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SPECTROSCOPIC INVESTIGATION OF THE FORMATION OF HYPOCHLORITE, RADIOLYSIS BY-PRODUCT IN 5 M NaCl FEATURING HIGH-ENERGY PROTON BEAM LINE EXPERIMENTS

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Introduction

Because geological salt formations are considered possible sites for radioactive waste disposal, plausible inundation scenario of salt repository will allow chloride brines to be formed, which consequently will be exposed to radiation from the waste. Key radioelements in Intermediate Level Waste (ILW), High Level Waste (HLW) or TRU waste have been found to be plutonium, americium, neptunium, uranium, and technetium.

Therefore, the effect of radiolysis on high-saline brine under simulated repository conditions are of particular importance because it results in oxidizing chlorine-containing species, such as hypochlorite (OCl^-), and hypochlorous acid (HOCl), which may oxidize actinide species to higher oxidation states [1-7].

Meaningful predictions of long-term redox conditions in a nuclear repository strongly rely on estimations of G-values of the irradiation-induced formation of the oxidizers OCl^- and HOCl. G-values not only depend on the total absorbed doses over the relevant timeframe, but also on the kind of irradiation involved. In fact, the G-values of hypochlorite produced by α-, β-, γ-, or neutron irradiation differ by an order of magnitude, depending on different LET cross-sections.

To overcome the serious constrains and obstacles of conventional radiochemical work within GBq/L activity levels, we are going to simulate α-irradiation of chloride brines by the adaptation of beam-line experiments.

Our long-term goal is to demonstrate how the main oxidizing chloride species such as hypochlorite caused by radiolysis may affect the overall behavior of actinides under salt repository conditions. This paper describes our first steps towards the production, the identification and the determination of these oxidizing species by beam line experiments.

Work Description

The chemical reagents are purchased from Aldrich Chemicals suprapure (99.99%), and are used without further purification. A 5 M NaCl solution was prepared by dissolving reagent grade NaCl in distilled water. All experiments are carried out in glass vessels at 24 ± 2 °C under normal atmosphere. The pH is adjusted by adding appropriate amounts of NaOH and measured during the experiment using a combination glass electrode ("Ross type, Orion Co). The chloride species are determined spectrophotometrically (Shimadzu Multispec 1501).

The Materials Science and Technology Division at Los Alamos National Laboratory offers capabilities to treat simulated brines with up to 6 MeV helium and protons to simulate the effect of irradiation on both solid and liquid media as well as the associated repository-related effects on actinide oxidation.

The perspective of these preliminary experiments is to be able to determine accurately the effects of α-activities up to kCi/L. Two preliminary experiments were performed: (1) A 4 mL quartz cuvette containing 5 M NaCl solution, pH 13 was attached to the 3 MV Tandem ion accelerator and irradiated by 4-6 MeV protons for three hours to reach a total absorbed dose of about 30 kGy. The temperature was (24 ± 2 °C). After irradiation, a UV Vis absorption spectrum of the irradiated brine was taken to identify the formation of hypochlorite.

(2) A 20 mL polyethylene test cell containing 5 M NaCl solution, pH 13 was attached to the 3 MV Tandem ion accelerator and irradiated with incremental step of 6, 12, 18, 24, and 30 micro Coulomb of 4.939 MeV protons producing absorbed doses of 1.48 kGy to

7.41 kGy. The temperature was (24 ± 2 °C). After each irradiation step, a UV Vis absorption spectrum of the irradiated brine was taken to monitor the formation of hypochlorite as a function of the absorbed dose.

Results

Results on preliminary test experiment 1

Some experiments were performed to test window material as well as to verify that the achieved dose rates within hour time-scale are adequate for the production of hypochlorite to be measured by using simple diode array UV-Vis spectrophotometry. The first test was performed using a 4 mL quartz cell, filled with 5 M NaCl solution, pH 13 after the addition of 1 M NaOH. As window material, we chose Havar®, a Co-based metal foil, to seal the ultra-high vacuum (UHV) of the primary beam-line towards the liquid cell. We applied a 3 nA proton beam for 3 hours until the Mylar foil showed serious radiation damage leading to a hole formation. However, a total absorbed dose of about 30 kGy could be introduced and the formation of hypochlorite associated with the accumulation of the introduced radiation energy was determined by UV Vis spectrophotometry (Figure 1).

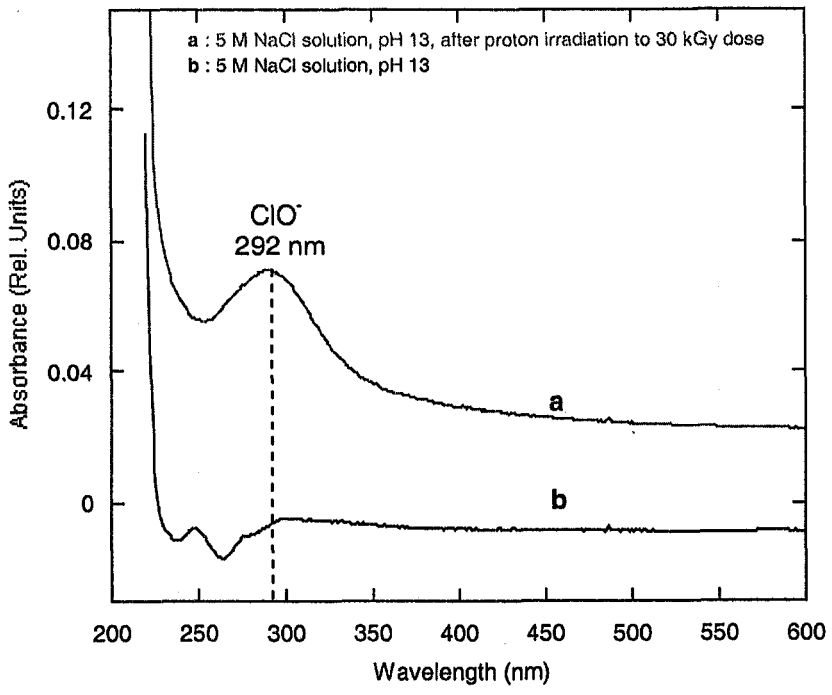

Figure 1: UV-Vis Absorption spectrum of 5 M NaCl, pH 13, after 4.4 MeV proton irradiation, achieving an absorbed dose of 30 kGy

Results on preliminary test experiment 2

4.9 MeV Proton beam was introduced in a 20 mL test cell containing 5 M NaCl. Furthermore, 12.5-micron Kapton® foil was used as window material sealing the high vacuum from the atmosphere and 2.5-micron Mylar® foil was used as interface to the 20 mL liquid test cell. The primary proton energy was set to be 5.755 MeV resulting to the proton energy in the liquid chloride target of 4.939 MeV. Selected UV Vis absorption spectra are plotted in Figure 2 in the wavelength range from 220 nm to 400 nm, after

introducing incremental step of 1.48 kGy radiation doses.

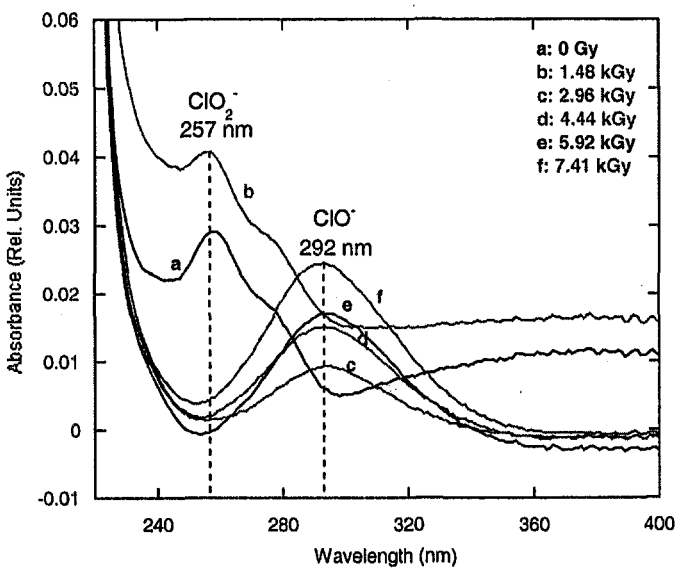

Figure 2: UV Vis absorption spectra of 5 M NaCl (pH 13) after introducing radiation doses of 1.48 kGy each producing a total absorbed dose of 7.4 kGy.

The spectrum at 0 Gy irradiation represents the non-irradiated 5 M NaCl, pH 13 and shows minor concentration of $NaClO_2$ probably due to the presence of NaOH. The apparition of the peak at 292 nm is attributed to the formation of hypochlorite in the solution. Similar peak has been observed for hypochlorite added to a 5 M NaCl solution [8]. While increasing the dose, the spectrum changed significantly in position and shape. The introduction of 6 micro Coulomb 4.9 MeV protons, associated with 29.6 Joule energy and 1.48 kGy dose, slightly increased the absorbance within the wavelength range

without changing speciation. The incremental introduction of 29.6 Joule energy, associated with 2.96 kGy, 4.44 kGy, 5.92 kGy, and 7.41 kGy total absorbed dose triggered the irradiation-induced formation of 34 μmol, 52 μmol, 58 μmol, and 81 μmol hypochlorite respectively (Figure 2).

Conclusion

We have quantified significant formation of hypochlorite at rather low dose and dose rate. The measured G-value for ClO^- formation in a 20 mL quartz cell containing 5 M NaCl solution, irradiated by proton ions is estimated to be 0.0949 molecules /100 eV, which is in fairly good agreement with the data published by Kelm et al. [1] of 0.0965 for alpha-self-irradiation using plutonium solutions of 3.7 GBq/L (1Ci/L). Of course, we have to take into consideration, that our experiment was not close to reach hypochlorite saturation, while the published data did. However, based on our 20 mL test experiment, we can assume that a 5 mmol ClO^- concentration, which may be sufficient to successfully oxidize actinides (U, Pu, Am) will be generated after introducing about 507 kGy dose or 10.14 kJ energy into the 20 mL liquid target, (considering the specific heat of water of 4.184 kJ kg^{-1} K^{-1}, 10.14 kJ energy will theoretically heat up the 20 mL target by 120 K when no cooling is applied). To be able to successfully estimate the long-term radiolytical considerations in a nuclear repository such as the Waste Isolation Pilot Plant, simulations including a wider range of irradiation and involved chemical constituents should be performed.

References

1. Kelm M., Pashalidis I., Kim J.I., *Spectroscopic investigation on the formation of hypochlorite by alpha radiolysis in concentrated NaCl solutions.* Applied radiation and isotopes, 1999. **51**: p. 637.
2. Kelm M., Bohnert E., *Radiation chemical effects in the near field of a final disposal site I: Radiolytic products formed in concentrated NaCl solutions.* Nuclear Technol., 2000. **129**: p. 119.
3. Magirius S., Carnall W., Kim J.I., *Radiolytic oxidation of Am(III) to Am(V) in NaCl solutions.* Radiochimica Acta, 1985. **38**: p. 29.
4. Büppelmann K., Magirius S., Lierse Ch., Kim J.I., *Radiolytic oxidation of Am (III) to Am (V) and Pu(IV) to Pu (VI) in saline solution.* J. Less Common Metals, 1986. **122**: p. 329.
5. Kim J.I., Lierse C., Büppelmann K., Magirius S., *Radiolytically induced oxidation reactions of actinide ions in concentrated salt solutions.* Mat. Res. Soc. Symp. Proc., 1987. **84**: p. 603.
6. Büppelmann K., Kim J.I., Lierse Ch., *The redox behavior of Pu in saline solutions under radiolysis effects.* Radiochimica Acta, 1988. **44/45**: p. 65.
7. Pashalidis I., Kim J.I., Lierse Ch., Sullivan J., *The chemistry of Pu in concentrated aqueous NaCl solution: Effects of alpha self-radiolysis and the interaction between hypochlorite and dioxoplutonium (VI).* Radiochimica Acta, 1993. **60**: p. 99.

8. P. Paviet-Hartmann, J. Dziewinski, T. Hartmann, S. Marczak, N. Lu, M. Walthall, A. Rafalski, Z. Zagorski, *"Spectroscopic investigation of the formation of radiolysis by-products by 13/9 MeV LAE in salt solutions"*, LA-UR-01-6300, 2002

9. Kelm M., Bohnert E., *Radiolytic compounds formed by dissolution of irradiated NaCl and $MgCl_2.6H_2O$ in water.* Radiochimica Acta, 1996. **74**: p154