

## **SUMMARY/PROGRESS REPORT**

**PROJECT TITLE:** Quantifying Silica Reactivity in Subsurface Environments:  
An Integrated Experimental Study of Quartz and Amorphous Silica to  
Establish a Baseline for Glass Durability

**DATE:** June 15, 2001

### **PRINCIPLE INVESTIGATOR:**

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### **GRADUATE STUDENTS:**

Mr. Colin Craven  
Mr. Troy Lorier  
Mr. Darren Wilson

### **UNDERGRADUATES:**

Ms. Christina Lopano (now graduate student at Penn State)

### **RESEARCH OBJECTIVE:**

An immediate EM science need is a reliable kinetic model that predicts long-term waste glass performance. A framework for which the kinetics of mineral-solution reactions can be used to interpret complex silicate glass properties is required to accurately describe the current and future behavior of glasses as synthetic monoliths or natural analogs. Reaction rates and mechanisms are essential elements in deciphering mineral/material reactivity trends within a compositional series or across a matrix of complex solution compositions. An essential place to start, and the goal of this research, is to quantify the reactivity of crystalline and amorphous SiO<sub>2</sub> phases in the complex fluids of natural systems.

Perhaps the most important motivation for quantifying SiO<sub>2</sub> reactivity in the fluids of subsurface environments is that an understanding of fundamental controls on the reactivity of simple Si—O bonded phases establishes baseline behavior for silica phases widely found in waste storage environments. Host rock silicate minerals dominate virtually every repository rock-water system. Further, complex silicate glasses will be the front line of defense in containing radioactive wastes in both interim and long-term storage strategies. However, we have little quantitative understanding of pure SiO<sub>2</sub> reactivity in the solutes of natural and perturbed groundwaters even though current EM strategy calls for dispersal of waste into silica-based glass materials. Findings will establish quantitative relationships between silica reactivity and complex solution chemistries never investigated which are presently speculative at-best. Further, we will be able to uncover an

underlying principle that governs how solutes affect silica reactivity in a systematic and predictable way.

## **RESEARCH PROGRESS AND IMPLICATIONS:**

The new research project was initiated on February 1, 2001. Therefore, our reporting period for this year spans only a few months of activity.

### **A. Interactions with Users: Tank Focus Area**

P.I. Dove has continued to interact with TFA scientists and engineers on the problems of waste glass properties. Mr. Colin Craven presented the results of EMSP research findings to a TFA subgroup at the Salt Lake City meeting in March of 2001 (Dove was expecting a new child and could not travel). Following this meeting, Mr. Craven traveled to PNNL and interviewed for a research position with the Applied Geochemistry group. Results of our EMSP-funded research have interfaced very well with the efforts of Dr. Pete McGrail and colleagues at PNNL. Continued linkages between Dove's former EMSP-funded postdoc, Dr. Jonathan Icenhower, and his group at PNNL has further facilitated information transfer from the 'university lab to user' environment. Similarly, former EMSP-funded graduate student from the Dove group, Troy Lorier, now works with the Glass Chemistry group (Dr. Bill Holtzscheiter) at Westinghouse Savannah River.

### **B. Publications:**

Karlsson, M., C.M. Craven, **P.M. Dove** and W.H Casey (2001) Surface charge concentrations on silica in different 1.0 M metal chloride background electrolytes and implications for dissolution rates. *Aquatic Geochemistry*, 7, p. 13-32.

Craven, C.M. and **P.M. Dove** (in review) Silica surface charge in alkali chloride solutions. *Geochimica Cosmochimica Acta*.

Lorier, T. and P.M. Dove (in preparation) The dissolution kinetics of quartz and amorphous silica in natural waters: A baseline for silica reactivity.

### **C. Awards:**

In the Spring of 2001, Mr. Colin Craven received the Outstanding Student Paper Award from the Hydrology Section of the American Geophysical Union.

## **PLANNED ACTIVITIES:**

Over the next year, we will be busy with the first full year of the project. During this time, Dove will also be working with Mr. Craven and Mr. Lorier to publish three papers from their two M.S. theses. In new work, we will be conducting experimental and theoretical analyses, to determine baseline relations and use this knowledge to address the problem of how complex solute mixtures

found in *real* solutions control long-term stability in corrosion. New student, Mr. Darren Wilson, will be finished with coursework and become active in a research plan to use an integrated experimental approach to construct a quantitative model of solute controls on the reactivity of crystalline and glassy SiO<sub>2</sub>. We will measure the dissolution rate of quartz and silica glass in a series of carefully selected mixed solute solutions over a range of pH and temperature. We will also determine the effect of reaction affinity on rates in DIW (control) and solute-bearing solutions by adjusting steady state silica concentrations produced during the dissolution reactions. With Dr. Selim Elhadj soon joining our group as a postdoctoral scientist, the kinetic portion of the study will be conducted in parallel with surface investigations of selected samples/conditions to resolve the controversy of reaction mechanism by conducting high-quality potentiometric surface titrations in the relevant solute-bearing solutions. This will settle long-standing questions of whether (how) solutes control mineral surface charge and reactivity. The quantitative information will be complemented by findings from *in situ* Atomic Force Microscopy (AFM) and *ex situ* analyses by XPS and Auger.

#### **OTHER ACTIVITIES:**

- 2001 Invited Speaker: Fall AGU special session Nanoparticles in the Environment, San Francisco
- 2001 Spring TFA Meeting, Salt Lake City

#### **INFORMATION ACCESS:**

web: [www.geol.vt.edu/geochem/pmd](http://www.geol.vt.edu/geochem/pmd)