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Method for the Determination of Residual Carbon Dioxide Saturation Using Reactive Ester Tracers

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TCCS-6 Trondheim (June 2011)

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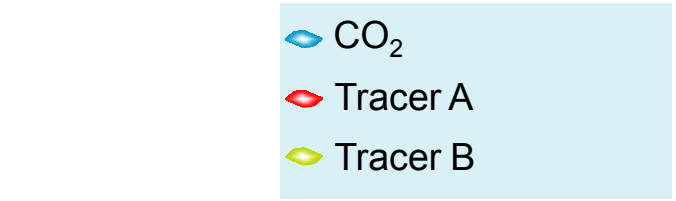
Outline

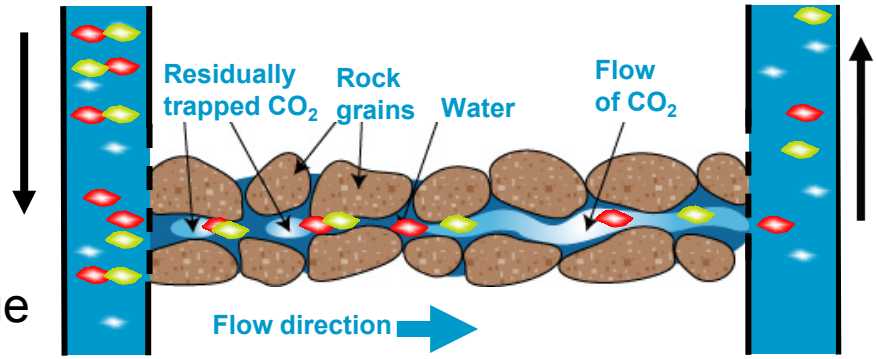
- Why use tracers?
- How tracers have been previously applied to CCS sites
  - Case studies from Frio and Otway
- Inert tracer behaviour
- Reactive tracer behaviour
- Proposed tracers and hydrolysis
- Laboratory determination of partition coefficients
- Computational modelling of reactive tracers vs. inert tracers for residual gas saturation
- Conclusions and ongoing work
  - Single well residual saturation test

    Otway Stage 2B (CO2CRC)

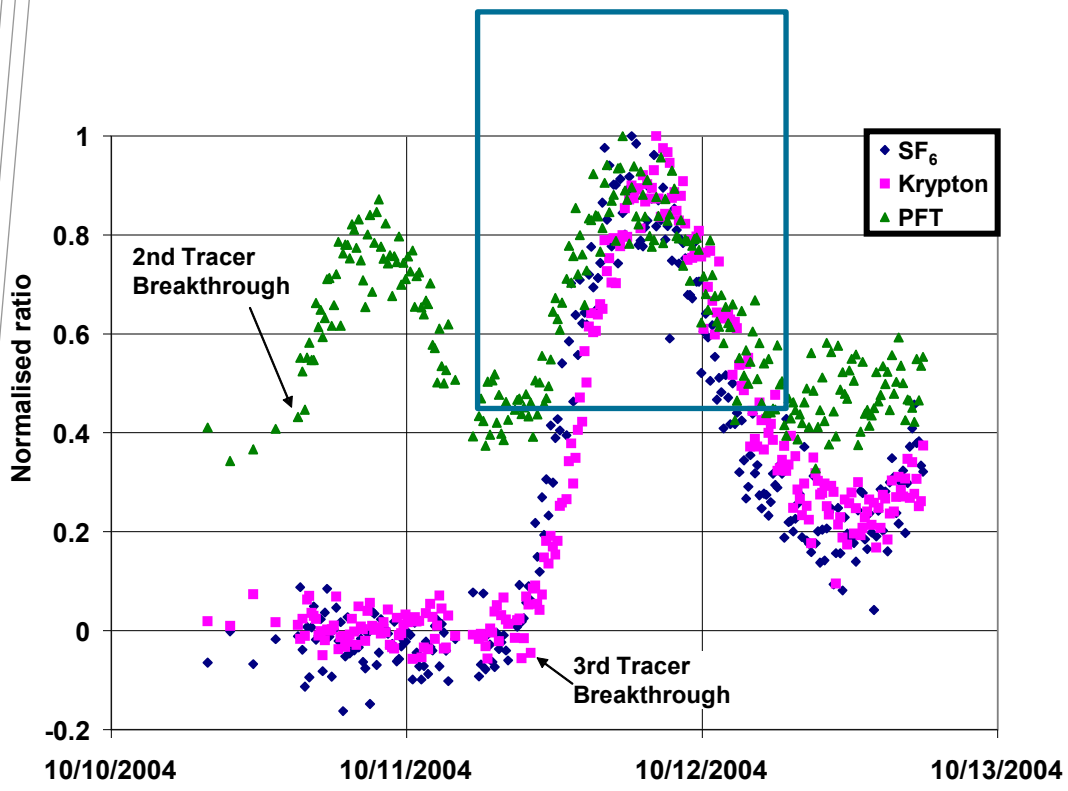
Why use tracers?

- Tracers can….
  - Verify the presence of injected CO_2
  - Confirm arrival at monitoring wells/demonstrate breakthrough
  - Show differences in behaviour in different sections of a formation
  - Assurance monitoring
    - overlying aquifers
    - soil gas
    - atmosphere
  - Potentially give information on storage capacity and saturation levels





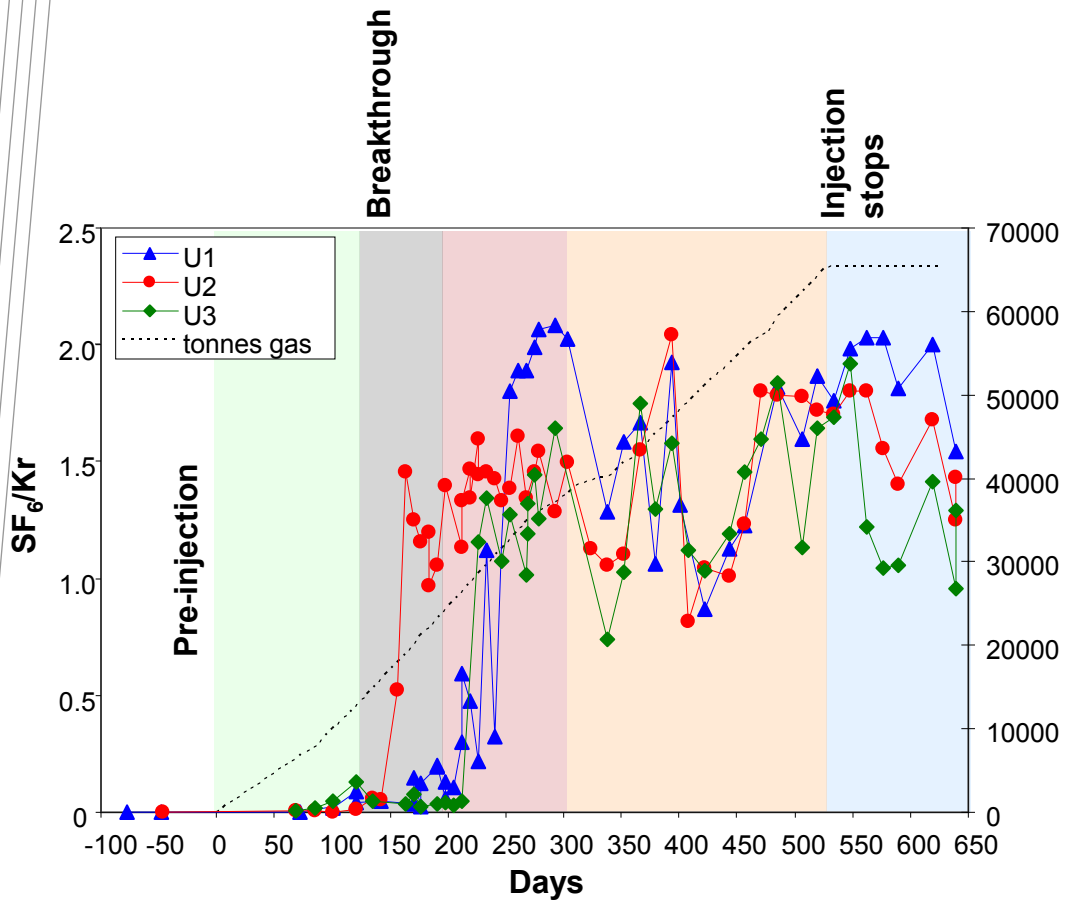
Case study – Frio Stage 1



From Freifeld et al., 2005

- Injection well to monitoring well
- 30 m distance
- 1500 m depth
- Arrival 51 hours
- Tracers used
  - Sulphur hexafluoride
  - Krypton
  - Perfluorocarbons
    perfluoromethylcyclohexane (PMCH)
    perfluorotrimethylcyclohexane (PTCH)
    perfluoromethylcyclobutane (PMCB)
    perfluorodimethylcyclohexane (PDCH)

Case Study – Otway

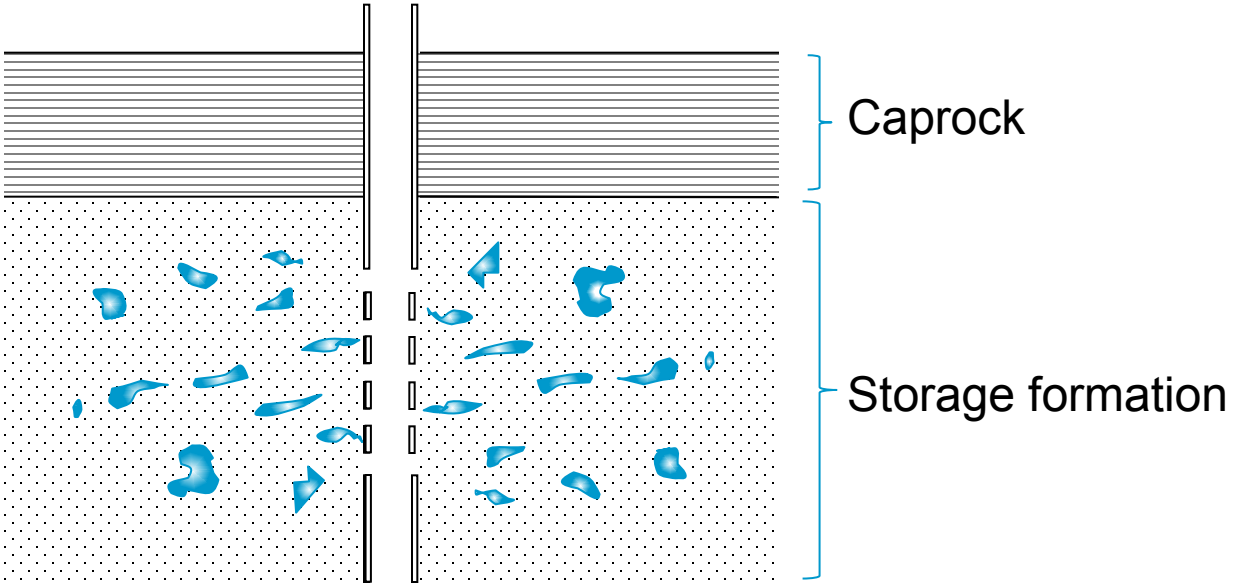


Data from Boreham et al., 2011

- Injection well to monitoring well
- 300 m distance
- 2000 m depth
- Arrival 101-121 days
- Tracers used
  - Sulphur hexafluoride
  - Krypton
  - Perdeuterated methane
  - 1,1,1,2-tetrafluoroethane

Single well test – Inert vs reactive tracers

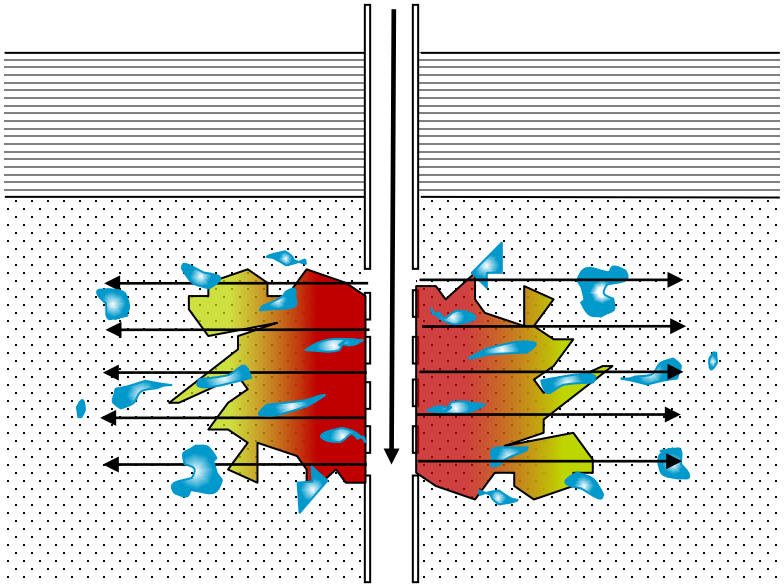
= residual CO_2

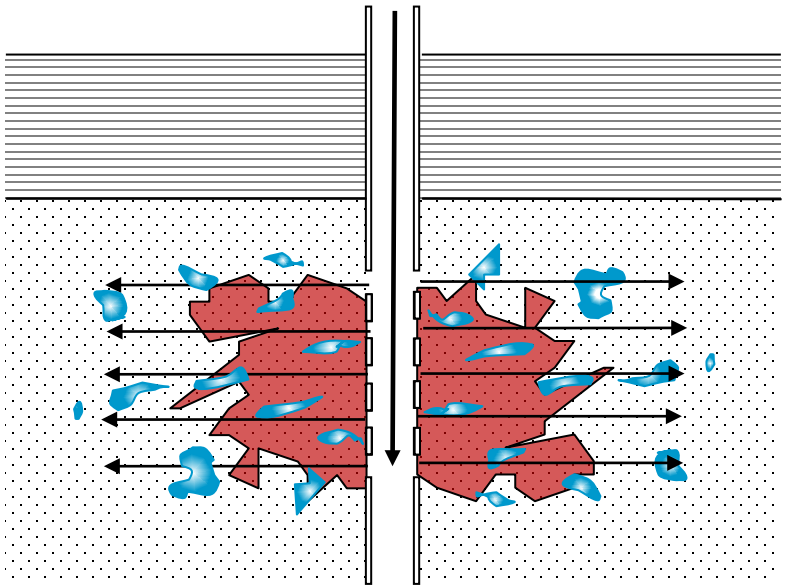


1. Tracer is injected with water and pushed out of the wellbore into the formation.
2. There it can partition between the water phase (where it is mobile) and the supercritical carbon dioxide phase (where it is stationary).
3. The velocity of the tracer in the formation is therefore dictated by the partition coefficient and the amount of residual CO_2 saturation.

Inert

Reactive





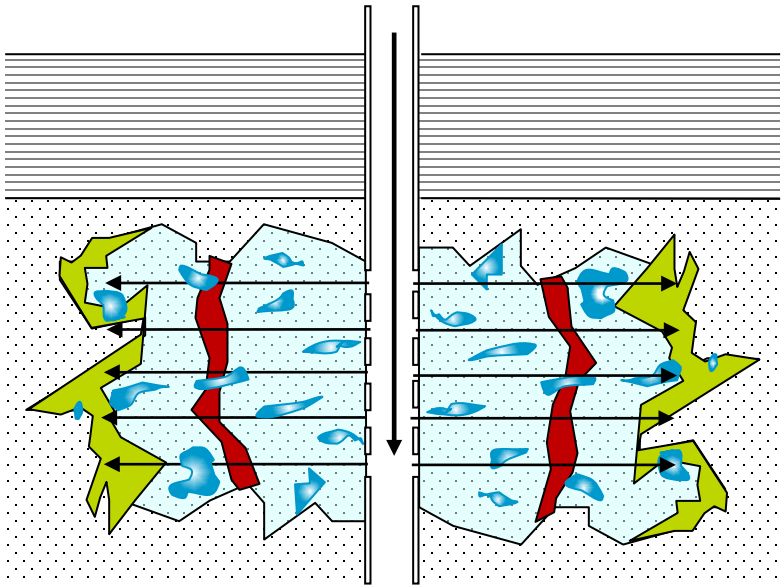
= Tracer 1: With higher partitioning coefficient into water (PC_{H2O})

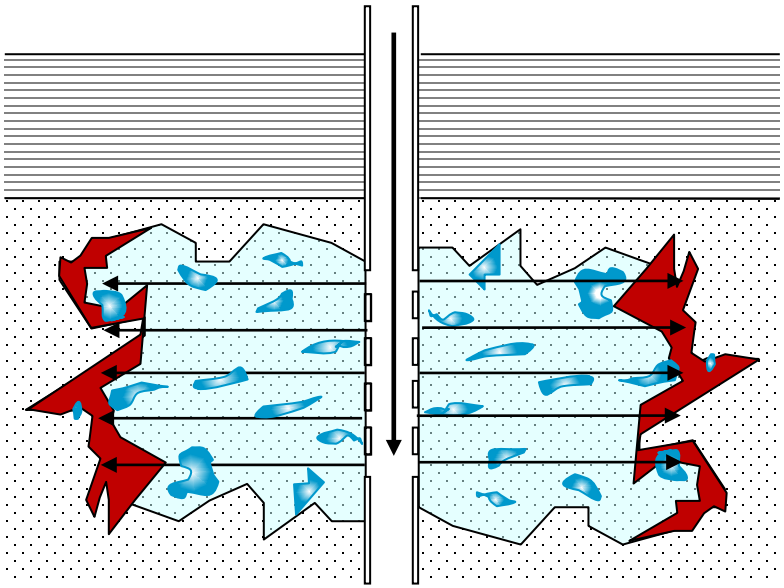
= Tracer 2: With higher partitioning coefficient into CO_2 (PC_{CO2})

= Parent tracer compound

Inert

Reactive





= Tracer 1: PC_{H2O}

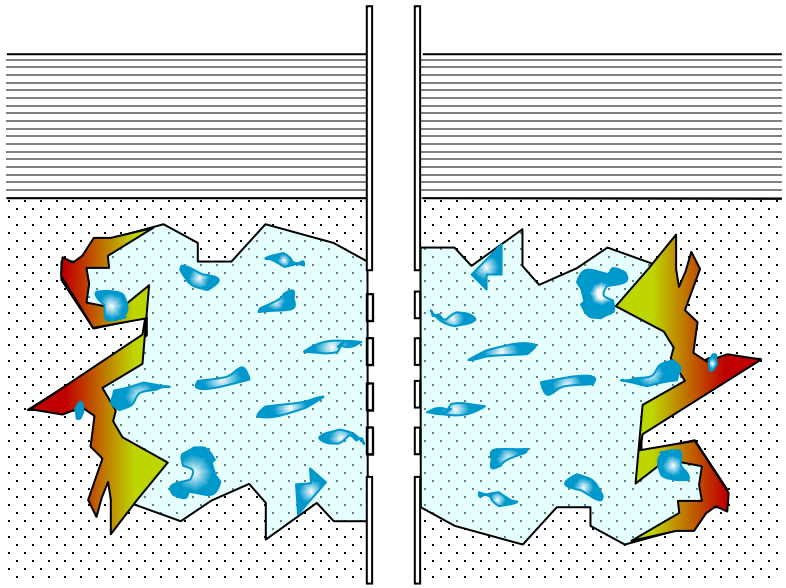
= Tracer 2: PC_{CO2}

= Parent tracer compound

Reactive

Reactive tracers require a “soak” time to hydrolyse. Some parent tracer will convert to multiple daughter products.

The daughter products have different functionality to the parent so have different partitioning properties.

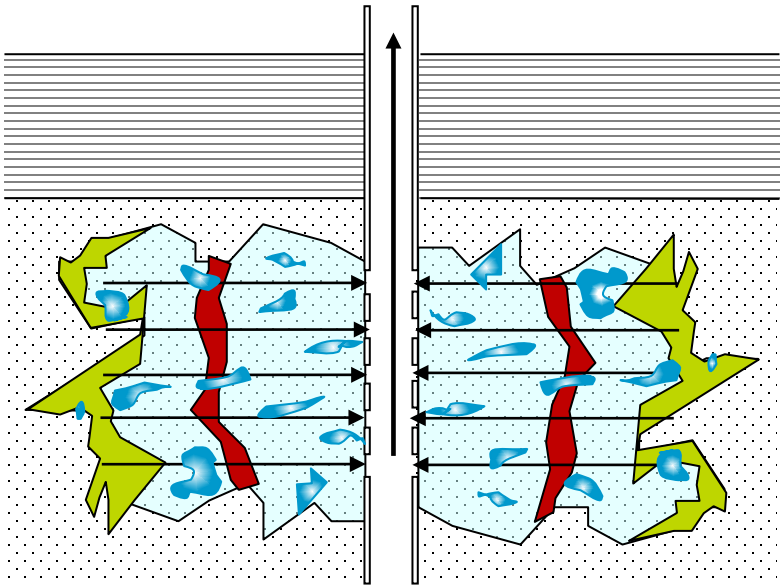


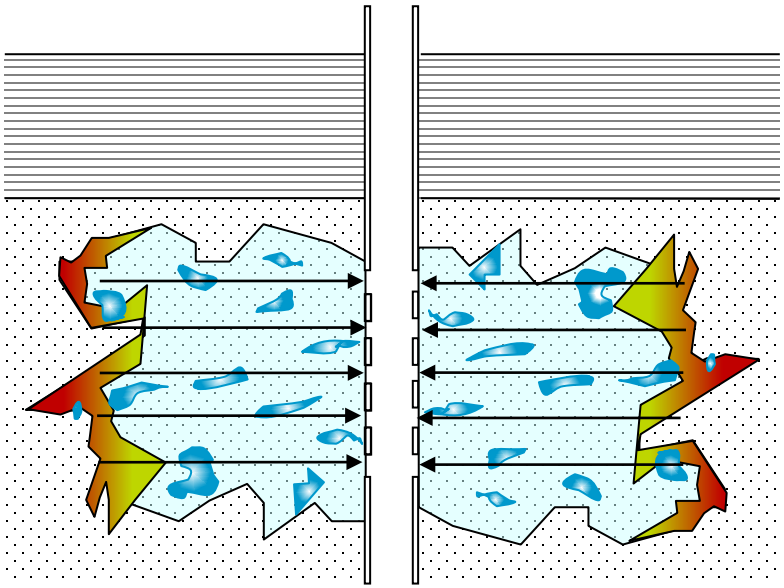
= Parent tracer compound

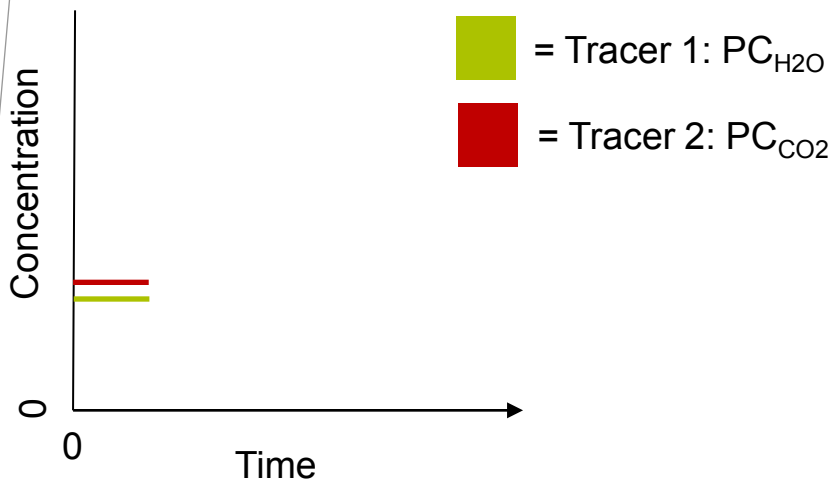
= Daughter hydrolysis compound(s)

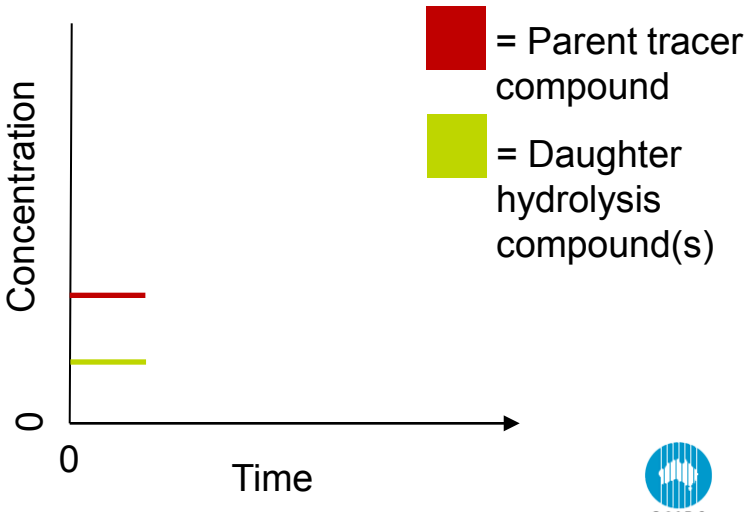
Inert

Reactive

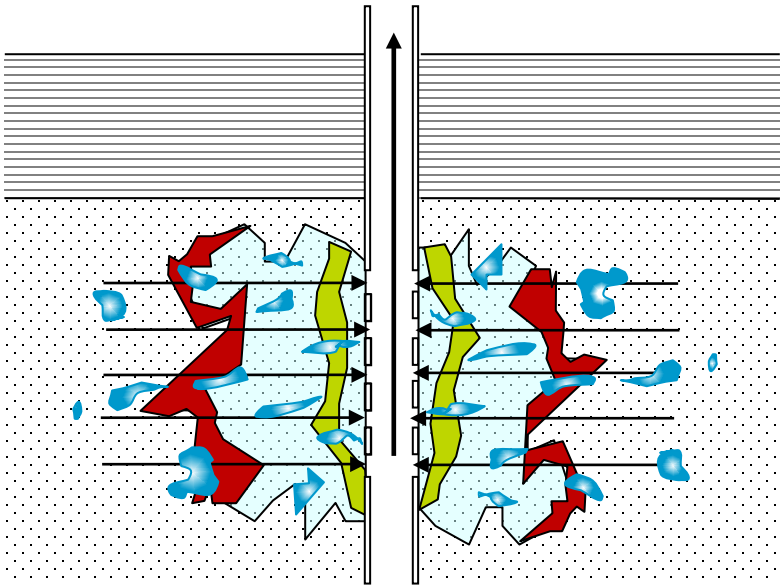


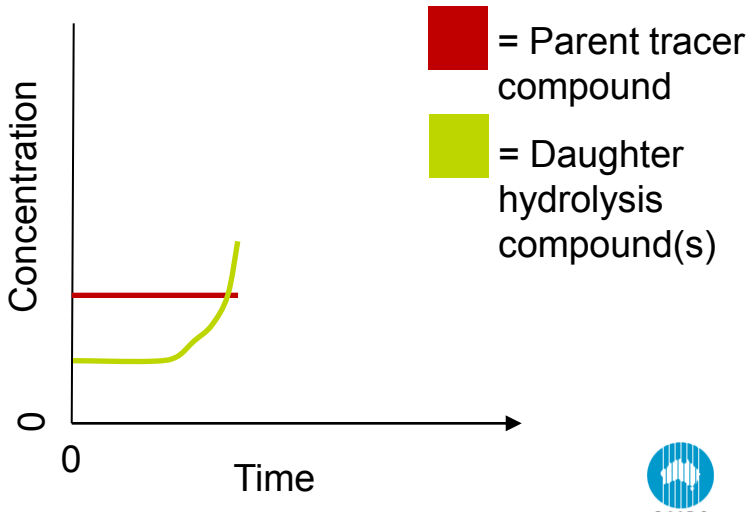






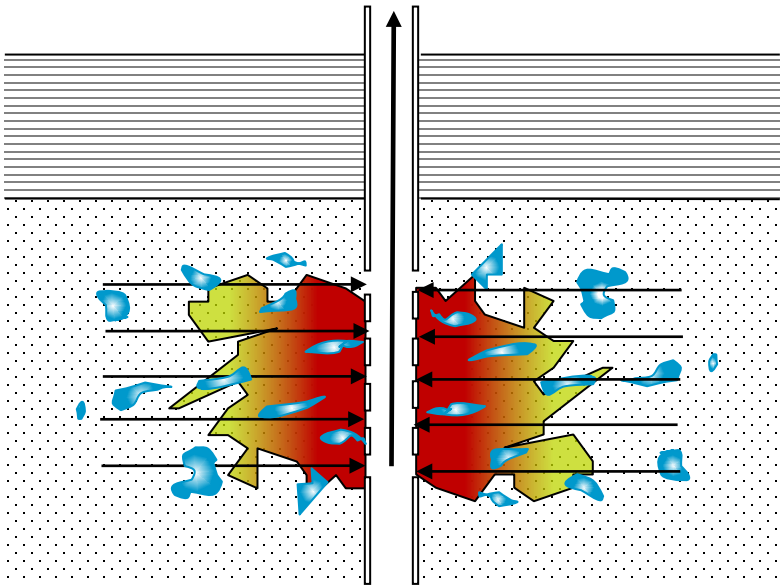
Reactive

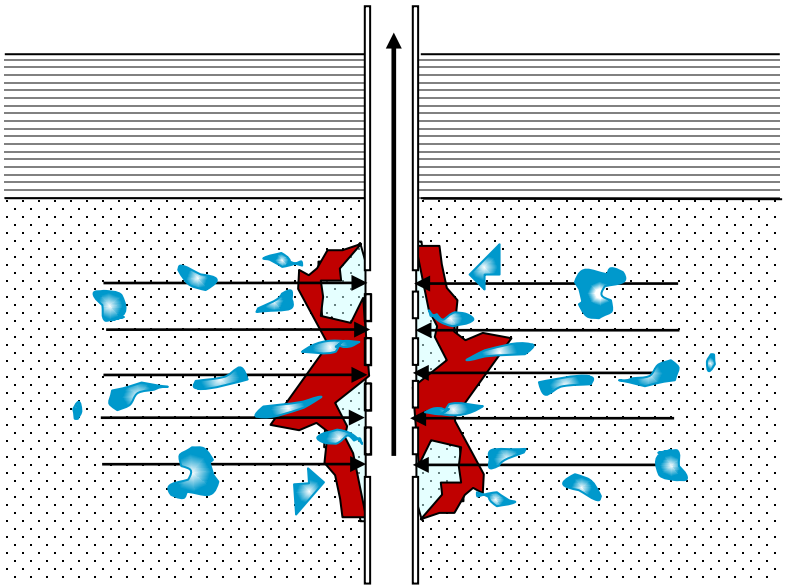


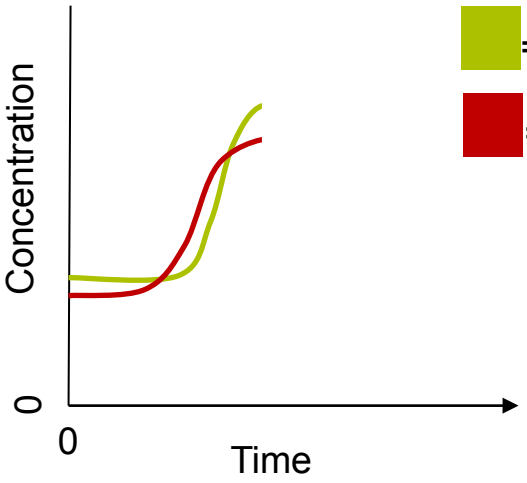

= Parent tracer compound
= Daughter hydrolysis compound(s)
Concentration
0
0
Time

Inert

Reactive

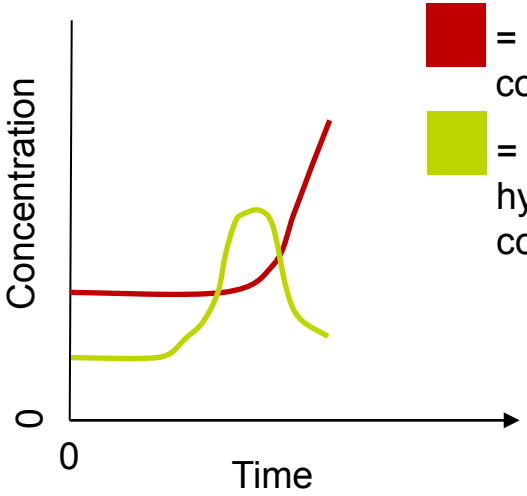






= Tracer 1: PC_{H2O}

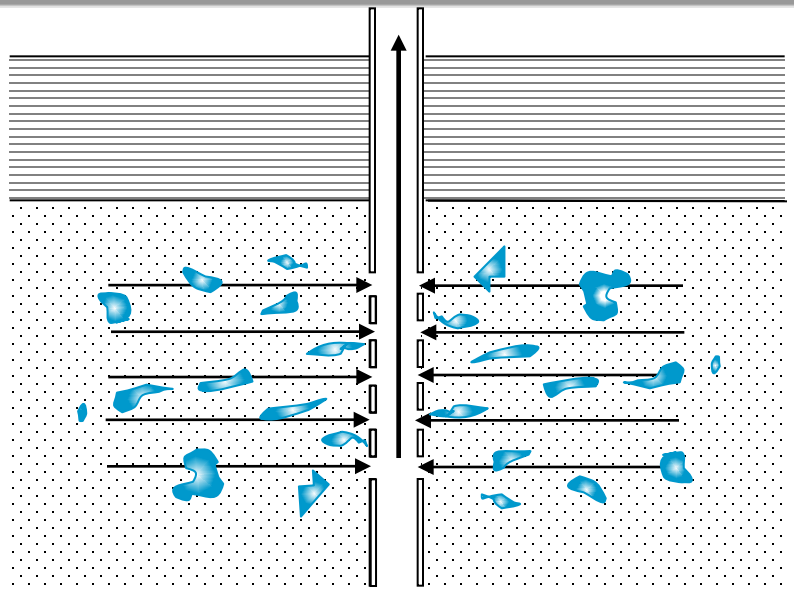
= Tracer 2: PC_{CO2}

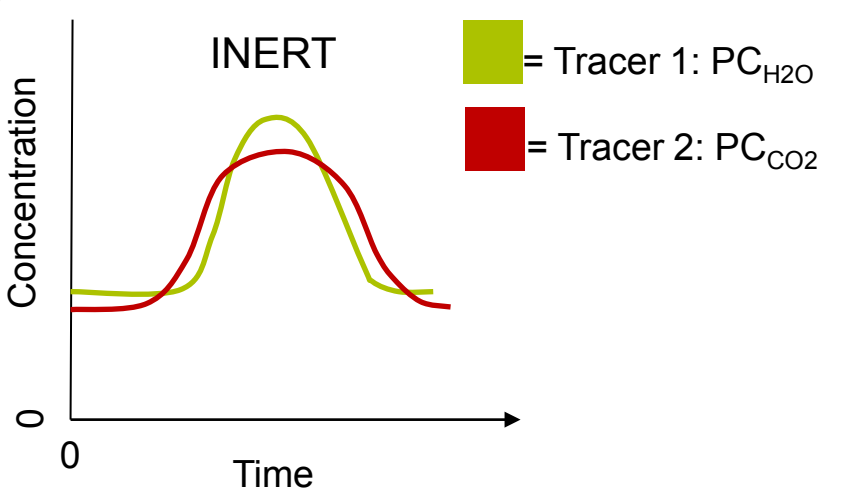


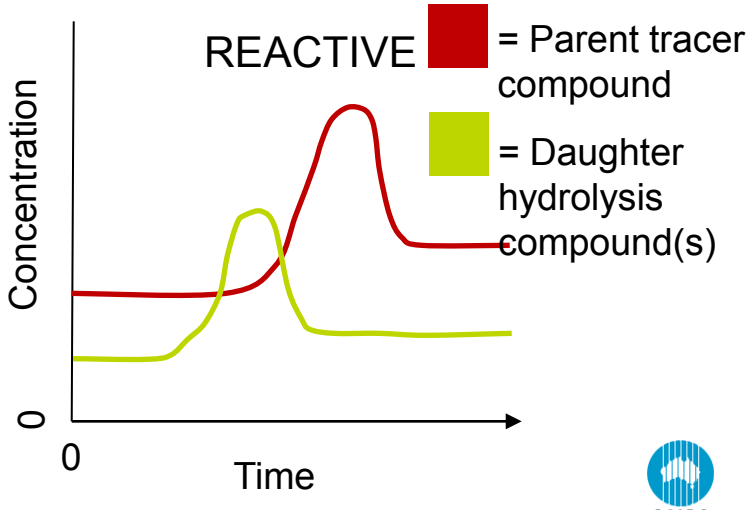
= Parent tracer compound

= Daughter hydrolysis compound(s)

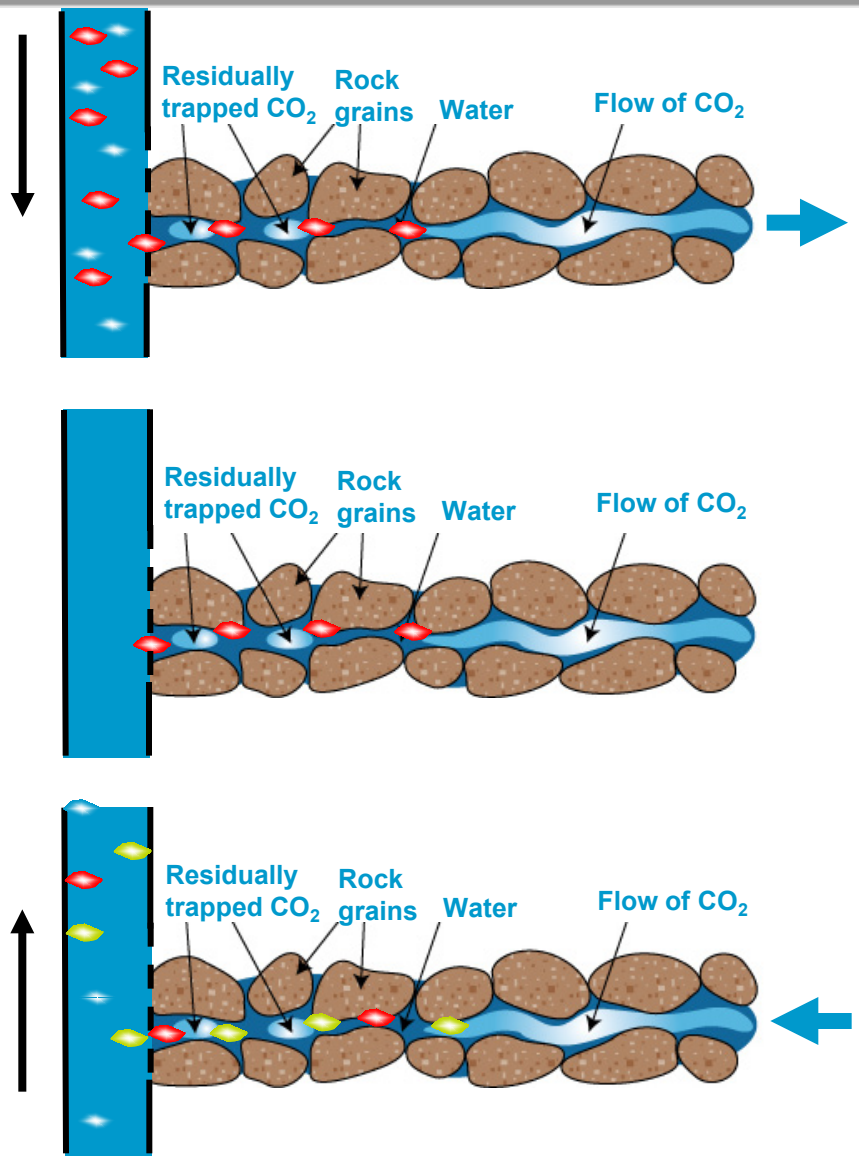
Single well test – Inert vs reactive tracers







Single well residual saturation test – Otway Stage 2B (CO2CRC)



CO_2
Parent tracer
Daughter product(s)

1. Reactive tracer injected and pushed into formation with CO_2/water.

2. Soak period to allow hydrolysis reaction.

3. Back production and recovery of parent tracer and daughter products.

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CO2CRC
CRC for Greenhouse Gas Technologies

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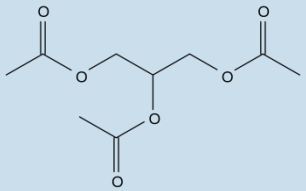
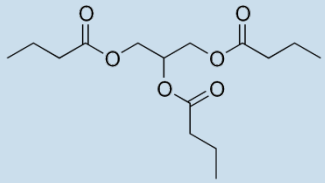
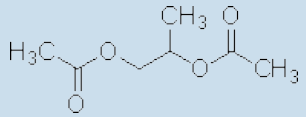
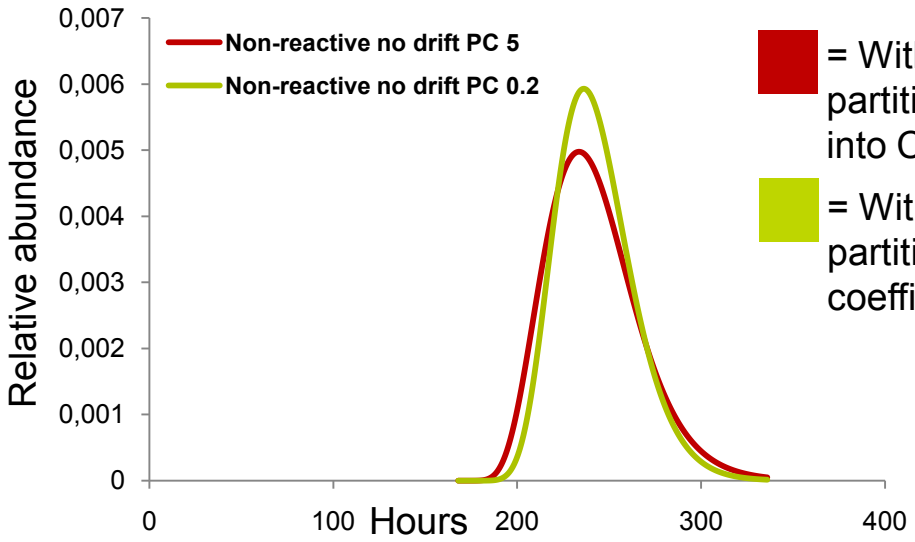
Tracers Proposed

	Triacetin	Tripropionin	Propylene glycol diacetate
Structure			
Formula	$C_9H_{14}O_6$	$C_{12}H_{20}O_6$	$C_7H_{12}O_4$
Breakdown/ daughter products	Glycerol Partially hydrolysed triacetin Acetic acid	Glycerol Partially hydrolysed tripropionin Propionic acid	Propylene glycol Partially hydrolysed propylene glycol diacetate Acetic acid
Partitioning coefficient	~10	~50	~4
Cost per Kg	$3	$8	$10
OHSE on parent and daughter compounds	Parent compounds are commonly used as food flavourings and cosmetic additives. The corresponding acids and alcohols (hydrolysis daughter products) are also food and cosmetic additives.		
Amounts required*	Solubility = 72g/L	Solubility = 2.6g/L	Solubility = 100g/L

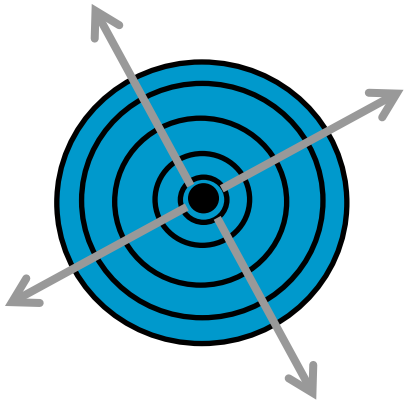
Summary of what we expect to see

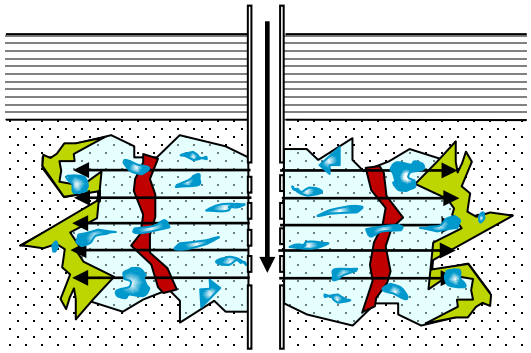


= With higher partitioning coefficient into CO_2

= With higher partitioning coefficient into H_2O

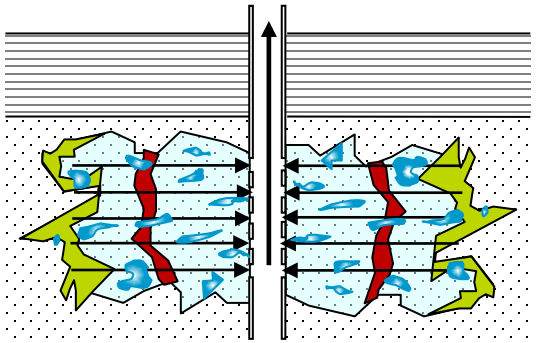
No drift





CO_2 saturation = 0.2

Tracers injected



CO_2 saturation = 0.2

Tracers produced

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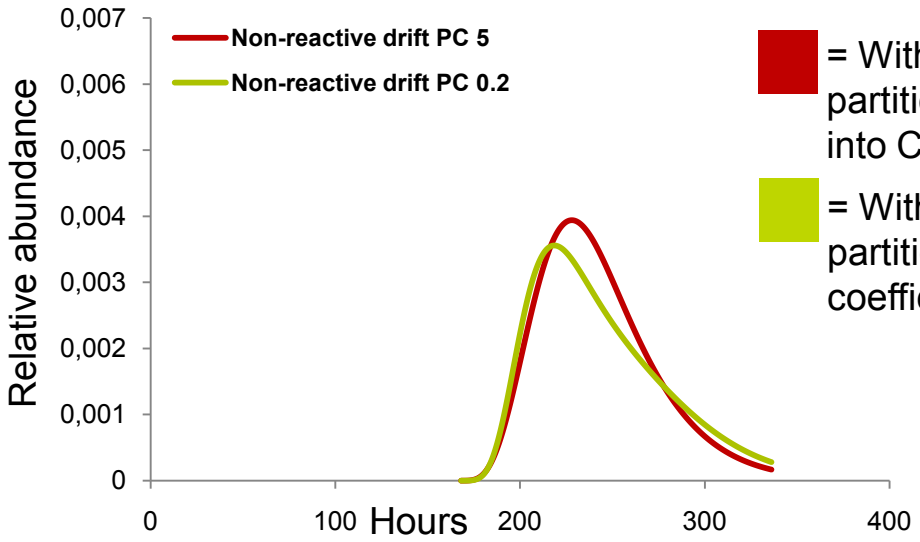
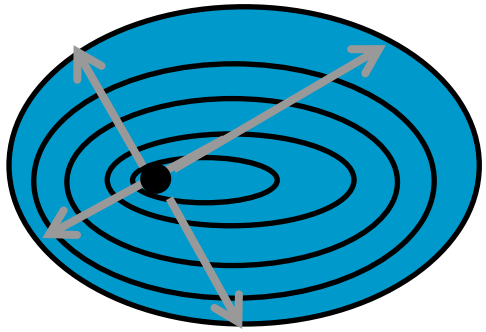
Summary of what we expect to see

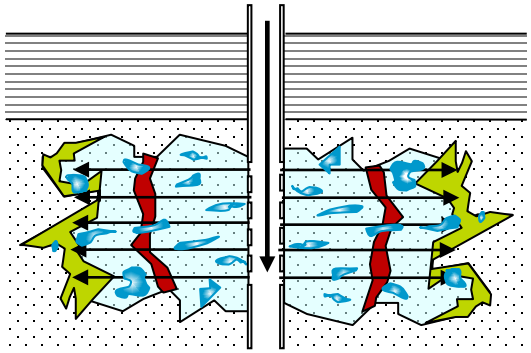


= With higher partitioning coefficient into CO_2

= With higher partitioning coefficient into H_2O

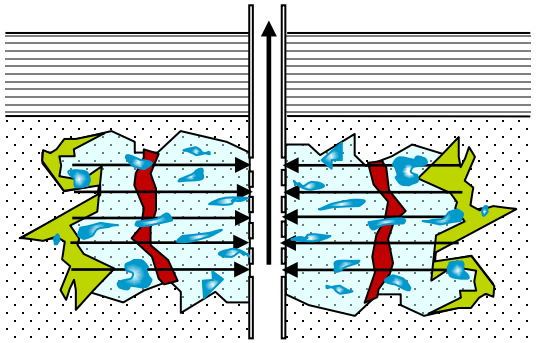
Drift





CO_2 saturation = 0.2

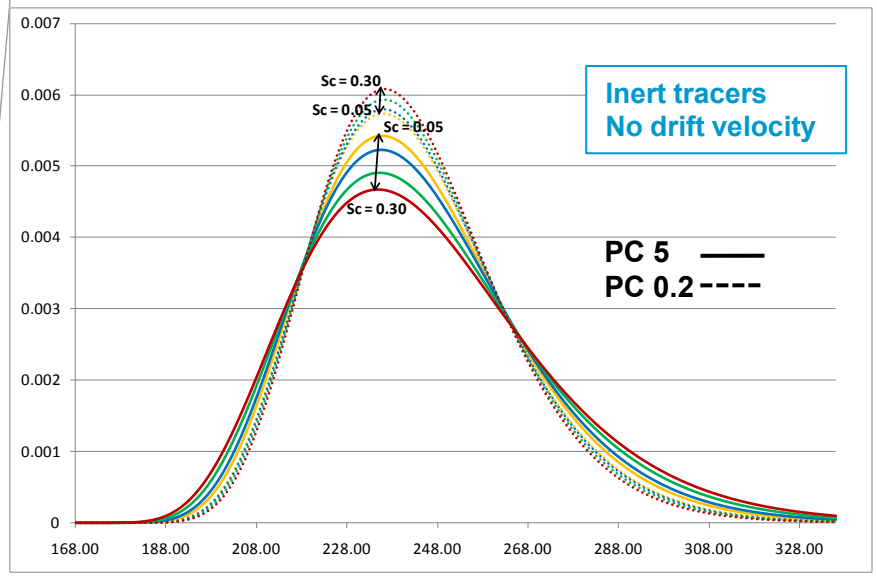
Tracers injected

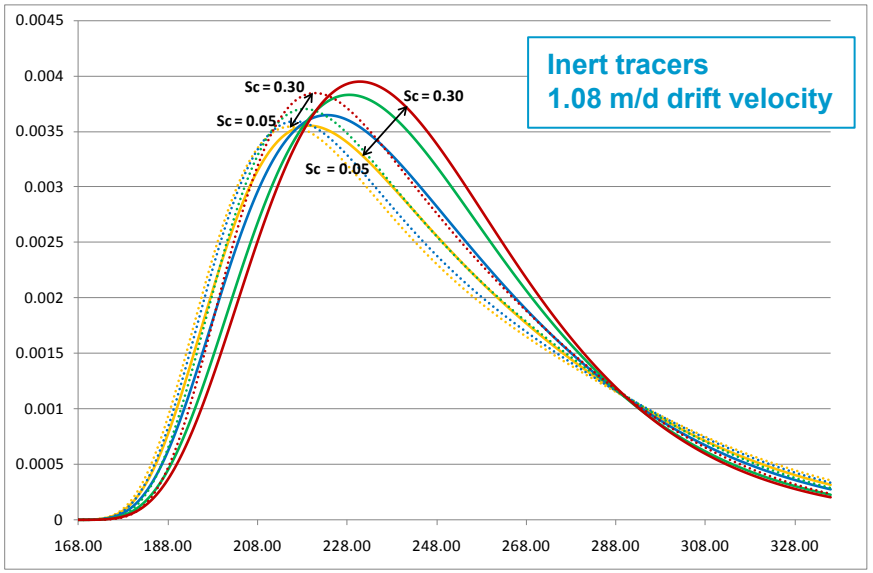


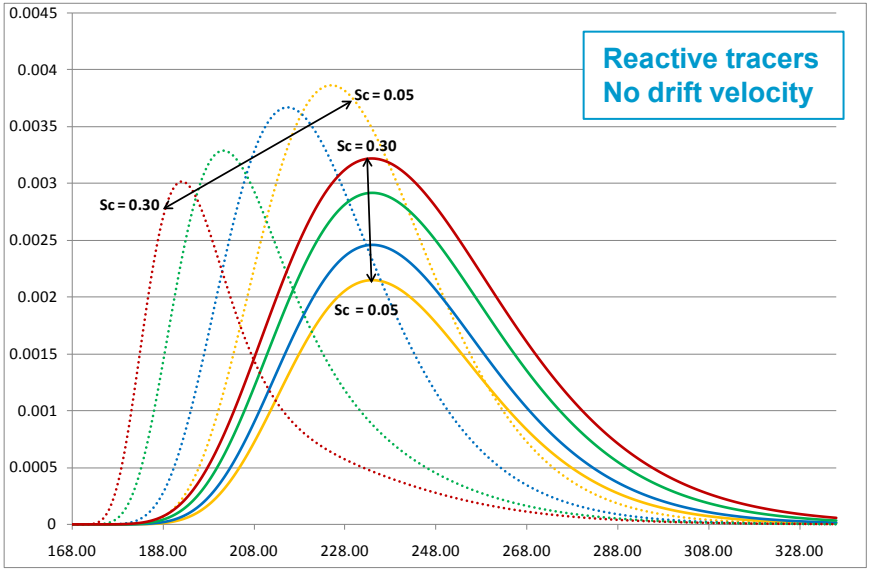
CO_2 saturation = 0.2

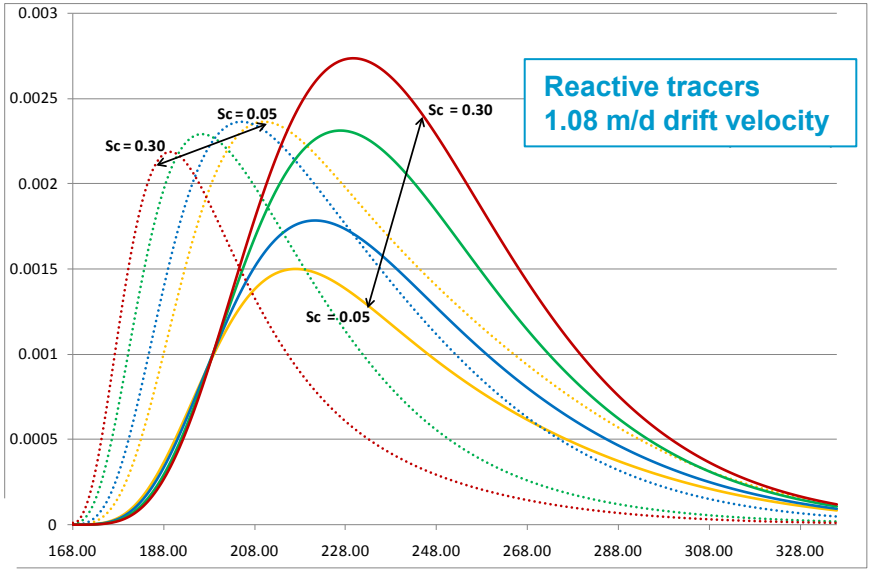
Tracers produced

Summary of what we expect to see









Conclusions & Ongoing work

- Conclusions
  - Reactive tracers are potentially more accurate and robust systems for determining residual saturation (including drift) compared to inert tracers
  - Choice of reactive tracer is dictated by
    - Residual saturation estimation
    - Temperature (reaction kinetics)
    - pH & salinity
    - Rock matrix (adsorption effects)
    - Toxicity
- Ongoing work
  - Field trials at CO2CRC Otway Residual Saturation Test
  - Analytical method development
  - Laboratory experiments to develop a package of partition coefficients and core flood experiments

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