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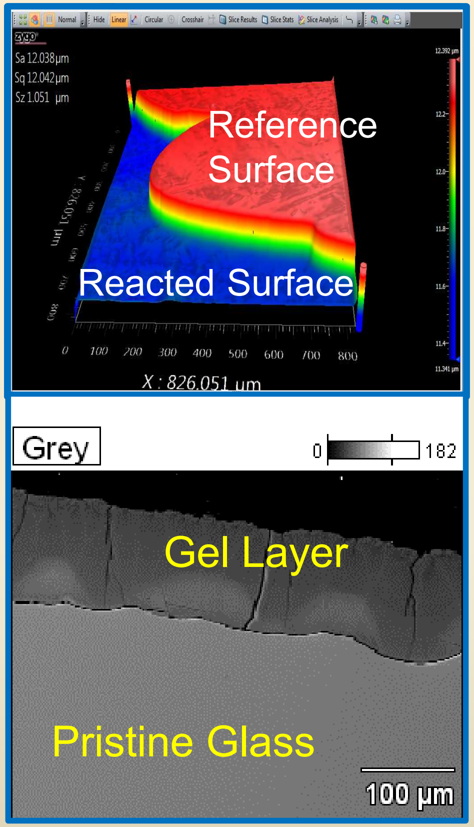

Dissolution of International Simple Glass (ISG) in Brine Solutions at 90°C

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Objectives

- Quantify the dissolution rate of the International Simple Glass (ISG) over a range of NaCl and $MgCl_2$ concentrations at 90^oC and pH(25^oC) = 9 using:
  - Chemical assay on powders
  - Chemical assay on monoliths
- Evaluate if dissolved NaCl enhances or suppresses rates.
- What mechanism controls the rate of glass dissolution in brine solutions?
- Potential role of $MgCl_2$.

Motivations—Both Practical and Theoretical

Practical Considerations

- No decision yet on the geologic setting of the repository for high level waste.
  - Granite
  - Shales/mudrocks
  - Tuff
  - Salt (brine solutions)
- Repeated cycles of evaporation/condensation result in high ionic strength brines.

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Theoretical Considerations—1

$$\text{rate} = k_{\circ} S \exp\left(\frac{-E_a}{RT}\right)^{\sigma} a_{H^+}^{\eta_{H^+}}\, g(I)\, f(\Delta G_r) \prod_i a_i^{\eta_i}$$

- Rate constant ($k_{\circ}$)
- Surface area (S)
- Activation Energy (E_a)
- Tempkin coefficient (σ)
- pH dependence ($a_{H^+}^{\eta_{H^+}}$)
- Ionic strength dependence ($g(I)$)
- Free energy dependence ($f(\Delta G_r)$)
- Catalysis / inhibition ($\prod_i a_i^{\eta_i}$)

Theoretical Considerations—2

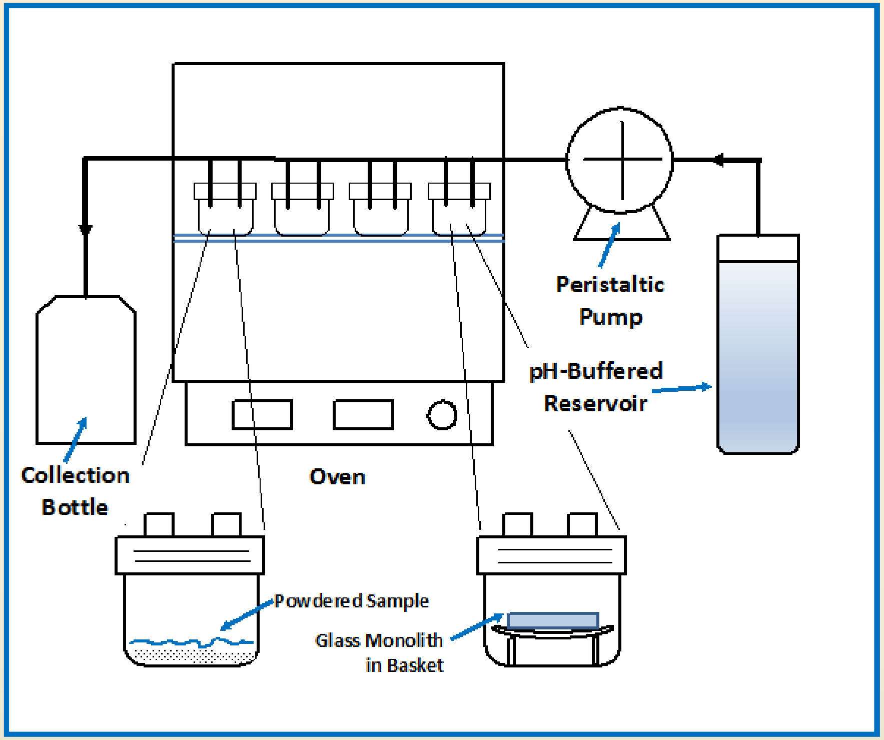
- How does ionic strength and the activity of water factor into the rate equation?

$$Rate = k_0 \cdot (a_{SiO_2}) \cdot (a_{H_2O})^2 \cdot \left(1 - \frac{Q}{K}\right)$$

  - Dove & Crerar (1990) GCA 54, 955-969

- Previous work indicates that the dissolution rates of silica polymorphs are enhanced by the presence of NaCl:
  - Dove & Nix (1997) GCA 61, 3329-3340—Quartz
  - Icenhower & Dove (2000) GCA 64, 4193-4203—Amorphous SiO_2
- Will multicomponent borosilicate glass behave the same way?

Experimental Setup



- Glass powder or monolith of known surface area.
- Solution flow rate constant.
- Reactors behave like a CSTR.
- Powder and monoliths in separate reactors, but at same *q*/S ratio.
- Effluent collected and analyzed for release of elements.

$$rate_i = \frac{(C_i^{out} - C_i^b)q}{f_i S}$$

Solution Preparation

- Solutions buffered with 0.015 M TRIS solution.
- A range of NaCl concentrations (no NaCl to 4.0 m NaCl)
- A range of $MgCl_2$ concentrations (no $MgCl_2$ to 1.5 m $MgCl_2$)
- Initial solutions at pH(25^{o}C) = 9.0
  - Correction factor required; determined analytically
  - $pC_H+ = pH_{obs} + A$
  - A = f(I) + b, where f = 0.180 and b = -0.098 for NaCl

A(0.5 molal NaCl) = 0

A(1.0 m NaCl) = 0.08

A(2.0 molal NaCl) = 0.26

A(3.0 m NaCl) = 0.44

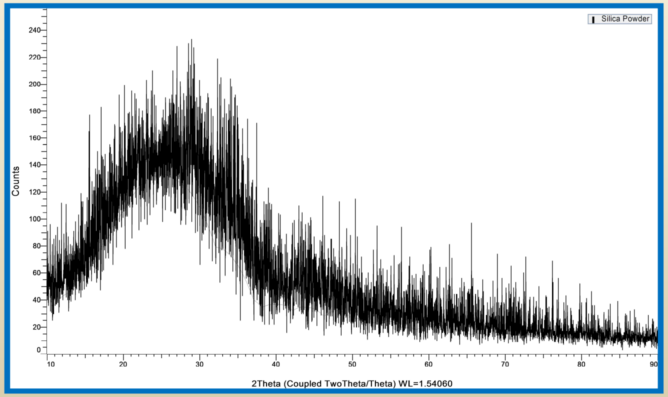
A(4.0 molal NaCl) = 0.62

Glass Preparation

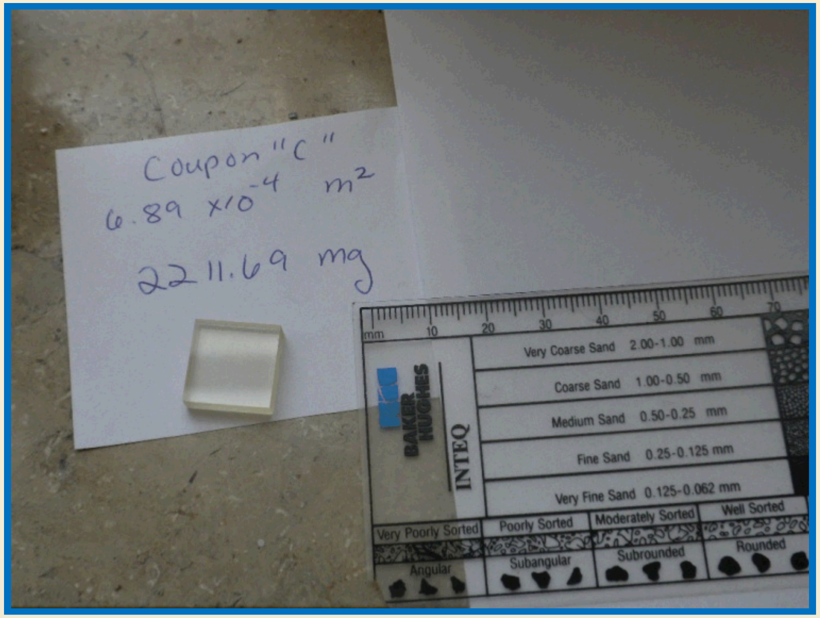
Powders

- 20 -30 mesh-size (850 – 600 micrometer diameter)
- BET SA: 5.7×10^{-3} m^2/g
- Geo SA: 3.3×10^{-3} m^2/g
- 0.20 g powder

XRD of ISG

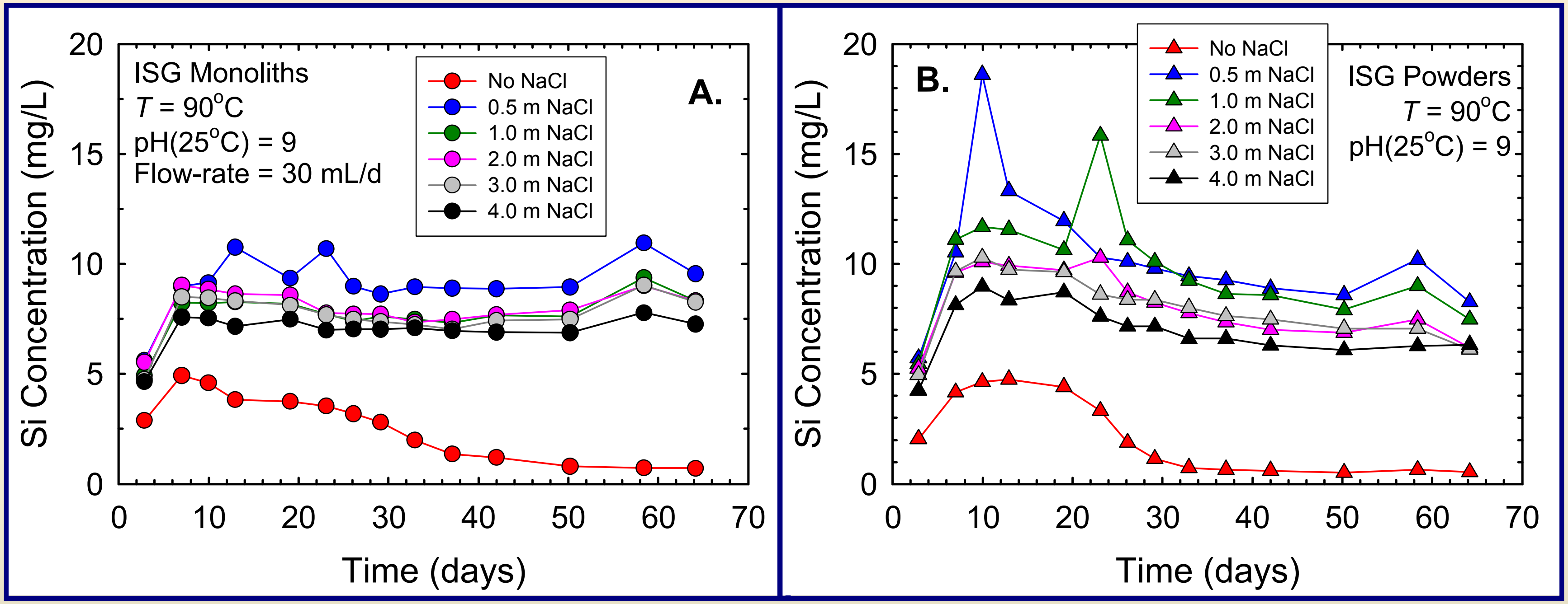


Monoliths

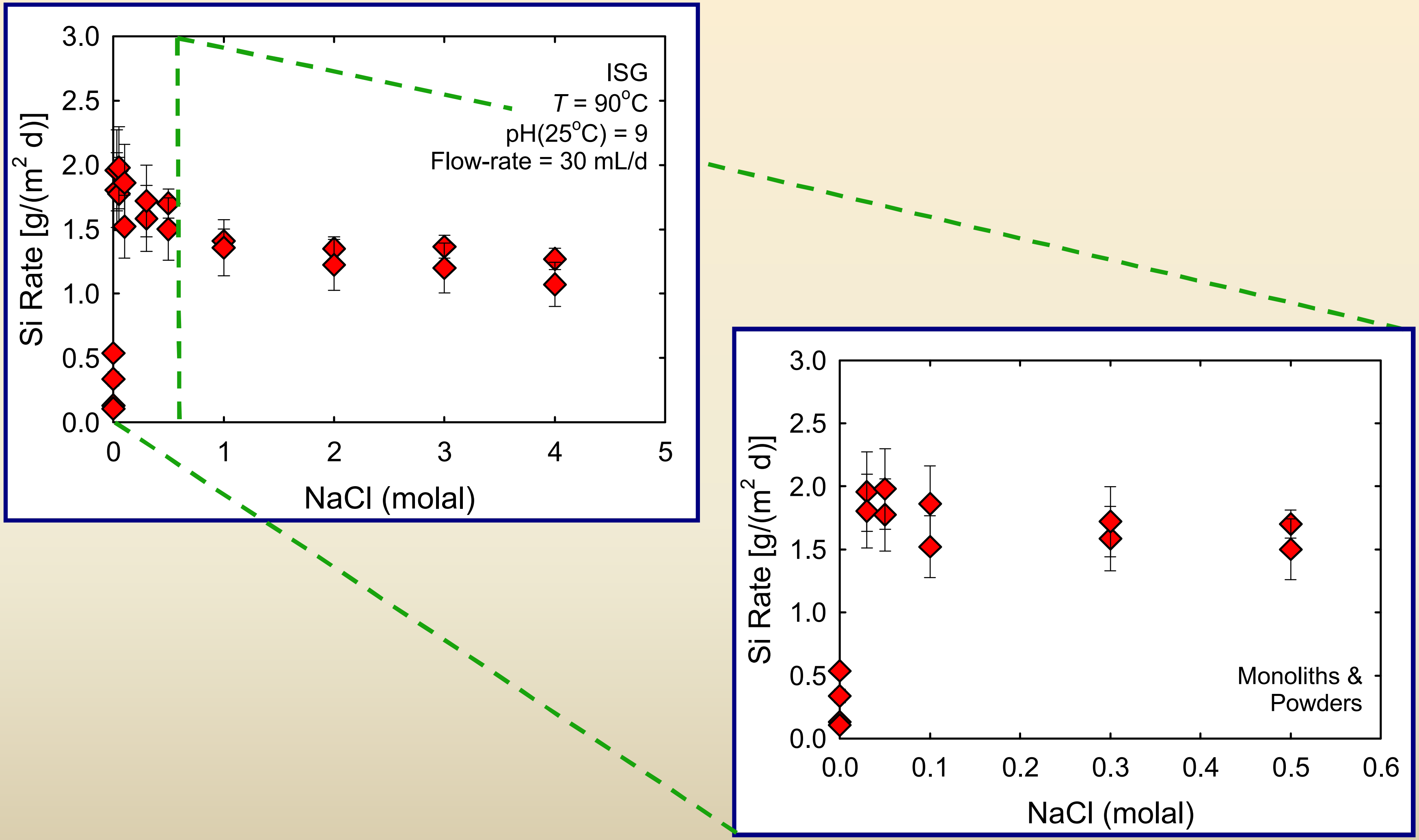


- Cut and polish glass monoliths.
- Measure monolith dimensions using calibrated electronic calipers.
- Better control over SA

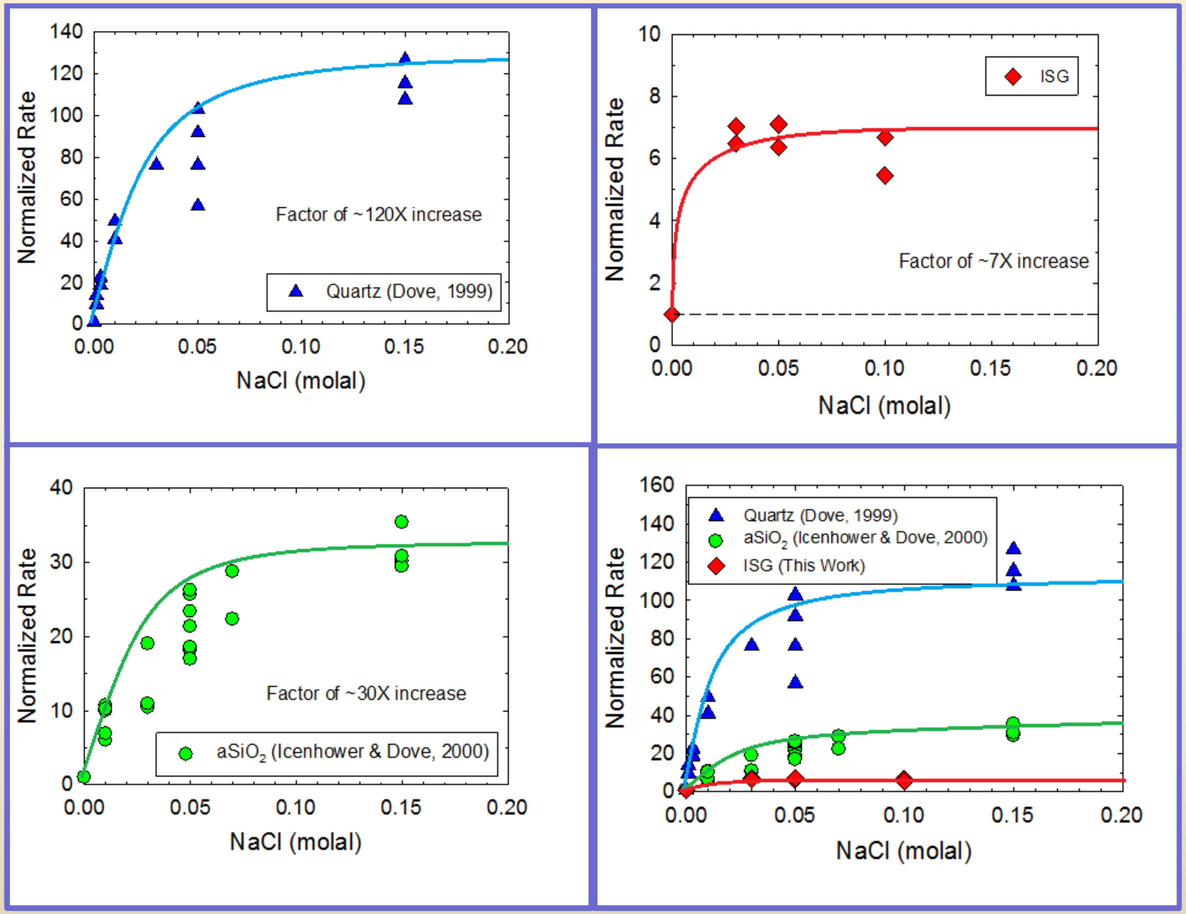
Approach to Steady-State



Rate Catalysis by NaCl

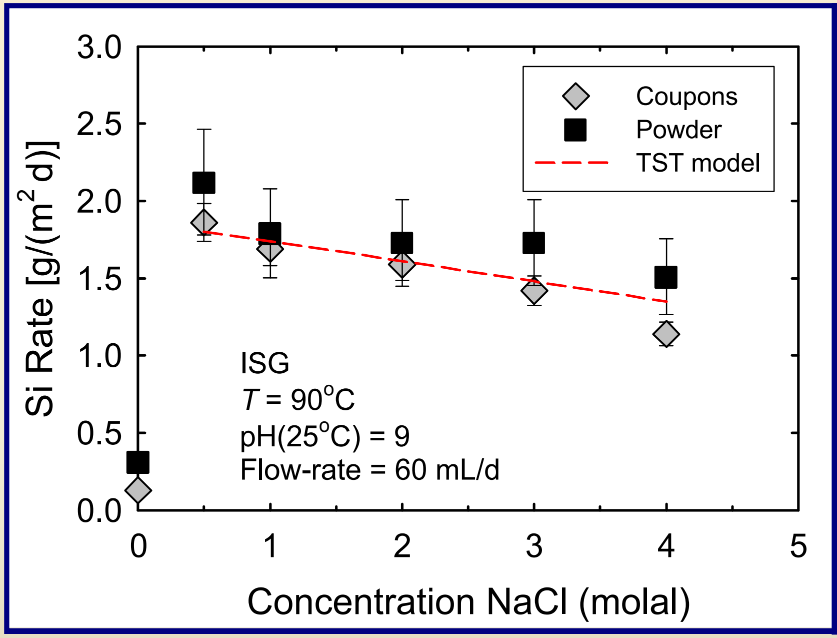


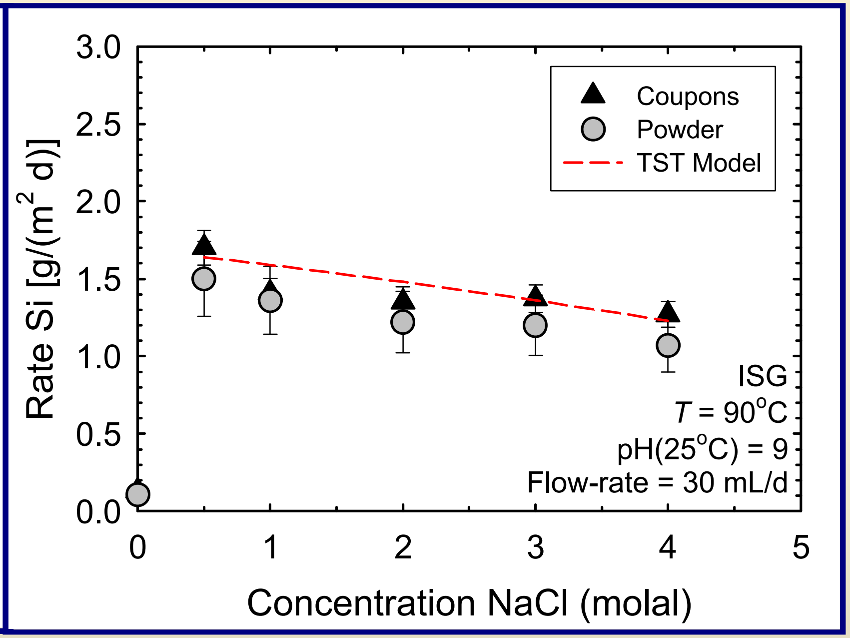
Enhancement of Rates by NaCl



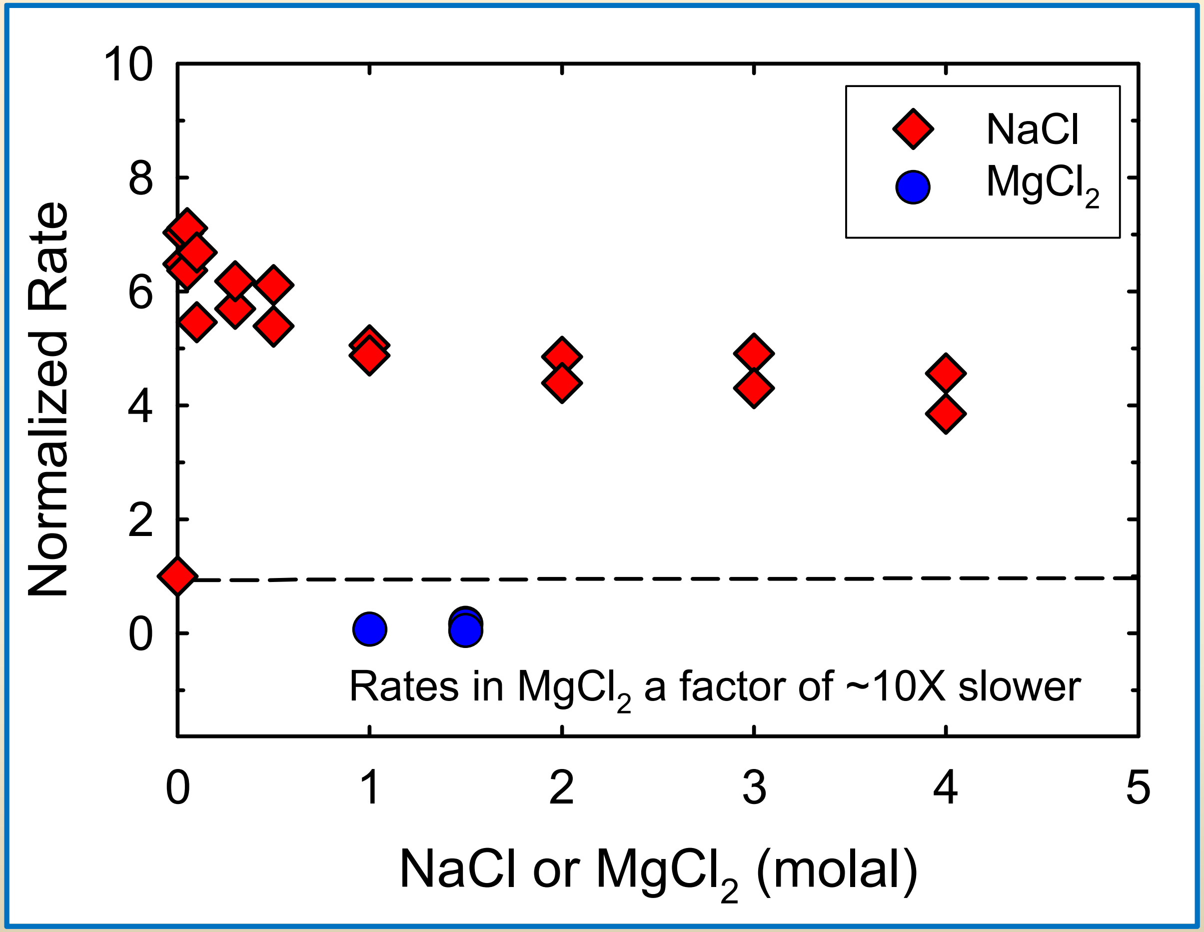
Dissolution Rate vs. Activity of Water

$$Rate = k_0 \cdot (a_{SiO_2}) \cdot (a_{H_2O})^2 \cdot \left(1 - \frac{Q}{K}\right)$$





Effects of $MgCl_2$ on ISG Rates



Conclusions

- Rates of powdered and monolithic ISG the same within error, assuming SA_{Geo}.
- With the addition of NaCl rates increase sharply.
- At higher concentrations of NaCl, the rates drop as the activity of water decreases, as predicted by TST.
- The rate catalysis behavior of ISG is similar, but smaller in magnitude, than that displayed by quartz and $aSiO_2$.
- This behavior indicates that rupture of the Si—O bond governs the dissolution of ISG in NaCl brine solutions.
- Preliminary work indicates rates ***decrease*** in $MgCl_2$ solutions.

Thanks for your attention!