U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

NUCLEAR WASTE TECHNICAL REVIEW BOARD
FULL BOARD MEETING

SUBJECT: GLASS MODELING

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Glass Waste-Form Testing: Activities

- Site-specific testing
  - Saturated
  - Unsaturated (drip)
  - Vapor phase
- Model development
- Model development testing
  - Rate constant
  - Affinity term
- Incorporate outside information

Glass Modeling: Status August 1990

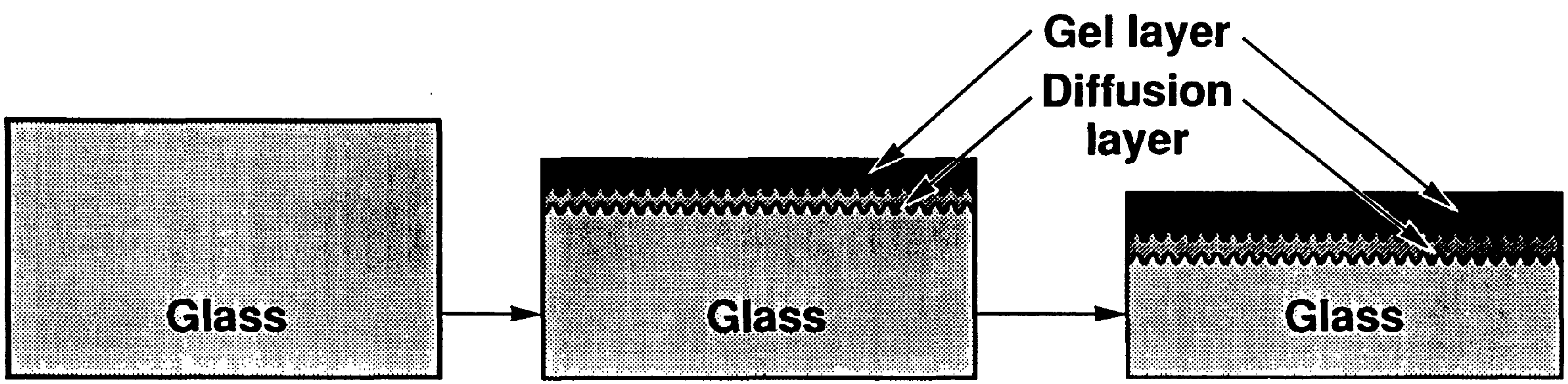
- Glass dissolution rate primarily controlled by solution composition (affinity effect) as opposed to diffusion/ transport control
- Simple mechanistic model developed in EQ3/6 code and successfully applied to a variety of glass dissolution tests
- Long-term rate control is related to saturation state of surface alteration layer, not glass
- Need for experimental program to provide model parameters independent of site-specific/validation test

Glass Dissolution Model

Hydration of the surface and ion exchange of alkalis

Diffusion layer thickens until rate of diffusion of alkalis equals rate of dissolution of network structure of gel

Diffusion and gel layers migrate into the glass maintaining a nearly constant thickness (steady state)



Dissolution of gel layer controls glass dissolution rates

Affinity Control of Glass Dissolution Rate

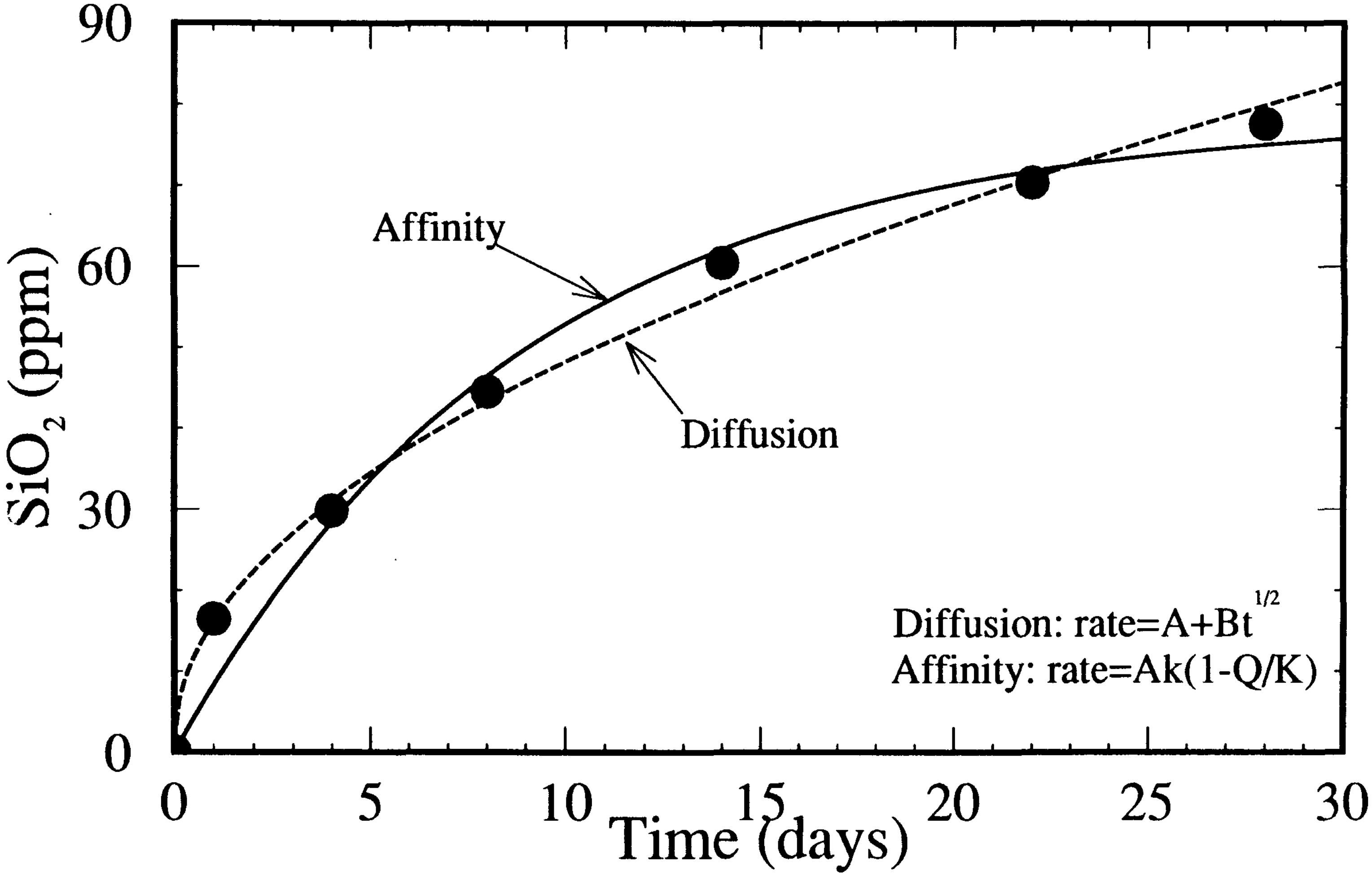
Rate = Surface area x Rate constant x Affinity term

- Rate constant is a function of temperature, pH, and solution composition
- Affinity term has form $(1-(Q/K)^m)^n$ where m and n must be determined experimentally
- Q is activity product for dissolving solid; K is equilibrium constant for dissolving solid

Current Models: Major Limitations

- Use model parameters as regression parameters in fitting experimental data
- Incomplete accounting for effects of solution chemistry on glass dissolution behavior
- Do not explicitly include effects of glass composition
- Do not account for glass/water interface surface chemistry

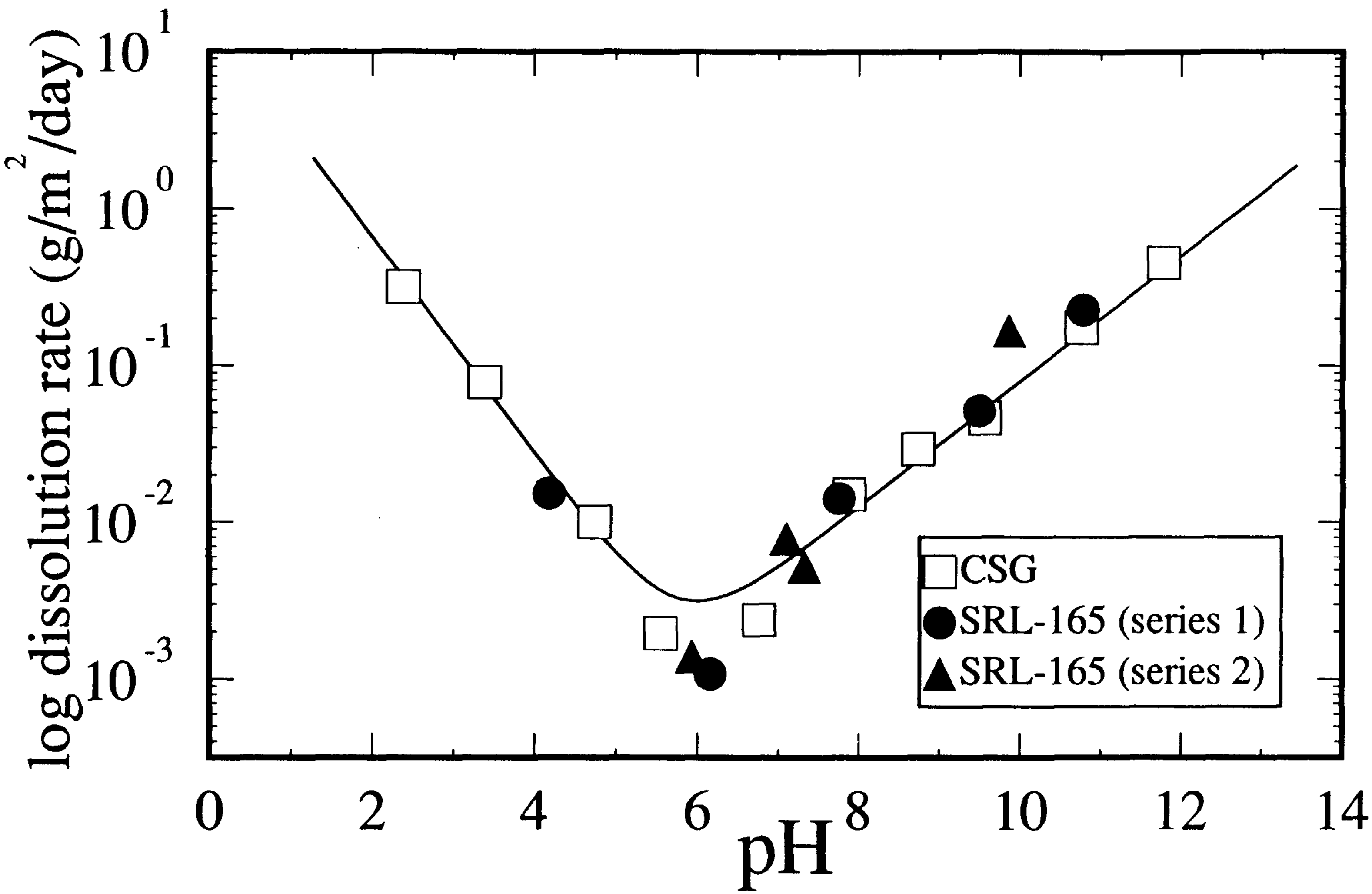
Affinity vs. Diffusion Rate Control



Status of Experimental Program to Provide Model Parameters

- Flow-through tests of 3 SRL glasses and simple analog glasses as a function of pH and temperature
  - Provide T and pH dependence of rate constant
- Completed test series of SRL-202 glass in Ca, Mg, Al, B, and Si-doped buffers
  - Provide interpretable information on effects of dissolved cations on dissolution rate under controlled conditions
- Measured SRL-165 analog glass dissolution rate in closed system from 100-250°C and used to define affinity term
- Beginning to systematically examine glass compositional effects on glass durabilities with flow-through experiments

Simple vs. Complex Glass



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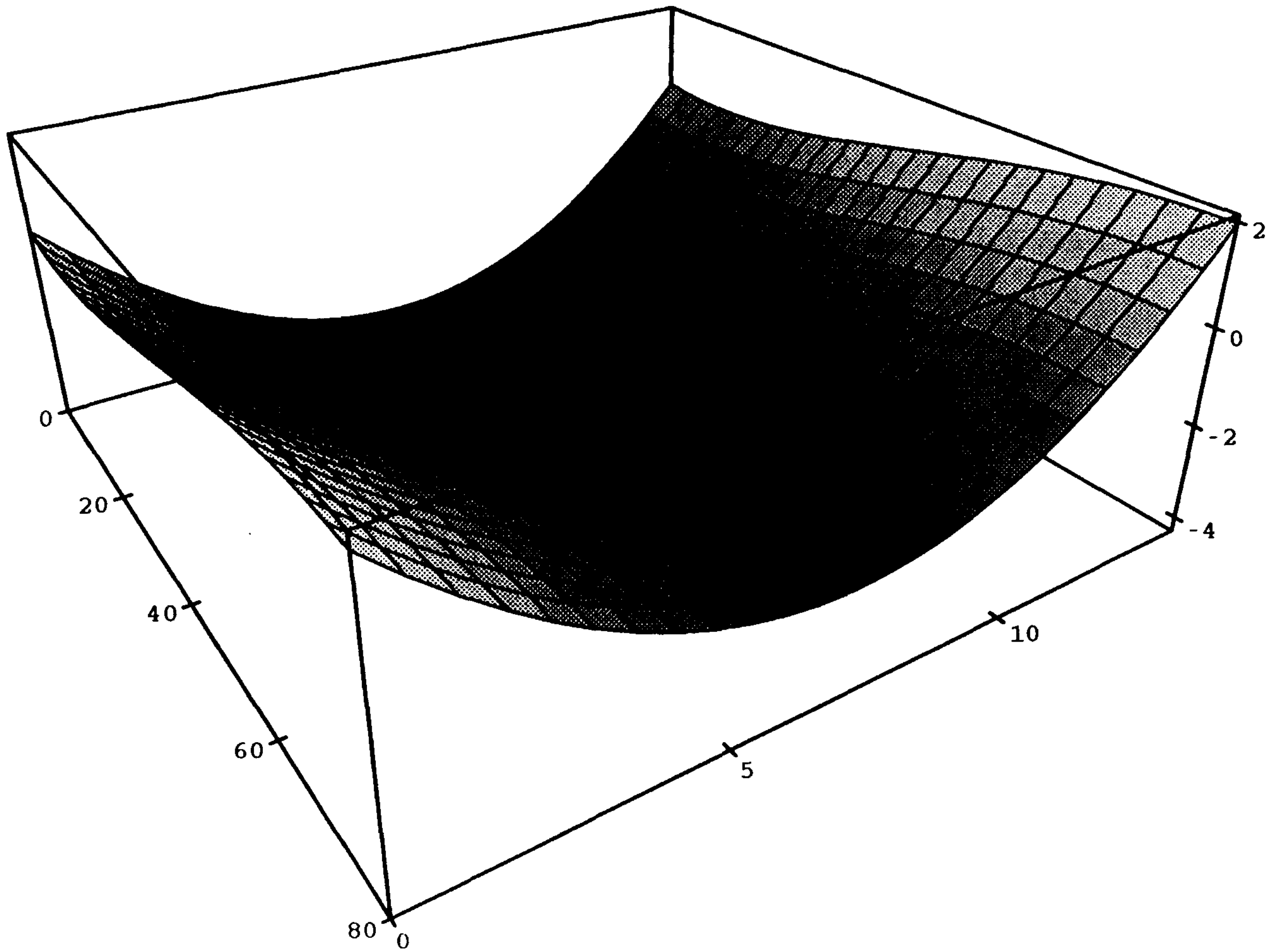
Temperature and pH Dependence of Glass Dissolution Rate



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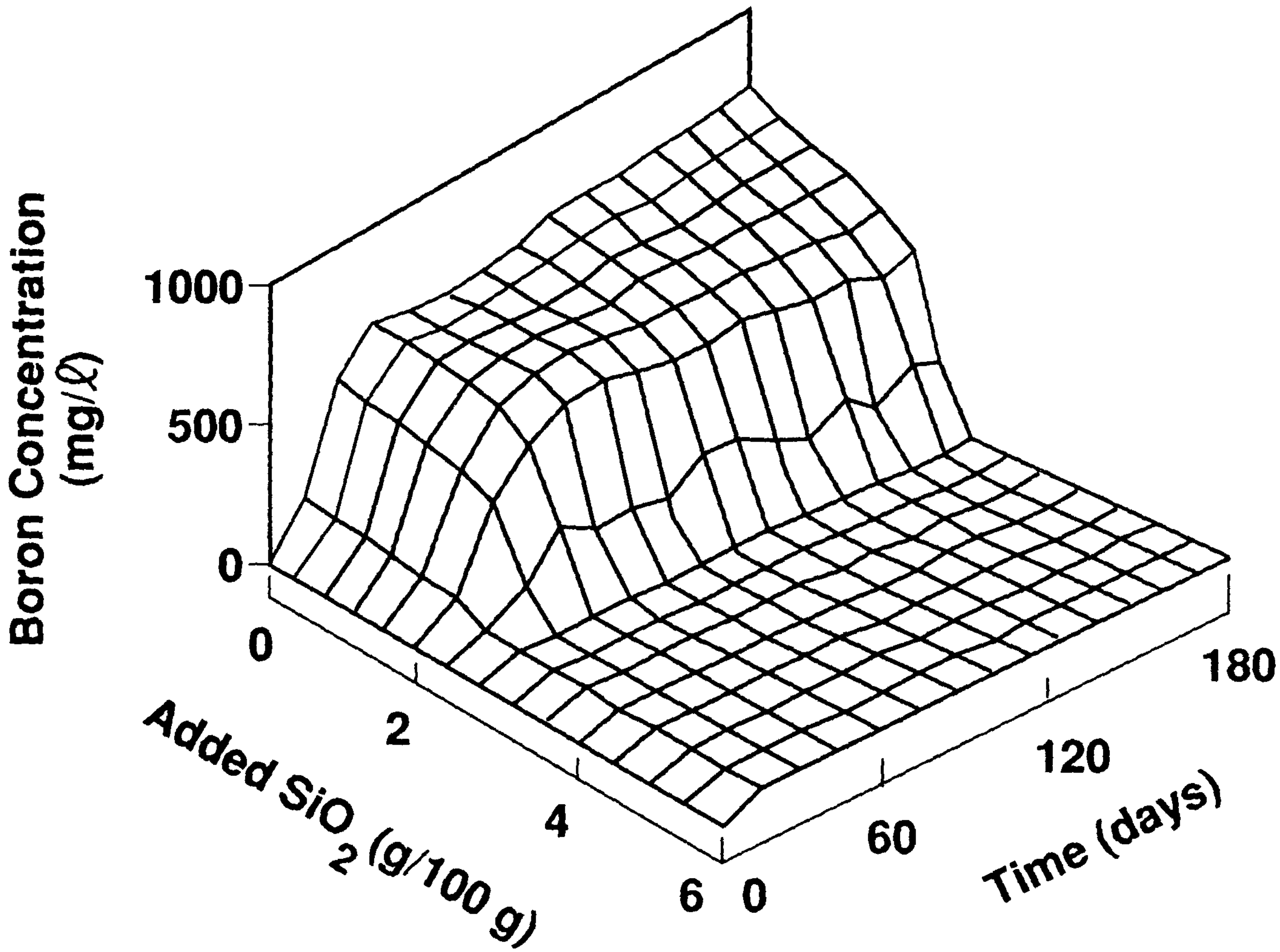
Dissolution Rate Dependence on Silica Concentration (WV205 Glass)



Modeling Applications

- Analysis of Surface Area/Volume* time scaling of experimental results
- Analysis of affinity control of glass dissolution rate

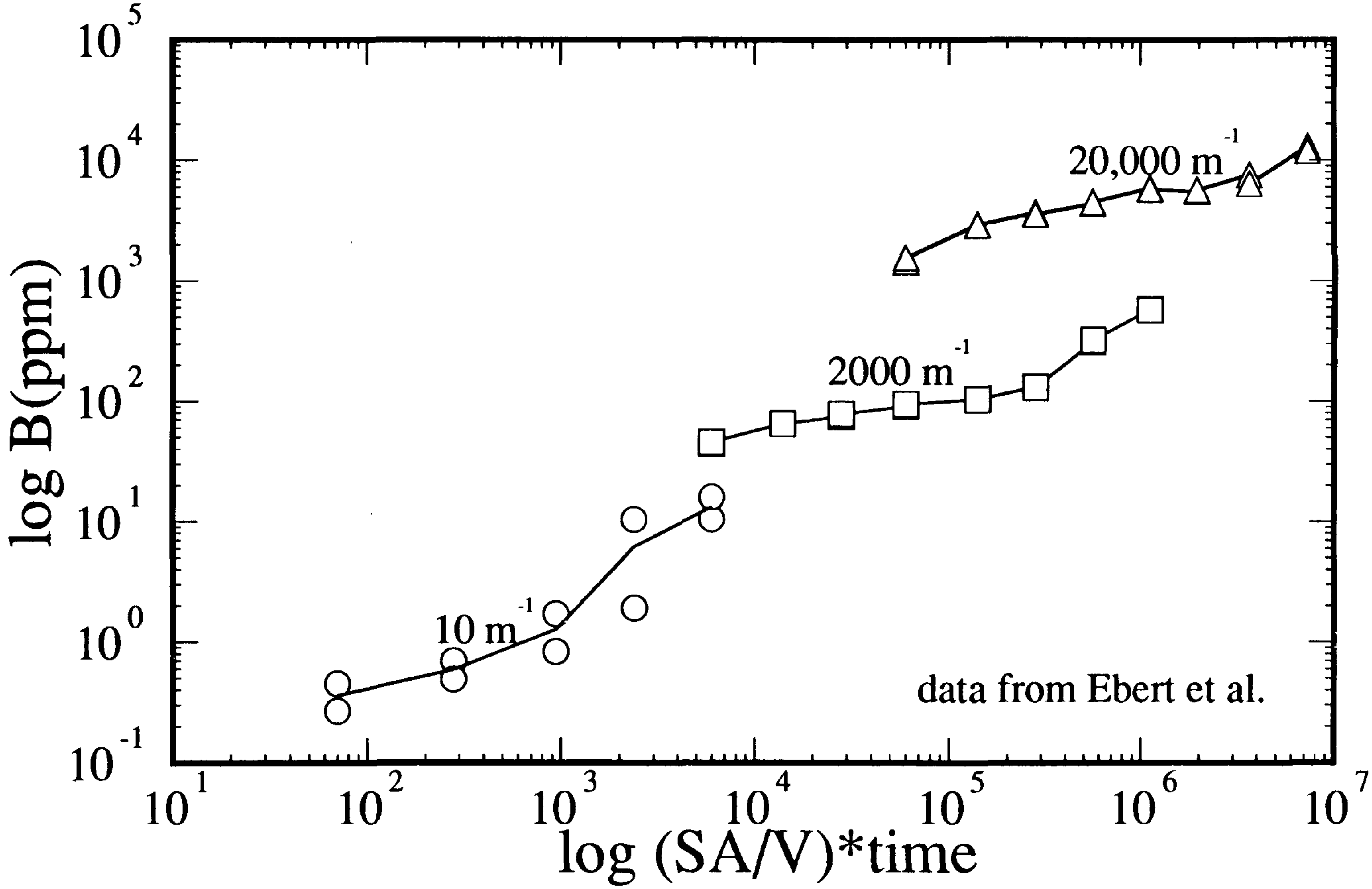
Application: Surface Area/Volume* (SA/V*) Time Scaling

- SA/V* time scaling follows from observations that dissolution rate is proportional to surface area and controlled by solution composition

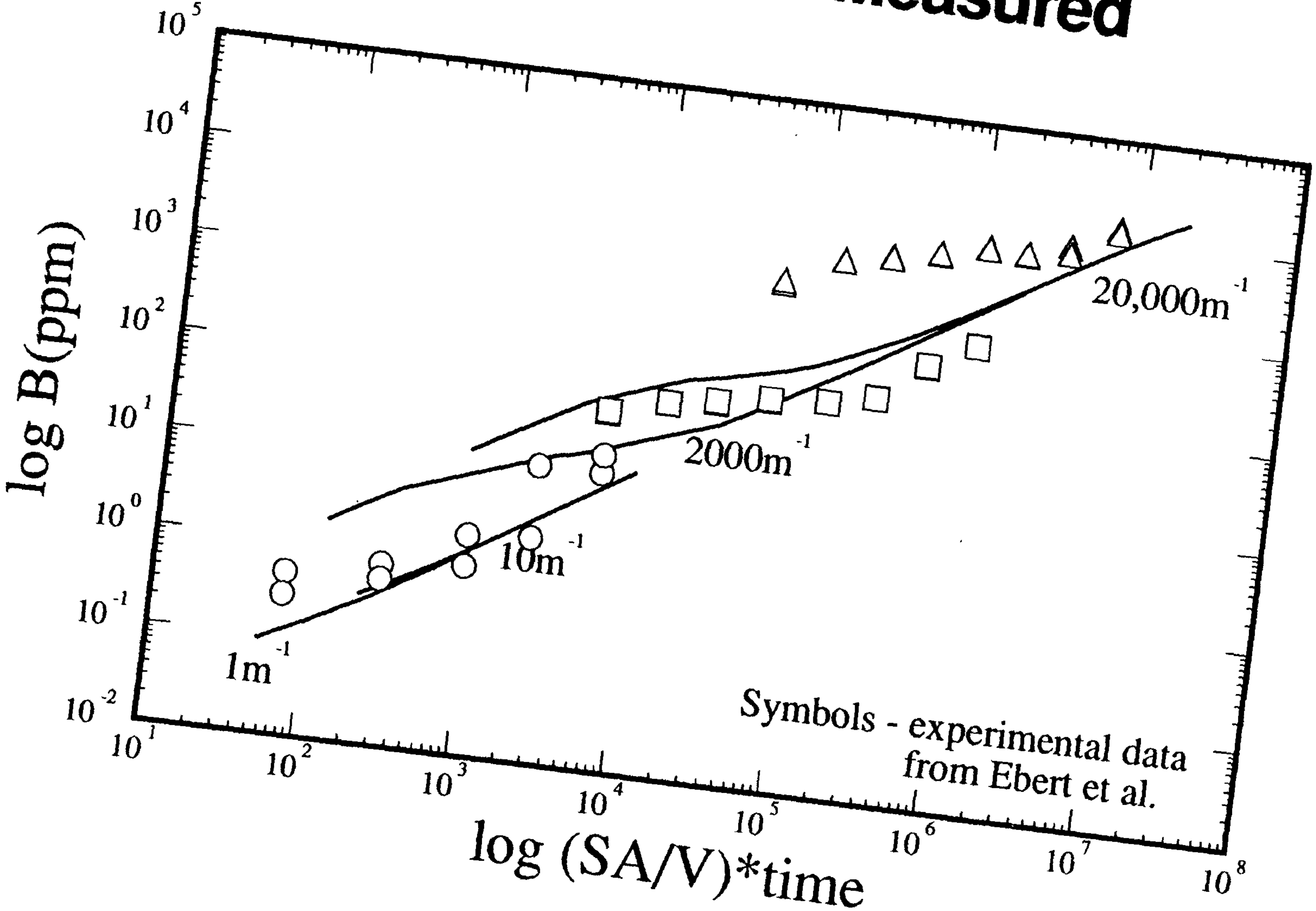
- SA/V* time scaling is not observed for most experiments. Why not?

- Simulate experiments over a range of SA/V ratios and scale according to SA/V* time

Surface Area/Volume (SA/V) Effects: Experimental Data



Surface Area/Volume (SA/V) Effects: Calculated vs. Measured



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Surface Area/Volume* (SA/V*) Time Scaling: Conclusions

- Rapid initial ion exchange of outer 50nm of glass surface is responsible for lack of SA/V* time scaling
- Use of high SA/V conditions to accelerate tests must be interpreted in context of functional relationships found in model results

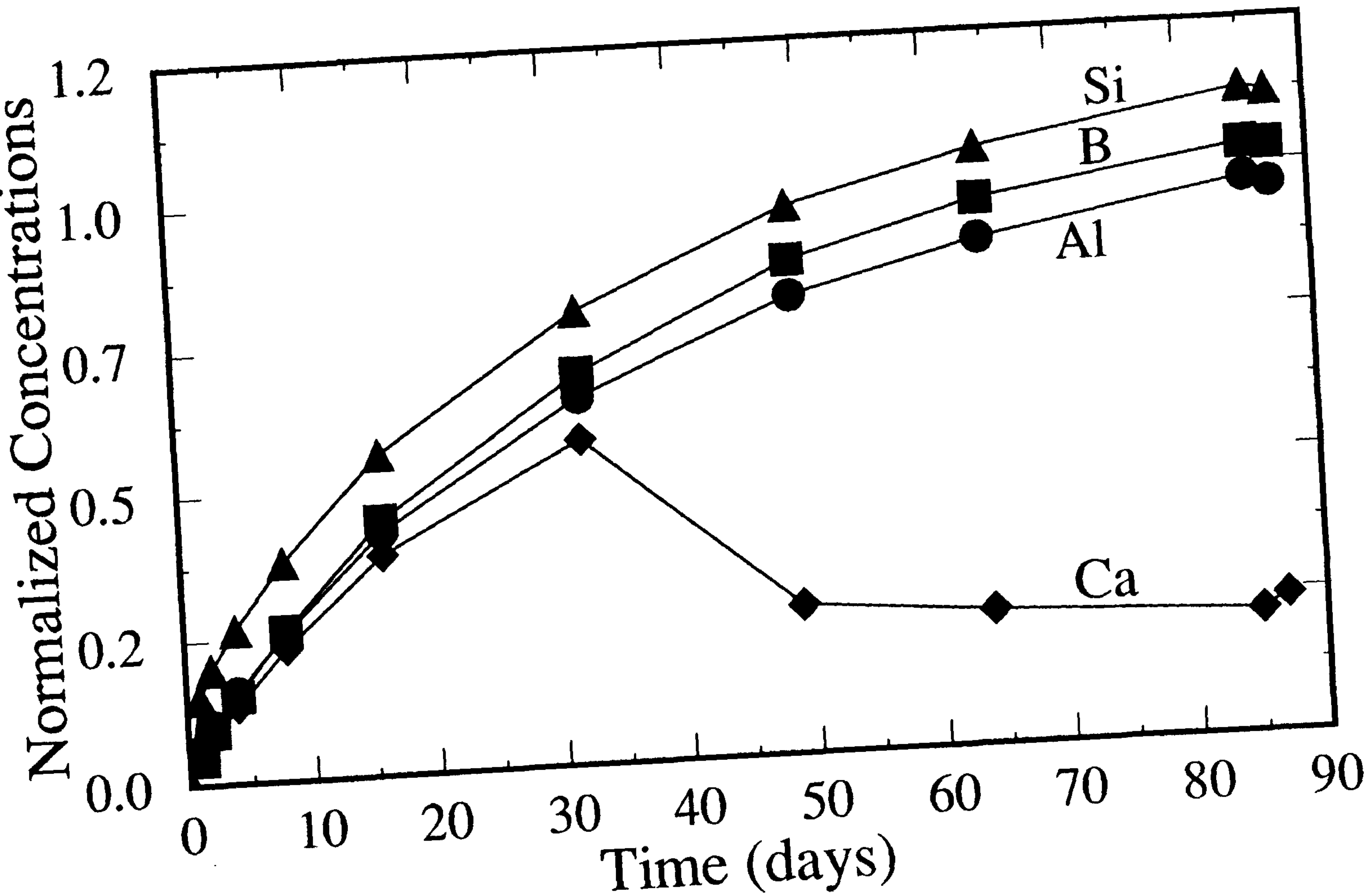
Application: Affinity Control

- Two questions:
  1. What is functional form of affinity term?
  2. What is solid controlling dissolution rate?

- Procedure:
  1. Extract release-rate data from well-characterized experiments
  2. Perform simulation using variety of reasonable solids as rate-controlling phases

- Find simple function that best fits release rate as function of time

CSG Glass (100° C)



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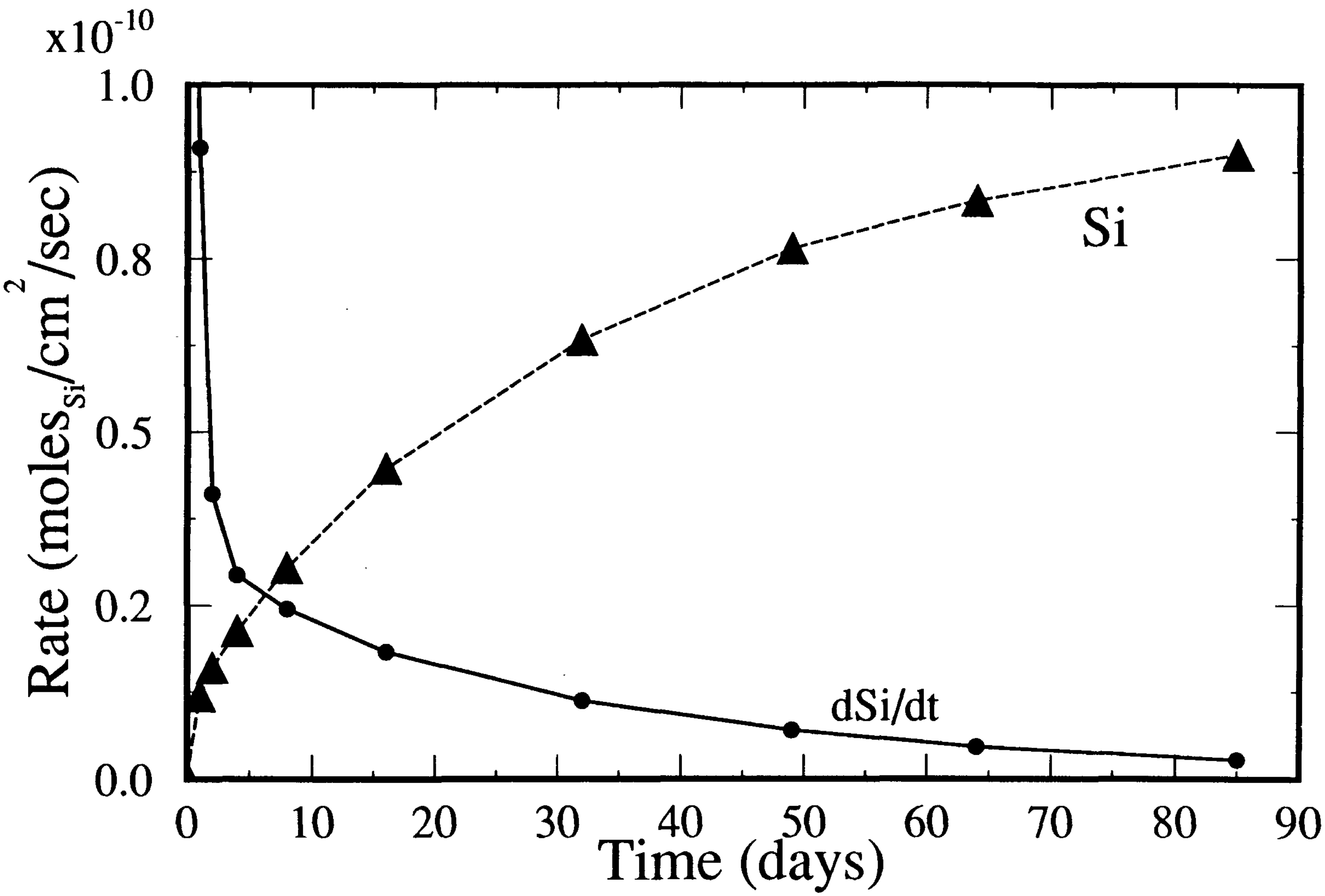
Silica Release Rate



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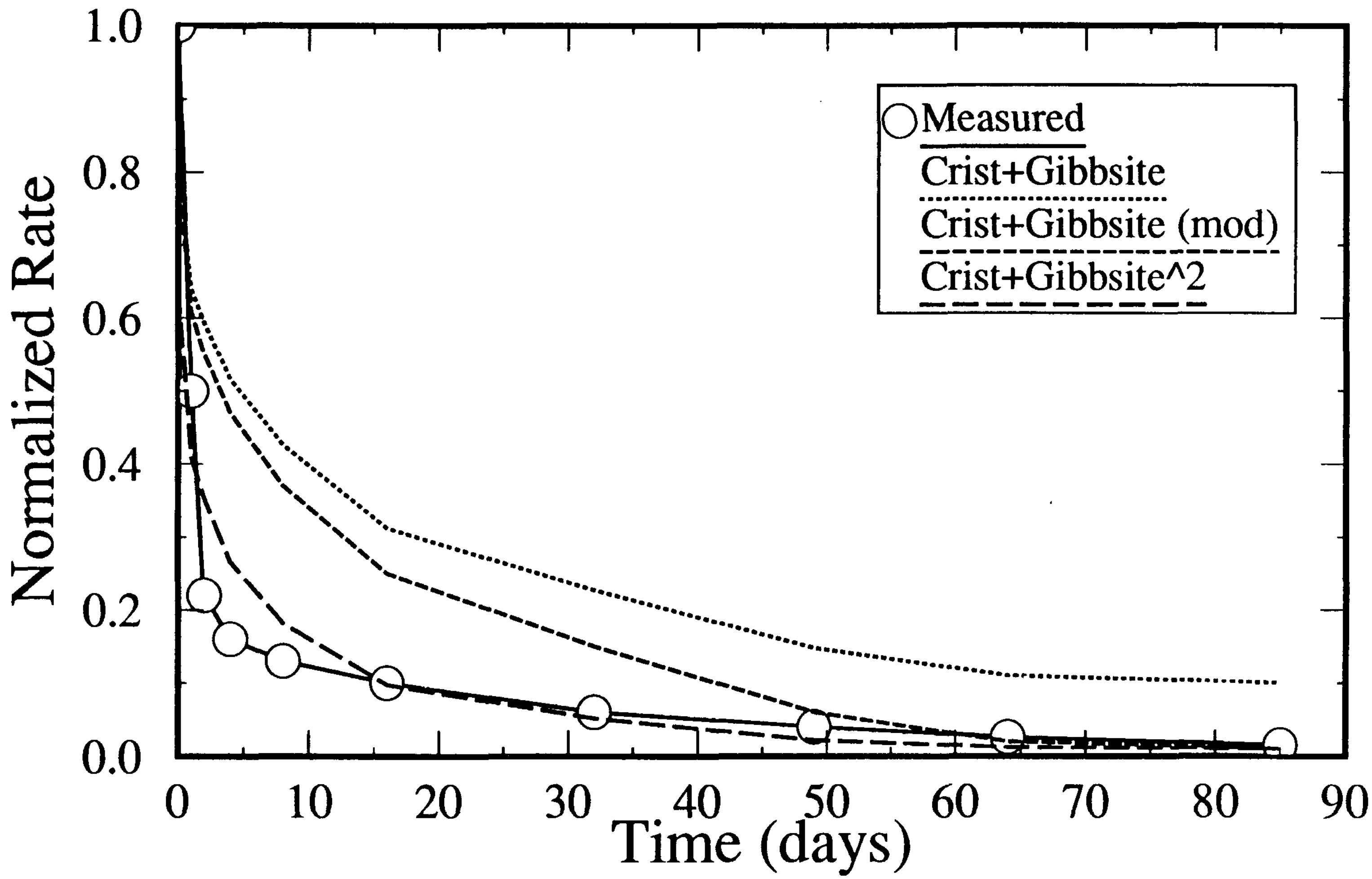
Dissolution Affinity



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Affinity Control: Conclusions

- Thermodynamic properties of bulk anhydrous glass do not control glass dissolution rate
- Glass dissolution rate consistent with control by hydrous surface layer
- Model will be further constrained with input from multiple independent test results with careful characterization of surface layers

Conclusions

- Have a mechanistic understanding of how glass dissolves but have not yet quantified critical parts of it
- The model is generic; not specific to the Yucca Mountain site
- The model is designed to be interfaced to mechanistic models for durabilities of other repository materials
- Understanding of glass dissolution is applicable to parallel studies of other waste-forms and repository materials