Modern Waste Water Treatment in Coke Making Plants

- A new way for Water Recycling!

Kerstin Stenzel
Dipl.-Ing.
ThyssenKrupp Industrial Solutions AG
Motivation for Process Development in Waste Water Treatment

- Environmental aspects
  - Rising requirements for environmental protection
  - Reducing liquid wastes like Cyanide, Thiocyanate, COD, PAH, BTEX etc…
  - Water shortage also in industrial countries

- Economical aspects
  - Investment costs
  - Utility costs

- Customer
  - Individual demands

COD = chemical oxygen demand
PAH = polycyclic aromatic hydrocarbons
BTEX = benzene, toluene, xylene, ethylbenzene
Standard Treatment of Coke Oven Gas

- Batteries
  - Down Comer
    - COG
      - Flushing Liquor
      - Tar/Water Separation
        - Tar Sludge
      - Gas Liquor/Coal Water
        - Coalwater Filter
          - Gas Liquor/Coal Water
  - Tar Water Separation
    - Crude Tar
      - ETP
      - Gas Exhauster
      - H₂S/NH₃ Scrubber
        - Benzene Scrubber
          - clean COG
          - crude BTX
          - Wastewater
            - WWTP
              - Wastewater
              - H₂S/NH₃ Vapours
                - Sulfur
      - Steam
      - Benzene Desorp.
      - H₂S/NH₃ Desorp.
        - Claus Plant
          - Sulfur
          - Tail Gas
Coke Waste Water Treatment in the past and today

- Concrete basins require much more floor space

<table>
<thead>
<tr>
<th></th>
<th>Flow Rate m³/h</th>
<th>Basin</th>
<th>JLR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>m²</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11,000</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>Area/Flow</td>
<td>m²/m³/h</td>
<td>122.22</td>
<td>66.67</td>
</tr>
</tbody>
</table>
Jet Loop Reactor
Membrane Filtration
Function of a Jet Loop Reactor (JLR)

- **Reaction zone**
  - nutrients delivered by the optimized mass transfer are degraded by the bacteria

- **Mass transfer zone**
  - two component jet nozzle produces dispersed air bubbles \(\rightarrow\) great surface for mass transfer
  - a lot of turbulence \(\rightarrow\) increases the mass transfer

*Optimized mass transfer \(\rightarrow\) lower retention time*
Coke Waste Water Treatment today

JLR & Ultra- (UF) & Membrane Filtration

**Detoxification:**
- HCN (Cyanide) and SCN (Thiocyanide) → NH₃

**Dephenolation:**
- C₆H₅OH (Hydrocarbon) → CO₂ + H₂O

**Nitrification:**
- NH₃ → NH₂OH → NOH → NO₂ → NO₃⁻

**Denitrification:**
- NO₃⁻ → NO₂⁻ → NO → N₂O → N₂ ↑
## Advantages and Disadvantages of JLR and membrane technology

### Advantages
- Less floor space required
- Lower retention time
  ⇒ Smaller treatment reactors
  ⇒ Lower recycle streams
- The waste water can be reused

### Disadvantages
- C-Source for Denitrification required
Experiences during Commissioning and Assistance of a German Waste Water Treatment Plant

- Consequences of a too old sludge age
  - Reduced ultrafiltration flow rate → feed waste water amount must be reduced
  - A great portion of dead biomass is existent. Biomass generates extracellular polymere substance which causes a reversible membrane fouling
  - Sludge shows no settlement

→ Continually centrifuging and intensive membrane cleaning could remove the fouling
Experiences during Commissioning and Assistance of a German Waste Water Treatment Plant

- Consequences of a too low dry solid matter
  - A too low dry solid matter is also not desirably → degradation rate will be reduced, limiting values might be failed
    → To prevent fouling and to reach the limiting values continually centrifuging and a high dry solid matter is necessary

- During the time it showed that although a high dry solid matter was existent a high ultrafiltration flow rate could be reached
  → Important continually centrifuging
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problems with the centrifuge
Experiences during Commissioning and Assistance of a german Waste Water Treatment Plant

Automation Optimization

- Wet-chemical online analyzers have high maintenance requirements and need a huge amount of chemicals
  - Ammonia and Nitrate sensors (ANISE and Nitratrax) were successfully tested, need less maintenance and no chemicals
  - Two different Oxygen sensors (LDO and Oxymax) have been tested → Both sensors are suitable
## Experiences during Commissioning and Assistance of a German Waste Water Treatment Plant

### Reachable degradation rates

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Max. Degradation rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Cyanide</td>
<td>98%</td>
</tr>
<tr>
<td>Thiocyanate (SCN)</td>
<td>98%</td>
</tr>
<tr>
<td>COD (chemical oxygen demand)</td>
<td>95%</td>
</tr>
<tr>
<td>Phenol</td>
<td>&gt; 99%</td>
</tr>
<tr>
<td>Ammonia (NH4-N)</td>
<td>&gt; 98%</td>
</tr>
<tr>
<td>Nitrogen composed of NH4-N, NO3-N, NO2-N</td>
<td>&gt; 95%</td>
</tr>
<tr>
<td>Sulfide</td>
<td>&gt; 99%</td>
</tr>
</tbody>
</table>
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- **Reachable outlet values**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reachable Outlet values [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH-Value</td>
<td>6-9</td>
</tr>
<tr>
<td>Suspension</td>
<td>Very small amounts because of the UF</td>
</tr>
<tr>
<td>COD</td>
<td>≤ 80</td>
</tr>
<tr>
<td>Ammonium-Nitrogen</td>
<td>≤ 2</td>
</tr>
<tr>
<td>Nitrogen composed of NH4-N, NO3-N, NO2-N</td>
<td>≤ 7</td>
</tr>
<tr>
<td>Total Phosphor</td>
<td>1 (depends on phosphoric acid dosage)</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>Very small amounts because of the UF</td>
</tr>
<tr>
<td>Volatile Phenole</td>
<td>≤ 0.03</td>
</tr>
<tr>
<td>Sulfide</td>
<td>≤ 0.04</td>
</tr>
<tr>
<td>Benzol</td>
<td>« 0.05</td>
</tr>
<tr>
<td>Free Cyanid</td>
<td>≤ 0.03</td>
</tr>
<tr>
<td>PAHs</td>
<td>« 0.05</td>
</tr>
<tr>
<td>Benzo(a) Pyren</td>
<td>« 0.25 µg/L</td>
</tr>
</tbody>
</table>
Experiences during Commissioning and Assistance of a German Waste Water Treatment Plant

- **Conclusion**
  - Continually centrifuging and intensive membrane cleaning could remove fouling.
  - To prevent fouling and to reach the limiting values continually centrifuging and a high dry solid matter is necessary.
  - Ammonia and Nitrate sensors (ANISE and Nitratrax) produce reliable results, don’t need chemicals and require less maintenance than wet-chemical online analyzers.
  - With the Jet Loop Reactor and Membrane Waste Water Treatment high degradation rates and low outlet values can be reached and the cleaned water can be reused.
Kerstin Stenzel
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ThyssenKrupp Industrial Solutions AG