New Chlorine Storage Material

Based on Polychlorides

Prof. Dr. Sebastian Riedel
Freie Universität Berlin

Chlorine Production in Europe and Germany

Cl 17
Chlorine
EN 3.16

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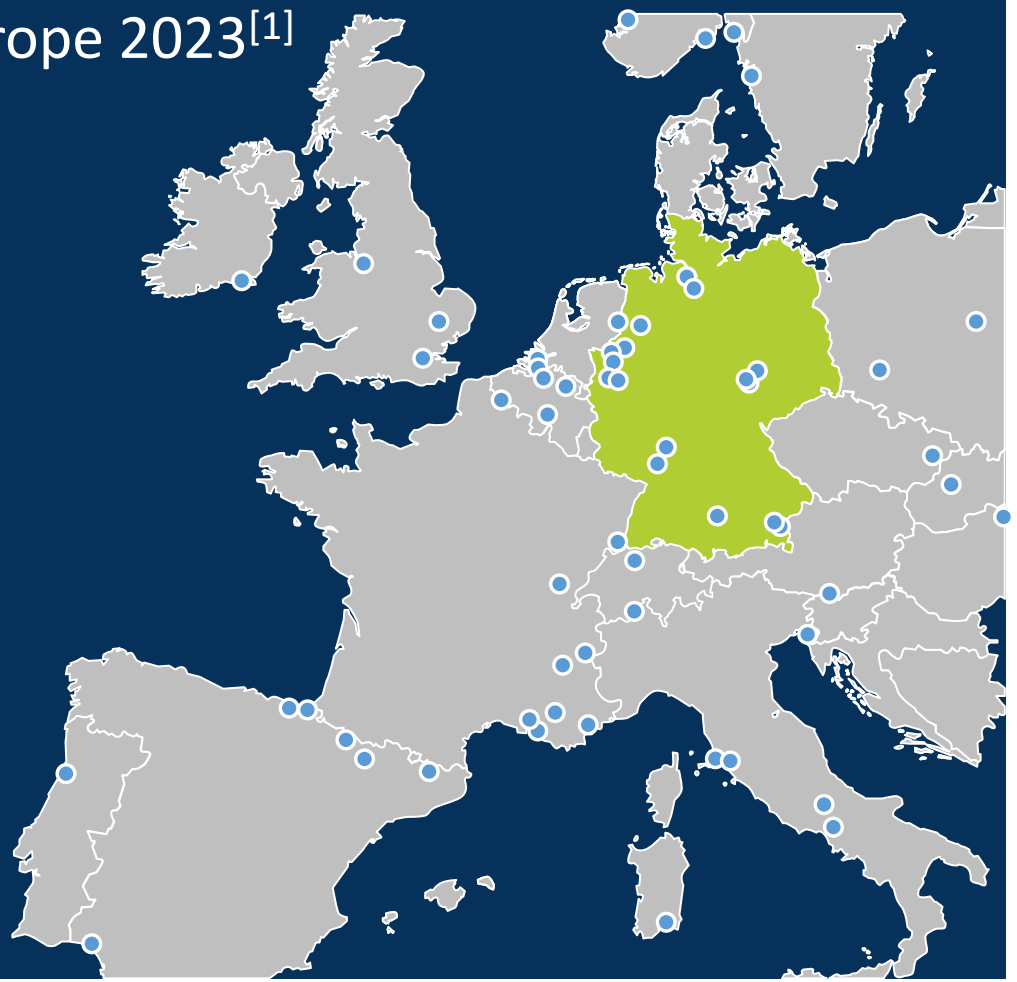
7.3 mio. t/a of chlorine are produced in Europe 2023[1]

≈55% of all industrial chemicals and polymers

In Germany 2022:

1,7% of the energy consumption[2]

Chloralkali electrolysis driven by electrical base load therefore CO_2 emissions



[1] Chlor-alkali industry review 2023/2024. **[2]** EuroChlor 2022

Chlorine Production Worldwide

Cl 17
Chlorine
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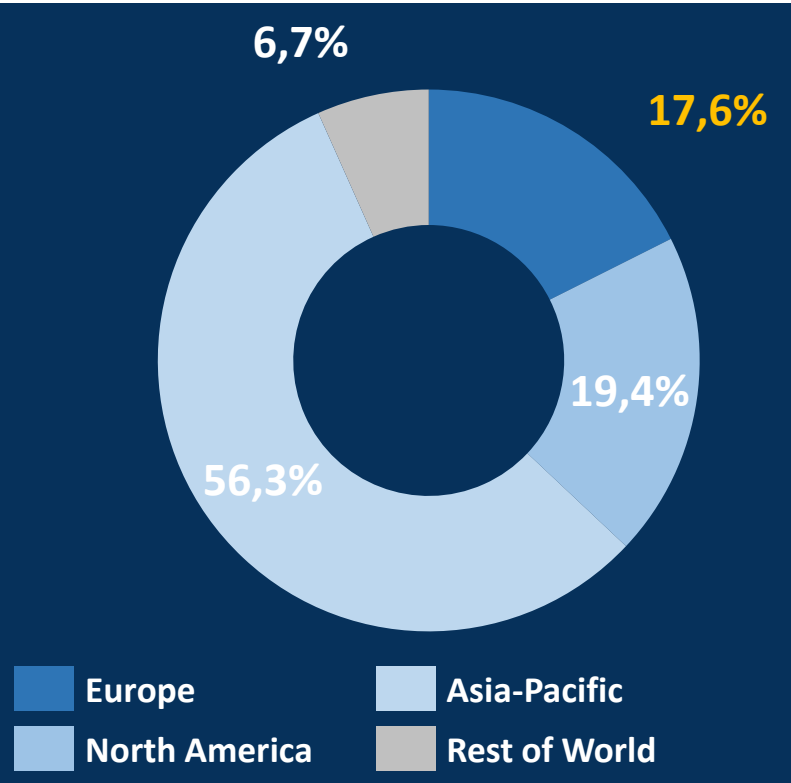

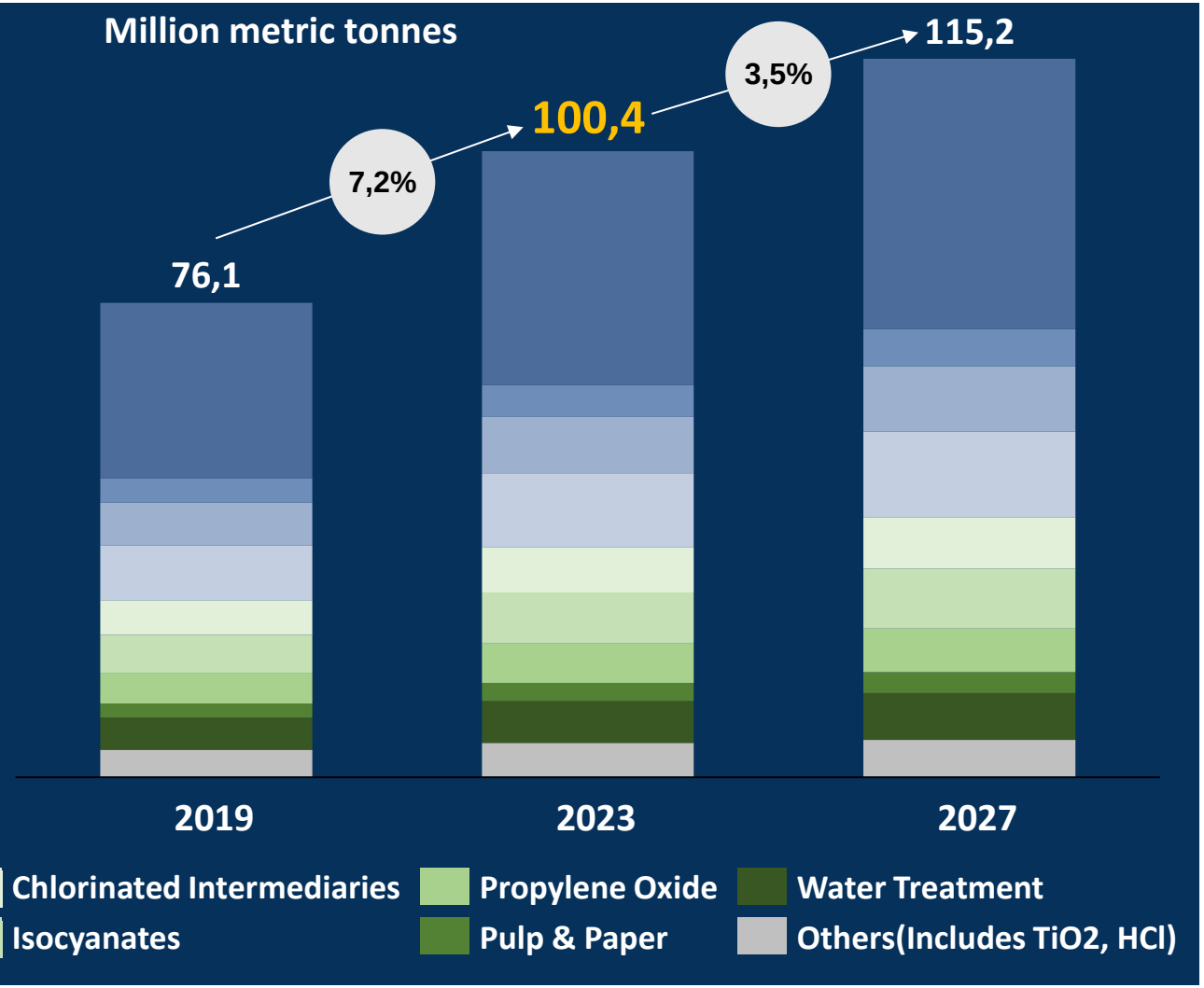

Source: ICIS Articles, Chemical Weekly, CMAI Price Reports, EuroChlor Publications, Company Annual Reports, Expert Interviews, and MarketsandMarkets Analysis, AgileIntel Research

Chlorine Storage & Safety

Cl 17
Chlorine
EN 3.16

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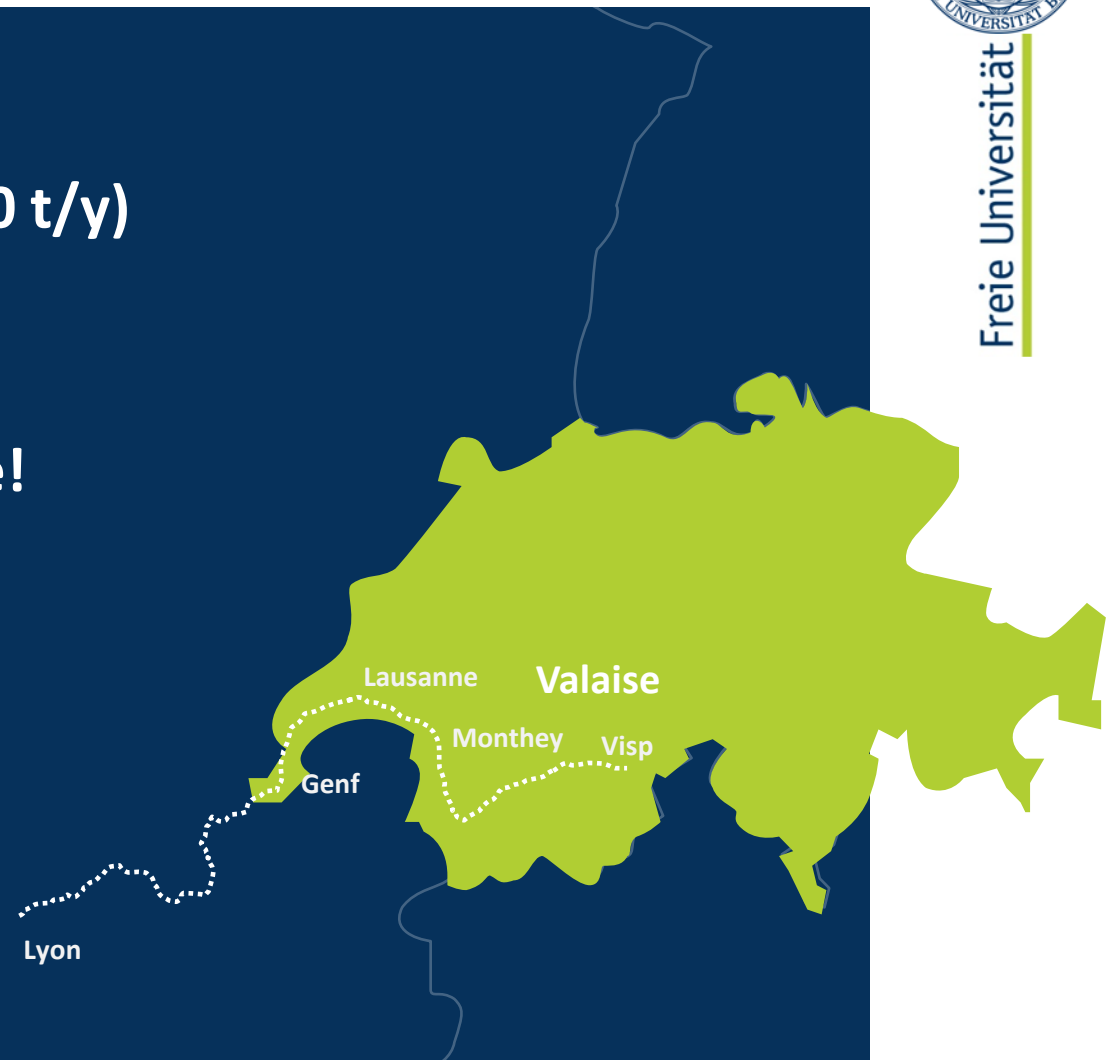
One production site in Switzerland (Pratteln, 47.000 t/y)

Difficult storage and **transportation** of elemental **chlorine** (Cl_2) due to **toxicity** and **pressure!**

Application of complex and expensive **safety equipment** and **materials**



Chlorine Accidents

Cl 17
Chlorine
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JACKRABBIT PROJECT

U.S. DEPARTMENT OF HOMELAND SECURITY

Chemical Security Analysis Center

CSAC

Expertise on Demand

Utah Valley University
https://www.chlorineinstitute.org/videos/jack-rabbit-chlorine-properties/

Chlorine Production has Major Challenges

Cl 17
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Potentially harmful to the environment / hazardous

Complex Transport & Storage

Energy intensive production

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New Chlorine Technology based on Ionic Liquids

Cl 17
Chlorine
EN 3.16

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$[NEt_4][Cl_3]$

Solid

$[NEt_3Me][Cl_3]$

Ionic Liquid

Chlorine IL

Low Gas Pressure

Simple Solution

Cheap, Scalable

35% Savings

Publications: S. Riedel, *et al. ACS Sustainable Chem. & Eng.* **2022**, *10*, 9525; S. Riedel, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202216586.
Cl-Technology Patents: WO 2019215037 A1 | WO 2021069757 A1 | WO2023020942 A1

Chlorine Storage

Cl 17
Chlorine
EN 3.16

Substrate	Mp. [°C]	Density at 25 °C [kg L^{-1}]	dyn. viscosity [mPa s]	Storage capacity [mol mol^{-1}][a]	Storage cap. by m. [kg kg^{-1}][b]	Storage cap. by V. [kg L^{-1}][c]
Cl_2	–101/–34	1.38			-	1.38
$[NBu_4]Cl$	5	1.30	684	2.18	0.55	0.46
$[NEtMe_3]Cl$	8	1.24	low vis.	1.44	0.82	0.56
$[NEt_2Me_2]Cl$	–19	1.20	16	1.57	0.8	0.54
$[NEt_3Me]Cl$	–10	1.21	19	1.68	0.79	0.53
$[NBuMe_3]Cl$	21	1.25	low vis.	2.57	1.19	0.68
$[NBuEt_2Me]Cl$	–19	1.30	46	2.72	1.06	0.67
$[NMePr_3]Cl$	9	1.23	141	2.13	0.77	0.54
$[NBu_2Me_2]Cl$	–27	1.17	low vis.	2.29	0.83	0.53

R. Wagner, M. Schwarze, T. Keilhack, M. Kleoff, S. Steinhauer, Y. Schiessel, M. Paven, S. Yogendra, R. Weber, S. Riedel
ACS Sustainable Chemistry & Engineering **2022**, *10*, 9525.

Chlorine Release by Heat

Cl 17
Chlorine
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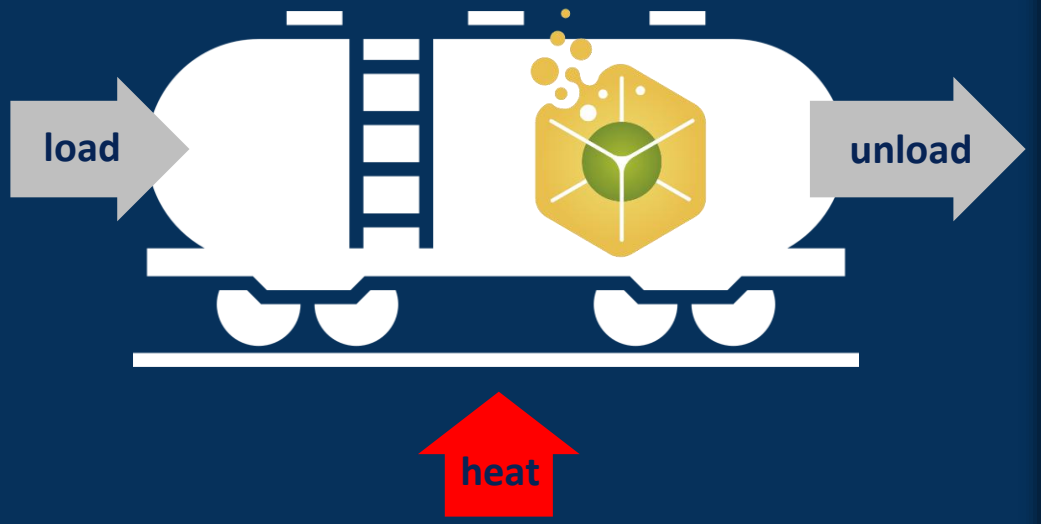
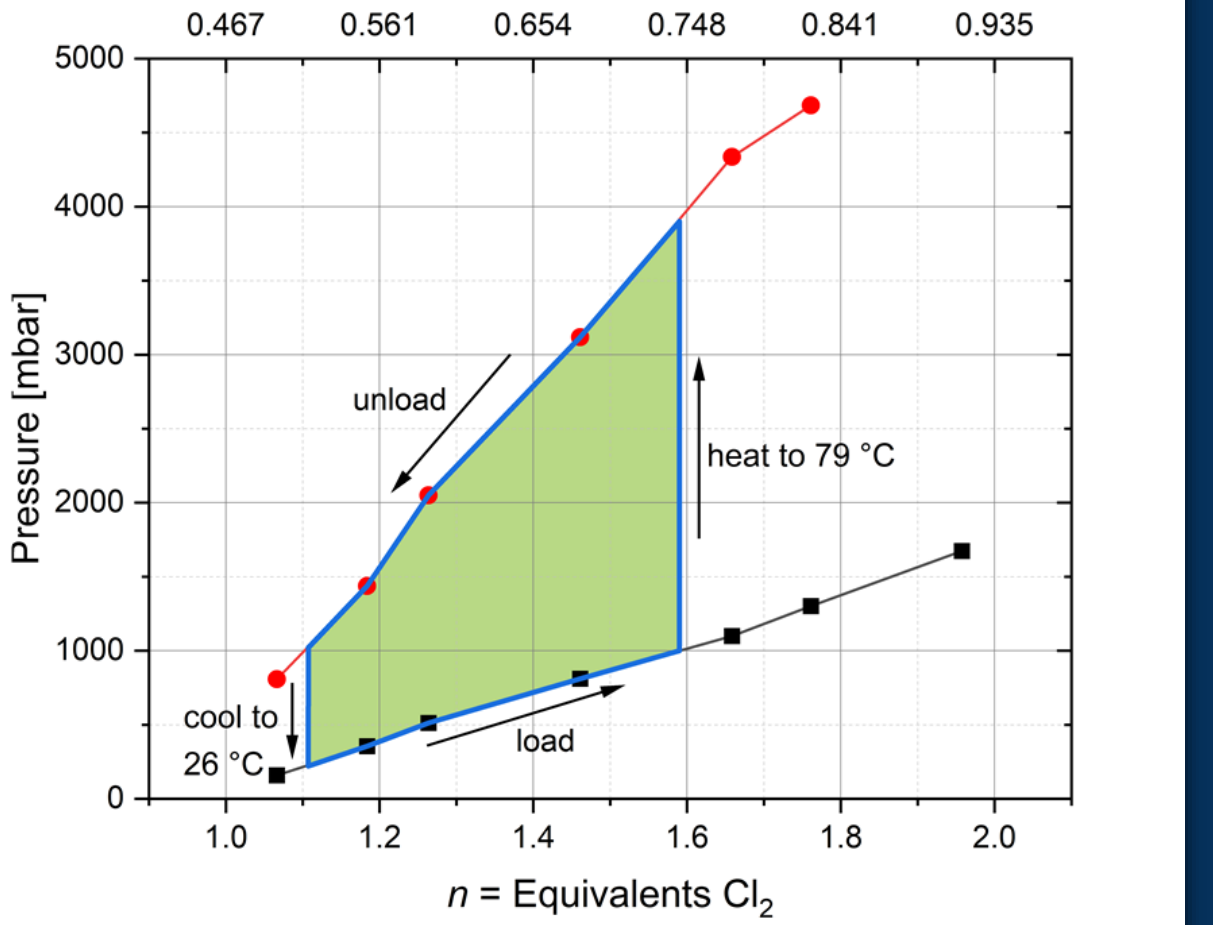


$[NEt_3Me][Cl_3]$



P. Voßnacker, N. Schwarze, T. Keilhack, M. Kleoff, S. Steinhauer, Y. Schiesser, M. Paven, S. Yogendra, R. Weber, S. Riedel *ACS Sustainable Chem. & Eng.* **2022**, 10, 9525

Patents: WO 2019215037 A1; WO 2021069757

Chlorine Release by Water

Cl 17
Chlorine
EN 3.16

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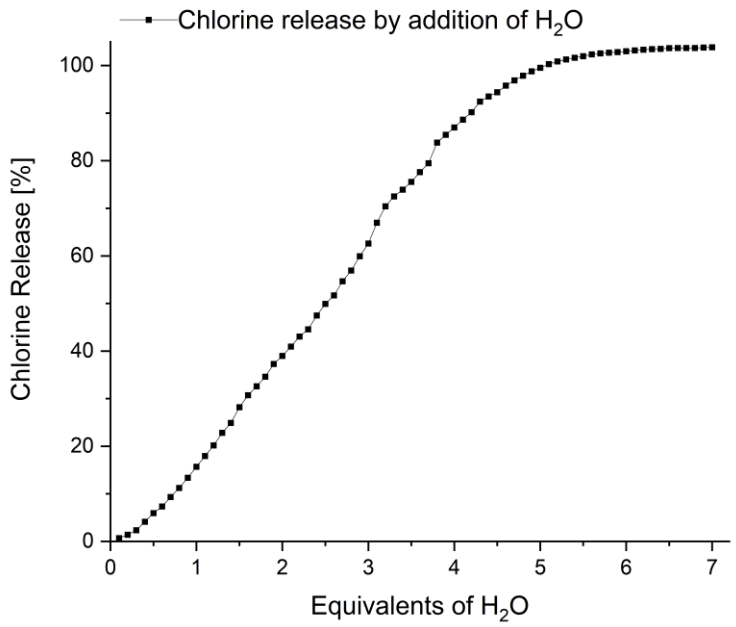
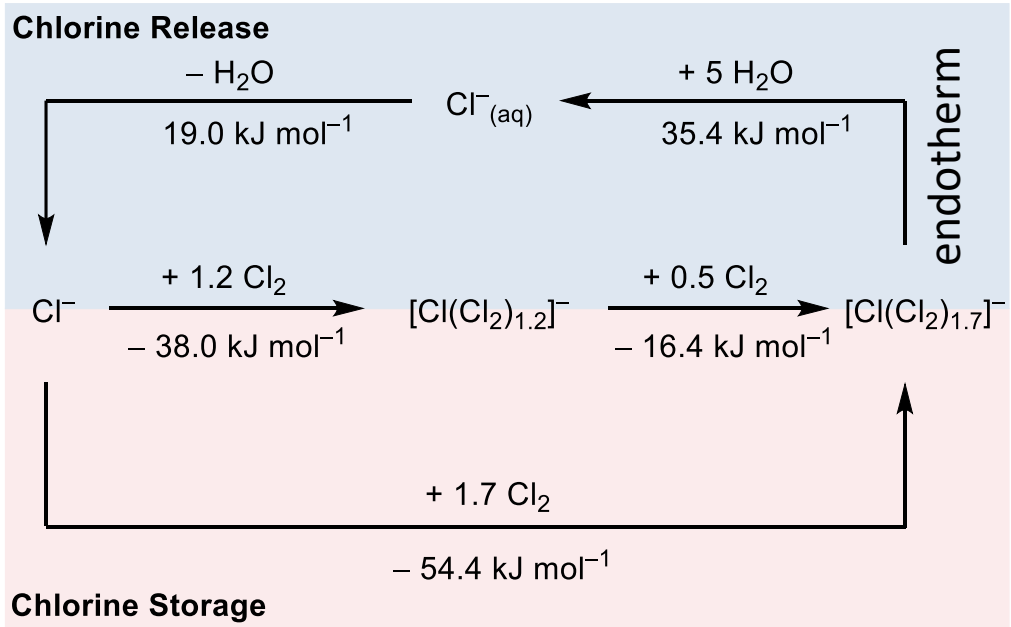
$$[NEt_3Me][Cl(Cl_2)_n] \underset{\text{storage}}{\overset{\text{release}}{\rightleftharpoons}} [NEt_3Me][Cl(Cl_2)_{n-x}] + x\,Cl_2$$





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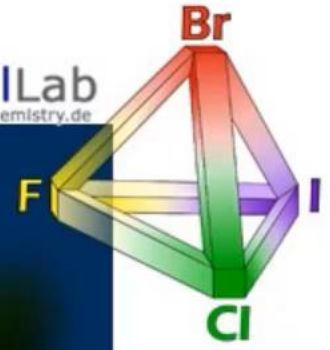
ACS Sustainable Chemistry & Engineering **2022**, *10*, 9525.

Patents:
WO 2019215037 A1, WO 2021069757

RiedelLab
www.fluorinechemistry.de



Polychloride based Ionic Liquids A Kind of Liquid Chlorine – Release by water

Prof. Dr. Sebastian Riedel
Freie Universität Berlin

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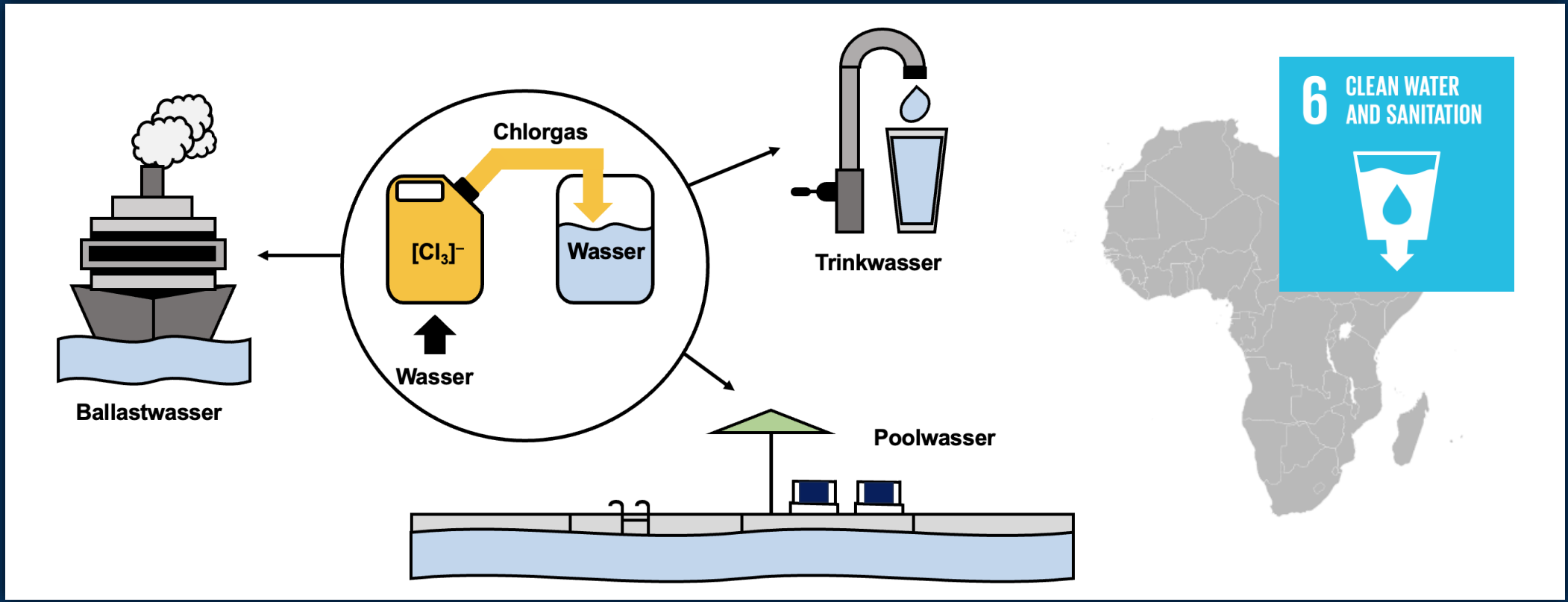
@RiedelLab

New Chlorine Technology based on Ionic Liquids

Cl 17
Chlorine
EN 3.16



A 20-litre canister of polychlorinated material (approximately 10 kg of chlorine) can be used for the purification of 20 Mio. L of water in accordance with the specifications set of DIN 19643.

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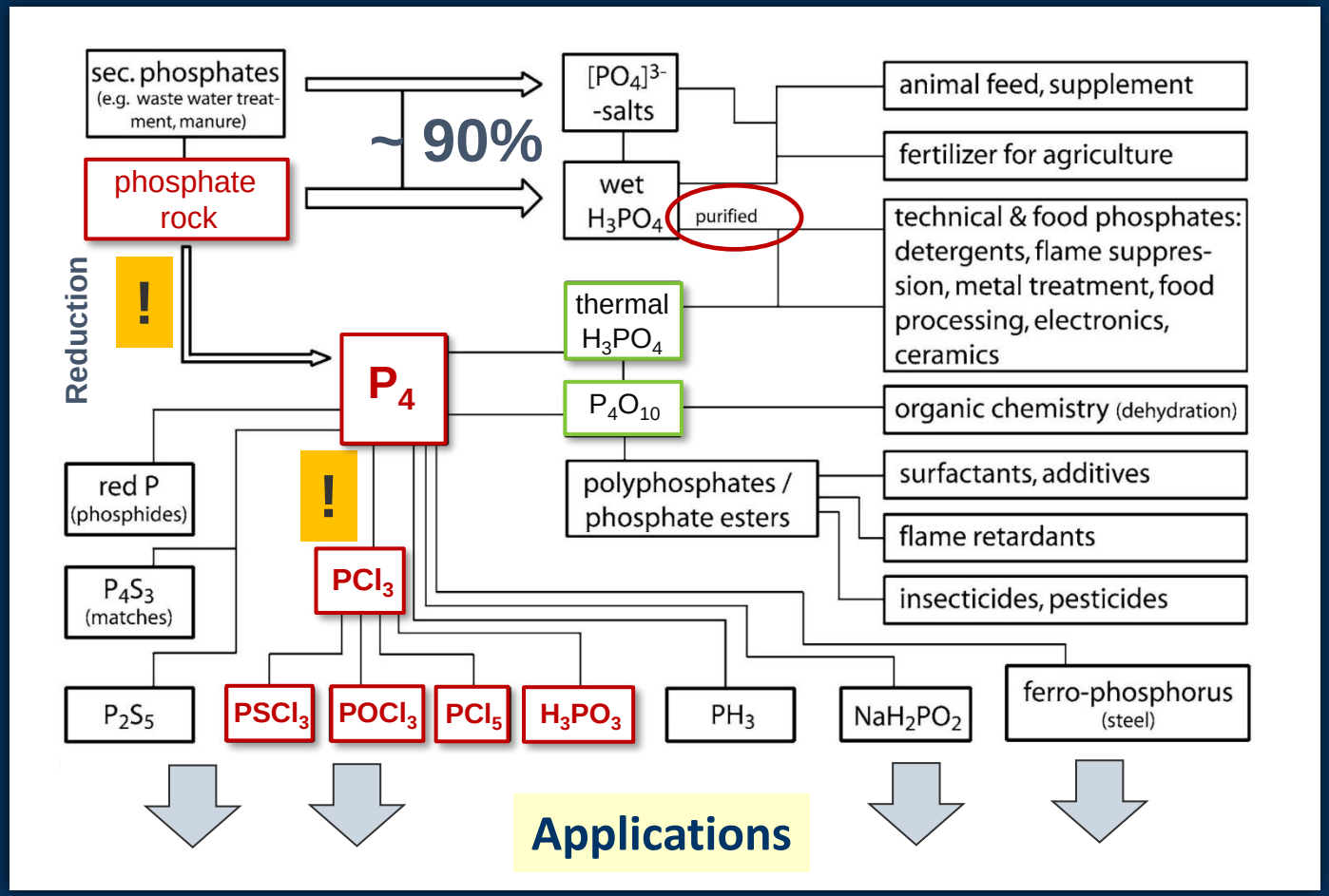
The P_4-Technosphere



Energy consuming

Chlorine-based syntheses

multi-step syntheses

toxic reagents

no P-recovery

waste

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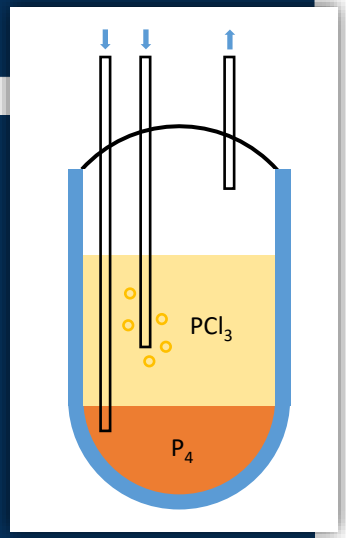
M. J. Ernst, M. Kleoff, P. Voßnacker, C. Müller, S. Riedel *Chem. Commun.* **2024**, *60*, 13372

Synthesis of PCl_3

$P_4 + 6\ Cl_2 \longrightarrow 4\ PCl_3$ Product

$PCl_3 + Cl_2 \longrightarrow PCl_5$ Byproduct

$P_4 + 6\ PCl_5 \longrightarrow 10\ PCl_3$ Product



$$5\ [NEt_3Me][Cl_3] + 2/4\ P_4 \xrightarrow[-20\ °C]{DCM} 2\ [NEt_3Me][PCl_6] + 3\ [NEt_3Me]Cl$$

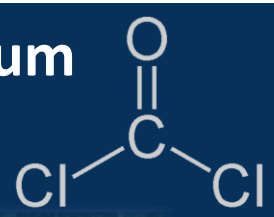
$$2\ [NEt_3Me][PCl_6] \xrightarrow{\Delta T} 2\ PCl_3\uparrow + 2\ [NEt_3Me][Cl_3]$$

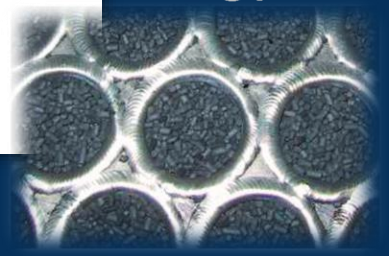
$$[NEt_3Me]Cl + PCl_5 \xrightarrow[72\ h,\ reflux]{DCM} [NEt_3Me][PCl_6]$$

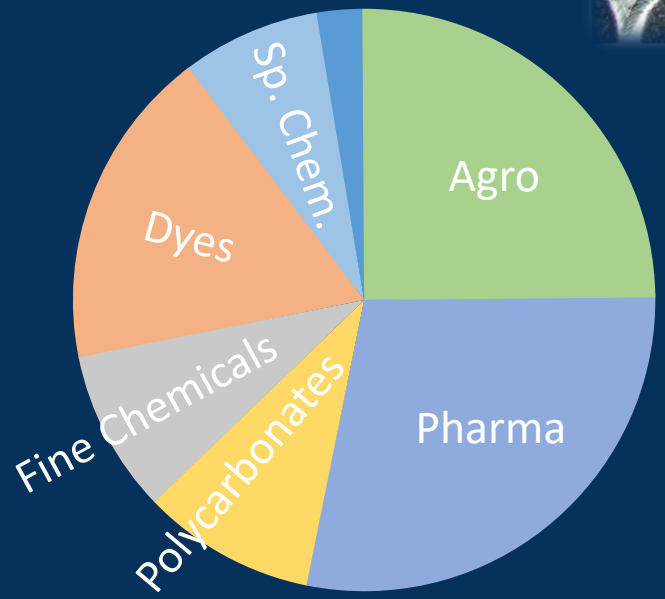
Industrial Production of Phosgene

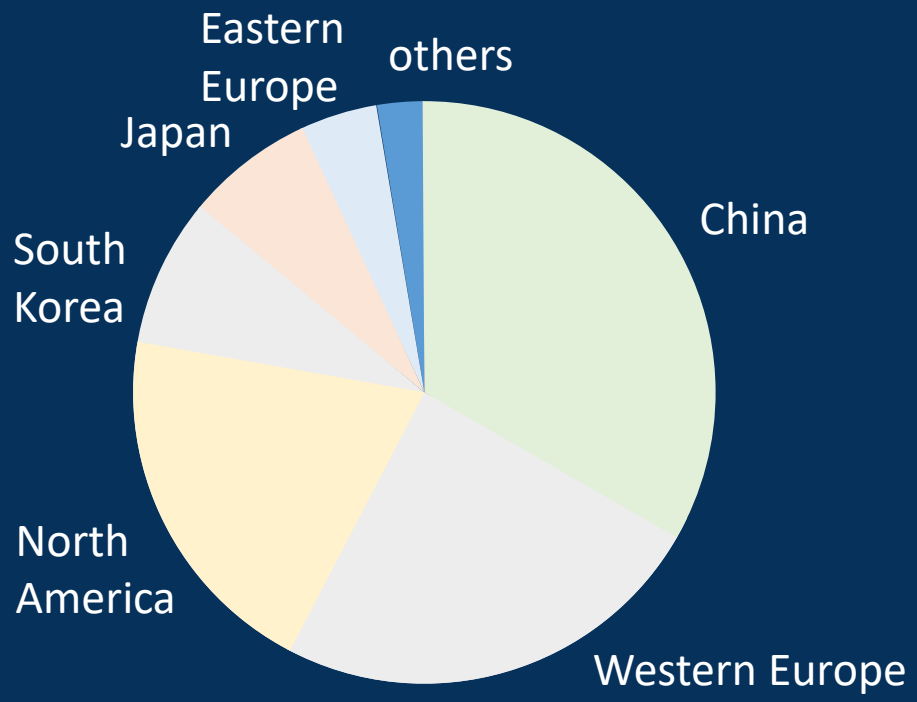
2023: 12 million tonnes per annum

$$CO + Cl_2 \xrightarrow[350 - 450\ °C]{\text{Carbon Cat.}} OCCl_2$$









World consumption of phosgene 2017 (%)

R. Hughes, G. E. Rossi, D. Lennon *React. Chem. Eng.* **2023**, *8*, 3150

IHS Market 2017

Freie Universität Berlin

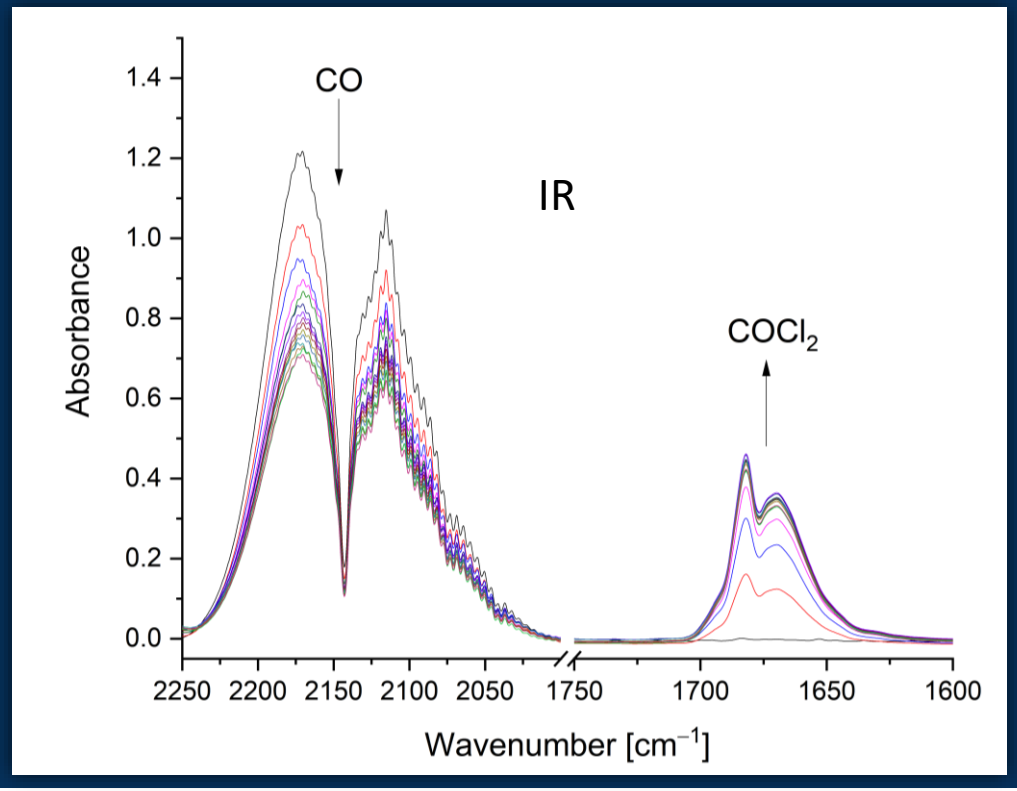
Synthetic Pathway for the Production of Phosgene

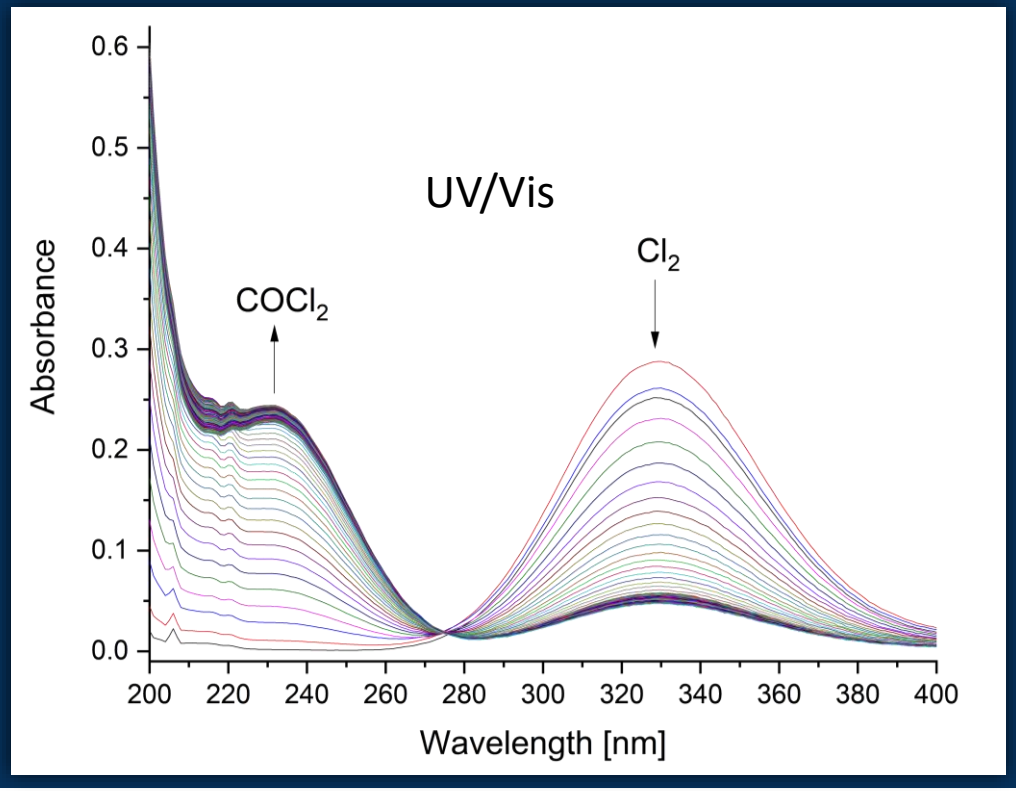
a) $CO_{(g)} + Cl_{2(g)} \xrightarrow{oDCB} C(O)Cl_{2(g)}$

b) $CO_{(g)} + Cl_{2(g)} \xrightarrow[NEt_3MeCl]{oDCB} C(O)Cl_{2(g)}$

c) $CO_{(g)} + [Cl_3]^- \xrightarrow{oDCB} C(O)Cl_{2(g)} + Cl^-$

d) $CO_{(g)} + Cl_{2(g)} \xrightarrow{NEt_4Cl} C(O)Cl_{2(g)}$





P. Voßnacker, A. Wüst, T. Keilhack, C. Müller, S. Steinhauer, H. Beckers, S. Yogendra, Y. Schiesser, R. Weber, M. Reimann, R. Müller, M. Kaupp, S. Riedel *Science Advances* **2021**, 7, 40: eabj5186

IR and UV spectra are shown with 30 min and 5 min intervals.

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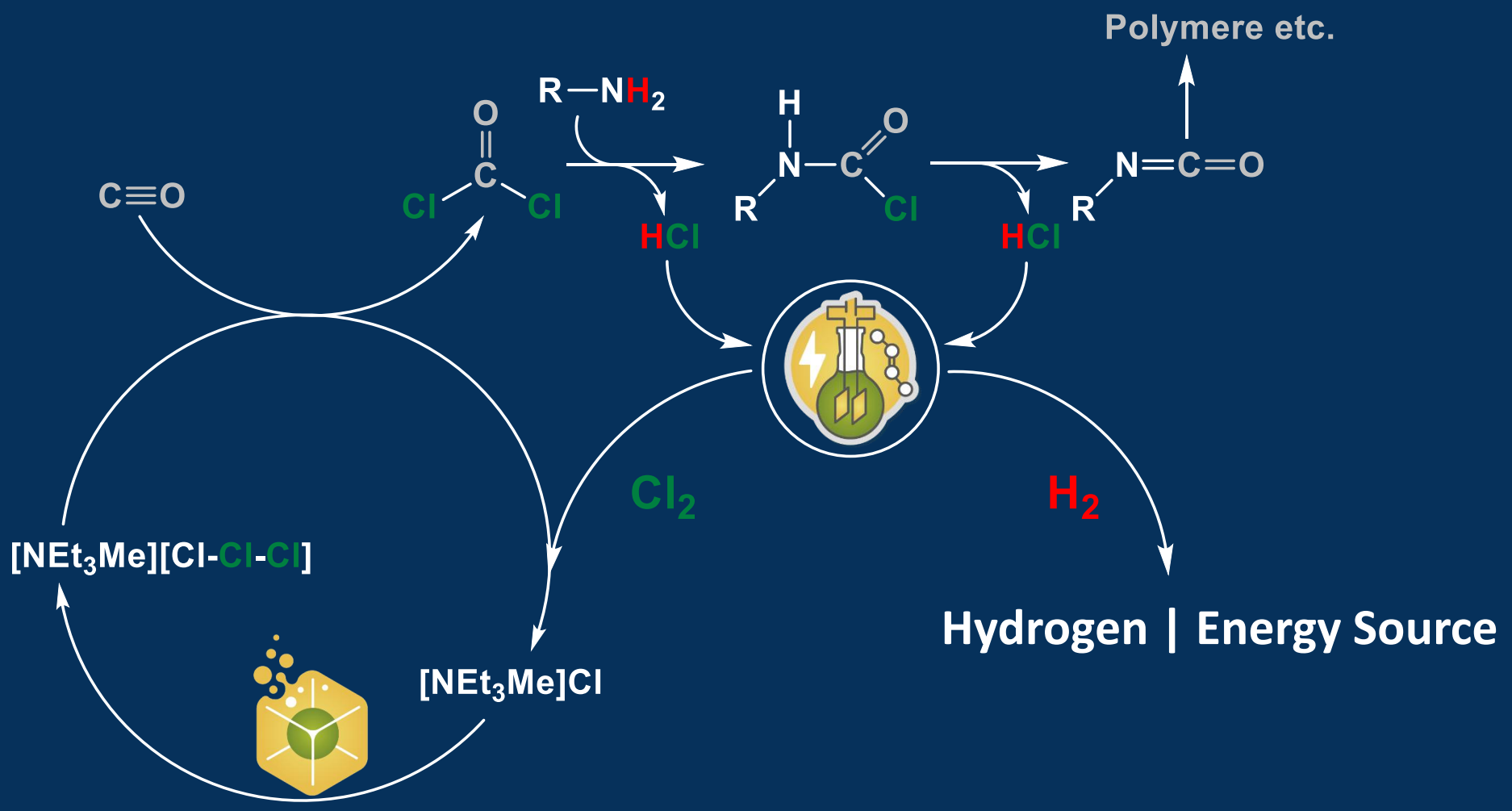
New and more Sustainable Chlorine Technology



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P. Voßnacker, A. Wüst, T. Keilhack, C. Müller, S. Steinhauer, H. Beckers, S. Yogendra, Y. Schiesser, R. Weber, M. Reimann, R. Müller, M. Kaupp, S. Riedel
Science Advances **2021**, 7, 40: eabj5186

Industrial Hydrogen Chloride (HCl)

Cl 17
Chlorine
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Aqueous Hydrogen Chloride

safer but more corrosive

limited applications

parasitic O_2 evolution

Gaseous Hydrogen Chloride

pressure-liquefied

useful base chemical

complex setup

Properties of the Bichloride IL

Cl 17
Chlorine
EN 3.16

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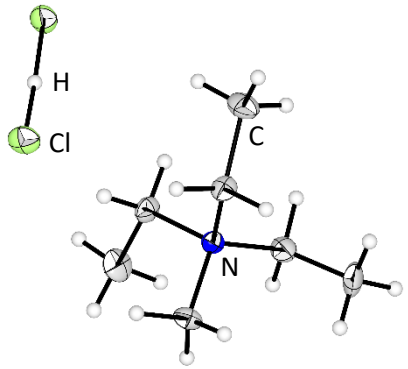
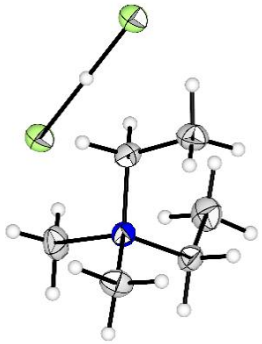
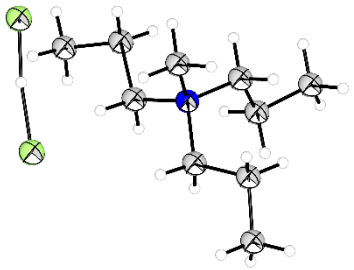
$[NEt_3Me][Cl(HCl)]$



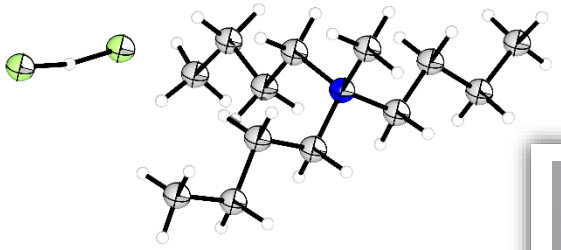
$[NEt_2Me_2][Cl(HCl)]$



$[NPr_3Me][Cl(HCl)]$



$[NBu_3Me][Cl(HCl)]$



Bichloride IL	Density	Dynamic Viscosity	Conductivity	Storage Capacity	
	[kg L^{-1}][a]	[mPa s][a]	[mS cm^{-1}][a]	[mol mol^{-1}][b]	[kg kg^{-1}][c]
$[NEt_3Me][Cl(HCl)_n]$	0.95	12	62.6	2.53	0.61
$[NEt_2Me_2][Cl(HCl)_n]$	0.94	7	70.1	2.39	0.63
$[NPr_3Me][Cl(HCl)_n]$	0.93	14	24.0	2.62	0.49
$[NBu_3Me][Cl(HCl)_n]$	0.92	26	9.8	2.70	0.42

Bichloride IL

G. H. Dreyhsig, P. Voßnacker, M. H. Baunis, N. Limberg, M. Lu, R. Schomäcker, S. Riedel *Science Advances*, **2024**, *10*, eadn5353

Patent: WO2023020942A1

Vapor Pressure of the Bichloride IL

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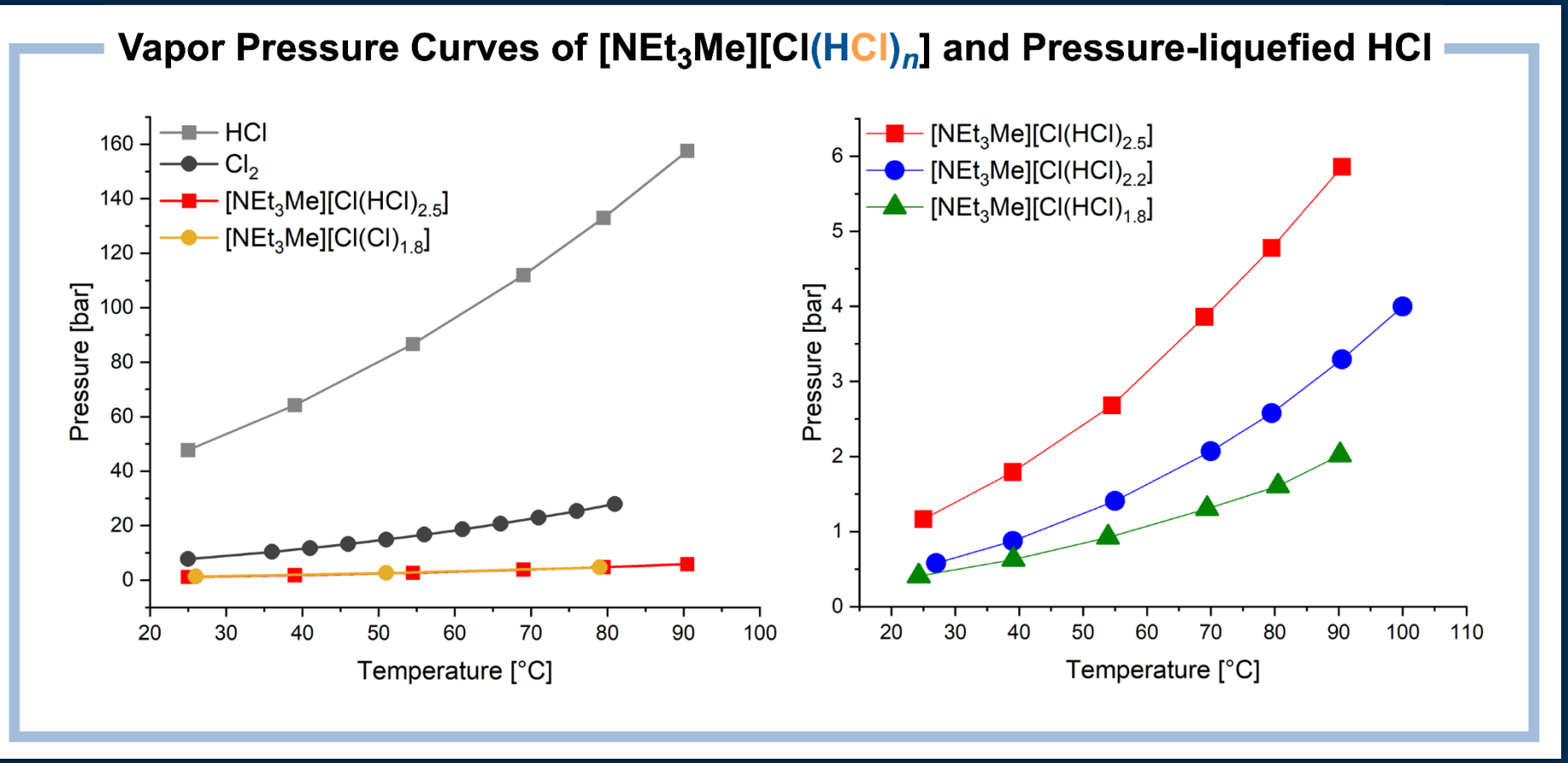

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Patent: WO2023020942A1

Bichloride-based Ionic Liquids

Liquid Hydrogen Chloride

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New Chlorine Technology based on Ionic Liquids

Cl 17
Chlorine
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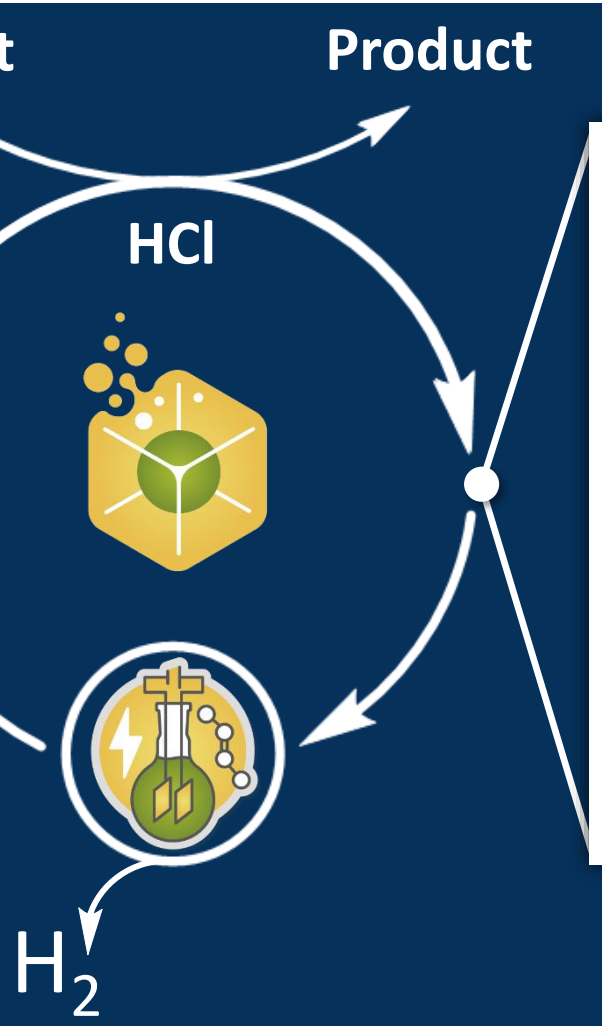
Chlorine IL



Bichloride IL

Low Gas Pressure

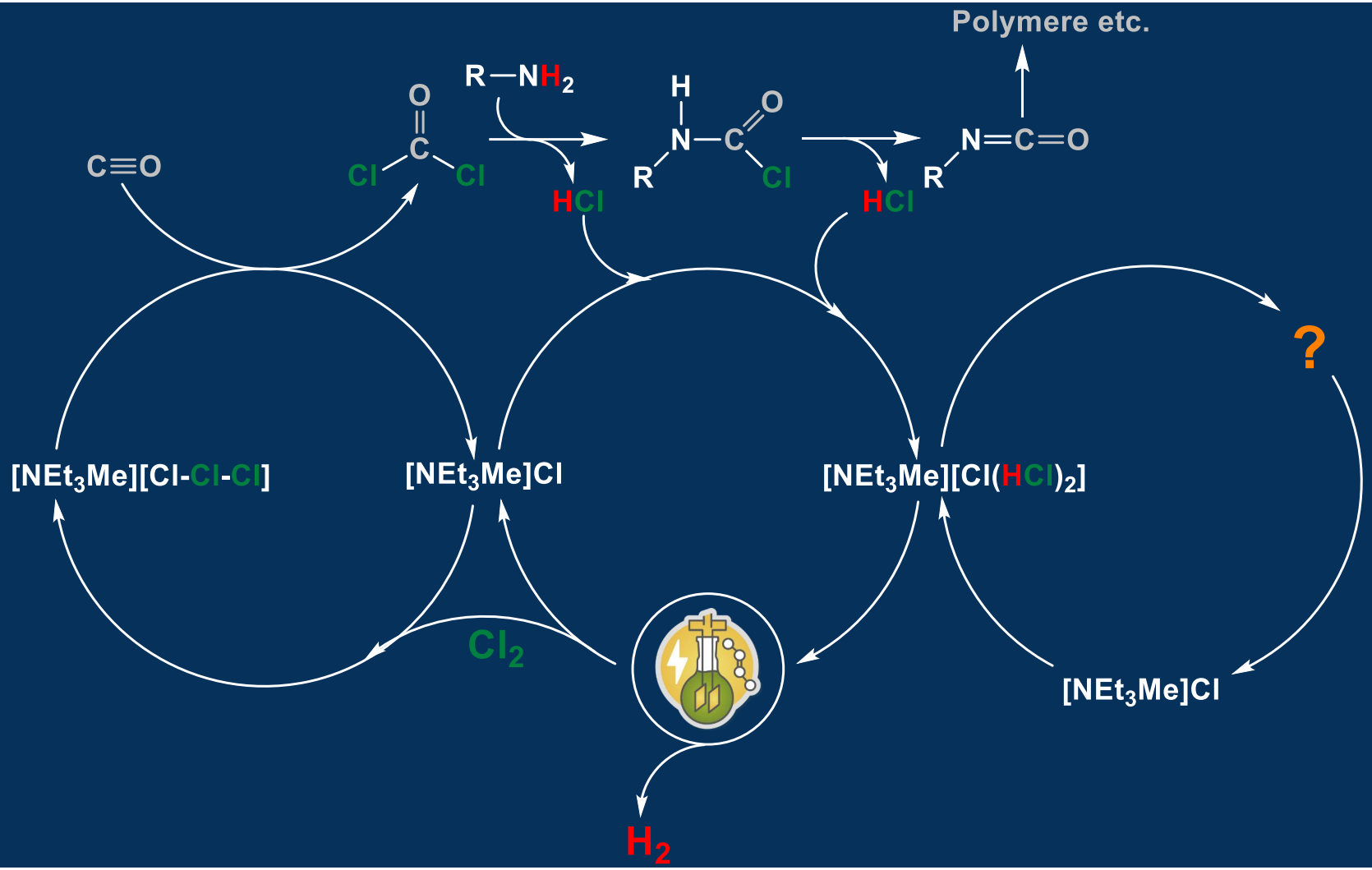
Simple Solution

Cheap, Scalable

Savings

Publications: S. Riedel, *et al. ACS Sustainable Chem. & Eng.* **2022**, *10*, 9525; S. Riedel, *et al. Angew. Chem.* **2023**, *62*, e202216586; S. Riedel, *et al. Science Advances* **2024**, *10*, eadn5353. **Cl-Technology Patents:** WO 2019215037 A1 | WO 2021069757 A1 | WO2023020942 A1

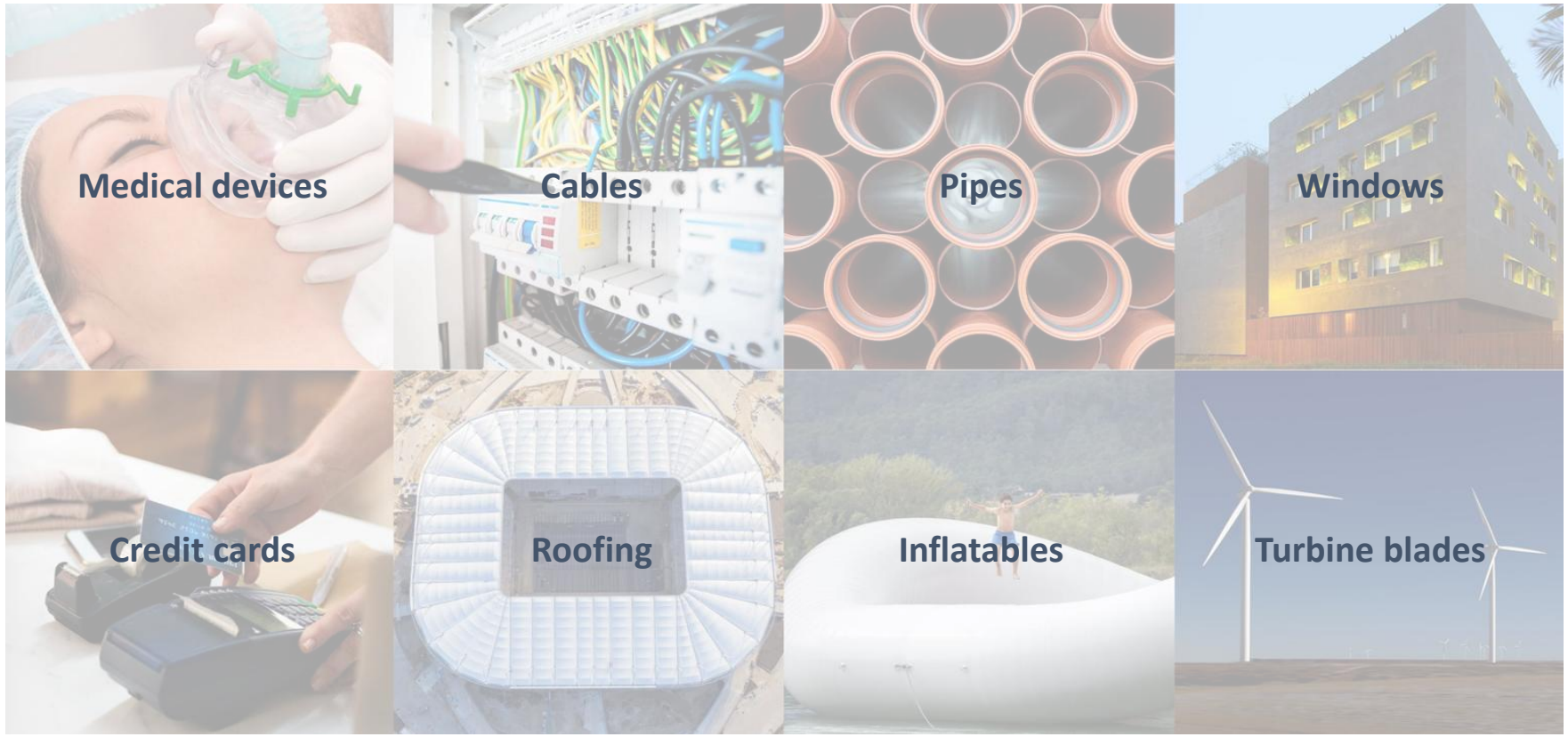
New and more Sustainable Chlorine Technology



Publications: S. Riedel, *et al. ACS Sustainable Chem. & Eng.* **2022**, *10*, 9525; S. Riedel, *et al. Angew. Chem.* **2023**, *62*, e202216586; S. Riedel, *et al. Science Advances* **2024**, *10*, eadn5353. **Cl-Technology Patents:** WO 2019215037 A1 | WO 2021069757 A1 | WO2023020942 A1

Production and Use of Polyvinyl Chloride (PVC)

PVC production volume of 5.1 mio. t a^{-1} in Europe



European Council of Vinyl Manufacturers (17. June 2024); https://pvc.org

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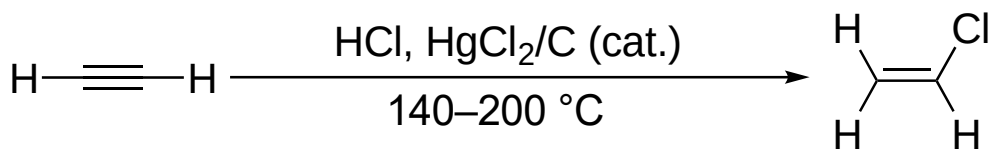
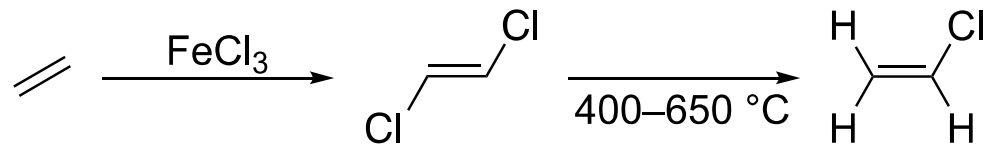
Production of Vinyl Chloride

Hydrochlorination of acetylene



Thermal cracking of 1,2-dichloroethane



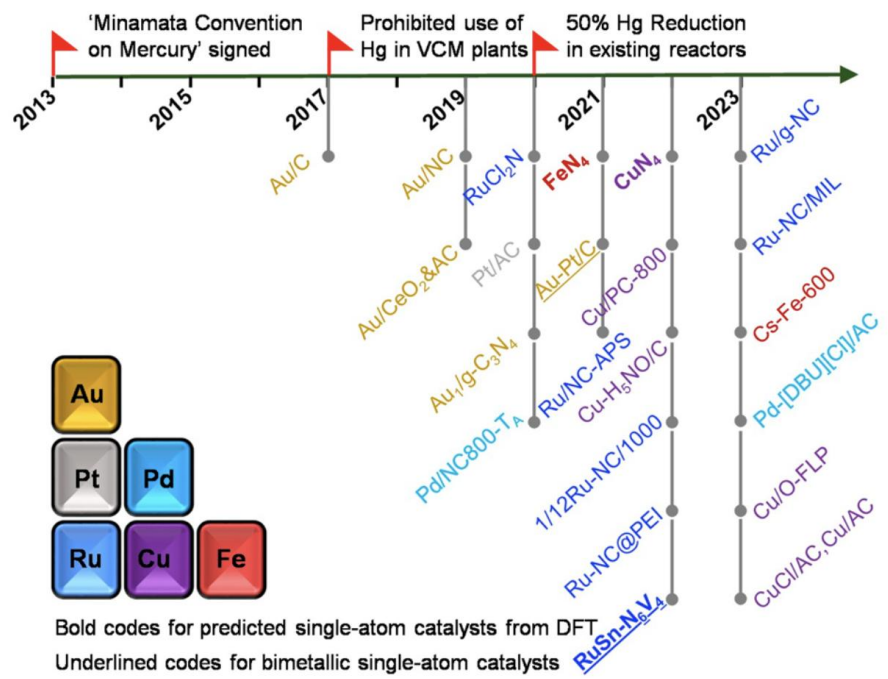
Mainly used by China (key global player in PVC market) due to vast coal reserves!
(13 mio. t a^{-1}, 80% by acetylene)

→ **Urgent need for technological solution to phase out use of mercury-based catalysts**

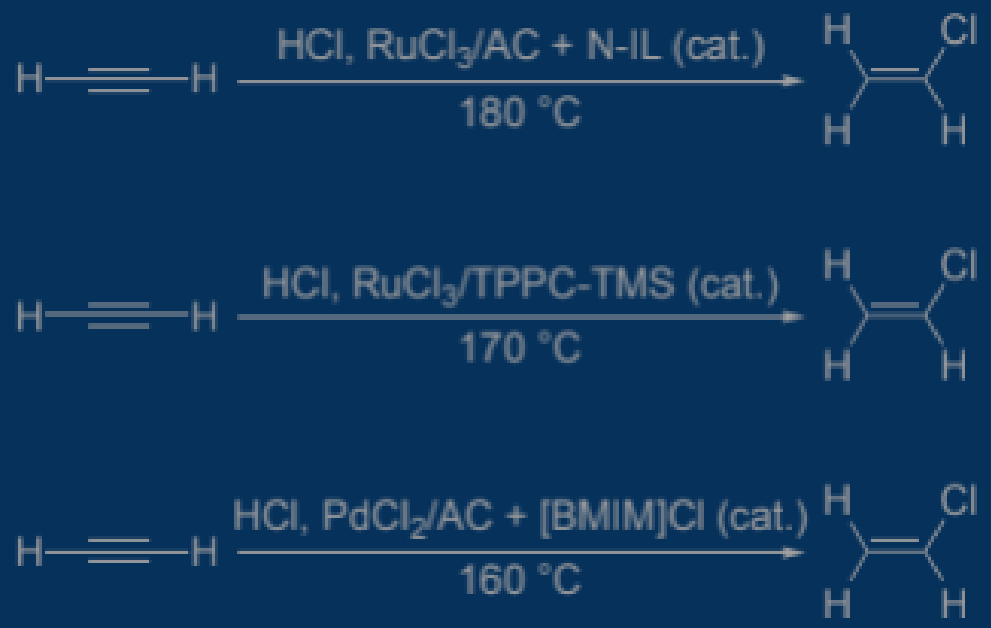
[1] E.-L. Dreher, *et al.*, L. H. Pottenger, Chloroethanes and Chloroethylenes in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, **2014**.
[2] G. Malta, *et. al.*, G. J. Hutchings, *Science* **2017**, *355*, 1399. [3] S. K. Kaiser, *et al.*, J. Pérez-Ramírez, *Nat. Nanotechnol.* **2022**, *17*, 606.

Mercury-Free Hydrochlorination of Acetylene

Single-atom catalysis



Catalyst promotion by Ionic Liquids



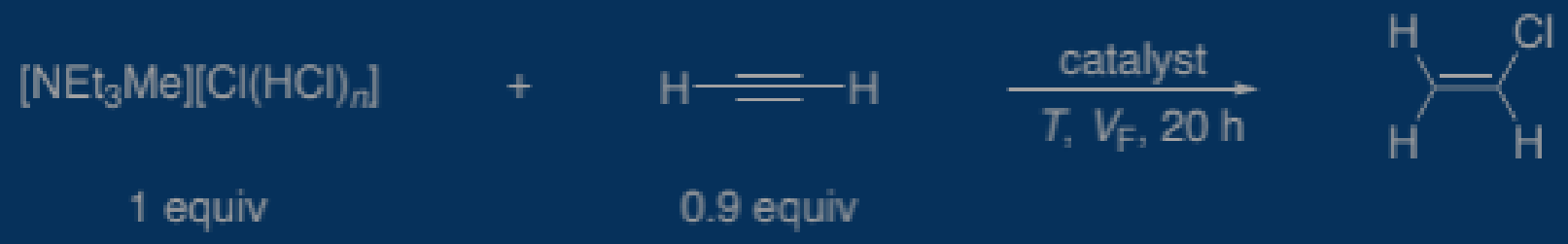
→ Catalyst in "supported-ionic-liquid-phase"

→ IL stabilizes catalytic active species

[1] Z. Chen, S. Wang, J. Zhao, R. Lin, *ACS Catal.* **2024**, 14, 965. [2] H. Whang, *et al.*, C. Wang, *Catal. Today* **2024**, *434*, 114696. [3] X. Wang, Y. Li, Z. Zhang, Z. Wang, Z. Zhang, F. Wang, X. Zhang, *New J. Chem.* **2024**, *48*, 5613. [4] J. Zhao, Y. Yue, G. Sheng, B. Wang, H. Lai, S. Di, Y. Zhai, L. Guo, X. Li, *Chem. Eng. J.* **2019**, *360*, 38.

Homogeneous Hydrochlorination of Acetylene using $[NEt_3Me][Cl(HCl)_n]$

Metal chloride experiments with $[NEt_3Me][Cl(HCl)_n]$



	Metal	Price per Ounce	Pre-Catalyst	Flask Volume	Temperature	Yield
1	Pd	899 €	$PdCl_2$ (0.5 mol%)	100 mL	100 °C	95%
2	Pt	974 €	$PtCl_2$ (0.5 mol%)	100 mL	100 °C	86%
3	Au	2167 €	AuCl (0.5 mol%)	100 mL	100 °C	48%
4	Bi	0.31 €	$BiCl_3$ (1 mol%)	250 mL	100 °C	10%

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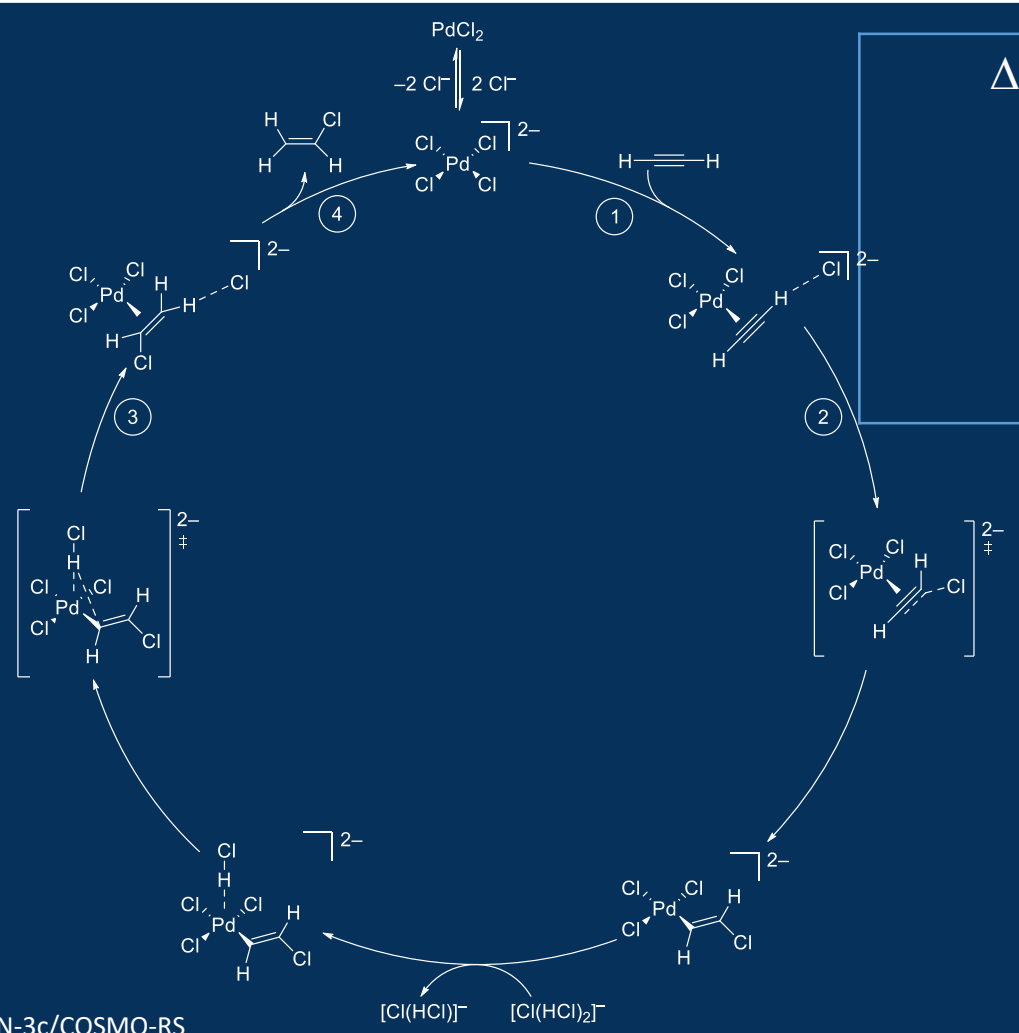
Strategic Metal Investments Ltd. (21. June 2024); http://strategic-metal.com/products/bismuth/bismuth-price/.
Goldpreis.de (21. June 2024); https://www.goldpreis.de.

Mechanism Using $[NEt_3Me][Cl(HCl)n]$ and $PdCl_2$

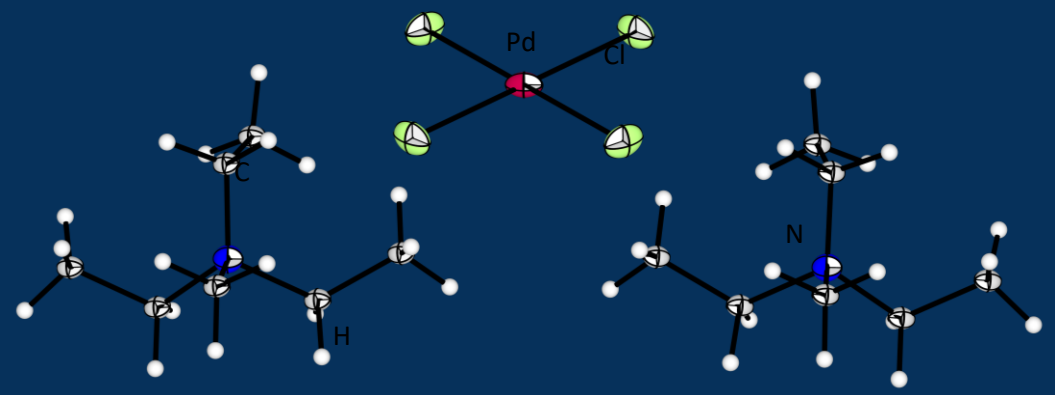


r2SCAN-3c/COSMO-RS

$\Delta G^{\ddagger}$ [kJ mol^{-1}]	
1	79
2	27
3	31
4	26

← **Rate-determining step**

Proposed active catalyst



R_1(all data) = 5.84%, wR_2(all data) = 12.16%, GooF = 1.187

G. H. Dreyhsig, V. Giulimondi, M. Kleoff, L. Lanfredi, M. Fuchs, N. Limberg, M. Reimann, M. Kaupp, J. Pérez-Ramírez, S. Riedel **2025** *submitted*

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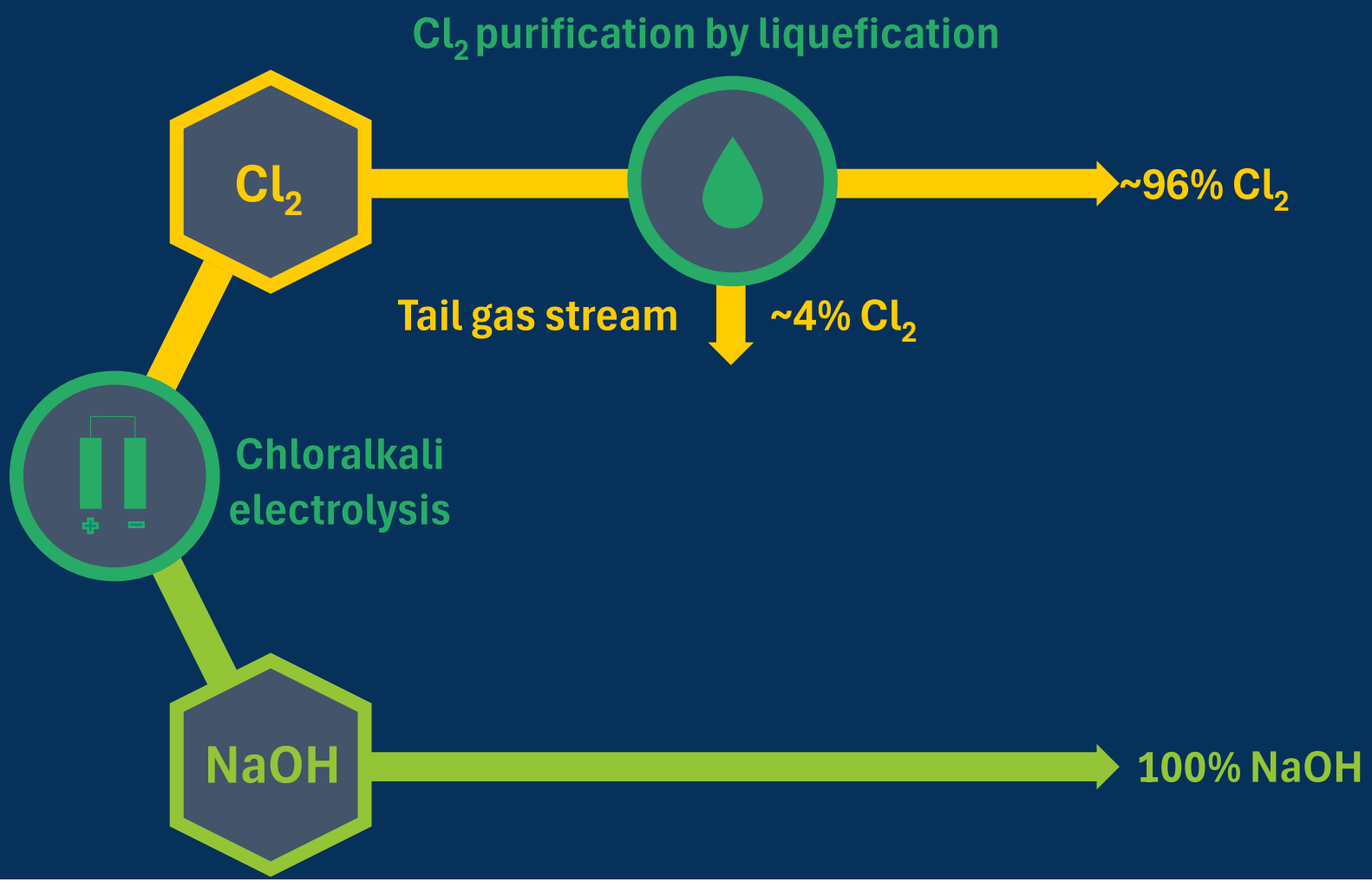
Tail Gas Streams of Chlorine Production



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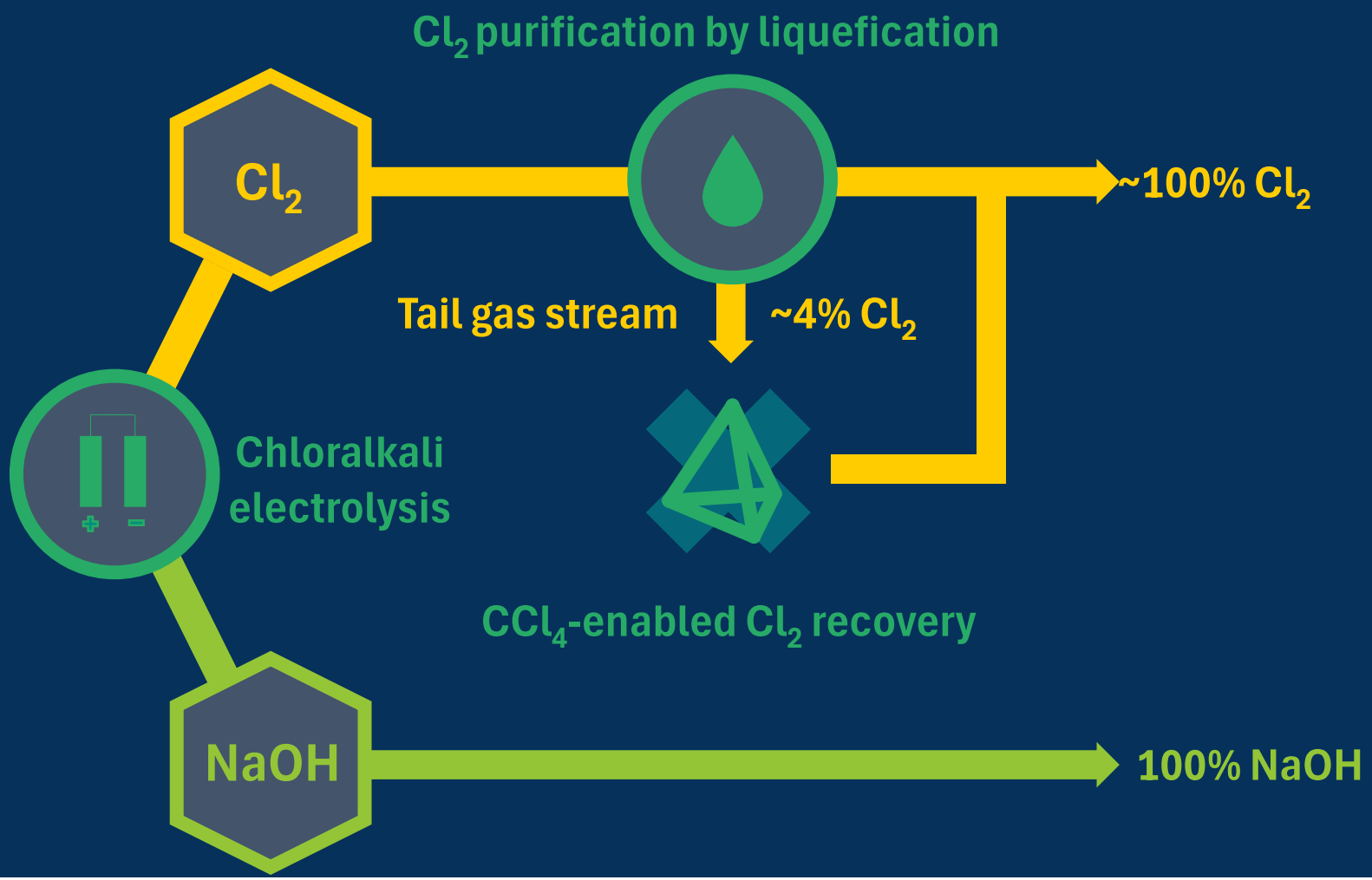
The Banned Solution: Tetrachloromethane (CCl_4)



- Until the 1990s, Cl_2 containing tail gas stream was washed with CCl_4 allowing selective Cl_2 adsorption and recovery
- Cl_2 and NaOH loss could be minimized
- CCl_4 is toxic and has high GWP and ODP

CCl_4 is prohibited since 1990

30 MONTREAL PROTOCOL

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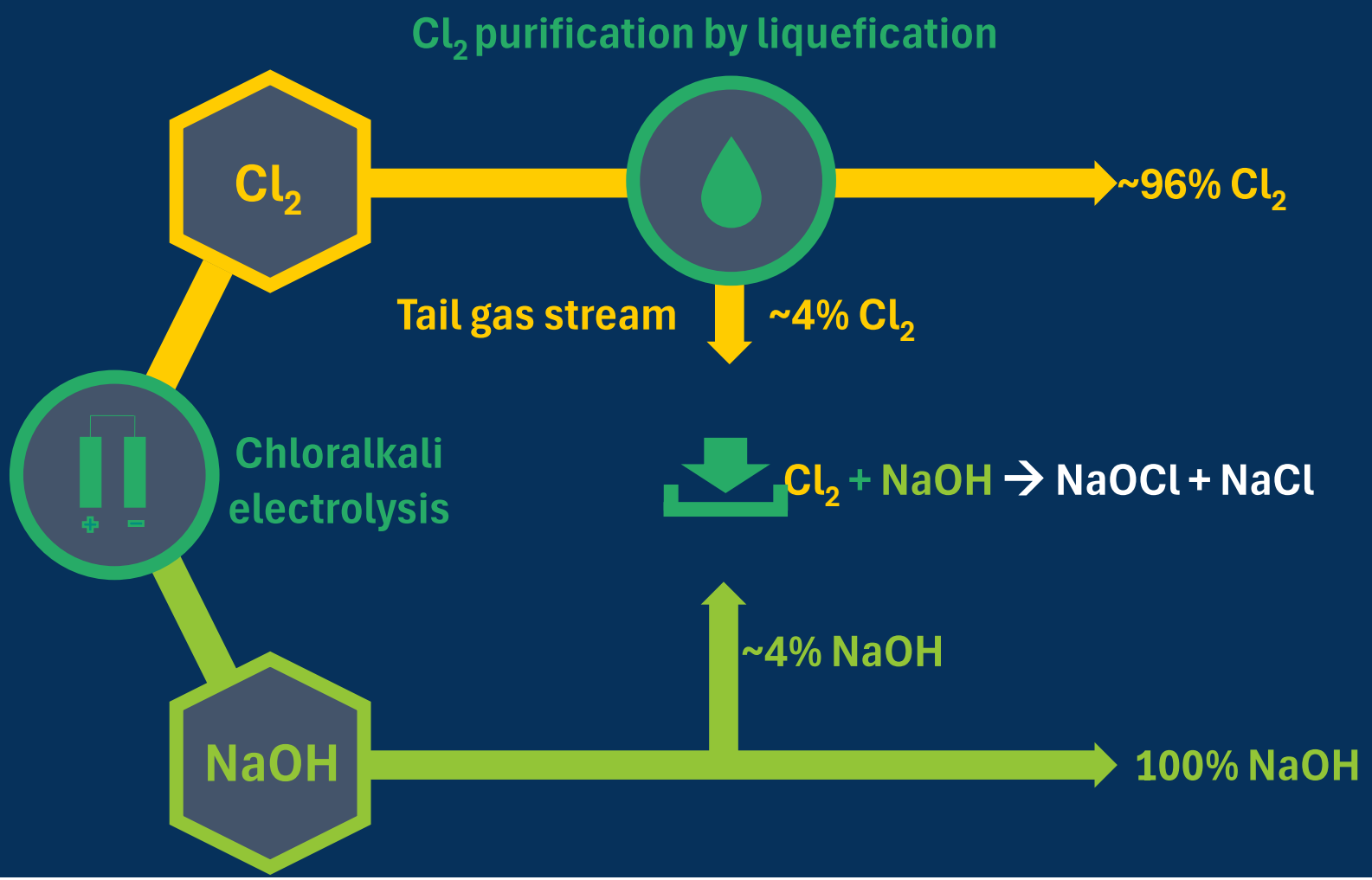
The Banned Solution: Tetrachloromethane (CCl_4)



- Real process: significant loss of Cl_2 and NaOH during Cl_2 purification
- Treatment of Cl_2 containing tail gas stream consumes large quantities of NaOH and forms NaOCl
- Amount of NaOCl exceeds its industrial demand and is mostly unwanted

Cl_2 containing gas streams and mixtures occur in **many** industrial processes and must also be **treated with NaOH**

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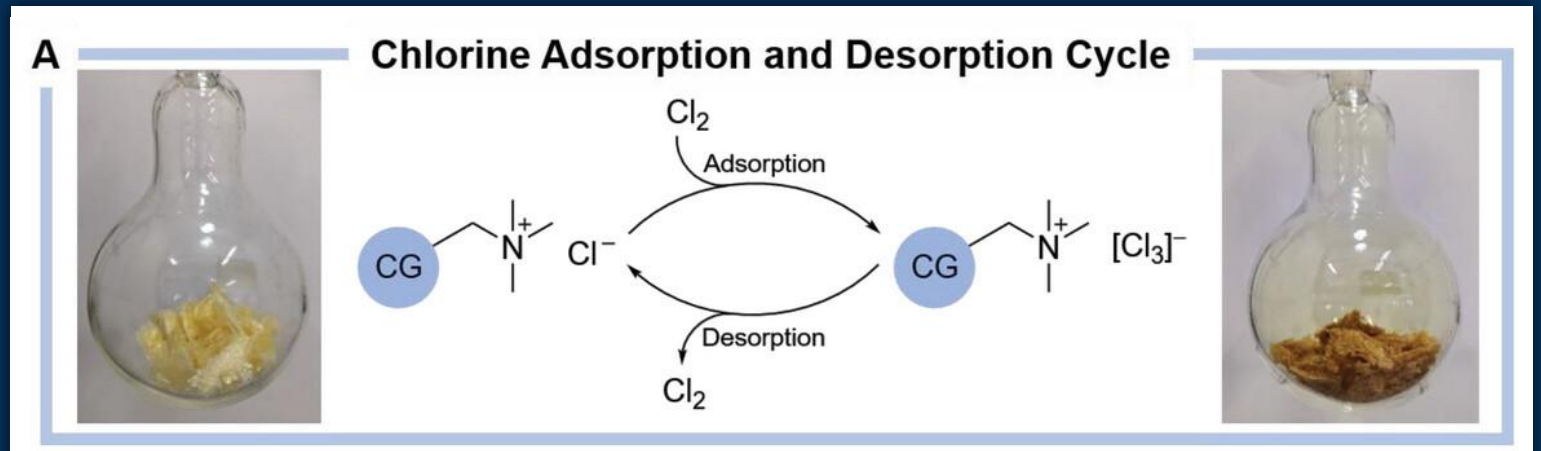
Polyethyleneimine-Based Cryogels



B

Chlorine Adsorption Capacities

Cryogel	Adsorption Desorption Cycle $m(Cl_2)/m(CG)$[a] (g/g) 1	2	3	Average
CG1[Cl]	0.29	0.24	0.22	0.25
CG2[Cl]	0.28	0.24	0.25	0.26
CG3[Cl]	0.24	0.22	0.21	0.22
nq-CG	0.16	0.16	0.15	0.15

[a] Corresponds to the total amount of Cl_2 reversibly adsorbed in the cryogel as $[Cl_3]^-$.

By applying heat and vacuum:

63% of the adsorbed Cl_2 was released within 3 h

72% was adsorbed within 16 h

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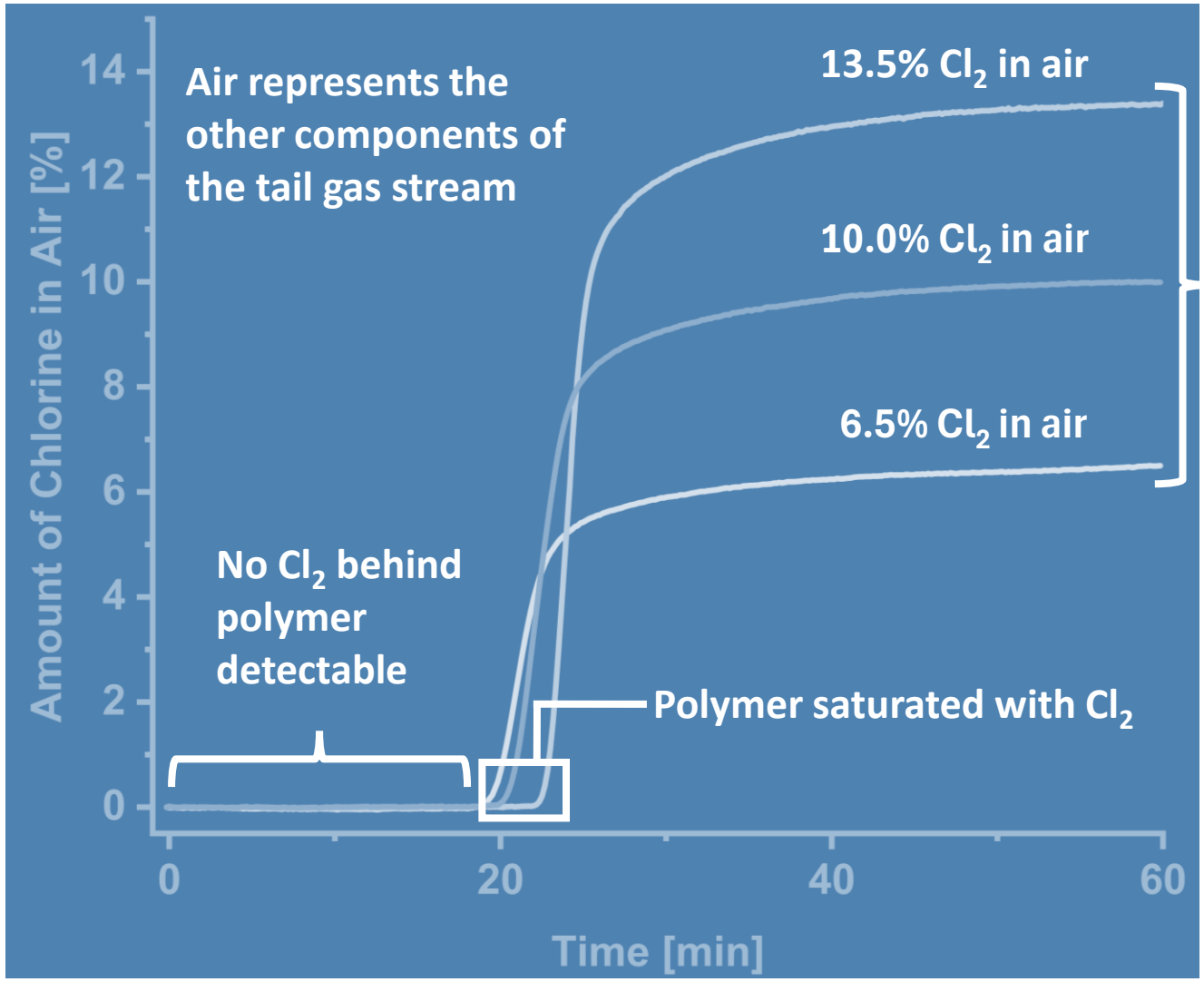
A. Lorente, J. S. Sturm, M. Kleoff, F. Lorenz, P. Voßnacker, O. Wagner, R. Haag, S. Riedel *Advanced Science* **2025**, *12*, 2414274

Influence of the Cl_2 Concentration



Independent from the Cl_2 concentration and shows a constant performance

Cl_2 behind polymer detectable

Simulation of different Cl_2-tail gas streams

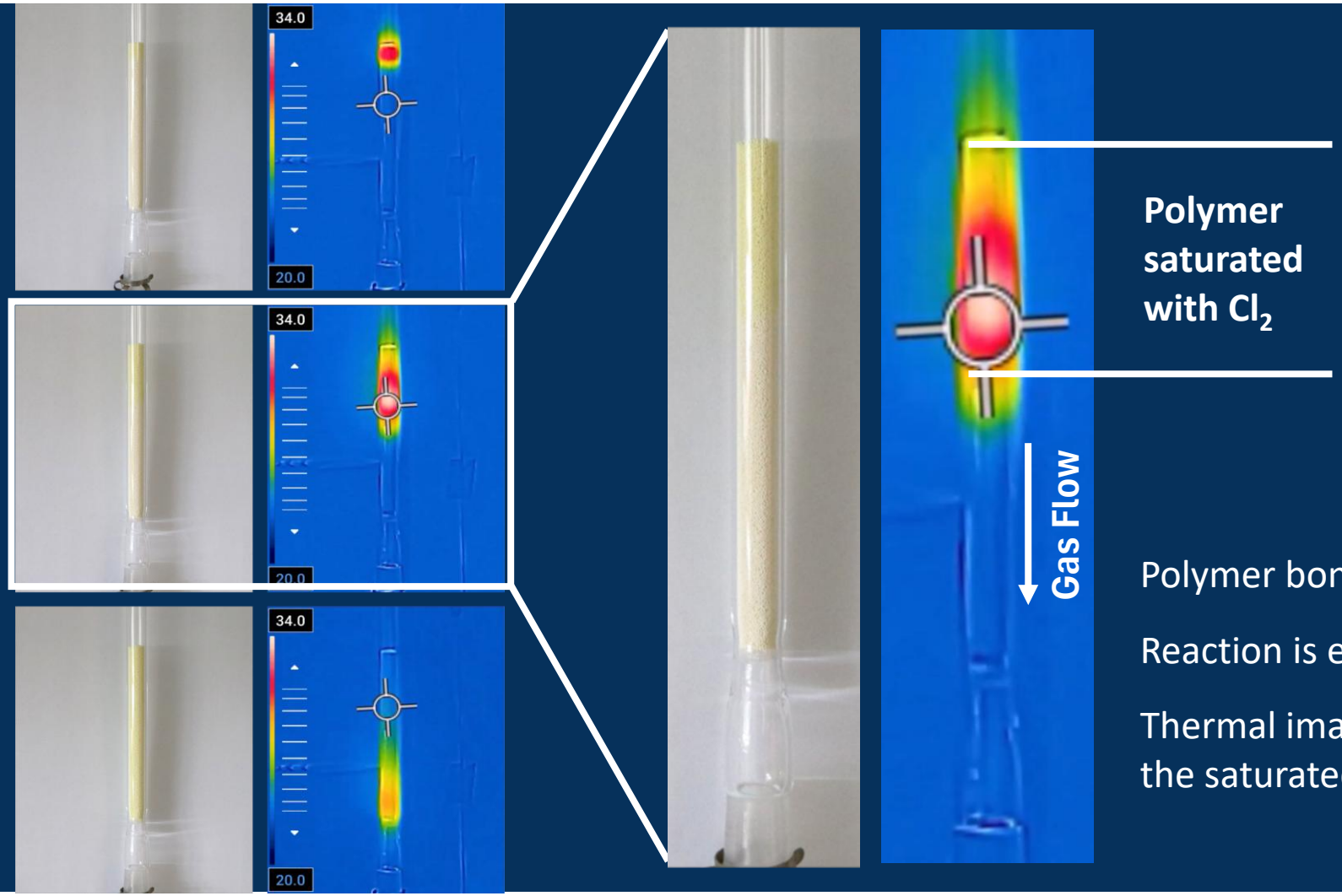
Cl_2-Saturation of the adsorbing polymer

Complete Cl_2 adsorption in the first 18-22 min

Time point of saturation depends on flow

Applied for Patent, **2023**, EP23206621.

Heat Evolution of Polymer-Loading with Chlorine



Exothermic polymer-loading with Cl_2 heats the polymer only up to 35 °C

Polymer bonds Cl_2 of tail gas stream selectively

Reaction is exothermic

Thermal imaging shows Cl_2 propagation along the saturated polymer

Applied for Patent, **2023**, EP23206621.

Perspective of a New Chlorine Technology

Cl 17
Chlorine
EN 3.16

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Transformation of the Chemical Industry and the Energy Sector

Bild: publish-industry / DALL-E

Upscaling for Industrial Application

Cl 17
Chlorine
EN 3.16

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CAE-Facility Leverkusen 1070 t/d

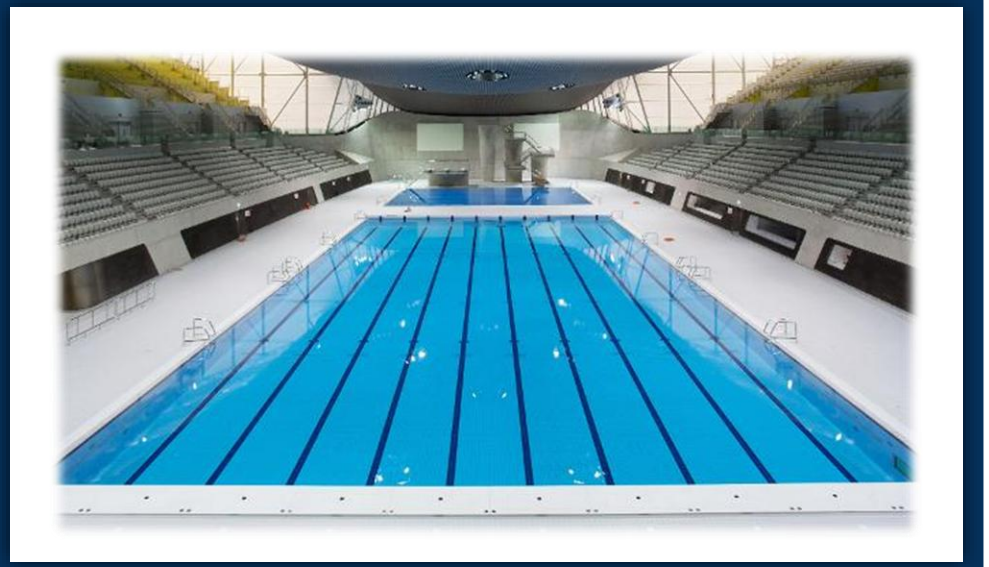
$[NEt_3Me]Cl$: 0.79 kg Cl_2/kg

Storage capacity for daily production Leverkusen:

1354 t $[NEt_3Me]Cl$ (100 t = ca. 20 k€)

Loaded storage material: **2003 m^3**

Comparison Olympic swimming pool: **2500 m^3**



EuroChlor **2023**; Riedel *et al. ACS Sustainable Chem. & Eng.* **2022**, *10*, 9525.

Indirect Energy Storage

Cl 17
Chlorine
EN 3.16

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Dark doldrum (two days)

Storage Material of **2708 t** → loaded material **4006 m³**

Production of 1 t of chlorine → **2.7 MWh**

Energy storage in 1 t of chlorine storage material → **1.2 MWh***

Two days eneregy storage → **5.8 GWh**

*Lithium-ion battery, has a high specific energy of approx. 90 - 240 kWh/t

EuroChlor **2023**; Riedel *et al. ACS Sustainable Chem. & Eng.* **2022**, *10*, 9525.

Direct Energy Storage

Cl 17
Chlorine
EN 3.16

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Pumped-storage power plant Wehr

Eneregy storage → **6.07 GWh**

Capacity of **4.4 million m³** water

1760 Olympic swimming pools

6,8 hours of energy support (45.000L/s)

Hornberg basin

Global Perspective of a New Chlorine Technology

Cl 17
Chlorine
EN 3.16

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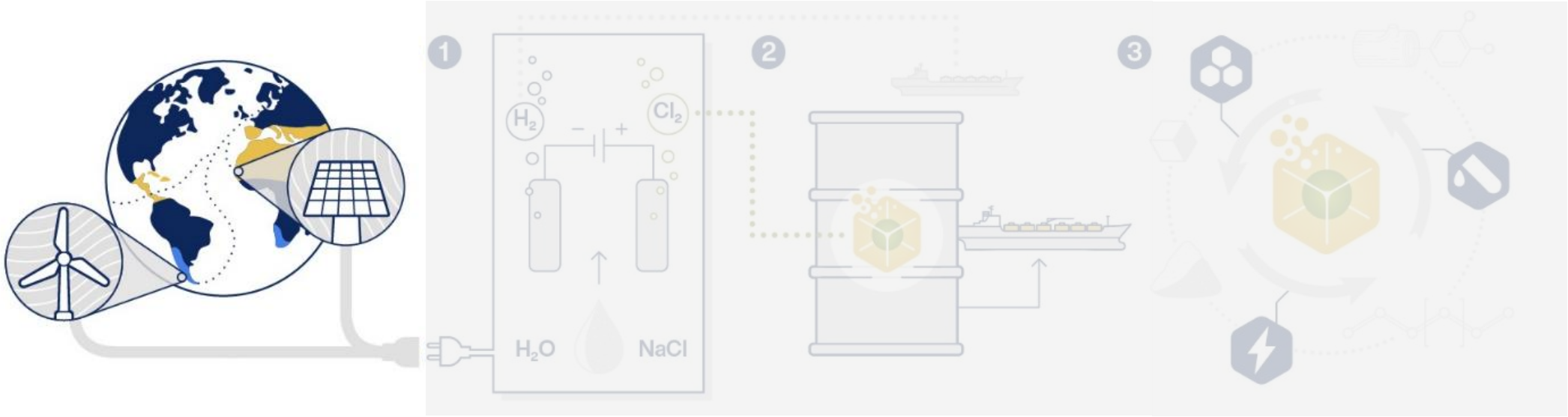
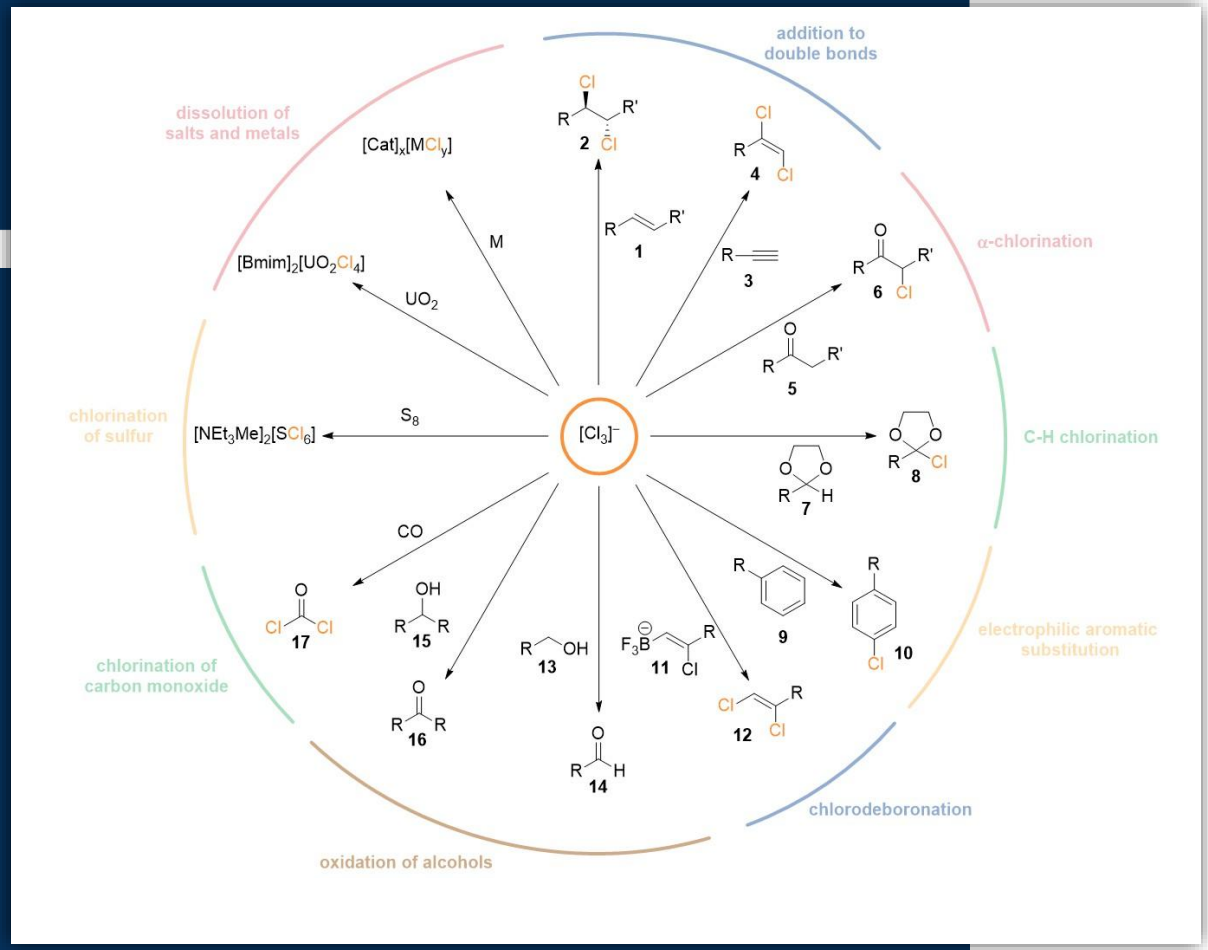
Renewable Energies | **Electrolysis** | **Material Carriers** | **Subsequent Value Chain**



Leopoldina: „Den kritischen Zeitpunkt nicht verpassen, Leitideen für die Transformation des Energiesystems“ **2023** | Diskussion Nr. 31
Publications: S. Riedel, *et al. ACS Sustainable Chem. & Eng.* **2022**, *10*, 9525; S. Riedel, *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202216586

$[Cl_3]^-$ Chemistry

M. Kleoff, P. Voßnacker, S. Riedel,
Angew. Chem. Int. Ed. **2023** *e202216586*



Rethinking Chlorine: Essential Chemical or Replaceable Risk?

J. Schwan, M. Kleoff, G. H. Dreyhsig, P. Voßnacker, T. Fiedler, M. Rosental, S. Riedel
ChemSusChem **2025**, DOI 10.1002/cssc.202402697

Acknowledgment

AK Riedel, FU Berlin April 2025

Freie Universität Berlin

RiedelLab
www.fluorinechemistry.de

Acknowledgment

CRC 1349 Fluorine-Specific Interactions

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