Influence of Radiolytic Products on the Chemistry of Uranium VI in Brines

Jean-Francois Lucchini, Donald Reed, Marian Borkowski, Andrzej Rafalski, James Conca,

Los Alamos National Laboratory, EES-12 Carlsbad Operations, Actinide Chemistry and Repository Science Program, + 1-505-234-5556, fax: +1-505-887-3051, lucchini@lanl.gov
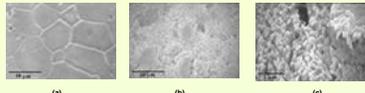
Introduction

Actinide chemistry in brines has been the subject of numerous investigations within the last two decades, because geological salt formations are being considered for radioactive waste disposal. Oxidation states, speciation and solubility of actinides in brine are a necessary step in the potential migration of actinides in the environment.

In the near-field chemistry of a salt repository of nuclear waste, ionizing radiations can strongly affect these processes, and thus the actinide mobility in concentrated saline solution. So the effects of radiolysis on high-saline brine under simulated repository conditions, and effect of the radiolytic by-products on actinide speciation are of particular importance.

The aim of this work is to give a non-exhaustive review of the chemistry of Uranium VI under the possible effects of irradiated NaCl concentrated solutions in alkaline medium.
We also introduce the experimental objectives planned to better understand the Uranium VI subsurface chemistry under the range of conditions expected in a nuclear waste repository.

Uranyl stability in brine

Concentration of uranium as a function of time in a $MgCl_2$ brine at pH 5 (experiment U-G5) and pH 7 (experiments U-G7 and U-G7-NC). Data for both unfiltered and 0.2μm-filtered solutions are shown.

☞ Steady-state uranium concentrations are obtained in the $MgCl_2$ brine, as well as in a NaCl brine (not shown in the figures)

Absorption Spectra for uranium in NaCl brine at pH 10 (experiment U-E10), in $MgCl_2$ brine at pH 5 (experiment U-G5). A featureless absorption spectrum is shown for uranium in both $MgCl_2$ brine at pH 7 (experiment U-G7) and NaCl brine at pH 10 in the absence of carbonate (experiment U-E10-NC).

Sharp spectral features in the U-E10 spectrum indicate the presence of a uranyl carbonate complex

XANES spectra of U(VI) hydroxide and the uranium precipitate recovered from the U-E10 experiment establish the precipitate as U(VI), rather than U(IV).

☞ Uranium is stable in NaCl brine in the +6 oxidation state, as a carbonate or hydrolytic complex

– Reed D.T. (1997). Unpublished data. "ANL Empirical Actinide Stability/Solubility" Project, Argonne National Laboratory.

• Uranium(VI) chloride complexes are so weak, that they are not significant species in brine above pH 5.

$UO_2^{2+} + n\ Cl^- \rightleftharpoons UO_2Cl^{(2-n)+}$ $\log \beta^*_1 = 0.17 \pm 0.02$

$UO_2Cl_{2(aq)}$ $\log \beta^*_2 = -1.1 \pm 0.4$

– Grenthe I., Fuger J., Konings R., Lemire R., Muller A., Nguyen-Trung C., Wanner H. (1992). Chemical Thermodynamics of Uranium. (Wanner, H. and Forest, I., eds.) OECD/NEA (1992)

• In synthetic NaCl-based brines containing Fe^0 (pcH 8 to 13), no significant reduction of U(VI) was observed within 55 days. The lack of reduction of U(VI) in brine solutions could be attributed to the lower reducing capacity of Fe powder in brines than in dilute solutions.

– Xia Y. Rao L., Rai D., Felmy A.R. (2001). "Determining the distribution of Pu, Np, and U oxidation states in dilute NaCl and synthetic brine solutions." Journal of Radioanalytical and Nuclear Chemistry 250:27.

Effect of H$_2$O$_2$ on uranyl in water: formation of uranyl peroxide

(a)   (b)   (c)

Scanning electron microscopy (SEM) images of (a) unleached UO_2 surface and, (b) and (c) leached UO_2 surface in water after 5 h of α-beam irradiation.

☞ Increase of the specific surface of the material and its solubility

• Tetrahydrate uranium peroxide (synthesized at room temperature) is reported to have a solubility product of log K_{sp} = 2.826 for the reaction : $UO_2^{2+} + H_2O_2 = UO_4.nH_2O + 2H^+$ in aqueous solution of a nearly neutral pH value.
• The two different polymorphs, which appear in nature as studtite ($UO_4.4H_2O$) and meta-studtite ($UO_4.2H_2O$), were found to have solubilities (measured in pH area close to 7) of 10^{-5} and $1.5.10^{-6}$ M respectively.
• UO_2 solubility is about 10^{-8} M in the same conditions.

– Amme M. (2002). "Contrary effects of the water radiolysis product H_2O_2 upon the dissolution of nuclear fuel in natural ground water and deionized water." Radiochimica Acta 90: 399.
– Lucchini J.F. (2001). "Effect of Water Alpha Radiolysis on the Spent Nuclear Fuel UO_2 Matrix." Thesis, University of Paris XI Orsay, France

Uranyl peroxide properties

• Studtite can form from schoepite in low peroxide concentrations : 1.1×10^{-14} M H_2O_2 (calculations).
• Studtite is the stable phase relative to dehydrated schoepite when hydrogen peroxide occurs.
• Studtite is thermodynamically unstable in systems with no peroxide, and at room temperature.

☞ Solution composition have an impact on precipitation of uranyl peroxide.

• The formation of uranyl peroxide is inhibited in high chloride concentration solutions (> 2.7M).
• Even at initial H_2O_2 concentration of 10^{-2}M, no uranyl peroxide forms if there is a scavenger of H_2O_2 in solution.
• However, if the peroxide concentration is high enough, the scavenging mechanism should be overruled and formation of UO_4 should take place, as in the case of natural formation of studtite minerals.
• Dissolution of uranyl peroxide occurs at low pH, or in presence of a strong oxidant (such as OCl^-) .

– Kubatko K.A.H., Helean K.B., Navrotsky A., Burns P.C. "Stability of Peroxide-Containing Uranyl minerals" Science 302, p.1191 11/14/2003
– Amme M. (2002). "Contrary effects of the water radiolysis product H2O2 upon the dissolution of nuclear fuel in natural ground water and deionized water." Radiochimica Acta 90: 399.
– Brown R.A. (1981) " Precipitation of uranium with hydrogen peroxide." Trans. Am. Inst. Min. Metall. Pet. Eng. Soc. Min. Eng. Aime 270 1694.
– Musikas C. (1989). "Quelques propriétés de l'uranium hexavalent en milieu alcalin." Radiochem. Radioanal. Letters 1/2: 134.

Influence of chloride concentrations on the radiolysis mechanism

At low solute concentrations, the solute does not greatly affect the molecular yield of radiolytic products in water. However, species that react with OH• or act as scavengers (such as Cl^- or Br^-) gradually lower the molecular yield of H_2O_2 as the concentration of the scavengers is increasing.

Radiolysis reactions of NaCl solutions: primary and secondary reactions and products
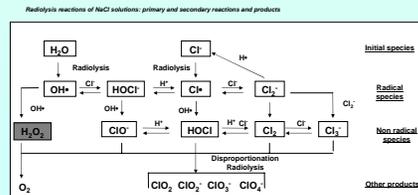
☞ The overall radiolytic production of H_2O_2 should be low in brines.

– Buppelmann K., Kim. J. I., Lierse Ch. (1988). "The redox behavior of Pu in saline solutions under radiolytic effects." Radiochimica Acta 44/45: 65.

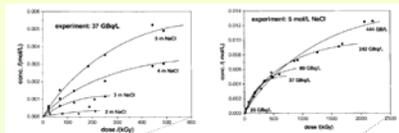## Hypochlorite formation in NaCl solutions

Fig. 1. Hypochlorite formed radiolytically in solutions of various NaCl concentrations at a constant alpha activity concentration of 37 GBq/L

Fig. 2. Hypochlorite formed radiolytically in 5 mol/l NaCl solutions containing various alpha activity concentrations.

☞ The formation of hypochlorite ion increases with the chloride concentration and the dose.

• Calculations show that the formation of hydrogen peroxide decreases when the chloride concentration increases in the solution.

– Kelm M., Pashalidis I., Kim J.I. (1999). " Spectroscopic investigation on the formation of hypochlorite by alpha radiolysis in concentrated NaCl solutions." Applied Radiation and Isotopes 51: 637.
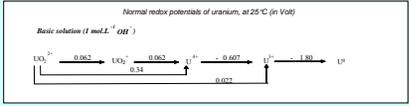
Radiolytic reactions in brines can cause…

❖ …the change in pH,
The initial effect of radiolysis of neutral saline solutions is a rapid decrease in pH locally to 4, followed by a gradual increase over a period of days to neutrality.

❖ …an increase of the redox potential (Eh) of the solution
The redox potential may reach about +1300 mV in acidic solutions. The solutions are then strongly oxidizing.

Species	λ_{max} (nm)	ε (L.mol-1.cm-1)	Redox potential (V)
Radicals			
Cl•	—	—	$E°$ (Cl•/Cl-) = 2.41
Cl_2^-	340	8800	$E°$ (Cl_2^-/2Cl-) = 2.09
HOCl•	350	3700	$E°$ (HOCl-/Cl-,OH-) = 1.09
ClO•	280	890	$E°$ (ClO•/Cl-) = 1.02 (calculated)
Non radicals			
Cl_2	333	135	$E°$ (Cl_2/2Cl-) = 1.40
Cl_3^-	325	190	$E°$ (Cl_3^-/3Cl-) = 1.38 (calculated)
HClO	235	100	$E°$ (HClO/Cl-) = 1.48
ClO-	292	350	$E°$ (ClO-/Cl-) = 1.69
ClO_2^-	260	160	$E°$ (ClO_2^-/Cl-) = 1.60
ClO_2	360	1000	$E°$ (ClO_2/Cl-) = 1.51

– Buppelmann K., Kim. J. I., Lierse Ch. (1988). "The redox behavior of Pu in saline solutions under radiolytic effects." Radiochimica Acta 44/45: 65.

Potential radiolysis effects on uranium chemistry in brines : no redox change…

Normal redox potentials of uranium, at 25°C (in Volt)

Basic solution (1 mol.L-1 OH-)

$UO_2^{2+} \xrightarrow{0.062} UO_2^+ \xrightarrow{0.062} U^{4+} \xrightarrow{-0.607} U^{3+} \xrightarrow{-1.80} U^0$
$\xrightarrow{0.34}$
$\xrightarrow{0.072}$

✓ Brine radiolysis should maintain uranium in solution as U(VI).

… but hypochlorite ion insertion into uranyl complexes ?

✓ In solubilities studies of schoepite $(UO_2)(OH)_2.xH_2O$ with hypochlorite ion in 0.1M NaCl at 25°C, under CO_2-free atmosphere, XRD patterns for the residual precipitates showed the introduction of hypochlorite ion in precipitates.

✓ Hypochlorite ion could displace hydroxide in $(UO_2)_2(OH)_x^+$, a predominant species in solution, to form a mixed complex and could also be incorporated into uranium precipitates. This would affect the overall uranium solubility.

– Kim W.H., Choi K.C., Park K.K., Eom T.Y. (1994). "Effects of Hypochlorite Ion on the Solubility of Amorphous Schoepite at 25°C in Neutral to Alkaline Aqueous Solutions." Radiochimica Acta 66/67: 45.

Effect of hypochlorite ion on schoepite

Fig. 1. Solubilities of uranyl hydroxide (schoepite) with hypochlorite ion (O) and without hypochlorite ion (●) in 0.1 M NaCl solution. $[UO_2^{2+}]_0 = 9.789 \times 10^{-6}$ M, $[OH-]_0 = 9.824 \times 10^{-5}$ M
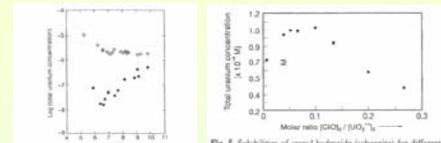
Fig. 5. Solubilities of uranyl hydroxide (schoepite) for different molar ratios of hypochlorite ion concentration to initial uranyl ion concentration in 0.1 M NaCl solution at pH 8.3, and $[UO_2^{2+}]_0 = 9.789 \times 10^{-6}$ M.

☞ The presence of hypochlorite ion enhanced the solubility of schoepite 10 to 100 times in the range of pH 6.0-9.8, compared with its solubility in the absence of hypochlorite ion
This effect is reduced when the molar ratio $[ClO^-]/[UO_2^{2+}]$ increases.

– Kim W.H., Choi K.C., Park K.K., Eom T.Y. (1994). "Effects of Hypochlorite Ion on the Solubility of Amorphous Schoepite at 25°C in Neutral to Alkaline Aqueous Solutions." Radiochimica Acta 66/67: 45.

Conclusion

This poster gives an overview of the literature about the chemistry of uranium(VI) in brines in the presence of radiolytic products.
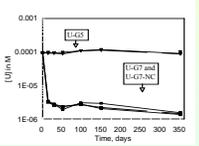
Major statements that can be made are:

❖ Some data exist on the effects of radiolysis on NaCl brines, but these are incomplete and do not fully define radiolytic effects in more realistic brines.

❖ U(VI) is not expected to be reduced in irradiated brines as a consequence of radiolysis. Non-radiolytic reduction pathways do exist and are currently under investigation, e.g., bio and iron.

❖ Radiolytic products (H_2O_2, OCl^-), as well as brine and repository components (Fe, Br, etc.), affect the speciation of uranium(VI) in brines.

❖ Issues related to precipitation/complexation effects on U(VI) speciation are being addressed experimentally.

Experimental objectives

Brine radiolysis presents a complex mechanism. The interaction of uranium with radiolytic species in solution remains a matter of investigation.
Our study will focus on the potential effects of radiolytic molecular products H_2O_2 and OCl^- on the uranium speciation in brines.
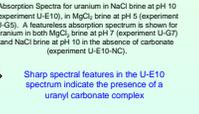
The overall reducing conditions of a repository (metals from containers, bioactivity) can mitigate the oxidizing effects of radiolysis and inhibit radiolytic products.
The redox stability of U(VI) in the presence of key repository components (e.g. iron) in brines will be addressed in our experimental studies.

Publications concerning the solubility of uranium are numerous in the literature, but very few were done in brine and under conditions that represent geological salt repository conditions.
The effective solubility of uranium(VI) as a function of key subsurface parameters will be established (e.g., brine composition, carbonate concentration, pH, and redox).
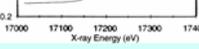
Los Alamos