INL/CON-16-37988-Revision-0

Controlling the distribution of microbially induced calcite precipitation in the subsurface

Yoshiko Fujita, Robert W. Smith, Timothy S. Ginn, Tess Weathers, Mehrdad Bastani

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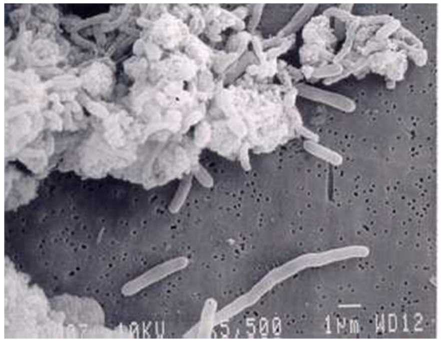
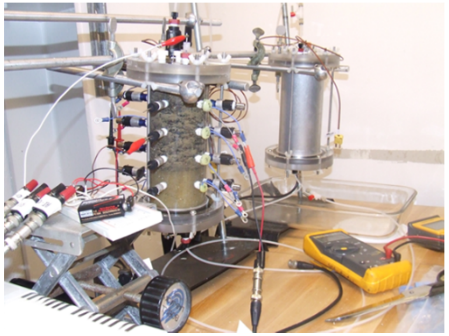
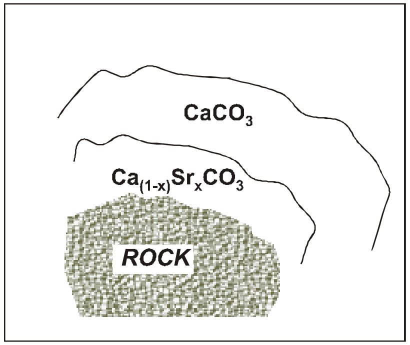


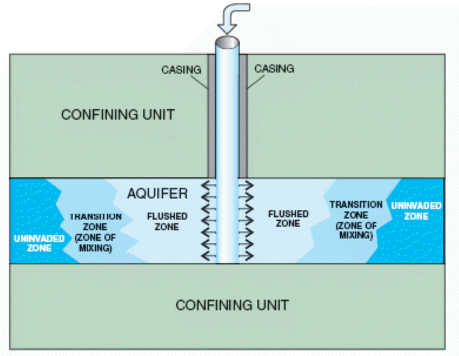


Potential applications of engineered precipitation in porous media

- Contaminant remediation (e.g., co-precipitation of ^{90}Sr in calcite, permeable reactive barriers)
- Permeability modification for energy resource or water recovery and management (including CO_2 sequestration)
- Consolidating geomedia by grain cementation

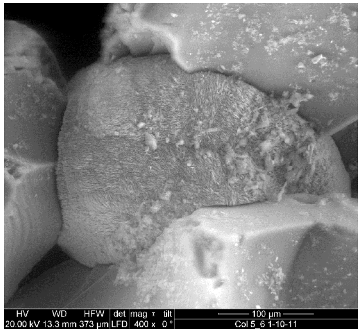
Formation of mixed Ca, Sr carbonate mineral phase.





Aquifer storage and recovery (Figure from USGS).

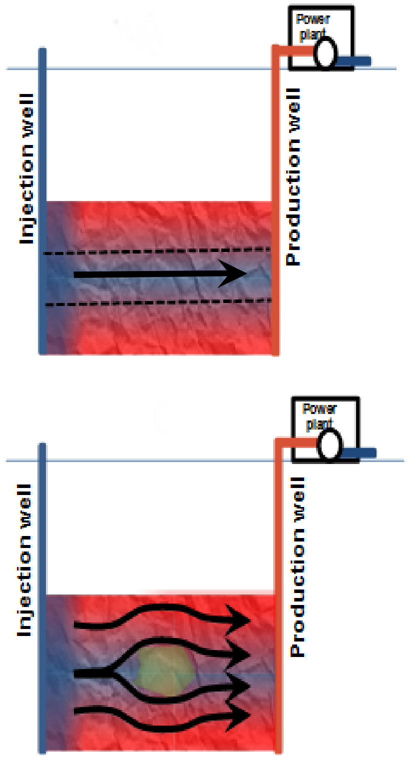
SEM image of $CaCO_3$ precipitated at grain contacts.



Given the intended purpose, how do we want to distribute mineral

- Uniformly throughout the subsurface volume?
  - Achievable for homogeneous medium?
  - Achievable for heterogeneous medium?
- Only at grain contacts, to increase consolidation of granular media (soil stabilization)?
- To create impermeable seals or zones at particular locations?
  - To encapsulate long-lasting contaminants in low permeability zones
  - To close off fractures and force longer residence times
  - To create impermeable caps over sequestered CO_2

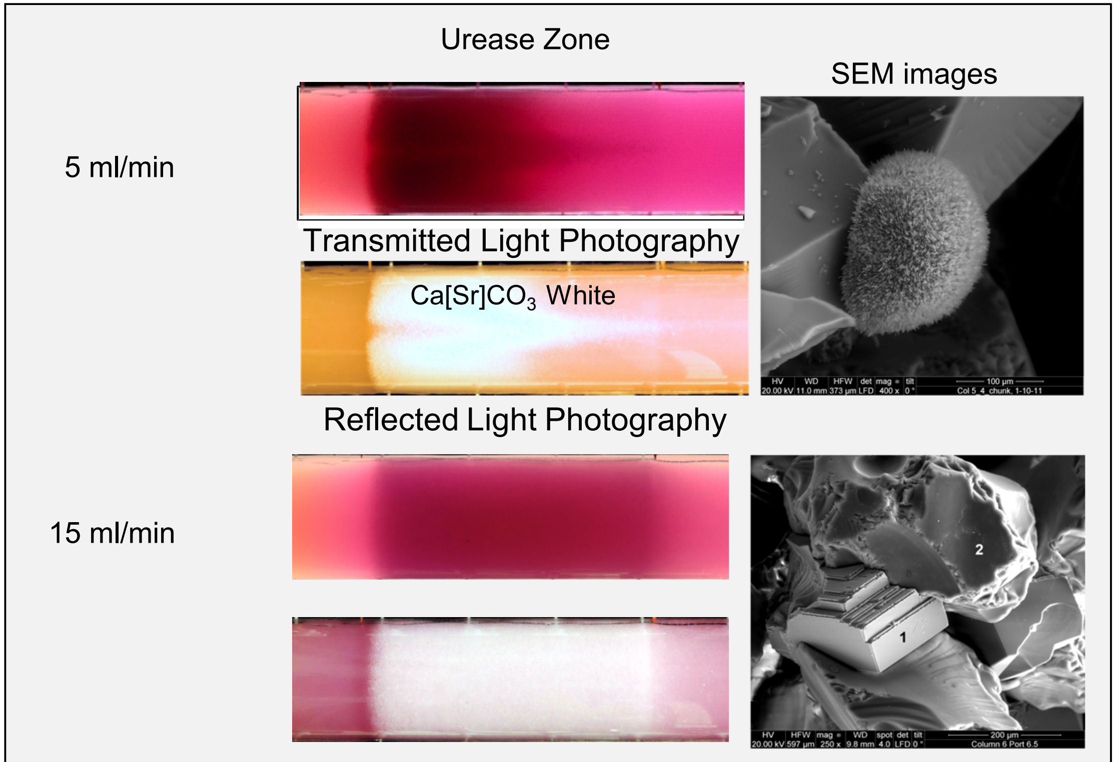
Example of how modifying permeability could prevent short-circuiting in EGS:



At depth, we have limited options

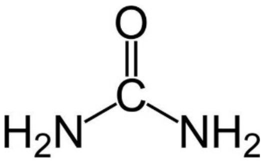
- We can manipulate:
  - Amendment introduction location(s),
  - Amendment introduction regimen,
  - Amendment composition (can include chemicals and or microbes)
- What we can't control well:
  - What other reactive agents (soluble or surfaces) or microbes are already in place and that can affect reaction kinetics
  - Transport (rate or path) of added constituents after injection—*but we may be able to impose temporary control of hydraulic boundary conditions.*

Example of transport effects:



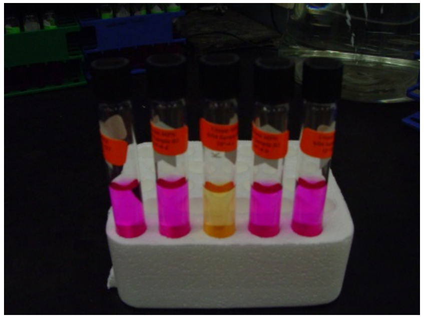
From Redden et al. (2014), *Environ. Sci. Technol.*, 48, 542-549.

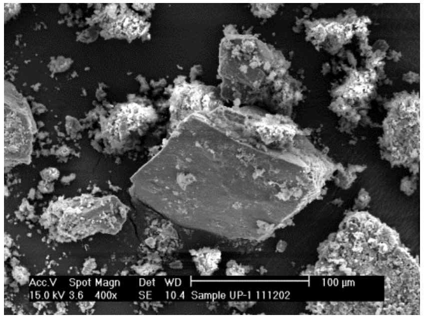
Some lessons from previous field experience with microbially induced calcite precipitation:



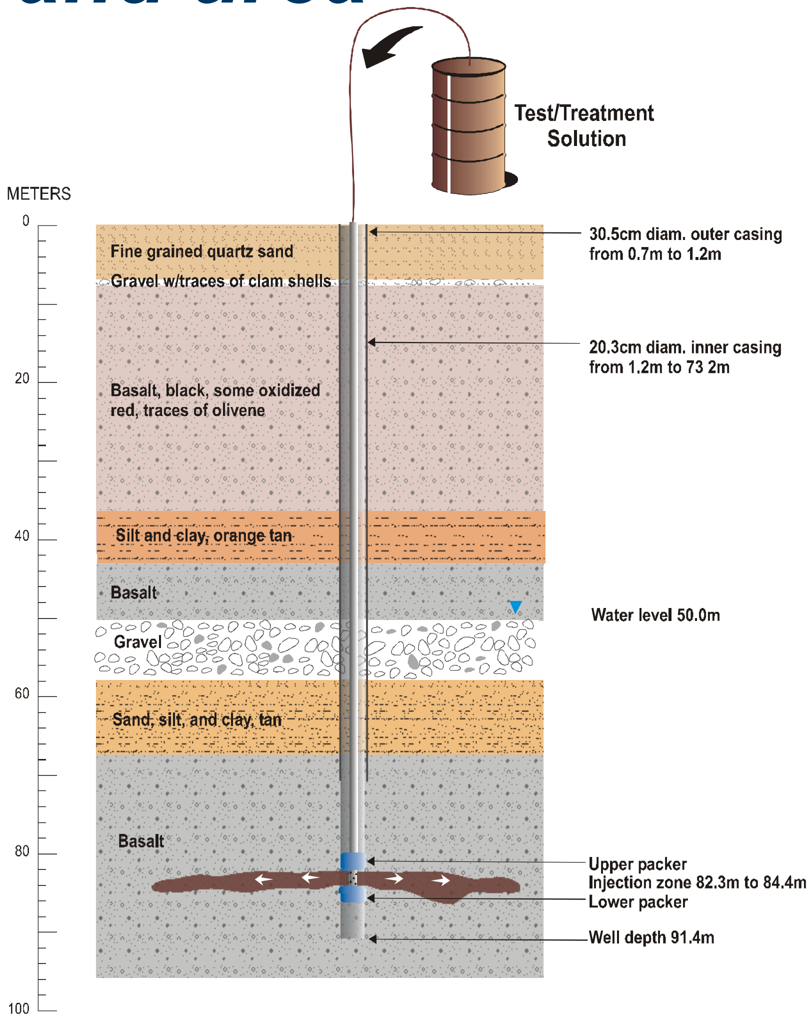
Urea

	$H_2NCONH_2 + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-}$	*Biotic*
	$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$	*Abiotic*
Net ppt.	--	
reaction:	$H_2NCONH_2 + 2H_2O + Ca^{2+} \rightarrow 2NH_4^+ + CaCO_3$	





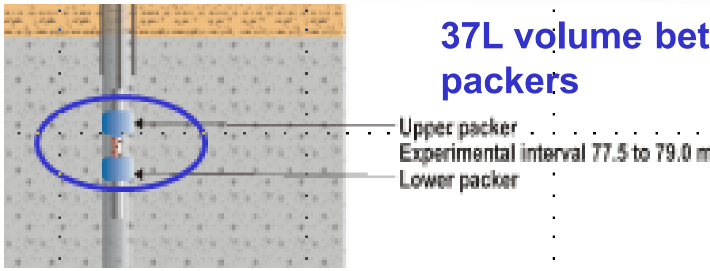
One well, separate injections of molasses and urea



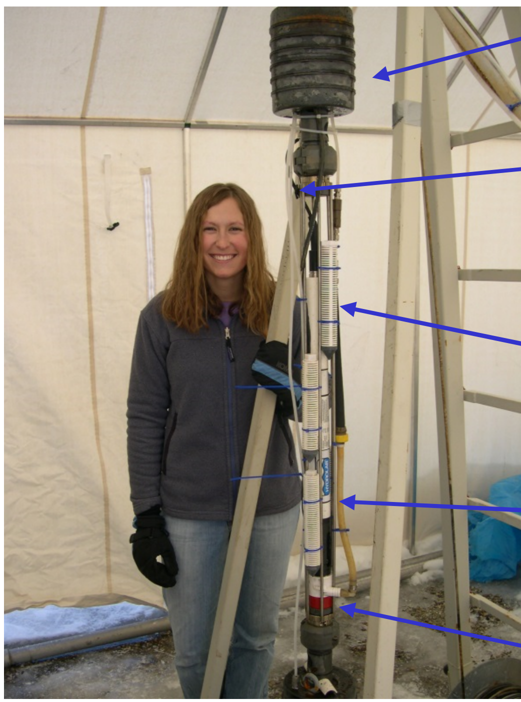
From Fujita et al. (2008), *Environ. Sci. Technol.* 42, 3025-3032.

- *Objective was to create bioactive zone around the well—"primed" system first with three injections dilute molasses (7.5 mg/L; 600-1500L), then added urea (50 mM, 600L).*
- *Within 24 hours of urea addition, well clogged and pump failed.*
- *Once bioactive zone is created, precipitation can be rapid and location depends on urea introduction.*

One well, assessments of attached activity



37L volume between packers



Inflatable packer (same at bottom)

Lines for amendment addition, sample withdrawal

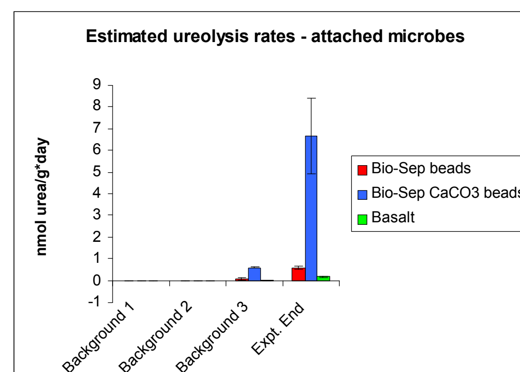
Slotted PVC canisters containing Bio-Sep beads or basalt

Hydrolab® (temp., pH, conductivity, Eh, D.O.)

Bilge pump for mixing in interval

Cheerful researcher willing to work during Idaho winter

- *Objective was to compare planktonic and attached activity.*
- *Daily low volume (250 ml) molasses for 7 days then molasses+urea for 7 days.*
- *Ureolysis rates for attached biomass 10X greater than water (volume basis).*



Multiple well experiment at Rifle, Colorado

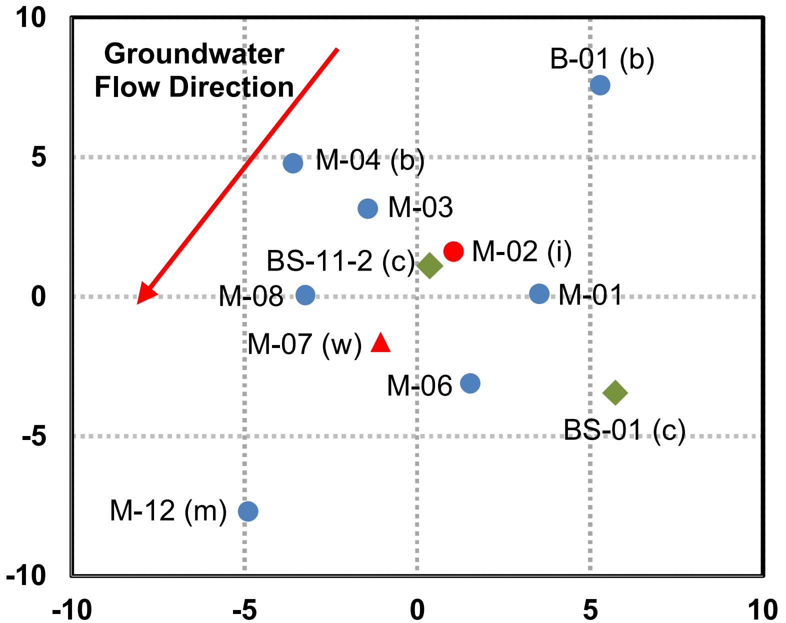
Experimental design assumptions:

- Attached indigenous microbes, capable of ureolysis.
- Must stimulate microbes and increase biomass before we see significant ureolysis activity.
- Hydraulic boundary conditions can be manipulated to create a localized, “well-mixed” reactor within which calcite deposition will be homogeneously distributed.

Rifle:

- Site of former uranium mill alongside Colorado River; tailings have leached U and other metals into sediments and aquifer
- Calcareous aquifer—already supersaturated with respect to calcite.
- Anaerobic system

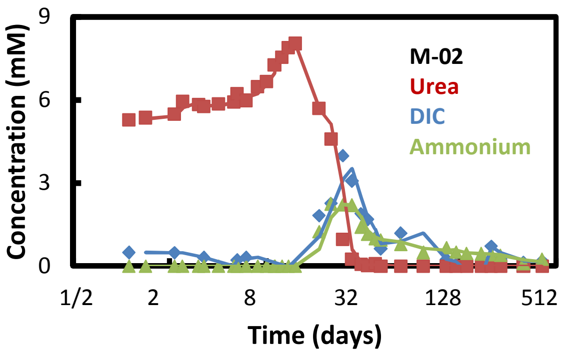
Rifle flow cell—recirculation for 12 days



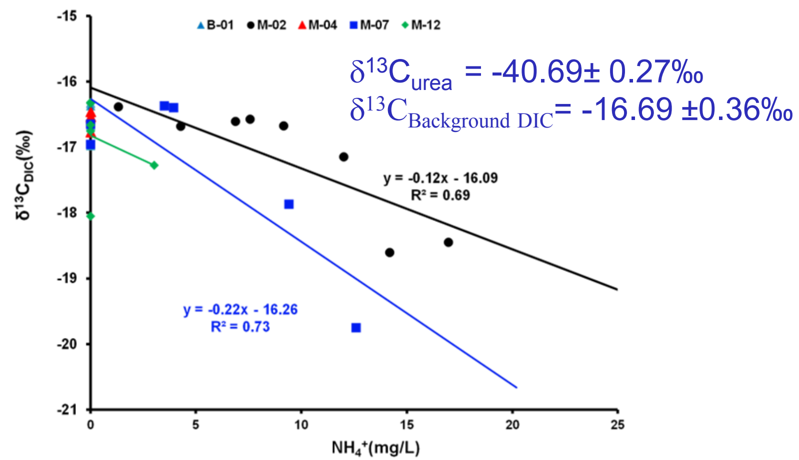
- Continuous two well recirculation experiment
  - 10.5 L min^{-1} (12 Days)
  - Recirculated 168,000 L
  - 42.5 kg Urea, 2.2 kg Molasses
- Extract from M-07 and inject in upgradient M-02
- Attached biomass collection
- Bromide tracer tests
- Geophysics tomography
- Long-term monitoring
  - Water sample collection
  - Hydrolabs
- Coring one year later
  - BS-11-2

Various indicators of ureolysis, and dominance of attached microbes

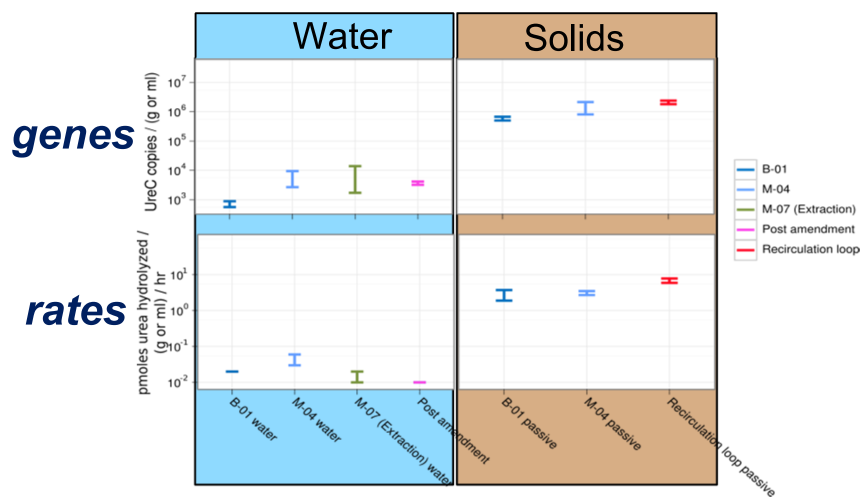
Disappearance of urea, appearance of ammonium:



δ^{13}C of DIC gets lighter as more urea hydrolyzed:



Both *ureC* gene numbers and ureolysis rates much higher for solids:

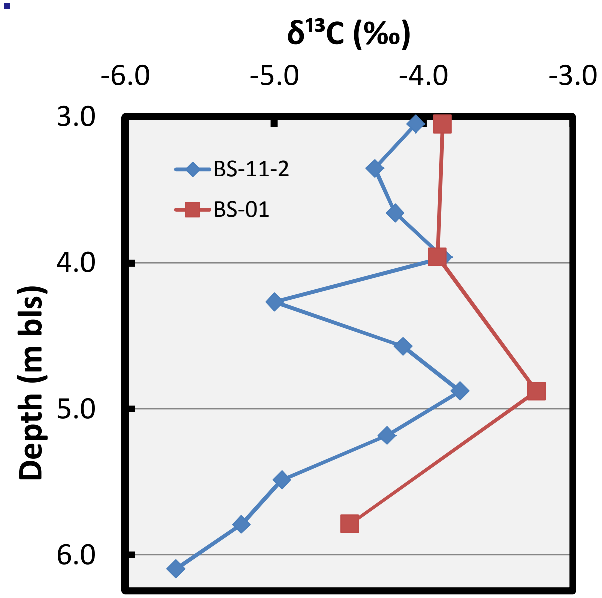


Various indicators of calcite deposition

Newly precipitated calcite difficult to detect directly:

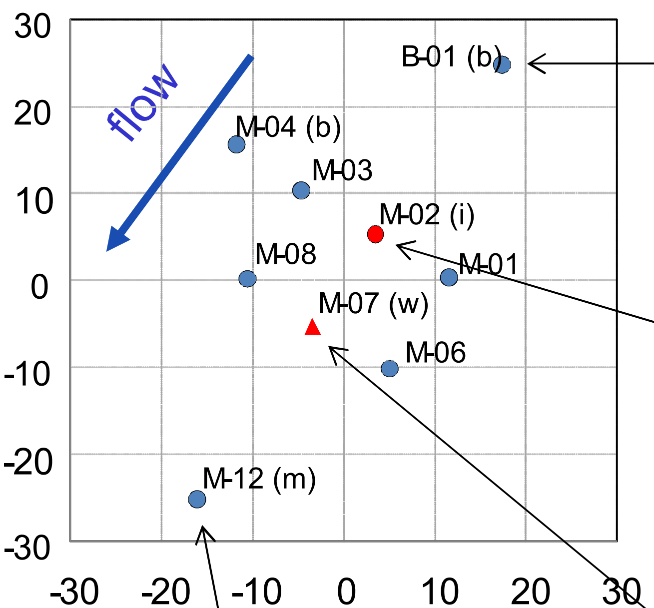
- Assuming complete conversion of added urea to calcite, total volume of new calcite 0.026 m^3, resulting in estimated 0.004% (v/v) increase in calcite in sediments.
- Background calcite at Rifle estimated at 0.6 to 2% (v/v).

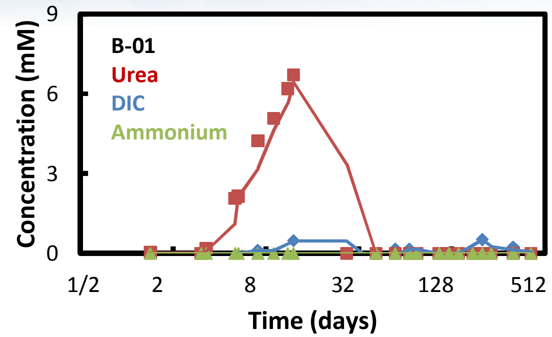
Post-injection core solid carbonate isotopically lighter:

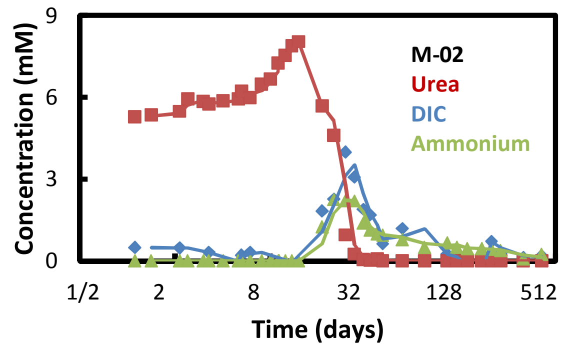


Depth to Sample (m)	Sediment Type
3.1	Sandy Cobble with some clay.
3.4	Sandy with some cobble. Traces of calcite.
3.7	
4.0	Sandy Cobble zone. Low amounts of calcite.
4.3	
4.6	Cobble dominated sandy zone with some reduced sediments. Medium amounts of calcite.
4.9	
5.2	
5.5	Highly reduced zone of cobble and sand zone. High amounts of calcite.
5.8	
6.1	

Reactive zone limited to recirculation zone

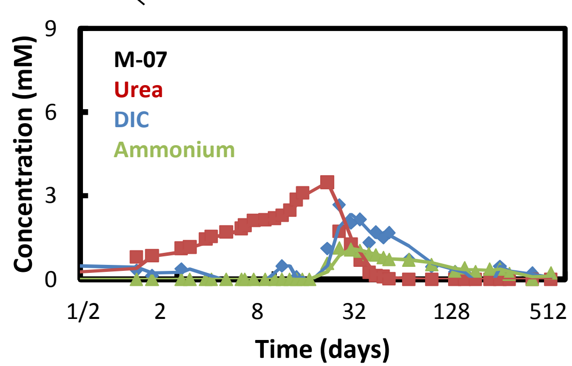


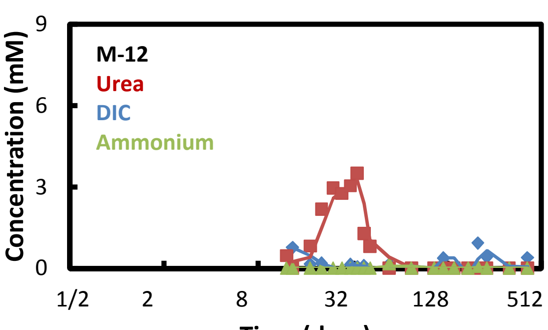


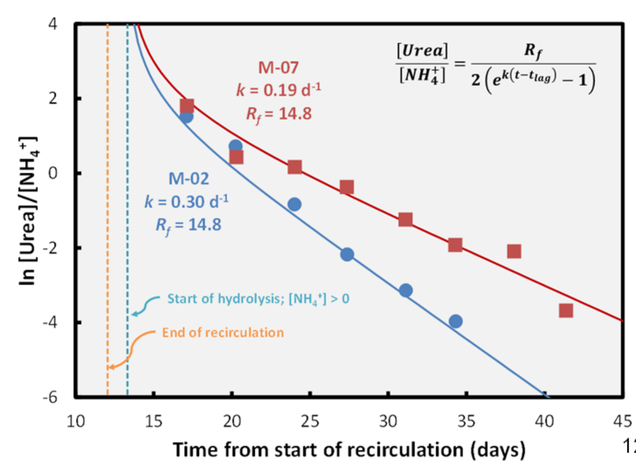


Ammonium never observed at B-01 or M-04.

Estimated 1st order ureolysis rate constants at M-02 and M-07 very similar; estimated lag time 13.3 days.

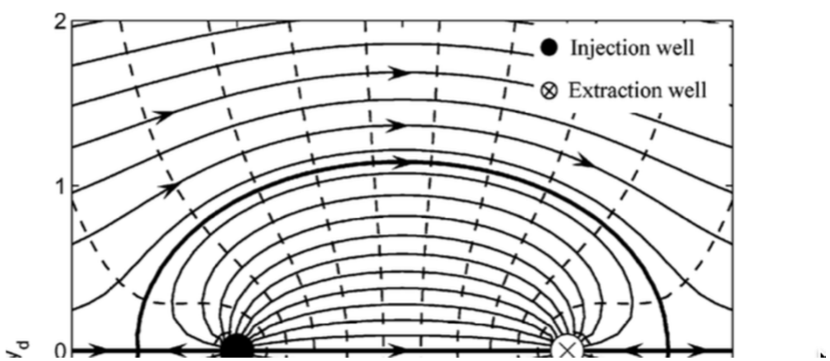




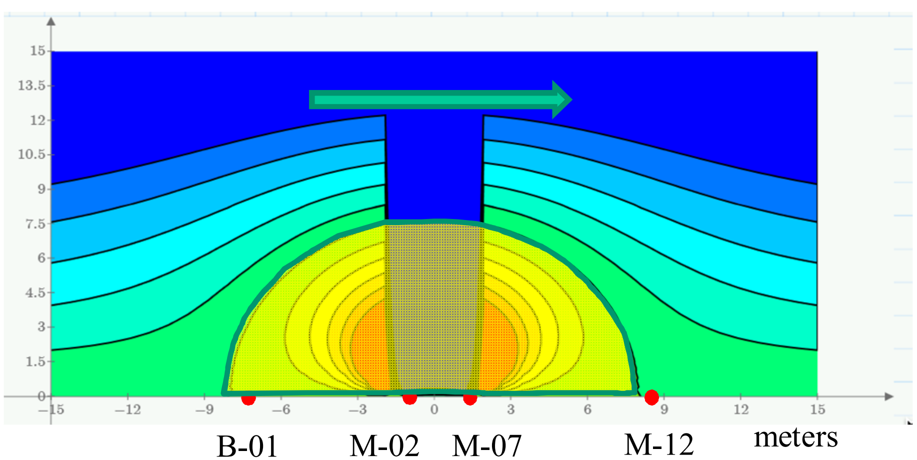


Mixing zone conceptual model

- Metabolic lag + recirculation allow assumption of mixing zone as batch reactor, 1st order kinetics.



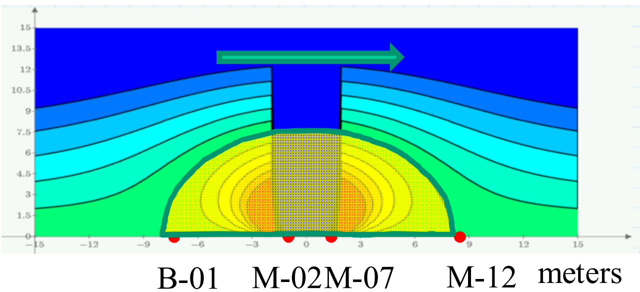
Charbeneau (*2000*)*; Luo and Kitanidis* (*2004*)

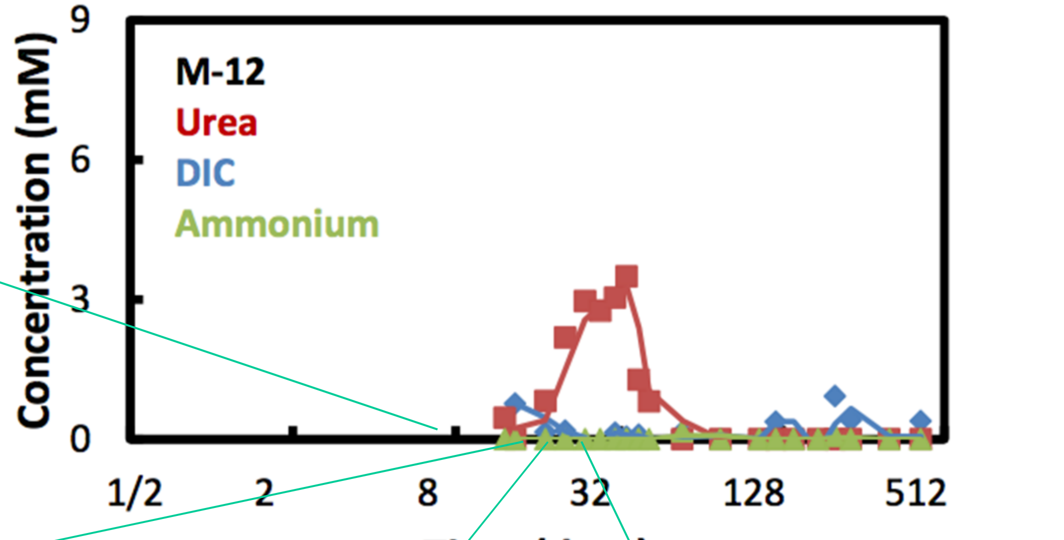


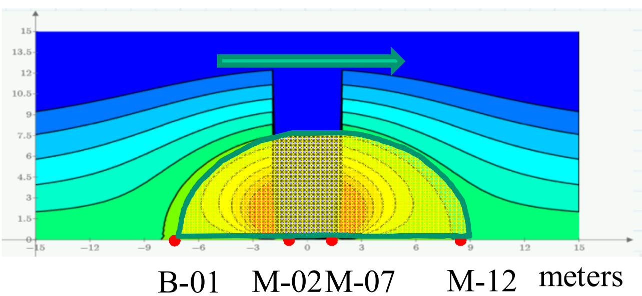
- Recirculation zone (half shown here in yellow) bounded by stream function contour $\Psi = 0$
- Water volume ~190 m^3
- Urea total = 42.5kg
- So, urea concentration at end of recirculation (before ureolysis) should be ~ 7mM
- Assume plume shifted upstream due to injection heterogeneity

Velocity 0.25m/d and b=2m gives homogenous C_{urea} of 7mM at end recirculation. C_{urea} measured at B-01 (7mM), M-02 (8mM), M-07 (4mM), M-12 (0mM)

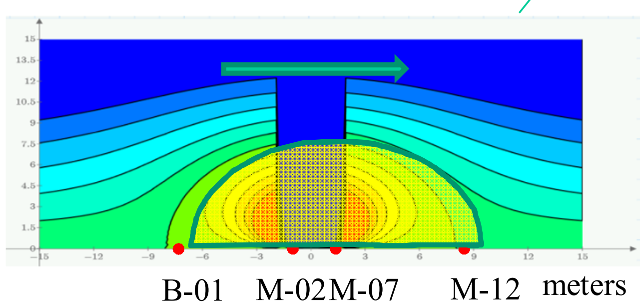
After recirculation ceased, urea “plume” moves downstream

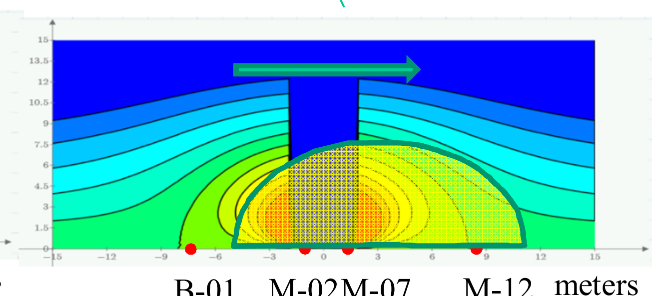






Assumed 99% of the microbes are attached and 1% are planktonic, moving with the plume. Therefore significant ureolysis only occurs within the original mixing zone., and though urea plume passes through M-12, no ureolysis.





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Conclusions

- Simultaneous injection of urea and molasses enabled us to take advantage of the metabolic lag time to widely distribute urea prior to development of a biologically active zone (BAZ).
  - BAZ consists primarily of attached microbes.
- Continuous recirculation allows us to control BAZ location; only wells within the recirculation zone exhibited significant ureolysis.
- Continuous recirculation also resulted in uniform reactive zone (similar rate constants).
  - ➢ *Shows promise as robust engineering technique for a* ***real (= heterogeneous)*** *medium.*

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Acknowledgments

- We are grateful to the countless colleagues who have contributed greatly to our MICP field research (especially Joanna Taylor, Mark Delwiche, James Henriksen, and Tsigabu Gebrehiwet for our Rifle experiment) and also to Phil Long, Ken Williams, Alison Montgomery and other members of the Rifle team.
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