

# Application of a hydroxylamine nitrate stability model to plutonium purification process equipment



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## ABSTRACT

A mathematical model that predicts hydroxylamine nitrate (HAN) ( $\text{NH}_2\text{OH} \cdot \text{HNO}_3$ ) stability is applied to aqueous solutions containing HAN, nitric acid and plutonium that are used in plutonium purification processes. The model estimates the stability of these solutions with respect to the rapid, hazardous, autocatalytic reaction of HAN with nitric acid that generates heat and gas. It also accounts for reaction kinetics, temperature changes, gas generation rates, solution volumes and flow rates, and distribution of plutonium and nitric acid between aqueous and organic phases. The model is applied to three typical process vessels used in solvent extraction purification of plutonium – a countercurrent aqueous/organic plutonium stripping column, an oxidation column used for HAN and hydrazine destruction, and a plutonium rework tank. Both normal and off-normal process scenarios are modeled. Two of the off-normal scenarios lead to the rapid autocatalytic reaction of HAN with nitric acid where heat and gas are generated and that could lead to damage of the process equipment and/or release of hazardous plutonium solution from the vessel. In these two cases, stationary aqueous solutions containing HAN, Pu(III), and nitric acid were allowed to slowly react until conditions for the autocatalytic reaction were reached.

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## 1. Introduction

A mathematical model for determining the stability of aqueous hydroxylamine nitrate (HAN) ( $\text{NH}_2\text{OH} \cdot \text{HNO}_3$ ) solutions used in solvent extraction purification of plutonium was described in an earlier publication (Barney and Duval, 2011). The model calculates rates of the reactions involved in oxidation of HAN under conditions existing in a typical plutonium purification solvent extraction process. Conditions for which the hazardous autocatalytic reaction of HAN with nitric acid occurs were predicted successfully with the model. This paper describes application of the model for predicting HAN stability in solvent extraction vessels where heat generation from chemical reactions, heat loss through vessel walls, gas generation rates, distribution of Pu(IV) and  $\text{HNO}_3$  between aqueous and organic phases, volume changes, and solution flow into and out of vessels must be considered in the stability calculations. The

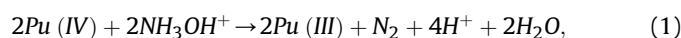
organic phase extractant considered in this paper is a 30% by volume tributyl phosphate (TBP) – branched paraffin hydrocarbon ( $\sim\text{C}_{12}$ ) solution. Examples of application of the model to three types of process vessels are described, along with normal operations and effects of off-normal conditions.

## 2. Heat and gas generation

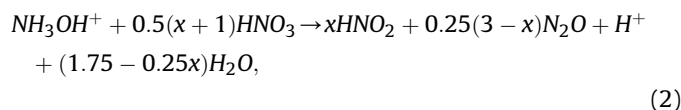
Chemical reactions at different stages of the process will produce heat and generate gases. These reactions will occur mainly in vessels where reagents are added to a solution in order to change oxidation states of plutonium or to remove reducing agents (mainly HAN or hydrazine) from the system. These vessels include the plutonium stripping column [where Pu(IV) is reduced to Pu(III) by HAN and removed from the organic phase], the oxidation column (where excess HAN and hydrazine are oxidized) and tanks downstream from the stripping column. The overall HAN reactions involved in heat and gas production are reduction of Pu(IV) to Pu(III),

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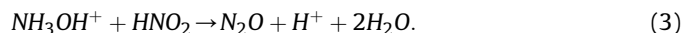
E-mail address: [scottbarney@hughes.net](mailto:scottbarney@hughes.net) (G.S. Barney).



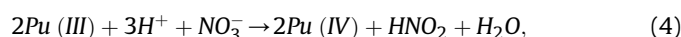
the autocatalytic reaction,



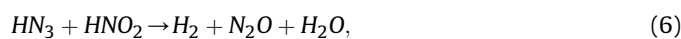
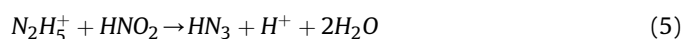
and the nitrous acid scavenging reaction,



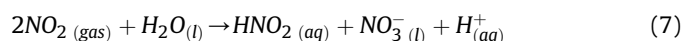
Other important heat producing reactions are reoxidation of Pu(III) with nitric acid,



oxidation of  $\text{N}_2\text{H}_5^+$  and  $\text{HN}_3$  with nitrous acid,



and absorption of  $\text{NO}_2$  gas in aqueous solutions,



The heats of reaction for each of these reactions are calculated from published standard heats of formation ( $\Delta H_f^\circ$ ) for the reactants and products (Dean, 1979). These reaction heats are used to calculate a temperature rise for the aqueous phase in processing vessels. The reactions occurring in a solution containing  $\text{HNO}_3$ ,  $\text{NH}_3\text{OH}^+$ ,  $\text{HNO}_2$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{H}_5^+$ ,  $\text{HN}_3$ ,  $\text{Pu(IV)}$ , and  $\text{Pu(III)}$  are considered.

The heat produced by these reactions is 50.78 kcal/mole of  $\text{Pu(IV)}$  (Reaction (1)), 23.76 kcal/mole of  $\text{NH}_3\text{OH}^+$  (Reaction (2)), 57.71 kcal/mole of  $\text{NH}_3\text{OH}^+$  (Reaction (3)), 10.23 kcal/mole of  $\text{Pu(III)}$  (Reaction (4)), 44.1 kcal/mole of  $\text{N}_2\text{H}_5^+$  (Reaction (5)), 82.49 kcal/mole of  $\text{HN}_3$  (Reaction (6)) and 12.8 kcal/mole of  $\text{NO}_2$  gas absorbed (Reaction (7)). The rate of each of these reactions is calculated by the model so that the contribution of each reaction to the total temperature rise of the solution is:

$$\begin{aligned} \frac{dT}{dt} = & k_1 \frac{[\text{Pu(IV)}]^2 [\text{NH}_3\text{OH}^+]^2}{[\text{Pu(III)}]^2 [\text{H}^+]^4 (K_d + [\text{NO}_3^-])^2} \left( \frac{50.78 \frac{\text{kcal}}{\text{mole}}}{C_{pL} \frac{\text{kcal}}{\text{L} \cdot ^\circ\text{C}}} \right) + k_2 [\text{NH}_3\text{OH}^+] [\text{NO}_2]^2 \left( \frac{23.76 \frac{\text{kcal}}{\text{mole}}}{C_{pL} \frac{\text{kcal}}{\text{L} \cdot ^\circ\text{C}}} \right) \\ & + k_3 [\text{NH}_3\text{OH}^+] [\text{HNO}_2] \left( \frac{57.71 \frac{\text{kcal}}{\text{mole}}}{C_{pL} \frac{\text{kcal}}{\text{L} \cdot ^\circ\text{C}}} \right) + (k_4 + k'_4 [\text{H}^+]) \frac{[\text{Pu(III)}] [\text{HNO}_2]^{0.5} [\text{H}^+]^{0.5} [\text{NO}_3^-]^{0.5}}{1 + \text{Beta} [\text{NO}_3^-]} \\ & \times \left( \frac{10.23 \frac{\text{kcal}}{\text{mole}}}{C_{pL} \frac{\text{kcal}}{\text{L} \cdot ^\circ\text{C}}} \right) + k_5 [\text{N}_2\text{H}_5^+] [\text{HNO}_2] [\text{H}^+] \left( \frac{44.18 \frac{\text{kcal}}{\text{mole}}}{C_{pL} \frac{\text{kcal}}{\text{L} \cdot ^\circ\text{C}}} \right) + k_6 [\text{HN}_3] [\text{HNO}_2] [\text{H}^+] \left( \frac{82.49 \frac{\text{kcal}}{\text{mole}}}{C_{pL} \frac{\text{kcal}}{\text{L} \cdot ^\circ\text{C}}} \right) \\ & + \frac{(\text{moles NO}_2 \text{ gas absorbed/second}) \left( 12.8 \frac{\text{kcal}}{\text{mole}} \right)}{(C_p \text{ kcal/L} \cdot ^\circ\text{C})(\text{solution volume, L})} \end{aligned} \quad (1)$$

The  $C_p$  term in this equation is defined as the total heat capacity (in kcal/K) of the aqueous and organic solutions in the vessel. The

$K_d$  and  $\text{Beta}$  terms are the dissociation constant for the  $\text{PuNO}_3^{3+}$  complex and the formation constant for the  $\text{PuNO}_2^{2+}$  complex, respectively. This equation is used in the model to calculate solution temperature as the reactions proceed.

The heat capacities of both aqueous and organic phases in the vessels are accounted for in the calculation since they will sometimes both be present and in thermal contact. The heat capacity of aqueous nitric acid solution and organic (30% TBP-hydrogenated propylene tetramer) phases are 0.946 kcal/K-L (for a 1.0 M  $\text{HNO}_3$  solution at 25 °C from Weast, 1980 p. D-119) and 0.387 kcal/K-L [for a 30% (vol.) TBP-hydrocarbon diluent mixture at 25 °C, Dean, 1979, pp. 7-206, 7-374, 9-77], respectively. Since the heat capacity of the stainless steel vessel is not accounted for in these calculations, the actual temperature increase is less than the calculated values.

Gas generation in process vessels during normal operations occurs by reactions that produce gases such as Reactions (1)–(3) and (6) as HAN solutions or  $\text{NO}_x$  gas (a mixture of  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ , and  $\text{NO}$  gases) are added to the vessel. These reactions will normally occur quite rapidly in the vessels so that gas generation rates will depend only on the feed rate of the aqueous solution or  $\text{NO}_x$  gas to the vessel and the concentration of reactants in the feed and in the vessel. However, the gas generation rate can be very high when the autocatalytic reaction occurs, depending on solution acidity, flow into and out of the vessel, and temperature conditions. This reaction is very fast once started and is strongly exothermic.

### 3. Heat loss from process vessels

Some of the heat generated by chemical reactions occurring in the process solutions will be lost to the air in the process cell/glove box atmosphere by three heat transport mechanisms: (1) conduction of heat through the solutions and the walls of the stainless steel vessel, (2) natural convection with heat being transferred from the outer surface of the vessel wall to a flowing layer of air in the cell/glove box, and (3) radiative heat transfer from the outside surface of the vessel to the cell/glove box. The assumption of instantaneous mixing of the entire contents of the vessel is used in the model and results in a uniform temperature throughout the vessel solutions. Heat conduction in the solutions is, therefore, not considered in the heat loss calculation. Heat transfer from the inner

surface of the stainless steel column to the outer surface will be rapid due to its high heat conductivity and relatively small

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