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The Redox-Behaviour of Plutonium in Saline Solutions under Radiolysis Effects

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*Plutonium/Radiolysis/Saline solution/Redox reaction/
ClO⁻ complexation*

Abstract

Auto-radiolytic redox reactions of Pu ions have been investigated in NaCl solution of different concentrations. The α -radiation induces the oxidation of the chloride ion. The NaCl solution containing an α -emitting nuclide becomes, therefore, an oxidizing medium. The Pu(IV) ion is readily oxidized to Pu(VI) in concentrated NaCl solutions (> 3 M), whereas the oxidation leads only to Pu(V) in less concentrated NaCl solutions (< 3 M). The redox kinetics are found to be dependent on the NaCl concentration, specific α -activity and pH of the solution. Explanations are given for probable radiolysis reactions and undergoing redox processes of Pu ions in each given system.

1. Introduction

The redox behaviour of Pu ions in natural aquatic systems is sensitively affected by given geochemical conditions [1]. In the near field the radiation effect controls additionally the redox reactions of Pu ions; such an effect is much pronounced especially in saline solutions [2–4]. The α -radiation induces oxidation of the Cl⁻ ion, producing strongly oxidizing species like HClO, ClO⁻ etc. via various transitory reactions [5–9]. As a result, the Eh value of saline solution containing α -emitting nuclides increases and hence the solution becomes a strongly oxidizing medium. The Pu ions of lower oxidation state become readily oxidized to Pu(V) or Pu(VI), depending on pH, salinity and specific α -activity of a given solution [2–4]. In some literature there are observations for the redox behaviour of Plutonium in saline solutions, e. g. reduction of Pu(VI) to Pu(IV) [10] and oxidation of Pu(IV) to Pu(VI) [11].

The present work deals with the basic redox reactions of Pu ions that may occur in saline solutions under the influence of their own α -radiation. The investigation is focused on radiolysis processes in NaCl solution as well as on speciation of redox reaction products of Pu ions. The speciation has been carried out by spectrophotometry.

2. Experimental

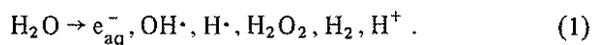
²³⁸Pu(IV) hydroxide and ²³⁸PuO₂ are used as solid phases. The latter is taken as a high temperature fired dioxide, whereas the hydroxide is precipitated by adding CO₂-free NaOH to an acidic solution of Pu⁴⁺. The ²³⁸Pu(VI) solution is prepared by fuming the Pu solution several times to near dryness with concentrated HClO₄ and dissolving the residue in 1 M HClO₄. The initial

specific α -activity for each experiment is varied from $2.6 \cdot 10^{10}$ to $3.0 \cdot 10^{11}$ Bq/L. Chloride solutions (0.9 to 5 M) are made by dissolving reagent grade NaCl in bi-distilled water. All experiments are carried out in glass vessels at 22 ± 1 °C under either normal atmosphere or anoxic CO₂-free condition (Ar). pH is adjusted by adding appropriate amounts of HCl or CO₂-free NaOH and measured during the experiment using a combination glass electrode ("Ross" type, Orion Co.). The redox potential (Eh) of solution is measured by a conventional platinum electrode (Ingold Co.). The Pu concentration is determined by liquid scintillation counting (LS 6800, Beckman Co.) after phase separation using ultrafiltration at different pore sizes from 1.3 to 220 nm. The speciation is made directly by spectrophotometry (Lambda 9, Perkin Elmer Co.).

3. Results and discussion

3.1. Radiolysis of chloride solution

The radiation chemistry of pure H₂O is well understood. In the course of water radiolysis the following radical, ionic or molecular species are formed [12]:



In the presence of dissolved oxygen, radicals like O₂⁻ and HO₂ can be produced additionally. Whereas the decomposition mechanism of water does not depend on the nature of radiation, the yield of each radiolysis product is directly influenced by the linear energy transfer (LET), which is much greater for α -particles than for γ -rays. The latter produces regions of high concentration of radical pairs, which are spaced along the way of the γ -ray at relatively large intervals. For α -particles the distance between spurs are very close and the expanding spurs will overlap from the moment of formation [13]. Combination of the radicals in the spurs produces H₂, H₂O₂ and H₂O. In pure water, the high LET radiation produces more molecular species than the radiation of low LET [14]. Although, at low solute concentrations, solute does not greatly affect each molecular yield, earlier works [15, 16] show that species which for example react with OH \cdot , like Cl⁻ or Br⁻, gradually lower the molecular yield of H₂O₂ as their concentration is increased. When the concentration of solute is more than a few percent of weight, it becomes necessary to consider the direct action of the radiation on the solute.

or dissociates to ClO^- at $\text{pH} > 7$ (cf. Eq. 10) in the presence of a high chloride concentration. The characteristic absorption peak, which is found at 235 nm only in chloride-free medium [19, 20], cannot be detected in 5 M NaCl due to the radiolytic gas generation that disturbs the absorption measurement in the UV-region. However, the production of HClO is evident from the reaction (9).

The consequence of α -radiolysis in concentrated saline solution is an increase of the redox potential (Eh) of a given solution system, which may reach about +1300 mV at $\text{pH} < 3$, changes to slightly lower values at $\text{pH} 3 \sim 7$ and then decreases linearly with further increasing pH [4]. Typical features of Eh changes in different NaCl concentrations at a constant specific α -activity ($1.7 \cdot 10^{11}$ Bq/L ^{238}Pu) are illustrated in Fig. 2. In 5.2 M NaCl, the Eh value increases rapidly to a saturation state (+1300 mV), while a slow Eh increase is obvious in 3.6 M NaCl. As shown in Fig. 3, radiolytic reactions cause the change in pH of the solutions as well. The initial pH 7.5 decreases rapidly to pH 4 and turns up to increase. The decrease and increase of pH becomes rapid and distinctive in 5.2 M NaCl, reapproaching to the original value of neutrality. The pH regaining process influences the Eh value which is then decreasing as shown in Fig. 2 (cf. 5.2 M NaCl), because they are reciprocally interdependent. In 3.6 M NaCl pH starts to increase slowly only after 30 days. The pH decrease in saline solutions results from the radiolytically induced reactions (9) and (10) as described above. As pH decreases the Pu(IV) hydroxide dissolves more, while being oxidized in the solution. Such an oxidative dissolution of the Pu(IV) hydroxide attributes to the pH increase (see below).

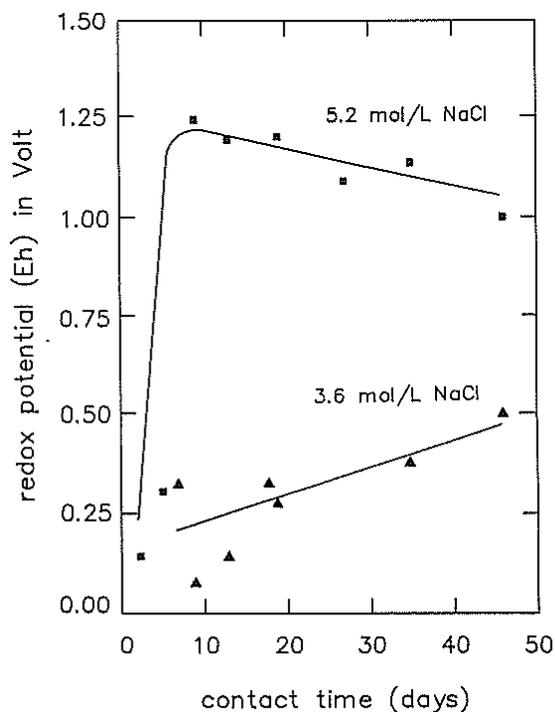


Fig. 2. The Eh change as a function of time in different NaCl concentrations at the specific α -activity of $1.7 \cdot 10^{11}$ Bq/L ($\text{pH} 4 - \text{pH} 7$).

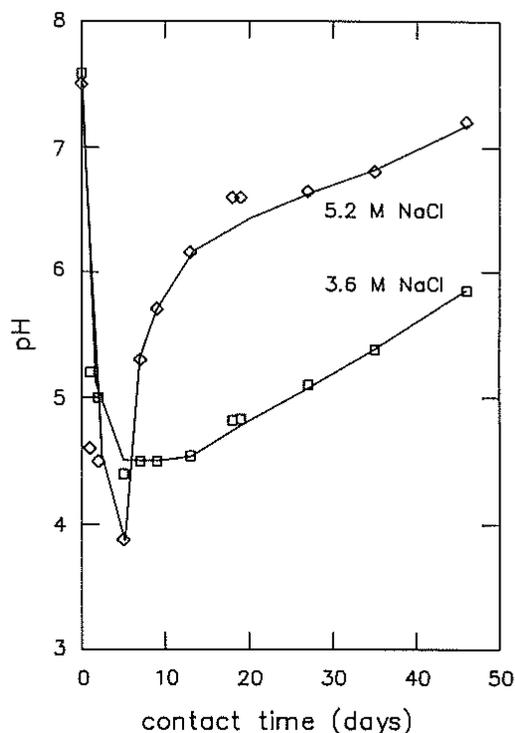
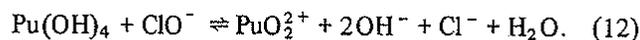
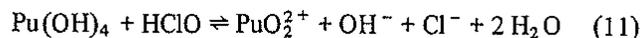


Fig. 3. The pH change as a function of time in different NaCl concentrations at the specific α -activity of $1.7 \cdot 10^{11}$ Bq/L.

3.2. Oxidation of Pu(IV)

In concentrated NaCl solutions the Pu(IV) hydroxide precipitate dissolves via production of the PuO_2^+ ion [4]. Among oxidizing chlorine species in the solution the predominant species, HClO and ClO^- , will oxidize Pu(IV) through the reactions:



The PuO_2^+ ion is expected to undergo chloride complexation or hydrolysis reaction depending on the pH of a given solution. The above two reactions demonstrate that the oxidative dissolution of $\text{Pu}(\text{OH})_4$ increases the pH of the solution (cf. Fig. 3). Absorption spectra of Pu(VI) produced by α -radiolysis in 5 M NaCl are demonstrated in Fig. 4. This solution is prepared by dissolving about 103 mg $^{238}\text{Pu}(\text{OH})_4$ in 200 mL 5 M NaCl at pH 1, adjusted to pH 12 by adding CO_2 free 5 M NaOH under Ar atmosphere, neutralized and allowed to stand for 4 weeks. The solubility of Pu is found to be 8.7×10^{-4} mol/L at pH 8.2, while the Eh value of the solution is increased to +900 mV. The first spectrum of this solution as shown in Fig. 4 (spectrum (a)) illustrates the two distinguished absorption bands at 852 nm and 863 nm, and one broad peak at 1013 nm. By lowering pH and allowing to reach the solubility equilibrium at each pH, the spectra (b), (c) and (d) are recorded. The absorption band at 863 nm decreases gradually and disappears at pH 5.7 and at this pH new absorption bands appear at 841 nm and 830 nm, while the absorption peak at 852 nm remains from pH

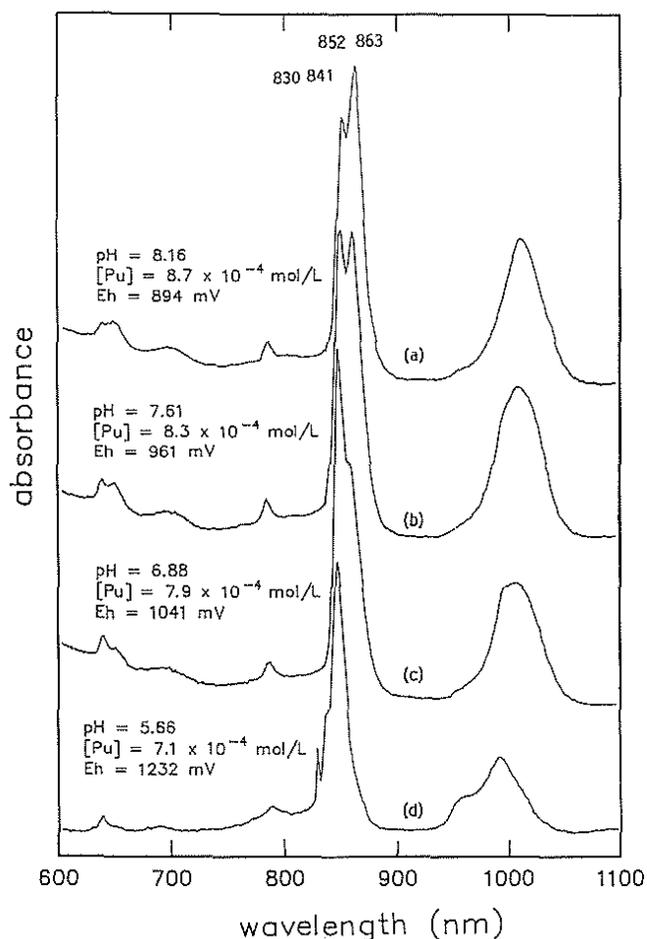


Fig. 4. Absorption spectra of Pu(VI) in 5 M NaCl ($2.2 \cdot 10^{11}$ Bq/l ^{238}Pu) at different pH.

8.2 to pH 5.7. The broad peak at 1013 nm is little by little shifted to the left and appears to be a composite of two absorption bands. At the same time the equilibrium concentration is decreased and the Eh value increased slightly at each pH lowering. From four distinguished absorption bands between 830 nm and 863 nm, four different Pu(VI) species are conceivable. The absorption band at 830 nm belongs certainly to the PuO_2^{2+} ion while the others are its complexed ions. In view of relatively high solubilities found in the pH range under investigation the presence of hydroxide species are considered to be not probable, since the hydroxide solubilities in this pH range are from one to four orders of magnitude lower [21]. The influence of chloride species is unlikely, because the chloride complexation is very weak (see below) suppressed by hydrolysis reactions. Only plausible species can be $\text{PuO}_2(\text{ClO})_n$ ($n = 1, 2, 3$). The ClO^- ion can be produced by α -radiolysis more than 10^{-3} mol/L in alkaline 5 M NaCl and its equivalent point is pH 7.5 with HClO [22]. The ClO^- concentration decreases slowly from pH 8.2 to pH 5.7, thus changing the $\text{PuO}_2(\text{ClO})_n$ species gradually. By removing Cl_2 from the solution, hence decreasing the ClO^- concentration via shifting the $\text{Cl}_2/\text{HClO}/\text{ClO}^-$ system [22], the solubility of Pu(VI) is decreased. This observation corroborates the possibility of the $\text{PuO}_2(\text{ClO})_n$ formation as postulated based on the

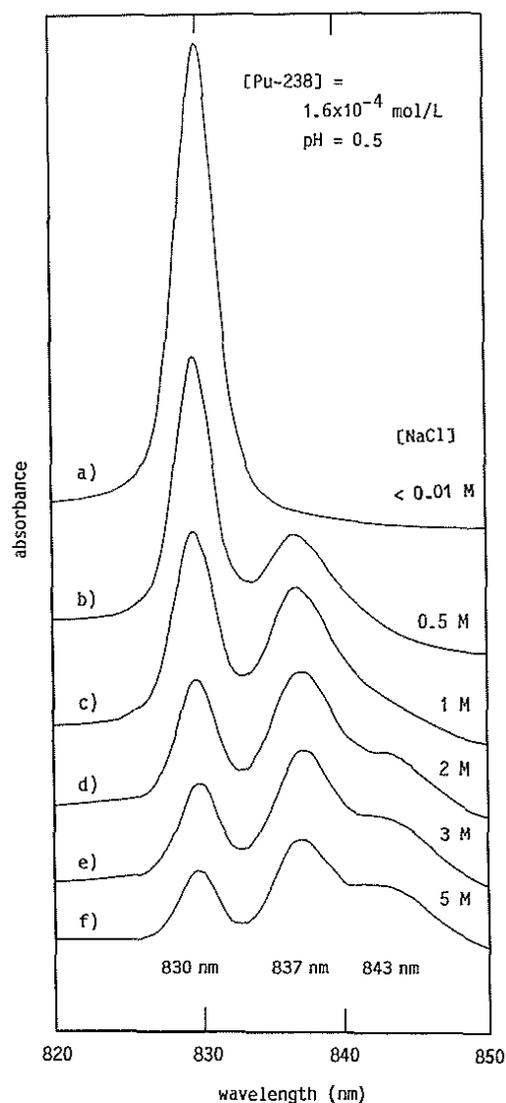


Fig. 5. Absorption spectra of Pu(VI) at pH 0.5 in different NaCl concentrations.

spectra in Fig. 4. The straightforward verification of the $\text{PuO}_2(\text{ClO})_n$ complexes is still in progress.

Further acidification to pH 0.5 results in the absorption spectrum as shown in Fig. 5, which reveals then the chloride species as described in the literature [23]: 830 nm for PuO_2^{2+} , 837 nm for PuO_2Cl^+ and 843 nm for PuO_2Cl_2 . By decreasing the NaCl concentration, a gradual change in the spectrum can be observed and in a diluted NaCl solution only the PuO_2^{2+} ion at 830 nm remains. The molar absorption coefficients of the three observed peaks in 5 M NaCl are evaluated to be:

PuO_2^{2+}	830 nm	$490 \text{ L mol}^{-1} \text{ cm}^{-1}$
PuO_2Cl^+	837 nm	$321 \text{ L mol}^{-1} \text{ cm}^{-1}$
PuO_2Cl_2	843 nm	$239 \text{ L mol}^{-1} \text{ cm}^{-1}$

The complexation constants are also determined as $\beta_1(\text{PuO}_2\text{Cl}^+) = 0.88 \pm 0.02$ and $\beta_2(\text{PuO}_2\text{Cl}_2) = 0.15 \pm 0.02$, which are comparable with the literature data [24].

In solutions $< 3 \text{ M}$ NaCl with the specific α -activity less than $1.8 \cdot 10^{11}$ Bq/L, Pu(IV) is oxidized only to

Pu(V). Relatively lower Eh values are attained in these solutions, in which the oxidation of Pu(IV) to Pu(VI) as well as the reduction of Pu(VI) takes place parallelly, hence producing Pu(V). Even at the relatively high specific α -activity, e.g. $1.7 \cdot 10^{11}$ Bq/L, the oxidation product appears to be only Pu(V) in spectroscopic observation. However, with further increase of activity ($> 1.8 \cdot 10^{11}$ Bq/L even in solutions < 3 M NaCl, the oxidation of Pu(IV) to Pu(VI) becomes complete (see below). As is evident from experiment, the radiolytic oxidation of Pu(IV) in saline solution is dependent primarily on the specific α -activity and NaCl concentration and secondarily on the pH.

3.3. Radiolytic redox reactions

The radiolysis process in non-saline aqueous solution will produce H_2O_2 as well as H_2 [12]. In $NaClO_4$ or $HClO_4$ solutions under α -radiolysis, no oxidation of Pu(IV) has been observed even with a high specific α -activity ($> 1.8 \cdot 10^{11}$ Bq/l). The reduction of Pu(VI) takes place instead. An experiment with 1.1×10^{-3} mol/l $^{238}Pu(VI)$ in 1 M $HClO_4$ ($1.7 \cdot 10^{11}$ Bq/l) shows autoradiolytic reduction of Pu(VI). A typical reduction process of Pu(VI) ends up, as shown in Fig. 6, with the production of Pu(IV) and Pu(III). The absorption band at 495 nm observed in the last spectrum of this figure is presumably ascribed to the $Pu(H_2O_2)_n^{4+}$ complex according to the literature [25]. The two main absorption peaks of Pu(III) are detectable: one at 560 nm is overlapped somewhat with one of Pu(IV) absorption bands (550 nm), while the other at 600 nm appears undisturbed.

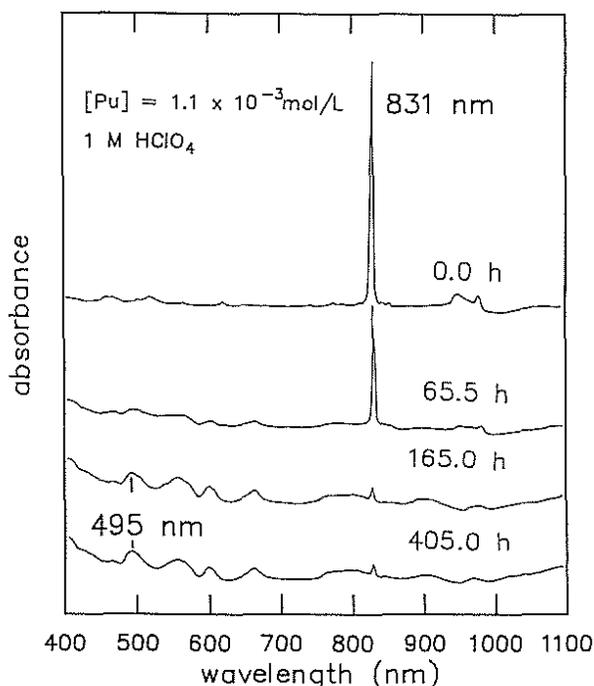


Fig. 6. Autoradiolytic reduction of Pu(VI) to Pu(III)/Pu(IV) in 1 M $HClO_4$ at the specific α -activity of $1.7 \cdot 10^{11}$ Bq/L.

One of the Pu solutions in 1 M $HClO_4$ is mixed with 3 M NaCl by a ratio of 1/10 and thus made to a 2.7 M NaCl solution at pH 1 with an increased specific α -activity of $2.2 \cdot 10^{11}$ Bq/L. As given in Fig. 7, the mixture of Pu(III) and Pu(IV) becomes slowly oxidized to Pu(VI). At the same time the Eh of the solution is increased from +200 mV to +1000 mV. The radiolytic oxidation has produced the PuO_2^{2+} and PuO_2Cl^+ ions which are to be observed in the upper spectrum of Fig. 7. The PuO_2Cl_2 species is not clearly visible, because of the relatively low NaCl concentration (2.7 M).

From the experimental results shown in Fig. 6 and 7 it appears evident that the radiolytic oxidation of Pu in saline solution undergoes reactions with oxidizing chlorine species which are produced by the radiolysis processes described in section 1.

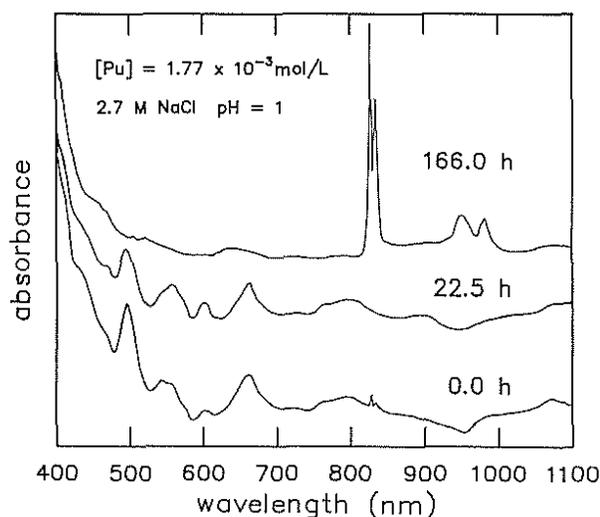


Fig. 7. Autoradiolytic oxidation of a mixture of Pu(III) and Pu(IV) to Pu(VI) in 2.7 M NaCl at the specific α -activity of $2.2 \cdot 10^{11}$ Bq/L.

Acknowledgement

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