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Constructing Eh-pH Diagrams of Plutonium by Using Its Thermodynamics Properties

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Abstrak

PEMBUATAN DIAGRAM Eh-JIH PLUTONIUM DENGAN MENGGUNAKAN SIFAT TERMODINAMIKANY A. Telah dibuat diagram Eh-pH Plutonium di dalam udara dengan tekanan dan suhu standar. Daerah stabilitas air ditentukan berdasarkan reaksi redoks air - oksigen dan air - hidrogen. Didapatkan dua pasang garis lurus yang hampir sejajar satu sarna lain. Reaksi redoks dari Plutonium menghasilkan 4 persamaan Nerst, tiap persamaan digambarkan dalam bentuk garis dan satu garis tegak akibat reaksi non redoks. Panjang setiap garis sangat bergantung pada garis - garis lainnya. Didapatkan dua pasangan garis yang saling tumpang - tindih kalau konsentrasi masing-masing spesiesnya sama dengan 10^{-9} M. Digambarkanjuga Ell-pH diagram untuk konsentrasi spesies Plutonium yang tidak sama.

Abstract

CONSTRUCTING Eh-pH DIAGRAMS of PLUTONIUM BY USING ITS THERMODYNAMIC PROPERTIES. Eh-pH diagrams of Plutonium under standard temperature and pressure (STP) condition are constructed. The stability domain of water is described based on redox reaction of water with oxygen and hydrogen. Two pair lines which are almost paralel to each other are found. Redox reaction of Plutonium poduces four Nerst equations; each equation is represented by one line and one vertical line as a result of non redox reaction. The length of each line depends on other lines. There are two pair lines which are overlapped each other if the concentration of each species equals to 10^{-9} M. It is also decribed Eh-pH diagrams for Plutonium with different concentrations.

Introduction

Plutonium is an important element for nuclear reactor. It occurs in nature in uranium ores as a result of neutron capture in U-238 causing spantaneous fission, and alpha - neutron reaction. Plutonium may be produced from U-238 in a reactor with any type of neutron spectrum.. A redox speciation of Pu ions is considered to be one of the most important chemical properties in the field of nuclear fuel preparation. Since chemical and physical properties of plutonium are hazardous, a special equipment is needed to manage plutonium. To obtain pure plutonium one needs separation process which have high recoveries efficiencies. For separating plutonium from irradiated uranium can be used two methods, i.e, aqueous solution and non-aqueous solution. The aqueous solution is based on the chemical differences espesially oxidation state of plutonium or redox processes, while the non-aqueous solution method is based on high temperature processes or pyrochemical and pyrometalurgical processes (1)

Though the concentration of plutonium in nature is very small, its existence is very important. Chemically plutonium has four (4) kinds of oxidation states, some of them have a tendency to undergo redox reaction with oxygen from the air, and at least one of them will react with *W* to form Pu^{4+} ion.

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Plutonium ion can also react with others lieands such as CNS-, organics matters etc. If the reaction of plutonium ion with organics matters is considered as a reaction between plutonium ion with oxygen, one will find complicated complex compound of plutonium-organics. Like others cations, some plutonium ions will undergo redox reaction such as iron which has two (2) kinds of oxidation states. In addition, plutonium is very poisoneous so it will be difficult to analyze plutonium composition, even using modem equipment. It is not all species of plutonium can be analyzed, sometimes one need specieal treatment. By analyzing one species of plutonium, the result can be used further to predict others species by using its thermodynamic properties.

Through the thermodynamic properties, such as Gibbs free-energy, enthalphy, equilibrium composition and its potential, the composition of plutonium and its species can be predicted. This information can be displayed graphically by Eh-pH diagrams

This paper will discuss the use of Gibbs free-energy and potential redox of plutonium in the aqueous solution for constructing Eh-pH diagrams. Redox reaction of plutonium was limited with oxygen only.

THEORY

The ability of a natural enviroment to oxidize some metals depends strongly on the acidity and potential of the environment. The enviroment potential or redox potential of a system is analogous to the pH of the system. Whereas pH expresses the acidity of solution, Eh describes the oxidation state of the system or taking up electrons from reducing agents. The pH of a solution can be expressed in acid solution or in natural and sea waters, the Eh can also be expressed in any solution.

Standard Electrode Potential and Equilibrium

The potential difference for a reaction is a measure of how far the reaction mixture condition deviates from ita equilibrium. The relationship of potential and free energy can be written as,

L'iGO=nfEo (1)

where n is the number of electrons transterred in the reaction, f is the Faraday constant, and E is the electrode potential for complete reaction. The value of f is commonly 96,500 coulombs. Under standard conditions, free energy and equilibrium are related by

L'iGo=RT In K (2)

If the pressure and temperature conditions or the concentrations of non-standard conditions are changed, the new value of L'iG should be converted from the AGO under standard conditions by

L'iG=L'iGo+RTln{[products]lReactants]} (3)

By intoducing L'iG=nfE and Eq.l into Eq. 3, one can obtain

NtE=nfP+ RTIn {[products ll[reactants]} . (4)

Both sides can be divided by n.f to have the Nerst equation,

E=Eo+RTln{[products]/[reactants]}/nf. (5)

Water is the most important substance in redox reaction. Its redox potential strongly depends on the siirroundings, and the ability of surface water to oxidize or reduce metals depends on the amount of oxygen or hydrogen. When the surroundings has more oxygen, the reaction can be written as follows [2, 3],

$$H_2O \ \Delta \ 1/2\ O_2 + 2H^+ + 2e^- \quad E^o=1.23\ V. \quad (6)$$

Nerst equation of the above redox reaction can be written as follows

$$E=E^o+0.059/2 \log\{[O_2]^{1/2}[H^+]^2/[H_2O]\}. \quad (7)$$

In the standard condition Eq. 7 becomes

$$E=1.23 + 0.059 /\{2 \log\{[O_2]^{1/2}[H^+]^2\}.$$

Usually, the concentration of oxygen in atmosphere is 20 %, therefore it can be taken as 0.2 atm for oxigen, since oxigen makes up about one-fifth of the atmosphere by volume. The potential of this half reaction depends on the pll, as shown by the Nerst equation.

Hence
Eh= 1.23+0.03 log (0.2) 1/2 + 0.059log [WI.,

Eh = 1.22-0.059 pH. (8)

Similarly for the lower (reducing) limit of stability of water by the evolution of hydrogen gas from water, the reaction can be written as follows,

$H_2 \Delta 2H^+ + 2e^-$ E^O=0.00 V (9)

E=EO+ 0.059 / 2 log {[W]2 / [H2]}

For which
E = 0.059/2 log [Wf - 0.03 log [H2]'

Since the pressure of hydrogen gas in near-surface enviroment cannot exceed I aim, the maximum possible reducing potential is

Eh = - 0.059 pH (10)

RESULT AND DISCUSSION
Oxidation and reduction (Redox) reactions play an important role in groundwater. The ability of natural enviroment to oxidize cations, such Fe^{2+} ,Pu3+. or reduction of others is called redox potential. Actually there are hundreds of cations or organics materials that can be found in the geological samples, so redox reaction in geochemical actually is very complicated. If plutonium is especially deposited in geological site where soil water, rain, oxygen and hydrogen from air can contact with plutonium, redox reaction of plutonium will take place. Those redox reactions are the simplest in the geochemical reaction. The result of the simple redox reaction between water, oxygen, hydrogen and plutonium itself can influence the composition of or speciation of plutonium because there is a transfer of electrons among them.

Constructing Eh-pH diagrams of iron and plutonium
As mentioned above, there are two lines in the Eh-pH diagrams of water redox rection. Those lines are parallel as can be seen in Figure 1. The lines are the basic for constructing Eh-pH diagrams of all metals reaction with oxygen and water as a simple redox reaction. Actually, a lot of organic and inorganic matter are found in geological water. If those elements involving in geological water are considered for redox reaction, the lines found will not parallel, because the value of oxidizing and reducing waters are not linear with Eh of those elements

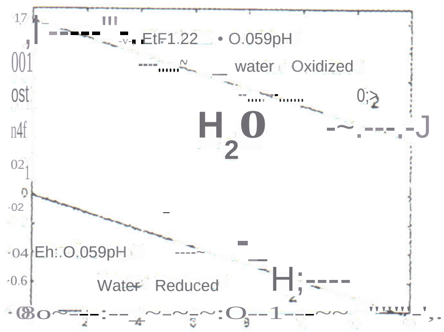

Figure I. Simple Eh-pH diagrams, the boundary lines are made by equations (8) and (10) of redox reaction between oxygen-water and hydrogen- water.

The Eh-pH diagram is constructed under normal pressure. When the pressure increases, the line of oxidized water moves upward and that of the reduced one moves downward. It makes water-domain stability increases. On the other hand, if the pressure decreases, water domain stability decreases. The pressure of the air, therefore, is very important in Eh-pH diagram. As a comparison, if the pressure of the air is 1 atm. and the amount of oxygen is 30 %, then the potential will be

Eh = 1.238-0.059 pH.

This line has the same tangent, but its intercept is higher. It means that domain stability increases.

meanwhile equilibrium constant and free energy should be calculated from thermodynamic properties.

Table 1 The redox reaction of plutonium(3)

Reduce species	Oxidized Species	~Gu k J mol .,	EO Vola
Pu J+	~ ~ l- e	-4828- (• 5::8'O"-.2~)-=-:-97	:-.4'--+--I~009-".~
Pu ,. + 2 Hi)'	PuO$_2$(s)+4 H; +e	.1001.8+5802 -2x238.1) ~-54.6	o.~6~
PuOz(s) + 4 H$^+$	Pu^{4+} + 2HzO	-482.8--2x238.1-(.IOOI.8)~428	0.443
PuO1 (5)	PuO1 + e	-8~3-(-lOOI.8)~ 148.8	U42
Pu" + 2 H$_2$O	PUOl$^+$ t 4H$^+$ tel	-853 _.(-482.8 -2 x 238.1)	1.l>Y1I

If the pressure of the air is less than I atm, the amount of oxygen in the air will also decrease, and the oxidation line has lower intercept than that of normal condition. It makes the domain stability decreases.

Oxidizing and reducing lines in the Eh-pH diagrams above are solely as a result of redox reaction between water - oxigen and water - hydrogen. If the geochemical sample has many metals and some organics materials, there will be a lot of redox reaction and Eh-pH diagrams. The diagram will become complicated.

Plutonium as a side product of nuclear reaction in a nuclear reactor sometimes is deposited as a geological deposit. Limited redox reaction of Pu - reduced water and Pu - oxidized water that will take place are very important, because notably organic matter is very rare in geological area. Those redox reactions will be added up to redox reaction between oxygen-water and hydrogen - water. If redox reaction between small amount of organic matter with plutonium takes place, the result of redox reaction could be ignored.

For constructing Eh-pH diagrams of plutonium, it can be made by two kinds of reactions, one is through Nerst equation for redox reaction, and Gibbs Free Energy formula for calculating equilibrium constant or for non redox reaction. Redox reaction depends on the potential and electron transfer, while non redox reaction depends on the equilibrium constant and free energy. Nerst equation is already known and used for reaction oxygen, hydrogen with water,

Thermodynamic properties such as free-energy, equilibrium, potential redox and the equation redox reaction of plutonium will end up in the calculation or prediction of plutonium speciation. The free energy of redox reaction, Pu^{3+} (aq)'v'Pu^{4+}+e, can be calculated by equation of AGo=Goproduct-GOreactantFirst ot all, Gibbs free-energy of plutonium has to be known[3] because the free energy has relationship with difference potential between oxidation state of plutonium which can be written t.G= n fE. Therefore, the E value can be calculated.

If the value of t.Go is negatif, the reaction will take place spontaneously, while if the t.Go value is positif, the reaction will not take place. It was found that for AGo= 97.4 k *J/mol* E equals to 1.009 V. The value of AGO for redox reaction of plutonium can be seen in Table I.

Table I shows that plutonium has four oxidanon states, I.e. Pu^{3+}, Pu^{4+} Pu^{5+} and PU022+ or Pu^{6+}. Each has a specific reaction, free energy and E values. Since each plutonium ion has different redox reaction with oxygen and hydrogen, each redox reaction has a different Eh-pH value.

There are five lines construct Eh-pH diagrams of plutonium; each has an equation from Nerst or Gibbs free energy.

1. Pu3+(aq) ~ t.Pu^{4+}+e^- . (11)

In this simple redox reaction of Pu3+ which does not involve *W*, only one electron involves. Reaction (12) has Nerst equation Eh=EO+ *0.0591* nf log{[Pu^{4+}]lPu3]}. This equation does not depend on the pH of the solution but on the concentration ratio of [Pu^{4+}(aq)]![Pu^{3+}]. The reaction has Eh=E = 1.009 Volts. This is simply a horizontal line.

II. Pu^{3+}+2H2O ~ Pu02+4W+e- (12)

Under standard conditions, Eh = EO, and for other Eh=EO-0.236pH.

III. Pu02(s)+4W ~ Pu4+2 H2O (13)

The above is not a redox reaction, so the Nerst equation can not be used. It does not depend on the potential of the reaction. The pH value should be calculated from the chemical equilibrium. The relationship between free energy with chemical equilibrium can be described as follows ~Go= -RT In K, K is the equilibrium constant, R is the gas constant (8. 314 J/ mol K) and T is the temperature. To simplify the calculation, a standard condition is considered.

K or equilibrium constant has 2 values, because AGO can be seen from two sides, first for the negatif value and the second for the positif value. First the calculation is done for K=3.1xlO-8. If [Pu^{4+}] is 10-6 M/kg, pH =0.6237. For [Pu^{4+}] = 1O~ M/kg, pH=-0.1228.

It produces a vertical line. Since the line is out of the range for small concentration, it I,s therefore, omitted from the Eh-pH diagram. If [Pu4+], however, is higher the line will be seen in the Eh-pH diagrams.

Second, the calculation is implemented for K = 318,007.36. If [Pu^{4+}]=10-6 M/kg, then pH=-0.3756. if [Pu^{4+}]=10-8 M/kg, then pH=-0.124. The higher concentration will produces a vertical line lies out of the range, but for the lower concentration the vertical line is seen close to zero.

IV. PU02(S) ~ PU02+ (aq) +e- . (14)

The value of Eh depends strongly on the concentration of [PU02+]. If [PU02+]=10^{-9} M/kg, Eh=1.009 V. This value is the same with that noted in Eq.[ll]. If [Pu021=10^{-6} M/kg, Eh=1.188Volts. This line is seen in the above of the line for [Pu021= 10^{-9} M/kg, but the lines are both horizontal.

For simplification of the Eh-pH diagram, it is better to take the same line instead of two lines that are very closed to each other.

V. Pu^{4+}(aq)+2H2O ~ Pu02+(aq) + 4W+e- (15)

This is another reaction between solid state of plutonium oxide and water. The reaction depends strongly on the pH, [Pu^{4+}] and [PuO/]. Under standard condition the value of Eh= ED. However, if *[W]* is changed from 1 to 10^{-1}, Eh= 0.853 Volts.

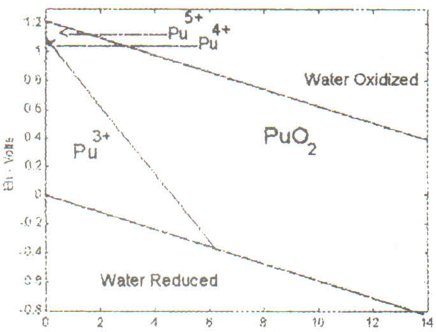

Figure 3 Four Nerst equationfonn Eh-pH diagram of plutonium

If [Pu^{4+}] and [PuO/] are the same and acidity is 1, the Nerst equation becomes very simple, because the value of Pu^{S+} and Pu^{4+} are canceled out in logarithmic equation. Those Nerst equations can be represented in Figure 3 for [pu^{3}1 and [Pu^{4}1, [Pu^{S}+] and [PuO/] as much as 10^{-9} M/kg.

For specific concentration of Pu, Pu^{4+} and Pu^{5+} becomes separating line of Pu 3+ and PU02. PU02 reaction in Eq. 13 Pu^{4+} and Pu^{5+} reaction in Eq.16 are overlapped. Actually, Nerst equation of reaction in Eq.16 itself is very short and that reaction in Eq.13 is rather longer. Those lines look like a single line. Eventhough Nerst equation of reaction in Eq.12 is not similar with reaction in Eq.l S, but the result of this equation is almost similar. Since the EO of both reaction is not difference enough and the value of PU02 is not big enough to overcome the value of 0.059 from its Nerst equation, so those lines looks like one horizontal line. When the value of *EO* of reaction in Eq.12 and Eq.15 is much different, it will bring about two lines on the Eh-pH diagrams of plutonium.

The consequence of those lines is the domain stability of Pu is very small, on the other hand the domain stability of PU02 is very large, Pu^{3+} stability domain is larger than the domain stability of Pu^{4+} but is smaller than the domain stability of Pu^{S+}. If the concentration of Pu^{3+}, Pu^{4+} and Pu^{S+} are higher than the above concentration, the line of reaction in Eq.14 is lower than that in Figure 3. The others line, however, are almost in the same position, but the Eh-pH diagrams will be different with the Figure 3 above. One line that is not desbribed in the Figure 3 is the result of calculation based on the Gibbs free energy, it is found pH = 0.6237 because it is

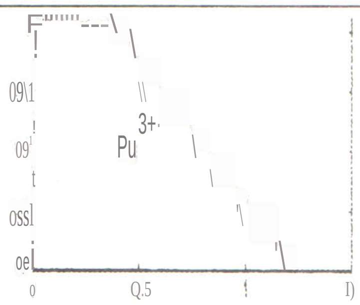

Figure 4; Four Nerst equations form Eh-pH diagram ofplutonium

too close to pH = zero.

In order to see the vertical line which separates Pu^{4+} and $PU0_2$, the scale of Figure 3 should be changed. If the concentration of Pu^{3+}, Pu^{4+} and Pu^{S+} as much as 10^{-9}, 10^{-9} and 10^{-7} M/kg respectively, then Figure 4 can be produced.

Not all part of the Eh-pH diagrams of plutonium is important, and it is needed to see all lines which are used to construct Eh-pH diagrams. In Figure 3, there seen two lines of plutonium reaction, but actually there are five lines. In Figure 4 those lines are shown, but the line for reduced water is not seen because that line is out of scale. On the other hand in this figure one can see clearly a vertical line which seperates Pu and PU02' This line is calculated by using Gibbs free energy because the reaction is not redox reaction. That line actually exists in the Figure 3, but it is not figured because it too small and closed to pH =0, so it was ignored.

CONCLUSIONS

1. For constructing the Eh-pH diagram of plutonium, there are four lines as a result of Nerst equation of redox reaction o of Plutonium, and one line as a result of its Gibbs free energy.
2. Eh-pH diagrams may be used to predict chemical speciation of plutonium in aqueous system
3. Since the chemical composition of natural water is complex, then for plutonium deposited in geological deposit its Eh-pH diagram will be more complicated.
4. Concentration of species of Pu strongly influences the value of its Nerst equations of redox reaction

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