

Contents lists available at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Technical Note

Interaction of NpO_2^+ with Cl^- in Na–Ca–Cl-type solutions at ionic strength of 6M: Effect of presence of Ca ion on interactionShinya Nagasaki ^{a, *}, Takumi Saito ^b, Satoru Tsushima ^c, Jared Goguen ^a, Tammy Yang ^d^a Department of Engineering Physics, McMaster University, 1280 Main Street West, Hamilton, Ontario, L8S 4L7, Canada^b Department of Nuclear Engineering and Management, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8654, Japan^c Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, P.O. Box 510119, 01314, Dresden, Germany^d Nuclear Waste Management Organization, 22 St. Clair Avenue East, Sixth Floor, Toronto, Ontario, Canada

ARTICLE INFO

Article history:

Received 12 June 2017

Received in revised form

1 August 2017

Accepted 14 August 2017

Available online xxx

Keywords:

 Cl^-

Density Functional Theory Calculation

Equilibrium Constants

Ionic Strength

 NpO_2^+ Presence of Ca^{2+}

ABSTRACT

The interaction of NpO_2^+ with Cl^- was studied using visible–near-infrared spectroscopy in NaCl–CaCl₂–NaClO₄, NaCl–NaClO₄, and CaCl₂–NaClO₄ solutions with ionic strength (*I*) of 6M. The spectra of NpO_2^+ around 980 nm varied with Cl^- concentration in the NaCl–CaCl₂–NaClO₄ and NaCl–NaClO₄ solutions at $[\text{Cl}^-] \geq 3.5\text{M}$, but not in the CaCl₂–NaClO₄ solution. Assuming the 1:1 interaction between NpO_2^+ and Cl^- , the apparent equilibrium constants at *I* = 6M were evaluated. The presence of Ca^{2+} was found to destabilize overall interaction between NpO_2^+ and Cl^- . The observations were consistent with the density functional theory calculation.

© 2017 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Sedimentary rocks in Canada are being considered as potential host rocks for a deep geologic repository for radioactive waste. Some of these rocks in Canada contain Na–Ca–Cl brine solutions with total dissolved solid concentrations of up to 350 g/L (e.g., Southern Ontario, Michigan Basin [1]).

Sorption of radionuclides onto host rocks surrounding a deep geologic repository and onto materials comprising the engineered barrier system is considered an important mechanism for retarding their transport from the repository to the biosphere [2].

The Nuclear Waste Management Organization has been maintaining a database of sorption distribution coefficient values of many elements including Np for Canadian sedimentary rocks and bentonite in saline conditions around neutral pH [the sorption database is targeting for the SR-270-PW reference brine, which is a Na–Ca–Cl-type with an ionic strength (*I*) of 6M] [3].

In our previous study [4], we found that the sorption distribution coefficients of NpO_2^+ for illite, shale, and MX-80 decreased in

the NaCl–CaCl₂–NaClO₄ solutions with *I* = 6M, as the Na/Ca molar concentration ratio (Na/Ca ratio) in the solution decreased from infinity to zero, and this could not be explained solely by the sorption competition of NpO_2^+ with Ca^{2+} . Because the sorption behavior of an element depends, in part, on its speciation, it is important to investigate the speciation of NpO_2^+ in Na–Ca–Cl brine solutions in order to understand the sorption mechanisms.

As Topin and Aupiais [5] pointed out, the reactivity of Cl^- with NpO_2^+ is considered to be very low. In the literature [6–14], the interaction of Cl^- with NpO_2^+ is treated as an interaction with one NpO_2^+ and one Cl^- (1:1) with an apparent equilibrium constant

$$\beta_{\text{NpO}_2\text{Cl}} = \frac{[\text{NpO}_2\text{Cl}]}{[\text{NpO}_2^+][\text{Cl}^-]} \quad (1)$$

The $\log\beta_{\text{NpO}_2\text{Cl}}$ values reported are as follows: -0.29 ± 0.05 in 2M HCl–HClO₄ solution by Gainar and Skyes [6], -0.42 ± 0.04 in 2M NaCl–NaClO₄ solution by Rao et al [7], 0.48 in 8.5M NaCl–NaClO₄ solution by Patil et al [8], and -0.05 ± 0.02 in 5M NaCl–NaClO₄ solution by Neck et al [9]. Guillaumont [10] argued that these studies did not take into account the variations in the medium when the data were processed, which resulted in bias in the

* Corresponding author.

E-mail address: nagasas@mcmaster.ca (S. Nagasaki).

equilibrium constants. The Nuclear Energy Agency (NEA) thermodynamic database [10] selected a $\log\beta_{\text{NpO}_2\text{Cl}} = 0.40 \pm 0.17$ ($I = 0\text{M}$ at 298.15 K), based on the studies by Cohen et al. [11] (HClO_4 solutions; $I = 3\text{M}$; $[\text{Cl}^-] = 0\text{--}2.7\text{M}$), Al-Niaimi et al. [12] (HClO_4 solutions; $I = 0.3\text{M}$, 0.4M , and 0.5M ; $[\text{Cl}^-] = 0.01\text{--}0.14\text{M}$), and Danesi et al. [13] ($\text{NaCl}\text{--}\text{HClO}_4\text{--}\text{NaClO}_4$ solutions; $I = 4\text{M}$; $[\text{Cl}^-] \leq 2.3\text{M}$).

Recently, Topin et al. [14] obtained a $\log\beta_{\text{NpO}_2\text{Cl}} = -0.40 \pm 0.07$ at 1M NaCl solution and corrected it to -0.12 ± 0.13 for $I = 0\text{M}$. However, the ionic strength conditions and the concentration range of Cl^- adopted by Topin et al. [14] and the NEA thermodynamic database [10] may be insufficient for brines.

By contrast, Giffaut [15] and Danesi et al. [16] concluded that there was no NpO_2^+ complexation with Cl^- in 4M NaCl or in 4M $\text{NaCl}\text{--}\text{HClO}_4\text{--}\text{NaClO}_4$ solutions, respectively. Allen et al. [17] investigated the interaction of NpO_2^+ and Cl^- in LiCl solution at $\text{pH} = 3$ by X-ray absorption fine structure spectroscopy and found that Cl^- was present in the equatorial region of the NpO_2^+ only in the solutions with $7\text{--}10\text{M}$ Cl^- and the coordination number of Cl^- was $0.6\text{--}1.0$. Furthermore, Petrov et al. [18] illustrated that the uncomplexed NpO_2^+ aquo ion could be considered to be the main unhydrolyzed Np(V) species even in 5.0M NaCl at $\text{pH}_m < 10.3$. As such, THEREDA (a German thermodynamic reference database containing Pitzer ion interaction parameters for brine solutions) [19] does not include the $\log\beta_{\text{NpO}_2\text{Cl}}$ value.

Richmann [20] has recently studied the interaction of NpO_2^+ with Cl^- in NaCl and NaClO_4 solutions with ionic strength up to 5M by visible–near-infrared (Vis–NIR) spectroscopy, observed the NpO_2Cl complex at $[\text{Cl}^-] \geq 3.5\text{M}$, and evaluated the $\log\beta_{\text{NpO}_2\text{Cl}}$ value as -1.5 ± 0.5 ($I = 5\text{M}$). The $\log\beta_{\text{NpO}_2\text{Cl}}$ value by Richmann [20] is indeed smaller than previously reported values [6–14]. Although many works have been conducted, nonnegligible discrepancy exists concerning the nature of the $\text{NpO}_2^+\text{--}\text{Cl}^-$ interaction. Furthermore, there is no study on the interaction of NpO_2^+ with Cl^- in the presence of Ca^{2+} in brine solutions. This paper studied the interaction of NpO_2^+ with Cl^- in $\text{Na}\text{--}\text{Ca}\text{--}\text{Cl}$ -type solutions at the constant high ionic strength of 6M , and the influence of Ca^{2+} on the interaction.

2. Experimental

2.1. Chemicals and Np solution

All chemicals used for preparing solutions were reagent grade and supplied from Fisher Scientific (112 Colonnade Road, Ottawa, Ontario, K2E 7L6, Canada). Deionized water from a Milli-Q Direct 8 was used. A Precise Controlled Atmosphere Glove Box (GB) supplied by Labconco (8811 Prospect Avenue, Kansas City, MO 64132-2696, USA) was filled with N_2 gas ($>99.999\%$) to exclude CO_2 . The concentration of O_2 in the GB was confirmed to be less than 1 ppm . The $\text{Np}\text{--}237$ solution was purchased from Stuart Hunt & Associates Ltd (5949 Ambler Drive, Mississauga, Ontario, L4W 2K2, Canada). Purchased Np in HNO_3 solution may contain Np(IV) , Np(V) , and Np(VI) . Pure NpO_2^+ in HClO_4 solution is prepared using the following procedures [6].

- (1) Np in HNO_3 solution was fed to an evaporation glass plate.
- (2) Np solution was evaporated and dried in the evaporation glass plate.
- (3) The Np dried in Step 2 was dissolved in a mixture of concentrated HNO_3 and concentrated HClO_4 solutions ($\text{HNO}_3/\text{HClO}_4 = 2:1$ by volume ratio).
- (4) The Np solution prepared in Step 3 was evaporated and dried.
- (5) The dry Np prepared in Step 4 was dissolved in a mixture of concentrated HNO_3 and concentrated HClO_4 solutions ($\text{HNO}_3/\text{HClO}_4 = 2:1$ by volume ratio).

- (6) The Np solution prepared in Step 5 was evaporated and dried.
- (7) The dry Np prepared in Step 6 was dissolved in 0.01M HClO_4 solution.
- (8) HONH_3Cl was added to the Np solution prepared in Step 7.
- (9) The NpO_2^+ solution was stored in the GB.

The Np oxidation states were confirmed by Vis–NIR spectroscopy (Agilent 8453 UV–Vis–NIR spectrometer (Agilent Technologies Canada 6705 Millcreek Dr, Mississauga, ON L5N 8B3, Canada); minimum wavelength dissolution = 1 nm). Experiments were conducted at 25°C . The procedure of pH_c [decimal logarithm of proton concentration (mol/L)] measurement was described elsewhere [6].

2.2. Interaction of Cl^- with NpO_2^+ in the presence and absence of Ca^{2+} by Vis–NIR spectroscopy

The SR-270-PW reference brine solution is $\text{Na}\text{--}\text{Ca}\text{--}\text{Cl}$ type, $\text{pH} = 6.0$, $I = 6.0\text{M}$, $[\text{Cl}^-] = 4.8\text{M}$, and Na/Ca molar concentration ratio = 2.7 [3]. In this study, $\text{NaCl}\text{--}\text{CaCl}_2\text{--}\text{NaClO}_4$ solutions at constant $I = 6\text{M}$ and constant Na/Ca molar concentration ratio = 2.7 with various Cl^- concentrations ($[\text{Cl}^-] = 3\text{--}4.9\text{M}$) were prepared. For comparison, $\text{NaCl}\text{--}\text{NaClO}_4$ and $\text{CaCl}_2\text{--}\text{NaClO}_4$ solutions with $I = 6\text{M}$ were also prepared. The Cl^- concentrations were $[\text{Cl}^-] = 3\text{--}4.5\text{M}$ for the $\text{NaCl}\text{--}\text{NaClO}_4$ solution and $[\text{Cl}^-] = 3\text{--}5\text{M}$ for the $\text{CaCl}_2\text{--}\text{NaClO}_4$ solution. The upper Cl^- concentrations (4.9M , 4.5M , and 5M) were limited by the solubility of NaCl and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ compounds. The lower Cl^- concentration (3M) was from the experimental results by Richmann [20]. In the $\text{CaCl}_2\text{--}\text{NaClO}_4$ solution, the Na/Ca molar concentration ratio was not kept constant at 2.7 . After we prepared the $\text{NaCl}\text{--}\text{CaCl}_2\text{--}\text{NaClO}_4$, $\text{NaCl}\text{--}\text{NaClO}_4$, and $\text{CaCl}_2\text{--}\text{NaClO}_4$ solutions, we applied the filtration (Vivaspin 6; 3000 MWCO (GE Healthcare Life Sciences 2300 Meadowvale Blvd., Mississauga, ON, L5N 5P9, Canada)) for 120 minutes at 8500 g at 25°C (Allegra X-30R; Beckman Coulter, LP, 7075 Financial Drive Mississauga, Ontario Canada), measured the concentrations of Na and Ca using inductively coupled plasma atomic emission spectroscopy (Varian Vista Pro (Varian Inc. (this company was purchased by Agilent Technologies in 2010.), Corporate Headquarters, 3120 Hansen Way, Palo Alto, CA 94304-1030, USA)) prior to and after the filtration, and confirmed that there were not any precipitates in all solutions.

A portion of NpO_2^+ stock solution was spiked to the $\text{NaCl}\text{--}\text{CaCl}_2\text{--}\text{NaClO}_4$, $\text{NaCl}\text{--}\text{NaClO}_4$, and $\text{CaCl}_2\text{--}\text{NaClO}_4$ solutions. The pH_c of solutions was adjusted by HCl and NaOH to 7.2 ± 0.5 for $\text{NaCl}\text{--}\text{CaCl}_2\text{--}\text{NaClO}_4$, 6.6 ± 0.3 for $\text{NaCl}\text{--}\text{NaClO}_4$, and 7.5 ± 0.3 for $\text{CaCl}_2\text{--}\text{NaClO}_4$ solutions. Because NpO_2^+ is dominant at pH_c up to 10 in aqueous solution in the absence of ligands [18], the difference of pH_c in this study was considered to be negligible. The concentration of NpO_2^+ was $1 \times 10^{-4}\text{ M}$. How to determine the concentration of Np is described elsewhere [4].

The principal $5f\text{--}5f$ transition (${}^3\text{H}_{4g}$ to ${}^3\text{I}_{2g}$) in the electronic absorption spectrum for NpO_2^+ in aqueous solutions is typically at around 980 nm [21,22]. This band follows a Beer–Lambert behaviour and is often used analytically to establish the concentration of NpO_2^+ in solution and to study its complexation behavior with a ligand as the band is affected by complexation [22,23]. In this study, the spectra of NpO_2^+ around 980 nm in the $\text{NaCl}\text{--}\text{CaCl}_2\text{--}\text{NaClO}_4$, $\text{NaCl}\text{--}\text{NaClO}_4$, and $\text{CaCl}_2\text{--}\text{NaClO}_4$ solutions were measured by Vis–NIR spectroscopy. As references, the spectra of NpO_2^+ in 6M NaClO_4 solution ($[\text{Cl}^-] = 0$) at $\text{pH}_c = 6.6$, 7.2 , and 7.5 were also measured.

2.3. Density functional theory calculation procedure

In order to theoretically study the effect of chlorine coordination to NpO_2^+ , we optimized the structures of $\text{NpO}_2(\text{H}_2\text{O})_5^+$ and

Download English Version:

<https://daneshyari.com/en/article/8083973>

Download Persian Version:

<https://daneshyari.com/article/8083973>

[Daneshyari.com](https://daneshyari.com)