

# Hydrated Portland Cement as a Carbonic Cement: The Mechanisms, Dynamics, and Implications of Self-Sealing and CO<sub>2</sub> Resistance in Wellbore Cements

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## The Problem

### Motivation:

#### Will wellbore cement maintain integrity?

A vast body of work has demonstrated that Portland-based wellbore cement can self-seal under some conditions following exposure to CO<sub>2</sub>-charged brine. This phenomenon is extremely important in long-term integrity of wellbores, because it counters earlier concerns that acidic brine would degrade cement.



Section of carbonated wellbore cement recovered from a mature CO<sub>2</sub>-EOR site, showing diffusively altered cement (orange zone) and silica+carbonate (gray zone) between cement & caprock — providing early evidence of self-sealing (Carey et al., 2007).

Despite the large body of work across the community, conditions that promote self-sealing remain somewhat uncertain, leaving open whether a wellbore will maintain integrity over time in the presence of carbonated brine. This ambiguity ties to the complexity of the system, which embodies a large chemical and mineralogical diversity, a wide range in downhole physical conditions and flow regimes, significant limitations on observing the dynamics directly, and uncertainty in the fundamental parameters needed to simulate all aspects of the dynamics exactly.

In this study, we focus on two questions facing CO<sub>2</sub> storage operations:

- What is a sufficient length of cement along the wellbore to maintain integrity over the design life of a project?
- What makes a cement “compatible” with a carbonated brine?

These questions are central to Class VI permitting.

We approach this through a synthesis of the body of knowledge combined with an extensive set of simulations that probe the diverse range of conditions, properties, and uncertainties alluded to above. Three elements differentiate our analysis from earlier studies: (1) exploration of a comprehensive range of thermodynamics and kinetics; (2) the use of constant fluid velocity as the critical variable; (3) coupling the analysis with a consideration of leakage rates.

## It is Critical to Capture the Uncertainty to Bound the Behavior of Self-Sealing

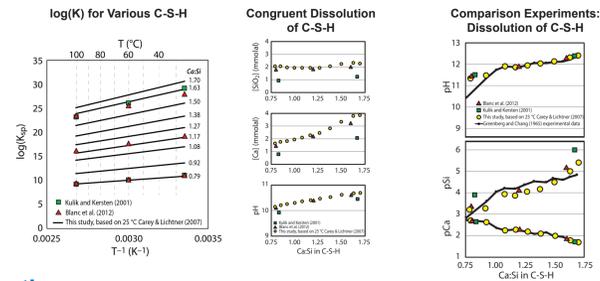
### Thermodynamics

A key uncertainty is the thermodynamic properties of calcium-silicate-hydrate (C-S-H):

- Different thermodynamic models have been developed from experimental data, and
- Variation in the composition of C-S-H can occur (as reflected in the Ca:Si ratio).

We comprehensively explored this variability to determine robustness of the predictions.

Below is logK for three published thermodynamic models and for the range of C-S-H composition as well as two examples of how predictions from these models compare.



### Kinetics

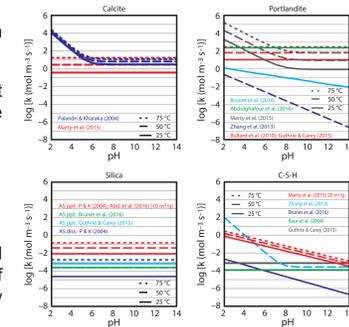
The kinetics of dissolution and precipitation are also uncertain.

Shown at right are the kinetic models that have been used in studies of the wellbore cement system. Two factors emerge:

- (1) rates used span orders of magnitude
- (2) calcite & (probably) portlandite are likely to be non-rate limiting.

We explored this entire range of kinetics and its impact on the predicted evolution of self-sealing conditions. The red curves show our base-case rates.

**Our analyses bounded behavior across the range in uncertainty.**

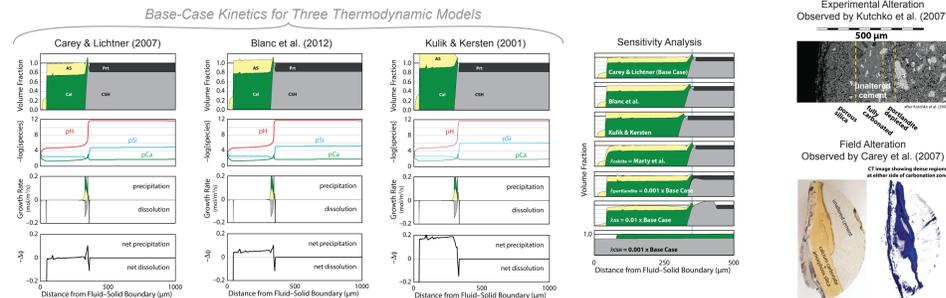


## The Analysis

### Reaction of Carbonated Brine & Hydrated Portland Cement

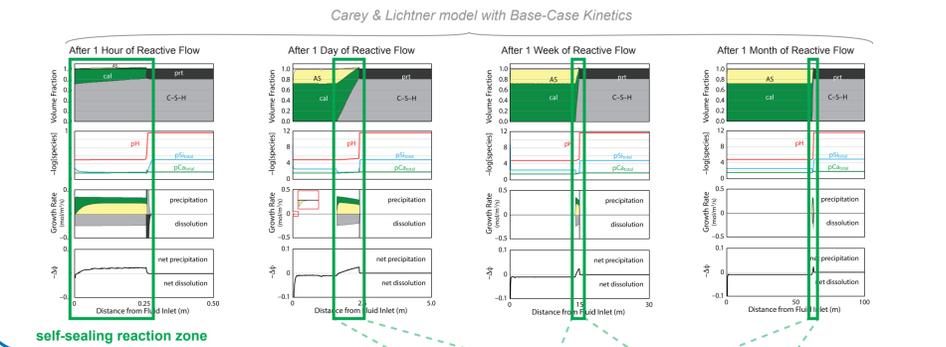
**Diffusion** Predicted evolution of diffusive alteration closely matches experiments & field.

- All three thermodynamic models predict similar mineralogical zones
- Carey & Lichtner and Blanc et al. correctly predict the observed zone of lower porosity at the interface.
- Base-case kinetics most closely match lab and field observations



**Advection** Predicted evolution of advective alteration at constant flow is broadly similar to diffusive alteration.

- Self-sealing occurs in a narrow reaction zone that moves over time.



## Self-Sealing Mechanisms and Dynamics

### Mechanism

Self-sealing consists of two reactions:

- At the interface with pristine hydrated Portland cement > Portlandite dissolves; C-S-H and calcite precipitate > Reaction is driven by pH and dissolved CO<sub>2</sub> and silica
- At the interface between carbonated cement and C-S-H > Portlandite dissolves; C-S-H and calcite precipitate

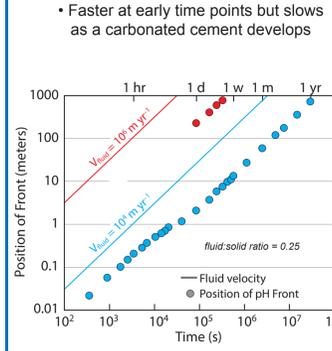
On either side of the self-sealing reaction zone, the system is i

- Hydrated Portland cement is stable downstream

### Dynamics

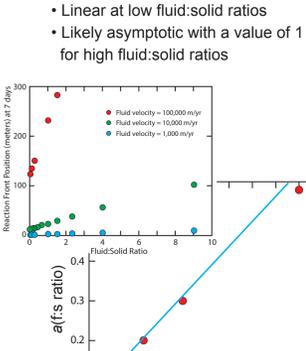
Self-sealing reaction zone migration is proportional to fluid velocity

- Faster at early time points but slows as a carbonated cement develops



Self-sealing reaction zone migration is proportional to fluid:solid ratio

- Linear at low fluid:solid ratios
- Likely asymptotic with a value of 1 for high fluid:solid ratios

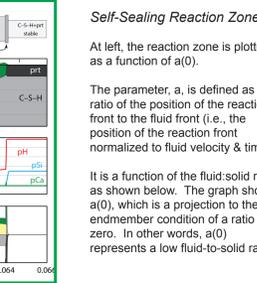


### Self-Sealing Reaction Zone

At left, the reaction zone is plotted as a function of a(t).

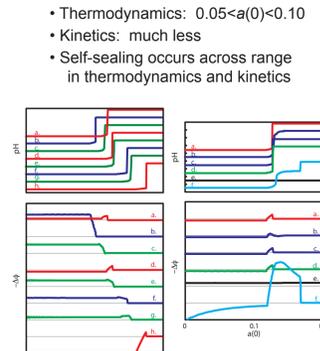
The parameter, a, is defined as the ratio of the position of the reaction front to the fluid front (i.e., the position of the reaction front normalized to fluid velocity & time).

It is a function of the fluid:solid ratio as shown below. The graph shows a(t), which is a projection to the endmember condition of a ratio of zero. In other words, a(t) represents a low fluid-to-solid ratio.



Self-sealing reaction zone is a function of thermodynamics & kinetics

- Thermodynamics: 0.05 < a(t) < 0.10
- Kinetics: much less
- Self-sealing occurs across range in thermodynamics and kinetics

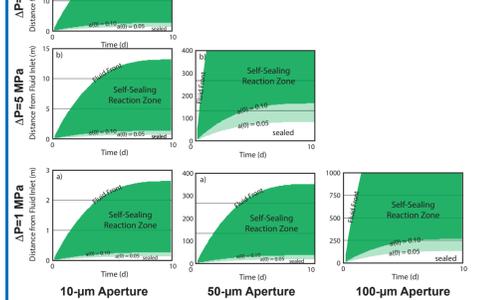


## Major Implications

### Many Factors Can Limit Migration of Self-Sealing Zone

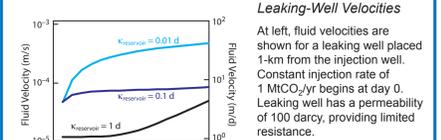
#### Aperture-Controlled

Small apertures should self seal. (Curves assume aperture flow follows the cubic rate law)



#### Permeability-Controlled

During early stages of injection, velocities can be limited to promote self-sealing, especially in higher permeability reservoirs.

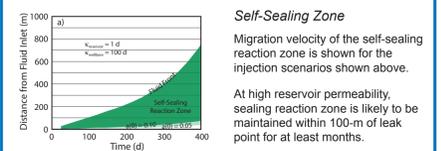


#### Leaking-Well Velocities

At left, fluid velocities are shown for a leaking well placed 1-km from the injection well. Constant injection rate of 1 MtCO<sub>2</sub>/yr begins at day 0. Leaking well has a permeability of 100 darcy, providing limited resistance.

#### Factors that Promote Self-Sealing

- Small fractures—microfractures likely not a concern
- Low reservoir pressures—active reservoir management promotes self-sealing conditions
- High reservoir permeability—higher permeability reservoirs dissipate pressures more readily, promoting self-sealing conditions at early stages of operation.
- Demonstrated zone of sealing in at least part of well, which would limit flow rates in fractures elsewhere



#### Self-Sealing Zone

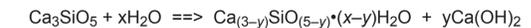
Migration velocity of the self-sealing reaction zone is shown for the injection scenarios shown above. At high reservoir permeability, sealing reaction zone is likely to be maintained within 100-m of leak point for at least months.

## Hydrated-Portland-Cement is a CO<sub>2</sub> Compatible Cement

We introduce the term *carbonic cement* as a parallel to hydraulic cement, which is a widely accepted description for materials that set and maintain integrity in the presence of water. Thus, carbonic cements set and maintain integrity in the presence of carbonic acid.

Portland-based cements are hydraulic cements. They consist of a mixture of anhydrous calcium phases that react with water, forming a mixture of hydrated calcium phases that are stable in water.

For example, a principal reaction in hydration of Portland cement is hydration of C<sub>3</sub>S to C-S-H + CH:



The reaction proceeds in the presence of water, and the resulting calcium silicate hydrate (C-S-H) is stable in water.

As shown in the extensive analysis of reactions above, hydrated Portland cement will react in a similar manner with carbonated brine, through a series of reactions that produce calcium carbonate and silica. An example reaction written for the above C-S-H is:



**The reaction products (silica and carbonate) are stable in carbonated brine. In other words, hydrated-Portland-cement is a CO<sub>2</sub> compatible cement; its reactivity is essential & beneficial.**

## Acknowledgements

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