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COMPUTER MODEL OF THE AUTOREDUCTION OF $^{238}\text{Pu(VI)}$
UNDER THE INFLUENCE OF ITS OWN α - RADIATIONS

G. L. Silver

AEC Research and Development REPORT

MONSANTO RESEARCH CORPORATION

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ABSTRACT

The autoreduction of hexavalent ^{238}Pu under the influence of its own alpha radiations can be simulated by adjusting the rate of reduction of Pu(IV) by radiation generated reducing agents and the rate of proportionation of Pu(III) , Pu(IV) and Pu(VI) via the equation $3\text{Pu(IV)} = 2\text{Pu(III)} + \text{Pu(VI)}$.

INTRODUCTION

One of the first discoveries about the aqueous chemistry of plutonium was the disproportionation reaction of the tetravalent plutonium ion in dilute acid,

The gradual reduction of the hexavalent state, PuO_2^{2+} , one of the products of the disproportionation reaction, has been attributed to the effects of the α -radiations of plutonium.^{1, 2, 3} While the nature of this reduction is not yet fully understood, recent work with ^{238}Pu suggests that the reduction can be understood in terms of an autocatalytic mechanism.⁴ A mathematical model of this reduction reaction has never been proposed, but the existence of a mathematical model of the reduction, which simulates the observed behavior of Pu(III), Pu(IV) and Pu(VI) during the course of the reduction reaction, would aid understanding of this reaction and may stimulate further research in this area. That the reaction might be autocatalytic has lead to the search for a computer model of the reduction reaction based on autocatalysis, α -generation of the catalytic agent, and reproportionation of the plutonium ions involved in the reduction reaction via equation (1). The model proposed in this paper reproduces the observed behavior of ^{238}Pu to a remarkable degree, and predicts some features of the autoreduction of $^{239}\text{PuO}_2^{2+}$. The reaction sequence on which the model is based is discussed elsewhere.⁴ Examination of this sequence reveals that it may be summarized by the following reactions:

It is one of the discoveries of this investigation that the autoreduction of Pu(VI) may be simulated by the equilibration of plutonium ions via equation (2), which is perturbed by continuous reduction of plutonium(IV) to plutonium(III) [equation (3)]. The assumption that only equation (2) is rate controlling is inadequate to explain the autoreduction of Pu(VI), as has been pointed out elsewhere.⁴ The model proposed in this paper assumes that both equations (2) and (3) are rate controlling, and that the autoreduction of Pu(VI) can be simulated by adjusting the

relative rates of alpha reduction of Pu(IV) and proportionation of Pu(III), Pu(IV), and Pu(VI) via equation (1). For a time during the autoreduction of Pu(VI), the rate of generation of Pu(IV) via equation (2) exceeds the rate of its removal via equation (3), leading to the appearance of a maximum in the concentration of Pu(IV) near the end of the reaction.⁴

The continuous readjustment of equation (2) to the perturbation caused by equation (3) leads to the ultimate reduction of most of the Pu(VI) in a manner similar to that experimentally observed.

A mathematical model of the autoreduction of Pu(VI) should incorporate several features, among them, (a) the tendency of Pu(III) and Pu(IV) to reach a steady state determined by the effects of the α -radiations on the solvent, (b) the tendency of Pu(III) and Pu(IV) and Pu(VI) to apportion according to equation (1), and (c) no reduction in the absence of lower oxidation states of Pu, the proposed catalytic agents.

DEVELOPMENT OF A MODEL FOR THE AUTOREDUCTION OF $^{238}\text{Pu(VI)}$

The first of the above requirements can be satisfied by ascertaining the steady state ratio Pu(III)/Pu(IV), called R, in a particular medium,⁴ and subtracting from this ratio the observed ratio of Pu(III)/Pu(IV), called P, in the same medium, so that the relative imbalance of the observed ratio is negative if Pu(III) is present in excess and positive if Pu(IV) is present in excess. The magnitude of the difference $[R - P]$ is then related to the magnitude of the imbalance of P from the steady state ratio, R, and the sign is related to the direction in which the relative concentration of Pu(III) and Pu(IV) must change in order to achieve the appropriate steady state ratio. The rate of change of Pu(III) in a solution in which P is inappropriate is proportional to $[R - P]$. When the sign of this difference is negative [i.e., an excess of Pu(III)], Pu(III) will be oxidized to Pu(IV), and when the sign of the difference is positive, Pu(IV) will be reduced until the appropriate steady state ratio, R, is obtained. Oxidation or reduction occurs via the oxidizing and reducing agents generated by the α -radiations of Pu on the solvent.⁴

While the tendency to adjust P to that ratio corresponding to steady state is related to the magnitude of the ratio imbalance, the rate of readjustment depends also on the quantity of Pu(IV) to be reduced. Thus, the rate of disappearance or appearance of Pu(III) as adjustment occurs in an irradiated solution may be stated as $[R - P][\text{Pu(IV)}](k)$, and the rate change of the concentration of Pu(IV), since mass must be conserved, is $[P - R][\text{Pu(IV)}](k)$, where k is a constant. Since the adjustment of P involves oxidation and reduction reactions, the constant k is related to the availability of oxidizing and reducing agents in the irradiated solution, or the rate at which such oxidants and reductants become available. As the specific activity of a plutonium isotope increases, the magnitude of k will also increase. Hence, in a solution of only Pu(III) and Pu(IV) not at steady state, the

concentration of Pu(III) may be postulated to change during successive time increments according to the equation

$$\text{Pu(III)}_{\text{new}} = (R - P_{\text{old}}) (k) [\text{Pu(IV)}_{\text{old}}] + \text{Pu(III)}_{\text{old}}, \quad (4)$$

and the concentration of Pu(IV) in the same solution will change in small increments of time according to the equation

$$\text{Pu(IV)}_{\text{new}} = (P_{\text{old}} - R) (k) [\text{Pu(IV)}_{\text{old}}] + \text{Pu(IV)}_{\text{old}}, \quad (5)$$

where P_{old} represents the concentration ratio of Pu(III) and Pu(IV) at a particular instant, and P_{new} represents the concentration ratio of Pu(III) and Pu(IV) an instant later. The size of the incremental concentration changes in a particular time interval can be adjusted by adjusting the value of k , the "radiation factor". Since Pu(VI) is not directly reduced at an appreciable rate to Pu(III) and Pu(IV) by reducing agents generated in nitric acid by the α -radiations of plutonium,⁴ the direct reduction of Pu(VI) to Pu(III) and Pu(IV) need not be considered.

In addition to α -induced oxidation and reduction reactions involving Pu(III) and Pu(IV), the species Pu(III), Pu(IV) and Pu(VI) are in equilibrium according to equation (1). The equilibrium concentration of Pu(III) may be found by solving the equilibrium expression, (1), for Pu(III), thus

$$\text{Pu(III)} = \left(\frac{[\text{Pu(IV)}]^3 (K_{\text{eff}})}{\text{Pu(VI)}} \right)^{\frac{1}{2}}, \quad (6)$$

where K_{eff} is the effective disproportionation equilibrium constant, and assumes a particular value in a particular acid.⁶ Likewise, the concentration of Pu(IV), when the concentrations of Pu(III) and Pu(VI) are specified, may be found by the expression

$$\text{Pu(IV)} = \left(\frac{[\text{Pu(VI)}][\text{Pu(III)}]^2}{K_{\text{eff}}} \right)^{\frac{1}{3}}. \quad (7)$$

The rate of disproportionation of Pu(IV), by equation (1), is proportional to the square of the concentration of Pu(IV), while the rate of reproporationation of Pu(III) may be taken as proportional to the product of Pu(III) and Pu(V).⁵ The rates of the forward and back reactions of equation (1), i.e., the rate of disproportionation and reproporationation, are also related to the specific reaction rate constants of the forward and back reactions. In simple reactions, the ratio of the specific

rate constants is the equilibrium constant of the reaction.⁷ For purposes of calculation with the proposed computer model, the specific rate of disproportionation of Pu(IV) is arbitrarily taken as unity. Since the value of the equilibrium constant⁸ for reaction (1) is about 0.001, simple reaction rate theory dictates that the specific reaction rate of the reproporationation reaction of Pu(III) and Pu(VI), via Pu(V), be about 1000. While simple reaction rate theory is not always adequate for complex reactions, it provides a basis for an initial assignment of the relative specific reaction rate constants for the forward and back reactions of equation (1) suitable for use in a system where equation (1) is perturbed in small increments.

From the above considerations of radiolytic adjustment of valence states and apportionment of valences via equation (1), it is possible to propose statements for the instantaneous concentrations of Pu(III), Pu(IV), and Pu(VI) which are easily translatable for computer processing:

$$\text{Pu(III)}_{\text{new}} = (R - P_{\text{old}})(k)[\text{Pu(IV)}_{\text{old}}] + \text{Pu(III)}_{\text{old}} + \quad (8)$$

$$2 \left(\frac{[\text{Pu(IV)}_{\text{old}}]^3 (K_{\text{eff}})}{\text{Pu(VI)}_{\text{old}}} \right)^{\frac{1}{2}} [\text{Pu(IV)}_{\text{old}}]^2,$$

$$\text{Pu(IV)}_{\text{new}} = (P_{\text{old}} - R)(k)[\text{Pu(IV)}_{\text{old}}] + \text{Pu(IV)}_{\text{old}} + \quad (9)$$

$$3 \left(\frac{[\text{Pu(III)}_{\text{new}}]^2 [\text{Pu(VI)}_{\text{old}}]}{K_{\text{eff}}} \right)^{\frac{1}{3}} [\text{Pu(III)}_{\text{new}}] [\text{Pu(VI)}] (1000),$$

$$\text{Pu(VI)}_{\text{new}} = \sum \text{Pu} - \text{Pu(III)}_{\text{new}} - \text{Pu(IV)}_{\text{new}}. \quad (10)$$

For the momentary concentration of Pu(III) in (8), the coefficient 2 derives from the fact that the disproportionation of Pu(IV) yields two Pu(III) ions; the coefficient 3 in (9) for the instantaneous concentration of Pu(IV) derives from the fact that reproporationation of Pu(III) and Pu(VI) yields three Pu(IV) ions. The decision to insert the coefficients (2,3) in the above equations is arbitrary, and the expressions for Pu(III) and Pu(IV) could also be written (1,3/2) or (2/3, 1). Coefficients are necessary, however, since equation (1) produces or consumes different numbers of Pu(III) and Pu(IV) ions for each incremental change to the left or right of the reaction. The coefficients, however, always bear the fixed relationship 2:3. The last terms in equations (8) and (9) are representations of the rate at which the concentration of Pu(III) and Pu(IV) change, via valence proportionation, and do not represent equilibrium concentration calculations. Zero order kinetics for Pu(VI) implies that this species is not directly involved in the rate determining steps;⁸ hence, the instantaneous concentration of this species is represented as the simple difference between the total quantity of Pu and that Pu in the (III) and (IV) states.

Since it is Pu(III) and Pu(V) which react directly in the reproporation reaction, the last term in equation (9) should have the form

$$\left(\frac{[\text{Pu(III)}]_{\text{new}}^2 [\text{Pu(VI)}]}{K_{\text{eff}}} \right)^{1/3} [\text{Pu(III)}]_{\text{new}} [\text{Pu(V)}], \quad (11)$$

involving the direct reaction of Pu(III) and Pu(V).⁵ Potential measurements made with a Pt electrode on nitric acid solutions of ²³⁸Pu, however, indicate that the steady state ratio of ²³⁸Pu(V)/²³⁸Pu(VI) is ≤ 0.1.⁴ Assuming for purposes of the model that Pu(V)/Pu(VI) ≈ 0.1 allows substitution of Pu(VI) in place of Pu(V), whose concentration is not easily followed, into equation (11). This substitution worked satisfactorily in the proposed model. To obtain a satisfactory time scale for the reduction reaction, the rates of alpha reduction and valence proportionation must be neither too fast nor too slow, or the reaction will proceed inordinately fast or inordinately slow. When the rate factor for valence proportionation is arbitrarily taken as 10⁻², the autoreduction of Pu(VI) is ordinarily complete in less than 100 computer calculation cycles, and this rate is convenient for testing properties of the computer model. The rate of valence proportionation of Pu(III), Pu(IV) and Pu(VI) should be practically the same for all isotopes of plutonium, whereas the "radiation factor" will depend upon the specific radioactivity of a particular plutonium isotope. Multiplying the valence proportionation terms in equations (8) and (9) by 10⁻² gives a convenient time scale for testing the model. It is then possible to test the effects of radiation by changing the value of the "radiation factor". Whatever the rationale of the constants used to adjust the rate of reproporation of Pu(III) and Pu(VI), and the rate of alpha reduction of Pu(IV), the salient point is that it is possible to simulate the behavior of ²³⁸Pu by proper adjustment of the rates of valence proportionation of Pu(III), Pu(IV), and Pu(VI) and alpha reduction of Pu(IV).

STATEMENT OF A PROGRAM SUITABLE FOR THE REPRESENTATION OF THE AUTOREDUCTION OF ²³⁸Pu(VI)

Since statements (8), (9), and (10) predict that the concentration of Pu(VI) will ultimately reach zero, and since it is observed that the concentration of Pu(VI) does not decrease to zero, but does reach a very small value, for example, in nitric acid solutions, it is necessary to correct, or to bypass, these statements near the end of the reduction reaction. Such a bypass must not disturb the in situ adjustment of P. In computer programming, such a bypass is easily achieved by means of the IF statement, and it then becomes easy to propose a computer model of the autoreduction of Pu(VI) based on α-reduction of Pu(IV) to Pu(III) and apportionment of valence according to equation (1):

IF $[\text{Pu(VI)}]_{\text{old}} = 0.03$ X, X, Y

$$\text{X } \text{Pu(III)}_{\text{new}} = (\text{R} - \text{P}_{\text{old}}) (k) [\text{Pu(IV)}_{\text{old}}] + \text{Pu(III)}_{\text{old}} \quad (12)$$

$$\text{Pu(IV)}_{\text{new}} = (\text{P}_{\text{old}} - \text{R}) (k) [\text{Pu(IV)}_{\text{old}}] + \text{Pu(IV)}_{\text{old}} \quad (13)$$

$$\text{Pu(VI)}_{\text{new}} = 0.03$$

$$\text{Y } \text{Pu(III)}_{\text{new}} = (\text{R} - \text{P}_{\text{old}}) (k) [\text{Pu(IV)}_{\text{old}}] + \text{Pu(III)}_{\text{old}} \quad (14)$$

$$+ (2)(10^{-2}) \left(\frac{[\text{Pu(IV)}_{\text{old}}]^3 K_{\text{eff}}}{\text{Pu(VI)}_{\text{old}}} \right)^{\frac{1}{2}} [\text{Pu(IV)}_{\text{old}}]^2$$

$$\text{Pu(IV)}_{\text{new}} = (\text{P}_{\text{old}} - \text{R}) (k) [\text{Pu(IV)}_{\text{old}}] + \text{Pu(IV)}_{\text{old}} + \quad (15)$$

$$+ (3)(10^{-2}) \left(\frac{[\text{Pu(III)}_{\text{new}}]^2 [\text{Pu(VI)}_{\text{old}}]}{K} \right)^{\frac{1}{3}} [\text{Pu(III)}_{\text{old}}] [\text{Pu(VI)}]_{\text{old}} (100)$$

$$\text{Pu(VI)}_{\text{new}} = \text{F} - \text{Pu(III)}_{\text{new}} - \text{Pu(IV)}_{\text{new}}.$$

In the above statements, the coefficient 100 in the expression for $\text{Pu(IV)}_{\text{new}}$ is an adjustment for the differing rates of the forward and back reactions of equation (1), and the factor 10^{-2} in the last terms of the expressions for $\text{Pu(IV)}_{\text{new}}$ and $\text{Pu(III)}_{\text{new}}$ adjusts the absolute rate of valence proportionation via equation (1) to provide a reasonable time scale for the reduction reaction. The total quantity of Pu in the system is represented by F.

In testing this model, the computer calculates the instantaneous concentrations of Pu(III), Pu(IV), and Pu(VI) given the initial conditions provided by the programmer. The instantaneous concentrations $\text{Pu(III)}_{\text{new}}$, $\text{Pu(IV)}_{\text{new}}$, and $\text{Pu(VI)}_{\text{new}}$ then become $\text{Pu(III)}_{\text{old}}$, $\text{Pu(IV)}_{\text{old}}$, and $\text{Pu(VI)}_{\text{old}}$ i.e., the initial conditions for the next calculation cycle. Instantaneous concentrations of the plutonium ions are then plotted versus calculation cycle number, which serves as an arbitrary time scale. By adjustment of the radiation factor, k, and the arbitrarily selected reaction rate constants of the forward and back reactions (1), sufficiently small changes in the concentrations of Pu(III), Pu(IV), and Pu(VI) may be obtained so that the plots of the concentrations of these species versus arbitrary time are nearly continuous.

PROPERTIES OF THE COMPUTER MODEL

To be an instructive and useful tool for the study of a chemical reaction, a proposed model should simulate the chemical system of interest as faithfully as possible, should embody as many properties of the system as possible, and should be so written that improvements are easily made and the effects of various changes in the chemical system easily tested. To an unexpected extent, the simple model proposed in this paper reproduces the properties of reducing solutions of $^{238}\text{Pu(VI)}$, and might therefore serve as a basis for further refinements as the nature of the autoreduction of Pu(VI) becomes better understood. Similarities of the model and experimental observations on reducing $^{238}\text{Pu(VI)}$ and $^{239}\text{Pu(VI)}$ are evident in many respects and are summarized below.

With appropriate values of k , the radiation factor, the model predicts an autocatalytic region for Pu(VI) early in the reduction reaction, and a zero order region for Pu(VI) as Pu(III) and Pu(IV) become abundant. This is the behavior demonstrated by $^{238}\text{Pu(VI)}$.⁴ Figure 1 illustrates the autocatalytic region and the zero order region of the reaction. The interesting behavior of the concentrations of Pu(III) and Pu(IV) during the autoreduction of Pu(VI) has been remarked elsewhere.⁴ The concentration of Pu(IV) increases to a maximum value near the end of the reaction, and then decreases until P is appropriate. The concentration of Pu(III) maintains a low value during the initial stages of the reaction, and increases near the end of the reaction until P reaches an appropriate value. Such behavior is illustrated both by ^{238}Pu and ^{239}Pu , and is an intrinsic part of the model as illustrated in Figure 1.

The rate of reduction of Pu(VI) in the zero order region should decrease as the level of radioactivity of the system decreases. Decreasing the radiation factor, k , results in a decrease in the rate of reduction of Pu(VI) , which nevertheless remains zero order. Such behavior is characteristic of ^{238}Pu . In the limiting case where the value of the radiation factor approaches a low value, the autocatalytic region disappears and the reduction of Pu(VI) is zero order throughout. Such behavior is characteristic of solutions of $^{239}\text{Pu(VI)}$, which have a relatively low level of radioactivity, and is reproduced by the model.⁹ Table 1 and Figures 1-3 illustrate the effects on the model of decreasing the radiation factor.

An increase in the concentration of catalysts, Pu(III) and Pu(IV) , results in an increase in the rate of reduction of Pu(VI) , at least in the case of ^{238}Pu , and decreases the residence time of Pu(VI) in the autocatalytic region. Such experimental results for ^{238}Pu are described elsewhere,⁴ and a similar effect is reproduced by the computer model as shown in Table 2 and Figures 4-6.

Changes in the rate of reduction of Pu(VI) in the zero order region with changes in R, the steady state ratio, have not been adequately studied experimentally. According to the computer model, the rate of the zero order reduction of Pu(VI) increases as P increases. While sufficient experimental data on real plutonium systems is lacking, such behavior in ^{238}Pu solutions is suggested by examination of Tables 3 and 4 of Reference 4. When R is changed, the effective equilibrium constant for reaction (1) is also changed. Also, in real systems, a change in R is probably accompanied by a change in the radiation factor. Table 3 describes the behavior of the model as R is changed. Figures 6-8 illustrate the behavior of changing the value of the steady state ratio on the autoreduction of Pu(VI).

Table 1

AUTOREDUCTION OF Pu(VI),
RADIATION LEVEL VARIABLE

<u>Radiation Factor k</u>	<u>$-\frac{d\text{Pu(VI)}}{dt}$^a</u>	<u>Remarks</u>
0.1	0.077	Figure 1
0.05	0.056	Figure 2
0.01	0.029	
0.001	Zero order region and autocatalytic region begin to merge.	Figure 3

Initial Conditions: $\text{Pu(VI)}_{0.1d} = 1.00$, $\text{Pu(III)}_{0.1d} = 0.01$, $\text{Pu(IV)}_{0.1d} = 0.01$,
 $F = 1.02$, $R = 0.50$, $K_{eff} = 0.02$.

^a Slope in zero order region.

Table 2

AUTOREDUCTION OF Pu(VI),
CATALYST CONCENTRATION VARIABLE

<u>Pu(III)_{old}</u>	<u>Pu(IV)_{old}</u>	<u>F</u>	<u>$-\frac{d\text{Pu(VI)}}{dt}$^a</u>	<u>Remarks</u>
0.01	0.01	1.02	0.062	
0.02	0.02	1.04	0.064	Figure 4
0.03	0.03	1.06	0.067	
0.05	0.05	1.10	0.075	Figure 5

Initial Conditions: $R = 0.60$, $k = 0.05$, $K_{eff} = 0.02$,
 $\text{Pu(VI)}_{old} = 1.00$.

^a Slope in zero order region

Table 3

AUTOREDUCTION OF Pu(VI),
STEADY STATE $\frac{\text{Pu(III)}}{\text{Pu(IV)}}$ RATIO VARIABLE

<u>Steady State Ratio, R</u>	<u>K_{eff}</u>	<u>$-\frac{d\text{Pu(VI)}}{dt}$^a</u>	<u>Remarks</u>
0.25	7×10^{-2}	0.038	Figure 6
0.50	2×10^{-2}	0.056	
1.00	5×10^{-2}	0.075	Figure 7
1.33	9×10^{-2}	0.080	
1.67	1.2×10^{-1}	0.091	Figure 8

Initial Conditions: $k = 0.05$, $\text{Pu(VI)}_{old} = 1.00$,
 $\text{Pu(III)}_{old} = 0.01$, $\text{Pu(IV)}_{old} = 0.01$,
 $F = 1.02$.

^a Slope in zero order region.

FIGURE 1 - Auto-reduction of Pu(VI),
radiation level variable.

FIGURE 2 - Auto-reduction of Pu(VI),
radiation level variable.

FIGURE 3 Auto-reduction of Pu(VI),
radiation level variable.

FIGURE 4 - Auto-reduction of Pu(VI),
catalyst concentration variable.

FIGURE 5 - Auto-reduction of Pu(VI),
catalyst concentration variable.

FIGURE 6 - Auto-reduction of Pu(VI), steady state
Pu(III)/Pu(IV) ratio variable.

FIGURE 7 - Autoreduction of Pu(VI), steady state Pu(III)/Pu(IV) ratio variable.

FIGURE 8 - Autoreduction of Pu(VI), steady state Pu(III)/Pu(IV) ratio variable.

ALTERNATE STATEMENT OF A COMPUTER PROGRAM SUITABLE FOR
REPRESENTATION OF THE AUTOREDUCTION OF $^{238}\text{Pu(VI)}$ UNDER
THE INFLUENCE OF ITS OWN ALPHA RADIATIONS

In the previous statement for the instantaneous concentrations of Pu(IV) , the concentration of Pu(V) was assumed to bear a fixed ratio to the concentration of Pu(VI) because of radiation-induced, potential controlling redox agents. The concentration of Pu(V) may also be established via the equilibrium

$$\text{Pu(VI)} + \text{Pu(III)} = \text{Pu(V)} + \text{Pu(IV)}$$

$$\text{Pu(V)} = \frac{K[\text{Pu(VI)}][\text{Pu(III)}]}{\text{Pu(IV)}} .$$

Since the value of K is about 0.1, substitution of Pu(V) into equations (9) and (11) leads to the following expression for the instantaneous concentration of Pu(IV) :

$$\text{Pu(IV)}_{\text{new}} \approx (\text{P}_{\text{old}} - R)(k)[\text{Pu(IV)}_{\text{old}}] + \text{Pu(IV)}_{\text{old}} +$$

$$(3)(10^{-2}) \left(\frac{[\text{Pu(III)}_{\text{new}}]^2 [\text{Pu(VI)}_{\text{old}}]}{K_{\text{eff}}} \right)^{1/3} \frac{[\text{Pu(III)}_{\text{new}}]^2 [\text{Pu(VI)}_{\text{old}}]}{\text{Pu(IV)}_{\text{old}}} (100) .$$

This form of the rate expression has been proposed by Rabideau.¹⁰ Combining this statement with the statements for the instantaneous concentrations of Pu(III) and Pu(VI) yields a model of the autoreduction of Pu(VI) with many of the same properties as the previously described model. These properties are described in Tables 4-6 and Figures 9-13.

Table 4

ALTERNATE MODEL OF AUTOREDUCTION OF
 $^{238}\text{Pu(VI)}$ - RADIATION FACTOR VARIABLE

<u>Radiation Factor, k</u>	<u>$-\frac{d\text{Pu(VI)}}{dt}$^a</u>	<u>Remarks</u>
0.10	0.050	Figure 9
0.05	0.034	
0.01	0.014	Figure 10
<0.01	Zero order and Autocatalytic Regions Begin to Merge	

Initial Conditions: $\text{Pu(III)}_{0.1d} = 0.01$, $\text{Pu(IV)}_{0.1d} = 0.01$,
 $K_{eff} = 0.02$, $R = 0.60$, $F = 1.02$,
 $\text{Pu(VI)}_{0.1d} = 1.00$

^a Slope in zero order region.

Table 5

ALTERNATE MODEL OF AUTOREDUCTION OF $^{238}\text{Pu(VI)}$,
CATALYST CONCENTRATION VARIABLE

<u>$\text{Pu(III)}_{0.1d}$</u>	<u>$\text{Pu(IV)}_{0.1d}$</u>	<u>F</u>	<u>$-\frac{d\text{Pu(VI)}}{dt}$^a</u>	<u>Remarks</u>
0.01	0.01	1.02	0.034	Figure 11
0.02	0.02	1.04	0.035	
0.03	0.03	1.06	0.036	
0.05	0.05	1.10	0.039	
0.10	0.10	1.20	0.051	

Initial Conditions: $\text{Pu(VI)}_{0.1d} = 1.00$, $R = 0.60$, $k = 0.05$,
 $K_{eff} = 0.02$

^a Slope in zero order region.

FIGURE 9 - Alternate model of autoreduction of $^{238}\text{Pu}(\text{VI})$ - radiation factor variable.

FIGURE 10 - Alternate model of autoreduction of $^{238}\text{Pu}(\text{VI})$ - radiation factor variable.

FIGURE 11 - Alternate model of auto-reduction of $^{238}\text{Pu}(\text{VI})$, catalyst concentration variable.

FIGURE 12 - Alternate model of auto-reduction of $^{238}\text{Pu}(\text{VI})$, steady state $\text{Pu}(\text{III})/\text{Pu}(\text{IV})$ ratio variable.

FIGURE 13 - Alternate model of autoreduction of $^{238}\text{Pu(VI)}$, steady state Pu(III)/Pu(IV) ratio variable.

Table 6

ALTERNATE MODEL OF AUTOREDUCTION OF $^{238}\text{Pu(VI)}$,
 STEADY STATE $\frac{\text{Pu(III)}}{\text{Pu(IV)}}$ RATIO VARIABLE

Steady State Ratio, R	K_{eff}	$-\frac{d\text{Pu(VI)}}{dt}$ ^a	Remarks
0.25	7×10^{-2}	0.015	Figure 12
0.50	2×10^{-2}	0.028	Figure 13
1.00	5×10^{-2}	0.048	
1.33	9×10^{-2}	0.059	
1.67	1.2×10^{-1}	0.070	

Initial Conditions: $k = 0.05$, $\text{Pu(III)}_{0.1d} = 0.01$,
 $\text{Pu(IV)}_{0.1d} = 0.01$, $\text{Pu(VI)}_{0.1d} = 1.00$,
 $F = 1.02$

^a Slope in zero order region.

Both computer models for the autocatalytic reduction of $^{238}\text{Pu(VI)}$ suffer shortcomings. Principal among these is the "calculation by increment" nature of the models. The instantaneous concentrations of Pu(III), Pu(IV) and Pu(VI) change by small increments instead of continuously as is the case in real ^{238}Pu solutions. Both programs are so written that the instantaneous concentrations of Pu(III) and Pu(IV) are allowed to adjust to the steady state ratio after the concentration of Pu(VI) drops below 0.03 without regard for the total quantity of plutonium present. This sometimes results in a small mass imbalance at the end of the reaction, i.e., the sum of Pu(III), Pu(IV) and Pu(VI) may exceed by a few percent the total quantity of plutonium initially present. Both models predict the complete disappearance of Pu(VI), necessitating the introduction of an IF statement. In the case of ^{238}Pu in dilute nitric acid, the concentration of Pu(VI) does not decrease to zero, but reaches a low steady state value.

Another shortcoming of the model lies in adding to both equations for the instantaneous concentration of Pu(IV) and Pu(III) a valence proportionation term. Obviously, the concentrations of Pu(III) and Pu(IV) cannot both increase simultaneously via disproportionation. One of these terms should be preceded by a minus sign.

The concentration of Pu(III) will be increased by disproportionation of Pu(IV) only near the end of the reaction when the concentration of Pu(IV) is near its maximum value. At the start of the reaction, when the concentration of Pu(IV) is low, the concentration of Pu(III) will be decreased by the disproportionation equilibrium. The question thus arises as to what time the valence proportionation terms should change sign. This problem has been obviated empirically in the present model. For example, at the beginning of a typical reduction sequence, when the concentrations of Pu(III), Pu(IV), and Pu(VI) are approximately 0.03, 0.10 and 0.89 respectively, the valence proportionation term in the equation for the instantaneous concentration of Pu(III) has a value of about 10^{-6} , and thus is small compared to the radiation term, which has a value of about (150) (10^{-5}). At the end of the reaction, the contribution from the valence proportionation term has increased, but may still be smaller than the radiation term, depending on the value of k . Likewise for Pu(IV), the value of the valence proportionation term is large near the beginning of the reaction and smaller near the end of the reaction, when the concentration of Pu(VI) is low.

A valence proportionation term is not included in the expression for Pu(VI) because this species is not directly involved in the rate determining steps. Moreover, since the total concentration of the three plutonium species is constant, the concentration of Pu(VI) is uniquely determined by specifying the concentrations of Pu(III) and Pu(IV). In addition, the concentration of Pu(VI) will not be augmented by valence proportionation except near the end of the reaction, since, for most of the reduction process, it is present in a concentration which exceeds its steady state value.

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