Operational experience from a 300 kg/h post-combustion capture test plant using Monoethanolamine

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One of the largest energy companies in Germany and Europe

Business segments:
electricity generation and trading, electricity grid and sales, gas, energy and environmental services

Annual revenue 2012: in excess of € 19 billion

Customers: some 5,5 million

Employees: some 20,000
## Place and characteristics of the Heilbronn test plant

**Heilbronn Combined Heat and Power Plant**
- Electric output (site): 1,020 MW
- District heating: 300 MW
- Electric output Unit 7: ~ 815 MW
- Commissioning of Unit 7: 1985
- Flue gas treatment: DeNOx, ESP, wet FGD, Sewage sludge cofiring (1998)

**Amine scrubbing test plant**
- Flue gas volume flow: ca. 1,500 Nm³/h (f)
  ~ 0.05 % of total flue gas volume flow of Unit 7
- CO₂ capture rate: ~ 90 %
- Captured CO₂ quantity: ~ 300 kg CO₂/h
- Design solvent: 30 wt.% Monoethanolamine (MEA), (20 – 50 w%)
- Space requirement: ~ 10 x 15 x 5 m, height: 40 m (absorber), 25 m
- Commissioning: March 2011
Process design of amine scrubbing test plant

- **Stainless Steel (1.4571/316TI)** (higher temperatures)
- **Polypropylene** (low temperatures)

**FGD**

- **Stack**
- **Pre-Scrubber**
- **Absorber**
- **Stripper**

- **CO₂-lean flue gas**

**Design and construction by**

- **Steam,** 1.2 bar, 135 °C
- **Stainless Steel (1.4571/316TI)** (higher temperatures)
Amine scrubbing test plant

Absorber top
Absorber water wash
Absorber inter-

Stripper top - overhead condenser

Inter-cooling and lean cooling HTX
Test plant operation in 2011

- 24/5 Operation
- Commissioning/Optimisation
- Operational problems
- Low availability of flue gas

Operational hours per calendar week (in h):

- Calendar Week 2011
  - Total operational hours in h
  - Operational hours per calendar week (CW) in h

Max. hours/week:
Solvent concentration of heat stable salts and metals

Rieder, A., Unterberger, S., GHGT-11, 2012
Observations points

Stack

CO\textsubscript{2}-lean flue gas

Absorber

Pre-Scrubber

Inter-Cooling

HX-Plate

Stripper

Stripper packing

Reboiler

Stripper sump

FGD

Polypropylene (low temperatures)

Stainless Steel (1.4571/316TI) (higher temperatures)
Observations after 1,600 h of test plant operation

- Stripper packing above rich inlet
- Stripper packing below rich inlet
- Sludge formation in inter-cooling storage
- Solids formation at stripper pressure retention valve

Lean-rich solvent cross heat exchanger inspection
SEM examination of the packing material grade 316 Ti

Surface without significant corrosion under the film

Packing material thickness: 0.25 mm
Partly covered by deposits

Deposit thickness $x$: approx. 50 µm

Deposit thickness $y$: approx. 25 µm

2 examples of pitting corrosion in the microsection approx. 10 µm at the non-covered surface
Metallurgic examination of cross heat exchanger plates grade 316 L

Surface: Visible grain boundaries on the cleaned material surface

Cross section: Slight corrosion under deposit

Rough surface without visible grain boundaries

Lean-rich cross heat exchanger plate (hot section)

Cross section: Pitting corrosion approx. 10µm

Rich solvent side

Lean solvent side
Deposit and sludge examination

Rich solvent side (hot)
Red to brown area

Analytical methods:
- EDS
  (Energy dispersive spectrometry)
- XRF
  (x-ray fluorescence)

Results of the EDS analysis:

<table>
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<th>Analyse 1 auf Belag 25kV</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
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<td>0.7</td>
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</table>

- With XRF, ferrous and chromium oxides, as well as ferrous carbonates could be confirmed
- The stripper sludge does not contain **nickel and molybdenum compounds**
  => These elements must stay in solution/do not precipitate for the entire temperature/pH conditions of the absorption/desorption cycle
Microstructure of stripper bottom / endoscopy of reboiler grade 316 Ti

Microstructure of stripper wall shows same characteristic surface as lean side of cross heat exchanger

Reboiler endoscopy shows rough surfaces, discoloration and corroded weld seams
Overview results from previous investigations

- Stainless Steel (1.4571/316TI) (higher temperatures)
- Polypropylene (low temperatures)

FGD → Stack → Absorber → CO₂-lean flue gas → Stripper → CO₂

- Pre-Scrubber
- Inter-Cooling
- HX-Plate
- Replica

Polypropylene (low temperatures)
Stainless Steel (1.4571/316TI) (higher temperatures)

No corrosion
Corrosion identified
Hypothesis: Degradation product-based corrosion cycle

Metal-complex induced corrosion generated by MEA degradation products

Dissolution of metals by corrosive attack/formation of complexes

Metal-rich deposits/dissolved metals in solvent

(Partial) Disintegration of metal ion carrier

Metal-complex induced corrosion generated by MEA degradation products

Catalyst (in solution)

from flue gas

Organic acids (i.e. formic, acetic, oxalic acid)

Corrosive agent(s)/metal ion carrier

absorber: cold lean solvent conditions
pH ~ 8.5; t ~ 40 - 100 °C

Destruction of the passive layer/corrosion of the metal surface

stripper: hot lean solvent conditions
pH ~ 10.5; t ~ 120°C

heat stable salts/organic acids/complexing agents

from flue gas

Monoethanolamine (MEA)
Conclusions

Results are plant- and solvent-specific – and still not complete
- First test campaign
- Confirmation required!
- Comparability questionable, due to 'used' material surfaces compared to 'new' conditions?

Corrosion effects clearly identified in the hot lean solvent area
- 'Critical' corrosion rate from a technical point of view?
- To be resolved by a corrosion allowance during equipment design?
- Use of alternative/higher-grade materials necessary? Suitable materials?
- Effect of self-accelerating solvent degradation on corrosion?
- Beneficial effect of reclaiming/solvent management to be investigated

Reaction/corrosion mechanism proposed

Further investigations on materials and components for:
- Further characterisation of corrosion mechanism
- Determination of corrosion rate
- Corrosion testing of selected materials
Thank you for your attention!

Questions?