Microbial methane in German coal associated gas (CAG)

Dr. Thomas Thielemann
Germany
Definitions of coal gases

**fossil:** thermal generation from coals and biological gas generation in geological periods of time; typical natural gas

**renewable:** recent biological gas generation
Classification of coal associated gases in Germany

- **Flözgas**
  - Coalbed Methane (CBM)
  - Gas from unworked coal measures
  - Methane: 90 – 95%

- **Grubengas**
  - Coalseam Methane (CSM)
  - Gas from active mines
  - Methane: 25 – 60%

- **Coalmine Methane (CMM)**
  - Gas from abandoned mines
  - Methane: 60 – 80%

Note: Grubengas (CMG) refers to gas from abandoned mines.
Global utilization of coal gases

Legend
- 0.28 2005: Production of coal gases in G.m³
- Hard coals
- Hard coal districts with gas utilization
2005: German reserves of natural gas vs. coal gases

**Natural gas:**

<table>
<thead>
<tr>
<th></th>
<th>Reserves</th>
<th>Production 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reserves</strong></td>
<td>270.0 Bill. m³ (9.535 Tcf)</td>
<td></td>
</tr>
<tr>
<td><strong>Production</strong></td>
<td></td>
<td>20.4 Bill. m³ (720.4 Bcf)</td>
</tr>
</tbody>
</table>

“static lifetime“:

<table>
<thead>
<tr>
<th></th>
<th>13.2 years</th>
</tr>
</thead>
</table>

**Coal gases:**

<table>
<thead>
<tr>
<th></th>
<th>Reserves</th>
<th>Production 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reserves</strong></td>
<td>30.0 Bill. m³ (1.059 Tcf)</td>
<td></td>
</tr>
<tr>
<td><strong>Production</strong></td>
<td></td>
<td>238.8 Mio. m³ (8.433 Bcf)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>125.6 years (theoretically)</th>
</tr>
</thead>
</table>

Thielemann, UNECE Ad Hoc Group of Experts on CMM   Geneva, 01.02.2006
2% or less of the existing methane volumes can be produced.
Recent gas leakage in the eastern Ruhr area, Germany
Mine Ewald-Fortsetzung: Past and Present

1950:  

2002:
Hydrocarbon mining concessions in the Ruhr area, Germany

Source: Abteilung Bergbau und Energie in NRW Bezirksregierung Arnsberg

31.12.2005

Thielemann, UNECE Ad Hoc Group of Experts on CMM Geneva, 01.02.2006
Coal Mine Methane Utilization in Germany 1998 to 2005

01.04.2000: renewable energy law
BGR-sampling sites

- Active hard coal mining 2001
- Abandoned hard coal mining 2001
- Sampling of coal gases 2002-2005
- Sampling of mine water 2003

Thielemann, UNECE Ad Hoc Group of Experts on CMM  
Geneva, 01.02.2006
Sampling

So far:

- eight sampling campaigns
- 132 gas samples analyzed
- mine water samples from six sites
- cuttings from different wells
Composition of coal gases

C_1/(C_2+C_3) vs. \delta^{13}C-Methane (‰ vs. PDB)

- Microbial gases
- Thermal gases

Mixture of thermal and microbial gases

- Gerling et al. (1995): Northern Germany
- Wingerning (1975): Ibbenbüren
- Lommerzheim (1988): S’ Münsterland
- Thielemann et al. (2003): Ruhr area
- Colombo et al. (1970): Ruhr area
- Kotarba (2001): Upper Silesia (Poland)
Maturity and Mixing Trends

δ^{13}C-Methane (‰)

C_{1}/(C_{2}+C_{3})

Microbial

More pronounced microbial influence in shallower gases

Thermal

Mixture of thermal and microbial gases

- Natural gas from more than 3.0 km depth
- Coal gases from about 1.5 – 3.0 km depth
- Coal gases from about 1.0 – 1.5 km depth
- Coal gases from about 0.2 – 1.0 km depth

Thielemann, UNECE Ad Hoc Group of Experts on CMM  Geneva, 01.02.2006
Methane generation:
hints from isotopic composition

Thielemann et al. (2003): Ruhr area
Lommerzheim (1988): Ruhr area
Gerling et al. (1995): Northern Germany
Kotarba (2001): Upper Silesia, Poland
Dusar (unpubl., 1994): Campine Basin, Belgium
Hosgörmez et al. (2002): Amasra, Turkey
Smith and Pallasser (1996): Australia (examples)
Natural Gas vs. Coal Mine Gas

- Maturity trend terrestrial 0.5-2.5 %VR
- Gerling et al. (1995): Natural gas, Northern Germany
- this study: Coal Mine Gas, Ruhr Basin, Germany

Admixture of microbial methane

\[ \delta^{13} \text{C-Methane} (\text{‰}) \]

\[ \delta^{13} \text{C-Ethane (‰)} \]
Natural Gas vs. Coal Mine Gas

Maturity trend terrestrial 0.5-2.5 %VR

- Gerling et al. (1995): Natural gas Northern Germany
- this study: Coal Mine Gas, Ruhr Basin, Germany

Admixture of microbial methane

why?

Samplings:
- = 02/2002
- = 11/2002
- = 03/2003
Why methane today seems to be considerably microbial:

Methane generated 312 Ma until today

Methane escaped within the last about 312 Ma, probably mainly thermal

remaining rest of thermal methane

(present and fossil) microbial methane

recent gas reserves

Thielemann, UNECE Ad Hoc Group of Experts on CMM   Geneva, 01.02.2006
Mine water

Sampling

Sample treatment

- transport to laboratory, refrigerated at 6°C and kept airless
**Mine water**

**Sample treatment**

- counting the natural microbial frequency (all species):

  cumulative cell number: 
  \[0.8 \times 10^4 \text{ to } 6.6 \times 10^5 \text{ per ml}\]

- nutrition fluid added to samples
  (Methanobacterium, DSMZ-Medium 119 with H\(_2\) as substrate)

- 4 weeks incubation in darkness at 30°C
Result four weeks after incubation in lab:

methanogenic archaea in 4 out of 6 samples

Cell division: A hint to living methanogenic archaea.

1 µm
Archaea: phylogenetic pedigree, based on 767 position analysis of 16S rRNA sequence

- Methanococcales
- Thermococcales
- Methanobacteriales
- Methanosarcinales
- Methanomicrobiales
- Methanoscps
- marine benthic Group D

ANME- anaerobe methane oxidizer - enriched culture 7 (ARB_37893411)
**Sulfolobus shibatae**

(hyperthermophilic acidophile Crenarchaeon)

**Mine Water Sample**

(nonthermophilic methanogen Archaeon)

---

Time (min)

<table>
<thead>
<tr>
<th>Relative Abundance</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>1304.01305.0</td>
<td>1302.01303.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NL: 1.25E7</strong></td>
<td><strong>NL: 5.38E6</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1300.01301.0</td>
<td>1298.01299.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NL: 5.71E6</strong></td>
<td><strong>NL: 1.25E7</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1296.01297.0</td>
<td>1294.01295.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NL: 2.99E7</strong></td>
<td><strong>NL: 9.80E7</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1292.01293.0</td>
<td>1290.01291.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NL: 6.20E7</strong></td>
<td><strong>NL: 2.32E7</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1288.01289.0</td>
<td>1286.01287.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NL: 5.35E6</strong></td>
<td><strong>NL: 3.88E5</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**NL: 4.46E5**

1304.0-1305.0

---

**NL: 1.01E6**

1302.0-1303.0

---

**NL: 9.74E3**

1300.0-1301.0

---

**NL: 1.46E4**

1298.0-1299.0

---

**NL: 6.32E4**

1296.0-1297.0

---

**NL: 2.02E4**

1292.0-1293.0

---

**NL: 1.19E4**

1290.0-1291.0

---

**Relative Abundance**

**Time (min)**

---

**Thielemann, UNECE Ad Hoc Group of Experts on CMM**

**Geneva, 01.02.2006**
Geochemical Results

1. MS-Analysis:
Mine water is rich in Caldarchaeol (typical of Archaea membrane fragments)

Example: DGC-I = Diglycosyl-Caldarchaeol, from Tomoaia-Cotisel et al. (1992)

2. DNA-Analysis: Archaea in the
mine water are *Methanocalculus pumilus*

(Picture from Mori et al. 2000)
Sketch of a mine producing thermal and microbial methane
Résumé

c coal gases in the Ruhr area =
Mixture of thermal and microbial methane

Methane emissions at the surface

in abandoned mines: waters with living
methanogenic archaea

microbial generation rates (time, volume) still
not clear
Future Activities

- extended sampling
- determination of microbial methane generation rates
- site-related mass balance
- enhancement of microbial methane generation in (deep) coal measures
Thank you for your attention