Dissolution theories for cementitious binders

A case for the interface

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Outline

- Introduction
- Rate controlling mechanisms
- Dissolution kinetics
- Implications for performance and durability
- Conclusions and perspectives
Introduction

- **Cementitious binder?**
  - **Glue** binding solid materials (through solid-solid grain boundaries that remain attractive in H$_2$O)
  - **Filler** of empty space between particles

- **Activation of (alumino-)silicates:**
  - Blended cement environment:
    - pH: 13 – 13.5
    - C-(A)-S-H products
  - Alkali activation
    - pH $>>$ 14
    - Product assemblage depend on material composition and activator
Why studying kinetics?

Hydration/reaction kinetics

- Availability of reactive species
- Reaction product formation
- Distribution of products: microstructure
- Strength development, heat generation
- Porosity, permeability: durability
Reaction kinetics in cementitious binders

- Chemical and microstructural processes are complex and interdependent
- Difficult to resolve individual mechanisms or parameters that determine kinetics

Fundamental approach: hydration as series of coupled processes (flow chart approach)
- Breaking down problem to study kinetics of individual mechanistic steps
- Foundation for understanding interactions among coupled phenomena
- Kinetics are often controlled by one significantly slower step

[Morrow et al., 2009]
Rate controlling mechanisms

$$ SCM + \text{water} (\pm X^{m+}) \xrightarrow{\text{pH, } T} \text{hydration products} $$

1. Surface dissolution control
2. Water availability
3. Space filling of reaction products
4. Diffusion through leached layer or reaction product layer
Rate controlling mechanisms

- Changes in reaction environment:
  - Solution composition (pH, [H$_2$O], solution saturation)
  - Availability of growth space
  - Leached layer/reaction product layer development

- Changes in rate controlling mechanism at different stages

[Snellings et al., 2012]
Rate controlling mechanisms

- Dissolution and precipitation processes are simultaneous
- Rate control depends on properties of reactants and hydration products
  - e.g. Alite hydration: rate control of main reaction by N & G
  - Reaction mechanisms and rates of glassy phases in solutions largely unknown

Global reaction rate

- Reactant dissolution (interface controlled)
- Reactant transport
- Product nucleation and growth
Theories for dissolution kinetics
Dissolution

- **Dissolution rate measurements**
  - In bulk: increase in concentration of solutes through time, solid mass loss
  - Rates are normalised to the total surface area (BET measurements or geometric calculation)
  - Initial *parabolic* kinetics followed by steady state rate (reported)

![Graph showing parabolic and steady state regimes](image)

[Hamilton et al., 2000]
Reactivity trends for mineral and glass dissolution

- **Congruent dissolution:**
  - Dissolution rates of MO oxides and orthosilicates scale with rate of exchange of inner sphere H$_2$O (kH$_2$O) from the ion in solution

[Casey & Westrich, 1992; Ohlin et al. 2010]
Reactivity trends for mineral and glass dissolution

- Incongruent (nonstoichiometric) dissolution:
  - Preferential leaching of elements from the surface
  - Leached surface layer of sparingly soluble components

[Casey & Westrich, 1992; Ohlin et al. 2010]
Reactivity trends for mineral and glass dissolution

- Polymer connectivity
  - Silicate network: the higher the connectivity, the lower the dissolution rate
  - Ab initio calculations indicate rate control of Q2 detachment

[Brantley et al., 2004; Brantley, 2008]
Surface dissolution control: driving force

- Saturation state of a solution with respect to a crystalline or amorphous solid

\[ aA + bB = cC + dD \]

\[ \Delta G = \Delta G^0 + RT \ln \left( \frac{[C]^c[D]^d}{[A]^a[B]^b} \right) \]

\( Q = \) reaction quotient

At equilibrium: \( \Delta G = 0 \) \( K_{sp} = \left( \frac{[C]^c[D]^d}{[A]^a[B]^b} \right)_{eq} \)

\( \Delta G^0 = -RT \ln K_{sp} \)

In general: \( \Delta G = -RT \ln K_{sp} + RT \ln Q = RT \ln \frac{Q}{K_{sp}} \)
Surface dissolution control: saturation state

- Saturation state $\sigma$

$$\sigma = \left( \frac{\Delta G}{RT} \right) = \ln \left( \frac{Q}{K_{sp}} \right)$$

- $\sigma < 0$ for dissolution

- e.g. dissolution of amorphous silica

$$SiO_2 + 2H_2O = H_4SiO_4^0$$

$$\sigma = \ln \left( \frac{Q}{K_{sp}} \right) = \ln \left( \frac{[H_4SiO_4^0]}{K_{sp}} \right)$$
Surface dissolution control: linear rate law

- Linear dependence of dissolution rate on driving force

\[
    r_{diss} = k_+ \left\{ 1 - \exp \left( \frac{\Delta G}{RT} \right) \right\} = k_+ \left\{ 1 - \left( \frac{Q}{K_{sp}} \right) \right\}
\]

- Assumptions:
  - One single, slow rate controlling step (first order reaction)
  - Based on bulk dissolution studies / empirical rate laws
  - Surface defects do not play a role

[Rimstidt & Barnes, 1980; Lasaga, 1981; Aagaard & Helgeson, 1982; Icenhower et al., 2004; Dove et al., 2008]
Surface dissolution control: exponential rate laws

- Problems:
  - Non-linear dependence: introduction of reaction orders \( n \)
    1) dissolution plateau at high degree of undersaturation
    \[
    r_{diss} = k_+ \left\{ 1 - \exp \left( \frac{n\Delta G}{RT} \right) \right\} = k_+ \left\{ 1 - \left( \frac{Q}{K_{sp}} \right)^n \right\}
    \]
    [Dove & Crerrar, 1990; Nagy & Lasaga, 1992]
    2) exponential dependence on driving force
    \[
    r_{diss} = k_+ \left\{ 1 - \exp \left( \frac{\Delta G}{RT} \right) \right\}^n = k_+ \left\{ 1 - \left( \frac{Q}{K_{sp}} \right) \right\}^n
    \]
  - Wide variation in reaction orders
  - Contradictions in rate law applicability

Control of surface defects on dissolution

[Burch et al., 1993; Schott & Oelkers, 1995]
Mechanistic description of congruent dissolution and growth

[ Cabrera et al., 1954; Lasaga & Lütge, 2001; Dove et al., 2005 ]

Depending on solution composition dissolution occurs:
1) At pre-existing surface steps (Q2 species at surface)
2) At dislocation defects intersecting the surface (crystals)
3) Homogeneously across the surface (or at impurities)

Parameters:
- Temperature $T$ (K)
- Saturation state $\sigma$
- Step edge energy $\alpha$ (mJ/m$^2$)
- Step kinetic coefficient $\beta$ (cm/s)

[ Development of theory in Dove et al., 2005 ]
Surface dissolution control: mechanistic description

- Quartz dissolution mechanism depends on $\sigma$, $T$, salt concentration, presence of adsorbate species, compositional impurities

[Brickmore et al., 2006; Dove et al., 2007]
Surface dissolution control: crystal vs. amorphous

- Step retreat = Q2 detachment, surface pitting = Q3 detachment
- Dissolution rate of amorphous phases is usually higher due to:
  - Lower interfacial energy
  - Greater strain on Si-O-Si bonds

Quartz

Amorphous SiO₂

[Dove et al., 2008]
Surface dissolution control: surface morphology

- Total dissolution is the combined sum of:
  - Step retreat velocity (depends on saturation state)
  - Nucleation of steps (formation of etch pits)

- Increasing the surface roughness (#steps) will increase initial dissolution rate:
  - Chemical etching (in acid, or at high undersaturation)
  - Grinding (creation of damaged, roughened layer)

$C_3S$ dissolution at high undersaturation

[Juilland et al., 2010]
Other rate controlling processes
Water availability

- Important in practice when low w/b ratios are used (high-performance applications)
- Consumption of water in hydration reactions
- Chemical shrinkage: $V_{\text{hydration products}} < V_{\text{reactants}}$
- Formation of gas filled porosity/decrease in RH
  - E.g. alite hydration stops when RH < 80% [Flatt et al., 2011]

![Graph showing chemical shrinkage over time](image)
Space filling by hydration products

- Main hydration period in Portland cement is controlled by nucleation and growth of products
- Eventual impingement of reaction products leads to growth deceleration

Hydration of polydisperse distribution of alite particles modelled using μic [Bishnoi, 2009]
1. Initial stage:
   - Incongruent dissolution leads to formation of leached/passivated layer
   - Congruent dissolution is reached when diffusion rate of leached cations and Si release rate equalize

[Tsomaia et al., 2003] [Hamilton et al., 2001]
Diffusion through leached/reaction product layer

- XPS BFS depth profiles:
  - Surface leaching
  - Precipitation of products

- Alite H concentration profiles through time

[Schweitzer et al., 2007] [Regourd et al., 1983]
2. Deceleration stage:

- Reconstruction and condensation of leached layer during corrosion of Ca-Na-B glass corrosion

- Dense and loose BFS hydration products in 30 yr old concrete

[Cailleteau et al., 2008]
Implications for Performance & Durability
Implications for performance and durability

- Linking kinetics and bulk mechanical properties:

  Do we really need the microstructure (complex)?
Does microstructure matter?

- Powers’ model
  - $X = 1$ – porosity
  - Same relation as found in numerous other rocks
  - Dependence only on amount, not on size or location
  - Calibration needed at 3 days compressive strength
  - Relationship varies for different systems

[Power, 1958]
Does microstructure matter?

- Thermodynamic modelling
  - Mass balance equations, thermodynamics indicate phase assemblage
  - Product properties need to be known (composition, solubility, density)

Broad correlation between total porosity (measured and calculated) and strength.

\[ f_c = 144(1 - 0.039P_t) \]
\[ R^2 = 0.91 \]

[Lothenbach et al., 2008]
Microstructure does matter

- Distribution of porosity-cracking behaviour

*After C. Dunant*
Implications for bulk properties

- Linking kinetics – microstructure – mechanics: many question marks remain…
  - Dissolution and reaction kinetics (how to measure degree of reaction?)
  - Reaction product properties: composition, density
  - Microstructural development: homogeneous or heterogeneous nucleation, nucleation density, growth (isotropic, planar, linear) behaviour, condensation,…

- Numerical modelling can help:
  - To model interactions between simultaneous processes, taking into account large numbers of factors and data
  - To compare, test and develop experiments and hypotheses

Available programs: CemHyd3D, HyMoStruc, Hydratica, µic
Conclusions and perspectives

- Dissolution theories describe rate dependency on:
  - Saturation state
  - Solution composition (pH, electrolytes,…)
  - Phase composition
  - Surface morphology

Modelling global weathering processes, nutrient release,…

- Extension of databases to synthetic phases/glass

Engineering of material reactivity, availability of reactive species
Conclusions and perspectives

- **Key to mechanistic understanding is isolating and analysing** the individual constitutive steps in hydration
  - e.g. insights into mineral dissolution kinetics

- **(Long term) scientific effort should focus on:**
  - Building and expanding of quantitative databases (reactant dissolution rates, product properties, microstructure development)
  - Application of new and improved analytical techniques to capture elusive parameters
  - Integration of experimental data in numerical models using improved process equations
Thank you for your attention!