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SPECTROSCOPIC INVESTIGATION OF THE FORMATION OF RADIOLYSIS BY-PRODUCTS BY 13/9 MeV LINEAR ACCELERATOR OF ELECTRONS (LAE) IN SALT SOLUTIONS

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ABSTRACT

In the near-field chemistry of a salt repository, the radiolytically-induced redox reactions in concentrated saline solution are of particular importance because the radiolysis of saline solutions results in oxidizing chlorine-containing species, which may oxidize actinide species to higher oxidation states. If the brines are irradiated, the solutions containing radiolytic species such as hypochlorite, hypochlorous acid or hydrogen peroxide, their pH and Eh may be altered. The oxidation and complexation states of actinides, which might be present in the salt brine, will change thus influencing their speciation and consequently their mobility. Furthermore, radiolytically formed oxidizing species such as ClO^- or H_2O_2 may enhance the corrosion of the canister material. Therefore, radiation effects on salt brines must be integrated into the database, which described the chemical processes near a disposal site. Investigations in that context usually focus on the radiation chemistry of solid NaCl however our focus is on the radiolytic products, which are formed when salt brines are irradiated by a 10 MeV linear accelerator of electrons (LAE). We attempt to quantify the irradiation-induced formation of typical radiolysis by-products such as the hypochlorite ion (OCl^-) by using a 13/9 MeV LAE with doses between 120 KGy to 216 KGy while monitoring the pH of the brine solutions

INTRODUCTION

In nuclear waste repositories, the radiation fields arising from the wastes may have an influence on the actinide speciation via the radiolysis products of water and more specifically the radiolysis products of NaCl or $MgCl_2.6H_2O$ i.e. hypochlorite, hydrogen peroxide in the case of a salt repository like the Waste Isolation Pilot Plant (WIPP) in New Mexico, USA or Gorleben in Germany. 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. These all have more than one accessible oxidation state under possible repository conditions. There is some probability to establish radiolysis as a mechanism for causing enhanced aqueous concentration of actinide and radionuclide in nuclear waste repositories near fields.

Furthermore, these experiments will help to understand under which assumed micro-environments in a salt repository, irradiation may produce enough oxidizing agents to increase actinide solubilities. The situation of a salt repository for actinide solubility and actinide speciation may be rather complex and reducing effects are in competition with oxidizing effects. It is important to correlate the salt repository situation to experimental results on radiolysis on the less-dimensional HLW systems. From the HLW experiments [1-5], we know that - in first order - the achievable hypochlorite concentrations entirely depend on the accumulated absorbed doses, while production rates depend on activity levels. Under this guideline, small activity levels can result in the formation of oxidizing radiolysis products after accumulating high enough doses. 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 identification and determination of these oxidizing species.

EXPERIMENTAL

The Chemical reagents were purchased from Aldrich Chemicals suprapure (99.99%), and were used without further purification. Two salts solutions 5 m NaCl and 3.7 m $MgCl_2.6H_2O$ as well as two synthetic salt brines, Brine 1 and Brine 2 (see table I) were prepared. The chloride solutions are made by dissolving reagent grade NaCl or $MgCl_2.6H_2O$ in distilled water. All experiments are carried out in glass vessels at 24 ± 2 °C under normal atmosphere. PH is adjusted by adding appropriate amounts of HCl or NaOH and measured during the experiment using a combination glass electrode ("Ross type, Orion Co). The chloride species are determined spectrophotometrically (Cary 500 and Perkin Elmer)

The linear electron accelerator, LAE 13/9 produces energies 5 to 13 MeV and has a power of 9 kW in the beam. It is equipped with a special electromagnet for the measurement of energy[6].

The four salt solutions (100 mL each) were transferred in a closed beaker and irradiated at 3 different doses: 120 kGy, 160 kGy and 216 kGy. The initial pH was 6.87 for 5 m NaCl, 4.42 for 3.7 m $MgCl_2.6H_2O$, 7.43 for brine 1, and 8.23 for Brine 2. The temperature was (24 ± 2 °C). After irradiation, a UV Vis absorption spectrum was taken.

Table I: Chemical Composition of Brine 1 and Brine 2

	Brine 1	Brine 2
Reagent	Mass Fraction	Mass Fraction
	g in 100 mL water	g in 100 mL water
Na_2SO_4	2.0684	2.37
NaBr	0.2246	0.113
$Na_2B_4O_7.10H_2O$	1.2343	0.60
NaCl	14.722	26.164
$NaHCO_3$		0.134
KCl	2.8553	0.723
$MgCl_2$•$6H_2O$	16.971	0.386
LiCl	0.0152	
$CaCl_2$•$2H_2O$	0.1666	0.176

RESULTS AND DISCUSSION

Irradiation caused some changes in the UV Vis absorption spectra of the brines (Figs. 1 and 2). These changes are relatively small for 5 M NaCl solution, a little larger for 3.7 M $MgCl_2$ solution and much larger for brines 1 and 2. The biggest change was observed for brine #1. Changes increased while increasing the radiation dose. Qualitative explanation of these changes in spectra will be discussed below.

Because geological salt formations are considered possible sites for radioactive waste disposal, numerous studies on the radiolysis effects of salt brines are reported in the literature [7].

Chloride ions in aqueous solution are inert towards e_{aq}^{-} and hydrogen but undergo rapid electron-transfer-type reactions with $OH^{\cdot}$ to give Cl_2^- which incorporate a second chloride ion and are stochiometrically equivalent to $Cl + Cl^-$:

$$OH^{\cdot} + Cl^- \xrightarrow{Cl^-} Cl_2^- + OH^- \qquad (1)$$

Dimerization of the species formed by the above reaction produces the corresponding halogen molecule (Cl_2) or an ion derived from it (Cl_3^-),

$$2Cl_2^- \longrightarrow Cl_2 + 2Cl^- (or\ Cl_3^- + Cl^-) \qquad (2)$$

Bjergbakke et al. [8] surveyed the compounds that may form in NaCl brines exposed to an assumed dose rate of 1Gy/s for 100s. They predicted by extrapolation the yields of the production of different chloride species. According to their observations, the concentration of hypochlorous acid (HOCl) remained in a steady-state at micromolar-level, and the concentration of chlorine gas was below the detection limit even for NaCl concentration of 5.5 M.

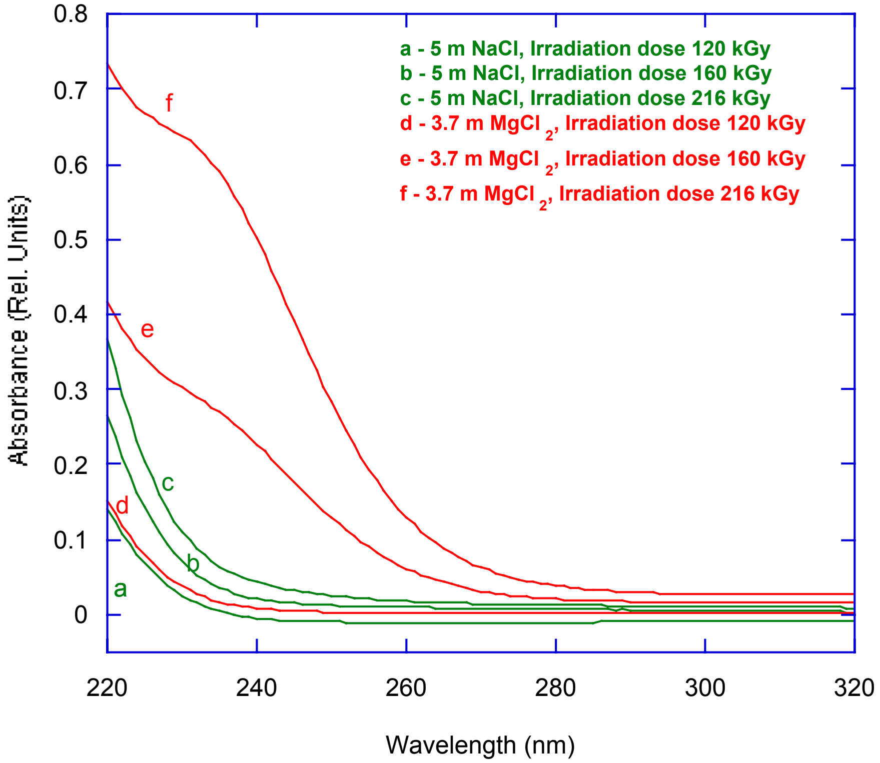

Fig. 1: Selected UV Vis absorption spectra of two pure salt solutions 5 m NaCl and 3.7 m $MgCl_2.6H_2O$ irradiated at three different doses: 120 kGy, 160 kGy, 216 kGy by a 13/9 MeV Linear Accelerator of Electrons (LAE).

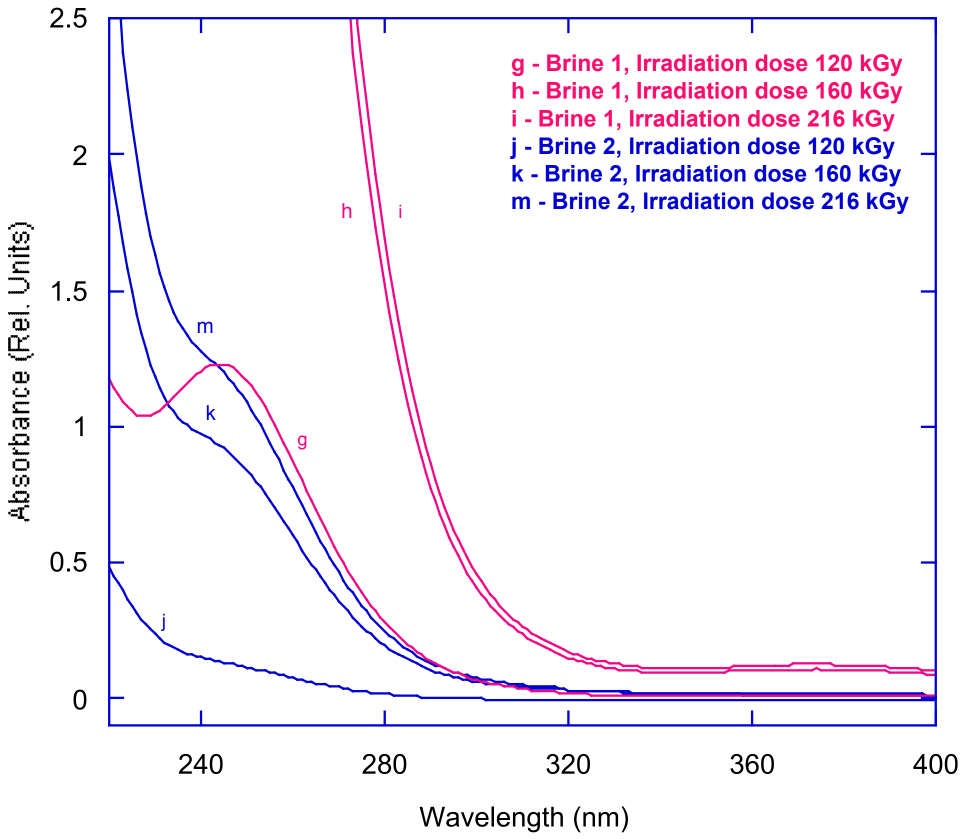

Fig. 2: Selected UV Vis absorption spectra of two synthetic brines irradiated at three different doses: 120 kGy, 160 kGy, 216 kGy by a 13/9 MeV Linear Accelerator of Electrons (LAE).

Alpha-particle irradiation of 5 M NaCl results in the formation of transitory equilibrium system of $Cl_3^-, Cl_2, HClO, ClO^-, Cl^-$ [9]. According to Büppelmann K., Kim J.I., and Lierse Ch., at pH<7, the formation of chlorine gas is favored. At 4<pH<7, the formation of hypochlorous acid (HClO) is observed while at pH>7, the formation of hypochlorite (ClO^-) is preferential [10]. This change may be easily explained by $H^+ + ClO^- \leftrightarrow^- HClO$ equilibrium (pK_a =7.23 in pure water).

Several chloride species have been identified in the literature [11-16]. The UV Vis absorption spectra of the individual species $HClO_2$, Cl_2, $KClO_3$, ClO^-, $NaClO_2$ and ClO_2 are plotted in Fig. 3. The generation of Cl_2 may be well distinguished by a relatively broad absorption band at 332.5 nm. ClO_2 formed by disproportionation radiolysis has also easy to detect, a broad absorption band at 360 nm. Hypochlorite ion ClO_2^- exhibits a peak at 260 nm and ClO^- - at 292 nm.

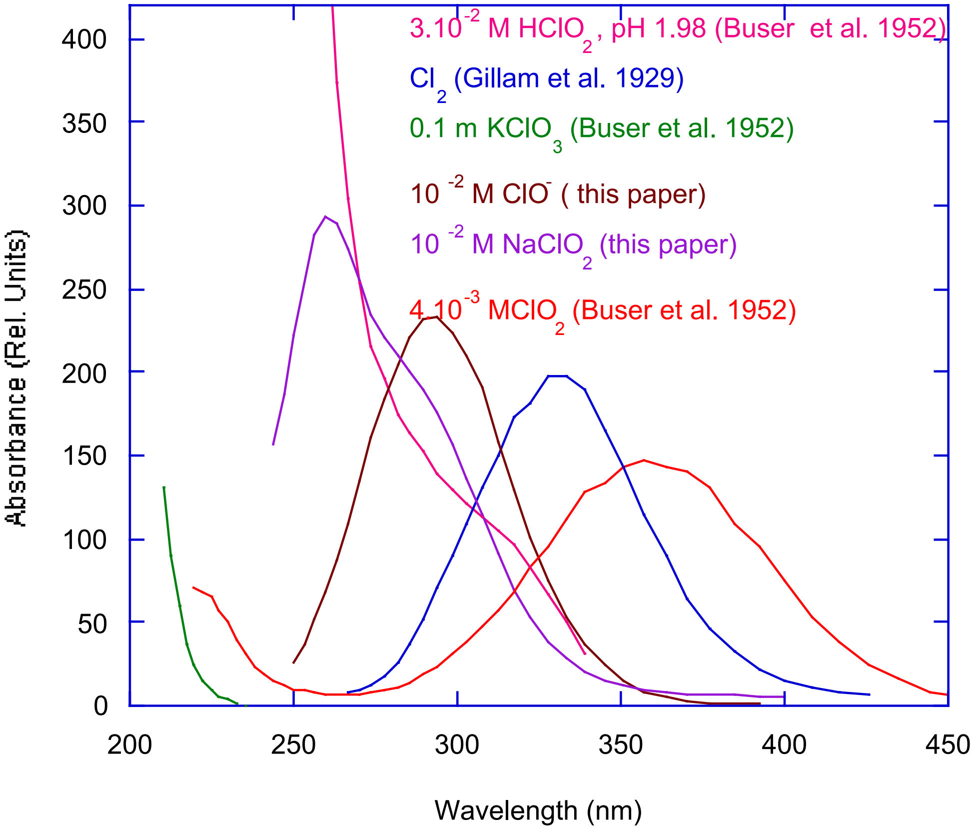

Fig. 3: UV Vis absorption Spectra of chloride species in water

The spectroscopic characteristics of important radiolysis products known in chloride solutions are summarized in Table II. The comparison of the data in Table II to the spectra of irradiated brines reveals that in our experiments Cl_2, Cl_3^- and ClO_2 were not the main products of radiolysis. Traces of Cl_2, Cl_3^- and ClO_2 may be suspected only for spectra "i" and "m" ("i"- brine 1 at 216 kGy, "m"- brine 2 at 216 kGy). Taking into account the molar absorption coefficients and very small rise in absorbance in region 330 – 400 nm, we conclude that non-ionic products of radiolysis are only a very small fraction of the radiolysis by-products.

The biggest changes in the spectra of irradiated brines are observed in the 220 – 300 nm region. This is the region where ClO^-, ClO_2^- and their protonated counterparts strongly absorb. We suspect that these ions (molecules) are the main contribution in the total overall radiolysis by-products.

The presence of higher oxidation steps of chlorine in irradiated brines cannot be confirmed by direct UV Vis spectrum. Chlorate and perchlorate have much too weak absorption of UV light to be determined by direct UV Vis spectroscopy.

The presence of oxochlorides seriously influences the stability of Pu waste-forms. In the absence of reductants, hypochlorite causes the high redox potential of the brine, which (1) may accelerate the dissolution of waste-forms, and (2) oxidizes actinides to their highest oxidation state, which is usually the most soluble. The complexing properties of ClO^- towards Pu(VI), as an example, can further increase its solubility. Besides its oxidizing properties, hypochlorite has the ability to form stable complexes with Pu(VI) [17, 18]. These complexes control the solubility of Pu in nearly neutral saline solutions.

Table II. Spectroscopic characteristics of important radiolysis products in water and chloride solutions

Species	Absorption band (nm)	ε (L mol^{-1} cm^{-1})	Reference
Cl_2	332.5	65	[11]
Cl_3^-	325	190	[9]
$HClO$	235	100	[9]
ClO^- in water, pH 7	290	163	This work
ClO^- in water, pH 13	292	345	This work
ClO^- in 5 m NaCl, pH 6.87	291	324	This work
ClO^- in 3.7 m $MgCl_2.6H_2O$, pH 4.42	284	197	This work
ClO^- in Brine 1, pH 7.43	370	60	This work
ClO^- in Brine 2, pH 8.23	330	49	This work
ClO_2^-	260	98	This work
ClO_2^- in 5 m NaCl, pH 6.87	259	108	This work
ClO_2^- in 3.7 m $MgCl_2.6H_2O$, pH 4.42	256	101	This work
ClO_2 in water	360	1000	[11]

We have determined the UV Vis absorption spectra of hypochlorite at different concentrations (10^{-1} M to 10^{-4} M) in water, pH 7 and in four different salt solutions, 5 m NaCl, 3.7 m $MgCl_2.6H_2O$, brine 1 and brine 2 (Fig. 4).

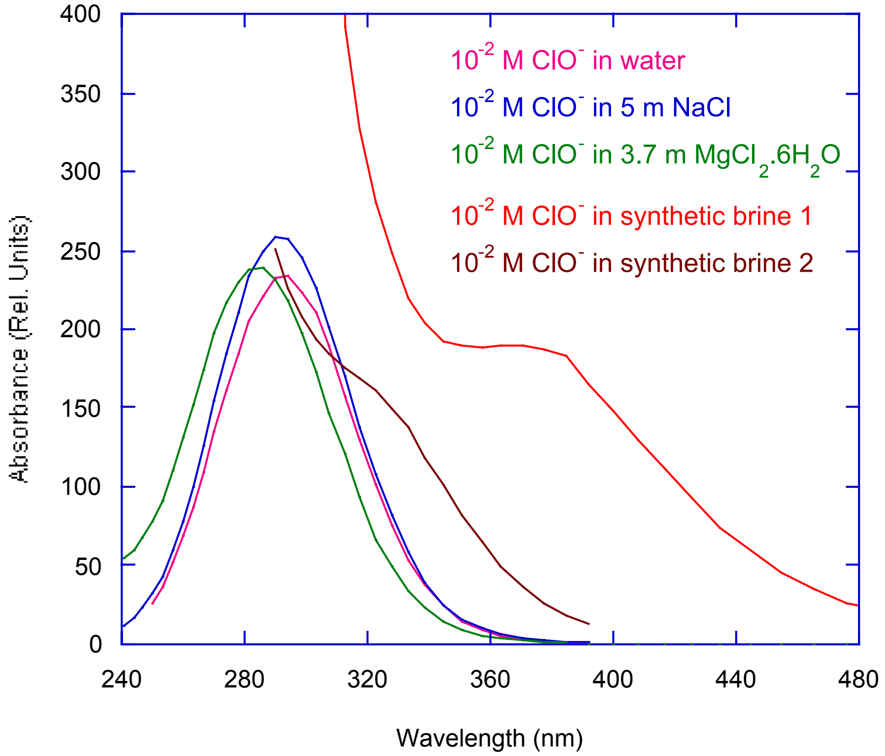

Fig. 4: UV Vis absorption Spectra of hypochlorite in water and in four different salt solutions

The formation of the ClO^- ion appears at pH 7, in water with a characteristic absorption spectrum at 291 nm, and a molar extinction coefficient ε of 163 ± 1.91. Depending on the medium, the absorption band is shifted towards lower wavelength at 284 nm for a 3.7 m $MgCl_2.6H_2O$ solution with a molar extinction coefficient ε of 197 ± 1.54, or towards higher wavelengths for brine 1 and brine 2, with an absorption band at 370 nm and 330 nm respectively and a molar extinction coefficient ε of 60.34 ± 1.65 for brine 1 and 49.21 ± 1.36 for brine 2. The absorption spectrum of ClO^- ion is depending strongly on the medium, as well as on pH.

CONCLUSION

From the preliminary experimental results, it appears evident that some radiolytically induced chloride species are produced by irradiating brines with different dose rate from a 13/9 MeV LAE. These oxidizing chlorine species, which are produced by the radiolysis processes of brines, may be responsible of the oxidation of actinides to their highest oxidation state, which is usually the most soluble. Much insight into the radiation process of brines and radiation induced radical reactions will be gained by means of the pulse radiolysis method, based on irradiation of brines with a short pulse of ionising radiation. We are planning to investigate the transient behavior of the radiolytically generated short-lived species by optical absorption spectroscopy. The time resolution will be in the nanosecond range.

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