Reclaiming of MEA with electrodialysis in post-combustion CO_2 capture: from lab results to pilot demonstration

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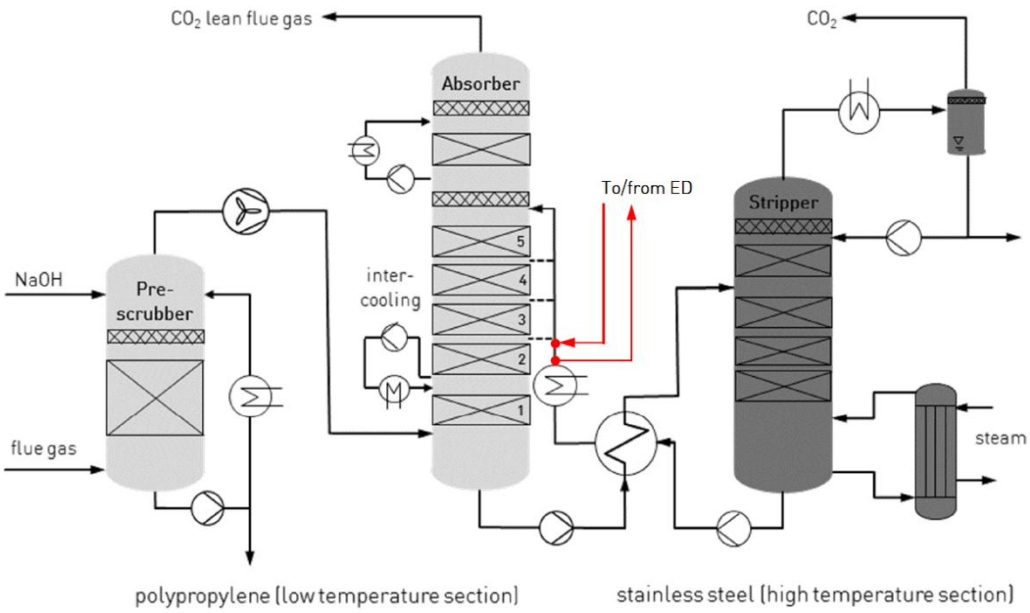
Post-combustion pilot unit in Heilbronn (EnBW)



A flue gas slipstream of about 1 500 Nm³/h is taken from the bituminous-coal fired unit.

The post-combustion pilot plant is designed to capture 7.2 tons of CO_2 per day at average CO_2-concentrations of the power plant and a capture rate of 90% with 30% aqueous MEA solution.

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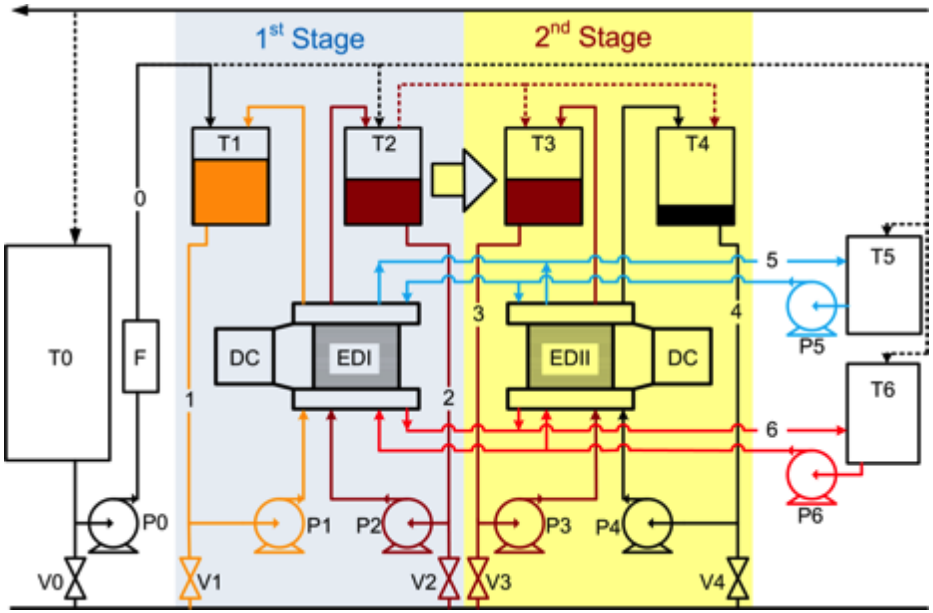
Electrodialysis Unit (EDU) at Heilbronn pilot site



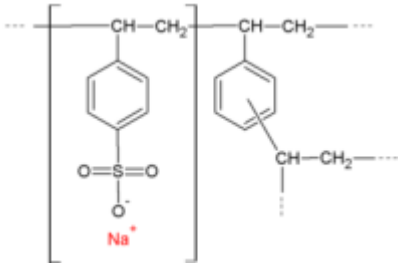
Electrodialyzers (ED) parameters:

- Active membrane area – 1.1 m^2
- 25 Desalting cells
- 24 Concentrate cells
- U=40-80 V; I=2–4.5 A
- Liquid flow – 150 l/h; V_{linear} = 0.5 m/s
- Commercial membranes MA-41 and MK-40
- MEA samples were taken after 200, 400, 535 and 972 hours of operation

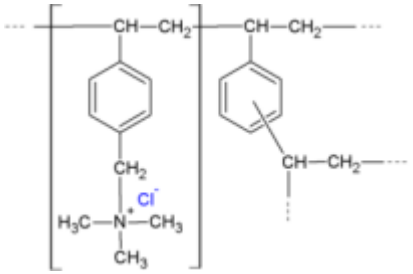
Analytical analysis:

- Anions – Formate, acetate, glykolate, oxalate, nitrite, nitrate, sulphate, chloride
- Cations – Fe, Ni, Cr, Ca, Mg, Na
- MEA concentration
- CO_2-loading
- Nitrosamines

Cation-exchange membrane MK-40



Anion-exchange membrane MA-41



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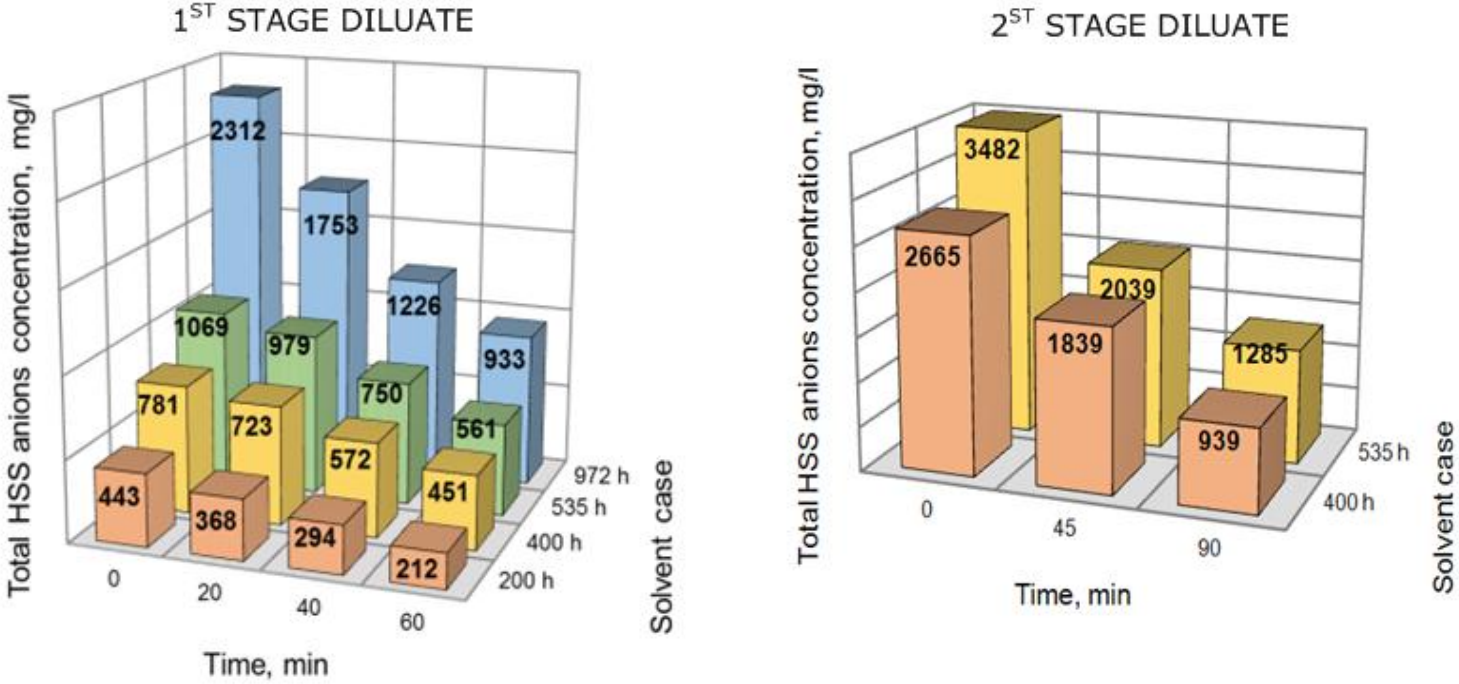
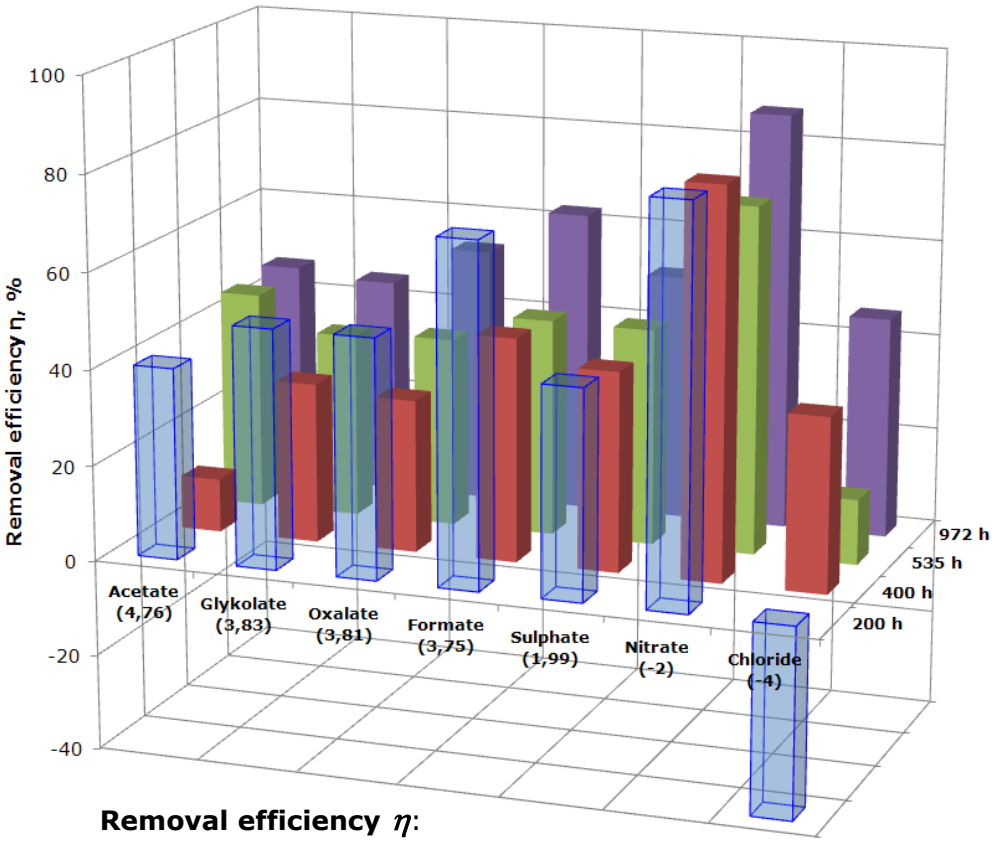
HSS anions removal from lean MEA in time during operation of 1st and 2nd stage of EDU



Change of volume and content of individual HSS anions in the concentrate during the reclaiming of differently degraded MEA samples (after all cycles)

MEA sample	Concentration change, meq/l						
	Formate	Oxalate	Acetate	Glykolate	Sulphate	Nitrate	Chloride
200 h	2.3→4.4	1.1→1.6	0.5→1.2	0.5→0.9	3.3→5.4	0.6→0.7	0.4→4.5
400 h	5.0→16.7	1.5→5.0	1.5→4.1	0.8→2.4	5.0→15.6	1.4→6.1	0.3→3.9
535 h	7.1→25.8	2.6→6.1	1.9→5.9	0.9→2.7	6.5→17.1	2.3→9.7	0.1→2.0
972 h	23.7→85.9	6.6→14.5	3.8→11.9	1.4→5.6	8.1→17.4	3.7→14.0	0.2→2.3

Removal efficiency for the individual HSS anions



Removal efficiency η:

$$\eta = \frac{\Delta C}{C_{t=0}} \times 100\% = \frac{C_{i,t=0} - C_{i,t=60}}{C_{i,t=0}} \times 100\%$$

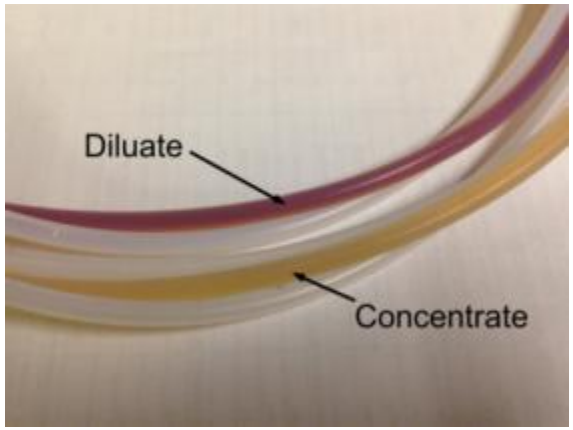
where $C_{t=0}$ is the initial concentration of *i* individual HSS anion before ED treating, meq/l; $C_{t=60}$ – the concentration of *i* individual HSS anion after 60 minutes of ED operation, meq/l (meq/l=milliequivalent/liter).

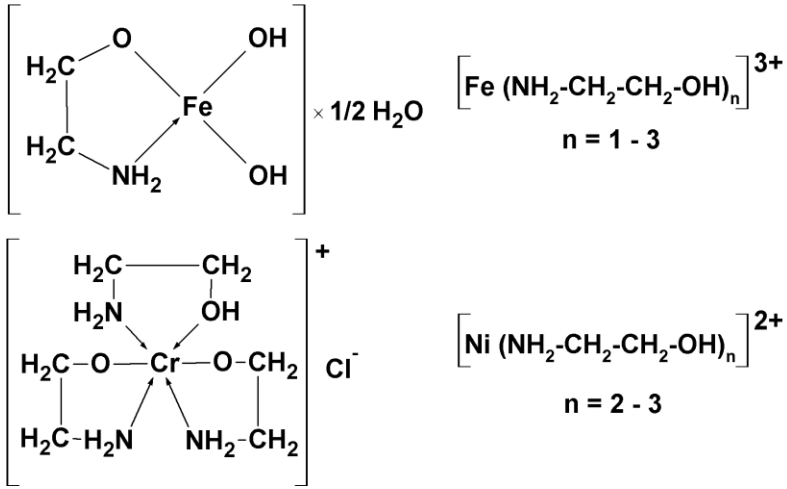
- Highest removal efficiency is achieved for nitrate ions
- Sulfuric acid is strong acid, but double charge hindered its transport
- Transport of bulky counter-ion $[MEAH]^+$ limits the mobility of anions in electrodialysis → generally quite small differences in removal efficiency
- Negative drop in removal efficiency for Cl^- is attributed by chloride ions releasing from the anion-exchange membrane

Solvent case	Sum of analyzed HSS anions, meq/l	
	Before ED reclaiming	After ED reclaiming
200 h	9.0	4.4
400 h	15.6	9.0
535 h	21.4	11.4
972 h	47.5	19.2

ED performance: removal of heavy metals

MEA	Concentration change, mg/l		
	Fe	Cr	Ni
200 h	11.0→12.0	4.2→4.8	2.4→2.7
400 h	19.0→20.0	6.3→6.6	3.3→3.4
972 h	311→334	195→217	124→138





- Heavy metals are presented as non-ionic species as colloidal particles or neutral complexes with MEA

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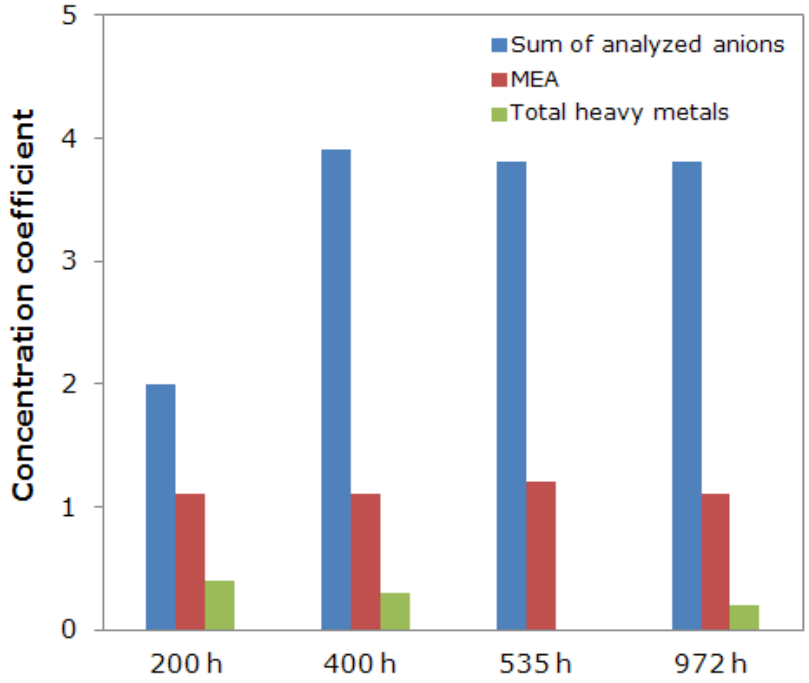
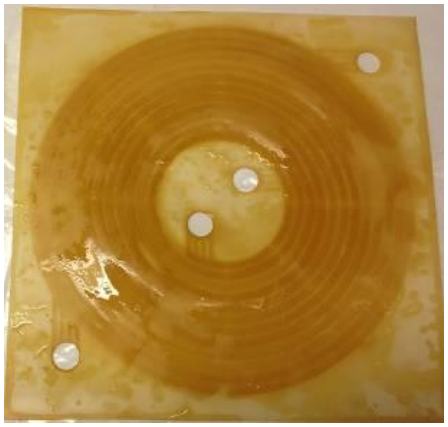
Overall transport of MEA, CO_2 and analyzed HSS anions

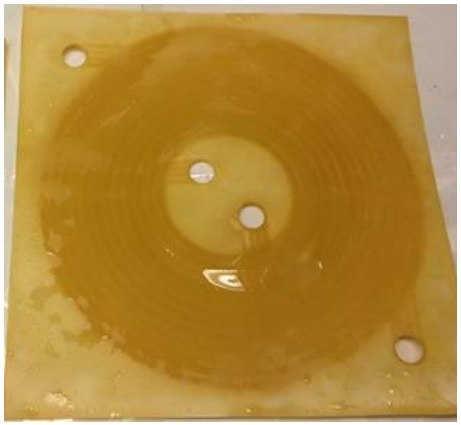
MEA	Initial content of analyzed HSS anions, meq/l	Amount of transported species, mole			MEA loss, mole/mole		
		MEA	CO_2	Sum of analyzed HSS anions	MEA/CO_2	MEA/analyzed HSS anions	MEA/ total HSS anions
200 h	9.0	23.19	7.00	0.09	3.3	258	116
400 h	15.6	25.95	8.37	0.21	3.1	124	70
535 h	21.4	25.58	8.63	0.28	3.0	91	57
972 h	47.5	20.81	5.93	0.71	3.5	29	24



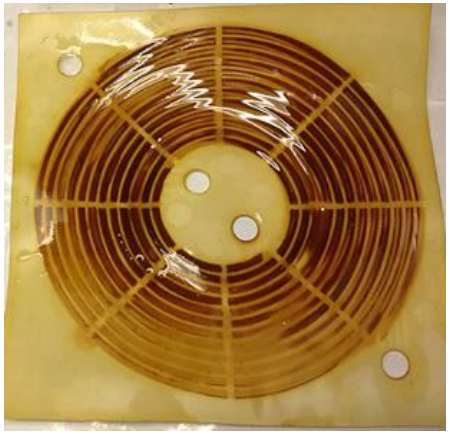
Membrane examination after ED campaign



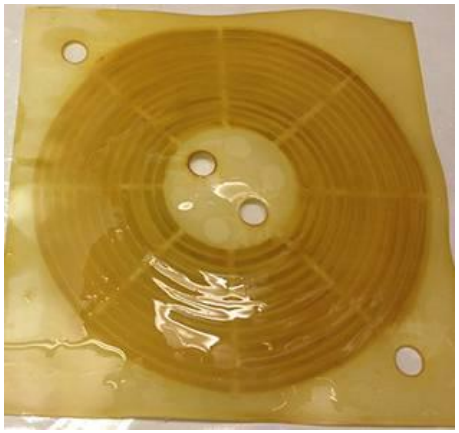
a) membrane MK-40 (diluate side)



b) membrane MK-40 (concentrate side)



c) membrane MA-41 (diluate side)



d) membrane MA-41 (concentrate side)

X-ray fluorescence analysis

Element (wt.%)	Membrane MK-40		Membrane MA-41	
	before	after	before	after
Na	19.7	2.5	0.6	-
Mg	0.5	0.4	0.2	0.4
Al	-	0.1	-	0.8
Si	0.9	1.0	0.2	3.6
S	72.8	91.8	0.6	4.9
Cl	-	0.1	93.4	28.4
K	0.2	0.6	0.2	0.1
Ca	0.3	0.2	0.1	0.2
Ti	1.4	1.0	3.1	4.9
Cr	-	0.2	0.2	1.2
Mn	-	-	-	1.2
Fe	**0.7**	**1.2**	**0.4**	**49.6**
Ni	-	0.1	-	0.4
Zn	0.4	0.8	0.1	2.3
Mo	-	-	-	1.3

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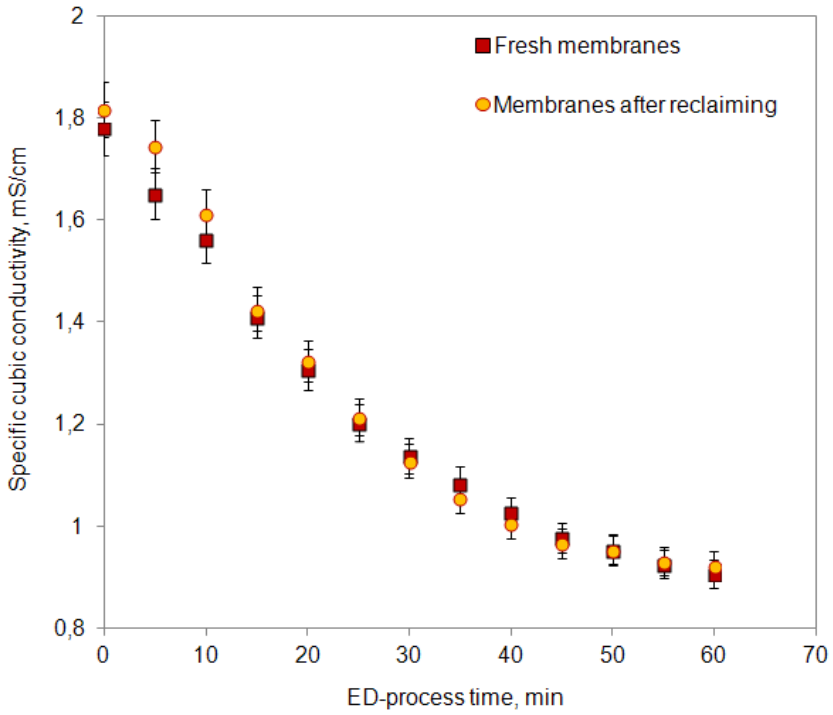
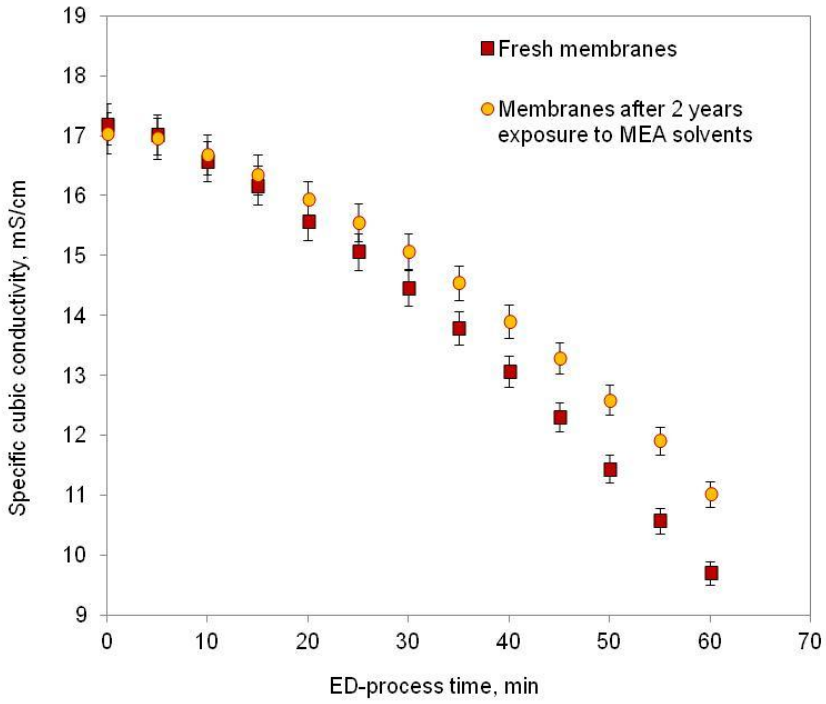
Membrane examination after ED campaign

"Real" degraded solvent



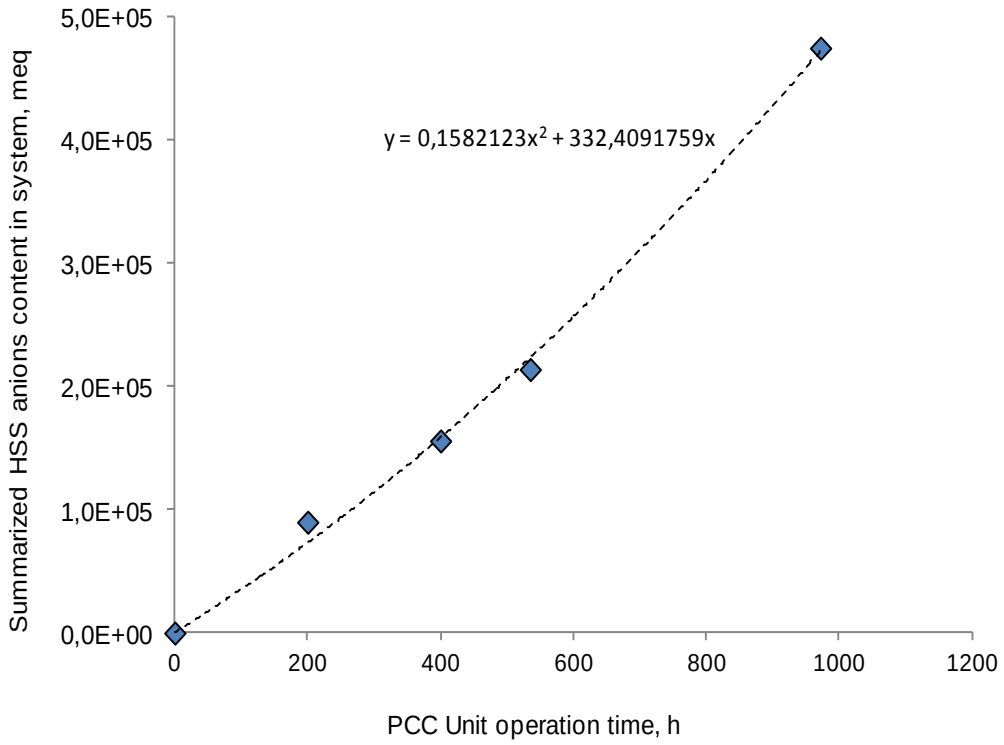
"Synthetic" degraded solvent



Membranes used in	Exposure time, days	
	Fresh MEA	Degraded MEA
Pilot-scale unit	6	12
Lab-scale unit	440	217

Rate of HSS anions build-up during PCC Unit operation

Case study: ED reclaimer for PCC Unit (10 m3 of 30 wt. % of MEA in the system)
The rate of removal of HSS anions by electrodialysis is equal to the build-up rate of the HSS anion content in the system



- Gradual increase of HSS in time during pilot Post-Combustion Capture (PCC) test

Estimated membrane surface area for different HSS anions content

Case study: ED reclaimer for PCC Unit (10 m3 of 30 wt. % of MEA in the system)
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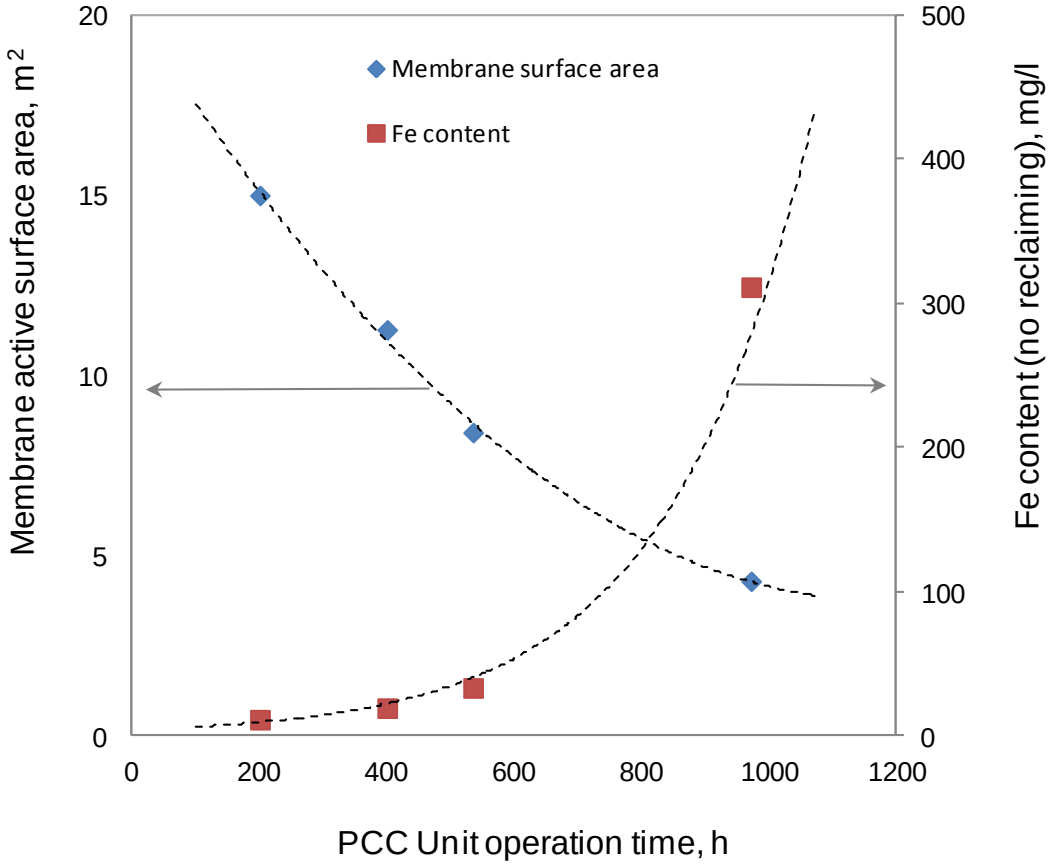

- Trade-off: Membrane surface area required and rate of Fe accumulation in the solvent.

MEA losses and flux of different components of degraded solution through the membranes

Case study: ED reclaimer for PCC Unit (10 m3 of 30 wt. % of MEA in the system)
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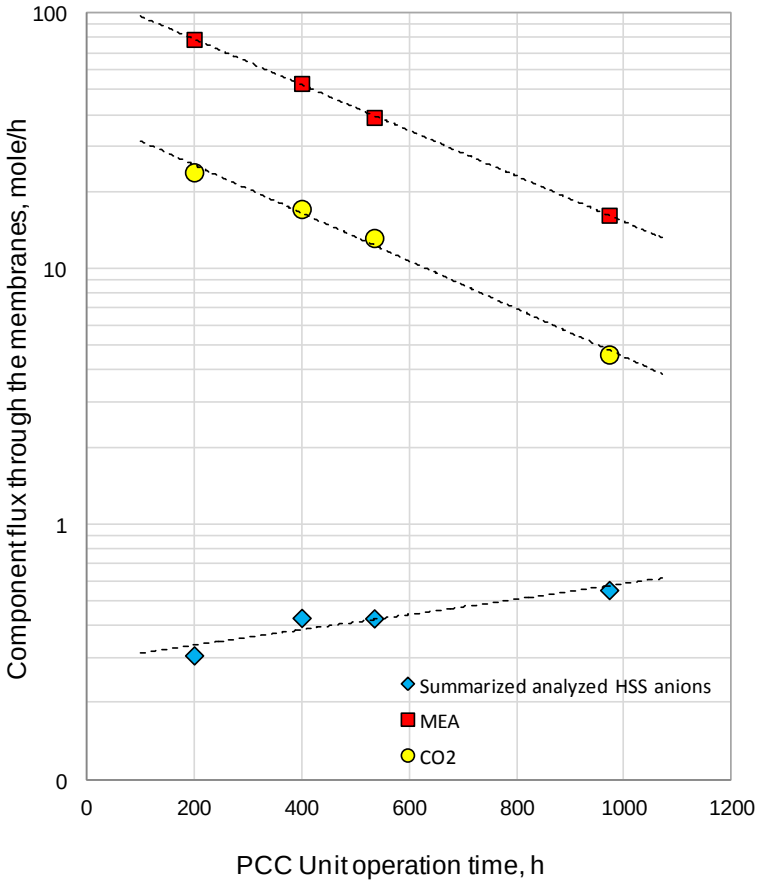

Increase of HSS content results:

- Increase of HSS removal rate
- Decrease of MEA losses

Final remarks

- Successful removal of HSS from real degraded MEA solvent can be achieved by electrodialysis
- No noticeable influence of heavy metals on the ED reclaiming
- Ion-exchange membranes possess stable performance under real conditions
- Further process optimization with the regards of CO_2 loading and mitigation of MEA loss is possible

Publications

- S.Bazhenov, A.Rieder, B.Schallert, V.Vasilevsky, S.Unterberger, E.Grushevenko, V.Volkov, A.Volkov. Reclaiming of degraded MEA solutions by electrodialysis: Results of ED pilot campaign at post-combustion CO2 capture pilot plant. International Journal of Greenhouse Gas Control 42 (2015) 593–601.

- S.Bazhenov, V.Vasilevsky, A.Rieder, S.Unterberger, E.Grushevenko, V.Volkov, B.Schallert, A.Volkov. Heat stable salts (HSS) removal by Electrodialysis: reclaiming of MEA used in post-combustion CO2-capture. Energy Procedia, 63, (2014), 6349 – 6356.

- A. Volkov, V. Vasilevsky, S. Bazhenov, V. Volkov, A. Rieder, S. Unterberger, B. Schallert. Reclaiming of Monoethanolamine (MEA) Used in Post-Combustion CO2-capture with Electrodialysis. Energy Procedia. 51 (2014), 148-153.

Thank you for your attention!

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