Oxygen, ozone and carbon dioxide in waste water treatment

Meeting EU regulations ....

**Directive 91/271/EEC**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>&gt; 2000* - 100.000 P.E.</th>
<th>&gt; 100.000 P.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[mg/l]</td>
<td>[% reduction]</td>
</tr>
<tr>
<td>BOD&lt;sub&gt;5&lt;/sub&gt;</td>
<td>25</td>
<td>70 - 90</td>
</tr>
<tr>
<td>COD</td>
<td>125</td>
<td>75</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>35 (60)</td>
<td>90 (70)</td>
</tr>
<tr>
<td>Phosphorus **</td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>Total nitrogen **</td>
<td>15</td>
<td>70-80</td>
</tr>
</tbody>
</table>

* Coastal water > 10.000 p.e.  ** Sensitive areas, one or both parameters

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* Biological treatment

* More stringent treatment
Oxygen, ozone and carbon dioxide in waste water treatment

....easily by using Oxygen, Ozone or Carbon dioxide in water treatment

- Neutralisation of industrial waste water: CO₂
- Prevent corrosion in canalisation and in treatment plant : O₂
- Capacity increase in activated sludge process: O₂
- Cracking of persistent COD with ozone: O₃
- Remediation of surface waters: O₂
Neutralisation of alkaline waste waters

Effluent discharge legislation in Europe: $6.5 < \text{pH} < 9.5$
Neutralisation curves of mineral acid and CO₂

Phase I

\[ \text{discharge limits} \]

\[ 2 \text{OH}^- + \text{CO}_2 \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \]

\[ \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- \]

Phase II

\[ \text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O} \]

Phase III

\[ \text{CO}_2 \text{ consumption} \]

\[ \text{Phase III mineral acid} \]
### Characteristics of CO₂ and mineral acids

<table>
<thead>
<tr>
<th>HCl &amp; H₂SO₄</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>• strong acids difficult regulation</td>
<td>• week acid, no over-acidification</td>
</tr>
<tr>
<td>• difficult to store and handle</td>
<td>• storage and handling simple and safe</td>
</tr>
<tr>
<td>• release of noxious fume</td>
<td>• inert gas</td>
</tr>
<tr>
<td>• corrosion</td>
<td>• no corrosion</td>
</tr>
<tr>
<td>• consent levels for discharge</td>
<td>• no salting up, ecologic</td>
</tr>
</tbody>
</table>
Oxygen, ozone and carbon dioxide in waste water treatment

CO₂ injection in waste or process water

- Pumped tube reactor with static mixer *
- Pumped tube reactor with multiple loops *
- Gas-liquid injector nozzles  dH > 40 °
- Diffusers
- Pressure vessel
- Submerged aerators
- Hose mats

* suited for injection of liquid CO₂
Oxygen, ozone and carbon dioxide in waste water treatment

Neutralisation of alkaline waste water with CO$_2$
Oxygen, ozone and carbon dioxide in waste water treatment

Compact units for gaseous CO₂

50 kg/h CO₂

75 kg/h CO₂
Advantages of Neutralisation with CO$_2$

- Safe and simple pH control, overdosing not possible
- Low investment costs
- No impact on salt content; reduced discharge fees
- Avoids corrosion problems when recycling effluents
Oxygen, ozone and carbon dioxide in waste water treatment

CO₂ Neutralisation References

• Beverage industry
• Dairies
• Pulp & Paper Mills
• Textile industry (Leather!)
• Galvanic processes
• Concrete handling
Oxygen, ozone and carbon dioxide in waste water treatment

Oxyduct: Oxygen addition in sewers

➢ Prevents sewer corrosion and hydrogen sulphide emissions
Calculated oxygen demand for pressurized sewers

*After Lohse 1987, ATV M 168*
Oxygen, ozone and carbon dioxide in waste water treatment

Oxygen injection through socket
Oxygen injection with pump-venturi in bypass

In Budapest
Advantages of oxyduct process with oxygen

- Proven technology
- High oxygen solubility
- Small gas flow compared to air
- Economic compared to nitrate and hydrogen peroxide
- Fast reaction compared to nitrate
Pure oxygen increases capacity and saves energy

**BIOX-Process**: first application at the WWTP ´Emschermündung´ in 1980. Since then our technology has been introduced in over 150 plants.

**Messer offers**
- Re-engineering of activated sludge process
- Retrofitting
- Oxygenation systems
- Gas supply
- Coached start-up
Oxygen, ozone and carbon dioxide in waste water treatment

Solubility of air and Oxygen in water

Oxygen mass transfer rate is one of the main factors influencing the performance of the activated sludge process.

Power of mass transfer is proportional to saturation deficiency: “Cs – Ct”

* i.e. set point 2 mg/l under atmospheric conditions
Oxygen, ozone and carbon dioxide in waste water treatment

BIOX Process

Oxygen bulk storage tank  vaporizer  control system

Oxygen probe

pure oxygen

activated sludge basin aeration

fine bubbles of oxygen are introduced over a wide area through specially developed oxygenation hose

epp 0200/9
Oxygen, ozone and carbon dioxide in waste water treatment

WWTP Ilsfeld (D): increased loads from textile industry
Oxygen, ozone and carbon dioxide in waste water treatment

WWTP Beggen (Lux): Peak loads from a dairy
Oxygen, ozone and carbon dioxide in waste water treatment

WWTP Leer (D): 120.000 P.E.
Deep shaft operated with pure oxygen;
Waste water 50 % municipal and 50 % oil mill
Oxygen, ozone and carbon dioxide in waste water treatment

WWTP Leer: 120.000 P.E.

Deepshaft operated with pure oxygen

- Increases capacity
- Saves energy
Oxygen, ozone and carbon dioxide in waste water treatment

Industrial waste water

Sequencing Batch Process

Fill
mixing, aeration

COD degradation
Nitrification
aeration, mixing, oxygenation

Denitrification
mixing

Sludge separation
sedimentation

Effluent draw
Surplus sludge withdrawal
Oxygen, ozone and carbon dioxide in waste water treatment

Sequencing Batch Reactors
Oxygen Demand Profile

Oxygen flow [m³/h]

Time [minutes]

Fill 1h,10min
7 h 00min
Sedimentation 2h 20min
Draw 1h 10min

Oxygenation, D.O. controlled
Oxygen, ozone and carbon dioxide in waste water treatment

Sequencing Batch Reactors
oxygen for cycle start in a dairy
Oxygen, ozone and carbon dioxide in waste water treatment

High rate SBR plant for treatment of sludge liquor

Advantages of the oxygen process
• Low investment costs
• Flexible operation mode
• Optimised sedimentation of sludge

WWTP Lingen (D)
Aerobic selector improves sludge settling

High concentration of „easy BOD“, e.g. waste water from potato processing or soft drinks, easily causes bulking sludge.

Aerobic selector:
- Short residence time
- Very high oxygenation rate

Aerobic selector in WWTP Overward (AT)
Oxygen, ozone and carbon dioxide in waste water treatment

Municipal + potato-processing waste water

Selector operated with pure oxygen

WWTP Hankensbüttel (D)
Oxygen, ozone and carbon dioxide in waste water treatment

Industrial waste water: membrane bioreactor

- superior effluent quality
- compact treatment
- exploit full potential with pure oxygen
Oxygen, ozone and carbon dioxide in waste water treatment

Membrane Bioreactor

additional oxygen increases capacity by > 50 %

NH₄ controlled oxygen dosage
Landfill leachate treatment
Horm (D)
Oxygen, ozone and carbon dioxide in waste water treatment

Nitrogen removal: Fundamentals

**Nitrification**

\[ \text{NH}_4^+ + \text{O}_2 \rightarrow \text{nitrifying bacteria} \rightarrow \text{NO}_3^- \]

**Denitrification**

\[ \text{NO}_3^- + \text{heterotrophic biomass} \rightarrow \text{N}_2 \]
Oxygen, ozone and carbon dioxide in waste water treatment

Conversion to Messer’s BIOX® N process

1. Primary settling tank
2. Aeration tank
3. Final clarifier
4. Inflow
5. Outflow
6. Return sludge
7. Excess sludge
8. BIOX® N process
9. Internal recirculation
10. Denitrification
11. Nitrification

Part of the Messer World

Dr. Hermans 32 / 09-05
Oxygen, ozone and carbon dioxide in waste water treatment

Conversion to Messer’s BIOX® N process : Retrofitting
Oxygen, ozone and carbon dioxide in waste water treatment

Sewage treatment plant Neustadt a/d Weinstrasse

Outlet values of nitrogen before and after conversion to BIOX® N

<table>
<thead>
<tr>
<th>Date</th>
<th>Total inorganic N (mg/l)</th>
<th>Before BIOX® N</th>
<th>BIOX® N process</th>
</tr>
</thead>
<tbody>
<tr>
<td>16. April</td>
<td>60</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>05. June</td>
<td>50</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>25. July</td>
<td>40</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>13. Sept.</td>
<td>30</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>02. Nov.</td>
<td>20</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>22. Dec.</td>
<td>18</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

Limit 18 mg/l

wine harvest

start-up BIOX® N
Oxygen, ozone and carbon dioxide in waste water treatment

The BIOX process-
This is how oxygen saves costs

Advantages:

- Increases treatment capacity
- Flexible operation mode
- Costly enlargements are avoided
- Reduction of yearly costs
- No additional energy demand
- Realised at short notice