

**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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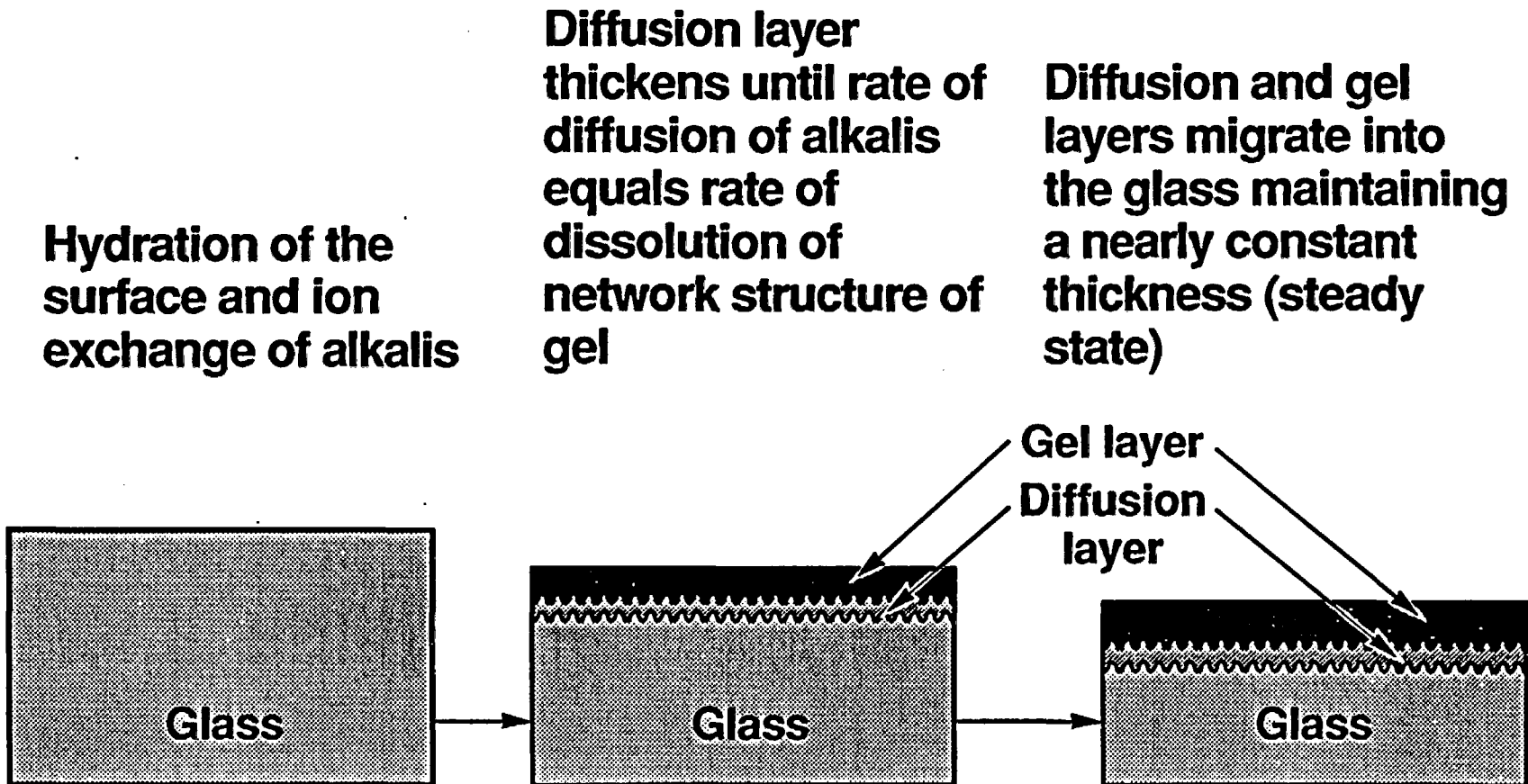
Glass Waste-Form Testing: Activities

- **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



Dissolution of gel layer controls glass dissolution rates

Affinity Control of Glass Dissolution Rate

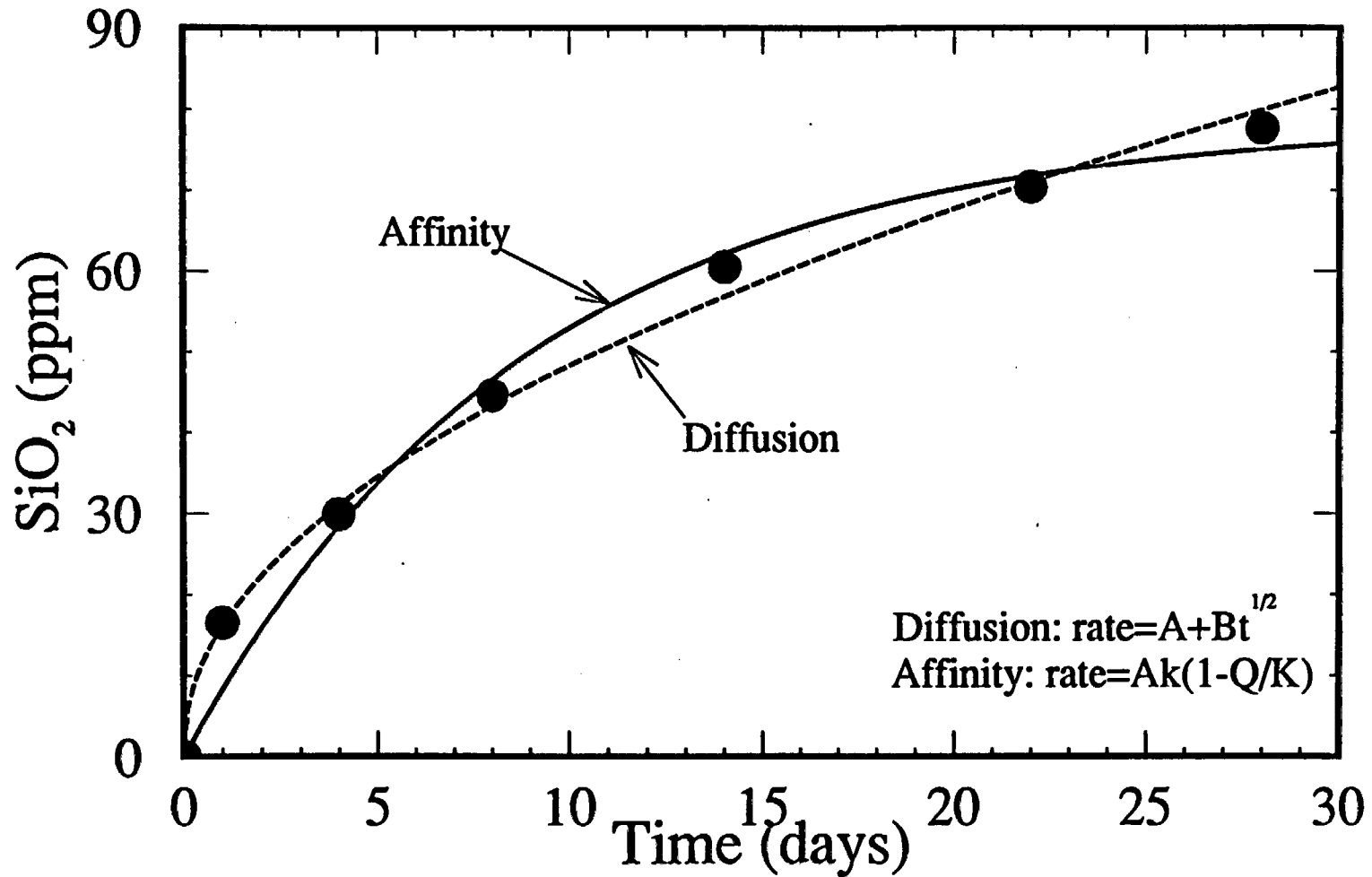
Rate = Surface area x Rate constant x Affinity term

- **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**

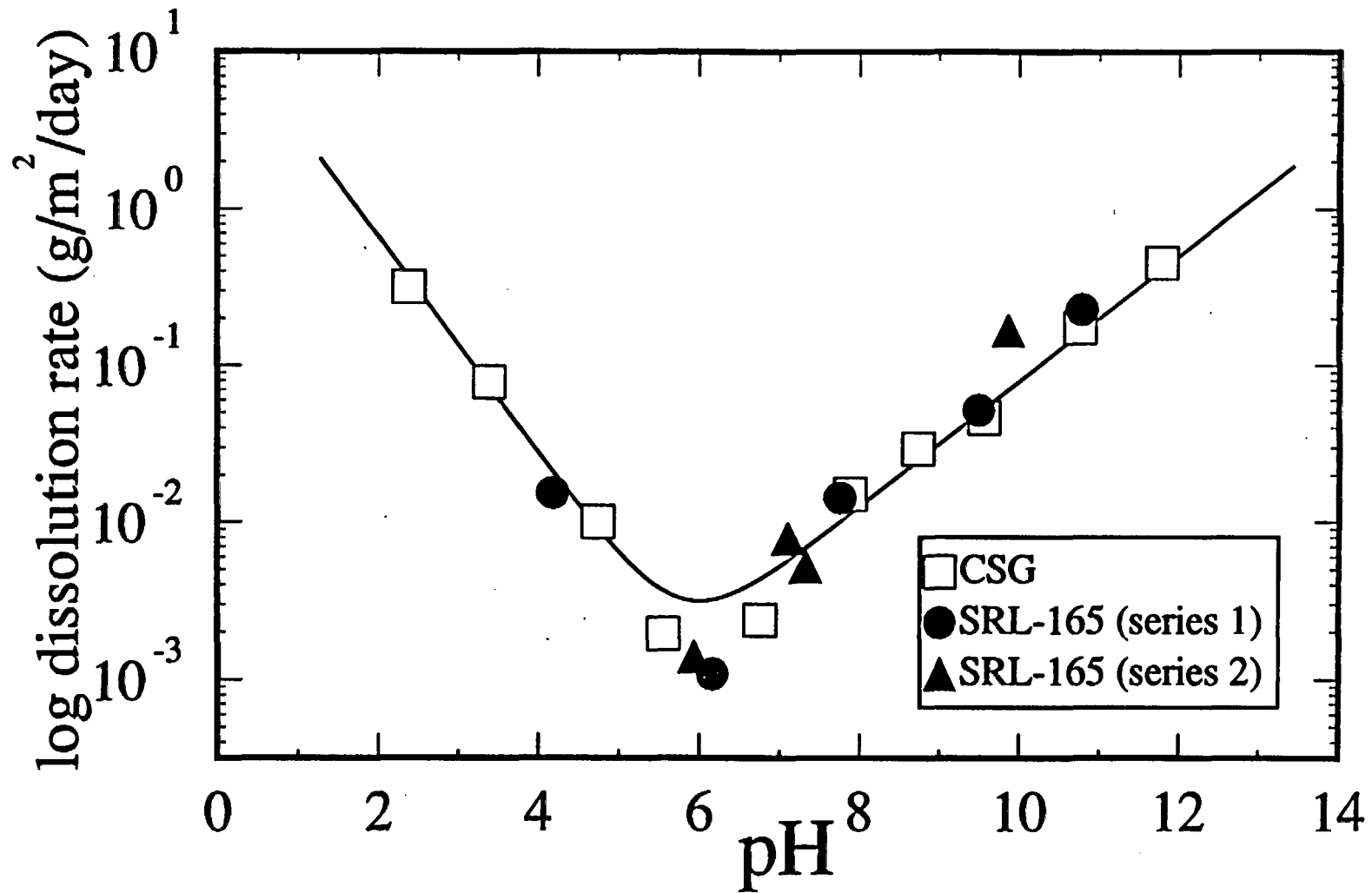
Affinity vs. Diffusion Rate Control



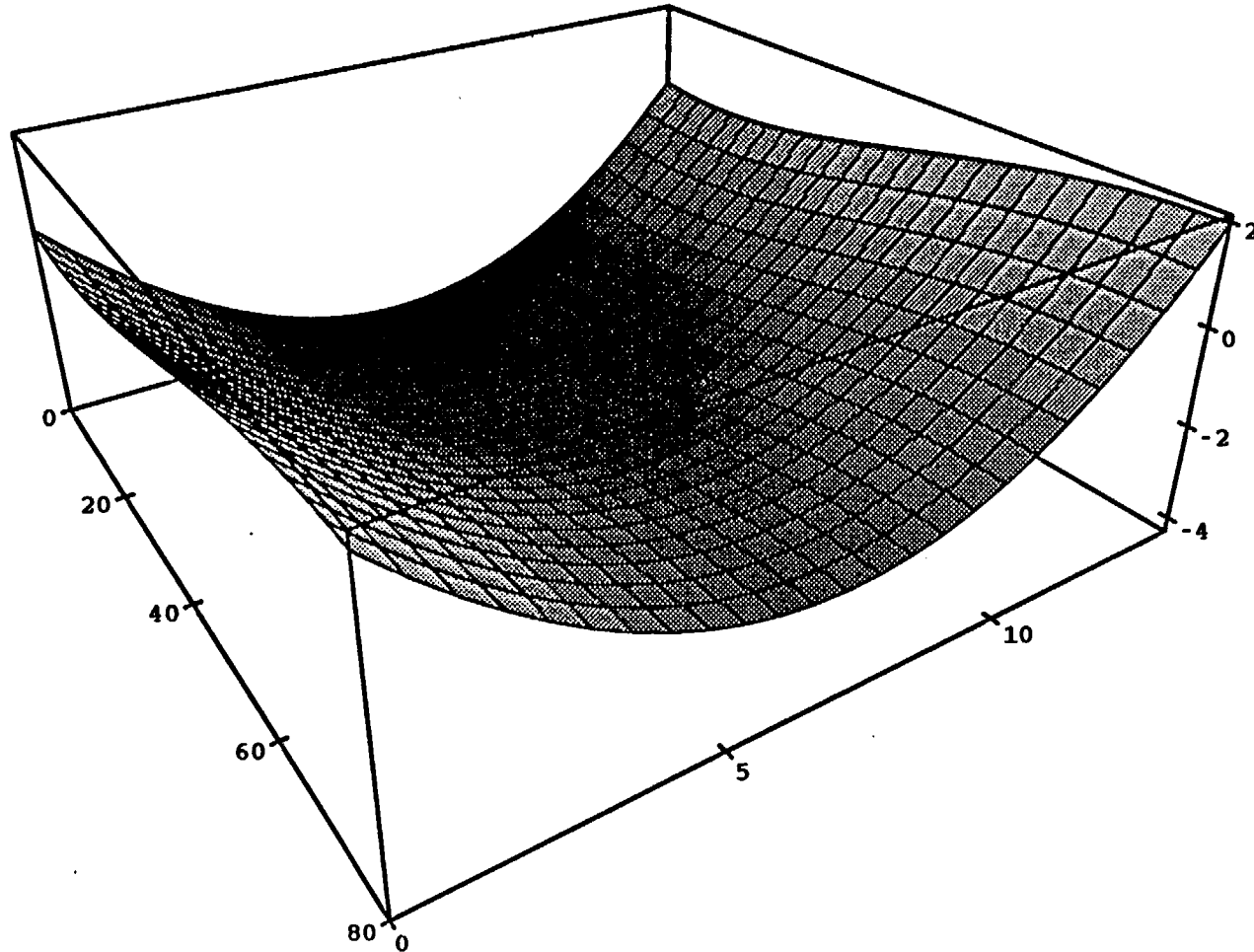
Status of Experimental Program to Provide Model Parameters

- **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**

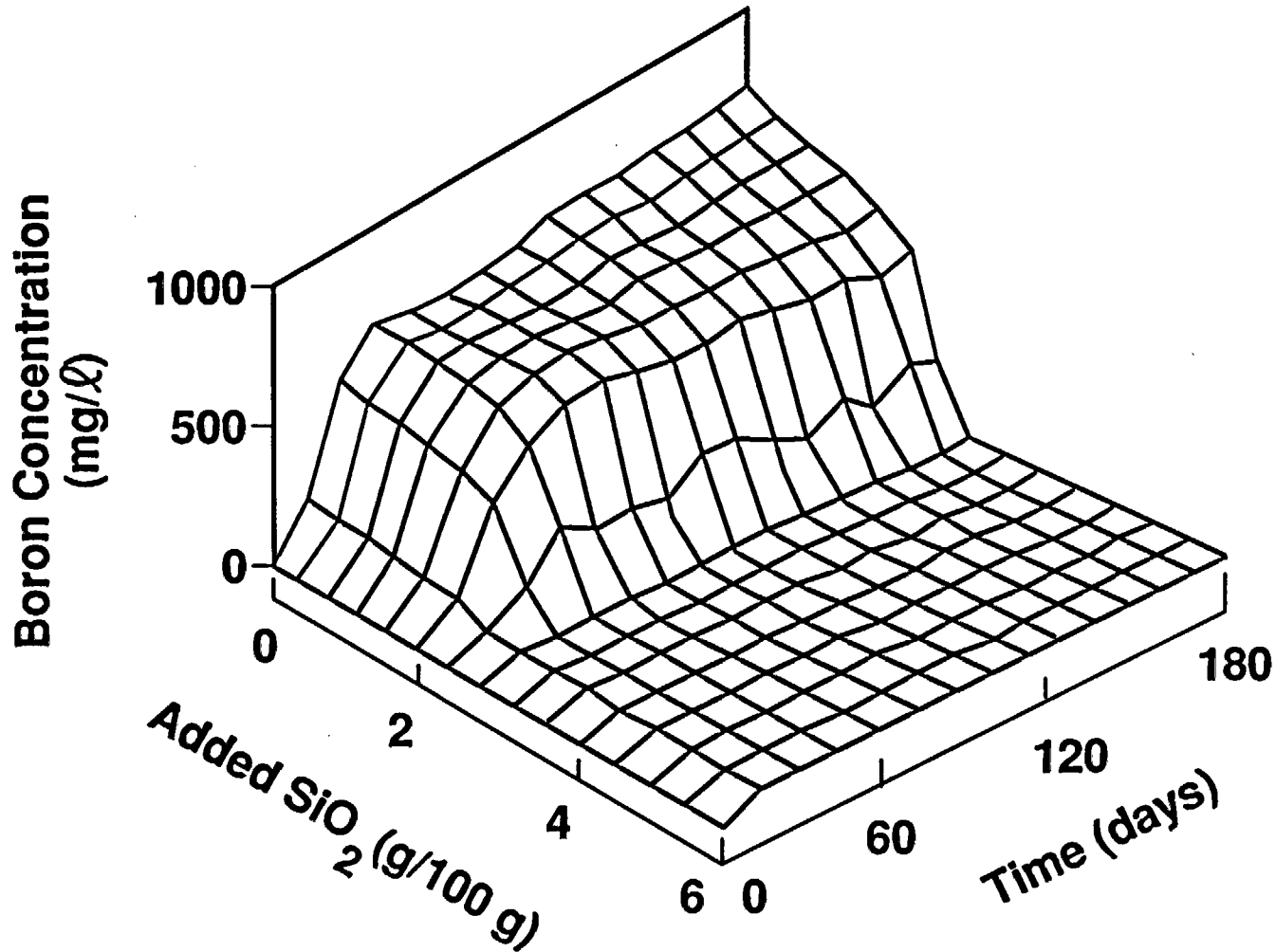
Simple vs. Complex Glass



Temperature and pH Dependence of Glass Dissolution Rate



Dissolution Rate Dependence on Silica Concentration (WV205 Glass)



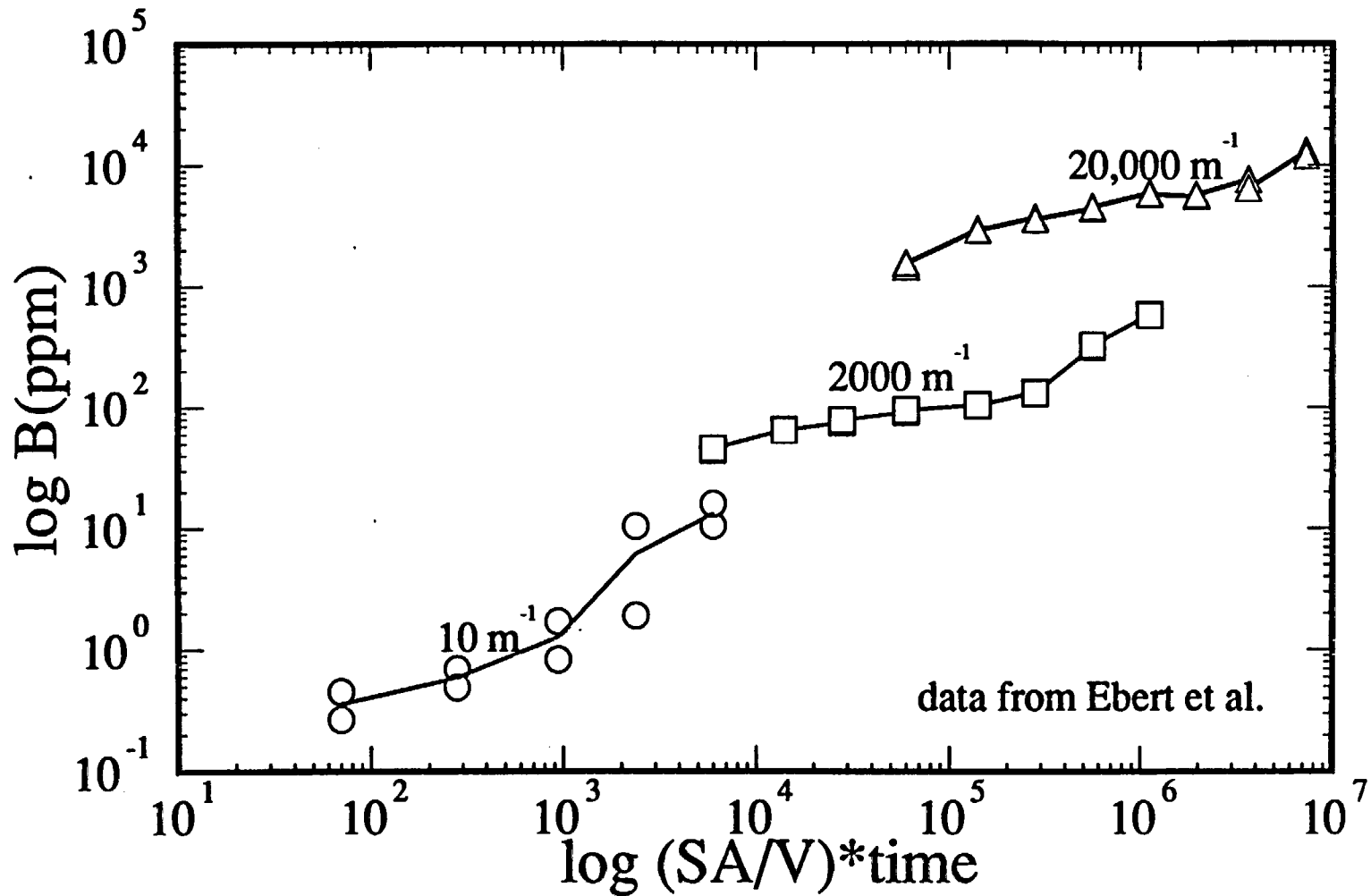
Modeling Applications

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

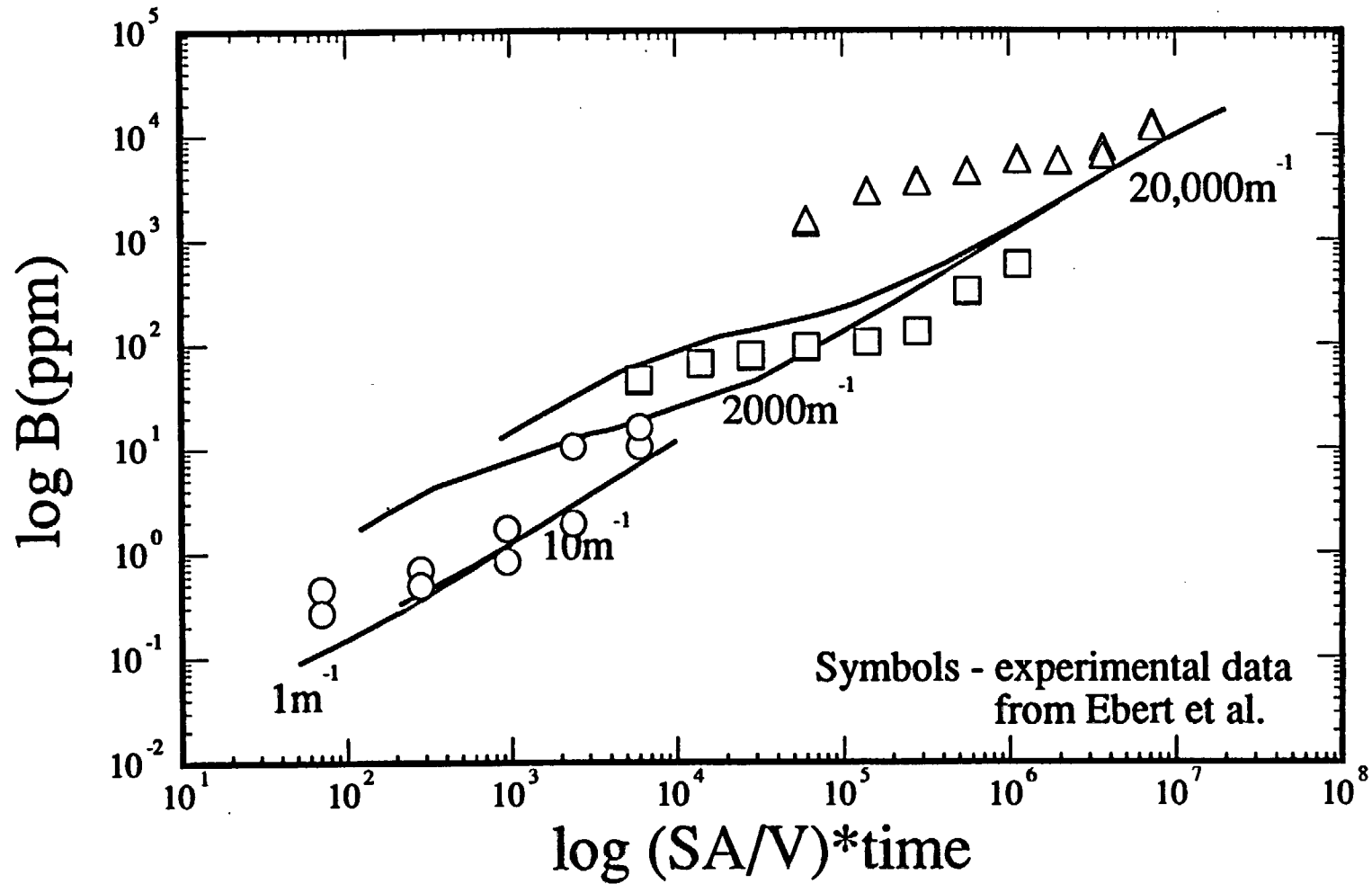
Application: Surface Area/Volume* (SA/V*) Time Scaling

- **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



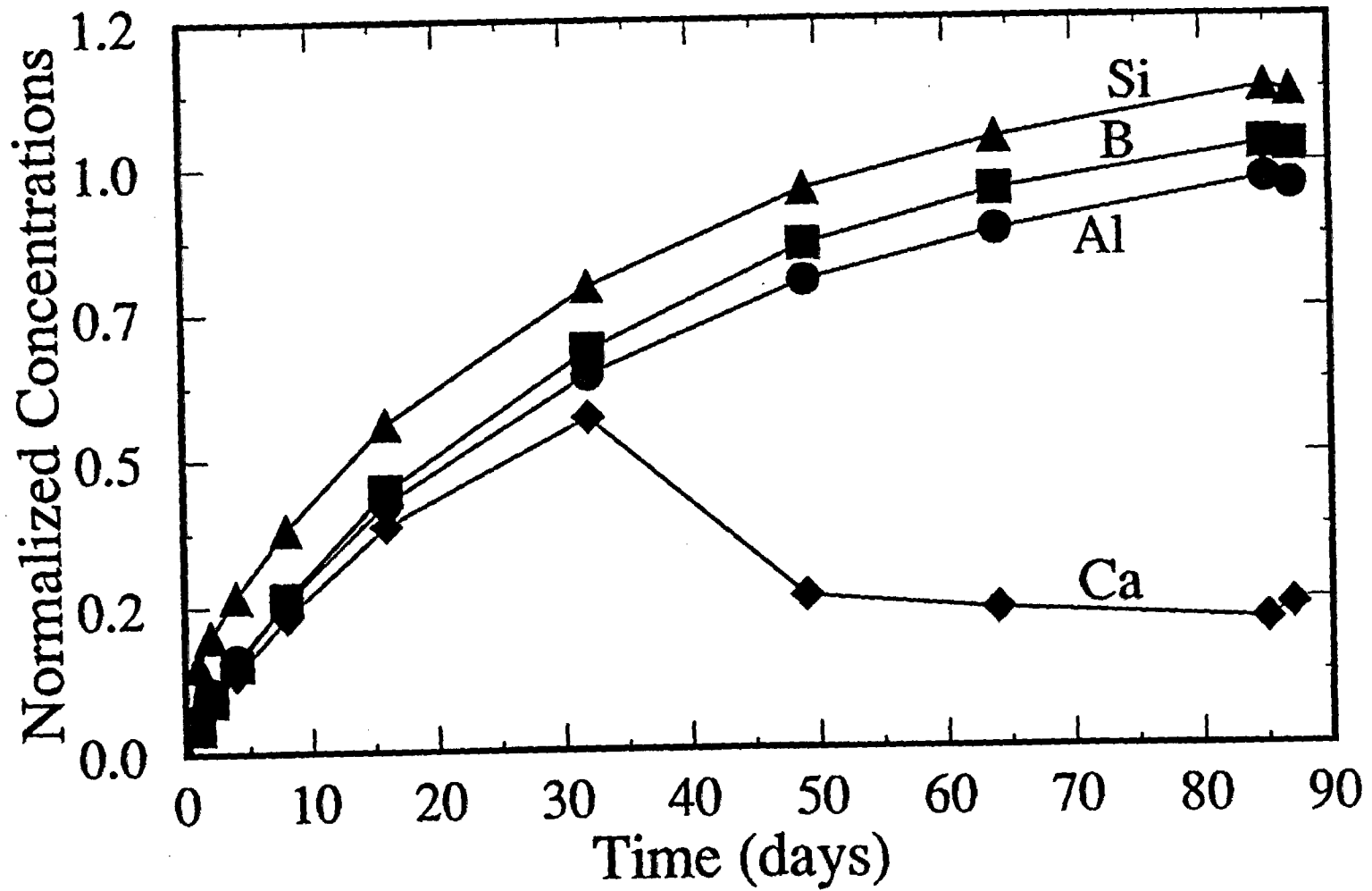
Surface Area/Volume* (SA/V*) Time Scaling: Conclusions

- **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**

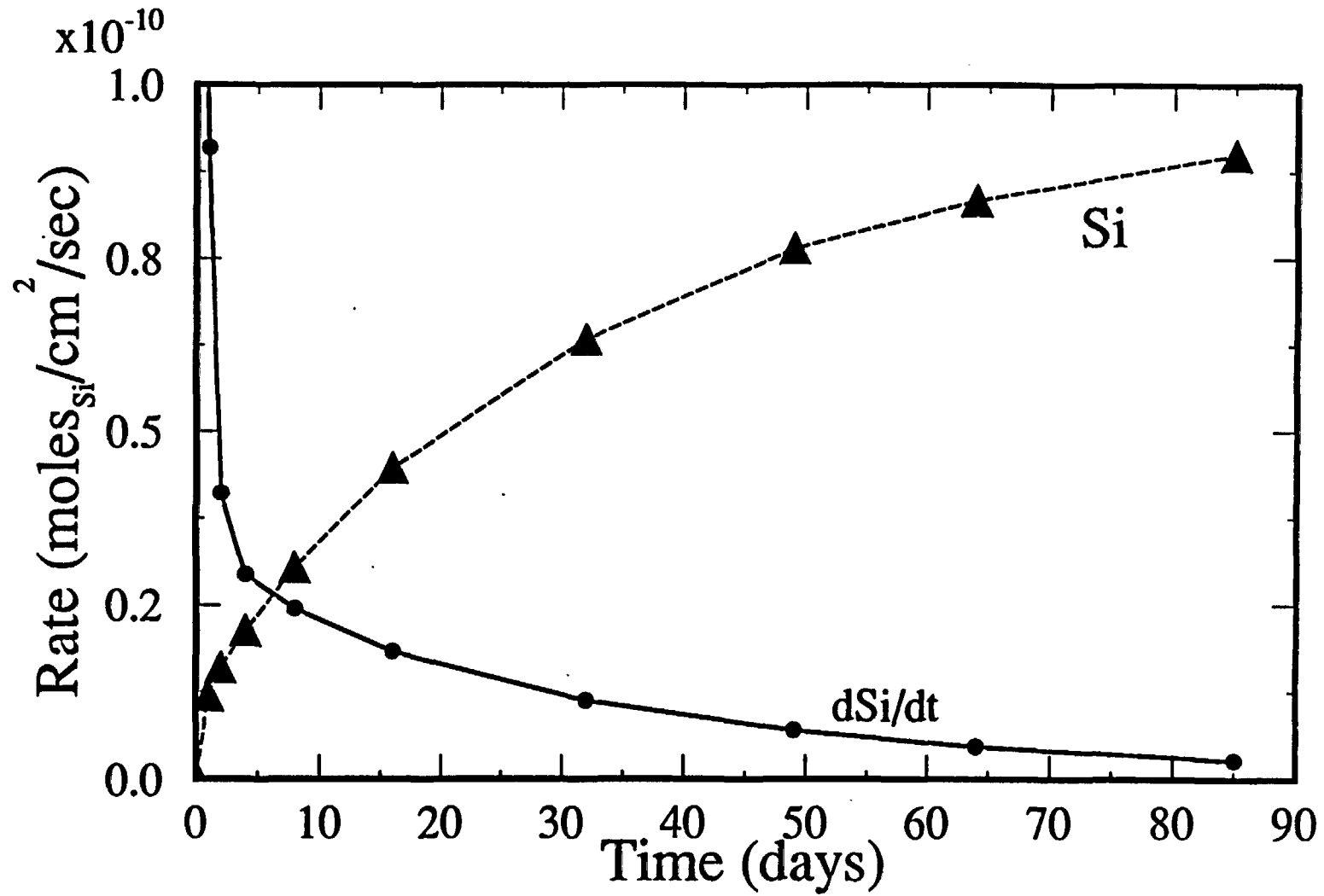
Application: Affinity Control

- **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**

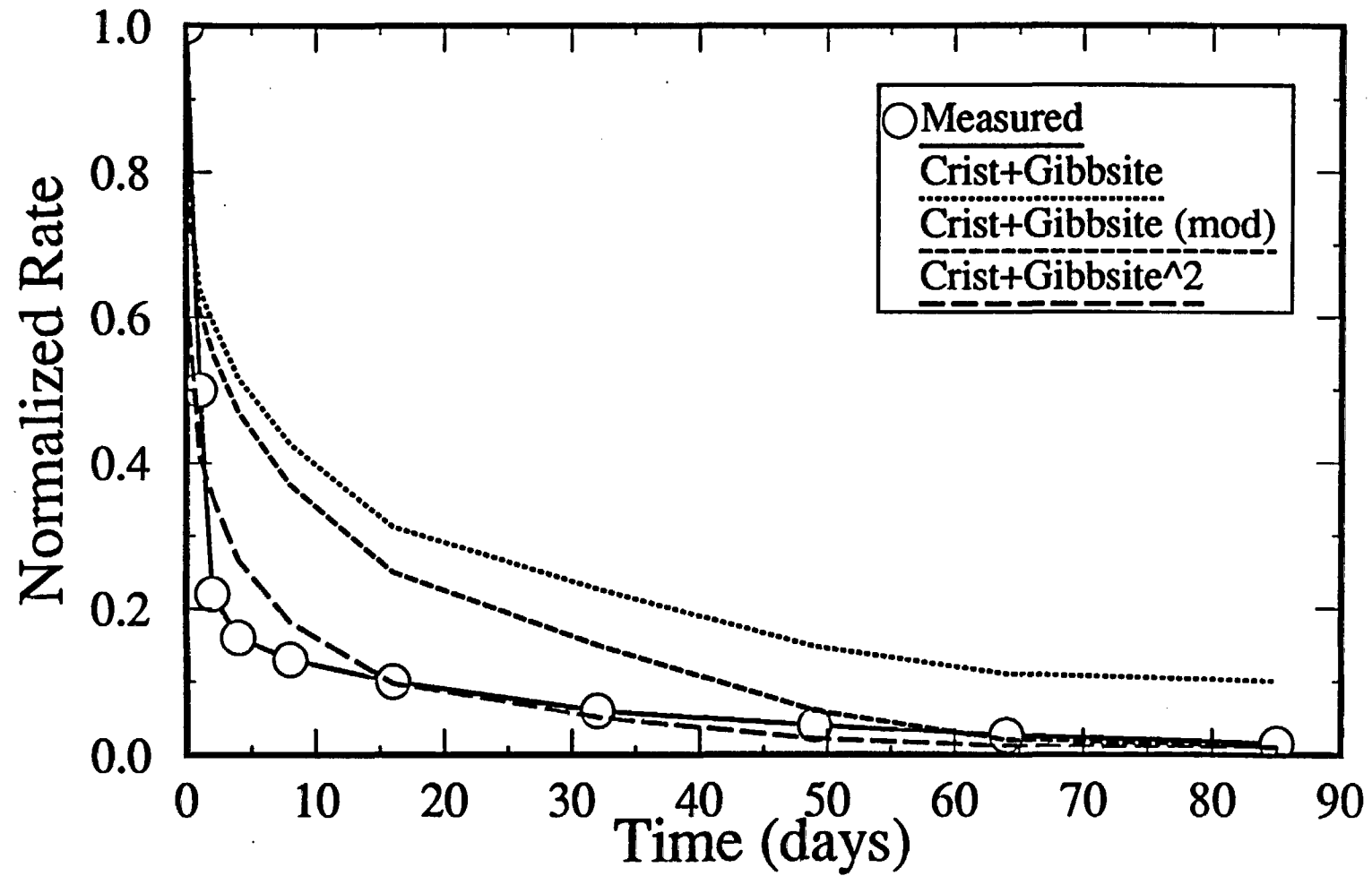
CSG Glass (100° C)



Silica Release Rate



Dissolution Affinity



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**