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A Novel Application of Pourbaix Diagrams for the *ad hoc* Prediction of Thermodynamic Behavior of Plutonium in Aquatic Environments

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Abstract: This short narrative focuses on the essence of the electrochemical potential E_h *vs.* pH relationships of the simplest plutonium species in aquatic environments. Of the many oxidation states reported of plutonium, only those with potentials within the limits of stability of water are expected to be thermodynamically stable. More importantly, the sole purpose of this work is to demonstrate the ways in which the Pourbaix method can be deployed for preliminary prediction of the behavior of plutonium in a hypothetical waste disposal scenario in a lake. This work is not an encyclopedic review of the intricate aqueous chemistry of plutonium ever published (although excellent literature is available for this purpose), and is not meant to be read as such. This discourse, however, facilitates the understanding of the ways in which the pair of parameters E_h and pH determine oxidation states and therefore speciation. This is fundamental to the interpretation of more advanced research in aquatic ecosystems. (31 references from 1960 to 2018).

Keywords: Plutonium, Pourbaix Diagram, Radioactive Waste, Water Pollution

1. Introduction

1.1. The Pourbaix (E_h *vs.* pH) Diagram

A Pourbaix diagram is a Cartesian plot with values of pH on the abscissa (x-axis) and electrochemical potential E_h on the ordinate (y-axis). The important redox chemistry of water itself limits the oxidation states that plutonium can exhibit, but together, the two parameters E_h and pH define the conditions under which any metallic species are thermodynamically stable in water, usually set at 25°C. The potential E_h is an indication of the propensity of water in aquatic ecosystems (which are in fact aqueous solutions containing many substances) to oxidize or to reduce, and it is related to pH by the Nernst Equation from which Pourbaix diagrams are constructed.

Acidity and alkalinity determine whether metallic ions stay in solution or undergo phase change and precipitate as solids. Therefore, solubility products (K_{sp}) are also used during compilation of these E_h-pH charts. Moreover, Pourbaix diagrams show reactions and products of known activities at equilibria, therefore displaying various predominate chemical species under hugely different combinations of E_h and pH. Diagrams that were originally prepared by the corrosion chemist Marcel Pourbaix were incorporated in his doctoral thesis, which he presented at the Université Libre de Bruxelles (Belgium) in 1939. The first English edition of the "Atlas of Electrochemical Equilibria" was published in 1966 [1] and has been updated continually. It is necessary to consider the stability of natural waters before dissolved plutonium species are considered.

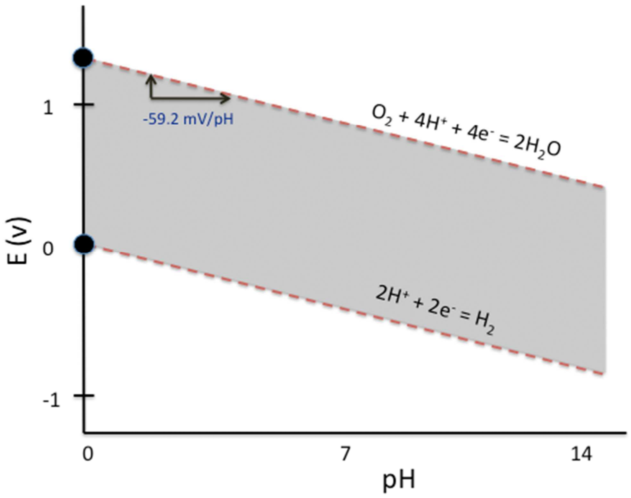

Figure 1. *The stability region of water on a Pourbaix diagram (adopted from [2]).*

Water may act as an oxidizing or reducing agent. As an oxidizing agent it is reduced to H_2 (*g*), therefore:

$$H_2O\ (l) + e^- \rightarrow \tfrac{1}{2}\ H_2\ (g) + OH^-\ (aq) \qquad (1)$$

For the equivalent reduction of protons at any pH, the ("reduction of water") half-equation is:

$$H^+\ (aq) + e^- \rightarrow \tfrac{1}{2}\ H_2\ (g) \qquad (2)$$

The corresponding Nernst expression when partial pressure of H_2 of 1 bar (~ 1 atmosphere) is:

$$E_h = -\ 0.059\ \text{V} \times \text{pH} \qquad (3)$$

When water acts as a reducing agent, it is oxidized to O_2. The half-equation is:

$$2\ H_2O\ (l) \rightarrow O_2\ (g) + 4\ H^+ + 4\ e^- \qquad (4)$$

The corresponding Nernst expression when partial pressure of O_2 of 1 bar (~ 1 atmosphere) is:

$$E_h = 1.23\ \text{V} - (0.059\ \text{V} \times \text{pH}) \qquad (5)$$

It can be seen that both the reduction potentials of H^+ and O_2 depend linearly on pH and the straight lines, equations (3) (5), are drawn accordingly on the graph of "Potential *vs.* pH", Figure 1. Any half-reaction with a value of E_h between the upper and lower lines which define the region of stability for water is generally immune to redox by H_2O.

Above the upper dotted line, equation (5) on Figure 1, water can be oxidized and becomes more acidic. Two examples are:

(a) Synthesis of hydrofluoric acid:

$$F_2\ (soln.) + 2H_2O\ (l) \rightarrow 2\ H^+F^-\ (aq) + O_2\ (g) \qquad (6)$$

$$F_2 + 2\ e^- = 2\ F^-;\ E^o = +2.87\ \text{V} \qquad (7)$$

(b) Stoichiometric conversion of Co(III) to Co(II):

$$4\ Co^{3+}\ (aq) + H_2O\ (l) \rightarrow 4\ Co^{2+}\ (aq) + 4\ O_2\ (g) + 4\ H^+\ (aq)\ (8)$$

$$Co^{3+} + e^- = Co^{2+};\ E^o = +1.92\ \text{V} \qquad (9)$$

Redox reactions with the $E_o > +1.23$V are many, *e.g.*, the reduction of Mn^{VII} to Mn^{II} (*i.e.*, MnO_4^- to Mn^{2+}) is driven by a potential $E^o = +1.5$ V. Kinetically, only a few species oxidize water rapidly, *e.g.*, the following observed reaction has been proposed:

$$4\ Ag^{2+}\ (aq) + 2\ H_2O\ (l) \rightarrow 4\ Ag^+\ (aq) + 4\ H^+\ (aq) + O_2\ (g) \quad (10)$$

However, the Belgian nuclear research centre called "SCK-CEN" demonstrated a five-step mechanism with the disproportionation reaction 2Ag(II) → Ag(I) + Ag(III) as the initiation step, followed by reductions of the intermediates H_2O_2 and the free radical $[O_2H]^\bullet$ as propagation steps, and the production of O_2 in the final step. The scheme allows both Ag(II) and Ag(III) as oxidants, and both are reduced to Ag(I), see [3].

Below the lower dotted line, equation (3) on Figure 1, H_2O and H^+ can be reduced, and the solution becomes more alkaline. Two examples are:

(c) Vigorous and highly exothermic reaction of soft metallic sodium with water:

$$2\ Na\ (s) + 2\ H_2O\ (l) \rightarrow 2\ Na^+\ (aq) + 2\ OH^-\ (aq) + H_2\ (g) \quad (11)$$

$$Na = Na^+ + e^-;\ E^o = -\ 2.71\ \text{V} \qquad (12)$$

(d) Dissolution of plutonium metal in strong, non-passifying acids:

$$2\ Pu\ (s) + 6\ H^+\ (aq) \rightarrow 2\ Pu^{3+}\ (aq) + 3\ H_2\ (g) \qquad (13)$$

$$Pu = Pu^{3+} + 3\ e^-;\ E^o = -\ 2.031\ \text{V} \qquad (14)$$

In general, when the potential of the oxidation of a metal to the metallic ion is negative, *e.g.*, $E = -2.03$ V, then the dissolution proceeds in concentrated acids. The reaction expressed by equation (13) can be carried out by dissolving pure α-phase plutonium metal in $HClO_4$ (6 mol dm^{-3}).

1.2. The Stability Region of Water on a Pourbaix Diagram

In 1 dm^3 of pure water there are 55.5 moles present. Usually, chemical species that are soluble and enter into redox relationships with H_2O are the limiting reagents and the rate of reaction is generally dependent on the concentration of the dissolved species alone. When the dynamic equilibrium $aA + bH_2O \rightleftharpoons cP_1 + dP_2 + ...nP_n$ is reached in a closed thermodynamic system, then the concentrations of all species remain constant. In an open thermodynamic system, a product in the gaseous state P_i (*g*) may be evolved, leaves the system, and displaces the equilibrium to the right continuously until reagent A is exhausted. Often, as in the case of the pair Co^{3+}/Co^{2+} in equation (8), the redox goes to completion and no Co(III) ions are left. The oxidative dissolution of metallic sodium in water, equation (11), also goes to completion.

The stability region of water, as shown in Figure 1, is defined by the range of values of E_h and pH for which H_2O is thermodynamically stable, *i.e*, it is inert under those circumstances. As we have seen, both oxidation and reduction of water have the same pH-dependence, testified by the slope of -0.0592 V (-59.2 mV) when redox potential is plotted against pH. The stability region is restricted to the area between the parallel lines with identical value of slope, of -59.2 mV. Any chemical species with an E_h more negative than that given by equation (3) can reduce water (actually as H^+) to give H_2 (*g*) and is confined below the lower line, and therefore the lower line defines the lower stability limit of water. Similarly, species with E_h higher than that predicted by equation (5) can liberate O_2 (*g*) and rests above the upper line, and therefore the upper line defines the upper stability limit of that of water.

2. Literature Survey of Pourbaix Diagrams for Plutonium Species in Natural Waters

2.1. Panorama of E_h-pH Conditions of Natural Waters

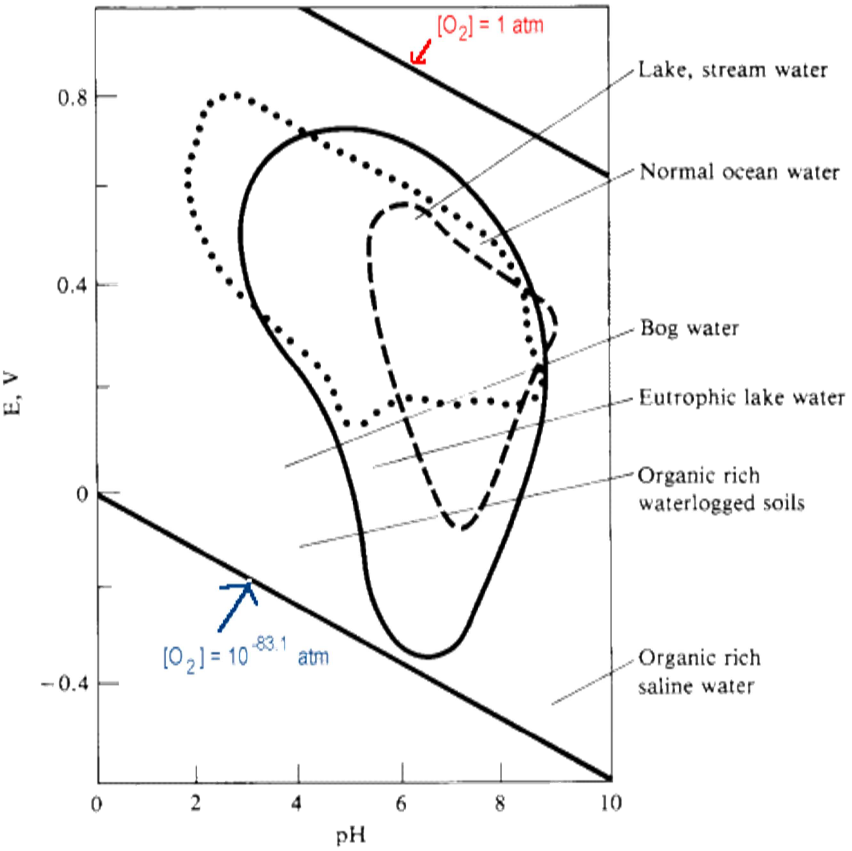

Figure 2. *Pourbaix diagram for natural waters showing their positions in the stability regime of water [5].*

Studies of the chemistry of water as ecological media can be carried out by using Pourbaix diagrams, albeit their rarity when plutonium species are present in solution and become the focus of attention. Becking *et al.* (1960) made a pioneer attempt to classify natural waters according to their E_h-pH characteristics by compiling data from hundreds of sources around the world [4]. The reported values of pH range from 4 to 10 in aerated waters, *e.g.*, mine runoff (pH = 4), streams (pH = 8), open seas (pH = 8) and brackish waters (pH = 10). In oxygen-deprived water-logged soils, pH is about 5, and for organic-laden brackish waters, pH is in the close vicinity of 10. Wulfsberg (2000) produced a similar but simplified diagram [5] and this is shown in Figure 2.

Note that all of the data points fall within the thermodynamic stability field of water displayed on Figure 1. The illustration shows that the collected pH values of these waters range from 2 to 9, with the majority of the data in the range $4 \le pH \le 8$.

Atmospheric CO_2 dissolves in H_2O to give the Brønsted-Lowry carbonic acid H_2CO_3, therefore,

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \ (pk_1 = 6.3) \quad (15)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \ (pk_2 = 10.3) \quad (16)$$

Respiration of aquatic organisms is another source of CO_2. The resulting acidity increases the redox potential. The opposing trend is photosynthesis, which consumes CO_2 and raises pH; thereby the redox potential becomes more negative. The Henderson-Hasslebach Equation [6] expresses the mole ratio between a weak Brønsted-Lowry acid HA and its conjugate base A^- at a specified pH of the bulk solution, therefore, in general:

$$pH = pK_a + \log_{10}([A^-]/[HA]) \quad (17)$$

Applying equation (17) to the carbonate-bicarbonate system gives the formula:

$$pH = pK_a + \log_{10}([CO_2^{2-}]/[HCO_3^-]) \quad (18)$$

Relative to the highest alkalinity of seawater at pH = 9 (Figure 2), one can calculate, by substituting $pk_2 = 10.3$ of H_2CO_3 into (18), the mole ratio of the two ions set in (16), with the result that $1 - [1/10^{(10.3 - 9)}] = 23\%$ of inorganic carbon of atmospheric origin is in the form of CO_3^{2-} and 77% as HCO_3^- ions.

Divalent cations such as the transition metallic ions Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} will remain in solution under very acidic conditions (when $[M^{2+}] \times [OH^-]^2 < K_{sp}$), but will form insoluble hydroxides, carbonates and hydroxy-carbonates in alkaline media (when $[M^{2+}] \times [OH^-]^2 > K_{sp}$). Documentation on the existence and properties plutonium-bicarbonate complexes is scarce and more work should be done to understand the roles that HCO_3^- play in keeping plutonium in aqueous solutions.

According to Figure 2, it is thermodynamically unfavorable for a water molecule in a lake to participate in a redox (electron transfer) reaction with any dissolved substance. The same assertion can be made for the other types of natural waters.

2.2. Aerobic and Anaerobic Aquatic Systems

The surfaces of natural bodies of water (*e.g.*, lakes and oceans) are in unhindered contact with air, and water which is free from pollutants contains adequate dissolved O_2 to render E_h close to E^o for the reduction of water to O_2. Well aerated waters facilitate the oxidation of metallic ions to higher oxidation states, and of the oxidation of many organic compounds. However, lakes suffering from eutrophication may give rise to algae blooms, and these lakes are often loaded with organic matter. The values of E_h can approach close to the H^+ reduction line. Natural waters may be oxidizing if saturated in O_2, or reducing if laden with organic matter, as in stagnant lagoons.

In bogs and organic-laden soils, water can become acidic due to high humic acid content. These are also strongly reducing conditions and they are ideal for the formation of CH_4 in marshes. Noxious gases such as NH_3, H_2S as well as the inflammable phosphine PH_3 also emanate from swamps. Conditions there may approach anaerobicity and are actively reducing, approaching the lower boundary of the reduction of water to hydrogen. These conditions may also be encountered in a lake severely polluted with organic matter which is high on biochemical oxygen demand (BOD) and/or chemical oxygen demand (COD), or at the bottom of a thermally stratified lake. A water column in such a lake has a temperature gradient. When the surface of the lake is warmer than the bottom layers, and if heat transfer from the surface of the lake to the bottom is slow, the lake will also be stratified in liquid density for some time, until convective mixing evens out the temperature profile. It is always sluggish for the colder and denser sedimentary materials to be transported to the well-aerated air/water interface, and there will also be a concentration gradient for dissolved oxygen. There will be less oxygen at greater depths; in water-logged sentiments the conditions can become anaerobic. Any aggregated particle constituted of $Fe^{III}O(OH)$ "molecules" (these are actually gigantic 3-dimensional networks) at the surface of the lake begins to sink when its specific gravity exceeds unity (S.G. > 1). Reducing agents such as organic matter will participate in the redox transformation Fe(III) → Fe(II) and release Fe^{2+} ions into aqueous solution to be hydrated as $[Fe^{II}(H_2O)_6]^{2+}$. These ions diffuse towards the surface according to Fick's Law of Diffusion, the driving force being the concentration difference in Fe^{2+} (*aq*) ions between the bottom and surface of the lake, created by redox itself. As Fe^{2+} (*aq*) ions rise to the oxygen-rich interface, they are easily oxidized and the resulting Fe(III) species will aggregate and settle again, thereby completing the cycle of events. Cobalt ions may behave similarly.

2.3. Aqueous Plutonium Species

The E_h-pH diagram for plutonium was published in the aforementioned 1st English edition of Marcel Pourbaix's "Atlas of Electrochemical Equilibria" [1]. Subsequently, the diagram has been utilized by scientists for specific tasks and it is necessary to present their findings in a meaningful and illustrative way, by inclusion of other species of relevance and focusing on their physical-chemical relationships with plutonium. For example, water from a well (labeled "J-13") at Yucca Mountain (Nevada, USA) contained plutonium at a concentration of 1×10^{-5} mol dm^{-3}. Other ions of significant in this water are OH^-, F^- and CO_3^{2-}. A diagram was constructed to reveal the aqueous species formed between the cationic species of plutonium and these inorganic anions [7], shown here as Figure 3.

Higher E_h values tend to stabilize the +V and +VI states of Pu. The red dots on the diagram are "triple points", so called because Pu can exist in three different oxidation states in equilibria. The region bounded by the solid black line is the E_h-pH conditions encountered in natural waters and falls within the stability region of water, as is evident in Figure 3. The comment made was that Pu(IV) is likely to be found in the oceans and groundwater, Pu(V) in rainwater and streams, and Pu(III) and Pu(VI) in other natural waters [7].

Professor Brian Powell at Clemson University (South Carolina, USA) has produced excellent education material and research papers on the environmental chemistry of actinides through the years. In personal communications (2018), he has acknowledged the fundamental importance of understanding the E_h *vs.* pH relationship in determining the oxidation states of plutonium and the role they play in directing the outcome of hydrolysis, complexation, colloid formation, precipitation and extent of sorption of Pu species [8]. The late Professor Heino Nitsche (1949 – 2014) of

University of California (Berkeley) devoted the early years of his academic career on the environmental chemistry of actinides but later developed a keen interest in the search for new heavy elements. His work on the adsorption of Pu(VI) by manganite MnO(OH) and hausmannite Mn_3O_4 deserves the attention of chemical engineers who are searching for naturally occurring adsorbents suitable for removing radioactive species from water [9], and aiming to design equipment for the unit operation of adsorption.

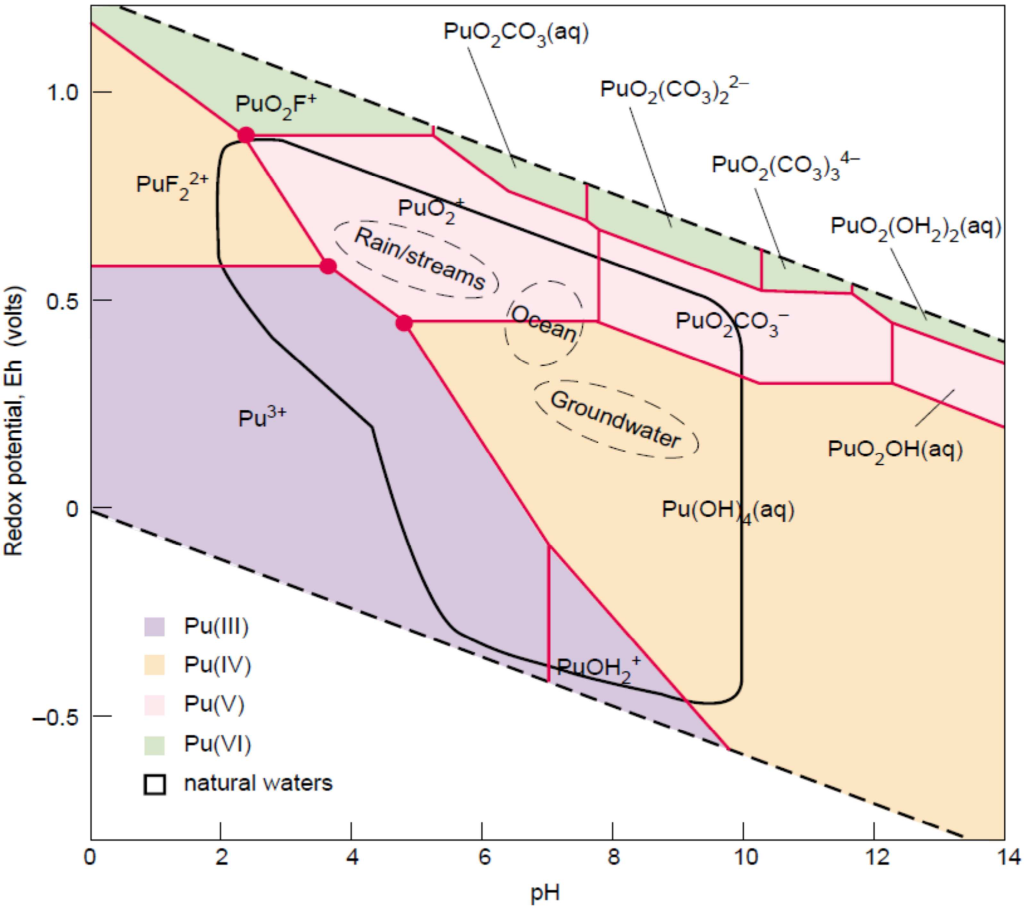

Figure 3. *Speciation of plutonium in oxidation states +IV to +V present in natural waters [7].*

3. Methodology: Using the Pourbaix Diagram as a Predictive Tool

For the sake of illustrating how a Pourbaix diagram such as the one on Figure 3 can be utilized, an attempt to answer a few questions posed by Wulfsberg [10] about a hypothetical radioactive waste disposal and/or accidental release into a lake is made here. This is a "thought experiment" in which consequential scenarios are posited by established scientific principles and knowledge, with this demonstrative work resting chiefly on chemical thermodynamics. (Figure 3 is chosen as the predictive tool purely for its clear identification of the thermodynamic stability regime for natural bodies of water. The aforementioned "J-13" water well in the Yucca Mountain does not play a part in this hypothetical situation). Suppose a nuclear weapons facility generated plutonium waste and its fate in a lake has to be predicted. The following technical questions (quoted *per verbatim* from [10]) can be raised during public enquiry and consultation.

Question 1: If the lake is well aerated and of normal pH, in what chemical form will the plutonium be found? Will it be present in solution or found in the sludge at the bottom of the lake?

Answer: "Normal pH" is interpreted to be pH = 7 and this is the commencement point of discussion. Since the water is well aerated, a vertical line emanating from the x-axis at pH = 7 hits the solid black line at E_h = + 0.7 V, at the boundary circumscribing the stability region for natural waters. The predominant species which can be stabilized by this E_h-pH condition is $[Pu^VO_2]^+$, an aqueous species, as indicated in Figure 3. Neck *et al.* (2007) reported that, in solubility studies, Pu(V) is dominant at pH > 3 and under air [11]. The diagram (Figure 3) gives no indication that $[Pu^VO_2]^+$ has combined with CO_3^{2-}, and Flury & Harsh (2003) commented that complexation with CO_3^{2-} is unimportant until pH exceeds 8 [12]. It is unlikely that plutonium will be found in the sludge at the bottom of the lake. Higher up the E_h axis at approximately +0.85 V, just below the (dotted) upper stability line for H_2O, the species $[Pu^{VI}O_2(CO_3)]^0$ (*aq*) exists.

Question 2: Will metallic plutonium dumped into the lake remain in the metallic form, or will it react with the water?

Answer: Metallic plutonium will react with water. The E_h-pH conditions required for H_2O to react chemically with another species are the ones outside the stability region for water. In fact, it is thermodynamically favorable for any metallic element M^0 (*s*) with its entire stability region below that of the lower stability line for water to release gaseous H_2 from water. In addition, Wulfsberg (2000) reported that if the stability regimes of an oxidizing and reducing agent do not overlap vertically on a Pourbaix diagram by more than 1 V, then the redox reaction will be highly exothermic [5]. The potential of the half-equation: $Pu = Pu^{3+} + 3\ e^-$ is $E^o = -2.031$ V [1]. The possibilities for dissolution of metallic plutonium are:

$$\text{Acidic medium } (-2 \leq pH < 7)\text{: } 2\ Pu\ (s) + 6\ H^+\ (aq) \rightarrow 2Pu^{3+}(aq) + 3H_2\ (g) \qquad (19)$$

$$\text{Alkaline medium } (7 < pH \leq 14)\text{: } 2\ Pu\ (s) + 3\ H_2O\ (l) \rightarrow (Pu^{III})_2O_3 + 3H_2\ (g) \qquad (20)$$

The species Pu_2O_3 in equation (20) appeared on the original Pourbaix diagram for plutonium [1]. Its entire stability region is below the lower stability limit for water, *i.e.*, its E_h stability range is too low (≤ -1 V) to be seen in Figure 3. Initially, Pu_2O_3 will be discrete molecules in solution but may flocculate in time. Note that there is a small area of predominance by the species labeled as $PuOH_2^+$ in the Pu(III) regime in Figure 3, directly above the lower stability line for H_2O, at pH = 8. (The species, as written, demanded that Pu acquired an oxidation state of +V). On reviewing the Pourbaix diagram presented by Runde [7], Flury & Harsh (2003) amended it to be $[Pu(OH)]^{2+}$ [12], keeping the oxidation state of Pu to be +III. This provides one extra possibility for dissolving the metal:

$$2Pu\ (s) + 6H_2O\ (l) \rightarrow 2[Pu^{III}(OH)]^{2+} + 3H_2\ (g) + 4OH^- \quad (21)$$

It has to be emphasized that while plutonium is attacked by pH-neutral freshwater very slowly, the corrosion is accelerated in sea water, after a finite induction period [13].

Question 3: Would any corrosion of the metallic plutonium by the water be most severe in acidic or in basic solution?

Answer: Corrosion will be most severe in acidic solution and proceeds according to equation (19). It is possible that, after initial redox in alkaline media, films of mixed plutonium oxides are formed on the surface of the metal, thereby passifying it by being a barrier to contact with water. The sesquioxide Pu_2O_3 on equation (14) has been known to be such a barrier [14], the stability region of which is directly above that of plutonium metal on the original Pourbaix diagram [1]. There is a related issue to be resolved. In the Pu(IV) stability region of Figure 3, within the stability regime for H_2O, the predominant species was branded as $Pu(OH)_4$ (*aq*), denoting that the electrically neutral species is in true solution. However, the solubility product for $Pu(OH)_4$ (solid) was reported to be $\log_{10}K_{sp} = -58$ at pH = 7, implying that the concentration of Pu(IV) species is in the vicinity of 10^{-11} mol dm^{-3}. (See [15 to 17]). With $[Pu_{Total}] = 10^{-5}$ mol dm^{-3} for the "J-13" well which instigated the drawing of the Pourbaix diagram in Figure 3, solid $Pu(OH)_4$ in the form of particulates or aggregates is likely to be dominant.

Question 4: If the lake is anaerobic and highly polluted with acid rain, in what chemical form will the plutonium be found? Will it be present in solution or found at the bottom of the lake?

Answer: The lake water has become highly reducing (assuming there is an abundance of organic material which consumed all the oxygen) and of acidic pH. The stability of water itself, however, does not depend on the presence of dissolved oxygen. Acidity renders the chemical reaction represented by equation (9) thermodynamically favorable, and therefore plutonium will be in its +III state, in the form of hydrated cations [18]:

$$Pu^{3+} + n\ H_2O\ (l) \rightarrow [Pu^{III}(H_2O)_n]^{3+}\ (soln.)\ (n = 8 \text{ or } 9) \quad (22)$$

4. Results

1. If a lake is well aerated and at normal pH, plutonium is expected to stay in aqueous solution in the form of the species $[Pu^VO_2]^+$.
2. Metallic plutonium deposited in such a lake is expected to react with water to form $(Pu^{III})_2O_3$ and $[Pu^{III}(OH)]^{2+}$ (*aq*). Initially, individual molecules of $(Pu^{III})_2O_3$ will be found in solution but may form aggregates in time.
3. Corrosion of plutonium metal is expected to be severe in acidic aqueous environments.
4. If the lake becomes anaerobic and acidic simultaneously, the predominant species is expected to be $[Pu^{III}(H_2O)_n]^{3+}$, which will stay in aqueous solution.

5. Discussions and Suggestions for Further Work

5.1. The Ecological Perspectives of Thermodynamic Predictions

When using a Pourbaix diagram to establish the predominance of a species, one must not infer that a particular species cannot possibly exist outside its stability region. The boundaries of a stability field are best interpreted as contours at which a unique species and an alternative may well be equally important, thermodynamically speaking. Also note that the boundary between a solid phase and a solution phase will depend on the concentration chosen for the aqueous species. This is traditionally set at 1×10^{-6} mol dm^{-3} (1 μM) but can be set at other values if desired. (Dr. Marcel Pourbaix seemed to prefer 1 μM.) Beyond the boundaries of its stability field, the species no longer dominates the population, and it becomes less and less prevalent the further conditions are adrift from those which define the stability field. Ecosystems are exceedingly complex, physically, chemically, geologically and biologically superimposed upon a backdrop of seasonal climate change. Even a micro-ecological niche may never reach “steady state” at all. It is often not possible to make precise measurements of the reduction potential. However, it is possible to obtain approximate values and recognize the conditions as being oxidizing or reducing, and predictions of the behaviour of aquatic ecosystems have been known to be precise therefrom.

The use of E_h-pH diagrams to support the observation of the chemical behavior of actinides remains a powerful conceptual tool in the forefront of aquatic ecological research. Romanchuk *et al.* (2016) have established E_h-pH stability regimes for many types of natural waters with a good reminder that the region of a Pourbaix diagram below the lower stability limit of water represents ecological environments which are “isolated” from the atmosphere [19]. The proliferation of plutonium carbonate complexes also substantiated the assertion of Flury & Harsh (2003) [12] that complexation with CO_3^{2-} becomes important when pH exceeds 8 (see answer to Question 1 above), and that the existence of a small stability field of $[Pu^{III}(OH)]^{2+}$ in the near-neutral region of pH = 7 is affirmed, Figure 4 [19].

Ewing (2015) produced Pourbaix diagrams for the speciation of uranium and plutonium, Figure 5, which originated from radwaste storage facilities of spent nuclear fuels, and the implications for geochemical pathways in the near-field of these facilities. Besides the oxides, hydroxides and oxocations of plutonium, the stability regions for the free, un-complexed anions $NO_3^-/NO_2^-/N_2$ and SO_4^{2-}/HS^- are shown to reflect near-field geochemistry [20]. The oxidation states +III to +VI of plutonium are all represented.

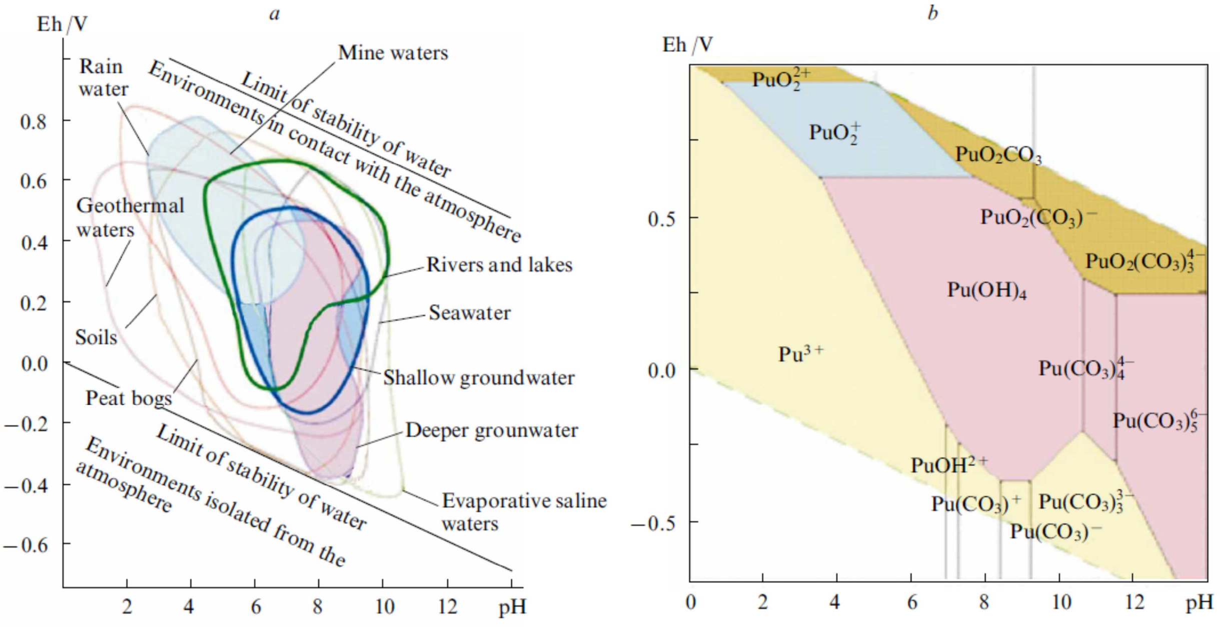

Figure 4. *Pourbaix diagrams for natural waters and plutonium [19].*

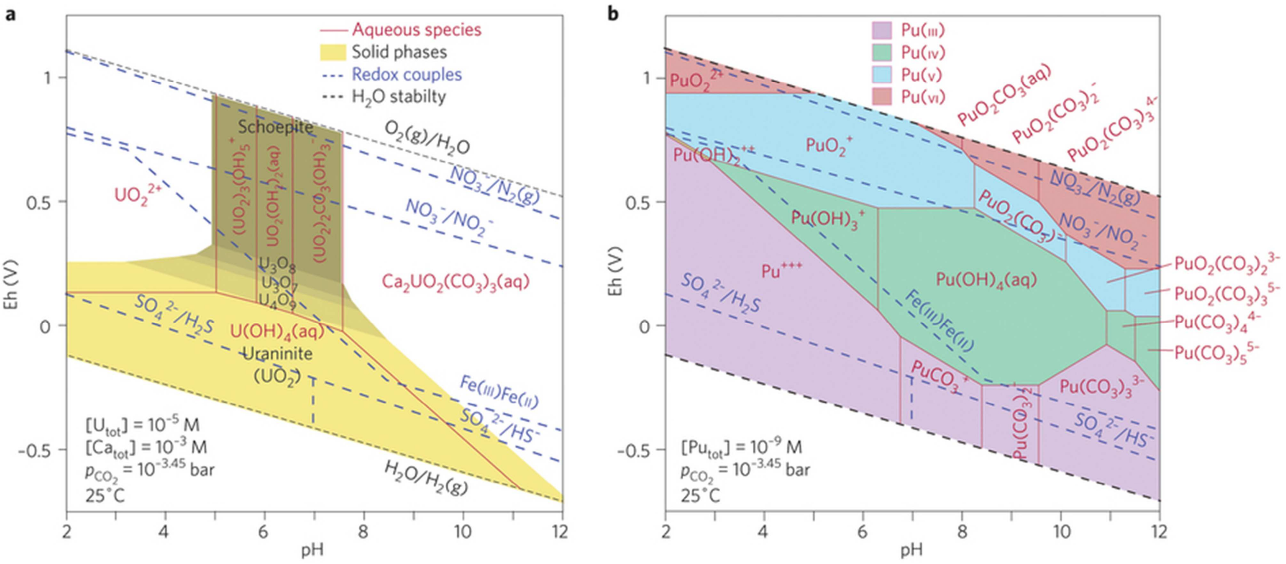

Figure 5. *Pourbaix diagrams for uranium and plutonium species, and of relevant minerals [20].*

5.2. Application of Pourbaix Analyses in Future Water Research

Four physico-chemical processes determine the amounts and forms of plutonium in aquatic environments: (i) precipitation (sedimentation), (ii) complexation and chelation, (iii) sorption, (iv) colloidal formation. This work has illustrated how the identity and relative abundance of even the simplest inorganic plutonium species can be governed by prevailing conditions such as pH and E_h (*e.g.*, availability of oxygen). Transport of plutonium in the natural environment and its biogeochemical cycle as an element is dependent upon its speciation fundamentally. To the observer, the most important indication of plutonium behaviour is its oxidation state because the extent to which the four processes are manifested in the aqueous phase seem to differ with each state, from +III to +VII. Input of plutonium into the hydrosphere of this planet include (i) fallout from nuclear weapons testing in the atmosphere in the last century, (ii) liquid discharges from nuclear processing plants, (iii) nuclear accidents: the research institute known as "Centre for Environmental Radiology" in Norway (2017) discovered that, in the immediate aftermath of nuclear accidents, "a major fraction of refractory radionuclides such as U and Pu will be present as particles, ranging from sub-microns to fragments". These particles "are an essential part of the source term [of dispersion], and particle characteristics are essential for the ecosystem transfer, accumulation and effects [21]". The aforementioned Norwegian research institution aims to "improve the predictive power of impact assessment models" within the time period 2017 – 2021.

The work of Dumas *et al.* (2018) resonates well with the sensibilities of the authors of the present work. In the process of literature search, both research groups detected huge gaps in the knowledge of "solubility, migration, and bioavailability of plutonium [because] experimental evidences are missing; we report here on X-ray Absorption Spectroscopy of plutonium in natural seawater. The observed valence state is +IV and its speciation correspond to PuO_2 type colloids [22]".

Colleagues over the world have carried out a colossal amount of high quality research on the many aspects of radionuclides in the environment. Subsequent to the Fukushima Daiichi accident in Japan in 2011, the focus is on monitoring air, marine and soil radioactivities. The World Nuclear Association (2016) reported that the main radionuclides released into the environment due to the Fukushima Daiichi accident in Japan in 2011 were ^{131}I and ^{137}Cs and that some ^{134}Cs and ^{90}Sr were also released [23], but this finding did not dampen the enthusiasm of Men *et al.* (2018) to innovate a method for "rapid analysis of Pu isotopes in seawater" to gauge the impact of the nuclear incident for themselves [24]. (In fact the Japanese themselves had provided evidence that plutonium was released into the environment as early as 2012 [25].) The International Atomic Energy Agency (IAEA) updates the world on the status of Daiichi, including all data pertaining to environmental radioactivity, at least once a month; the latest installment of news was deposited on its website on 8th March 2018 [26].

Interest on the toxic yet exotic element known as plutonium has never waned. Of the 237 papers and books amassed and updated to 26th March 2018 by the organization called "Interdisciplinary Study on Environmental Transfer of Radionuclides from the Fukushima Daiichi NPP Accident", 22 focused on the fate of plutonium [27]. Batlle *et al.* (2018) posed the review question, "After the Fukushima Daiichi nuclear accident: Are we better positioned to understand the impact of radionuclides in marine ecosystems?" [28]. China seems to be concerned about the "accumulation" of plutonium in the South China Sea; samples collected between 2012 to 2014 by Wu *et al.* were analyzed and the results published in 2018 [29]. The authors of this work believe that a systematic way to make deeper sense of field data pertaining to the impact of plutonium on any coastal environment is to prepare detailed Pourbaix diagrams that will represent each set of conditions under which the data was collected, and interpret them within the framework of the four liquid phase processes stated above.

Management of the aftermath of the Fukushima has been complicated by the fact that on-site water was mixed with seawater as a coolant for the damaged reactors. Kim *et al.* (2016) attempted to remove the radionuclides of Co, Mn, Sb, Ru, and Sr by a ferric floc, subsequent to separation of Cs by adsorption [30]. It would be interesting to test the efficacy of the separation processes for Pu, developed by chemical engineers especially for the nuclear fuel cycle, with the liquid to be decontaminated being a process stream of naturally occurring water, *e.g.*, water from the small lake hypothesized in this work. The Purex Process, a multi-step treatment method involving liquid-liquid extraction and ion-exchange, comes to mind. The success of the process depends heavily on speciation, and Pourbaix diagrams such as Figures 4 and 5 presented in this work will aid the initial experimental investigations and interpretation of results.

Researchers always need to address the hydrolysis of species with Pu in its various oxidation states from +III to +VII since this parameter will govern whether the resulting products will stay in solution, form colloids, or precipitate. The simplest hydrolysis is expressed in equation (22). Moreover, there are important types of chemical reactions which need attention in a thorough examination of a Pu population in a laboratory. One is the distinct possibility of mixed ligands in natural waters which will quench the high positive charge of a central Pu ion. This has scarcely been investigated. The other is the redox phenomena of "Disproportionation and Reproportionation". This requires explanation. A species undergoes disproportionation when it oxidizes and reduces itself simultaneously. The reverse of this reaction is reproportionation, whereby two Pu ions of different oxidation states participate in redox to produce two Pu ions of the same state. The following equilibrium can be established in acidic media:

$$2\ \mathrm{Pu}^{4+}\,(aq) + 2\ \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{Pu}^{3+}\,(aq) + [\mathrm{Pu^{V}O_2}]^{+}\,(aq) + 4\ \mathrm{H}^{+}\,(aq),\ \text{slow step.} \tag{23}$$

After the rate-determining step (23) has produced Pu(V) ions, they will react with Pu^{4+} ions in the mixture, with the result that all four oxidation states +III to +VI exist in the same solution. At equilibrium:

$$\mathrm{Pu}^{4+}\,(aq) + [\mathrm{Pu^{V}O_2}]^{+}\,(aq) \rightleftharpoons \mathrm{Pu}^{3+}\,(aq) + [\mathrm{Pu^{VI}O_2}]^{2+}\,(aq),\ \text{fast step.} \tag{24}$$

Solutions with a single-state Pu component can be prepared in the laboratory, albeit not in nature. However, note that the initial species which trigger disproportionation can be Pu(V) instead of Pu(IV):

$$2\ [\mathrm{Pu^{V}O_2}]^{+}\,(aq) + 4\ \mathrm{H}^{+}\,(aq) \rightleftharpoons \mathrm{Pu}^{4+}\,(aq) + [\mathrm{Pu^{VI}O_2}]^{2+}\,(aq) + 2\ \mathrm{H_2O}\,(l) \qquad (25).$$

Plutonium in its +V state disproportionates in acid, but is stable in neutral and alkaline solutions. The disproportionation is followed by the reaction between Pu^{4+} and $[Pu^{V}O_2]^{+}$ ions as in equation (24), but the attainment of equilibrium, whereby all four oxidation states coexist, is not immediate. It will actually take several hours [31]. Also, radiolysis of water by α-particles from Pu isotopes produces short-lived free radicals such as $HO^{\bullet}$, $O^{\bullet}$ and $H^{\bullet}$ and they have great propensity to participate in redox reactions. A good topic for research is to discover whether the equilibria of disproportionation shift to the left or right during the long-distance transport in the environment. It would be most interesting to produce Pourbaix diagrams representing such situations because speciation is likely to change with time. At present, no work on the time-dependent disproportionation of plutonium species with mixed ligands derived from natural waters has been done. The authors are ready to take up this challenge.

6. Conclusion

The Pourbaix (E_h *vs.* pH) diagrams of water and that of the simplest inorganic plutonium species in aqueous solution are introduced. A broad classification of natural bodies of water using these diagrams is briefly described. The Pourbaix method of interpretation of stability has been applied to the thermodynamic prediction of the behavior of plutonium species in a hypothetical waste disposal situation in a lake, with no assumptions other than imposed conditions. The merits of the utilization of the Pourbaix analysis has been discussed, and future work is proposed in the light of recent literature.

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