Crystallization of salts in a porous medium

A tribute to Gilles Chanvillard

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Salts in a porous medium

- What is the problem?
- Gilles’ approach to the equilibrium state
- Non equilibrium considerations
- Experimental study of growth in pore networks
Mirabilite in Limestone

- Indiana limestone pores contain thenardite ($\text{Na}_2\text{SO}_4$)

- Precipitation of mirabilite ($\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}$) destroys stone
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Stress from Mirabilite

- Dry salt dissolves until solution is saturated with respect to thenardite

- That solution is highly supersaturated with respect to mirabilite
Driving Force for Growth: Supersaturation

- Dissolution of hydrated salt

\[ \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons 2\text{Na}^+ + \text{SO}_4^{2-} + 10\text{H}_2\text{O} \]

Solubility product:

\[ Q = [\text{Na}^+]^2[\text{SO}_4^{2-}][\text{H}_2\text{O}]^{10} \]

Equilibrium constant:

\[ Q = K[T] \]

- Pressure needed to suppress growth of a macroscopic crystal

\[ p = \frac{RT}{V_M} \ln \left[ \frac{Q}{K[T]} \right] \approx \frac{R_g T}{V_M} \ln \left[ \left( \frac{c}{c_s} \right)^3 \right] \]
As degree of saturation with crystals increases, mole fraction of solute decreases
Saturation versus Pore radius

* Crystals progressively invade smaller pores, reaching full saturation as $r_p \to 0$
Crystallization pressure vs Radius

- As smaller pores are invaded, the pressure applied to the pore walls, $P_A$, increases

$$P_A = \gamma_{CL} \left( \frac{2}{r_{p, eqm}} - \frac{1}{r_{pk}} \right)$$
Equilibrium state corresponds to osculating rectangle

\[ \beta(x) = \frac{Q}{K - 1} \]
Approaching equilibrium

- First cycle from arbitrary starting point
Approaching equilibrium

✦ Second cycle
Approaching equilibrium

- Third cycle
Approaching equilibrium

- Fourth cycle → approaching equilibrium
Inaccessible pores

✲ Initial concentration limits size of pores that salt can enter
Crystal saturation

- Equilibrium box bounds salt-filled pores
Effect of concentration

- Decreasing $x$ decreases pressure on pore walls
Effect of concentration

- Raising $x$ increases pressure on pore walls

![Diagram showing the effect of concentration on pore walls](image)
Coarsening

- Diffusion of salt out of the body reduces $P_A$
External source of salt

- Entry of salt, evaporation, or cooling raises $x$ and $P_A$
Wetting / Drying Cycles

- Rewetting with salt-rich solution raises $x$ and $P_A$
Limitations of equilibrium analysis

- Pores in stone are usually too large for curvature to affect solubility significantly
- All pores fill simultaneously
- Propagation from large into small pores leads to diffusion control, so no pressure
Solubility versus Pore size

• Freundlich equation relates solubility product, $K$, to crystal size

\[ \frac{2 \gamma_{CL}}{r_p - \delta} = \left( \frac{RT}{V_M} \right) \log \left[ \frac{K[r_p]}{K[\infty]} \right] \]

$r_p = 0.1 \mu m \rightarrow 9\%$ enhancement
Indiana Limestone

- Bimodal pore size distribution
  - Peaks near 0.3 and 30 µm
  - Few pores smaller than 0.1 µm
Kinetic considerations

- Interface- versus Diffusion-controlled growth
- Frequency of nucleation
- Transport in the film
- Growth through a network of pores
Interface Control

- Rate of growth is determined by the kinetics of attachment of atoms to the interface
- Not all sites are equally likely to accommodate attachment
- Driving force for growth is supersaturation, $Q/K - 1$
Crystall Growth

- Interface attachment kinetics

- Growth rate, \( G \), depends on mobility, \( \eta \), driving force, \( \Delta G_f \) and accommodation probability (interface site factor, \( f \))

\[
G = \frac{f kT}{2 \pi \lambda^2 \eta} \left( 1 - \exp \left[ -\frac{\Delta G_f}{kT} \right] \right)
\]

- Precipitation: \( \Delta G_f = kT \ln \left( \frac{Q}{K} \right) \equiv kT \ln (\beta) \)

\[
G = \frac{f kT}{2 \pi \lambda^2 \eta} \left( \frac{\beta - 1}{\beta} \right)
\]
Diffusion control

- If the supply of atoms is small, the rate of arrival of atoms may be slower than the rate of attachment.
- Concentration at interface reaches equilibrium solubility.
- Since no supersaturation exists, no pressure can be exerted.
Growth in pores

- Pores in Indiana limestone
Model Networks

- Polyhedral grains with cylindrical pores along edges
- For typical stone with 15% porosity, 0.5 m²/g surface area, node spacing is 4-6 times the pore diameter
Crystallization Pressure

- Crystallization pressure is possible only if the crystal is in contact with a supersaturated solution.

\[ p_c \approx \frac{R_g T}{V_M} \ln \left[ \left( \frac{c}{c_s} \right)^{\nu} \right] \]

- Under diffusion control, the interface concentration is \( c_s \), so it cannot grow against resistance.

- Crystallization pressure is present only if the crystal is growing under interface control.
Pore - Filling

- Volume fraction of salt is insufficient to fill the pores

\[ \text{Vol Frac} \]

Sodium sulfate
Pore - Filling

- Volume fraction of salt is insufficient to fill the pores
Pore - Filling

- Volume fraction of salt is insufficient to fill the pores

To generate pressure, must diffuse salt from adjoining pores while maintaining supersaturation.
Generating Pressure

- Expect heterogeneous nucleation on pore walls

- No pressure generated unless crystal touches the opposite wall

- When a spherical crystal makes contact (radius = diameter of pore) its volume is

\[ V_{sphere} = 8 \left( \frac{2\pi}{3} - \frac{8}{9} \right) r_{pore}^3 \]

\[ = \pi r_{pore}^2 \ell v_{frac} \]

so solute comes from pore length

\[ \ell \approx 3 r_{pore} / v_{frac} \]
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Diffusion Control?

- Solute must come from distance $\ell / 2 \approx 1.5 r_{\text{pore}} / \nu_{\text{frac}}$
- Time for crystal to grow into contact is $t = 2 r_{\text{pore}} / G$
- Distance homogenized by diffusion in this time is
  \[ x \approx \sqrt{D t} \approx \sqrt{2 r_{\text{pore}} D / G} \]
- Is $x > \ell / 2$ ?

- For sodium sulfate heptahydrate, $G \sim 1-6 \mu m / s$, $D \approx 0.65-2 \times 10^{-9} m^2 / s$, so if pore radius is $r_{\text{pore}} \approx 2 \mu m$, $x \approx 20-90 \mu m \approx 10-45 r_{\text{pore}} > \ell / 2$ for $\nu_{\text{frac}} > 0.03-0.15$
- Stress from hepta exerted w/o diffusion control
Nucleation on Walls

- Expect heterogeneous nucleation on pore walls
- Few sites have favorable contact angle
- If number of nuclei $\geq 1$ between nodes, the amount of solute is not sufficient to allow the crystal to grow into contact with the opposite side of the pore
- Nucleation must be rare to generate crystallization pressure
Nucleation on Walls

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Pore Network

- Network consists of cylindrical pores and nodes (junctions)
- What happens when a crystal reaches a node?
  - Branch into all, some, or none of the intersecting pores?
Branching at Nodes

* Can crystals branch freely at nodes, or are they trapped?

In this case, a single crystal can transform all the pore volume.

In this case, diffusion to the trapped crystal generates crystallization pressure.
Growth in a Network

- Nucleation must be rare to allow crystals to fill pores
- Diffusion must be fast compared to growth to allow interface concentration to be high ($\beta > 1$)
- If nuclei are not too far apart, neighborhood (red zone) has uniform concentration
Nucleation must be rare to allow crystals to fill pores

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Growth & Branching

- If the crystal branches into all pores at junctions, a region with radius $r$ transforms, but the growth distance is $\ell = r \tau$, where $\tau$ is the tortuosity of the pore network.

- Stress determined by composition of film between crystal and wall.

- If diffusion in film is very slow, high pressure can be sustained on the pore wall.
Trapping of Film

- Film of solution is trapped between crystal and pore wall
- Whether composition of film equilibrates with pore solution depends on diffusivity in the film
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Fast diffusion in Film

- Suppose that growth is interface controlled
- Concentration in pore liquid decreases as crystal grows, but interface concentration equals average composition, and film composition is in equilibrium with pore liquid
Fast diffusion in Film

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  - Concentration in pore liquid decreases as crystal grows, but interface concentration equals average composition, and film composition is in equilibrium with pore liquid

- Solid curve is crystallization pressure
- Dashed curve is fraction of pore filling with crystals
- $R_g T / V_M \approx 13 \text{ MPa}$
Slow diffusion in Film

- Suppose that growth is interface controlled

- Concentration in pore liquid decreases as crystal grows, and interface concentration equals average composition, but *film concentration does not equilibrate with pore*
Slow diffusion in Film

- Suppose that growth is interface controlled.
- Concentration in pore liquid decreases as crystal grows, and interface concentration equals average composition, but film concentration does not equilibrate with pore.
- $R_g T/V_M \approx 13 \text{ MPa}$
Comparison to Data

- NMR measurements of average solution concentration during growth of hepta in pores of stone

- Plot of normalized volume fraction versus normalized time indicates $R_O \approx 1 \text{ cm}$

- If a single crystal grows that far, it must enter diffusion control
Comparison to Data

- DSC data for hepta in limestone
- Fit implies $R_0 \approx 0.3$ mm (similar to size of DSC sample)
- Implies growth of few crystals with high tortuosity or difficulty branching at nodes in network
Comparison to Data

- DSC data for mirabilite in limestone (symbols) agree well with theory.
- Duration of transition longer than time for one crystal to grow across the sample.
- Implies growth of one crystal with high tortuosity or difficulty branching at nodes in network.
Branching at Nodes

Can crystals branch freely at nodes, or are they trapped?

In this case, a single crystal can transform all the pore volume.

In this case, diffusion to the trapped crystal generates crystallization pressure.
Test of Growth in Channels

- Channels 5 \( \mu \text{m} \) wide & deep etched into Si, covered with glass
- Channels filled with solution (3 molal \( \text{Na}_2\text{SO}_4 \))
- Cooled to induce supersaturation
Channel structure

- Triangular pattern allows growth in straight line, but hexagonal pattern requires turn at every junction
Growth in Channels

- 3 molal Sodium sulfate
Branching

- Crystal enters
Branching

- Crystal passes junction, no branching
Branching

- Branch occurs
Conclusions

- Existence of crystallization pressure implies growth controlled by interface kinetics, not diffusion
- If branching occurred freely, pores would fill quickly
- Slow transformations observed experimentally imply blocking at nodes in pore network
- Blocked crystals probably grow intermittently at high supersaturation
- Images show delayed branching of sodium sulfate in lithographic channels
- Need more control over nucleation, better images, numerical simulation of diffusion and growth kinetics
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PDMS Channels

- Pattern originally made in PDMS
- Channels distorted by crystallization pressure
- Therefore, created new pattern in silicon