AWARD No. :	**DE – FG 07 – 99 ER15023**
AWARDEE NAME :	**Florida State University**
ACCOUNT No. :	**EMSP 86753**
PROJECT TITTLE :	**"The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica and Uranium Species to High Concentration"**
PERIOD COVERED :	**EMSP Annual Report for 6/1/02 – 5/31/03**
P.I. :	**GREGORY R. CHOPPIN**

Research Objective:

The objective of this research project is to develop the necessary thermodynamic data, including aqueous phase stability constants and Pitzer ion-interaction parameters, to predict the changes in aqueous phase chemistry that occur when high ionic strength , highly basic tank wastes enter the vadose zone.

Research Progress and Implications:

Polymerization Behaviour of Silicic acid

The presence of considerable amounts of silicic acid in natural waters may possibly be one of the reasons for the migration of radionuclides into natural waters and environment from the waste depository site. This has stimulated interest in studying the complexation behaviour of silicate with the radionuclides likely to be present at the disposal sites of wastes from treatment processes of nuclear weapons and nuclear reactor fuel. Further, the stability constants of the complexes of 5f element cations and o-silicate anion may be necessary parameters in modelling behaviour of the longlived actinides in the environment.

Experiments were carried out on the polymerization of silicic acid to better understand its behavior under different experimental conditions of pH, temperature, silicic acid concentrations and aging time. The effect of pH on the change in o-silicic acid concentration for various aging times in solutions having an initial concentration of o-$Si(OH)_4$ of 0.025M at a fixed ionic strength of 0.2M ($NaClO_4$) at 25^0C is shown in Figure 1. The rate of polymerization was slow at low and high pH and was a maximum in the range of pH 6-8.

The rate of polymerization was found to increase with temperature and aging times and the data was consistent with second order kinetics (Figure 2). The values of rate constant (k) at different temperature (Table 1) were found to decrease with temperature from 10-25^{0}C, but increased in the 25-60^{0}C temperature range. Such a behavior in the rate constants of the polymerization reaction of silicic acid indicates two different mechanisms.

The experimental data on the degree of polymerization (P) of silicic acid against aging time (t_{ag}) at varying initial concentration of silicic acid [$(SA)_i$] at constant pH and temperature (Figure 3) has been determined and utilized to develop a mathematical equation correlating P with t_{ag} and $(SA)_i$. The mathematical equation:

$$P = \{ (137.53 \pm 26.93[(SA)i]^{0.65\pm0.06}) \times t_{ag}^{([-1.71\pm0.18 \times (SA)i + 0.35\pm0.09])} \}$$

allow prediction of the degree of polymerization of silicic acid at different aging times and different initial silicic acid concentrations.

The results on polymerization of silicic acid have provided the conditions for its complexation study with metal ions. Experiments were carried out on complexation behaviour of UO_2^{2+} ion with silicic acid from 0.2M $NaClO_4$ using solvent extraction technique employing di-(2-ethyl hexyl phosphoric acid), (HDEHP, H_2A_2 in dimer form) in heptane. In the lower pH range (1.0 to 2.0), the data was consistent with the stoichiometry of the extracted species $[UO_2(A_2H)]$ in the organic phase as per the extraction reaction:

$$UO_2^{2+}{}_{(a)} + 2[H_2A_2]_{(o)} \overset{K_{ex}}{\Leftrightarrow} [UO_2(A_2H)_2]_{(o)} + 2H^+{}_{(a)}$$

where K_{ex} is the equilibrium constant and (a) & (o) represent the aqueous and organic phases respectively. However, in the higher pH range (2.0 to 5.0), the slope of log D (distribution ratio) vs pH were observed to be less than 1, though the D values increase with increased pH and the material balance of activity of ^{233}U was within the experimental error limit of < 3% . In the presence of silicic acid, the extraction of UO_2^{2+} ion increased to pH 4.0 and then decreased as the pH increased to 5.0. The D values for extraction of UO_2^{2+} in the presence of silicic acid were found to be smaller in comparison to those in the absence of silicic acid. Further work at different pH values (1.50, 3.0 & 3.5) on the extraction of UO_2^{2+} at fixed silicic acid concentrations and also at different temperatures will be performed.

Publications / Paper submitted:

1. A manuscript on " Study on Polymerization Behavior of Silicic Acid" based on the work of this project, is ready for transmitted to a journal for publication.
2. An abstract " Study on the Role of Silicate Complexes in the Migration of Radionuclides in Environment" has been submitted for the presentation in 226th ACS meeting scheduled to be held at New York during September 7-11, 2003.

This research is conducted by Dr. Dhruva Kumar Singh.

Planned Activities:

In the next project year, the following is the research plan. To minimize hydrolysis of U(VI) at higher pH, the experiments on silicate complexation have been planned at the pH values of 1.50, 2.50, 3.0 and 3.50 with varying concentrations of o-silicic acid (0.01 to 0.07M). Further, to incorporate the contribution due to the polymeric fraction of o-silicic acid in complexation reactions, similar experiments under the same conditions will be carried out with aged solutions. The effect of temperature (0, 25, 40, 50^0C) on complexation reaction will also be studied to obtain the stability constants and thermodynamic parameters for the such reactions. It is planned to follow these experiments with studies of the complexing behavior of o-silicic acid with Cm(III), Am(III) & Sr(II).

TABLE 1

Initial rate constant, k , values for the polymerization of silicic acid

$[0\text{-}Si(OH)_4] = 0.05M$, $I = 0.20M$ ($NaClO_4$) ; pH = 6.0.

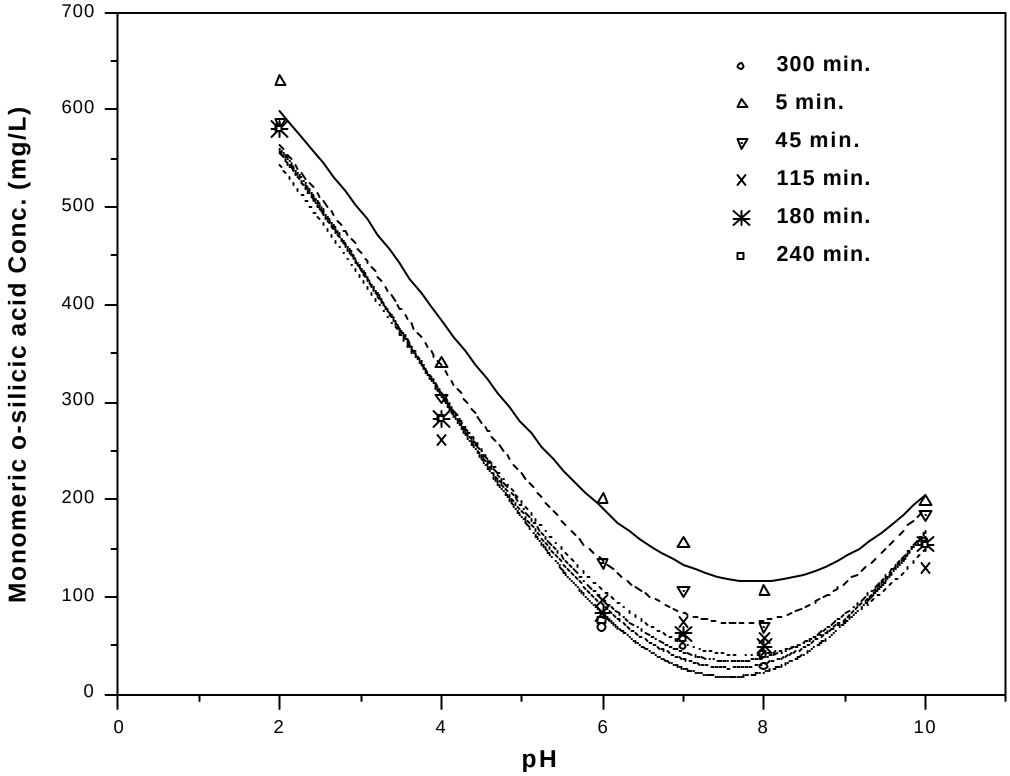
Temperature (^0C)	k ($M^{-1}min.^{-1}$)	Correlation coefficient
10	1.48 ± 0.17	0.94
20	1.36 ± 0.08	0.96
25	1.30 ± 0.08	0.98
40	1.68 ± 0.07	0.99
60	2.28 ± 0.15	0.97

Figure Captions:

Figure -1: Variation in monomeric silicic acid concentration as a function of pH for different aging times. The initial concentration of o-$Si(OH)_4$ was 0.025M at I = 0.2M ($NaClO_4$), T = 25^0C.

Figure -2: Second order plots for the polymerization reaction at different temperatures. ●- 10^0C, ○- 25^0C, ▼- 40^0C, ▽- 60^0C.

Figure -3: Dependence of the degree of polymerization (P) at various concentrations of o-$Si(OH)_4$; I = 0.2M ($NaClO_4$), pH = 6.0, and T = 25^0C.; ●- 0.025M, ○- 0.040M, ▼- 0.050M, ▽-0.060M, ■- 0.075M.



Monomeric o-silicic acid Conc. (mg/L)
pH
0
100
200
300
400
500
600
700
0
2
4
6
8
10
300 min.
5 min.
45 min.
115 min.
180 min.
240 min.

Figure 1

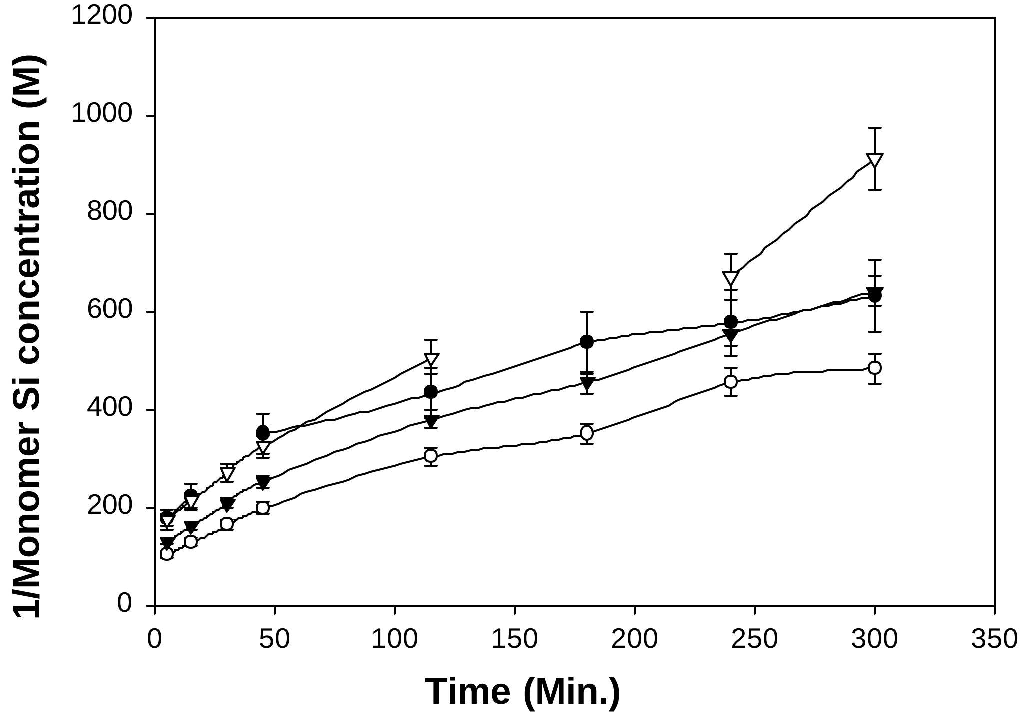
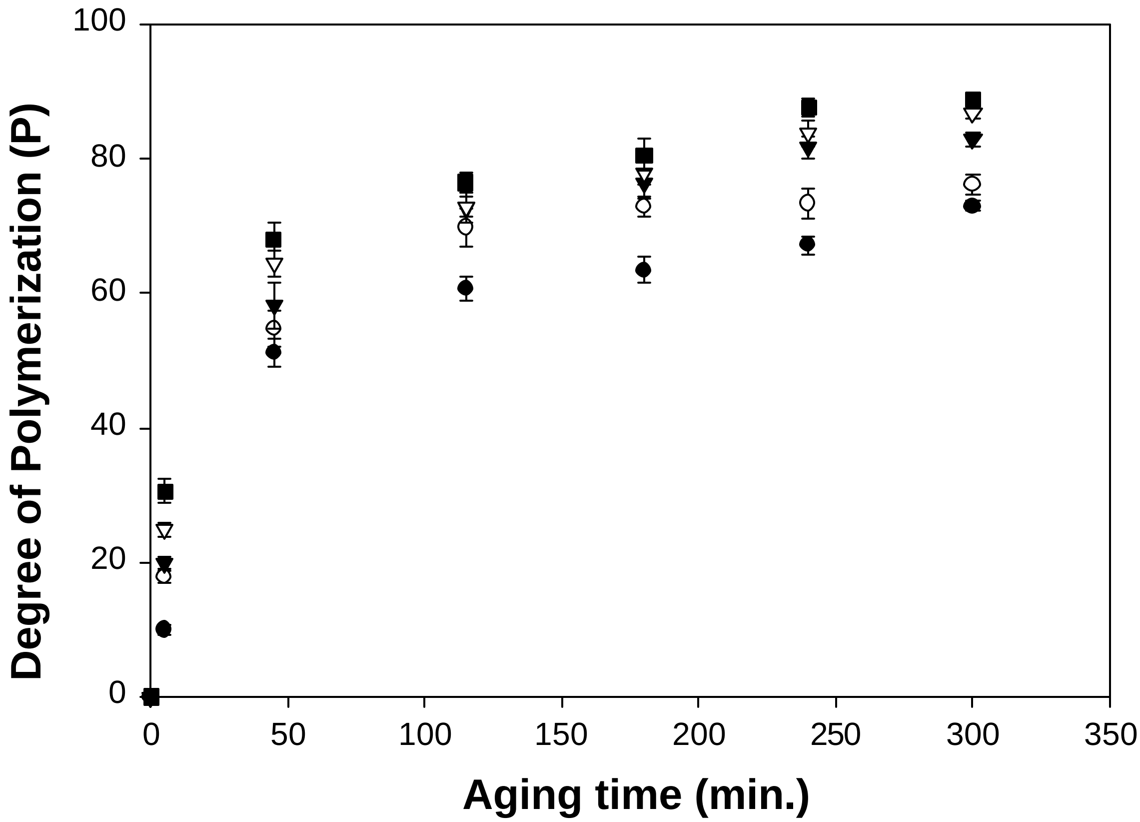

1200
1000
800
600
400
200
0
1/Monomer Si concentration (M)
0
50
100
150
200
250
300
350
Time (Min.)

Figure 2



Degree of Polymerization (P)
Aging time (min.)
0
20
40
60
80
100
0
50
100
150
200
250
300
350

Figure 3