Impacts of $CO_2$ on indigenous microbial populations and implications for groundwater quality

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Outline

• Introduction
• CCS and microbes
• Microbiological impacts
• Physical impacts
• Impacts on CO$_2$ containment and groundwater
• Chemical impacts – an assessment approach
• What does this mean to risk assessments?
Introduction

- Microbes live in many subsurface environments (biofilms)
- Mass of subsurface microbes may exceed the mass of biota on the Earth’s surface
- Microbes will exist in geological settings relevant to CCS
- Growth and activity constrained by nutrient and energy supplies which can be introduced
- Microbes can also be introduced...

Microbes in biofilms on disused mine wall
Ways to inject microbes and nutrients/energy into the deep subsurface...

Drilling muds
Each CO$_2$ migration scenario will also impact on indigenous microbial populations...
CCS and microbes

• Unlikely to survive supercritical CO₂
• Many will survive and thrive in contact with CO₂ gas or dissolved phases generating biofilms
• CO₂ movement would generate a slow moving redox front
• CO₂ alteration of groundwater pH will change population makeup

Microbial cells on fresh framboidal pyrite. Biofilm filaments also visible (Courtesy A E Milodowski, BGS)
CCS and microbes

- CO₂ can act as an oxidant (energy source) by methanogens in strongly reducing conditions
- ? Impact of microbial methanogenesis and associated oxidation of minerals eg sulphides
- Effects of impurities eg H₂S, SOₓ, NOₓ?

Microbial cells on fresh framboidal pyrite. Biofilm filaments also visible (Courtesy A E Milodowski, BGS)
Study sites – Potential CO₂ storage sites in Germany within the “North German Basin” as model sites for research – includes microbiology
Background and Motivation

Hypothetical effects of CO$_2$ in the system*

- pH variation
- toxic/non toxic compounds
- availability of nutrients

Adaptation of the community

- cell number
- metabolic activities
- community composition

Characterization of microbial activities and community composition in potential reservoirs and the effect on industrial CCS application

What does this mean?

- **Physical impacts** – alteration of porosity impacting on injectivity/transport of CO$_2$/Corrosion/biodegradation of structures (e.g. Ketzin)

- **Chemical impacts** – change in pH; redox conditions -> intracellular or extracellular mineral formation/degradation -> mobilisation of potentially harmful elements in groundwater

![CryoSEM image of rod-like cells and biofilaments in mudstone fracture](image1)

![Gallionella spp showing precipitated spiral iron minerals](image2)

![Redox front at Poços de Caldas, Brazil](image3)
Approach for evaluating microbial impacts on rock physical properties? Ketzin

Biological flow cell

Injected with microbes

Microbes and biofilms on pyrite grains

Analysis of core showing biofilm formation

No injection of microbes

Change in flow due to cycling of biofilm formation/breakthrough of fluid
Impacts of CO$_2$ on Biofilms

> Understand the interactions between CO$_2$ rich waters and biofilms in the deep subsurface using:

- Batch experiments
- Flow-through experiments under *in-situ* conditions with *D. geothermicum*
- Sandstone from Keuper aquifer in the Paris basin

*Desulfotomaculum geothermicum*  
(Dupraz et al., 2011)
Microbes and groundwater quality - background

• **Why?** – Regulatory frameworks require environmental impacts of CO$_2$ leakages to be assessed (e.g. EU Directive)

• Impacts of CO$_2$ (trace metal mobilisation) on groundwater ‘an unacceptable risk’ – GreenPeace

• IEA-GHG workshop (2008) defined focus of research in this area. Included examining impacts on groundwater

• US EPA guidelines for wells for CCS to protect groundwater
Microbes and groundwater quality - background

- Few field and laboratory data available (e.g. New Mexico NA, ZERT, EU RISCS project now started). Several reactive transport modelling studies mostly in US context.
- Mobilisation of trace metals is site specific (Lemieux, 2011). Transport of co-injected impurities into aquifers.
- Models do not consider microbes which CATALYSE GEOCHEMICAL PROCESSES.

Acid mine drainage – pyrite oxidation catalysed by *Thiobacillus spp*. 
Microbes and groundwater quality

- Microbial effects may be small or undetectable in initial period of storage
- Many reactions will become autocatalytic e.g. pipeline corrosion, underground construction (Ketzin)
- Effects of CO$_2$ injection needs to be evaluated (precautionary principle)
- Use of CO$_2$ and waste stream impurities as microbial energy source can be assessed using a chemical thermodynamic approach
Chemical impacts - Thermodynamic approach for evaluating microbial activity in CO\(_2\) injection streams

- Redox half reactions can be used.
- Pyrite oxidation (by microbes) can be coupled to CO\(_2\) reduction
- Impurities in injected CO\(_2\) can also be coupled to CO\(_2\) reduction
- Other redox half reactions could also be considered e.g. impurities such as oxygen coupled to pyrite oxidation to assess overall energy availability

**The technical stuff**

**CO\(_2\) reduction**

\[ CO_{2(aq)} + 8H^+ + 8e^- \rightarrow CH_4(aq) + 2H_2O \]

where the free energy of reaction per electron consumed is:

\[ \Delta G_r^{1e} = [\Delta G_r^{ss} + 8RT\ln(10)pH + RT\ln(10)(aCH_4/aCO_2)]/8 \]

**Pyrite oxidation examples**

\[ FeS_2 + 10H_2O \rightarrow FeOOH + 2SO_4^{2-} + 19H^+ + 15e^- \] (3)

where the free energy of reaction per electron produced is:

\[ \Delta G_r^{1e} = [\Delta G_r^{ss} + 19RT\ln(10)pH + 2RT\ln(10)\log(aSO_4^{2-})]/15 \] (4)

\[ FeS_2 + 2H_2O \rightarrow FeOOH + 2S^0 + 3H^+ + 3e^- \]

where the free energy of reaction per electron produced is:

\[ \Delta G_r^{1e} = [\Delta G_r^{ss} + 3RT\ln(10)pH]/3 \]
Chemical impacts - Thermodynamic approach for evaluating microbial activity in CO$_2$ injection streams

- Free energy of some impurity half reactions and CO$_2$ reduction half reaction at STP
- SO$_2$ oxidation can be coupled to CO$_2$ reduction above pH 3
- Methanogenesis and drop in pH
- Approach can be used for site-specific evaluations on microbial activity/chemical impacts – NEXT STEP

(West et al GHGT10)
Conclusions

• Effects of CO$_2$ stream on indigenous microbes is an area of uncertainty
• Precautionary principle suggests impacts need to be quantified especially for groundwater quality
• Risks may only apply to certain geological settings and/or specific waste streams
• Microbial energetics approach can be used with existing data. Would also identify data gaps for...
• Generic experimental and field observations are needed
• Site specific assessments are likely to be needed (including existing and planned storage sites)