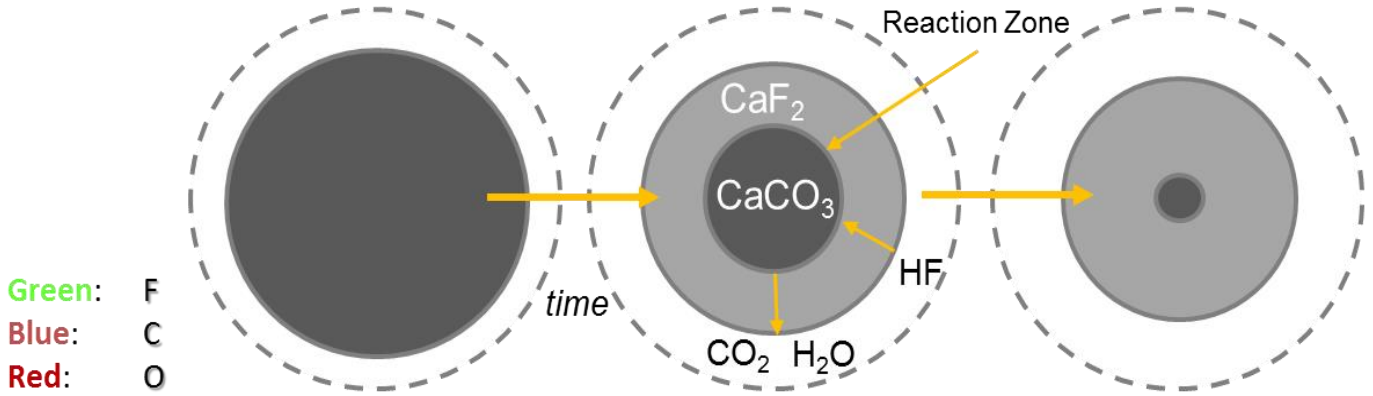
Conversion of calcite into syn-spar

Feedstock recycling

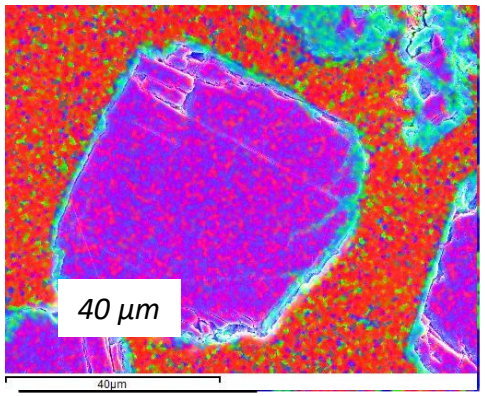
Chemisorption & conversion: $CaCO_3 + 2\ HF \rightarrow CaF_2 + CO_2 + H_2O$

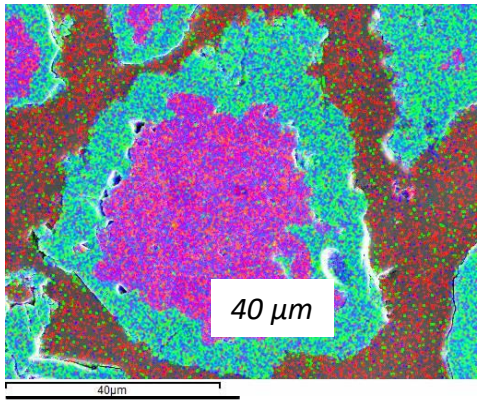
Shrinking unreacted-core Modell:

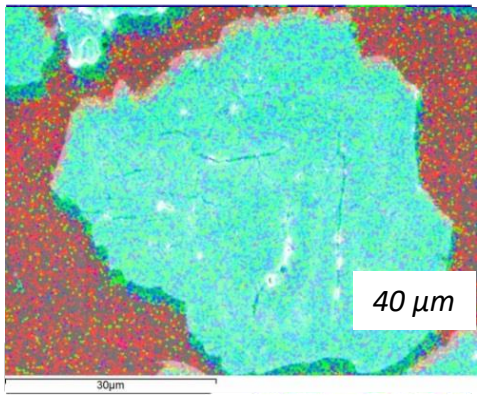
- Core-Shell-structure
- Steady movement of the reaction front into the core



Green: F
Blue: C
Red: O



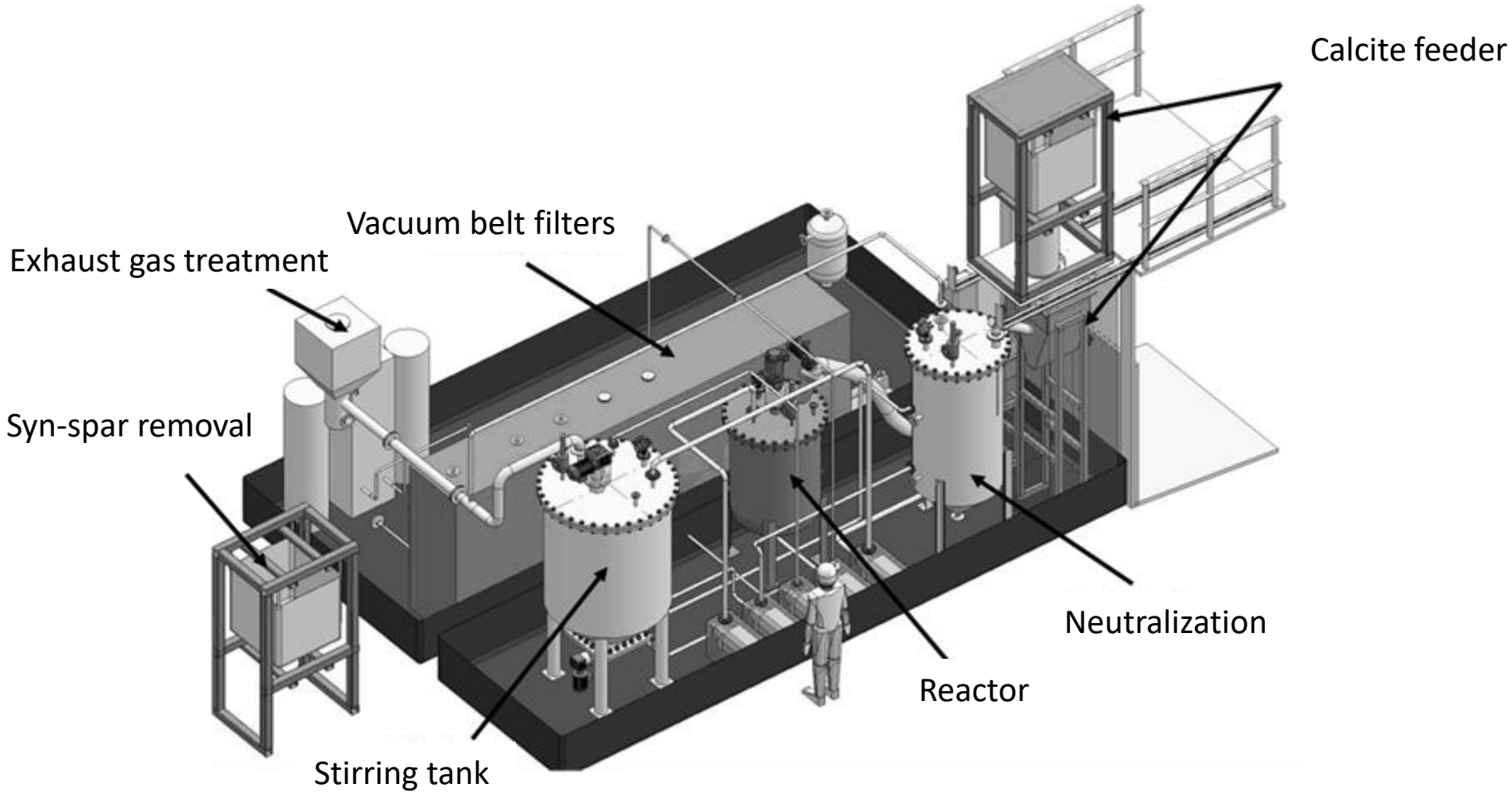




EDX-Mapping

Time

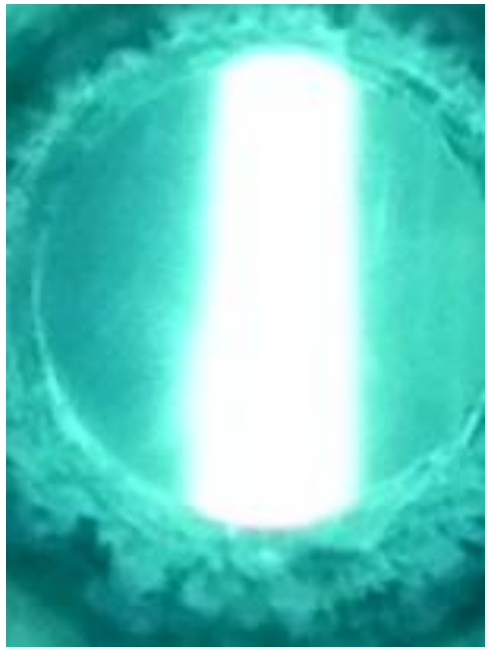
Design of a 900t p.a. plant for syn-spar production from HF

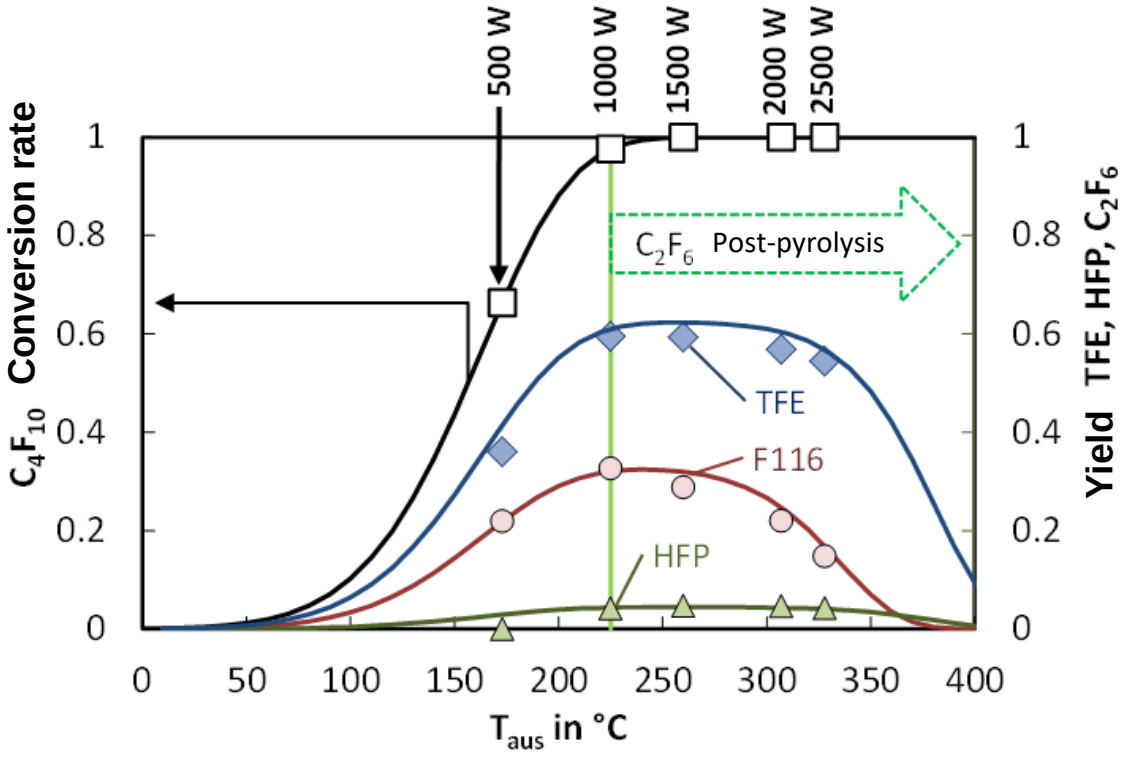


Monomer Recycling:

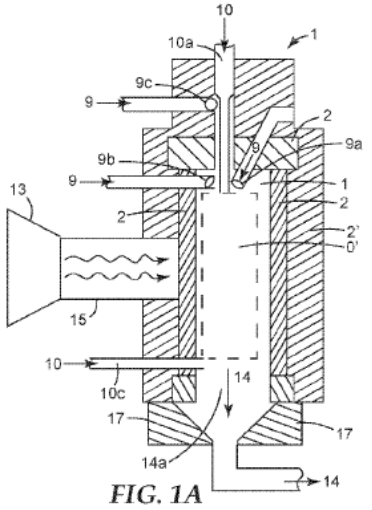
Plasma-pyrolysis of perfluorinated alkanes

Plasma converting alkanes (<C4) into alkenes



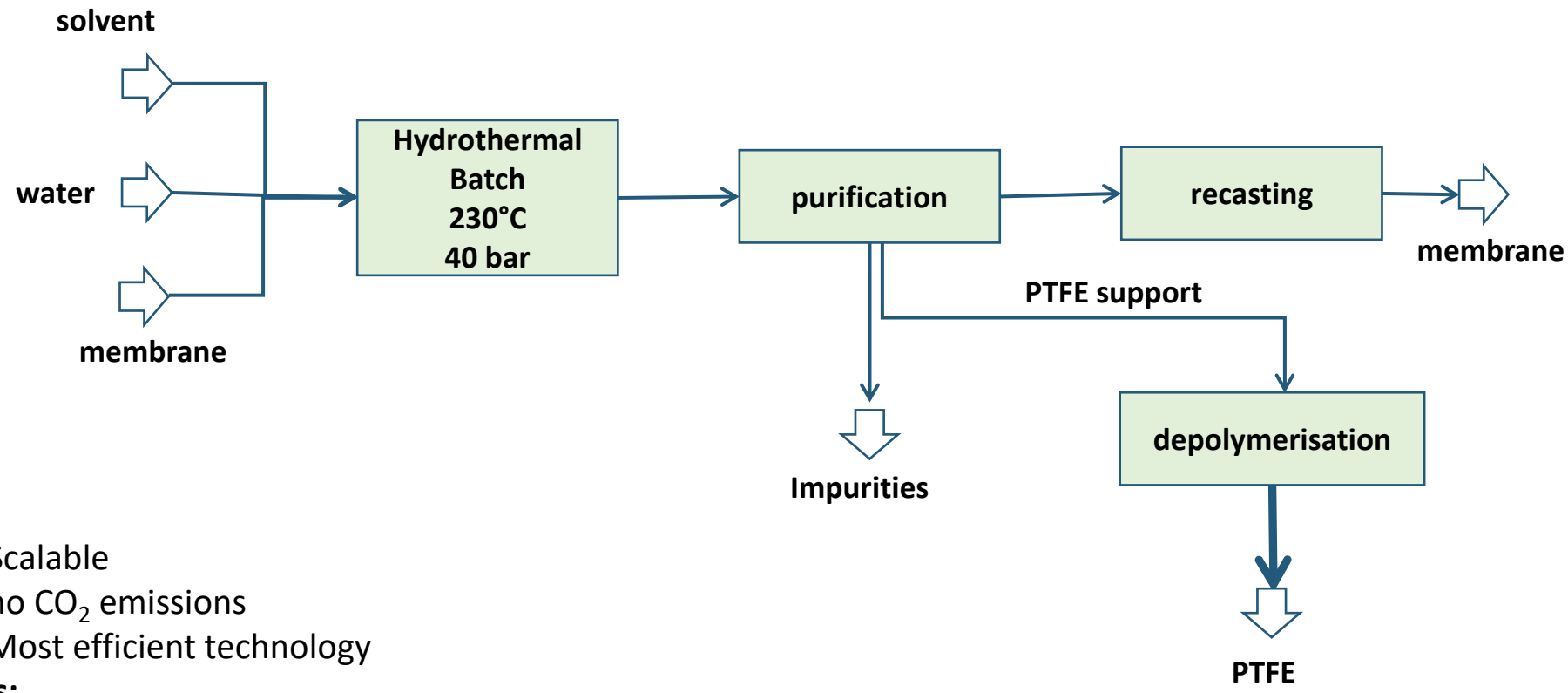


Process and apparatus for producing fluorinated alkenes



WO2016/054246 A1

Molecule recycling: Dissolving of ionomer membranes



Pro:

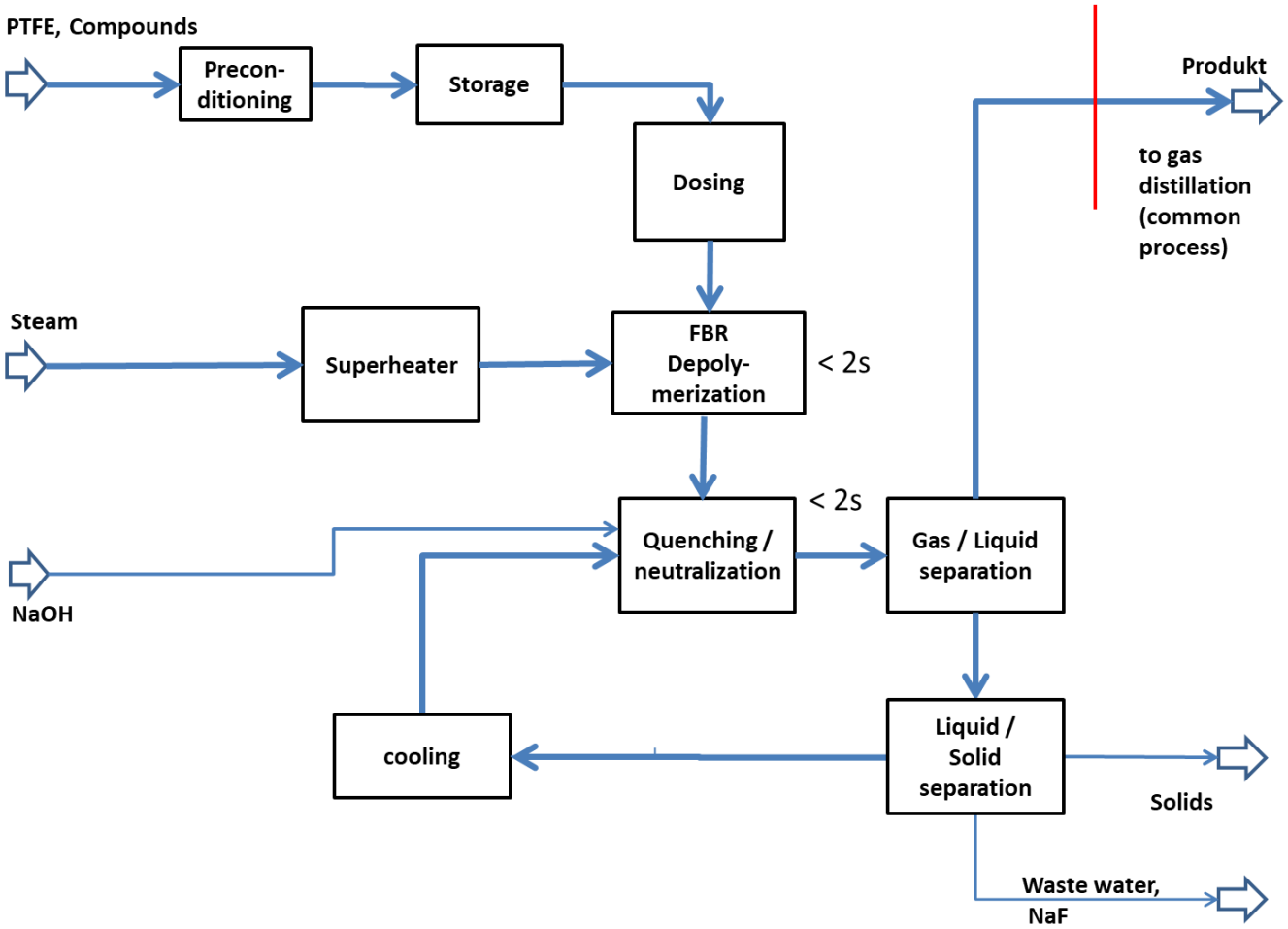
- Scalable
- no CO_2 emissions
- Most efficient technology

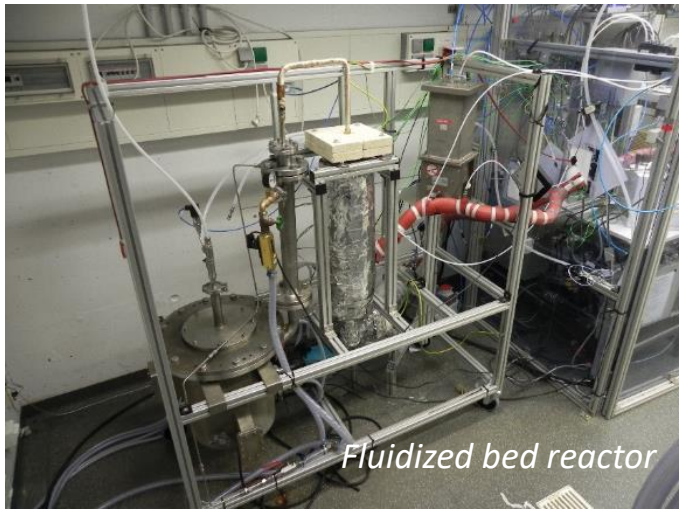
Cons:

- not established
- TRL~4
- Purification steps not defined

Yield: 90%
Energy demand: app. 166 MJ/kg

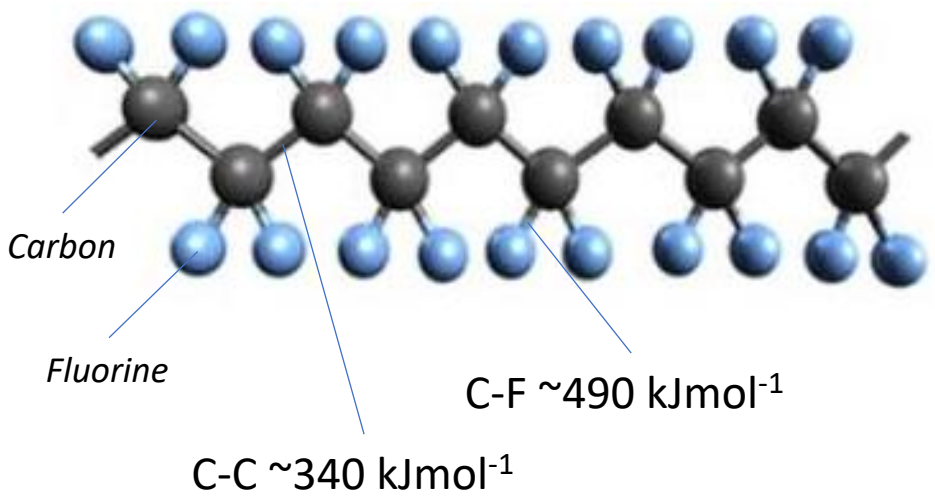
Monomer Recycling: Depolymerisation of PTFE





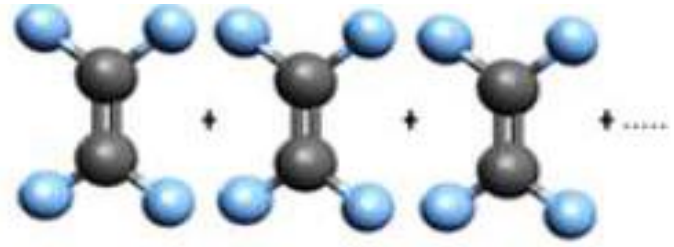
Thermal decomposition (pyrolysis) of PTFE

PTFE



Heat

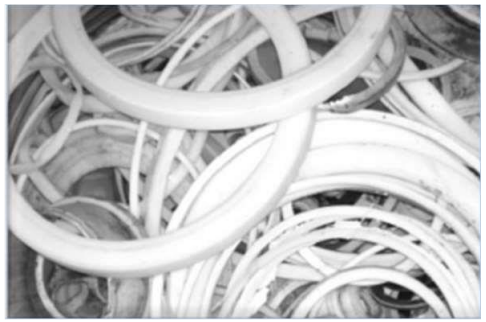
TFE (Tetrafluoroethylene)

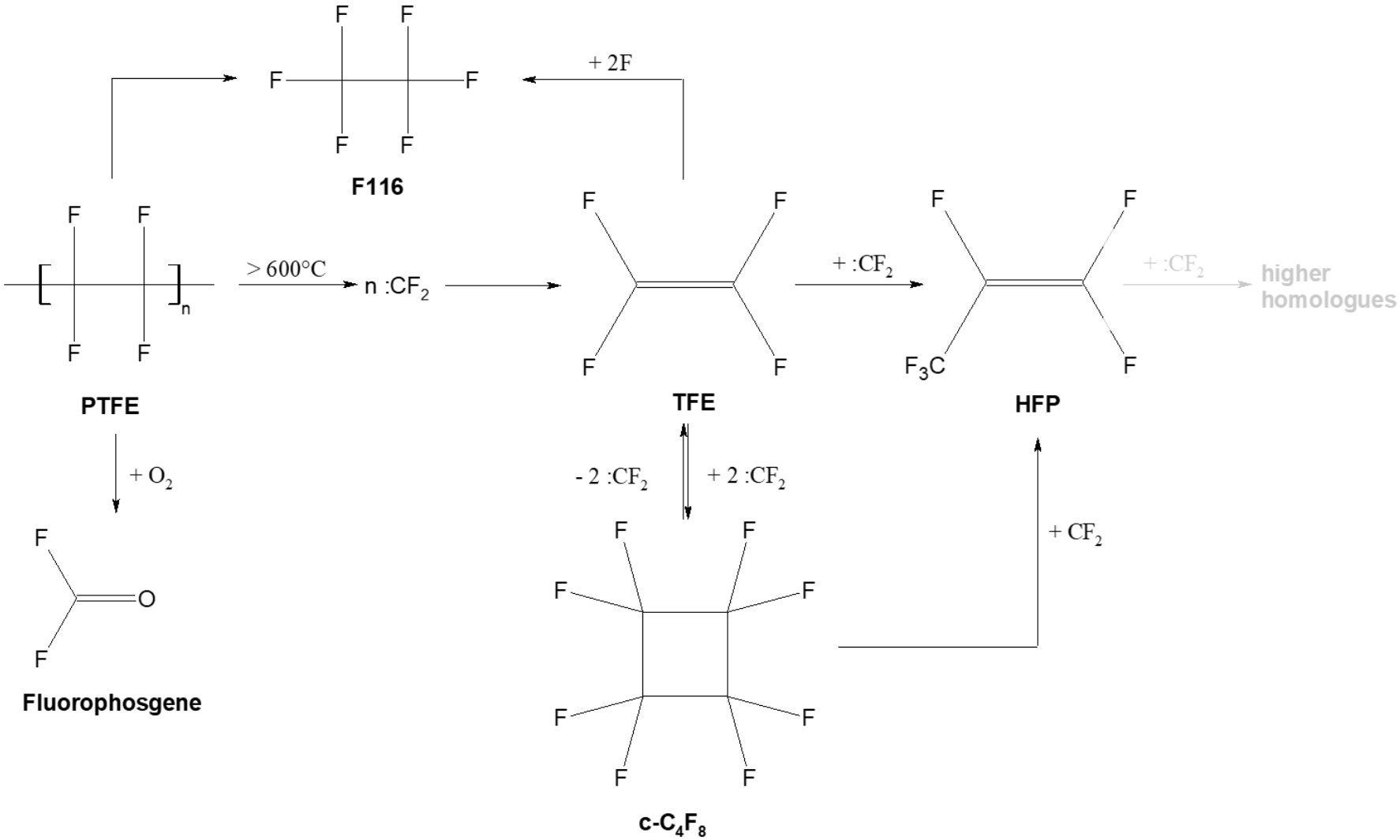


- Fluorine as the most electron-negative element builds very strong bonds with carbon

Depolymerisation of PTFE

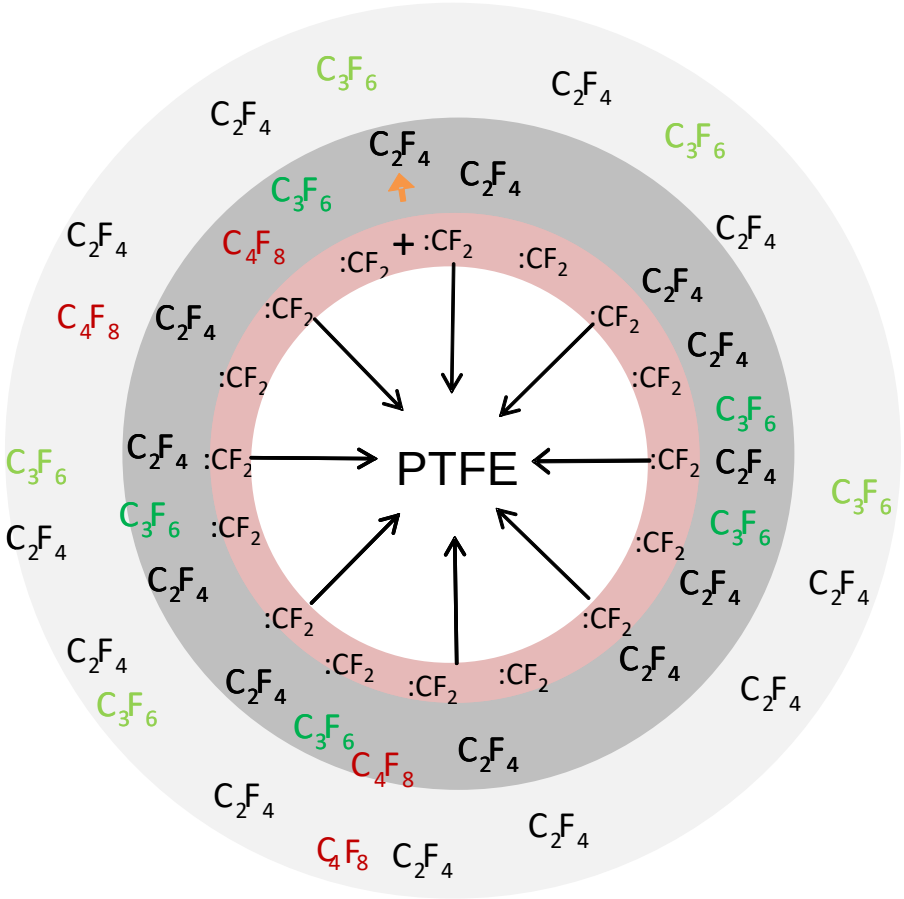
Monomer recycling





Depolymerisation of PTFE particles in a fluidized bed

Monomer recycling



Temperature rises to >500 °C

↓

$:CF_2$ is formed on the particle; particle shrinks

↓

$2\ :CF_2 = C_2F_4$ (TFE); C_2F_4 removal; reproduction

↓

$CF_2 + C_2F_4 = C_3F_6$ (HFP)

↓

C_3F_6 removal; reproduction

↓

$CF_2 + C_3F_6 = 2\ C_4F_8$

↓

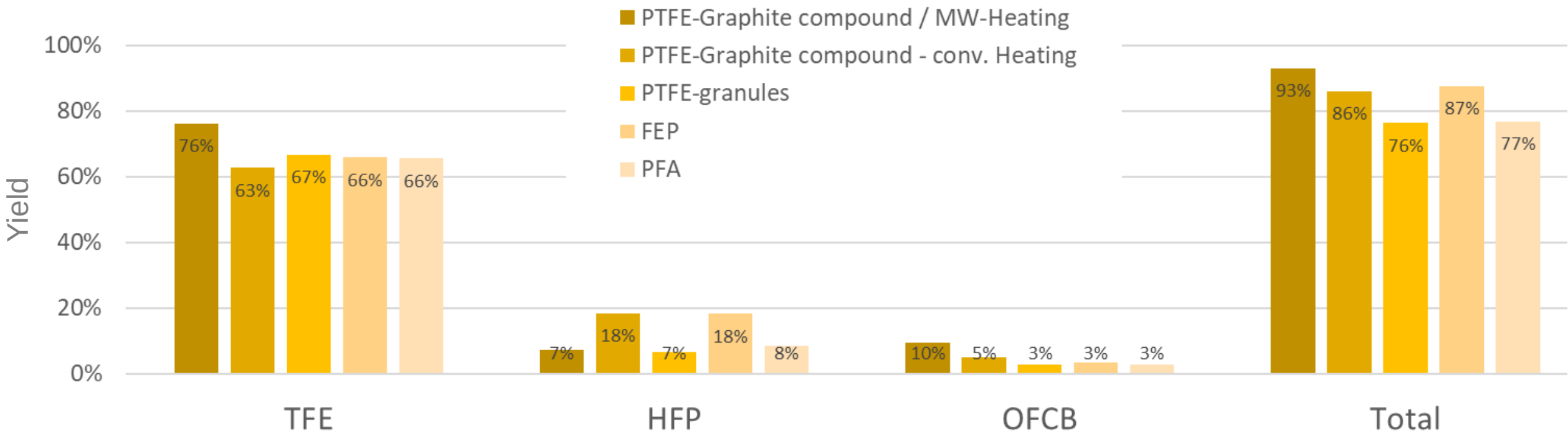
C_4F_8 removal; reproduction

↓

no reaction of 2 C_4F_8 due to too low concentration

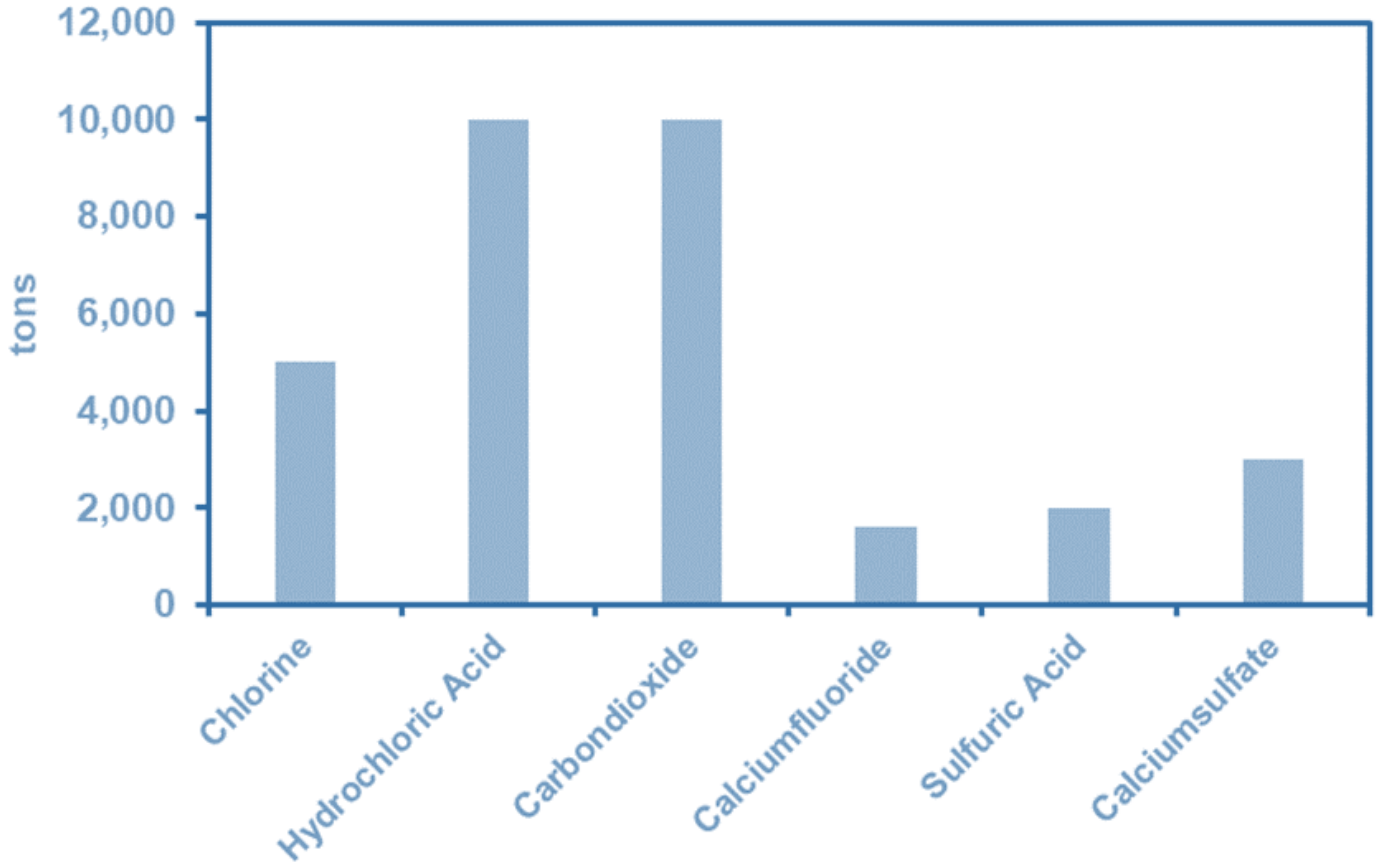
Influence of the fluoropolymer on the product gas

Monomer recycling



Environmental benefit from depolymerisation of PTFE

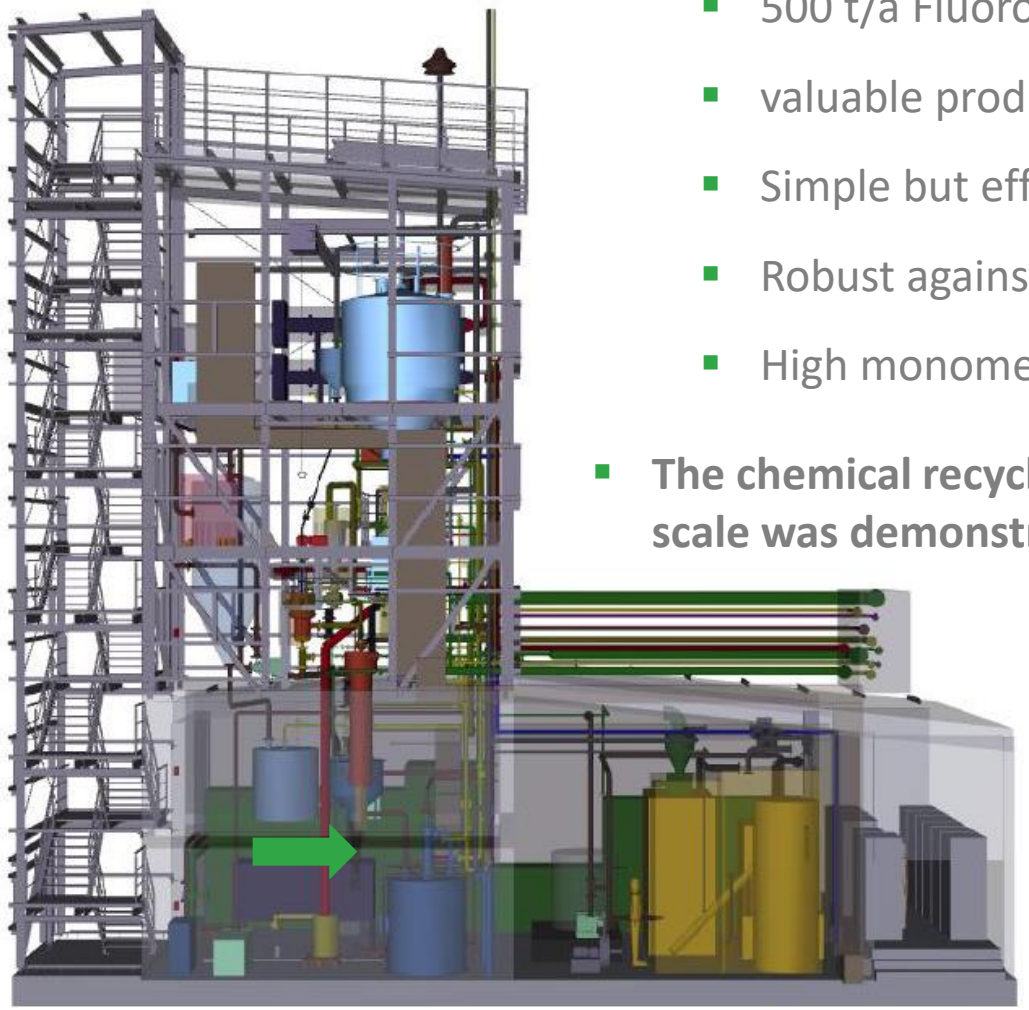
Monomer recycling



Related to the production of 1000 t PTFE

PTFE pyrolysis plant at 3M / Dyneon

Monomer recycling



- 500 t/a Fluoropolymers
- valuable products: TFE, HFP, cyclo C_4F_8
- Simple but efficient process design
- Robust against impurities
- High monomer yield

- **The chemical recycling of fluoropolymers on a technical scale was demonstrated successfully.**

Summery

- Chemical recycling is mandatory to ensure the sustainable future of fluoropolymers
- Depending on the kind and composition of EoL fluoropolymers, the type of chemical recycling has to be adapted:
  - Molecular Recycling
  - Monomer recycling
  - Feedstock recycling
- For all variants of chemical recycling, a TRL of at least 4 has been demonstrated
- Due to the quite differentiated uses of fluoropolymers, proper recycling is complex
- Production waste recycling is the "low hanging fruit”
- It is not the lack of suitable concepts but the “valley of death” in process scaling that is currently hindering development

Closing the fluorine loop partners & sponsors

Activities along the process chain

- Development of business models for EoL-material based fluorochemicals
- Development of waste management strategies for end-of-life materials
- Quality management for secondary raw materials
  (quality control and pre-treatment of EoL-material)
- Design and engineering of Up-Cycling plants

- In cooperation with
  - Producers of fluorochemicals/-polymers
  - Processors of fluoropolymers / end users
  - Recycling companies
  - Associations & policy makers

element 9
closing the loop
www.element9.de

The mission / Bussines Units

Engineering & Up-Cycling plants

- Establishing processes for the chemical recycling of fluoropolymers by bringing together diverse skills and resources
- Supporting waste management strategies

Green Fluoropolymer Factory

- R22-free production of fluoropolymers based on secondary raw materials