# Heterogeneity Development and Its Influence on Long-Term PRB Performance: Column Study

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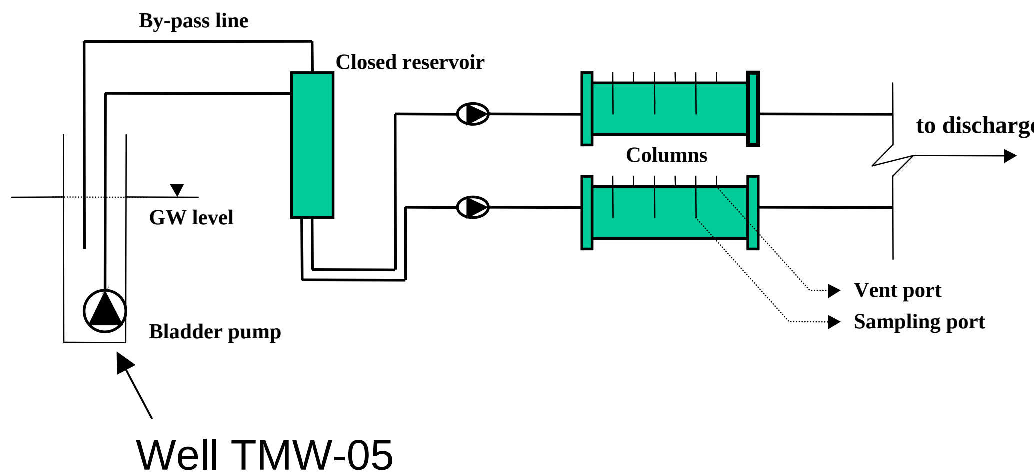
# Acknowledgements

- **Funding provided by DOE’s Subsurface Contaminant Focus Area**
- **Todd Hart, PNNL**

# Scope

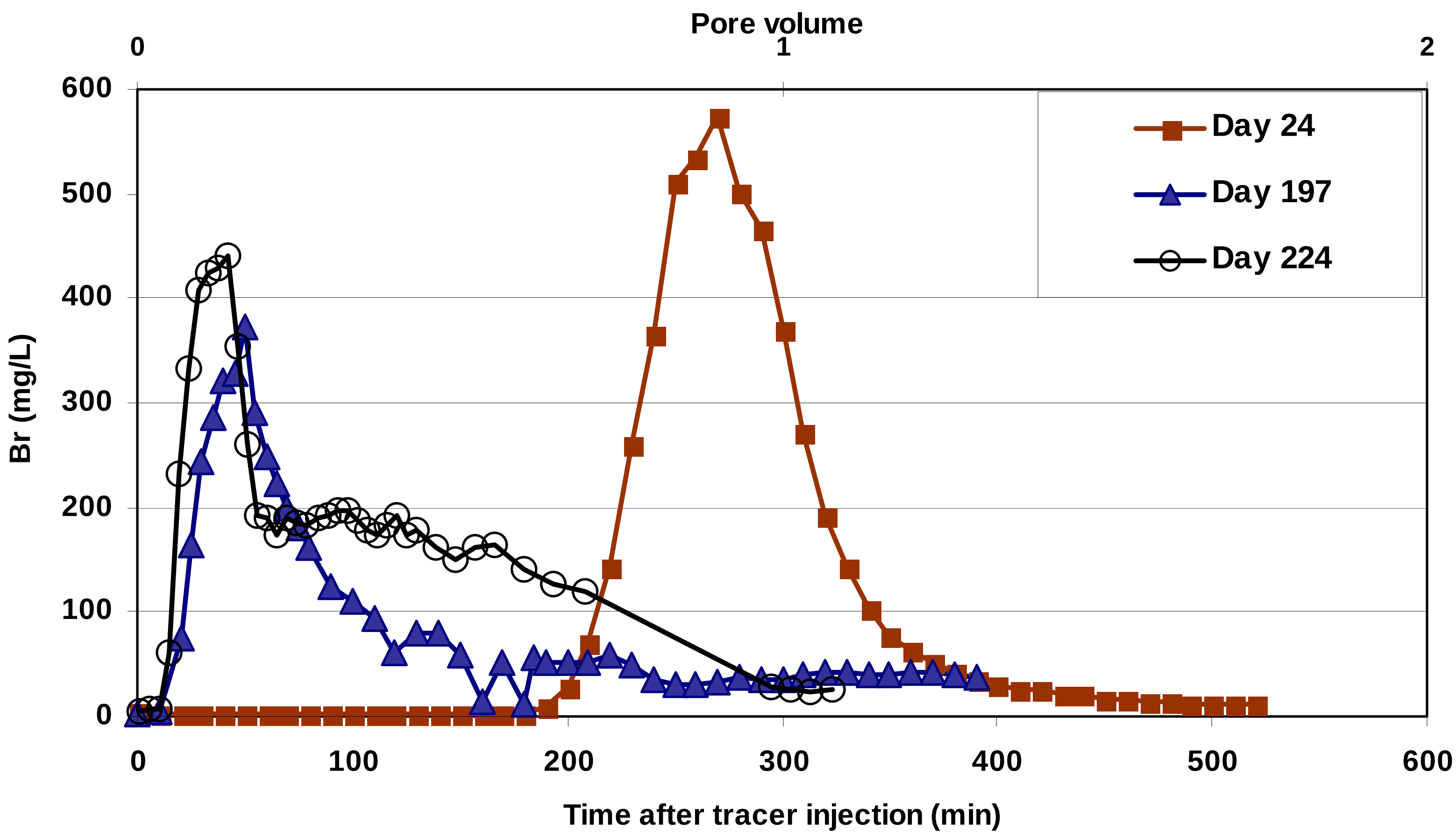
- The performance of existing permeable reactive barriers (PRBs)
- Field Column Study
  - Geochemistry
  - Hydrology
  - Gas production
  - Microbial activity
  - Mineralogy
  - Key indicator for PRB performance
- Laboratory column study
  - Gas production and entrapment

# Field Column Studies at the Y-12 PRB Site

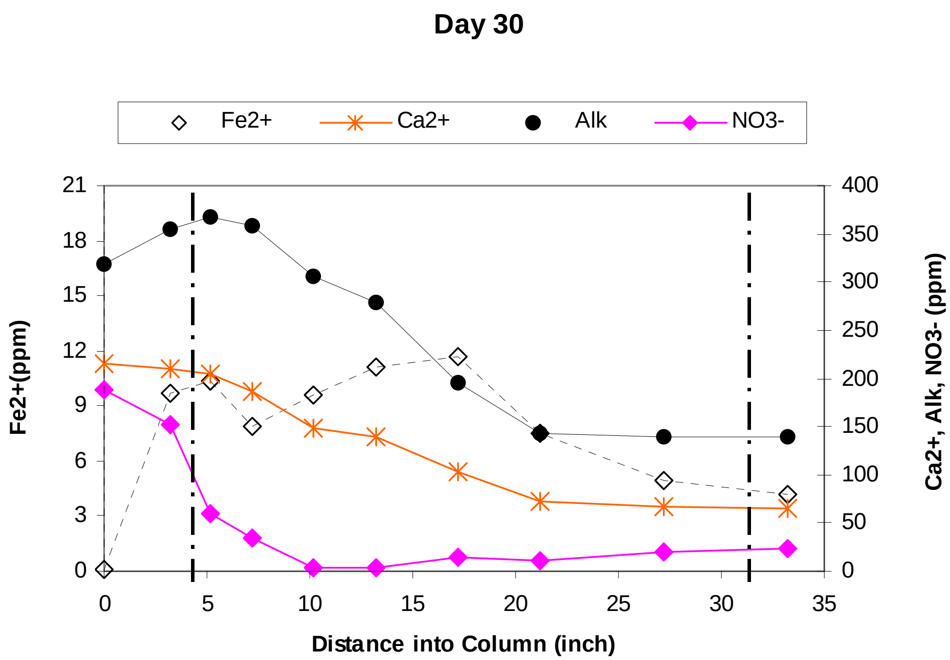


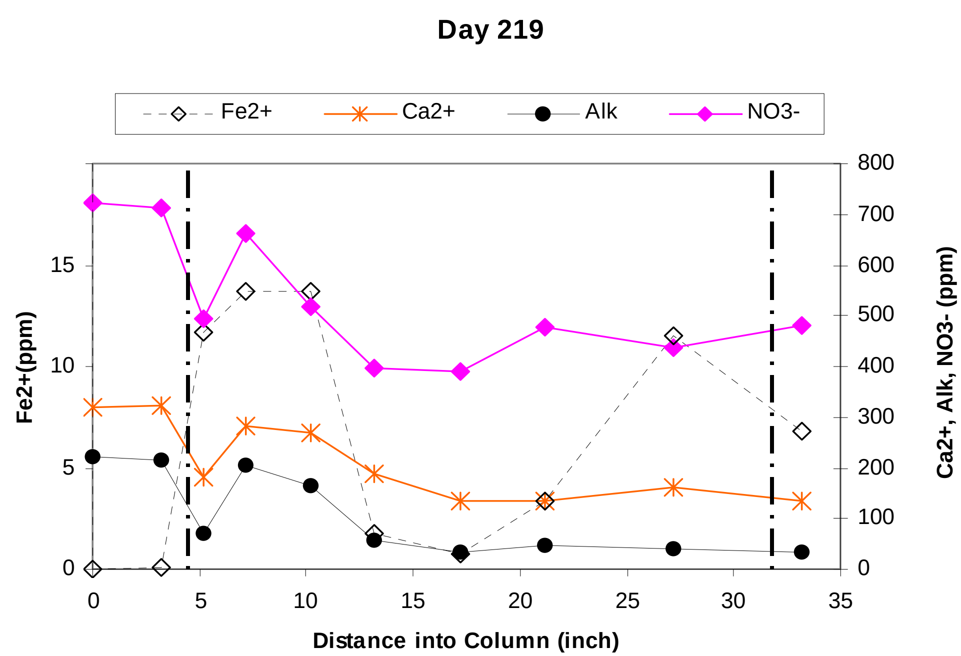

- **Fe-filings in 6-in Ø, 36-in columns; 680 days of operation.**
- **2 columns: accelerated- and slow-flow.**
- **Objective: to understand geochemical and hydraulic changes and establish key performance indicators.**
- **Monitoring: geochemical parameters at multiple ports; tracer tests**
- **Geochemical and hydrological modeling**
- **Mineralogical study: Identification and quantification**

# Hydraulic changes reflected by tracer tests

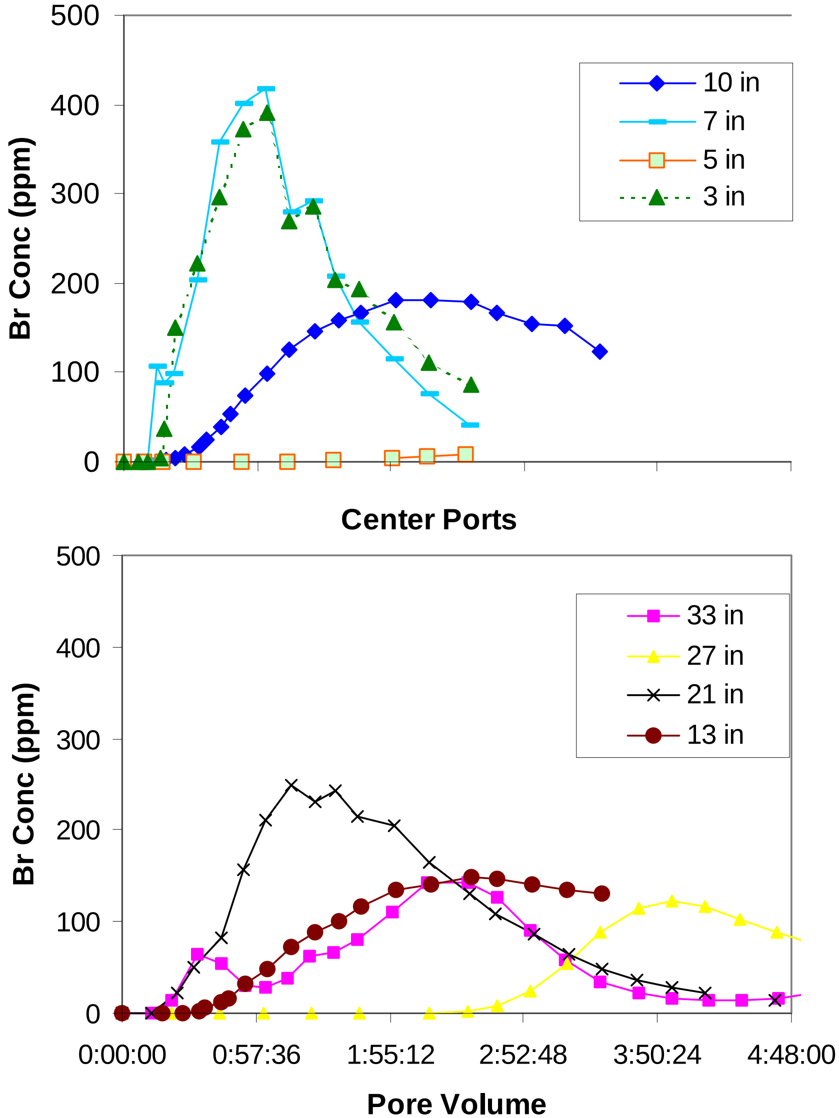


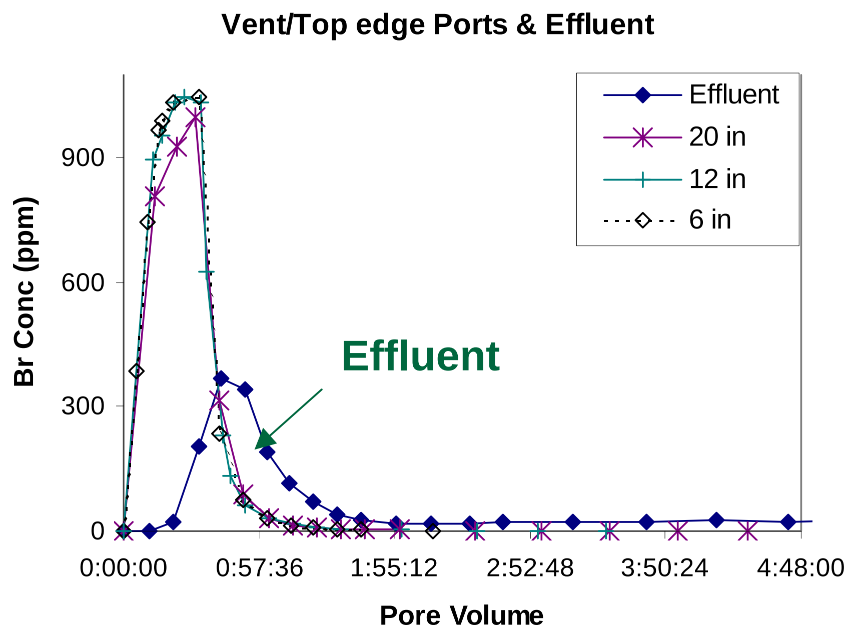
# Heterogeneity Development as shown in aqueous ionic profiles over time



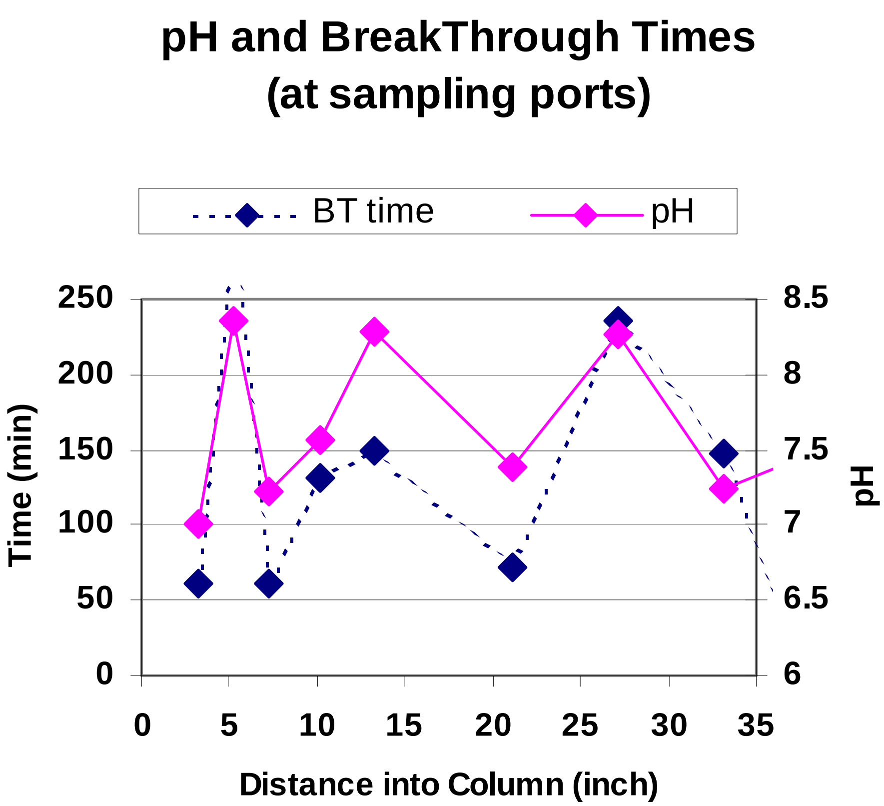



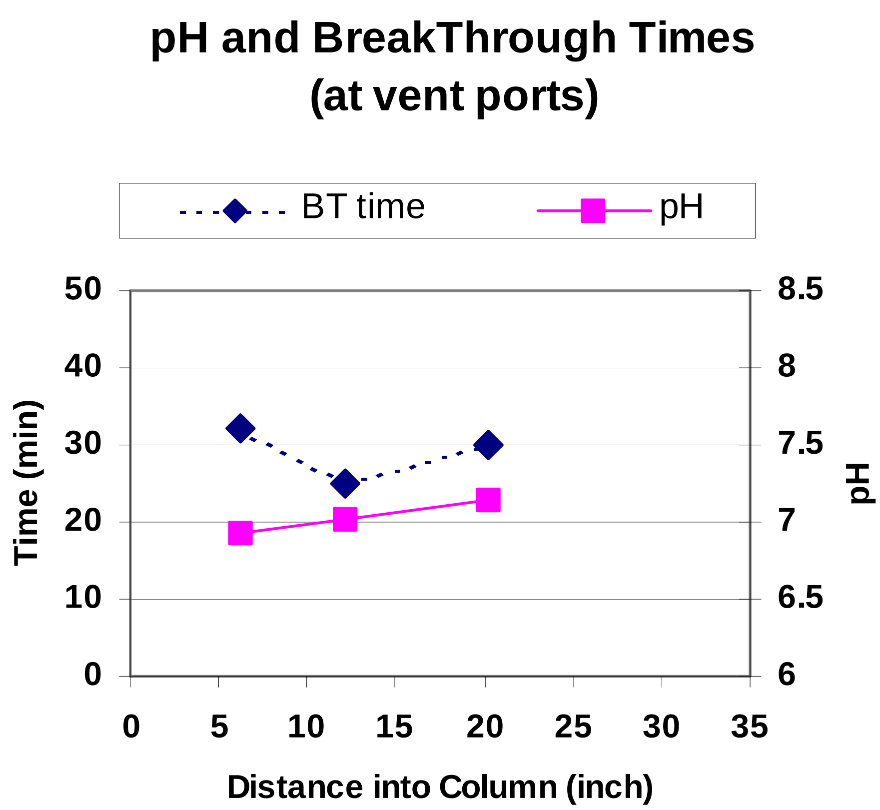
# Preferential flow paths reflected by comprehensive tracer test at Day 247.



# Correlation between pH and tracer breakthrough time



# Gas production

- **Collection and Quantification: Tedlar bags attached to the vent ports**
- **Composition: mainly nitrogen gas**
- **Minimal effect on the initial development of flow heterogeneity– the gas production was significant after the flow heterogeneity development.**
- **Nitrate reduction:**
  - **Abiotic** $4Fe^0 + NO_3^- + 7H_2O = 4Fe^{2+} + NH_4^+ + 10OH^-$
  - **Biotic** $5Fe^0 + 2NO_3^- + 6H_2O = 5Fe^{2+} + N_2 + 12OH^-$

# Precipitate mass and volume (from mass balance in aqueous phase)

**1) as $CaCO_3$ and $Fe_3O_4$**

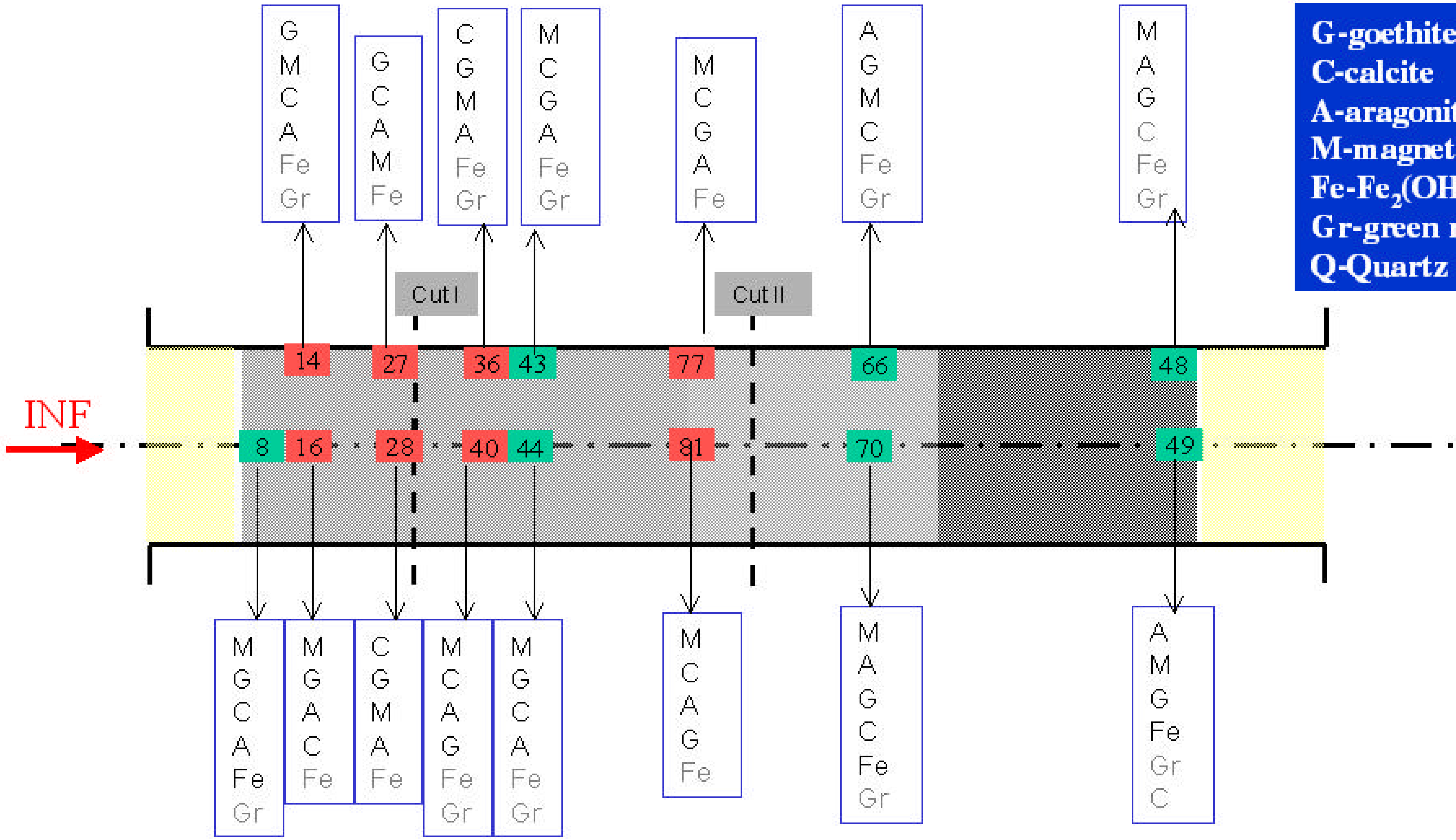
| Day | Total Weight (%) | | Total Porosity Loss (%) | | Corrosion rate |
|---|---|---|---|---|---|
| | (uniform, 30 in) | (20 in) | (uniform, 30 in) | (20 in) | mM/kg.day |
| 30 | 5.1% | 7.6% | 4.4% | 6.5% | 17.0 |
| 72 | 9.7% | 14.6% | 8.8% | 13.1% | 10.1 |
| 215 | 14.2% | 21.3% | 12.7% | 19.0% | 3.1 |
| 399 | 23.8% | 35.7% | 13.4% | 20.1% | 4.5 |
| 666 | 31.4% | 47.1% | 20.8% | 31.2% | 2.5 |

**2) as $CaCO_3$ and FeOOH**

| Day | Total Weight (%) | | Total Porosity Loss (%) | | Corrosion rate |
|---|---|---|---|---|---|
| | (uniform, 30 in) | (20 in) | (uniform, 30 in) | (20 in) | mM/kg.day |
| 30 | 5.7% | 8.5% | 6.3% | 10.5% | 17.0 |
| 72 | 10.8% | 16.2% | 12.4% | 20.6% | 10.1 |
| 215 | 15.8% | 23.7% | 18.0% | 29.9% | 3.1 |
| 399 | 26.4% | 39.6% | 18.4% | 30.5% | 4.5 |
| 666 | 34.8% | 52.2% | 28.4% | 47.1% | 2.5 |

# Column disassemble

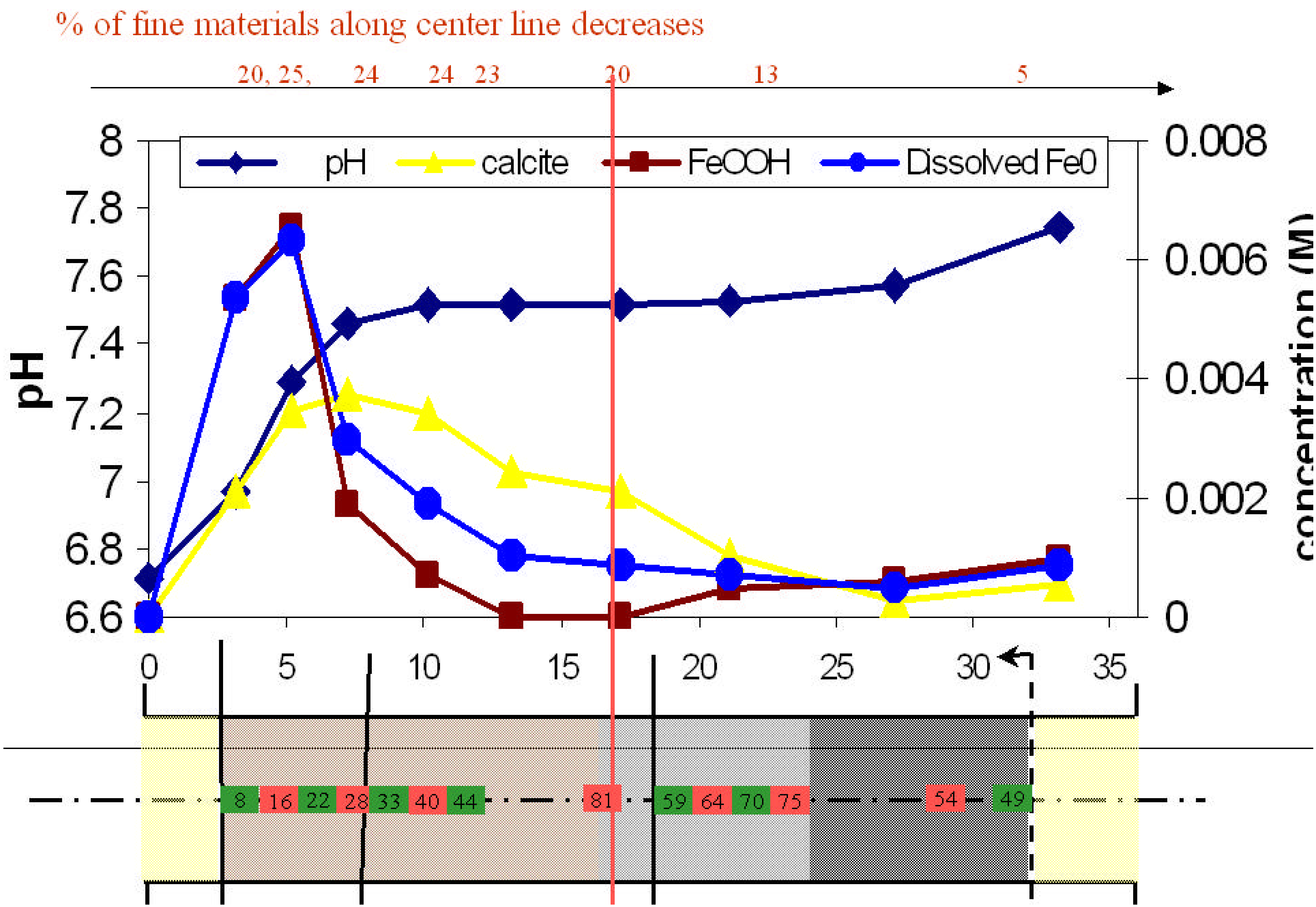
# Phase Identification (XRD)



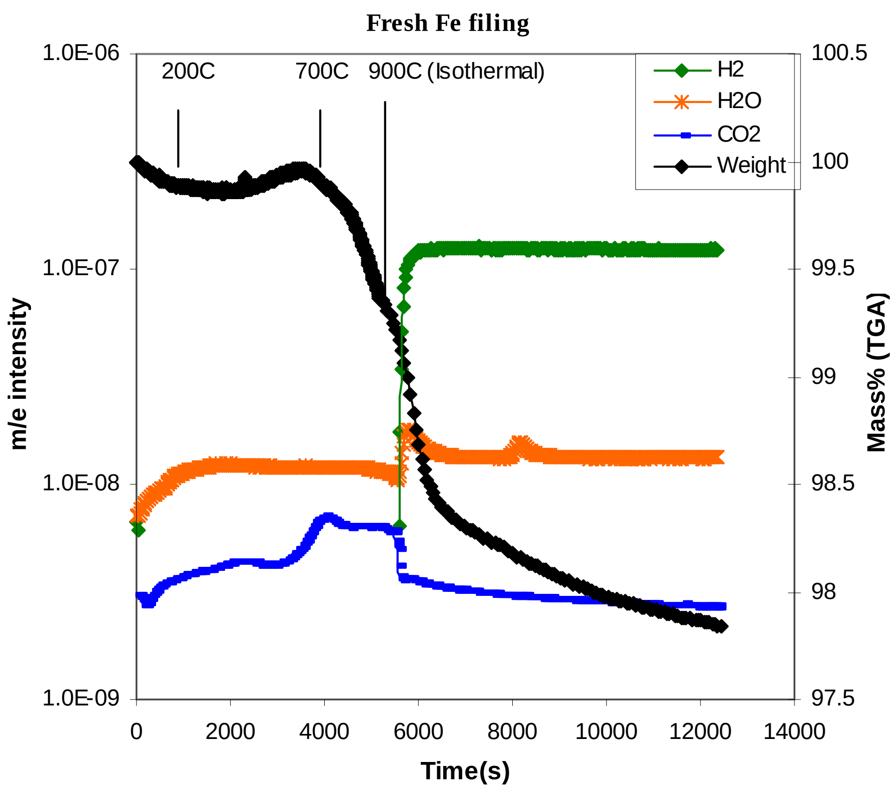

**G-goethite**
**C-calcite**
**A-aragonite**
**M-magnetite**
**Fe-$Fe_2(OH)_2CO_3$**
**Gr-green rust**
**Q-Quartz**

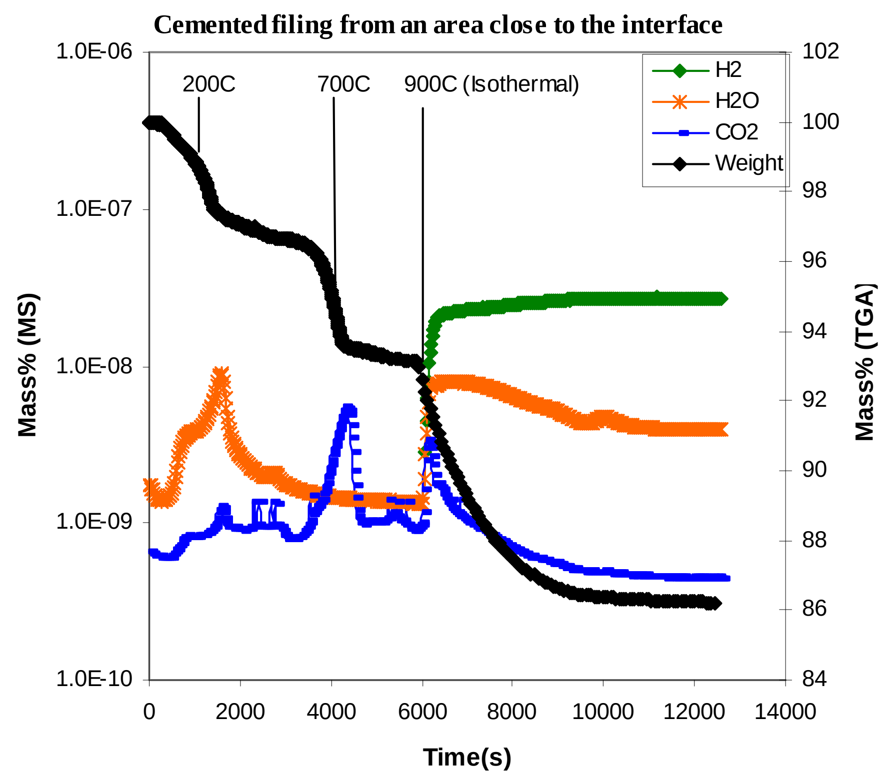
- Calcite decreases, while aragonite increases along the column
- Goethite along upper boundary, magnetite along center line

# Equilibrium dissolution of Fe (0)



# Quantitative analysis of precipitants (a new approach using TGA-MS)




**250-400C :** $2FeOOH = Fe_2O_3 + H_2O$

**~700C :** $CaCO_3 = CaO + CO_2$

**900C ($2\%H_2$) :** $3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O$

$Fe_3O_4 + H_2 = 3FeO + H_2O$

$FeO + H_2 = Fe + H_2O$

# Precipitate Mass and Corrosion Rate (TGA result)

| Iron | Precipitate mass (%) | | | Total precipiatate mass (%) | | Corrosion rate (mM/kg.day) | |
|---|---|---|---|---|---|---|---|
| | 600-800C | 900C (iso) | | | | | |
| | as $CaCO_3$ | as $Fe_2O_3$ | as $Fe_3O_4$ | as $Fe_2O_3$ | as $Fe_3O_4$ | as $Fe_2O_3$ | as $Fe_3O_4$ |
| **Fresh iron** | | 5.1 | 5.6 | 5.1 | 5.6 | | |
| **Influent** | 6.9 | 23.5 | 25.5 | 30.4 | 32.4 | 5.3 | 5.9 |
| **Mid-span** | 16.7 | 19.8 | 21.4 | 36.4 | 38.1 | 5.1 | 5.8 |
| **Effluent** | 4.5 | 16.8 | 18.2 | 21.3 | 22.7 | 3.5 | 3.9 |

# Conclusion

- **A comprehensive field column study over two years shows:**
  - Heterogeneity development due to precipitation of mineral phases. Gas production and microbial activity have minor contribution to the process
  - Flow heterogeneity development is expected within 1 year in the PRB subjected to the same water characteristics.
  - pH is a good indicator on hydraulic flow distribution when Fe(0) maintains its reactivity
  - Aqueous chemical sampling is a good way to assess the extent of precipitation (instead of coring and solid phase analysis)
  - TGA proves to be a good methodology to quantify major phases in precipitants, calculate corrosion rate of iron.
- **Couple the quantitative result with geochemical and hydrological model—description of in situ PRB performance.**
- **The scaling from field column to in situ barrier is underway. A preliminary assessment show that the extent of clogging as seen in the accelerated flow column would occur in in-situ PRB in 20 years, with heterogeneous distribution**
- **Contributed to key findings in a document on long-term performance monitoring of PRBs collaborating with DoD and EPA**