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RADIOLYTIC OXIDATION OF AMERICIUM(III) TO AMERICIUM(V) AND PLUTONIUM(IV) TO PLUTONIUM(VI) IN SALINE SOLUTION*

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Summary

The redox behaviour of americium and plutonium in concentrated NaCl solutions (more than 1 M NaCl) under the influence of their own alpha radiation is investigated. The α radiation (greater than 0.5 Ci l^{-1}) induces the oxidation of the Cl^- ion and hence creates a strongly oxidizing medium in which americium(III) and plutonium(IV) present initially become oxidized to americium(V) and plutonium(VI) respectively. The oxidation kinetics depend on the α-radiation dose, NaCl concentration and pH of the solution. Americium(V) remains stable at pH >8 and plutonium(VI) in a wide range of pH.

1. Introduction

Radiolysis reactions in saline solutions are known to produce Cl_2^- as a major transitory species which is supposed to show absorption at 340 nm [1, 2]. In α-radiation induced reactions it is observed that the production of the ClO^- ion as well as the undissociated HClO appears to be predominant [3]. Whatever the products may be, the resulting effect is the creation of a strongly oxidizing medium in which actinide ions become readily oxidized to higher oxidation states in a wide range of pH. A somewhat similar effect is observed in concentrated K_2CO_3 solutions, but the equivalent effect is only attained with a much higher radiation dose [4].

The present paper reports the α-radiation induced oxidation of americium(III) to americium(V) and plutonium(IV) to plutonium(VI) in saline solutions of various NaCl concentrations. Primary radiolysis reactions of the aqueous chloride solution and subsequent oxidation of americium(III) and plutonium(IV) are discussed.

2. Experimental details

A typical experiment is carried out with 150 ml NaCl solution in a thermostat vessel (at 25 °C) containing americium-241 hydroxide, plutonium-

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238 oxide or hydroxide under either argon or normal atmosphere. Variations are made for the α-radiation dose, 0.75 - 15 Ci l^{-1}; the NaCl concentration, 1 - 5 M and pH, 2 - 11. The two different atmospheres chosen for experiment enable the examination of possible gas effects on the radiation induced redox reactions of actinides under investigation. For the experiment under argon atmosphere, CO_2-free chemicals are used in order to preclude any possible influence of carbonate ions on the redox reaction of actinide ions. Soluble actinide species are characterized by either UV–VIS spectrophotometry for less dilute solutions or laser induced photoacoustic spectrometry (LPAS) [5] for dilute solutions (less than 10^{-5} mol l^{-1}).

3. Results and discussion

3.1. Primary radiolysis reactions and Eh change in saline solutions

In aqueous NaCl solutions, radiolysis reactions with energetic α particles are expected to involve first of all the following primary reaction:

$$H_2O \longrightarrow H^{\bullet} + OH^{\bullet} + \ldots \qquad (1)$$

and as secondary reactions:

$$OH^{\bullet} + Cl^- \rightleftharpoons Cl^{\bullet} + OH^- \qquad (2)$$

$$2\,Cl^{\bullet} + H_2O \longrightarrow H^+ + Cl^- + HClO \qquad (3)$$

$$Cl^{\bullet} + Cl^- \rightleftharpoons Cl_2^- \qquad (4)$$

$$2\,Cl_2^- + 2\,OH^- \longrightarrow 3\,Cl^- + ClO^- + H_2O \qquad (5)$$

and at the relatively high pH (6):

$$HClO \rightleftharpoons H^+ + ClO^- \qquad (6)$$

Spectroscopic measurements indicate that under argon atmosphere the ClO^- ion is produced predominantly at $pH > 7$ and Cl_2 at $pH < 4$. At pH 4 - 7, where HClO is expected to be present, no characteristic absorption peak (235 nm) can be identified, because in the range 190 nm to 270 nm a strong absorption of the solution overlaps it. The production of Cl_2 and ClO^- in experimental solutions is verified by comparing the spectra with those measured separately for the Cl_2 gas and NaClO solution, which show the same absorptions at 325 nm and 286 nm respectively. The transitory species Cl_2^- is not observed. The radiolysis products Cl_2, HClO and ClO^- evidenced at different pH corresponding unambiguously to the chlorine species calculated by the Eh–pH function [6].

In experiments under aerobic conditions, another radiolysis product is observed in addition to the products determined under argon atmosphere. This product appears at pH 5 - 9 and shows a distinctive absorption at 365 nm, which corresponds to the band once characterized as ClO_2 by Buxton and Subhani [7]. Whether or not such a species is produced under present experimental conditions is subject to further verification.

Figure 1 shows a typical Eh–pH diagram for chlorine species in 5 M NaCl, taking account of 1.59 V for $HClO + H^+ + e^- \rightleftarrows + \frac{1}{2}Cl_2 + H_2O$, 1.40 V

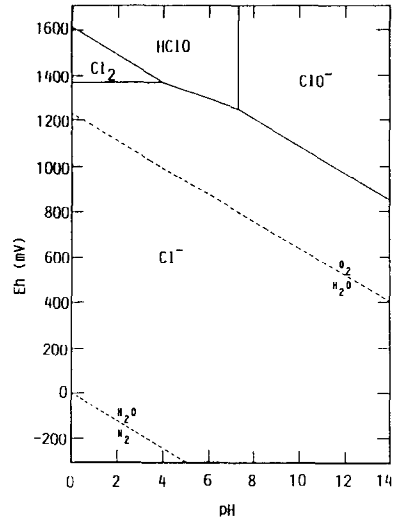


Fig. 1. The Eh–pH diagram of chlorine species (see text).

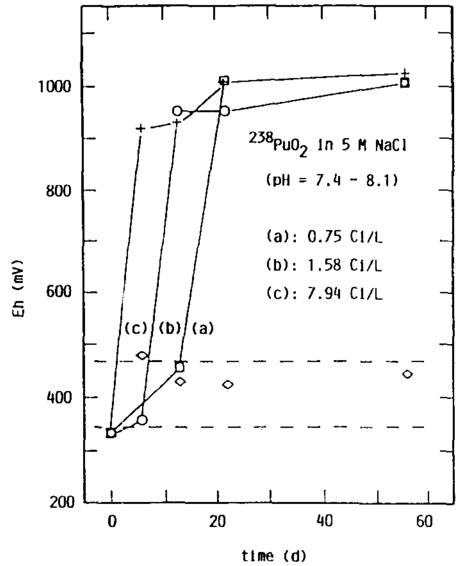


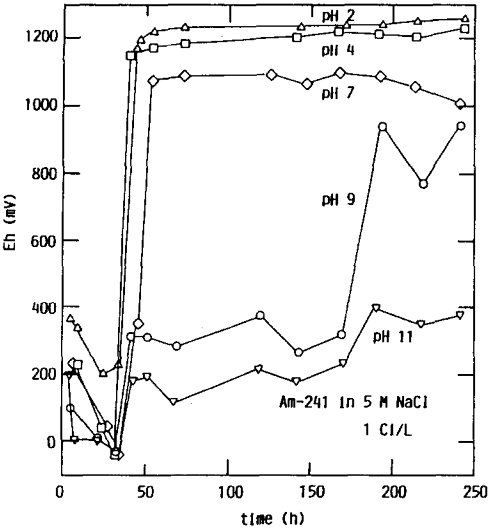
Fig. 2. The α-radiation induced Eh increase in 5 M NaCl for different specific α activities as a function of time (aerobic conditions).

for $\frac{1}{2}Cl_2 + e^- \rightleftarrows Cl^-$ and $\lg K = -7.3$ for $HClO \rightleftarrows H^+ + ClO^-$ [6]. This diagram demonstrates that under oxidizing conditions the major species are Cl_2, HClO and ClO^-, which corroborate straightforwardly the radiolysis products observed in the present experiment at different pH values.

Figure 2 illustrates Eh changes in 5 M NaCl solutions with different activities of $^{238}PuO_2$. The higher the α-radiation dose the faster the Eh value increases. Eh changes at different pH values with constant α activity can be seen in Fig. 3, which demonstrates the distinctive pH influence. Experiments shown in Figs. 2 and 3 are carried out under aerobic conditions. Saturated Eh values measured separately in 5 M NaCl under a Cl_2 atmosphere are given in Fig. 4, which lie close to the border line of Cl_2, HClO and ClO^- generation indicated in Fig. 1. The major radiolysis products observed spectroscopically are approximately indicated in this figure. The dotted line represents the expected values. In the course of the experiment started from the lower pH, the Cl_2 partial pressure upon 5 M NaCl is gradually diminished as the experiment proceeds to higher pH and as a consequence the measured Eh values are accordingly lower than those expected.

3.2. Oxidation of americium(III) and plutonium(IV)

For comparison, the standard potential diagrams for americium and plutonium are shown in Fig. 5. With data given in this figure together with the Eh values in Fig. 4 and hydrolysis constants known from the literature, it is possible to evaluate the probable oxidation states of americium and plutonium in salt solutions of oxidizing medium.



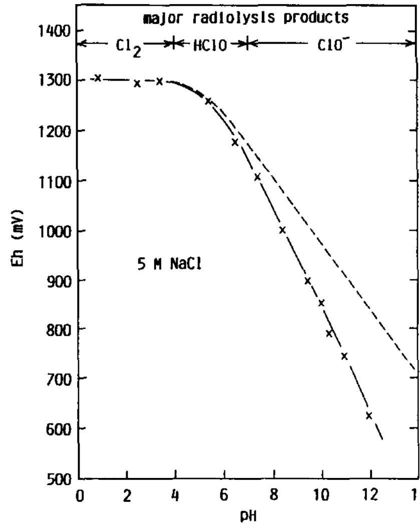


Fig. 3. The α-radiation induced Eh increase in 5 M NaCl at various pH values as a function of time (aerobic conditions).

Fig. 4. Experimental Eh–pH function in 5 M NaCl under Cl_2 atmosphere. The dotted line reflects expected values.

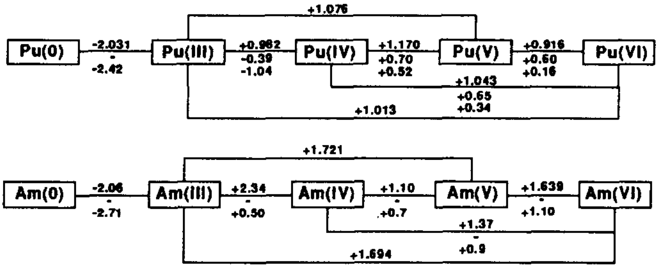


Fig. 5. Redox potential diagram for plutonium and americium: in 1 M $HClO_4$ [9] (upper), at pH 8 [10] (middle) and at pH 14 [9, 10] (lower).

In 5 M NaCl americium(III) will be oxidized to americium(V) at pH >7, whereas in the same solution any oxidation state of plutonium will result in plutonium(VI) in the full pH range. Oxidation experiments are carried out in 5 M NaCl by means of solubility measurements of americium(III) and plutonium(IV) hydroxides with which the α-radiation dose in solutions is maintained to a certain threshold level (more than 0.75 Ci l^{-1}), as discussed below.

3.2.1. Oxidation induced dissolution of americium(III) hydroxide

Starting with the freshly precipitated americium(III) hydroxide of 1 Ci l^{-1} in 5 M NaCl at different pH values, measurements of its dissolution are followed as a function of time. As shown in Fig. 6, at pH 7 the solubility equilibrium is attained immediately, while at pH 8.5 the concentration started with 10^{-8} mol l^{-1} increases slowly to saturation after only one week.

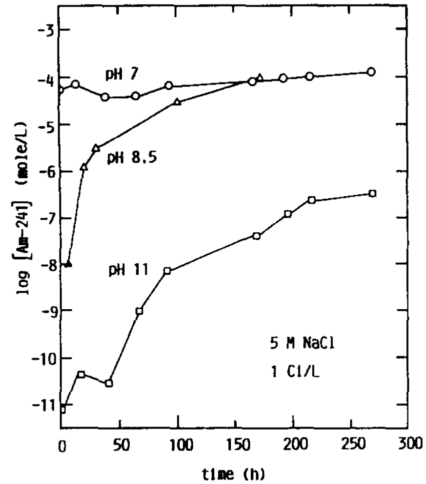


Fig. 6. Solubilities of the americium hydroxide precipitate in 5 M NaCl at different pH values as a function of time; the solubility increase is due to radiolytic oxidation of americium(III) to americium(V) (anaerobic conditions).

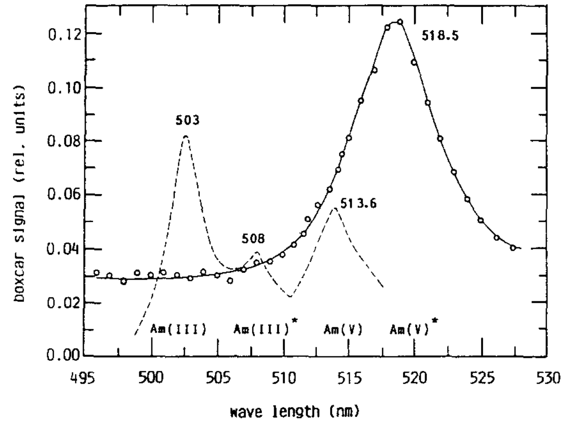


Fig. 7. Photoacoustic spectra of americium(V) carbonate species (1×10^{-5} mol l^{-1}) at pH 11 and americium(III)–americium(V) mixture (3.4×10^{-6} mol l^{-1}; broken line) at pH 8.3 [3] (*, carbonate species).

At pH 11 the solubility equilibrium is observed after 11 days. In these solutions the major soluble species is found as americium(V) and no other oxidation state can be detected. Figure 7 illustrates the absorption spectra of an americium(V) carbonate species which is present in the solution at pH 11 (cf. Fig. 6). At this pH value, the CO_2 absorption in the solution is considerable and hence more than 1 M carbonate species is expected to be produced by air contact of the solution. The absorption band of the americium(V) carbonate species at 518.5 nm is considerably shifted from the absorption of the AmO_2^+ ion at 513.6 nm ($\epsilon = 41$ l mol^{-1} cm^{-1}) [3]. There is no trace of absorption visible at 508 nm, which is assigned to be an americium(III)

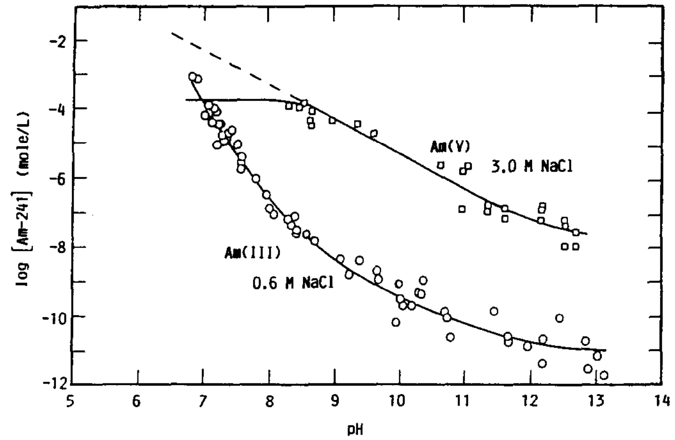


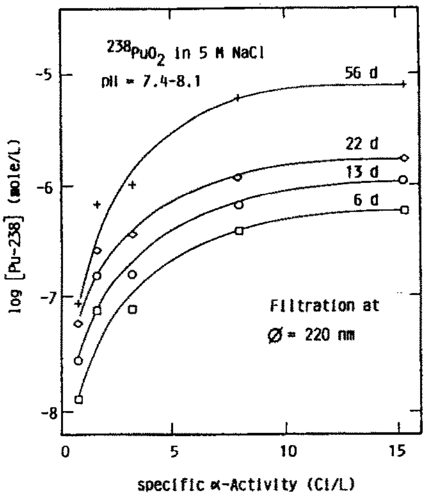
Fig. 8. Solubilities of americium(III) and americium(V) hydroxides in 0.6 M NaCl and 3 M NaCl as a function of pH (for both solutions: 1 Ci l^{-1}) (anaerobic conditions).

carbonate species. This has an LPAS sensitivity of 5×10^{-8} mol l^{-1}. For comparison, a spectrum (dotted line) is given in order to indicate appropriate peak positions of the species otherwise expected, when the oxidation is incomplete.

Figure 8 illustrates the solubilities of americium(III) and americium(V) hydroxides under argon atmosphere in 0.6 M NaCl and 3 M NaCl respectively. The total amount of americium in each solution is maintained at 1.2×10^{-3} mol l^{-1} (1 Ci l^{-1}). Americium(III) remains unoxidized in 0.6 M NaCl, whereas in 3 M NaCl the initially introduced americium(III) is completely oxidized to americium(V) at pH >8 and only partially to americium(V) at pH 7. At pH <7 the oxidation of americium(III) requires Eh >1300 mV, which is not attainable by α-radiation induced radiolysis reactions in 3 M NaCl. This fact is corroborated by spectroscopic measurements of the solutions at pH <7, which reveal the presence of americium(III) only. In 0.6 M NaCl the solubility pattern as a function of pH resembles closely that observed for americium(III) hydroxide in 0.1 M $NaClO_4$ [8].

3.2.2. Oxidation induced dissolution of plutonium(IV) dioxide

Solubilities of $^{238}PuO_2$ are determined, as shown in Fig. 9, in 5 M NaCl at pH 7.4 - 8.1 with varying amounts of the oxide, containing α-radiation doses from 0.75 - 15.5 Ci l^{-1}. The higher the α-radiation dose, the faster the dissolution takes place. The speciation of the major soluble species verifies the presence of plutonium(VI) alone at all pH values. A typical photoacoustic spectrum is given in Fig. 10, which indicates the presence of PuO_2^{2+}, PuO_2Cl^+ and $PuO_2Cl_2^0$ species, showing absorptions at 830, 836.5 and 845 nm, respectively. This photoacoustic spectrum is taken after acidification of the solution (pH 8), in which the hydrolysed plutonium(VI) species show an extremely low absorption coefficient and are therefore difficult to speciate spectroscopically. In solutions of lower pH, plutonium(VI) is also



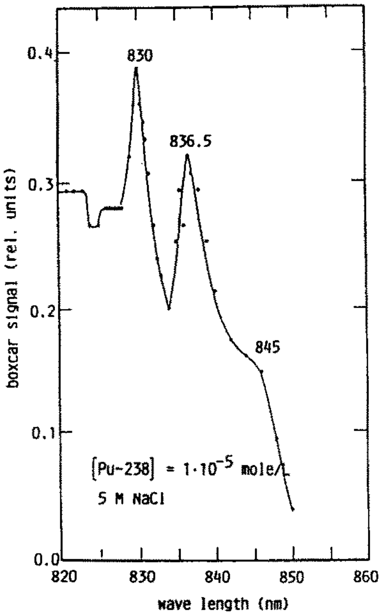


Fig. 9. Solubilities of PuO_2 in 5 M NaCl at different contact times as a function of the specific α activity.

Fig. 10. Photoacoustic spectrum of plutonium(VI): 830 nm for PuO_2^{2+}, 836.5 nm for PuO_2Cl^+ and 845 nm for PuO_2Cl_2.

found as the only species present and remains stable without becoming reduced with time.

The present experiment demonstrates an interesting chemical process that can be beneficial for the preparation of higher oxidation states of americium and plutonium without using external oxidizing agents or electrochemical elaboration. On the other hand, the results appear significant for the chemical assessment of nuclear waste repositories in salt deposits.

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