INTRODUCTION

The protection of the environment is growing more and more in the focus of public interest worldwide. Therefore the requirements for reducing the impact of pollution is rising in all industrial areas, including the coke plant business. To identify and tackle the challenges of tomorrow for our clients, ThyssenKrupp Industrial Solutions (TKIS) - Process Technologies (formerly known as Uhde) continuously conducts research for environmentally friendlier processes and technologies.

Modern waste water treatment facilities of coke making plants use the Jet Loop Reactor and membrane filtration technology. With this process waste water can be recycled for either reuse at the same site or reuse in other applications. Besides the benefit of reducing liquid emissions and thus minimizing the environmental impact an additional economic improvement can be achieved: Compared to a conventional waste water treatment plant equipped with basins, the Jet Loop Reactor requires much less space.

The paper presents a brief abstract about the main topics of this technology as well as the latest beneficial results of the validating performance and operational data from a full scale plant.

DISCUSSION

Waste Water Treatment in Coke Making Plants

The following block diagram (Figure 1) gives an overview of the standard coke oven gas treatment including the waste water treatment. It shows that the water which should be cleaned in the waste water treatment consists of purge water from the desorption. This purge water contains parts of filtered coal water, wash water from the H₂S/NH₃-scrubber and steam condensate.
Coke Waste Water Treatment in the past and today
Figures 2 and 3 are show a conventional concrete basin waste water treatment plant and a pilot plant which consists of a Jet Loop Reactor and a membrane filtration. The pilot plant has been used by TKIS at a German coke plant to test the technology before building a full scale industrial sized waste water treatment plant.
The first step of our waste water treatment development was to reduce the necessary floor space. Concrete basins require much more floor space than the waste water treatment with Jet Loop Reactor and membrane filtration because the Jet Loop Reactors can be built much higher than concrete basins. For example, the basin waste water treatment at a Korean coking plant requires an area to flow rate ratio of 122 m²/ (m³/h). By comparison, an industrial size Jet Loop Reactor waste water treatment plant which has been built at a German coking plant only requires an area to flow rate ratio of 67 m²/ (m³/h).

**The function of a Jet Loop Reactor (JLR)**

The Jet Loop Reactor consists of two zones: the mass transfer zone and the reaction zone.

The waste water enters the mass transfer zone together with air from a compressor through a two component jet nozzle. This jet nozzle produces dispersed air bubbles in the water. The bubbles have a very large surface which is used for mass transfer. There are also extra obstacles installed in the mass transfer zone to create turbulence and increase the mass transfer. The nutrients, the impurities which should be degraded, and the oxygen are transported to the bacteria. The jet nozzle and the obstacles create the first loop as shown in Figure 4 below.

From the mass transfer zone the water-air mixture is flowing up to the reaction zone. There the nutrients, the impurities and the air which has been transported to the bacteria in the mass transfer zone are degraded by the bacteria. On top of the reaction zone there is a degasing zone where the surplus air escapes from the water and leaves the reactor to the open atmosphere. Because of the escaping air bubbles, a density difference is created, causing the denser part of the water to flow down the inside of the reactor. This creates the second loop of the Jet Loop Reactor. The remaining portion of the water can exit the reactor and proceed to ultrafiltration or the outer reactor circulation.
Because of the optimized mass transfer, a lower retention time is needed in a Jet Loop Reactor than in a conventional waste water treatment basin. A lower retention time has the advantage that the equipment can be designed smaller and lower recycle streams are needed. This results in lower investment and operating costs.

**Coke Waste Water Treatment today**

Figure 5 below shows a new coke waste water treatment process. This process includes Jet Loop Reactors and membrane treatments.

**Disinhibition:** HCN (Cyanide) and SCN (Rhodanide) → NH₃

**Dephenolization:** C₆H₅CH₂OH (Hydrocarbon) → CO₂ + H₂O

**Nitrification:** NH₄ → NH₂OH → NOH → NO₂⁻ → NO₃⁻

**Denitrification:** NO₃⁻ → NO₂⁻ → NO → N₂O → N₂
The stripped water from the H₂S/NH₃-distillation is sent together with air to the first stage of the new waste water treatment. The first stage consists of a Jet Loop Reactor for disinhibition and dephenolation and an ultrafiltration step. During disinhibition cyanides and rhodanides are degraded to ammonia. The hydrocarbon phenol is degraded to carbon dioxide and water. The ultrafiltration removes the bacteria from the water and sends them back to the Jet Loop Reactor so that they can specialize on the inhibitors.

Nitrogen removal takes place in the second stage. It consists of a Jet Loop Reactor for nitrification, a basin for denitrification and final aeration and an ultrafiltration step. The denitrification and the final aeration are taking place in a conventional concrete basin. During nitrification the ammonia is degraded to nitrate and during denitrification the ammonia is degraded to nitrogen which escapes into the atmosphere. In the final aeration the bacteria degrades surplus COD (chemical oxygen demand). The ultrafiltration holds back the bacteria and returns it to the nitrification in the Jet Loop Reactor. The bacteria in the second stage are thereby specialized on degrading ammonia and nitrate.

Surplus sludge can be removed from both ultrafiltration units and sent to a centrifuge.

Downstream from the second ultrafiltration, the filtered waste water is cleaned, fulfilling the actual German regulatory limiting values and can be safely discharged. A waste water treatment plant which consists of these two described stages has been built and commissioned by TKIS at a German coke plant.

To reach even stricter limiting values or to completely reuse the cleaned water on site, a third stage may be necessary. Depending on the requested limiting values, the third stage can consist of different membrane treatment combinations.

**CONCLUSIONS**

**Advantages and disadvantages of the Jet Loop Reactor and membrane technology**

Figure 6 summarizes the advantages and disadvantages of the Jet Loop Reactor and membrane technology in comparison to the conventional basin technology:

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>+ less floor space required</td>
<td>- C-Source for Denitrification required</td>
</tr>
<tr>
<td>+ lower retention time</td>
<td></td>
</tr>
<tr>
<td>⇒ smaller treatment reactors</td>
<td></td>
</tr>
<tr>
<td>⇒ lower recycle streams</td>
<td></td>
</tr>
<tr>
<td>+ the waste water can be reused</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6, Advantages and disadvantages of the Jet Loop Reactor and membrane technology

Because a Jet Loop Reactor can be built higher than a conventional basin less floor space is required. By using a two component jet nozzle and some flow obstacles a high turbulence with a great mass transfer can be reached so that lower retention times, smaller treatment reactors and lower recycle streams are sufficient. When a third stage is also installed, some or all the treated waste water, depending on the required limiting values, can be reused. The Jet Loop Reactor and membrane process has only the slight disadvantage that a c-source for the denitrification is required. This can be called a slight disadvantage because some conventional waste water treatments also need a c-source.

**Reachable degradation rates of the Jet Loop Reactor and ultrafiltration waste water treatment**

The following figures show the degradation rates which could be reached during commissioning the two stage German waste water treatment plant.
Figure 7, Degradation rate free cyanide

A degradation rate of 98% could be reached

Figure 8, Degradation rate of thiocyanate

A degradation rate of 98% could be reached
A degradation rate of 95% could be reached.

Figure 9, Degradation rate of COD

A degradation rate greater than 99% could be reached.

Figure 10, Degradation rate of phenol
Degradation rate Ammonia [%]

A degradation rate greater than 98% could be reached

Figure 11, Degradation rate of ammonia

Degradation rate Ntot (NH4N+NO3N+NO2N)

A degradation rate greater than 95% could be reached

Figure 12, Degradation rate of Ntot (NH4N+NO3N+NO2N)
The following figure shows the reachable degradation rates according to the experience TKIS has made during commissioning the German two stage Jet Loop Reactor and ultrafiltration waste water treatment.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Max. Degradation rate [%]</th>
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<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>
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