Application of ODACON® – Amine Technology in the Water and Steam Cycle of Power Plants and Industrial Boilers

Ronny Wagner
Managing Director
REICON
REICON – short introduction

- Over 30 years of expertise in development and application for chemical water treatment in:
  - Power plants
  - District heating networks
  - Cooling circuits

- Economical and ecological proceedings for cleaning, preservation and operation of water- and steam cycles

- Innovative technologies and product solutions, self developed and produced product ODACON®

- Individual support service with skilled service engineers and own laboratory
Agenda

- Main benefits of ODACON application
- Characteristics and effectiveness of ODACON®
- Experiences in power plants
- Application of ODACON
  - Standstill preservation
  - Continuous treatment program
  - Turbine cleaning
- Summary
Benefits by the use of ODACON

- Protection of the whole water- and steam system
- Protection in a full, partially empty and empty state
- No additional activities necessary during downtime
- Preservation can be done during operation or shut-down procedure
- No depreservation is needed before recommissioning
- Reduced corrosion product transport during recommissioning
- Reduction of commissioning time
- less personnel expenditure
### Benefits by the use of ODACON

<table>
<thead>
<tr>
<th>Preservation</th>
<th>In Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protection of the whole water- and steam system</td>
<td>Protection against erosion, FAC and stress corrosion cracking</td>
</tr>
<tr>
<td>Protection in a full, partially empty and empty state</td>
<td>Removal of existing deposits from surfaces in boiler and from turbine</td>
</tr>
<tr>
<td>No additional activities necessary during downtime</td>
<td>Reduction of iron transport in water steam cycle</td>
</tr>
<tr>
<td>Preservation can be done during operation or shut-down procedure</td>
<td>increase of the heat transfer at the condenser surfaces by changing from film condensation to dropwise condensation</td>
</tr>
<tr>
<td>No depreservation is needed before recommissioning</td>
<td>Substitution of oxygen scavengers e.g. Hydrazin</td>
</tr>
<tr>
<td>Reduced corrosion product transport during recommissioning</td>
<td>No extra preservation activities needed before shut-down</td>
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<td>Reduction of commissioning time</td>
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Characteristics of ODA and ODACON

- **substance Octadecylamine (ODA):**
  - Long-chain, aliphatic amine with chemical structure $\text{C}_{18}\text{H}_{37}\text{NH}_2$
  - Primary amine content $> 99\%$
  - Waxy, solid substance, non-soluble in water
  - The substance in its pure form is not useful for industrial application.

- **ODACON Emulsion**
  - Stable, pure, watery emulsion
  - No admixtures of emulsifiers, polyacrylates or poly-amines
  - Does not form organic acids by thermal decomposition
  - No hazardous substance, biodegradable
  - Certified for the application in nuclear power plants
General characteristics of ODACON®

- ODACON® is a pure and stable watery emulsion of Octadecylamine (ODA)
- the emulsion contains no admixture of phosphate, Hydrazine, other (poly-) amines or emulsifiers
- REICON guarantees the chemical purity of the emulsion as follows:

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<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Chloride</td>
<td>&lt; 2 ppm</td>
<td>Silikate</td>
</tr>
<tr>
<td>Fluoride</td>
<td>&lt; 2 ppm</td>
<td>Acetate</td>
</tr>
<tr>
<td>Sulfate</td>
<td>&lt; 2 ppm</td>
<td>Natrium</td>
</tr>
</tbody>
</table>

- ODACON® is a biodegradable, non-toxic product

<table>
<thead>
<tr>
<th>biodegradability</th>
<th>81 % in 28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.06 ppm*</td>
</tr>
<tr>
<td>BSB₅</td>
<td>0.98 ppm*</td>
</tr>
<tr>
<td>CSB</td>
<td>1.85 ppm*</td>
</tr>
<tr>
<td>TOC</td>
<td>0.39 ppm*</td>
</tr>
</tbody>
</table>

*Valid for an ODA concentration of 1 ppm (Dr. Roth bioTEST 1995)
Thermal stability of ODACON®

- No thermal decomposition up to 450°C
- Decomposition equilibrium at 520°C
- Decomposition products contain no harmful organic substances such as low molecular organic acids
- Results are gained in an autoclave test under static conditions

Adsorption of ODACON®

- formation of mono or bimolecular protection layers by
  - 1. Physosorption between metal surface and polar part
  - 2. Chemisorption and ion bonding
→ strong and durable connection of ODA molecules at the surface leads to a long term preservation effect
Mobilizing effect of ODACON®

- ODACON® has a mobilizing effect on oxides and corrosion active deposits
- these deposits are gradually and carefully removed
- chloride or similar harmful substances are displaced during adsorption

- Protection against stress crack corrosion even in crevices

With ODA

Without ODA

autoradiograph of clamped samples
(density level = rate of chloride accumulation)
Mobilizing effect of ODACON® - Example

- Cleaning effect on heat transfer surfaces of the steam generator from corrosion products (from 200 g/m² to 120 g/m²) and salts e.g. Chloride

Cl⁻ [µg/l]

comparison of blow down water at unit 2 of NPP Kola (VVER design)
Decrease of surface tension

- ODACON® is lowering the surface tension of water whereby the droplet diameter is scaling down strongly.

T dependence of the surface tension of pure water (1) and saturated ODA solution (2)

Distribution of the droplet size, curve (1) without ODA and curve (2) with ODA.
Impact on droplet characteristic

- Improvement of wettability
- Faster diffusion of droplets
- Reduction of the maximum force on the surface during impact
- Films at the rear edge of turbine blades will be sprayed into small droplets

Without ODACON

With ODACON

slow motion of drop impact on a solid surface
Influence to abrasion through erosion

- Forming stable protective layers in steam and condensate system
- Decrease of material removal through erosion
- Protection against stress crack corrosion and corrosion fatigue

**Graphs:**

1. Abrasion through erosion at different sorts of steel as a function of time.
   - pH = 8.5
   - t = 170 °C
   - w = 50 m/s
   - C-Stahl
   - 13 Cr Mo 4.4
   - ohne ODA
   - mit ODA

2. Abrasion through erosion in wet steam as a function of temperature.
   - γ = 30 h
   - w = 150 m/s
   - pH = 8.5
   - 25%
During condensation the droplets are diffused faster, which causes significantly weaker damages on surfaces.

Removal rate caused by droplet impact erosion on C-steel as a function of the flow velocity.

Stereo microscopic measurement (magnification 1:12) of material probes.
Effect to condensate polishing resins

- The capacities reached by the SAC of the FFA-test do not differ significantly from the blind test´s results.

- The resin from FFA-test shows fouling symptoms which decrease after regeneration to a level comparable to the blind test resin.

- ODACON is removed down to a presumably tolerable residual level during usual technical regeneration.

- after seven cycles of loading with ODACON containing feedwater, there are no vital negative effects on the model plant detectable

- During 4 years of operation at NPP Greifswald no negative effect to the resins because of ODA treatment were detectable

Extract of a study from MIONTEC GmbH Leverkusen, 2010
Effect on online measurement system

- “... On pH, ion selective sodium measurement as well as on a Clark-type oxygen probe, no negative influence could be observed. ...”

<table>
<thead>
<tr>
<th></th>
<th>FFA no. 1</th>
<th>FFA no. 2</th>
<th>FFA no. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating on SC probe</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>pH drift</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Retention capacity</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
</tr>
</tbody>
</table>

Table 3:
Summary of results on specific conductivity, pH drift, and resin retention.

<table>
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<th>FFA no. 2</th>
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<tbody>
<tr>
<td>pH stability</td>
<td>No influence</td>
<td>No influence</td>
<td>No influence</td>
</tr>
<tr>
<td>Sodium step response</td>
<td>No influence</td>
<td>No influence</td>
<td>No influence</td>
</tr>
<tr>
<td>Sodium calibration</td>
<td>No influence</td>
<td>—</td>
<td>—</td>
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Table 4:
Summary of results on pH stability, sodium step response, and sodium calibration.

Extract from PPChem 14(9), 2012 “Impact of Film Forming Amines on reliability of online analytical instruments”
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Example 1: STEAG Power Plant Weiher

- **Plant characteristics**
  - Hard coal fired Benson boiler
  - Steam capacity max: 2130 t/h
    - min: 500 t/h
  - Max pressure: 178 bar
  - Steam temperature: 525 °C
  - Electrical output: 700 MW

- since Mai 2017 in reserve operation mode

- Used only for Re-dispatch for grid stabilization
Example 2: STEAG Power Plant Bexbach

- **Plant characteristics**
  - Hard coal fired Benson boiler
  - Steam capacity max: 2200 t/h, min: 400 t/h
  - Max pressure: 195 bar
  - Steam temperature: 535 °C
  - Electrical output: 780 MW

- since Mai 2017 in reserve operation mode

- Used only for Re-dispatch for grid stabilization
During revision a sample pipe was cut and compared to an older one without ODACON preservation.

The surface with ODACON protection layer looks smoother and cleaner.

No corrosion is detectable.
Example 3: CCPP Statkraft Hürth (Germany)

- CCPP Unit 1 of STATKRAFT Markets GmbH at Chemiepark Knapsack

- Total power output: 800 MW
  - 2 x gas turbines each 267 MW
  - 1 x steam turbine 270 MW

- 2 x heat recovery steam generator
  - Design parameters: 114 bar, 555°C
  - Total steam capacity: 700 t/h

- No condensate polishing plant

- Unscheduled cycling operation mode
  - Frequent shutdowns with unknown standstill time
  - Daily starts and stops when operating
Cycle treatment with ODACON® improves the corrosion protection during shutdown and has a positive effect on re-commissioning at Knapsack 1:
- The total commissioning time is reduced from about 8 hours to 4 hours.
- The time for reaching the standard conductivity levels in steam during commissioning is decreased from 5 - 6 hours to 2 - 3 hours.

No impact of ODACON® injection was detected to the reliability of on-line measurement equipment.

During preservation no pH-decreasing decomposition products were detected.

Because of the successful application and the good results at Knapsack 1, STATKRAFT decides to use ODACON® also for preservation at Unit 2.
Example 3: CCPP Statkraft Hürth (Germany)

- **Situation without ODACON**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formel</th>
<th>unit</th>
<th>LP steam</th>
<th>IP steam</th>
<th>HP steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Iron</td>
<td>Fe</td>
<td>µg/l</td>
<td>&lt; 20</td>
<td>&lt; 80</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>Iron\textsubscript{AAS}</td>
<td>Fe\textsuperscript{2+} / Fe\textsuperscript{3+}</td>
<td>µg/l</td>
<td>3</td>
<td>29</td>
<td>3</td>
</tr>
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- **Situation with ODACON**

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<td>Iron\textsubscript{AAS}</td>
<td>Fe\textsuperscript{2+} / Fe\textsuperscript{3+}</td>
<td>µg/l</td>
<td>6</td>
<td>8</td>
<td>5</td>
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- Even with longer standstill periods and with no additional measures the iron values during start up are decreased in IP parts → reduction about ca. 70%
Example 3: CCPP Statkraft Hürth (Germany)

Condenser

Last stage turbine blades
more references
(abstract – thermal power plants)

- EDF Centrale Thermique de Porcheville (France)
  - Fuel oil fired, forced circulation boiler, 600 MW, 190 bar, 542 °C, 1800 t/h

- MIBRAG Power Plant „Buschhaus“ (Germany)
  - Lignite fired, Benson boiler, 390 MW, 192 bar, 535 °C, 1000 t/h

- CHP Varna (Bulgary)
  - Coal fired power plant TP 100A, 210 MW, 150 bar, 545 °C, 640 t/h

- power plant Shangan (China)
  - gravity circulation boiler 350 MW, 167 bar, 538° C, 1000 t/h

- CHP Beijing 2 (China)
  - gravity circulation boiler 50 MW, 100 bar, 540 °C, 220 t/h

- envia power plant Bitterfeld Wolfen (Germany)
  - HRSG 75 MW, 90 bar, 490°C, 90 t/h

- Syrdarya Power Plant (Uzbekistan)
  - natural gas fired power plant, 10x 300 MW, 255 bar, 540 °C, 1000 t/h
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Standstill preservation

- **Benefits:**
  - Protection of the whole water steam cycle against idle corrosion
  - Preservation can be done during shut-down procedure, no extra time or additional activities are necessary.
  - Protective layer remains stable irrespective if the systems is drained or stays filled.
  - No depreservation is needed before start up
  - Time to reach standard operating values after standstill is reduced
  - Iron transport in the water steam cycle after re-commissioning is reduced
Standstill preservation

- preservation technology:

  - ODACON® injection in condensate or feed water lines
  - Condensate polishing plant should be bypassed
  - ODACON® demand for a boiler with an average capacity of 1,000 t/h: 2,000 kg
  - ODACON® consumption for follow up preservation about 50% lower
  - Water chemical operating values will be affected during injection

- ODACON® injection 3 – 5 days before shutdown
  ODACON dosage rate: 40 – 60 ml/t

- Standstill Months or Years

- max. ODACON concentration: 2.0 ppm

- Load

- 100 %
Continuous treatment program

Benefits:

- Minimization of corrosion in the whole water steam cycle
- Protection against flow accelerated corrosion as well as stress corrosion cracking
- Removal of existing deposits and inhibition of re-depositing
- Iron transport in the water steam cycle is reduced during operation
- Condensate polishing plant can be switched off after implementation
- Improvement of heat transfer by intensified droplet condensation
- Substitution of oxygen scavengers like Hydrazine
- No extra preservation procedures necessary, faster start-up times
Continuous treatment program

- Dosing technology:

  - ODACON® injection in main condensate after condensate polishing plant or at the suction side of feed water system
  - Condensate polishing plant can be operated only during implementation
  - ODACON® demand for a boiler with an average capacity of 1,000 t/h and 8,000 operating hours per year: 5,000 – 8,000 kg
  - Water chemical operating values will be affected during implementation phase but will return to normal operating values within 2 weeks

Diagram:
- ODACON dosage rate: 1 – 10 ml/t
- Ø ODACON concentration: 50 – 500 ppb
Using ODACON® the turbine is cleaned without the addition of aggressive acids. The linings are gently washed away from the surface and the base material is not damaged.

Procedures:

Cleaning with saturated steam:
After shut down the turbine is exposed with ODACON® treated saturated steam. During application the turbine must be operated with turning gear. Because water steam cycle is not in operation, higher ODACON® concentrations are acceptable which reduces the application time.

Cleaning during operation
ODACON® is injected in the feed water or directly in the steam line in front of the turbine.

The treatment will need some weeks or month due to the kind of deposits because the ODACON® concentration is limited by the cycle chemistry.
Example 1: combined cycle power plant Wiesengrund in Eisenach:

- Heat recovery steam generator
  - Type: Standart Fasel
  - thermal capacity: 50 t/h

- Tap condensing turbine
  - Type: ABB G 25
  - Capacity: 10 MW

- Back pressure turbine
  - Type: KKK CFR 5
  - Capacity: 3,3 MW
Turbine cleaning with ODACON

Example 2 Cleaning with saturated steam:

- Injection of ODA emulsion during wet stream operation directly in front of the turbine
- ODA concentration > 2 ppm, maximum concentration depends on the temperature in the condenser
- Steam parameter and turbine speed is the same as during normal wet steam cleaning

Example: 200 MW turbine before and after cleaning
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Summary

- ODACON® offers a variety of advantages and benefits opposed to other technologies for preservation or continuous treatment of the water steam cycle in power plants with reference to costs, usability, efficiency and environmental sustainability.

- ODACON® preservation has a long term effect, whether the boiler is drained or remains (partly) filled.

- The commissioning process after standstill is improved regarding the time to reach the parameters for turbine operation and the consumption of water and fuel.

- REICON offers substantial know-how regarding ODACON®, the effectiveness, the procedures and application.
Contact details

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