KNX™ and PRAVO® – a Perfect Duo for Mercury Capture
Recent Industrial Applications in Waste Incineration

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German Licensees of Vosteen Consulting applying KNX™ and PRAVO® industrially

Town Karlsruhe – Wastewater Treatment Plant
2 Stationary Fluidized Bed Combustors for Sewage Sludge applying NaBr and PRAVO® since 2007
Martin Maurer, Roland Milz

EGLV – Central Sludge Treatment Plant Bottrop
2 Stationary Fluidized Bed Combustors for Sewage Sludge applying NaBr since 2004
Testing PRAVO® in 2004 and again in April 2008
Falko Lehrmann, Günter Schwabe
**KNX™**

is a registered trade mark of ALSTOM Power - ECS, standing for the bromine based mercury oxidation technology of Vosteen Consulting

**PRAVO®**

was developed in 2004 - 2007 and is applied for a registered trade mark of Vosteen Consulting

Patents on the combined application are pending

*PRAVO® is a proprietary anorganic polysulfide in different formulations (depending on the specific application)*
PRAVO® - Production, Laboratory R&D:

VOSTEEN Consulting GmbH
Thermal Engineering and Environmental Protection

PAN-Chemie Dr. G. Fülöp e.K.
Gabor Fülöp

Martin-Luther-University Halle-Wittenberg
Institute for Environmental Engineering
Heinz Köser, Jan Schütze
Application of KNX™ and PRAVO®

in the

Communal Waste Water Treatment Plant
Karlsruhe-Neureuth
Karlsruhe has 285,000 inhabitants – Wastewater Treatment Plant Neureut (875,000 PE)
Wastewater Treatment Plant Karlsruhe-Neureut
with 2 Fluidized Bed Combustors (FBC) for sewage sludge

„No mercury into the air“

„No mercury into the neighbouring river Rhine“
FBC Unit 2

ESP  WFGC  stack

CEM  FBC

Rotor of Decanter
<table>
<thead>
<tr>
<th>Process Description</th>
<th>Temperature</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge Sedimentation</td>
<td>4 – 5 % dry matter</td>
<td></td>
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<tr>
<td>PE-Sludge Conditioning</td>
<td></td>
<td></td>
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<tr>
<td>Mechanical Dewatering</td>
<td></td>
<td></td>
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<tr>
<td>Centripress (25 % dry matter)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Contact-Drying</td>
<td>43 % dry matter</td>
<td></td>
</tr>
<tr>
<td>Heat Recovery Boiler</td>
<td>25 bar, 300 °C</td>
<td></td>
</tr>
<tr>
<td>ESP</td>
<td>170 °C</td>
<td></td>
</tr>
<tr>
<td>WFGC</td>
<td>2 stages + wet Venturi (System LAB, 1997)</td>
<td></td>
</tr>
</tbody>
</table>
NaClO₂ to be substituted by NaBr (40 %) and TMT15® to be substituted by PRAVO®100

70 °C

First stage:
- pH = 0.5 … 1
- 2 m³, 0.1 m³/hour
- \( t_{R1} = 20 \) hours

Second stage:
- pH = 7.2
- 4 m³, 0.75 m³/hour
- \( t_{R2} = 5.3 \) hours
Injection of diluted NaBr into FBC-Freeboard with 3 lances
Most advanced German High Tech
emptying plastic bottles
filled with diluted PRAVO (no Rhine wine)

counting droplets
Results from November 2007

Hg at the stack [µg/Nm³ dry, 11 vol% O2]

S²⁻/Hg mass ratio [mg/mg]

Br/Hg [mg/mg]

Hg at stack [µg/Nm³ dry]

S²⁻/Hg scrubbers 1 + 2 [mg/mg]

S²⁻/Hg scrubber 2 [mg/mg]

150 µg Hg/Nm³ dry in the raw gas

KNX via lances
Variation of PRAVO

KNX to sludge
Variation of KNX

Variation of KNX via lances

Variation of PRAVO

# of parametric variation in November 2007
How to achieve 95% mercury removal rate

- NaBr added to sludge
- NaBr injected via 3 lances

**Diagram:**

- **Hg removal [%]** vs **S²⁻/Hg mass ratio [kg/kg]**
- **PRAVO variation**
  - KNX not strictly constant
- **KNX variation** under high PRAVO
Variation of Br⁻/Hg and S²⁻/Hg mass ratio (1)

PRAVO is permitting lower KNX
Mode of KNX injection not important

- NaBr added to sludge
- NaBr injected via 3 lances

**High Br**

- High PRAVO
- S²⁻/Hg mass ratio = 20
- mainly to Scrubber 1 (pH = 0.5)

**Low PRAVO**

- S²⁻/Hg mass ratio = 2.5
- only to Scrubber 2 (pH = 7)
Constantly achieved:
Hg = 10 µg Hg/ Nm³ dry, 11 % O2 at stack

Day without parameter variations
Br/Hg = 252 mg/mg,  S²⁻/Hg = 19.9 mg/mg
Hg = 8 ... 25 µg Hg/ Nm³ dry, 11 % O₂ at stack - „Only high PRAVO is not enough“

Interrupting KNX-feed to sludge

Br/Hg = 202 mg/mg -> 0 -> 202 mg/mg

S²⁻/Hg = 19.9 mg/mg = const.
Hg = 15 → 25 µg Hg/Nm³ dry, 11 % O₂ at stack

„Only low KNX is not enough“

S²-/Hg = 19.9 mg/mg -> 0 -> 19.9 mg/mg

Br/Hg = 256 mg/mg = const

 Interruption of PRAVO®-feed to scubber 1
Wastewater Treatment Plant Bottrop and Central Sludge Treatment Plant Bottrop
NaClO₂ substituted by NaBr since August 2004

> 90 % mercury capture

PRAVO® already tested in 2004
Bottrop Project Team  (Dezember 2003 und July 2004)

Bernhard Vosteen

Günter Schwabe
Operations Manager

Yearly savings in Bottrop: 300,000 €
Ecotoxicological Assessment of the Waste Water Treatment with PRAVO®100

Preliminary results, under revision testing PRAVO®100, density: 1.28 g/l (at 20 °C)

Marine Algal Growth not inhibited
(tests according to DIN ISO 10253-L45)

Aquatic Toxicity of PRAVO®100
(tests according to OECD)

\[
\begin{align*}
\text{LC}_0 &: \quad 640 \text{ mg/l} \quad \text{(dilution 1 : 2,000)} \\
\text{LC}_{50} &: \quad 2660 \text{ mg/l} \quad \text{(dilution 1 : 500)} \\
\text{LC}_{100} &: \quad 5120 \text{ mg/l} \quad \text{(dilution 1 : 250)}
\end{align*}
\]

Diluted PRAVO®100 safe to handle
dissociation products: S, SO\(_4\)\(^2-\) limited H\(_2\)S-formation (even at pH < 1)
Specific additive costs much < 100 US $/ gHg

2.90 €/kg Br⁻ (pure)
15.2 €/kg S²⁻ (pure)
1 € = 1.35 US$

KNX™ and PRAVO® – a perfect duo indeed
Conclusions

1. KNX™ highly effective in wet and dry mercury capture
2. PRAVO® enhancing wet mercury capture
3. KNX™ + PRAVO® make sure > 90 % removal rate
4. PRAVO® in WFGD alone less effective than KNX alone
5. PRAVO® most effective in presence of Br⁻
6. PRAVO® lowers need of KNX™ (cost optimisation)

Patents pending
Thanks for Your attention

Questions?