IMPACT OF EDTA ON THE SOLUBILITY AND REDOX BEHAVIOUR OF URANIUM IN DILUTE TO CONCENTRATED NaCl SOLUTIONS

E. Yalcintas[1], D. T. Reed[2], X. Gaona[1], M. Altmaier[1]

[1]*Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal,*
*Postfach 3640, 76021 Karlsruhe - Germany*
[2]*Los Alamos National Laboratory, USA*

The impacts of EDTA on the solubility and speciation of uranium were evaluated as a function of ionic strength, redox conditions, and pH. EDTA is both a strong complexant of U(IV/VI) and, under many conditions, can act as a reducing agent towards U(VI). An accurate knowledge of this aquatic chemistry and, more generally, the thermodynamics of actinides are fundamental needs that support nuclear waste disposal concepts. The availability of complete and correct chemical and thermodynamic models helps provide reliable geochemical model calculations and source-term estimations for the safety assessment of nuclear waste repositories.

Uranium typically comprises the largest inventory in treated TRU and HLW radioactive waste and is the key component of spent fuel. In this context, understanding its chemistry is important in its own merit as well as being potentially useful as an analog of the An(VI) and An(IV) actinides. U(VI) is the most stable oxidation state of uranium under anoxic and oxidising conditions, whereas U(IV) prevails in strongly reducing environments, forming the sparingly soluble UO_2(am,hyd) in the absence of complexing ligands. EDTA is a strong complexing ligand used for decontamination purposes in nuclear reactors, clean-up operations and for the separation of radionuclides. Previous studies available in the literature have shown that both An(IV) and An(VI) form strong complexes with EDTA, eventually leading to significant increase in the solubility compared to EDTA-free systems [1-3]. However, most of these studies have been performed under acidic conditions, and accordingly the NEA–TDB review selected only binary U–EDTA complexes [3], both for +IV and +VI redox states. In the alkaline to hyperalkaline pH conditions, which are most relevant to nuclear waste repositories, the formation of ternary U–OH–EDTA complexes is also to be expected, as recently reported for the Pu(IV) system [4–5]. Additionally, such complexes can importantly affect the solubility and redox transitions between U(IV) and U(VI). In this context and based on a combination of solubility experiments and spectroscopic measurements, this work aims at evaluating the impact of EDTA on the solubility and redox phenomena of uranium and, ultimately, at developing complete and correct chemical and thermodynamic models for U(IV) and U(VI) in EDTA-containing systems, valid for dilute to concentrated salt systems and covering the entire pH range.

The solubility of U(IV) and U(VI) in the presence of EDTA was investigated from both undersaturation and oversaturation conditions. Experiments were performed in an inert gas atmosphere with < 2 ppm O_2 at $T = (22 \pm 2)$ °C. Oversaturation solubility experiments were conducted with $[U]_0 = 10^{-3}$ M (either as +IV or +VI), whereas undersaturation solubility experiments were performed with approximately 3 mg of UO_2(am,hyd) or $Na_2U_2O_7 \cdot H_2O$(cr) per sample. In the case of UO_2(am, hyd), strongly reducing conditions (pH + pe < 2) were fixed in each independent solubility sample with $SnCl_2$. Background electrolyte solutions were prepared with [EDTA] = 0.001 and 0.01 M, constant ionic strength $I = 0.5$ and 5.0 M Na_4EDTA–NaCl–HCl–NaOH, and covering the pH_m range 0–13 (with $pH_m = -\log [H^+]$). Uranium concentration, pH_m and E_h values were monitored at regular time intervals. Thermodynamic equilibrium was assumed after repeated measurements with constant [U] and pH_m. After attaining equilibrium conditions, selected samples were characterized by UV–vis-NIR (supernatant solutions), XRD and quantitative chemical analysis (solid phases). Additionally, spectroscopic measurements were performed with U(IV) as a function of EDTA concentration in 0.5 M HCl (see Figure 1), and as a function of pH at constant EDTA concentration to identify the changes in the aqueous speciation. The results obtained on the impact of EDTA on the aqueous speciation, redox state and solubility of uranium will be presented in this contribution, discussed in the context of the presence/absence of ternary species, and evaluated as an analog for An(IV) actinides.

Figure 1. Uranium-EDTA absorption spectra as a function of [EDTA] in 0.5 M HCl. Isobestic points are clearly seen at a number of wavelengths indicating the formation of one EDTA complex (presumably the neutral U-EDTA complex).
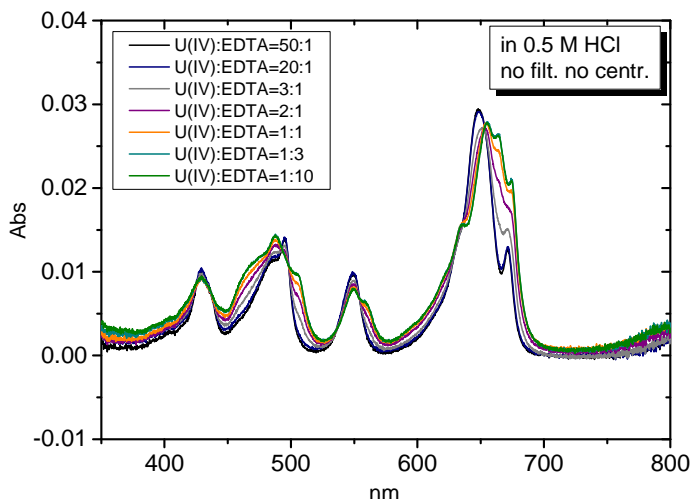
[1] Carey G. H. and Martell, A. E., (1968), "Formation, hydrolysis and olation of Uranium (IV) chelates", J. of American Chemical Society, 90:1.

[2] Borkowski, M., Lis, S. and Choppin, G.R., (1996), "Complexation behaviour of NpO_2^+ and UO_2^{2+} ions with several organic ligands in aqueous solutions of high ionic strength", Radiochimica Acta 74, 117-121.

[3] Hummel, W., Anderegg, G., Rao, Linfeng, Puigdomenech, I. and Tochiyama, O. "Chemical thermodynamics of compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands", OECD Nuclear Energy Agency (ed.), Vol. 9, Issy-les-Moulineaux (France), Elsevier (2005).

[4] Boukhalfa, H., Reilly, S. D., Smith, W. H., and Neu, M. P., (2004), "EDTA and Mixed-Ligand Complexes of Tetravalent and Trivalent Plutonium", Inorg. Chem., 43, 5816-5823.

[5] Rai D., Moore, D. A., Rosso, K. M., Felmy, A. R. and Bolton, H. Jr., (2008), "Environmental Mobility of Pu(IV) in the Presence of Ethylenediaminetetraacetic Acid: Myth or Reality?", J. Solution Chem., 37: 957–986.
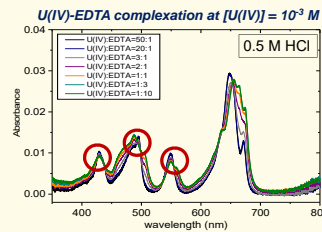
Impact of EDTA on the solubility and redox behaviour of uranium in dilute to concentrated NaCl solutions

Karlsruhe Institute of Technology

Los Alamos NATIONAL LABORATORY EST. 1943

LA-UR-17-27827

E. Yalcintas[(a,b)], D. T. Reed[(b)], X. Gaona[(a)], M. Altmaier[(a)]

[(a)]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Germany

[(b)]Los Alamos National Laboratory, USA

Introduction

- Uranium typically comprises the largest inventory in treated TRU and HLW radioactive waste and is the main component of spent fuel. Understanding its chemistry is important in its own merit as well as being potentially useful as an analog of the An(VI) and An(IV) actinides.
- Most relevant oxidation states of U:
  - **U(VI)** shows an amphoteric behaviour and precipitates as $UO_3 \cdot 2H_2O(cr)$ and M–U(VI)–OH(s) with M = Na, K, Ca under acidic and alkaline conditions, respectively.
  - **U(IV)** forms sparingly soluble hydrous oxides (UO_2(am,hyd)).
- EDTA is a strong complexing ligand used for decontamination purposes in nuclear reactors, clean-up operations and for the separation of radionuclides.
- This work aims at evaluating the impact of EDTA on the solubility and redox phenomena of uranium and, ultimately, at developing accurate chemical, thermodynamic and activity models for U(IV) and U(VI) in EDTA-containing systems for the long-term safety assessment of currently in operation (WIPP) and future nuclear waste repositories.

Experimental

Undersaturation experiments
- Experiments at [EDTA] = 0.001, 0.01 M and 0.05 M and I = 0.5 M and 5.0 M Na_4EDTA–NaCl–HCl–NaOH
- Approximately 3 mg of UO_2(am,hyd) or $Na_2U_2O_7 \cdot H_2O$(cr) per sample
- Strong reducing conditions set by 2 mM Sn(II) systems in the case of U(IV)
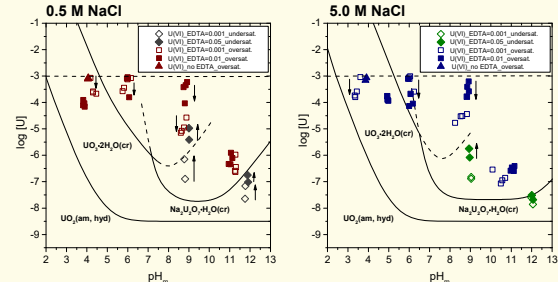
Oversaturation experiments
- $[U]_0 = 10^{-3}$ M (either as +IV or +VI)
- Experiments at [EDTA] = 0.001, 0.01 M and 0.05 M and I = 0.5 M and 5.0 M Na_4EDTA–NaCl–HCl–NaOH

Measurements
- pH : $pH_m = -\log m_{H+} = pH_{exp} + A_m$ [1]
- E_h : Pt combination electrodes with Ag/AgCl
- [U] by ICP-MS after ultrafiltration (3 and 10 kD)
- Speciation measurements by UV-vis

U(VI) and U(IV) complexation with EDTA

- **U(VI):** UO_2edta^{2-}, UO_2(Hedta)$^-$ and $(UO_2)_2$edta(aq) species selected in NEA-TDB [2], although complexity of the system highlighted due to the formation of polynuclear complexes
- U(VI)-EDTA-OH species expected to prevail in alkaline pH conditions are not considered in the current model
- **U(IV):** Spectroscopic measurements as a function of [EDTA] clearly indicate the formation of single EDTA complex => **U(edta)(aq)**
- No evidence for the formation of polynuclear species observed by increasing the U(IV):EDTA ratio

U(IV)-EDTA complexation at $[U(IV)] = 10^{-3}$ M

0.5 M HCl

U(IV):EDTA=50:1
U(IV):EDTA=20:1
U(IV):EDTA=3:1
U(IV):EDTA=2:1
U(IV):EDTA=1:1
U(IV):EDTA=1:3
U(IV):EDTA=1:10

U(VI) solubility in the presence of EDTA

Experiments at $[EDTA]_{tot}$ = 0.001, 0.01 and 0.05 M, I = 0.5 and 5.0 M

0.5 M NaCl

5.0 M NaCl

- Significant increase in U(VI) solubility with increasing [EDTA] at $6 \le pH_m \le 9$
- Precipitation observed at $pH_m \sim 4$, hinting towards (UO_2)-EDTA(s) ?

U(IV) solubility in the presence of EDTA

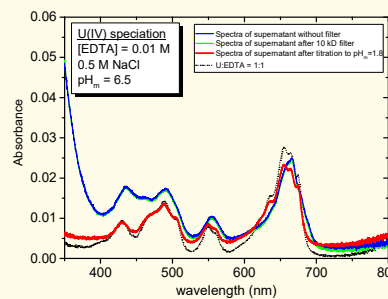**Undersaturation experiments at $[EDTA]_{tot}$ = 0.001 and 0.01 M, I = 0.5 and 5.0 M**

0.5 M NaCl

5.0 M NaCl

NEA-TDB model
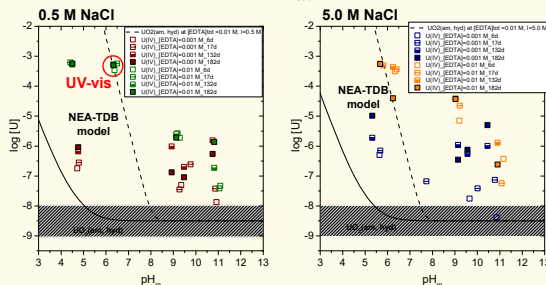
UV-vis

- Significant increase of solubility at $pH_m < 12$, chemical species not defined above pH > 7 in NEA-TDB [2] => formation of $U(OH)_n$EDTA$^{(n-)}$ in analogy to $Pu(OH)_n$EDTA$^{(n-)}$ [3,4] ?

UV-vis measurement from U(IV) solubility data

U(IV) undersaturation solubility sample at pH_m = 6.5 in 0.5 M NaCl

U(IV) speciation
[EDTA] = 0.01 M
0.5 M NaCl
pH_m = 6.5

Spectra of supernatant without filter
Spectra of supernatant after 10 kD filter
Spectra of supernatant after titration to pH_m=1.8
U:EDTA = 1:1

- Filtration results show that no colloids (>5 nm) are present in the system
- Sample re-acidification results show that the higher-pH complex is reversible and no U(VI) is present
- Changes in the higher-pH absorption spectra suggest the presence of ternary species: => **$U(OH)_n$EDTA$^{(n-)}$** ?

Summary and Outlook

- Very significant changes were observed in the chemistry of U(IV) and U(VI) in the presence of EDTA.
- Decrease of U(VI) solubility in acidic pH region and consequent precipitation hint towards the formation of (UO_2)-EDTA(s). Formation of U(VI)-EDTA-OH might play a role at $pH_m \ge 9$.
- U(IV) strongly complexes with EDTA in the acidic pH region, whilst solubility increases up to 3 orders of magnitude at repository relevant pH conditions.
- Combination of solubility and spectroscopic observations suggest the formation of binary U(IV)–EDTA and ternary U(IV)–OH–EDTA complexes which are not considered so far in NEA-TDB model.
- Longer equilibration time as well as further solubility experiments and spectroscopic investigations are needed to develop complete chemical, thermodynamic and activity models.

References

- [1] Altmaier et al., Geochimica et Cosmochimica Acta, **67(19)**, 3595–3601, (2003).
- [2] Hummel et al., Chemical Thermodynamics Vol. 9. Elsevier, Amsterdam, (2005).
- [3] Boukhalfa et al., Inorganic chemistry, **43**, 5816-5843, (2004).
- [4] Rai et al., J. Solution chemistry, **37**, 957-986, (2008).