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# *Gas Dehydration Glycols in the Subsurface Environment*

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# *Program Funding*

| | |
|---|---|
| DOE-NETL | $800,000 |
| GRI | $800,000 |
| Environment Canada | $105,000 |
| Total | $1,705,000 |

- Period of performance is Oct. 1, 2000 - Sept. 30, 2003
- Funding shown in Canadian dollars using 65% exchange rate

# *Program Goals and Objectives*

Goals:

- Develop techniques for the management and/or remediation of wastes associated with natural gas production and processing.

Objectives:

- Develop data to predict the subsurface transport and fate of gas production and processing wastes.

- Integrate data into Risk Based Corrective Action (RBCA) models and develop Environmentally Acceptable Endpoints (EAE) criteria for glycol-based dehydration wastes.

# *Background*

- Glycol-based dehydration units are used to remove water from the natural gas stream.
  - Located at wellheads & transmission/distribution facilities
  - Over 40,000 dehydration units in United States
  - Triethylene glycol (TEG), diethylene glycol (DEG), and ethylene glycol (EG) are most commonly used

# *Background*

## Key Results of 2000-2001Laboratory Research

- Condensates and glycols commonly occur together, sometimes in concentrations that are above water quality standards.
- Glycols appear to significantly enhance the mobility of condensates, including BTEX, in soils from North Dakota, New Mexico, Louisiana, and Alberta.
- Glycols that are high in BTEX ("rich" glycols) are less biodegradable than pure glycols.
- Soil conditions affect biodegradability and magnitude of cosolvency effect.

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# *2002 Field-Based Studies*

- Sites with historical data for condensates and glycol
- Sites with different soil types

# *Field Work Plan*

- Collect  and analyze sediment samples.
- Collect and analyze water samples from existing monitoring wells.
- Install new wells where deemed necessary.
- Sampling points selection based on historical data.

# *Analytical Work Plan*

- Glycol determinations in sediments and water conducted at EERC using GC/MS.

- BTEX determinations in water conducted by commercial lab using GC/FID.

# *Research Sites*

- Wind River Basin of Wyoming
  - Natural gas compressor station
  - Sandy subsurface
  - Average depth to groundwater = 15 ft

- Northern Alberta
  - Natural gas processing plant
  - Gravel pad on muskeg (clay, high organic content)
  - Average depth to groundwater = 3 ft

# *Glycol in Groundwater (mg/L)*
# *Wyoming Site*

| | June 2002 | | September 2002 | |
|---|---|---|---|---|
| Well# | DEG | TEG | DEG | TEG |
| 3 | 1 | 10 | ND | 6 |
| 4 | 64 | 1390 | 104 | 3051 |
| 6 | ND | ND | ND | ND |
| 12 | 241 | 3352 | 300 | 3484 |
| 16 | ND | ND | ND | ND |
| 18 | 2 | 8 | ND | 6 |

ND = Non detect (detection limit was 1 mg/L)

Values shown are the mean of triplicate runs of each sample.

EG was not detected in any sample.

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# *Glycol in Groundwater (mg/L)*
# *Wyoming Site*

## September 2002

| Well# | DEG | TEG |
|---|---|---|
| 20 | ND | ND |
| 21 | ND | ND |
| 22 | 9 | 189 |
| 23 | 10 | 200 |
| 24 | 5 | 78 |
| 25 | ND | ND |

ND = Non detect (detection limit was 1 mg/L)
Values shown are the mean of triplicate runs of each sample.
EG was not detected in any sample.

# *Glycols in Water - Alberta Site*

| Well | EG (mg/L) | | DEG (mg/L) | | TEG (mg/L) | |
|---|---|---|---|---|---|---|
| | June | Oct | June | Oct | June | Oct |
| MW 00-1 | ND | ND | ND | ND | ND | ND |
| MW 00-3 | ND | ND | ND | ND | ND | ND |
| MW 01-10 | ND | ND | ND | ND | ND | ND |
| MW 01-11 | ND | ND | ND | ND | ND | ND |

ND = Non Detect (Detection Limit was 5 mg/L)

# *Glycol in Soil (ppm)*
# *Wyoming Site*

## June 2002

| Location (depth) | DEG | TEG |
|---|---|---|
| P1 (14') | <1 | <1 |
| P2 (20') | <1 | <1 |
| P3 (16') | <1 | <1 |
| P4 (14') | <1 | <1 |
| P5 (17') | <1 | <1 |
| P6 (15') | <1 | <1 |
| P7 (20') | <1 | <1 |
| P8 (19') | <1 | <1 |

# *Glycol in Soil (ppm)*
# *Alberta Site*

## June 2002

| Location (depth) | EG | DEG | TEG |
|---|---|---|---|
| • HA1 (2’) | 22 | <1 | <1 |
| • HA2 (3’) | 7581 | 43 | 63 |
| • HA3 (2’) | <1 | <1 | <1 |
| • SB2 (2’) | <1 | <1 | <1 |
| • SB2 (13’) | 23 | <1 | <1 |
| • SB3 (2’) | <1 | <1 | <1 |
| • SB3 (8’) | <1 | <1 | <1 |
| • SB3 (10’) | 11200 | 28 | 64 |
| • SB3 (13’) | 1040 | <1 | <1 |
| • SB4 (2’) | <1 | <1 | <1 |
| • SB4 (8’) | 255 | <1 | <1 |
| • SB4 (13’) | 56 | <1 | <1 |

# *Comparison of Organic Carbon in Soil Wyoming site vs. Alberta site*

| | TOC (%) Range |
|---|---|
| Wyoming | 0.02 - 0.16 |
| Alberta | 0.35 - 7.9 |

# *Key Observations*

- In Wyoming glycol was found in the groundwater, but not the sediments.
- In Alberta glycol was found in the sediments but not the groundwater.
- Glycol degrading microbes were present in sufficient numbers in the subsurface at both sites to suggest attenuation was occurring.

# ASTM Colorometric vs. GC Analytical Methods

| | Colorometric | GC | |
|---|---|---|---|
| WY Well# | Total Glycol | DEG | TEG |
| 3 | 400 | 0 | 0 |
| 4 | 150 | 104 | 3051 |
| 6 | 600 | 0 | 6 |
| 12 | 400 | 300 | 3484 |
| 16 | ND | 0 | 0 |
| 18 | 300 | 0 | 6 |
| 20 | ND | 0 | 0 |
| 21 | ND | 0 | 0 |
| 22 | ND | 9 | 189 |
| 23 | 200 | 10 | 200 |
| 24 | 600 | 5 | 78 |
| 25 | ND | 0 | 0 |

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EG was not detected in any GC sample.

# *Explanation for Differences*

- Interferences are cited in ASTM method description. Method was originally developed for automotive industry.
- False positives caused by aldehydes and/or other organic compounds.
- False negatives caused by lack of ability to detect DEG and TEG.

# Conclusions

- Nature of the sediment (TOC) controls the partitioning of glycol.
- Glycol transport in the subsurface does not appear to be overly extensive or particularly problematic compared to condensates.
- Glycols do not appear to affect the transport and fate of condensate plumes.
- Commercial lab analytical techniques may not provide accurate assessment of glycol occurrence.

# *Project Benefits*

- Previously unavailable data allows for scientifically-based decisions regarding the management and/or remediation of subsurface glycol contamination.
- Data can be used to develop EAE or RBCA protocols for gas processing wastes.
- The use of ASTM method for glycol analysis in soil and water should be reconsidered.