

APPLICATION OF HIGH ENERGY BEAM-LINE EXPERIMENTS ON MgCl₂ SOLUTION TO SIMULATE RADIOLYSIS IN THE NEAR FIELD OF A NUCLEAR REPOSITORY

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ABSTRACT

In the event of inundation of a nuclear waste repository located in a geological salt formation, chloride brines in contact with nuclear waste will be exposed to different kind of radiation depending on waste-form conditions. Ionizing radiation, however, has the ability to significantly affect groundwater chemistry through the formation of free radicals, ionic- and molecular species. Alpha-radiation emitted from light actinides contained in the waste (U, Np, Pu, Am, and Cm) will induce the formation of radiolysis by-products in the brine solution such as hypochlorite (OCl⁻), and hypochlorous acid (HOCl). In the absence of reductants e.g. metal ions, released through the corrosion of waste container, and microbial activity, hypochlorite can cause high redox potential in brines, which may (1) enhance dissolution rate of waste-forms, and (2) oxidize actinides to their highest oxidation state, and consequently enhance actinide migration. Addressing the needs of performance assessment in respect to the consideration of experimental data on the impact of radiolysis towards the geochemical-radiochemical system, we are presenting a “cold” experimental approach to determine radiation-induced formation rates of radiolytic species such as OCl⁻ and HOCl. To overcome the constraints of conventional radiochemical work, we are simulating alpha-irradiation in chloride brines by the adaptation of ion-beam-line experiments. We irradiated 3.7 M MgCl₂ x 6H₂O targets as surrogates for the groundwater of the WIPP Salado formation to doses up to 7.1 kGy with protons, and up to 5.6 kGy with double-charged helium ions. The irradiation-induced formation rates of OCl⁻ and HOCl were determined by UV-Vis spectrophotometry. The knowledge about the radiation-induced production of oxo-chloride species is a first step towards the assumption of their steady-state concentrations in the repository near-field. Considering a worst-case repository situation with high 0.001 M ²³⁹Pu concentration (602 MBq/L) in the groundwater brine of the repository near-field, the “cold” irradiation experiment as presented here reflects 163 days of dose accumulation and radiolytic species formation simulated by a one-day experiment.

INTRODUCTION

The quality of a disposal strategy for nuclear waste is determined by its isolation capacity towards the actinide elements as the most radiotoxic radionuclides. As an administrative measure, the quality of the disposal strategy is evaluated by performance assessment, which should conclude on experimental data on thermodynamic and kinetics, unfolding the most dominant processes relevant to potential mobilization of radionuclides from the primary waste-forms, retention in secondary actinide-host phases, and the migration of radionuclides from the geochemical environment of the repository near-field. The generally accepted conception for nuclear waste disposal is burial in deep geologic repositories chosen to ensure that the radiotoxic constituents of nuclear waste will remain confined as a result of the geochemical constitution and the addition of engineered barriers, in order to minimize the potential of radionuclide release from the repository near-field into the biosphere. Hereby, one of the greatest concern and a potential worst-case scenario for environmental sound disposal is groundwater intrusion. Groundwater intrusion into a nuclear waste repository in deep salt formations may cause the repository to be inundated with brine from surrounding aquifers and the chloride-dominated brines to be exposed to radiation from degraded nuclear waste. In groundwater brines, alpha- and gamma radiation emitted from light actinides will induce the formation of radiolytic species such as hypochlorite (OCl^-) and hypochlorous acid (HOCl), [1-6] which, in the absence of reductants, can cause higher redox potentials [7, 8], enhanced waste-forms dissolution rates, and furthermore promote higher actinide oxidation states, as well as higher solubilities. Addressing these needs for experimental data on the impact of radiolysis towards the geochemical-radiochemical repository system, we are presenting a “cold” experimental approach to determine radiation-induced formation rates of radiolytic species by applying beam-line experiments. We have already simulated the effect of alpha-irradiation on liquid media by treating 5 M NaCl solution as well as 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and synthetic MgCl_2 -based brine with 4.9 MeV protons [4-6]. The far goal of these research activities is to understand radiolysis in the repository near-field and to determine steady-state concentrations of the radiolytic species to affect the repository Eh-pH system within the time frame to be considered by performance assessment.

EXPERIMENTAL

The chemical reagents are purchased from Aldrich Chemicals suprapure (99.99%), and are used without further purification. The salt solutions 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was prepared by dissolving the proper reagent grade chemicals in distilled water. All experiments are carried out in glass vessels at 24 ± 2 °C under normal atmosphere. The pH is measured during the experiment using a combination glass electrode (Ross type, Orion Co). This set of experiments is designed to (1) assess if either OCl^- or HOCl can be formed directly by applying high-energy ion-beam experiment, and (2) determine the irradiation induced HOCl/OCl^- formation as a function of the absorbed irradiation dose, using a 20 mL test cell, attached to the 3 MV Tandem ion accelerator via a doubled-window interface [5-6]. This doubled window consists of a 10- μm Harvar™ foil to seal the ultra-high vacuum of the beam-line and an 8- μm Kapton™ foil as a membrane towards the test cell containing salt solutions. The experimental details are displayed in Table I.

The salt solution was irradiated using a similar approach as described in [3, 5, 6]. After introducing 6 μC of either 5.2 MeV He^{++} ions or 4.9 MeV protons into the liquid cell, a UV-Vis absorption spectrum (Spectrophotometer Shimadzu Multispec 1501) was taken to determine the progress of radiolysis by-products formation, knowing that the HOCl spectroscopic

characteristics in 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at pH 4.42 [6] are: (1) absorption band at 232 nm, and (2) molar extinction coefficient ϵ 13044 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. Each incremental irradiation step of 6 μC 5.2 MeV He^{++} ions and 6 μC 4.9 MeV protons is associated with 15.49 J and 29.61 J energy, increasing the absorbed irradiation dose in the test cell by 618 Gy and 1.18 kGy, respectively. In this experimental set-up, total absorbed doses of 5.6 kGy and 7.1 kGy were achieved by using 5.2 MeV He^{++} ions or 4.9 MeV protons, respectively.

Table I. Experimental Details the Liquid-Cell Test Experiment: Irradiation-Induced Hypochlorous Acid Formation in 20 mL 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ Solution using Proton and Helium Ions Irradiation.

Target	3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
	pH 4.42	pH 5.07
	4.9 MeV proton irradiation	5.2 MeV He^{++} ion irradiation
Ionic strength	3.7	3.7
Chloride concentration (mol/L)	7.4	7.4
Mass to be irradiated (kg)	2.50×10^{-2}	2.50×10^{-2}
Source energy after acceleration (eV)	5.50×10^6	8.80×10^6
Energy (eV) after the UHV window (Harvar TM 10 μm)	5.022×10^6	6.030×10^6
Energy (eV) after test-cell window (Kapton TM 8 μm)	4.935×10^6	5.164×10^6
Total cumulative energy (J)	177.6	139.4
Total introduced dose (kGy)	7.10	5.60

We used Monte Carlo simulation (SRIM) [9] for information on (1) stopping and (2) the associated ionization of 4.9 MeV protons and 5.2 MeV He^{++} ions in 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ salt solution used as a surrogate for Salado-brine. The primary interaction between 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and either 4.9 MeV protons or 5.2 MeV He^{++} ions is limited to the first 299 μm ($\pm 0.6 \mu\text{m}$) or 33.6 μm ($\pm 0.4 \mu\text{m}$) brine layer, respectively, of the 20 mL brine salt solution, situated behind the 8- μm KaptonTM window (Fig. 1).

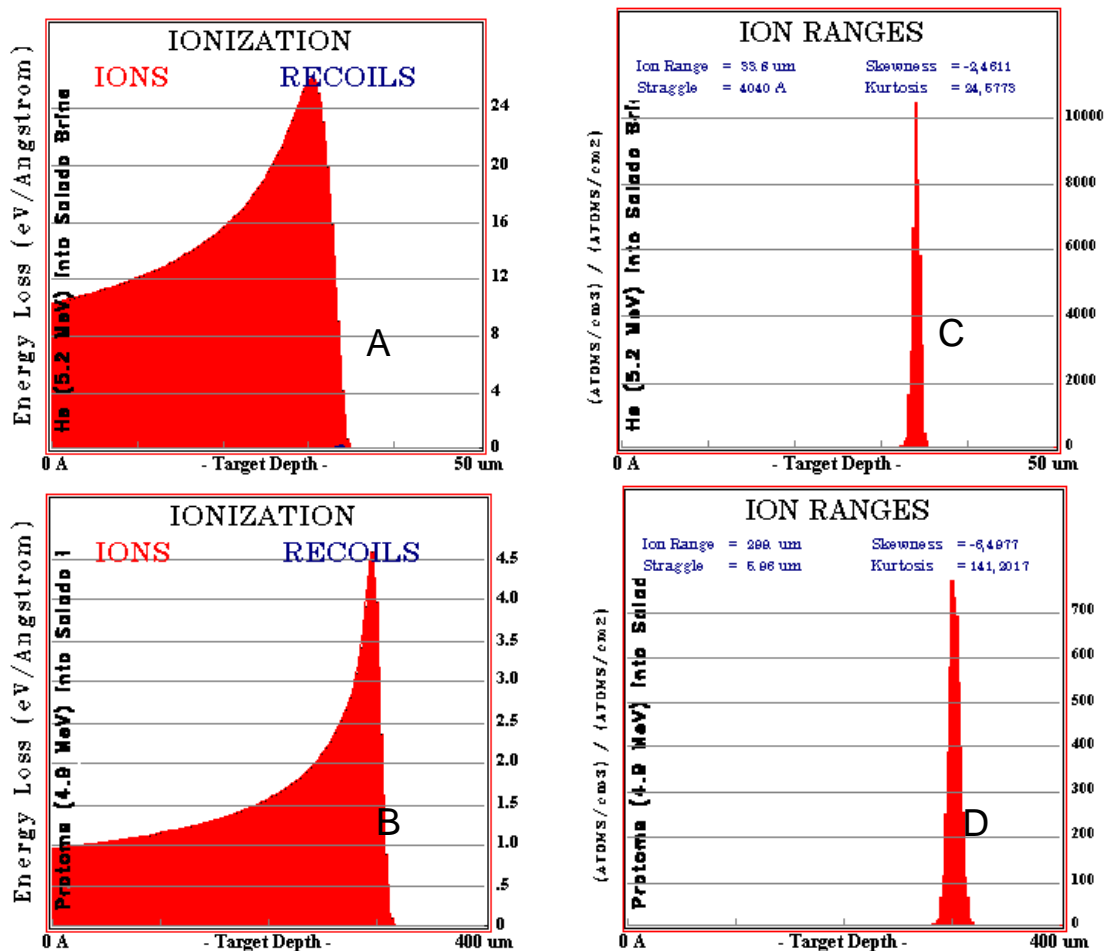


Fig. 1. The Monte Carlo Simulation (SRIM) of the collision events within the liquid cell towards the beam-line: (1) ionization of the constituents in 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution by (A) irradiating with 5.2 MeV He^{++} ions, (B) irradiating with 4.9 MeV protons, and (2) ion ranges in 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution of (C) 5.2 MeV He^{++} ions: 33.6 μm ($\pm 0.4 \mu\text{m}$), and (D) 4.9 MeV protons: 299 μm ($\pm 0.6 \mu\text{m}$).

RESULTS AND DISCUSSION

We successfully simulated alpha-radiolysis in a repository near-field via a “cold” experimental approach by attaching a test cell to a Tandem ion accelerator, and formation rates for the radiolytic species were determined. The irradiation of 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ by using either 4.9 MeV protons or 5.2 MeV He^{++} ions up to doses of 7.1 kGy and 5.6 kGy, respectively, led to the formation of hypochlorous acid (HOCl) determined spectrophotometrically at 232 nm (Fig. 2). The measured formation rates of radiolytic HOCl in 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were determined to be 0.004 (± 0.0004) mmole * kGy⁻¹ irradiated by 4.9 MeV protons, and 0.011 (± 0.001) mmole * kGy⁻¹ using 5.2 MeV helium ions. The $G_{(\text{HOCl})}$ values (100 eV yield) for the formation of hypochlorous acid were measured to be 0.0389 ± 0.004 for 4.9 MeV protons, and 0.107 ± 0.01 for 5.2 MeV helium ions, respectively.

In order to gain basic phase constitutional information of the system being investigated, UV-Vis absorption spectra of the individual species ClO^- and Cl_3^- in 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ are plotted as a function of pH in the wavelength range of 190 nm to 400 nm (Fig. 2). The formation of Cl_3^- is well characterized by its broad absorption band at 325 nm, while hypochlorite ions ClO^- exhibit a distinguished peak shifted towards lower wavelength at 282.7 nm ($\epsilon = 197 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). In the pH range 4 to 6, the concentration of hypochlorous acid (HOCl) is in a steady-state at micromolar-level with a molar extinction coefficient $\epsilon = 13044 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ [5, 6].

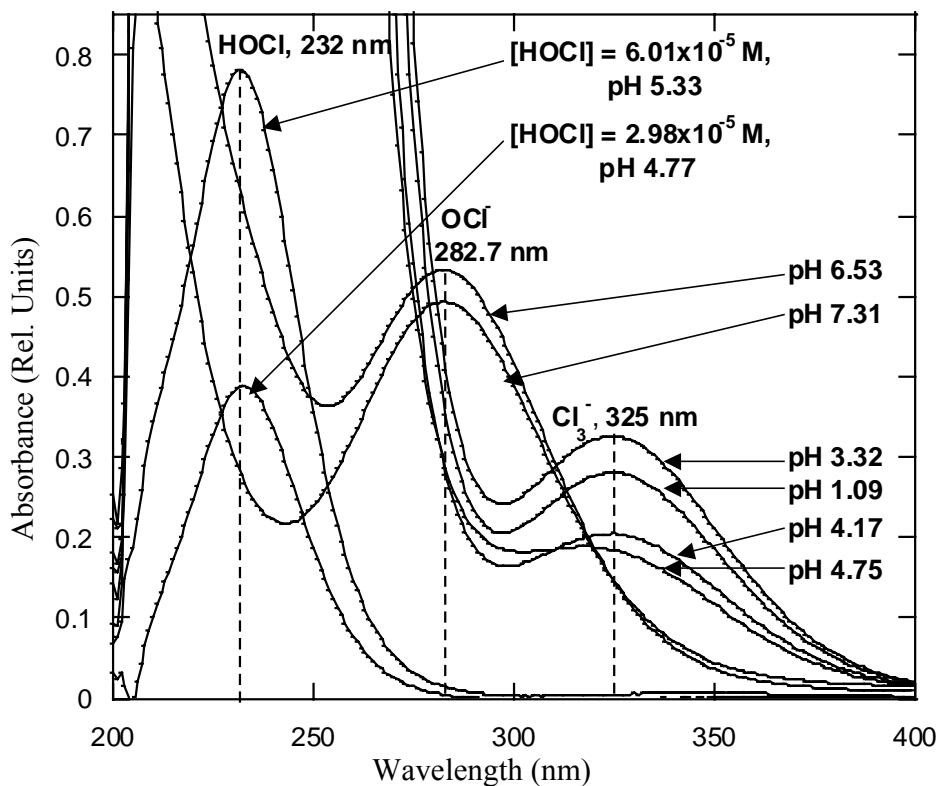


Fig. 2. UV-Vis Absorption spectra of chloride species in 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as a function of pH.

To simulate radiolytic effects on repository brine like chloride solutions expected for the WIPP, e.g. through Pu self-irradiation after groundwater intrusion and waste-form degradation, we irradiated 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution (1) with 5.2 MeV He^{++} ions by incremental steps of 618 kGy to a final absorbed irradiation dose of 5.60 kGy and (2) with 4.9 MeV protons by incremental steps of 1.18 kGy to a final absorbed dose of 7.1 kGy. UV-Vis absorption spectrophotometry was used to determine radiolytic constitution and species concentration as a function of absorbed dose, and a spectrum was taken after each irradiation step (Fig. 3).

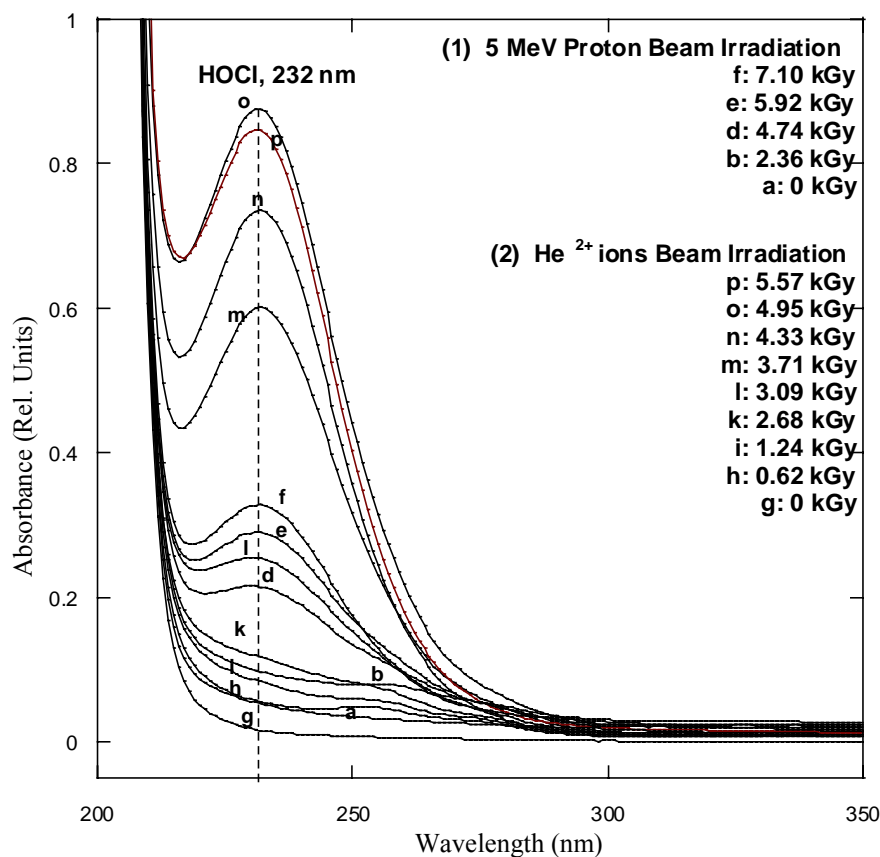


Fig. 3. UV-Vis absorption spectra of 3.7 M MgCl₂.6H₂O irradiated by (1) 4.9 MeV protons, pH = 4.42, and (2) 5.2 MeV He⁺⁺ ions, pH = 5.072

The spectrum at 0 Gy irradiation represents the non-irradiated 3.7 M MgCl₂.6H₂O solution. By using either 4.9 MeV protons or 5.2 MeV He⁺⁺ ions, the formation of ClO₂⁻, as an intermediate species, is observed at 256 nm with an assumed concentration in the micromolar range. After introducing a dose of about 4 kGy into the brine solution, by 4.9 MeV protons and 5.2 MeV He⁺⁺ ions, this intermediate chloride species has mainly disappeared and the formation of HOCl is observed, associated with a peak at 232 nm. The formation of HOCl was confirmed in parallel experiments by adding hypochlorous acid to a 3.7 M MgCl₂.6H₂O solution [5, 6]. The progress of HOCl formation as a function of absorbed dose shows considerable scattering and is characterized by alternating an overall linear growth, independently if the brine solution was irradiated by 5.2 MeV He⁺⁺ ions or by 4.9 MeV protons (Fig. 4). This alternation could be caused by the presence of intermediate chloride species (radicals) such as ClO₂⁻, as well as through rapid reactions of radiolytic hypochlorous acid with the brine. Considerable scattering in the radiolytic product formation as a function of absorbed dose was not observed in previous experiments by applying a similar experimental approach, irradiating NaCl-based brine with 4.9 MeV protons [6]. At this point, no intermediate radiolytic species formation as well as no considerable scattering in the radiolytic species formation with increasing dose was observed. Therefore, it can be assumed that the experimental set-up provides sufficient homogeneity within

the irradiated brine solution and the data scattering is rather caused by secondary chemical effects than by poor intermixing.

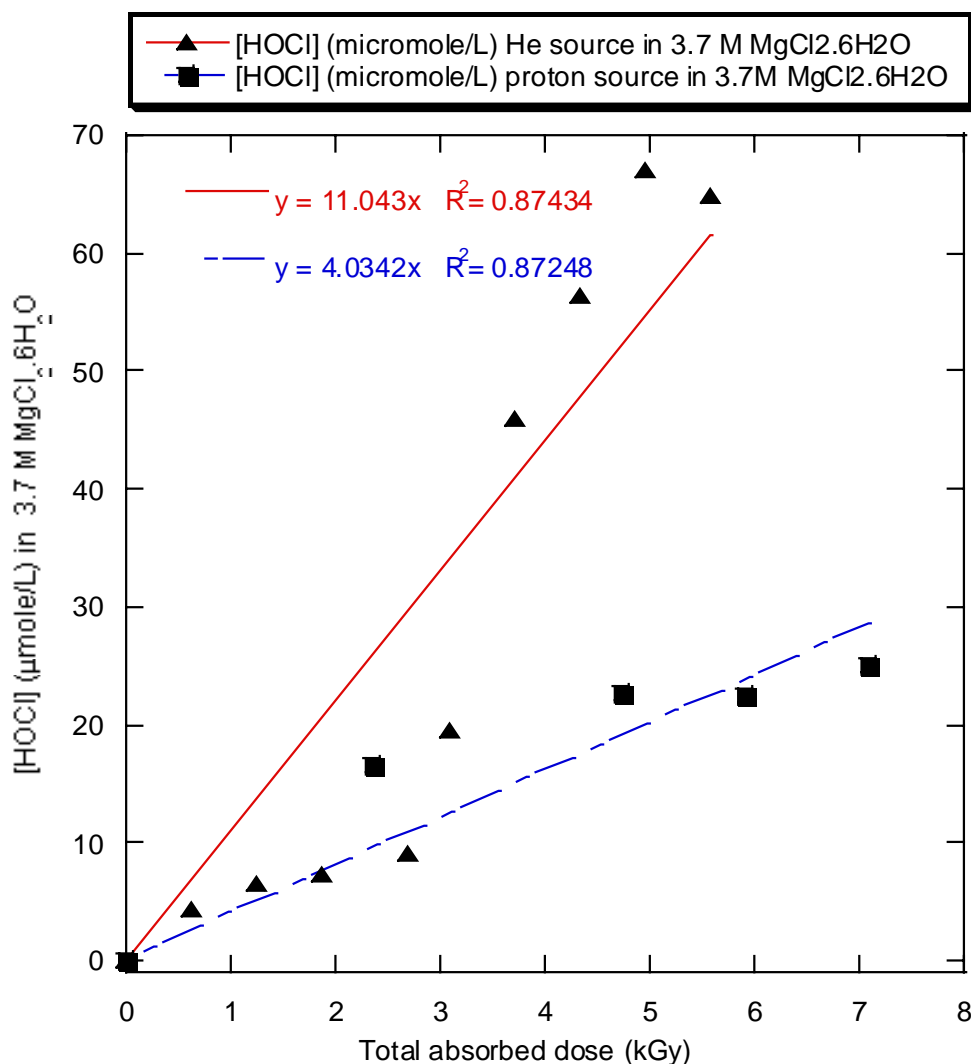


Fig. 4. Irradiation-induced formation of hypochlorous acid as a function of total absorbed dose. 20 mL of 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution was step-wise irradiated either with double-charged 5.2 MeV He ions or with 4.9 MeV protons to total doses of 5.6 kGy and 7.1 kGy, respectively. Based on linear data fitting, formation rates of radiolytic HOCl in 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were determined to be $0.004 (\pm 0.0004) \text{ mmole} \cdot \text{kGy}^{-1}$ when irradiated by 4.9 MeV protons, and $0.011 (\pm 0.001) \text{ mmole} \cdot \text{kGy}^{-1}$ by using 5.2 MeV helium ions.

The irradiation of brine by using 5.2 MeV He^{++} ions results in significant higher radiolytic product yields than by using 4.9 MeV protons, and a strong LET dependency was observed. The highest radiolytic product concentration of 66.7 μmol HOCl was measured after introducing a 4.9 kGy dose by 5.2 MeV He^{++} , based on the molar extinction coefficient of $13044 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 232 nm. Based on stopping and ion ranges (Fig. 1), the LET of 5.2 MeV He^{++} and 4.9 MeV protons were calculated to be 154 eV/nm and 16.5 eV/nm, with an increased LET within the last

10% in ion range from 220 eV/nm to 260 eV/nm and from 25 eV/nm to 46 eV/nm, respectively (Fig. 1A, Fig. 1B). It appears that in Salado-type brine, high ionization densities and dense overlays of ionization tracks are favoring higher radiolytic yields relative to dose. As a result of the about 9 times higher ionization density and hence higher local radical concentration, in the irradiation experiment using 5.2 MeV He⁺⁺ ions compare to using 4.9 MeV protons, the formation rate of hypochlorous acid in 3.7 M MgCl₂.6H₂O solution is enhanced by a factor of 2.75. The measured G-value (100 eV yield) for the formation of radiolytic HOCl in 3.7 M MgCl₂.6H₂O solution are 0.107 ± 0.01 molecules /100 eV by using 5.2 MeV He ions, and 0.0389 ± 0.004 molecules /100 eV by irradiation with 4.9 MeV protons (Tables II).

Table II. G_(HOCl) Value (100 eV yields) for 3.7 M MgCl₂.6H₂O

	4.9 MeV proton irradiation	5 MeV He ⁺⁺ ion irradiation
[HOCl] (mmole/kGy)	0.0040 ± 0.0004	0.0111 ± 0.001
Sample Mass (kg)	0.025	0.025
Dose per μC (Gy)	1.97*10 ²	1.03*10 ²
Target Energy (eV)	4.94*10 ⁶	5.16*10 ⁶
G _(HOCl) (number of HOCl molecules formed per 100 eV)	0.039 ± 0.004	0.107 ± 0.01

This considerable LET dependency in the radiolytic yield of MgCl₂.6H₂O brine solution might provide a reasonable argument for improved waste-form qualities and as low as possible corrosion rates of waste container material in contrast to current strategies allowing intense waste container (mild-steel) corrosion for providing reducing near-field conditions. In the situation of waste-form degradation and Pu-self-irradiation in the repository near-field, radiolytic yields will be significantly enhanced through alpha-radiolysis compare to gamma-radiolysis. Reducing repository conditions on long terms might not be achieved but most likely actinide migration through the formation of radiolytic oxo-chloride species and the consequential changes in actinide speciation.

In previous experiments, we have quantified the formation of hypochlorite in Castile-type brine at rather low dose and dose rates. By applying proton irradiation, the measured G-value for ClO⁻ formation in a 20 mL test cell containing 5 M NaCl solution was determined to be 0.095 molecules /100 eV [3], which is a good agreement with the data published by Kelm et al. [2] of 0.0965 molecules / 100 eV applying alpha-self-irradiation using plutonium solutions of 37 GBq/L. It seems reasonable that the results of the simulation of radiolysis in 3.7 M MgCl₂.6H₂O brine as presented, will also be in agreement with Pu-self-irradiation experiments to come. Our radiation experiments are mainly focused in the determination of radiolytic yields rather than measuring long-term steady-state concentrations and are considered as a first step in the determination of long-term near-field conditions. On longer terms, the decomposition of hypochlorous acid should be considered and the hypochlorous acid concentration will reach saturation as the result of irradiation-induced formation and of disintegration of hypochlorous acid by autocatalysis and/or photolysis. The long-term steady-state concentration of hypochlorous acid in a repository will depend on an array of criteria which are given by the individual geochemical site and by the waste-form constitution, among them (1) the presence and concentrations of the constituents (mainly metals) which could enhance the decomposition of

hypochlorous acid, and (2) kinetic of waste-form degradation and the actinide mobility, to define dose rates and ionization characteristics at the interface waste-form - brine.

CONCLUSION

We demonstrate that applying non-radioactive beam-line experiments is a durable approach to generate valuable data on the formation-rates of radiolytic constituents without the experimental and administrative constraints of radioactive bench top or glove-box work. Information on formation rates of radiolytic species are crucial in order to assess the impact of radiolysis on geochemistry and to evaluate actinide-migration from nuclear salt repositories on long terms, and consequently, provide support for related performance assessment efforts. In current geochemical models to assess actinide solubilities under the individual repository conditions, steady-state concentration of radiolytical species such as hypochlorite and hypochlorous acid are not considered, basically because radiolysis expected in salt repositories after water intrusion and waste-forms degradation is highly complex and data are only available for simplified systems. At the current state of our experiment, we can directly determine the irradiation-induced formation of hypochlorite and hypochlorous acid as a function of absorbed dose. The G-values (100 eV yields) for HOCl formation in a 20 mL cell containing 3.7 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution were determined to be 0.107 ± 0.01 molecules /100 eV when irradiated by 5.2 MeV He^{++} ions, and 0.039 ± 0.004 molecules /100 eV when applying 4.9 MeV proton irradiation. Anyhow, for performance assessment efforts, steady-state long-term concentrations of radiolytic species are of great importance and therefore data on formation rates of radiolytic species in specific repository brines should be completed by data on radiolytic species decomposition by including all relevant constituents. In a realistic system, to reflect repository near-field conditions, the assessment of effects of radiolysis is, because of its complexity, an intriguing task, and constituents also in very minor concentrations might trigger both, the formation or the disintegration of radiolytic species. To give an example, the presence of metal corrosion constituents, also in very minor concentration, will participate in the catalytic decomposition of radiolytic products such as hypochlorous acid or hypochlorite. It has to be pointed out, that beam-line experiments on non-active samples as performed here, mainly focus on radiolytical formation rates rather than on the determination of steady-state concentrations, but the knowledge about the radiation-induced production of oxo-chloride species is considered as a first step towards the assumption of their steady-state concentrations in the repository near-field. Considering a worst-case repository situation with high $0.001 \text{ M } ^{239}\text{Pu}$ concentration (602 MBq/L) in the groundwater brine of the repository near-field, the "cold" irradiation experiment as presented here reflects 163 days of dose accumulation and radiolytic species formation simulated by a one-day experiment.

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