

Practical experiences from projects with conversion from mercury to membrane electrolysis technology

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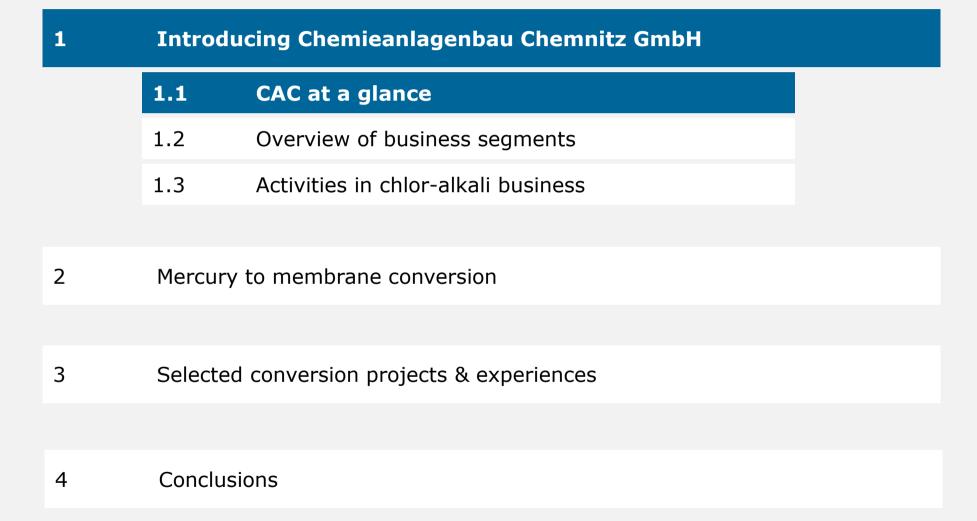
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Dr. Franziska Herrmann

Monterrey, November 15th, 2018





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More than 50 years of experience



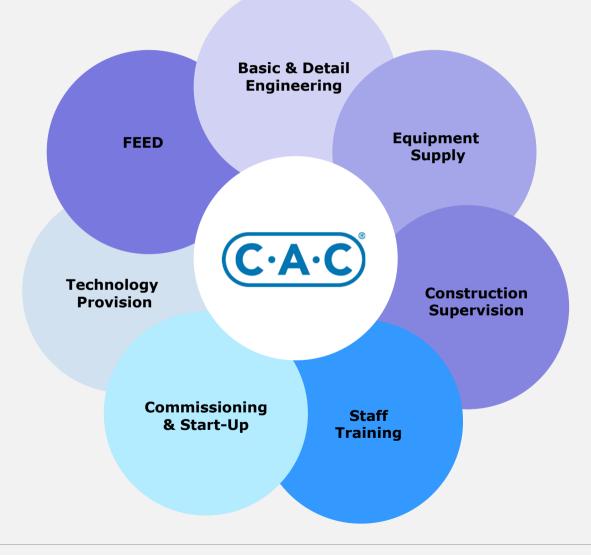




1964	Plant engineering and contracting division within the factory "Germania"
1970	Directorate plant engineering in collective combine CLG
1990	Foundation of "Lurgi Anlagenbau Chemnitz GmbH" and integration in the Lurgi group
2004	Foundation of an independent plant engineering company in Chemnitz and foundation of "Chemieanlagenbau Chemnitz GmbH"
2005	Foundation of HUGO PETERSEN within the CAC group of companies
2006	Take-over of the majority stake of BiProTech Sp.z.o.o. in Kraków, Poland



CAC offers all services for construction, reconstruction or expansion of your plant





1	Introducing Chemieanlagenbau Chemnitz GmbH		
	1.1	CAC at a glance	
	1.2	Overview of business segments	
	1.3	Activities in chlor-alkali business	
2	Mercury	to membrane conversion	
3	Selected	conversion projects & experiences	

4 Conclusions

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Targeted Industries & Market Segments



Refinery & Crude Oil Processing

- Refinery Engineering
- Atmospheric Distillation
- Vacuum Distillation
- Hydro-desulphurisation
- Reforming / Zeoforming
- Bitumen
- Isomerisation
- Demercaptanisation
- Lube Oil Refining



Gas Engineering

- Natural Gas
 Underground Storage
- Gas Compressor Stations
- Gas Treatment
- Pre-treatment
- Purification
- Gas Scrubbing
- Separation of higher hydrocarbons
- Gas Compression
- Sulphur Recovery
- Demercaptanisation



Petrochemicals

- Expandable Polystyrene
- Ammonia
- Urea
- Melamine
- Butadiene
- Maleic Anhydride
- Butanediol
- Nitric Acid



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Inorganics

- Sulphuric Acid
- CI-Alkali Electrolysis
- Chlorine Purification
- Ammonium Sulphate
- Poly-aluminium Chloride
- Ferric Chloride
- Calcium Chloride



1.1	CAC at a glance
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- 1.2 Overview of business segments
- **1.3** Activities in chlor-alkali business
- 2 Mercury to membrane conversion
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Track record of the chlor-alkali business

1964	1 st Chlor-alkali electrolysis (mercury) built for BASF AG, Germany
1976	1 st Chlorine plant (diaphragm) built for Sameit Alkali, Norway
1983	1 st Chlorine plant (membrane) built for United Srichai Chemicals, Thailand
2004	Transfer of Lurgi's chlor-alkali business to Chemieanlagenbau Chemnitz GmbH
2010	Acquisition of Krebs Swiss chlor-alkali technology from GEA Messo, France



CAC is Associate Member of EuroChlor

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BASIC & DETAIL ENGINEERING – C/A PLANTS					
No.	CLIENT	LOCATION	PLANT CAPACITY (in thousand tons per year)	YEAR (start-up)	REMARKS
1	OAO NAVOYAZOT	Navoi, Uzbekistan	23 Chlorine26 Caustic Soda	2001	FS BE NEW PLANT
2	SAYANSKCHIMPLAST I.	Sayansk, Russia	150 Chlorine 168 Caustic Soda	2006	FS BE CONVERSION
3	MOSVODOKANAL	Moscow, Russia	10 Chlorine 11.3 Caustic Soda	2013	BE DE NEW PLANT
4	SAYANSKCHIMPLAST II.	Sayansk, Russia	180 Chlorine 202 Caustic Soda	2013	BE DE EXPANSION
5	SODA CHLORAT	Beresniki, Russia	26 Chlorine40 Caustic Potash	2014	FS BE DE CONVERSION
6	JSC BELARUSKALI	Soligorsk, Belarus	16.5 Chlorine 25 Caustic Potash	2015	BE DE NEW PLANT

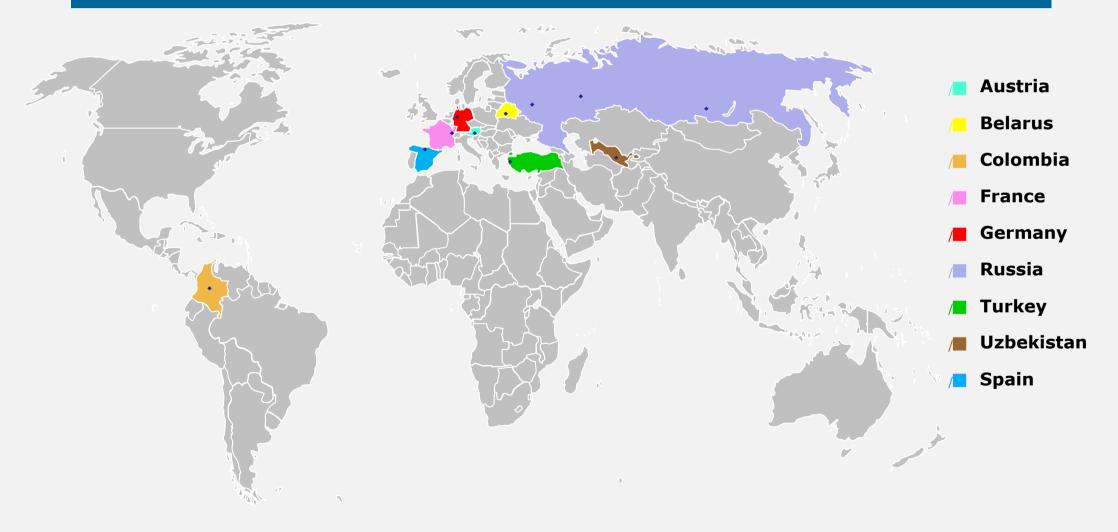




BASIC & DETAIL ENGINEERING – C/A PLANTS					
No.	CLIENT	LOCATION	PLANT CAPACITY (in thousand tons per year)	YEAR (start-up)	REMARKS
7	TESSENDERLO GROUP	Loos, France	 54.0 Chlorine 61.0 Caustic Soda or 40.7 Chlorine 64.5 Caustic Potash 	2012	PDP CONVERSION
8	DONAUCHEMIE	Brueckl, Austria	31.6 Chlorine 35.7 Caustic Soda	2015	BE DE EXPANSION
9	POTASSE ET PRODUITS CHIMIQUES SAS	Thann, France	43.2 Chlorine 68.4 Caustic Potash	2015	BE DE CONVERSION
10	BRINSA S.A.	Zipaquirá, Colombia	27 Chlorine30 Caustic Soda	2016	BE DE CONVERSION
11	JV AKZO / EVONIK	Ibbenbueren, Germany	82 Chlorine 130 Caustic Potash	2017	BE CONVERSION
12	PETKIM PETROKIMYA HOLDING A.Ş.	Aliağa, Izmir, Turkey	103 Chlorine 113 Caustic Soda	2019	BE, DE CONV. MON/BIP
13	Altamira-Electroquimica del Cantabrio, S.A. (BONDALTI GROUP)	Torrelavega, Spain	68 Chlorine 76 Caustic Soda	2019	CONVERSION



> 600,000 t/a of chlorine are produced in our reference plants



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Mercury to membrane conversion

- **2.1** Electrolyser technologies
- 2.2 Re-use of equipment
- 2.3 Arrangement
- 3 Selected conversion projects & experiences

4 Conclusions

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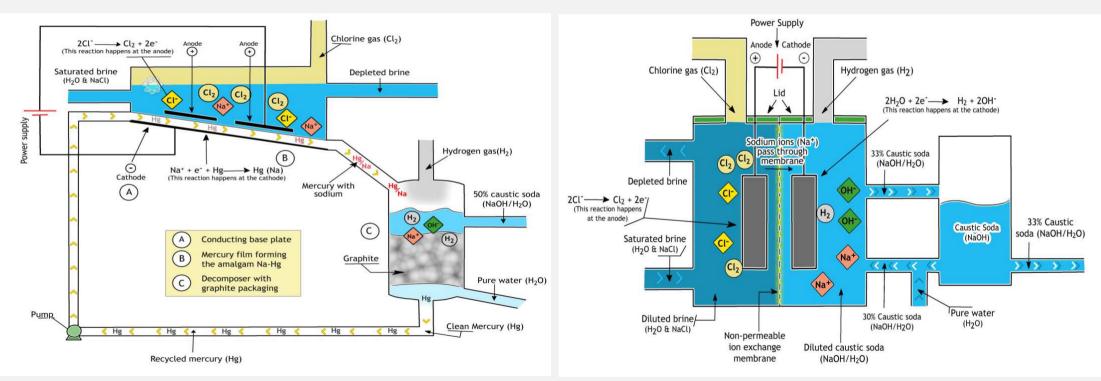
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Electrolyser technologies

Mercury electrolyser

Membrane electrolyser



source: EuroChlor

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Advantages of membrane vs. mercury process

Environmental impact & improvements

- Complete reduction of the mercury emissions to the air
- Exclusion of contamination of mercury to the soil
- No waste water and waste disposal contaminated with mercury
- Significant reduction of electrical power consumption up to 30% less!
- **Essential savings of operational costs** due to:
 - No further mercury treatment & disposal required
 - Up to 50% less operational staff required
 - Less maintenance costs

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14 12 10 HCI 8 Mio. t Cl2 Na Mb 6 Hg Dia 4 2 0 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018

chlorine production in Europe

data source: EuroChlor

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Re-usable equipment

- ✓ Salt dissolver, tanks, heat exchangers
- ✓ Gas treatment sections (coolers, drying towers, blowers, compressors...)
- ✓ Filters and columns: usually too big, but no problem (more retention time)
- X Pumps: not recommended especially brine pumps are usually too big
- X Transformer/rectifier: not recommended different requirements for current & voltage
- Physical and static conditions of the equipment & piping have to be checked carefully
- Cleaning of filters, tanks, pumps etc. has to be done properly with water or with diluted hypo solution
- Check for elementary mercury at low points
- Change precoating agent from perlite/harborlite to cellulose (avoid Al & SiO₂ contamination)
- Install additional ion exchanger column with special Hg resin (to protect Ca+Mg resin)

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Location / placement

- New equipment can be installed:
 - Greenfield, next to old plant
 - In old building \rightarrow re-use cell room after decontamination
- Decontamination (EuroChlor TSEM 05/311, TSEM 11/378, TSEM 11/389):
 - Mercury is everywhere → concrete structure & ground need to be removed or not touched at all
 - Sand should not be brought back in place \rightarrow to be removed & decontaminated
- Space requirements:
 - Membrane electrolysers require higher cell room
 - Space required underneath membrane electrolysers

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2 Mercury to membrane conversion

3	Selected	conversion pro	jects & ex	periences

3.1	Latest references
3.2	Parallel operation
3.3	Re-use of equipment
3.4	Health, safety, environment

4 Conclusions

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OAO Sajanskchimplast

- Location: Sayansk, Russia
- Plant: Chlor-Alkali Electrolysis
- Capacity: 169,000 t/a Caustic Soda 150,000 t/a Chlorine

Electrolyser Technology: Asahi Kasei Corporation, Japan AsahiKASEI

Services:

- Project Management
- Basic and Detail Engineering
- Design specification for civil works, steel structure, HVAC
- Deliveries
- Construction Supervision Assistance
- Supporting of start-up phase
- Training of personnel

Project Completion: 2006



Special conditions:

- First Chlor-Alkali Membrane Electrolysis in Russia
- Consideration of the Russian Regulation on Chlorine
- Financed through ECA-covered loan by Euler-Hermes Credit Insurance

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Potasse et Produits Chimiques SAS

- Location: Thann, France
- Plant: Chlor-Alkali Electrolysis / Bromine Recovery Unit
- **Capacity**: 68,400 t/a Caustic Potash 43,200 t/a Chlorine 4,000 t/a Bromine

Electrolyser Technology:

Chlorine Engineers Corporation, Japan

Contract: EPC

Services:

- Project Management
- Basic Engineering
- Detail Engineering
- Procurement & Supplies
- Construction & Construction Management
- Training of personnel & Start-up

Project Completion: 2016



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Evonik Industries AG & Akzo Nobel Industrial Chemicals GmbH

- Location: Ibbenbueren, Uffeln, Germany
- Plant: Chlor-Alkali Electrolysis
- Capacity: 130,000 t/a Caustic Potash 82,000 t/a Chlorine

Electrolyser Technology: Asahi Kasei Corporation, Japan

Asahi **KASEI**

Services:

- Project Management
- Basic Engineering
- Detail Engineering & Procurement
- Construction Management
- Commissioning support & Training

Project Completion: 2017



Akzo Nobel - Location at Ibbenbueren/Germany

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2 Mercury to membrane conversion

3 Selected conversion projects & experiences

- 3.1 Latest references
- **3.2 Parallel operation**
- 3.3 Re-use of equipment
- 3.4 Health, safety, environment

4 Conclusions

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Parallel operation of Hg & Mb electrolysis

- Advantage: minimise downtime by establishing
 - one combined brine loop for treatment of brine to/from Hg electrolysis as well as membrane electrolysis and
 - proper tie-in points for common product handling
- Disadvantages:
 - requires more time for planning and establishing of tie-in points
 - possibly creates unwanted interferences from one system to the other (e.g. back pressure, interlocks, Hg contamination...)
 - requires additional step(s) for removal of mercury (precipitation and/or ion exchanger)

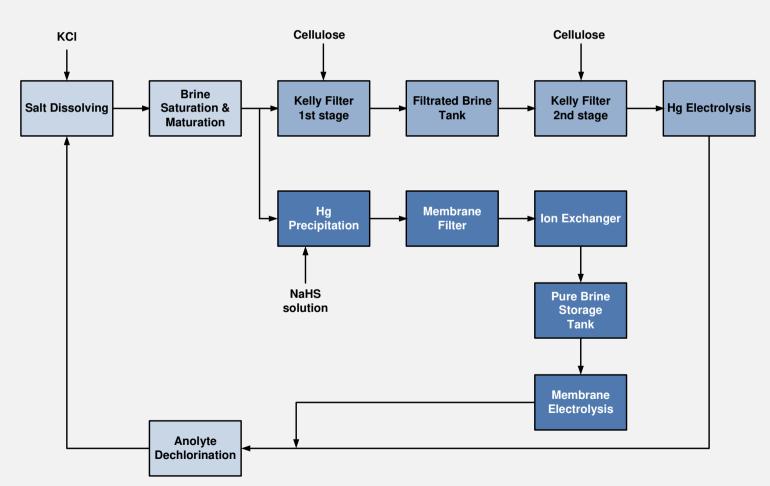
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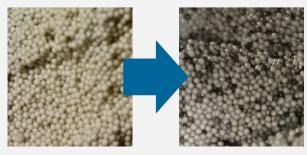
Parallel operation: practical example



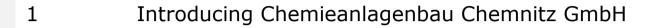
strainer of filtrated brine pump: covered by HgS



ion exchanger resin for Hg (TP214): covered and partially blocked by HgS







2 Mercury to membrane conversion

3	Selec	Selected conversion projects & experiences			
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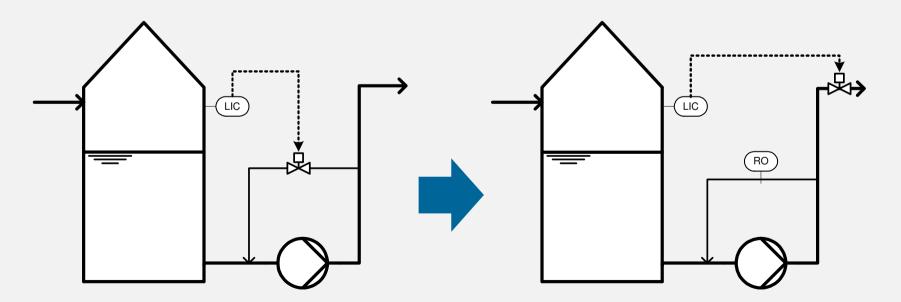
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Re-use of equipment: brine pumps

- brine flow in Hg plant is **2.5-fold** than in Mb plant
- pumps could be equipped with variable frequency drive (VFD) or
- control philosophy has to be adjusted → otherwise such big pumps would operate not at their optimum point or beyond their performance curve



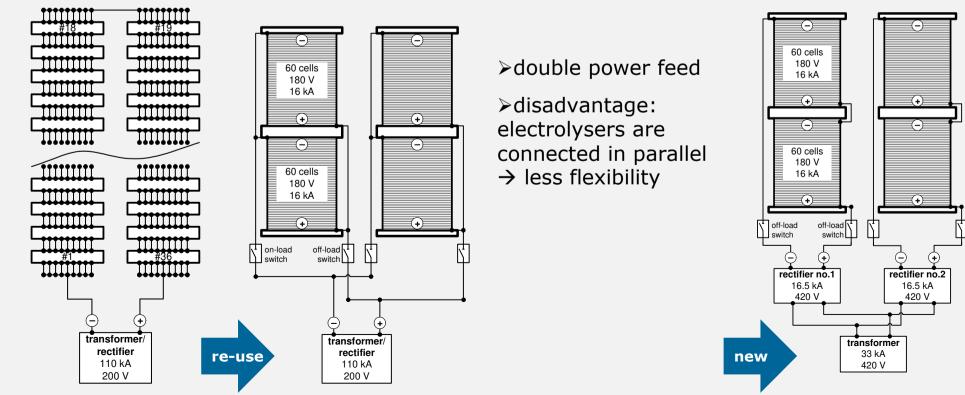
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Re-use of equipment: transformer/rectifier

- Traditionally Hg electrolysis requires relatively high current and low voltage
- Area of membrane cells is smaller and current density is smaller than in Hg cells
 → more cells are connected in series resulting in higher overall voltages
- Example: Hg cell room with 36 cells (10 m²) \rightarrow converted to 4x60 Mb cells



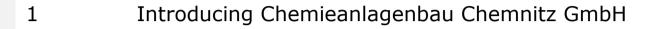
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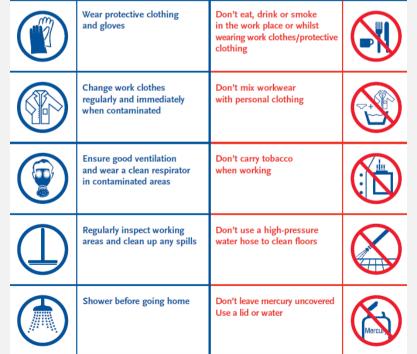


Separation of contaminated area & construction area

- Personal safety → high risks of operating personnel as well as personnel of construction company due to
 - Mercury emissions
 - Chlorine emissions
- Protective equipment, cleaning and hygiene is of high importance
 → EuroChlor TSEM 05/305 →
- Create separation between normal operating area and new construction area



Housekeeping DO'S and DON'TS when working in mercury cell rooms



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Example:

wooden wall for separation of Hg electrolysers (in operation) and construction site







- 2 Mercury to membrane conversion
- 3 Selected conversion projects & experiences

4 Conclusions

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Conclusion / summary

- Conversion from mercury to membrane technology is beneficial in terms of operating costs and from environmental point of view
- Cell room building and some equipment can be re-used (after decontamination) to reduce investment costs
- It should be evaluated carefully how much of the existing equipment is re-used and how the conversion should be done (time schedule)
- Training of operating personnel is also very important because requirements for brine quality are higher

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Thank you for your attention!

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