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A GEOCHEMICAL AND MICROANALYTICAL STUDY OF SILICA SCALE DEPOSITION IN GEOTHERMAL BRINES

U.S. DEPARTMENT OF ENERGY, GEOTHERMAL ENERGY PROGRAM

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Project Background and Status

The tendency of siliceous sinters to precipitate from geothermal fluids presents both industrial and environmental challenges. The deposition of silica scale on metal surfaces leads to the clogging of re-injection pipes and the corruption of fluid handling equipment (Axtmann, 1976). If uncorrected, the precipitation of the silica-rich scales can necessitate the costly extraction and replacement of pipes, wellheads, and other processing components. In brines of especially high ionic strength, uncontrolled deposition can be extreme; Salton Sea fluids, for example, may precipitate silica scale in excess of 50 cm yr⁻¹ (Gallup, 1989). Moreover, if fluids are re-injected into the ground rock after their withdrawal, silica precipitation may diminish the porosity of the reservoir, thereby degrading the flow characteristics of the field. As silica deposition concentrates heavy metal ions into the solid phase, disposal of silica scales in an environmentally acceptable fashion also can prove problematic.

We have completed a series of baseline experiments using a model brine solution in which we monitored the evolution of colloidal silica and silica precipitate. These results will serve as a reference for our current investigations of silica coagulation in the presence of scale inhibitors. By comparing the behavior of dissolved silica in the presence and in the absence of inhibitors, we will be able to determine the mechanisms by which the inhibitors operate and to suggest new approaches for scale inhibition.

Project Objectives

The overarching question that we are addressing for this project is as follows:

What factors control the condensation of colloidal silica to form amorphous precipitates in geothermal brines?

Researchers have proposed a number of hypotheses to account for the coagulation of silica polymers and the resultant formation of silica gels in aqueous fluids of high ionic strength. Hypotheses have included: 1) a lowered activity of the water component in brines due to electrolyte hydration (Marshall and Warakowski 1980); 2) a decrease in the "shielding" of the silica surface by water molecules in response to surface dehydration at neutral to high pH (Matijevic 1973); 3) an increase in the effective zpc of silica due to the incorporation of metal cations in the surfaces of silica colloids (Yokoyama et al. 1993); and 4) interparticle coagulation based on the inner-sphere bonding of sorbed metal cations (Yates et al. 1998).

In collaboration with research scientists from the Geothermal and Power Operations Division of the Unocal Corporation, we are performing experiments that will allow us to test these hypotheses. Specifically, we will examine individual steps in the reaction sequence by which monomeric silica transforms to amorphous opal. By separating this reaction pathway into discrete events, we will be able to monitor with high specificity the interactions between aqueous silica with dissolved metal ions of interest. Once the nature of these sub-reactions is established, geothermal industries will be able to inhibit the formation of scale by targeting those factors that induce coagulation with precision.

Approach

We are approaching the formation of silica scale by a combination of exhaustive wet-chemical

analytical assays that can distinguish monomeric and polymeric silica and by novel chromatographic methods that we have helped to develop. The chemical parameters of our experiments were designed with the participation of Dr. Darrell L. Gallup, a Consulting Chemist with the Unocal Corporation, and the fluids are based on brine compositions from the Salton Sea Known Geothermal Resource Area (SSKGRA) in southern California's Imperial Valley, a site with 10 generating plants and a 330 MW net capacity.

Using the Salton Sea Brine composition (4598 ppm Na⁺, 978 ppm K⁺, 200 ppm Ca²⁺, 8330 ppm Cl⁻, 45 ppm HCO₃⁻), we are systematically exploring the effects of time, pH, ionic strength, and initial silica concentration on the deposition of silica precipitates. Silica solutions with initial concentrations of 250, 750, and 1250 mg/L silica (SiO₂) were prepared from pH 3 to pH 11 and with ionic strengths of 0.015 and 0.24. Silica concentrations of 250, 750, and 1250 mg/L SiO₂ were chosen for these experiments because they encompass the range of concentrations observed in hydrothermal fluids at the geothermal sites of interest to the Unocal Corporation. Values of pH include 3, 4, 5, 6, 7, 9, and 11. Silica sols exhibit maximum stability between pH 2 and 3. Above pH values of 11, silica becomes extremely soluble. Between these pH limits, silica coagulates most rapidly.

Results

Nanocolloidal Silica Characterization

We have tested ultrafiltration and developed other techniques for sizing nanocolloids. In our previous efforts to size silica colloids using calibrated gel filtration chromatography (GFC), we observed that the first colloids to appear in solutions containing 500 to 1000 mg/kg silica at pH 7 for both low (0.005 M) and relatively high (0.24 M) ionic strengths measured 20 to 40 kD. We determined that these weights correspond to sizes of 3 to 4 nm for these incipient colloids, and we confirmed these results by light scattering, atomic force microscopy (AFM), and transmission electron microscopy (TEM).

Wet Chemical Experiments

Typical results from our wet chemical baseline analyses of the concentrations of monomeric silicic acid, nanocolloidal silica, and silica precipitate are presented in Figure 1. These results yield the following insights:

1) For all silica concentrations and ionic strengths, the deposition of precipitate is extremely dependent on solution pH. The sensitivity is slightly less pronounced with higher ionic strength, but, in all cases, reaction rates are maximized between pH 5 and 7 and markedly lower outside this range.

2) Relatively small increases in silica concentration and in ionic strength can dramatically enhance the deposition of silica scale. Whereas no precipitate appears over several months in 0.015 M solutions with 250 mg/L silica, the deposition of scale occurs over hours when ionic strength is 0.25 M or silica concentrations are 1250 mg/L.

3) Nanocolloidal silica consistently appears as an intermediate reaction product. Even in solutions that deposit silica precipitate within hours, a transient nanocolloidal population can be detected.

Our initial studies of the effects of a sulfite inhibitor (50 mg/L) on the nucleation and precipitation of nanocolloidal silica (Fig. 2) lead to the following conclusions:

1) The magnitude of the sulfite inhibition of silica precipitation is strongly dependant on the pH of the solution. Sulfite is more effective at inhibiting precipitation at pH values of 5 and below.

2) The magnitude of sulfite inhibition on silica precipitation is strongly dependant on the initial concentration of silica. Sulfite is less effective at inhibiting silica precipitation at higher concentrations than at lower concentrations.

3) Monomeric and nanocolloidal silica fractions were stabilized by sulfite in all solutions.

Planned FY 2002 Milestones

The major goals for the coming year are as follows:

1) Inhibition of silica polymerization by carboxylic acids. Silica solutions with concentrations of 250, 750, and 1250 mg/L ppm silica will be prepared as standard Unocal brines with EDTA, acetic acid, and citric acid. Polymer evolution will be assayed by wet chemical analysis and ICP-AES to ascertain the stages of polymerization that are interrupted by these inhibitors. 2) Titration of coagulated silica solutions. Solutions with concentrations of 2000 mg/L silica will be prepared and allowed to achieve steady state monomer/polymer concentrations. A suite of Groups I and II and transition metal cations will be added to these solutions in a range of concentrations to determine CCCs.

Technology Transfer/Collaborations

The Geothermal and Power Operations Division of the Unocal Corporation has sponsored basic and applied research on the formation of silica scale for 23 years. In 1996, Unocal awarded a 2-year grant to one of the principal investigators (Heaney) to investigate the feasibility of soft-gel chromatography for geothermal fluid analysis. This grant provided half-support for a postdoctoral scholar (Dr. Douglas M. Yates), who refined the technique and performed a series of experiments in conjunction with Unocal. Results of this work have been presented at national meetings (Yates and Heaney 1997, 1999; Heaney and Yates 1997, 1998) and in written and oral Final Reports to Unocal.

For this DOE-sponsored project, we are maintaining our strong partnership with Unocal. As noted above, we are studying brine compositions specified by Unocal, and we are performing research along avenues developed in collaboration with research scientists at Unocal, particularly Drs. Darrell L. Gallup and Philip A. Molling. None of our research results are proprietary. The DOE grant supports one undergraduate student and one postdoctoral researcher. The postdoctoral researcher, Dr. Gary Icopini, has presented our initial colloidal sizing data at the 11th Annual Goldschmidt Symposium in May 2001 (Icopini et al. 2001), and shortly we will be submitting two papers on our work to date to *Geochimica et Cosmochimica Acta* and to *Geothermics*.

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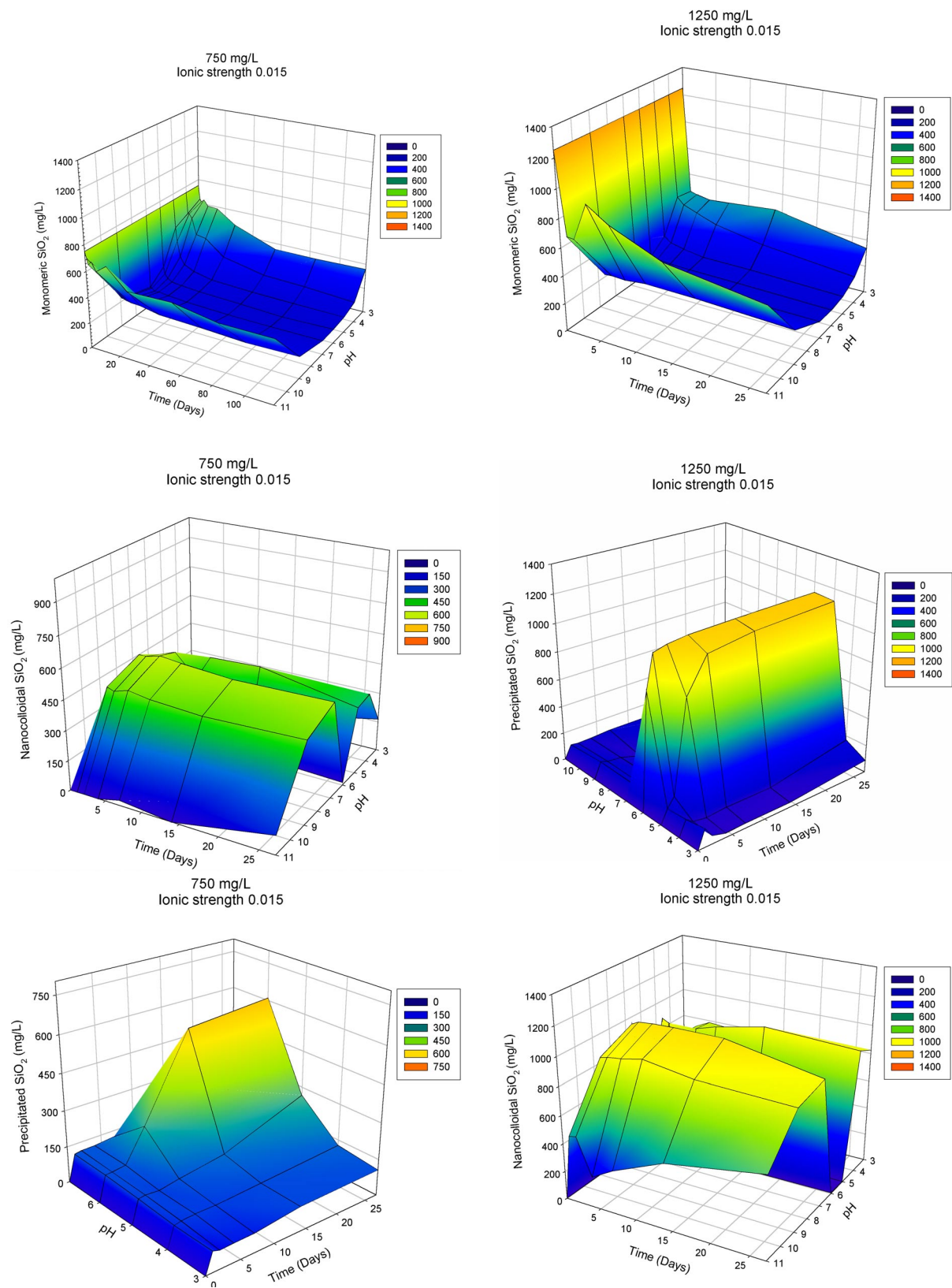


Figure 1. Variation of monomeric, nanocolloidal, and solid silica concentrations as a function of time and pH for solutions of low ionic strength (0.015 M) and an initial concentration of 750 and 1250 mg/L SiO_2 .

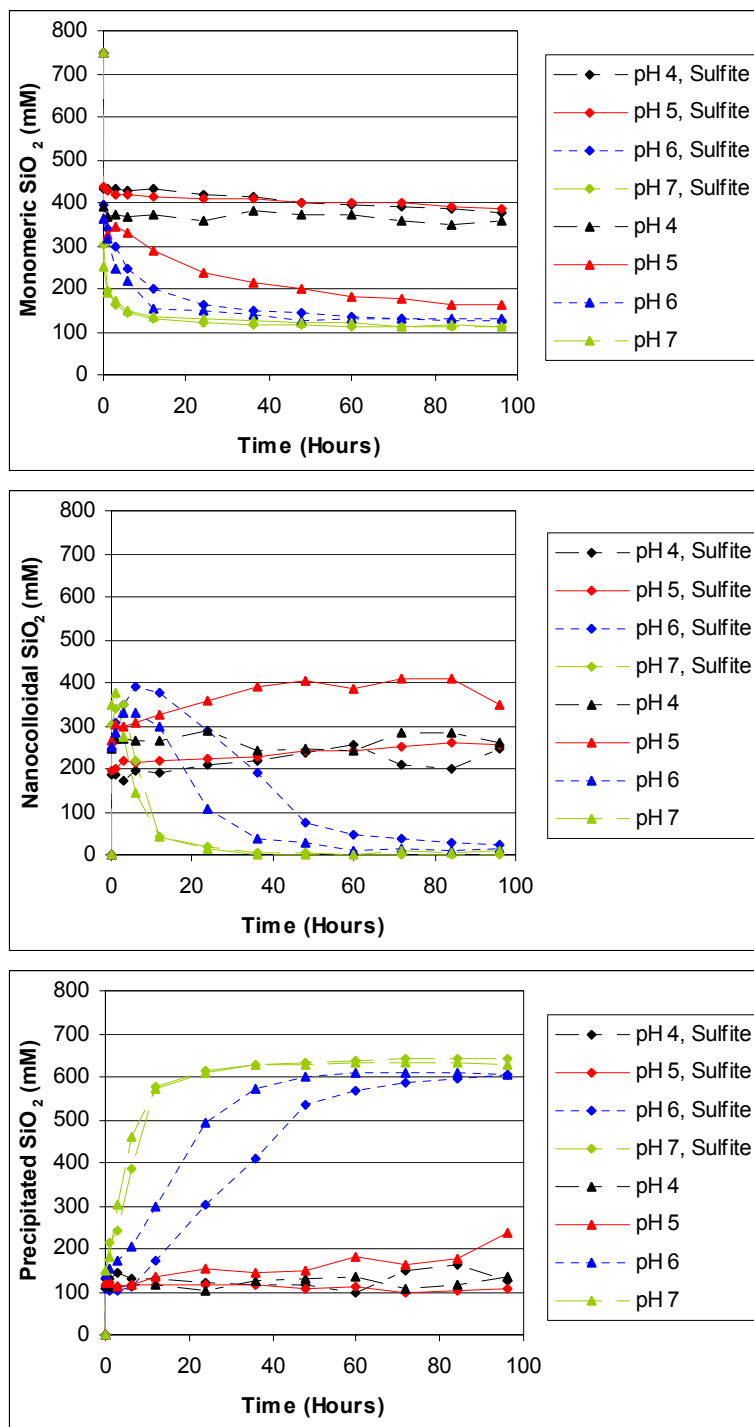


Figure 2. Variation of monomeric, nanocolloidal, and solid silica concentrations as a function of time and pH for solutions of high ionic strength (0.24 M) and an initial concentration of 750 mg/L SiO₂. The diamonds indicate solutions to which 50 mg/L sulfite was added to the simulated brine.