WORLD chlorine council

Global chlor-alkali industry: on the move to phase-out mercury cell-technology

ICMGP Edinburgh 29 July 2013

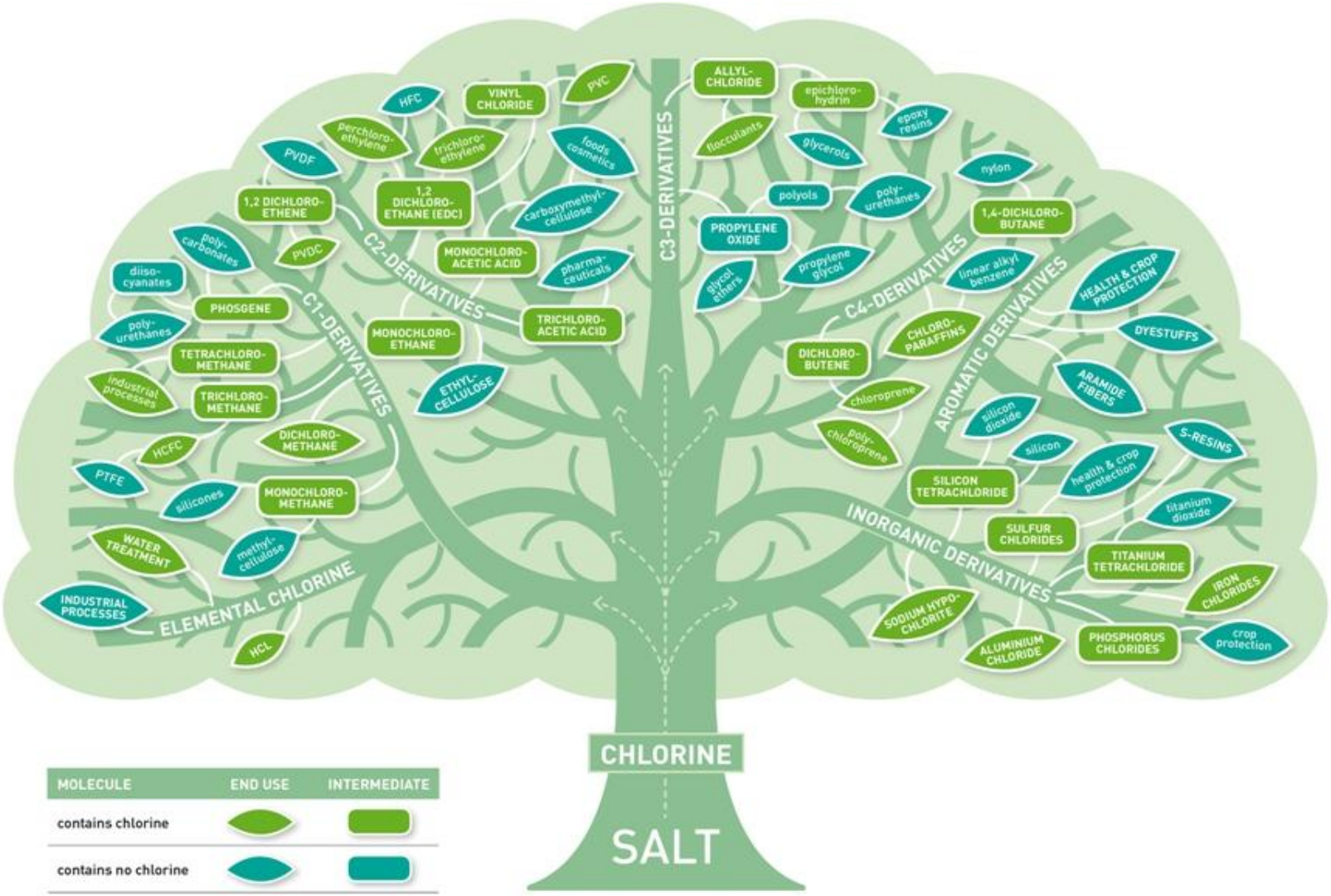
Dolf van Wijk
Jean-Pol Debelle, Allan Jones

Content

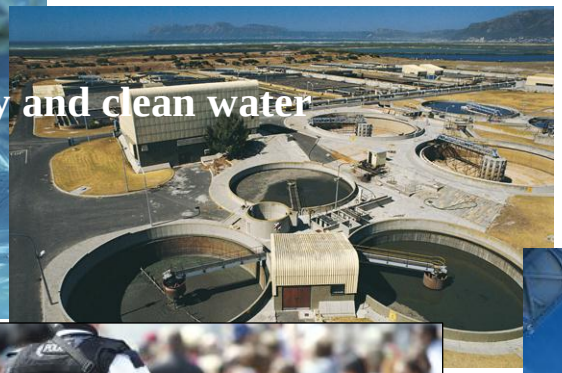
- Introduction
  - Chlorine and its products
  - Chlorine manufacturing
- Mercury and the chlor-alkali industry
  - Declining use
  - Declining releases
- Mercury phase-out key factors
- Mercury handling and storage

Chlorine – a versatile chemical building block

- Add electrical energy to a brine solution
  (=electrolysis of NaCl)
- Gives Cl_2 with built-in energy pack
  (+ H_2 and NaOH)
- Cl_2 reactive versatile building block essential in many modern life materials and products


CHLORINE
SALT
ELEMENTAL CHLORINE
C1-DERIVATIVES
C2-DERIVATIVES
C3-DERIVATIVES
C4-DERIVATIVES
AROMATIC DERIVATIVES
INORGANIC DERIVATIVES
HFC
VINYL CHLORIDE
PVC
perchloro-ethylene
trichloro-ethylene
PVDF
foods cosmetics
1,2 DICHLORO-ETHENE
1,2 DICHLORO-ETHANE (EDC)
carboxymethyl-cellulose
poly-carbonates
PVDC
MONOCHLORO-ACETIC ACID
pharma-ceuticals
diiso-cyanates
PHOSGENE
TRICHLORO-ACETIC ACID
poly-urethanes
MONOCHLORO-ETHANE
TETRACHLORO-METHANE
ETHYL-CELLULOSE
industrial processes
TRICHLORO-METHANE
DICHLORO-METHANE
HCFC
PTFE
silicones
MONOCHLORO-METHANE
WATER TREATMENT
methyl-cellulose
INDUSTRIAL PROCESSES
HCL
ALLYL-CHLORIDE
epichloro-hydrin
epoxy resins
flocculants
glycerols
nylon
polyols
poly-urethanes
1,4-DICHLORO-BUTANE
PROPYLENE OXIDE
propylene glycol
linear alkyl benzene
glycol ethers
HEALTH & CROP PROTECTION
CHLORO-PARAFFINS
DYESTUFFS
DICHLORO-BUTENE
ARAMIDE FIBERS
chloroprene
silicon dioxide
poly-chloroprene
silicon
S-RESINS
health & crop protection
SILICON TETRACHLORIDE
titanium dioxide
SULFUR CHLORIDES
TITANIUM TETRACHLORIDE
IRON CHLORIDES
SODIUM HYPO-CHLORITE
ALUMINIUM CHLORIDE
PHOSPHORUS CHLORIDES
crop protection
MOLECULE
END USE
INTERMEDIATE
contains chlorine
contains no chlorine

Chlorine applications



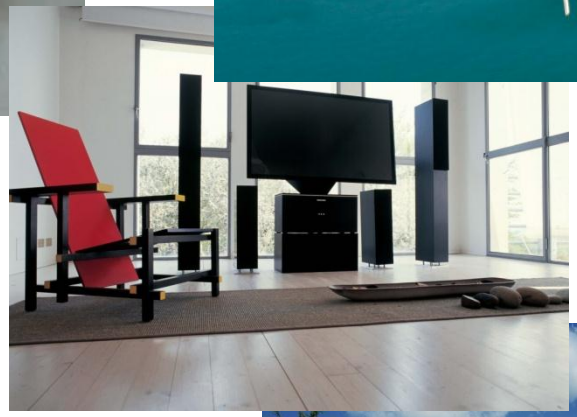
WORLD chlorine council

Helmet glass poly-carbonate

Polycarbonate Stool and TV

Solar cells and polycarbonate ‘glass’ – light and strong

Nylon and PVC



PVC construction materials

Pictures: Bayer MaterialScience, Tessenderlo Chemie, Solvay /Solar Impulse

WORLD chlorine council

Different routes to manufacture chlorine

- the membrane cell process, nowadays most widely used:

- the mercury cell process, where mercury is used as the cathode
- the diaphragm cell process
- Production capacities: Mercury: 7%; Membrane 77%

Mercury in use in chlor-alkali plants (situation 2012)

Country or region	**Hg plants** (end 2012)	**Capacity** kt Cl2/yr	**t Hg** (**)
Europe	34 (31)	3668	*6602*
India	3 (1)	98	*176*
Brazil + Argentina (1) + Uruguay (1)	6	321	*578*
North America + Mexico	(4)	380	*684*
Russia	3	414	*745*
Sub-total WCC	**50** (45)	**4881**	**8785**
Non WCC members estimate	< 43 (*)	< 1000	*< 1900*
Grand total	**< 93**	**< 5881**	**< 10685**

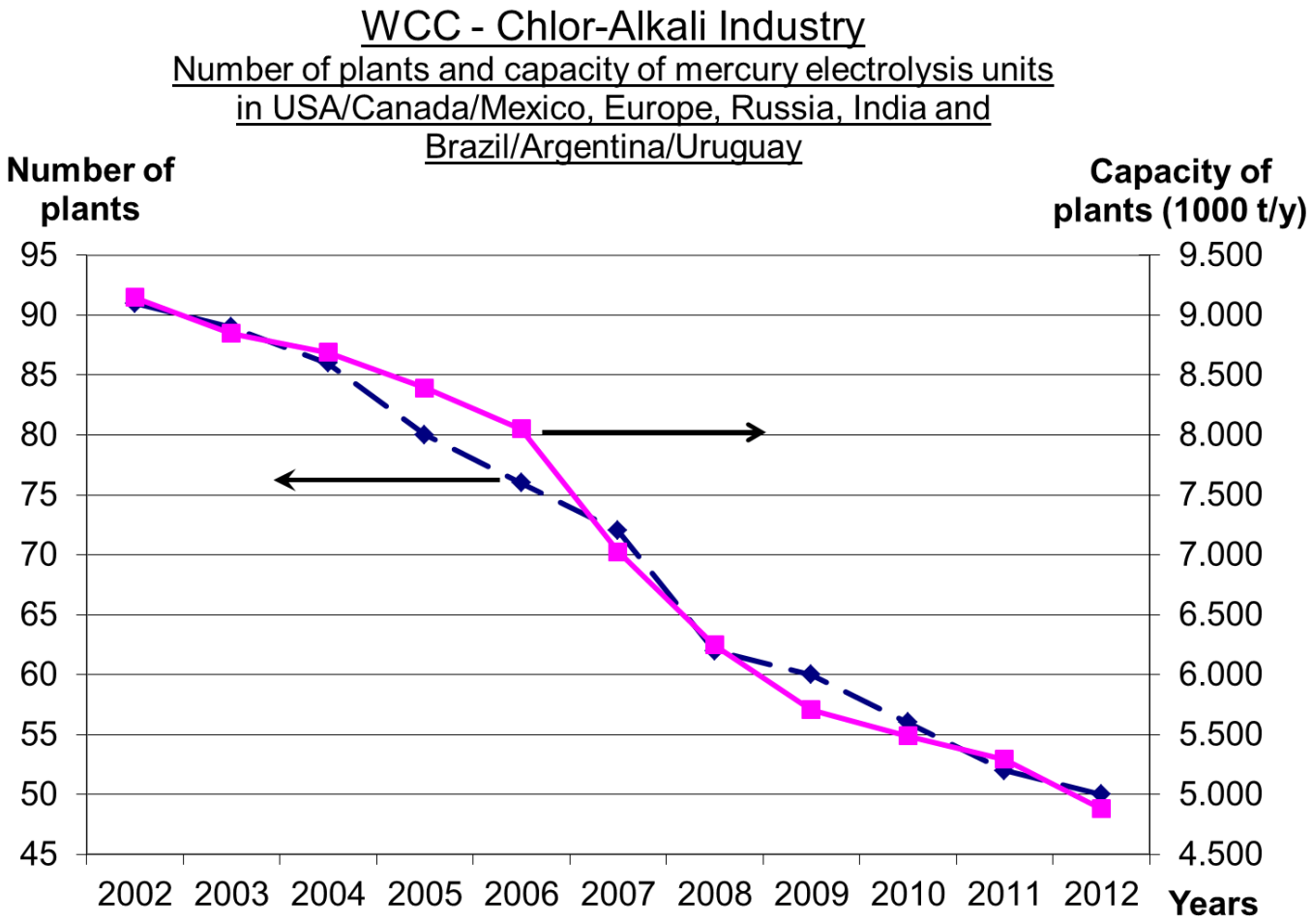
(*) but for less than 1 Mt Cl_2/yr on a total of 5.9 Mt/yr
(**) rounded values based on an average of 1.9 t Hg/kt Cl2 capacity

Mercury in use in chlor-alkali plants (situation 2012)

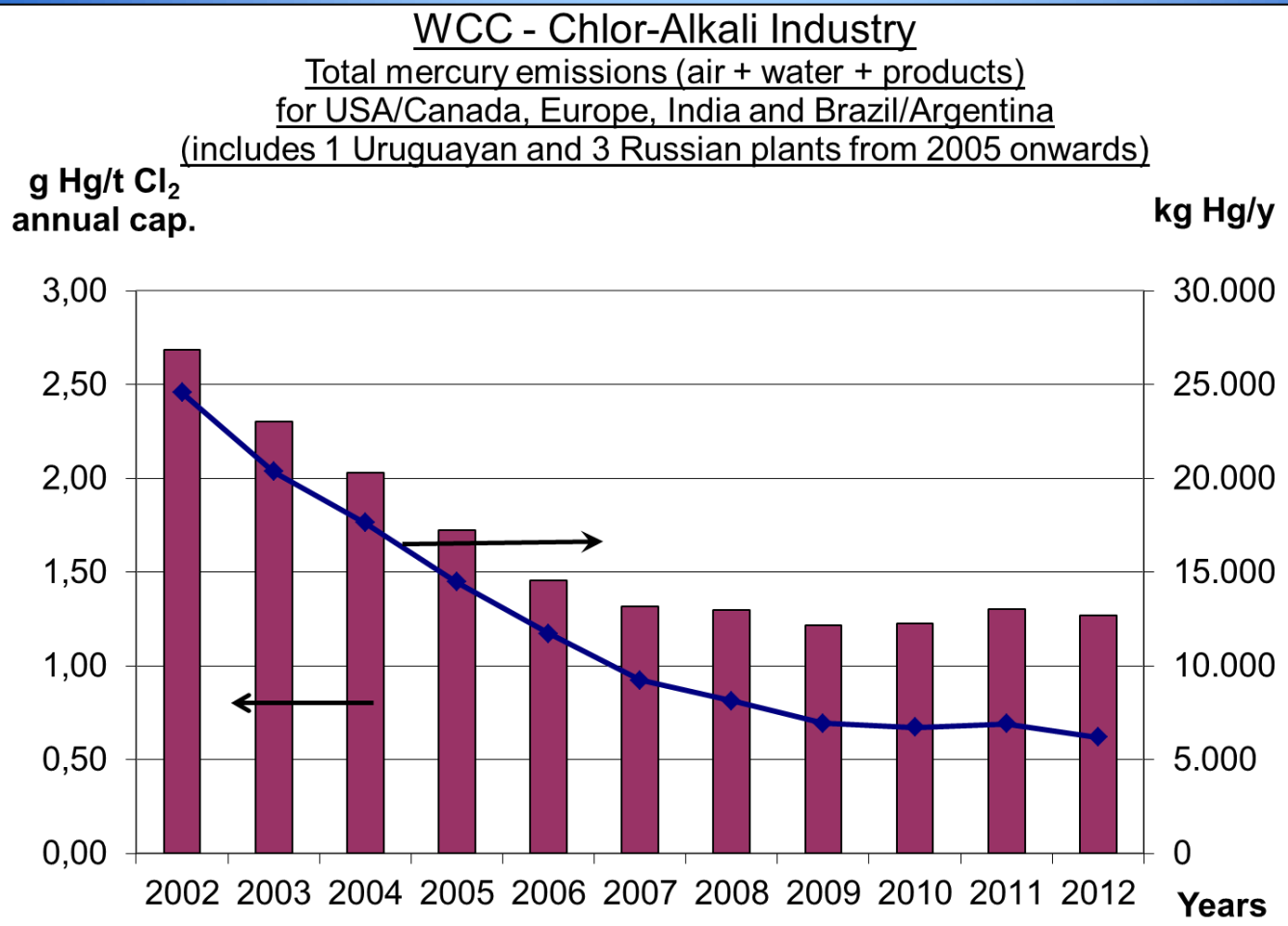
Country or region	**Hg plants** (end 2012)	**Capacity** kt Cl2/yr	**t Hg** (**)
Europe	34 (31)	3668	*6602*
India	3 (1)	98	*176*
Brazil + Argentina (1) + Uruguay (1)	6	321	*578*
North America + Mexico	(4)	380	*684*
Russia	3	414	*745*
Sub-total WCC	**50** (45)	**4881**	**8785**
Non WCC members estimate	< 43 (*)	< 1000	*< 1900*
Grand total	**< 93**	**< 5881**	**< 10685**

(*) but for less than 1 Mt Cl_2/yr on a total of 5.9 Mt/yr
(**) rounded values based on an average of 1.9 t Hg/kt Cl2 capacity

Mercury process by WCC member companies



Mercury releases WCC member companies



WORLD chlorine council

Mercury phase-out – key factor is costs

Membrane advantages versus mercury:

- Lower energy cost: 22-30%
  - But steam needed to concentrate caustic
- Easier operation and maintenance

→ Conversion is financial-investment issue

- Long-term investments needed
- In mature markets payback time is over 10 years

Handling and storage of mercury in CA industry

- Safe handling and storage of liquid mercury is long-standing practice
- Good housekeeping; continued training; regular controls are key elements
- WCC guidance documents shared; several topics, e.g. housekeeping, minimisation of emissions, analytical methods, decommissioning, mercury storage …

http://www.unep.org/hazardoussubstances/Mercury/PrioritiesforAction/ChloralkaliSector/Reports/tabid/4495/language/en-US/Default.aspx

Safe handling practices during operation

Cell room

Respiratory equipment during cleaning

Safe handling practices during operation

Vapour extraction and
active carbon filtration

Confinement with aeration

Safe handling during conversion

Installation of dedicated
area to change PPE:
Personal protective equipment

Frequent air measurements

Safe handling during conversion

Fluorescent x-ray measurements

Contaminated waste handling

Mercury storage

- Storage options under consideration globally:
  - Aboveground – belowground (e.g. salt mines)
  - Liquid – solid (stabilised)
  - Studies ongoing on feasibility and safety
- Chlor-alkali industry interested in pursuing permanent storage solutions

Mercury sulphide disposal in landfill and salt mines has been applied since many years

- Technical solutions operational in Germany (industrial unit), Spain (lab scale)
- Results show transformation of mercury is complete; no metallic traces detectable in solid
- Germany: industrial installation running successfully since >3 years (>1000 tonnes treated)
- Spanish project for building industrial plant launched summer 2011, including collection and transport; Project on hold due to financial constraints

Stabilisation of mercury (German company)

Brought to full scale, licensed and commercially used

The end product from the stabilisation is the non toxic mercury sulphide, also known as cinnabar.

Thank you for your attention

For further information:

Contact Dolf van Wijk - WCC Secretariat

dvw@cefic.be

…and: