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Thermodynamics and Complexation Reactions of Anionic Silicate Species

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The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica Species to High Concentration: Effects on Neutralization of Leaked Tank Wastes and Migration of Radionuclides in the Subsurface

Highly basic tank wastes contain several important radionuclides, including ^{90}Sr , ^{99}Tc , and ^{60}Co as well as actinide elements (isotopes of U, Pu and Am). A fraction of these wastes are known to have leaked into the vadose zone at the Hanford Site. Upon entering the sediments in the vadose zone, such highly basic solutions dissolve concentrations of silica from the silica and aluminosilicate minerals present in subsurface. These dissolution reactions alter the chemical composition of the leaking solutions, transforming them from highly basic (as high as 2 M NaOH) solution into a pore solution with dissolved silica and significantly reduced pH. This moderately basic (pH 9 to 10), high-silica solution has the potential to complex radionuclides and promote migration through the subsurface. This path of radionuclide migration currently is not a recognized transport mode in the factors that are modeled for radionuclide transport through the vadose zone beneath leaking tanks. The goal of this project is to ascertain the free monosilicic acid concentration, and the degree of polymerization as a function of pH and total concentration of silicate ions, and to use this data to measure the interaction of radionuclides of Co(II), Sr(II), Nd(III), Eu(III), Am(III), U(VI) and Th(IV) with the ionic silicate.

Part I

Dependence on pH and total silicate concentration of monosilicic acid concentration, and degree of the polymerization

Determination of the silicate concentration

Silicic acid was prepared from sodium silicate nanohydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$). The appropriate quantity was dissolved in a polyethylene vessel in about 90 ml water and quickly brought to pH = 2 with concentrated HClO_4 . The resulting solutions were adjusted to a volume of 100 ml, a pH of 2,5 and an ionic strength of 0.2 M (Na, H) ClO_4 using dilute NaOH and HClO_4 solutions. Silicic acid solutions were freshly prepared for each experimental run. A spectrophotometric method used for the determination of the silicic ion concentration and the degree of polymerization involved formation of the yellow β -silicomolybdate anion ($\text{SiMo}_{12}\text{O}_{40}^{4-}$) [1] by silicic acid with acidic molybdate reagent.

The acidic molybdate reagent was prepared by mixing of 10 ml 10% $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 1.18 M NH_4OH with 50 ml water adding 10 ml 1.5 M H_2SO_4 .

The resulting solution was 0.0707 M in MoO_4^{2-} , 0.148 M in NH_4^+ ion, and 0.188 M to SO_4^{2-} , at pH ca. 1.2. This dilute molybdic acid reagent solution is stable for a week.

The production of silicic acid (monosilicic acid $\text{Si}(\text{OH})_4$) by acid hydrolysis of tetramethylorthosilicate $\text{Si}(\text{OCH}_3)_4$ (TMOS) was studied as an alternative to production from $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ TMOS (98% purity, Aldrich). TMOS was distilled prior to use and stored over P_2O_5 . For each set of measurements, o-silicic acid was prepared by addition of 50 μl of TMOS to 10.0 ml deionized H_2O and the pH adjusted with HClO_4 to ca. pH 2.3. The solution was shaken vigorously to obtain complete hydrolysis. For the measurements, working solutions were prepared by dilution of appropriate volumes of this stock solution (ca. 34 mM).

Procedure.

To 4.0 ml of the molybdic reagent as much as 1.00 ml of sample solution containing not more than 200 mg SiO_2 per liter (3.33 mM) was added. The volume was adjusted to 5.0 ml and the absorption measured at 400 nm wavelength. A silicate atomic absorption standard solution (1.000 g per liter in 2 wt% NaOH) was used for calibration of the silicic acid determinations.

Determination of the polymerization degree of silicic acid

The degree of polymerization of silicic acid was investigated as a function of increasing $\text{Si}(\text{OH})_4$ concentration and various pH values. Samples of silicic acid obtained by hydrolysis of sodium silicate were mixed with the molybdic reagent and the adsorption spectra recorded at 20 seconds intervals in the range of 380 to 420 nm wavelength over a period of 15 minutes. As proposed by Coudurier et al. [2], the fraction of the polymeric silicic acid which does not react with the molybdic reagent in the first 15 minutes was determined by extrapolation of the linear part of the absorption curve between 10 and 15 minutes to $t = 0$. The polymerization data with time is shown in Figure 1.

In Figure 2 the change of absorbance at 400 nm with time for 0.01, 0.025, 0.05 and 0.09 M total silicic acid concentration at pH = 1.28 are presented. The degree of polymerization of silicic acid increases with increasing concentration and with pH for the investigated solution, the polymerization degree 0.025 M o-silicic acid was changed from 9.3 to 56.9 to 71.9 % for pH 1.28, 3.73 and 8 40, respectively.

Interaction of silicic acid with chosen elements

The interactions of UO_2^{2+} , Eu^{3+} , Am^{3+} , Co^{2+} and Ni^{2+} with monosilicic acid were investigated by a solvent extraction method.

Under the experimental conditions used, the complexation reaction in aqueous phase between the radioactive elements (M^{n+}) and the anion of orthosilicic acid (L^-) can be written as:



The distribution coefficient of the metal ions between the organic and aqueous phases in the presence of the ligand can be described by:

$$1/D = 1/D_0 (1 + \beta_1[L^-] + \beta_2[L^-]^2 + \dots) \quad (2)$$

where D_0 is the distribution coefficient measured in the absence of the ligand and L^- is the free ligand concentration calculated from the total ligand concentration, and the measured pH after reaching extraction equilibrium. The literature value of $pK_a = 9.587$ [3] was used for the ionization to form $OSi(OH)_3^-$.

Uranyl ion (UO_2^{2+})

The solvent extraction system used to determine the complex formation constants UO_2^{2+} with silicic acid was an organic phase of 2.5 mM HTTA (thenoyl trifluoroacetone) in toluene. Several series of extractions of UO_2^{2+} , with silicic acid varied between 0.03 to 0.07 M at varying pH from 2.7 to 4.7 were made. The distribution ratios of uranium were measured by liquid scintillation counting. Duplicate aliquots of 1.00 ml of both phases were introduced to Ecolite Scintillation cocktail and measured with a Beckman 6500 LSC.

The distribution ratio for UO_2^{2+} was measured as a function of pH. The D_0 values were corrected for any variation in pH by interpolation from the calibration curve. The plot $(D_0/D - 1)$ versus free ligand concentration was fitted by a parabolic equation to determine the two stability constants $\log \beta_1 (= 6.72 \pm 0.5)$ and $\log \beta_2 (= 13.4 \pm 0.7)$ for formation of $UO_2(OSi(OH)_3)^+$ and $UO_2(OSi(OH)_3)_2$, respectively.

The first stability constant obtained in this work is smaller than that reported in the literature [4], ($\log \beta_1 = 7.38 \pm 0.08$), probably because the literature data was not corrected for the second stability constant. All calculations were performed under the assumption that the total dissolved silicic acid was present in solution as the orthosilicate anion.

Europium (III)

Preliminary experiments showed that Eu(III) distributions ratios were not large enough with TTA, so HDEHP (di-2-ethylhexyl phosphoric acid) was chosen to provide larger extraction coefficients.

A 3×10^{-5} M solution of HDEHP in heptane was used in the extraction experiments to determine the formation constant of the Eu – silicate complex. Extraction

experiments of Eu(III) with the same amount of o-silicate in each from 0.03 to 0.09 M, at pH = 4.5 (all in I = 0.20 M (NaCl)), were performed. The distribution ratios of europium were measured, as for UO_2^{2+} , by liquid scintillation counting.

The first formation constant, β_1 , was calculated from the slope of linear regression plot of $(D_o/D - 1)$ vs. the free ligand concentration $[L^-]$ and found to have a value of 7.04 ± 0.10 . No evidence was found for the existence of a second Eu – silicate complex for these experimental conditions.

Cobalt (II)

The organic phase in the solvent extraction systems used to determine the stability constants of Co^{2+} with o-silicate ion was 0.01 M HDEHP and 5.28×10^{-3} M HDEHP in heptane, at pH = 5.5 and 6.5, respectively. The ionic strength was 0.20 M (NaClO_4).

Two series of extraction of Co(II) in which the silicate concentration varied from 0.03 to 0.09 M were conducted. The distribution ratios of cobalt as a function of $\text{Si}(\text{OH})_4$ were measured by gamma counting using duplicate aliquots 1.00 ml of each phases measured in an Isoflex Automatic Gamma Counter. The plot of $(D_o/D - 1)$ versus concentration of free ligand is presented in Figure 3. This plot was fitted by parabolic equation to determine the two stability constants, $\log \beta_1 = 4.8 \pm 0.5$ and $\log \beta_2 = 9.6 \pm 0.7$.

Nickel (II)

Solvent extraction was used to determine the stability constant of complexation of Ni^{2+} with silicic acid. The organic phase was 0.0055 M HDEHP in n-heptane. The aqueous phases contained different concentrations of free silicate ions. Fresh silicic acid was prepared before each experiment by hydrolysis of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) in I = 0.20 M (Na, H) ClO_4 . Several series of extractions of Ni^{2+} were made. In each series the constant total concentration of silicic acid was kept at a pH from 5.0 to 6.5 and the total concentration of silicic acid varied between 0.00 to 0.07 M. ^{63}Ni tracer used for the distribution ratio determination was measured by liquid scintillation counting. The 1 : 1 complex formation constant, $\log \beta_1$, calculated from the slope of the plot of $(D_o/D - 1)$ versus the free ligand concentration $[L^-]$ (at a constant pH) by linear regression, was 5.41 ± 0.23 ($R^2 = 0.93$).

The possible sorption of nickel on the polymeric silicic acid was investigated. The aqueous phase after extraction was filtered through the 0.45 μm Nalgene filter and the mass balance in the aqueous and organic phases was compared with the activity of ^{63}Ni in the blank. The sum of the activity in the filtered phases was within $\pm 3\%$ agreement with the blank. This suggests that sorption of nickel on the polymeric form of silicic acid is negligible.

Figure 1. Development of polymerization degree with time of two solutions of $[\text{Si}]_{\text{T}} = 10 \text{ mM}$, $\text{pHr ca. } 9.7$, $I = 1.0 \text{ M NaClO}_4$; \blacklozenge , \diamond are samples from the separate solutions.

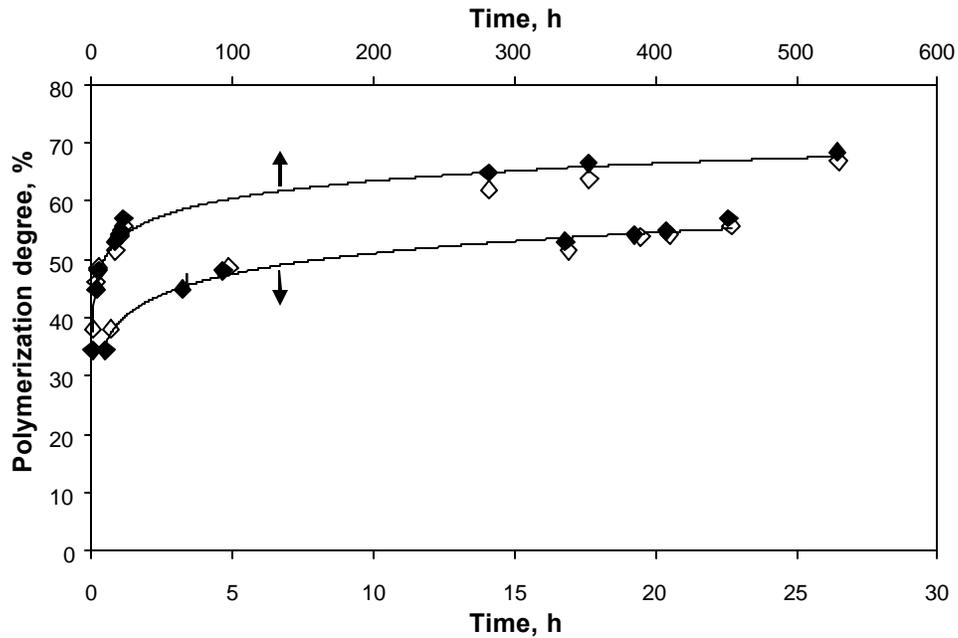


Figure 2. The changes of absorbance in time for difference total concentration of silicate acid at $\text{pH} = 1.28$; $I = 0.20 \text{ M (NaClO}_4)$.

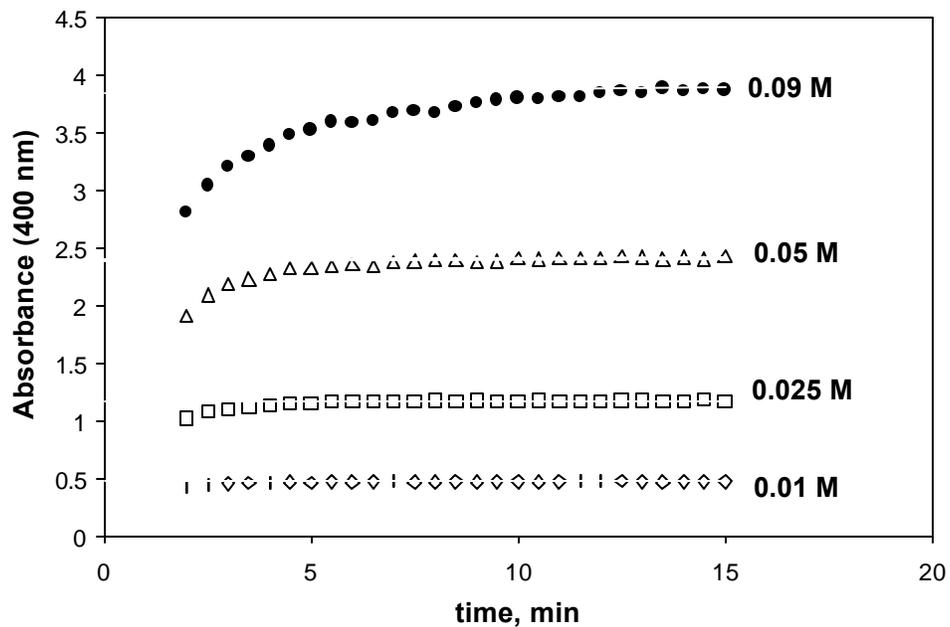
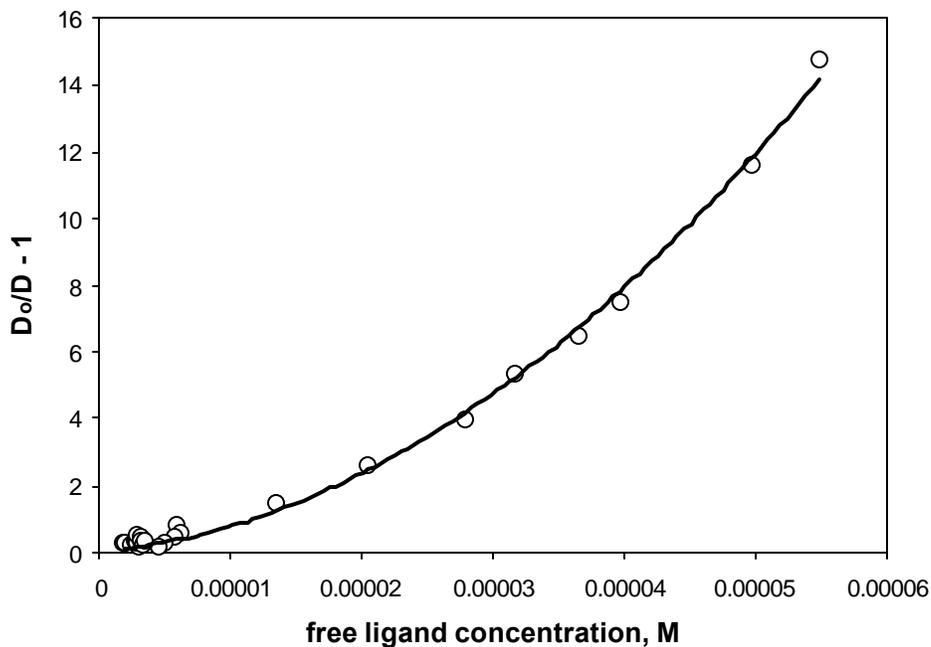


Figure 3. Plot of $D_0/D - 1$ for Co(II) as a function of free silicate ion concentration; pH = 6.0, I = 0.20 M (NaClO₄).



References

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Part II

In the next +contract period, collection of data on the stability constants of o-silicate with Sr(II), Eu(III) and UO_2^{2+} will be completed. Characterization of the Eu(III) and UO_2^{2+} complexes by laser fluorescence spectroscopy will also be continued.

The stability constants will be determined for these metals plus Ni(II) and Co(II) at several other ionic strengths to obtain the necessary constants for use of the Pitzer equations. This will allow speciation of these silicate complexes in media of different salt concentrations.