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**An Estimate of Chlorine-Induced Volatilities of Actinides
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Abstract

An estimate is made of the effects of chlorine on volatilization of actinides during combustion in the RFP Fluidized Bed Incinerator. The volatile species are assumed to be $\text{UO}_2\text{Cl}_2(\text{g})$, $\text{PuO}_2\text{Cl}_2(\text{g})$, and $\text{AmO}_2\text{Cl}_2(\text{g})$. Available thermodynamic data are used to calculate vapor pressures of $\text{UO}_2\text{Cl}_2(\text{g})$. Recent thermodynamic data on $\text{PuO}_2(\text{OH})_2(\text{g})$ volatilities are used to provide predictive thermodynamic data for $\text{PuO}_2\text{Cl}_2(\text{g})$. The $\text{AmO}_2\text{Cl}_2(\text{g})$ vapor pressure is assumed to be the same as the $\text{PuO}_2\text{Cl}_2(\text{g})$ vapor pressure but reduced by the $\text{AmO}_2(\text{s})$ mole fraction in $\text{PuO}_2(\text{s})$. Assuming that chlorine in the waste produces an $\text{HCl}(\text{g})$ pressure of 10^{-2} atm in the combustion chamber, the actinide volatilization rates in the offgas are calculated to be of 1.5 g/y U, 22 $\mu\text{g/y}$ Pu, and 4.4 ng/y Am.

Introduction

The purpose of this report is to provide an estimate of the chlorine-induced volatilities of actinides in the Rocky Flats Plant Fluidized Bed Incinerator.

The volatilization of actinides that occurs during combustion of mixed wastes in incinerators and other thermal oxidation processors leads primarily to condensation of the actinides on fine flyash particulates ($< 1 \mu\text{m}$) or to formation of actinide-containing aerosols in the offgas. The flyash contains actinide oxides formed in the combustion process, and some small fraction of this flyash is in the $< 1 \mu\text{m}$ size range. Particulates in this size range are of concern because they are difficult to filter out and may result in air emissions from the process. HEPA filters are effective at removing $\sim 99.97\%$ of these particulates. It is important to understand the volatilization contribution of actinides to the fine particulates in order to determine the extent of concentration of actinides on these particulates.

We have previously made measurements of U, Pu, and Am volatilities in the presence of steam and oxygen to evaluate the extent of gaseous actinide oxide and oxyhydroxide species that form under combustion conditions [1]. We were able to quantitatively establish the U species volatilities, assuming equilibrium conditions prevail in the combustion process. For Pu and Am species, the volatilities were found to be very low, and we were only able to establish upper limits for the volatilities. The data are still very useful for evaluating volatility limits in thermal oxidation processors. We have made some further measurements on Pu volatilities (work supported by DOE Defense Programs), which will be discussed in this report.

When chlorine or fluorine are present in the combustion, actinide volatilization as oxychloride or oxyfluoride species is expected in addition to the oxide and oxyhydroxide species. We are interested here in estimating the Cl-induced volatilities. Thermodynamic measurements are available for $\text{UO}_2\text{Cl}_2(\text{g})$ [2], although the volatilizing species was only assumed and not identified in the study. We assume the identification to be correct for our purposes here, and that $\text{UO}_2\text{Cl}_2(\text{g})$ is the only important uranium oxychloride species. There are no thermodynamic data for Pu and Am oxychloride gases. Predictions are made herein of thermodynamic data for the Pu and Am oxychloride species based on bond energy comparisons between U species and Pu species.

Recent Pu Volatility Measurements

Since our last report [1], further transpiration measurements have been made at higher temperatures on $^{238}\text{PuO}_2$ volatilities in the presence of $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. This work was done under DOE Defense Programs funding, and has not yet been written up. Please refer to our previous report [1] for experimental

details. We give here the results for the highest temperature runs at 1475 K, which indicate the presence of both $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$. These runs were made without the silica glass wool filter in place in front of the collection tube. It appeared that the PuO_2 sample had sintered sufficiently as to reduce dust carryover to below the volatility levels.

The transpiration data are summarized in Table 1. For runs 106, 107 and 111, which only had $\text{O}_2(\text{g})$ present, we take Pu to be volatilized only as $\text{PuO}_3(\text{g})$. The volatilization reaction and equilibrium constant are given by

$$K_1 = p(\text{PuO}_3)/a(\text{PuO}_2)p(\text{O}_2)^{1/2},$$

where the activity of $\text{PuO}_2(\text{s})$ is unity. We find the average value of K_1 at 1475 K to be $4.03 \times 10^{-11} \text{ atm}^{1/2}$ for the three runs. For volatilization to $\text{PuO}_2(\text{OH})_2(\text{g})$, the reaction and equilibrium constant are given by

$$K_2 = p(\text{PuO}_2(\text{OH})_2)/a(\text{PuO}_2)p(\text{O}_2)^{1/2}p(\text{H}_2\text{O}).$$

Values for $p(\text{PuO}_2(\text{OH})_2)$ are obtained from runs 105, 108, 109 and 110, by deducting $p(\text{PuO}_3)$ values (calculated using K_1) from the experimental $p(\text{Pu total})$. The K_2 values are then calculated (see Table 2). The average value of K_2 at 1475 K for the four experiments is 5.77×10^{-10} . The dependence of Pu volatility on H_2O pressure is illustrated in Fig. 1 where $p(\text{Pu total})/p(\text{O}_2)^{1/2}$ is plotted as a function of $p(\text{H}_2\text{O})$ for the experimental data. The solid line represents the K_1 and K_2 values derived herein. The variation of Pu volatility with H_2O pressure is consistent with formation of $\text{PuO}_2(\text{OH})_2(\text{g})$.

Based upon the K_1 value at 1475 K obtained herein and using auxiliary thermodynamic data given earlier [1], we calculate a $\Delta H^\circ_{f,298}$ for reaction (1) of $500.03 \pm 5.0 \text{ kJ/mol}$, and a $\Delta H^\circ_{f,298}$ for $\text{PuO}_3(\text{g})$ of $-555.77 \pm 5.5 \text{ kJ/mol}$. Similarly, based upon the K_2 value at 1475 K obtained herein, we obtain a $\Delta H^\circ_{f,298}$ of $337.97 \pm 9.0 \text{ kJ/mol}$ for reaction (2) and a $\Delta H^\circ_{f,298}$ for $\text{PuO}_2(\text{OH})_2(\text{g})$ of $-959.66 \pm 9.5 \text{ kJ/mol}$. The uncertainties are taken only from the experimental scatter of the most recent data. If previous data is taken into account, the uncertainties are considerably larger.

Table 1. Transpiration data for Pu volatility from $^{238}\text{PuO}_2(\text{s})$. Measurements were all made at 1475 K.

run #	time (min)	tot. moles gas	p(O ₂) (atm)	p(H ₂ O) (atm)	p(Ar) (atm)	Pu (ng)	p(Pu total), (atm)
105	120	0.638	0.389	0.611	--	19.2	1.27×10^{-10}
106	120	0.248	1.000	--	--	2.48	4.20×10^{-11}
107	240	0.124	1.000	--	--	1.59	5.39×10^{-11}
108	120	0.758	0.0654	0.699	0.235	21.5	1.19×10^{-10}
109	120	0.345	0.144	0.338	0.518	8.03	9.79×10^{-11}
110	120	0.266	0.186	0.144	0.670	4.21	6.64×10^{-11}
111	360	0.186	1.000	--	--	1.11	2.51×10^{-11}

Table 2. Determination of p(PuO₂(OH)₂) by difference, and calculation of K_{eq} for the reaction $\text{PuO}_2(\text{s}) + 1/2 \text{O}_2(\text{g}) + \text{H}_2\text{O} = \text{PuO}_2(\text{OH})_2(\text{g})$.

run #	p(O ₂) (atm)	p(H ₂ O) (atm)	p(Pu total) (atm)	calc. p(PuO ₃) (atm)	diff. p(PuO ₂ (OH) ₂) (atm)	K _{eq} (atm ^{-1/2})
105	0.389	0.611	1.26×10^{-10}	2.51×10^{-11}	1.01×10^{-10}	2.66×10^{-10}
108	0.065	0.699	1.19×10^{-10}	1.03×10^{-11}	1.09×10^{-10}	6.08×10^{-10}
109	0.144	0.338	9.79×10^{-11}	1.53×10^{-11}	8.26×10^{-11}	6.44×10^{-10}
110	0.186	0.144	6.64×10^{-11}	1.74×10^{-11}	4.90×10^{-11}	7.90×10^{-10}
ave.						5.77×10^{-10}

Figure 1. Plot for data at 1475 K illustrating the dependence of Pu volatility on $\text{H}_2\text{O}(\text{g})$ pressure.

Prediction of Thermodynamic Values for $\text{PuO}_2\text{Cl}_2(\text{g})$

Consider the reactions:

Thermodynamic data are known for all of the species in these reactions except for $\text{PuO}_2\text{Cl}_2(\text{g})$. Enthalpy changes ($\Delta H^\circ_{r,298}$) for the reactions represent bond energies for breaking of two bonds, i.e., in reaction (3) two U-OH bonds are broken, in reaction (4) two U-Cl bonds are broken, and so forth. We make the approximation that the ratio of bond energies of reaction (3) to reaction (4) is the same as the ratio of bond energies of reaction (5) to reaction (6). This then gives a value for the enthalpy change for reaction (6), which allows us to calculate a value for the enthalpy of formation of $\text{PuO}_2\text{Cl}_2(\text{g})$. Free energy function data will need to be estimated using the molecular constant method to complete the required data for $\text{PuO}_2\text{Cl}_2(\text{g})$.

The sources of thermodynamic data that are needed for the reactions above are as follows. The $\Delta H^\circ_{f,298}$ value for $\text{UO}_2(\text{OH})_2(\text{g})$ is given in our previous report [1], and for $\text{PuO}_2(\text{OH})_2(\text{g})$ is given above. The $\Delta H^\circ_{f,298}$ values for $\text{OH}(\text{g})$ and $\text{Cl}(\text{g})$ are from the JANAF tables [3]. The $\Delta H^\circ_{f,298}$ value for $\text{UO}_2(\text{g})$ is given by Green [4]. For $\text{UO}_2\text{Cl}_2(\text{g})$, a $\Delta H^\circ_{f,298}$ value of $-969.20 \pm 2.0 \text{ kJ/mol}$ is obtained from a third law analysis of volatility data by Cordfunke and Prins [2]. The free energy functions for $\text{UO}_2\text{Cl}_2(\text{g})$ are calculated from estimated molecular constants (see Table 3). For $\text{PuO}_2(\text{g})$, a $\Delta H^\circ_{f,298}$ value of $-413.36 \pm 12.5 \text{ kJ/mol}$ was obtained from a third law analysis of transpiration measurements by Pardue and Keller [5] of $\text{PuO}_2(\text{s})$ volatility under 1 atm O_2 pressure. Free energy function data for $\text{PuO}_2(\text{g})$ were calculated from molecular constant data given by Green [4]. The $\Delta H^\circ_{f,298}$ values used for the uranium and plutonium oxides, oxyhydroxides, and oxychlorides are summarized in Table 4.

Utilizing the $\Delta H^\circ_{f,298}$ data, we obtain the $\Delta H^\circ_{r,298}$ values shown in equations (3) to (5), and taking the ratio of bond energies for reaction (3) to (4) to be the same as for reaction (5) to (6), the $\Delta H^\circ_{r,298}$ value shown in equation (6) is obtained. With this value of $\Delta H^\circ_{r,298}$ for equation (6), and using the known

Table 3. Estimated molecular constants and calculated standard entropies, heat capacities, and free energy functions for $\text{UO}_2\text{Cl}_2(\text{g})$ and $\text{PuO}_2\text{Cl}_2(\text{g})$.

Molecular constants for $\text{UO}_2\text{Cl}_2(\text{g})$: MW = 340.934 g/mol, degeneracy of ground state = 1, structure is C_{2v} with sigma = 2, U-O bond length = 0.2538 nm, U-Cl bond length = 0.180 nm, vibrational frequencies (in cm^{-1}): 776.1, 765.43, 348, 323, 92, 91, 225.2, 225.2, and 70.

Molecular constants for $\text{PuO}_2\text{Cl}_2(\text{g})$: MW = 341.95 g/mol, degeneracy of ground state = 9 ($f^{2-3}\text{H}_4$ ground state), structure is C_{2v} with sigma = 2, Pu-O bond length = 0.2538 nm, Pu-Cl bond length = 0.180 nm, vibrational frequencies (in cm^{-1}): 776.1, 765.43, 348, 323, 92, 91, 225.2, 225.2, and 70.

$$C_p = A_1 + A_2 \times 10^{-3}T + A_3 \times 10^{-6}T^2 + A_4 \times 10^{-9}T^3 + A_5 \times 10^{-12}T^4, T = 298-2300 \text{ K}$$

	S°_{298} J/mol-K	A_1 J/mol-K	A_2 J/mol-K ²	A_3 J/mol-K ³	A_4 J/mol-K ⁴	A_5 J/mol-K ⁵
$\text{UO}_2\text{Cl}_2(\text{g})$	373.36	72.847	91.215	-91.6491	40.3818	-6.49615
$\text{PuO}_2\text{Cl}_2(\text{g})$	391.66	72.847	91.215	-91.6491	40.3818	-6.49615

T (K)	$-(G^\circ_T - H^\circ_{298})/T$	
	$\text{UO}_2\text{Cl}_2(\text{g})$ (J/mol-K)	$\text{PuO}_2\text{Cl}_2(\text{g})$ (J/mol-K)
800	408.633	426.939
900	416.361	434.667
1000	423.718	442.023
1100	430.702	449.007
1200	437.329	455.634
1300	443.620	461.925
1400	449.600	467.905
1500	455.293	473.598
1600	460.720	479.026

Table 4. Summary of $\Delta H^\circ_{f,298}$ values for uranium and plutonium oxides, oxyhydroxides, and oxychlorides.

species	$\Delta H^\circ_{f,298}$ (kJ/mol)	
UO ₂ (g)	-466.30 ± 5.0	from ref. [4]
UO ₃ (g)	-788.21 ± 7.0	from ref. [1]
UO ₂ (OH) ₂ (g)	-1151.61 ± 7.5	from ref. [1]
UO ₂ Cl ₂ (g)	-969.20 ± 2.0	3 rd law calc.
PuO ₂ (g)	-413.36 ± 12.5	3 rd law calc.
PuO ₃ (g)	-555.77 ± 5.5	3 rd law calc.
PuO ₂ (OH) ₂ (g)	-959.66 ± 9.5	3 rd law calc.
PuO ₂ Cl ₂ (g)	-780.61	estimated

$\Delta H^\circ_{f,298}$ values for $\text{PuO}_2(\text{g})$ and $\text{Cl}(\text{g})$ in equation (6), a $\Delta H^\circ_{f,298}$ value of -780.61 kJ/mol for $\text{PuO}_2\text{Cl}_2(\text{g})$ is obtained. To complete the thermodynamic data for $\text{PuO}_2\text{Cl}_2(\text{g})$, we have calculated free energy functions as shown in Table 3. The standard entropy and a heat capacity equation for both $\text{PuO}_2\text{Cl}_2(\text{g})$ and $\text{UO}_2\text{Cl}_2(\text{g})$ are also given in Table 3.

Application to RFP Fluidized Bed Incinerator

We now apply the thermodynamic data to estimate the Cl-induced actinide volatilities in the RFP Fluidized Bed Incinerator. Combustion of chlorinated hydrocarbons produces $\text{HCl}(\text{g})$ as a combustion product. The $\text{HCl}(\text{g})$ further reacts with the $\text{Na}_2\text{CO}_3(\text{s})$ in the bed to form $\text{NaCl}(\text{s})$ and reduces the $\text{HCl}(\text{g})$ pressure to a very low level. The reaction is given by

Assuming equilibrium for the reaction, we calculate (see JANAF [3] for thermodynamic data) $K_{\text{eq}} = 3.4 \times 10^{-7}$ for the reaction at 823 K, and with $p(\text{H}_2\text{O}) = 0.05$ atm and $p(\text{CO}_2) = 0.1$ atm, we find $p(\text{HCl}) = 3.40 \times 10^{-7}$ atm. If however, $\text{HCl}(\text{g})$ does not fully equilibrate with $\text{Na}_2\text{CO}_3(\text{s})$, then higher $\text{HCl}(\text{g})$ pressures will be present and can enhance the volatilities of the actinides. We will assume higher $\text{HCl}(\text{g})$ levels to evaluate the effects on volatilities.

We also need to know the chemical forms of the actinide oxides that result from the combustion process. For uranium, we had previously [1] taken the form to be $\text{Na}_2\text{UO}_4(\text{s})$. This form had been taken on the assumption of thermodynamic equilibration which gives a very low $\text{HCl}(\text{g})$ pressure (see above). As $\text{HCl}(\text{g})$ pressures are increased, Na_2UO_4 will no longer be stable, but uranium will form $\text{U}_3\text{O}_8(\text{s})$. This is shown by the reaction,

which we calculate (see refs. [1,3] for sources of thermodynamic data) to have a K_{eq} of $1.53 \times 10^7 \text{ atm}^{-5/6}$ at 823 K, and with $p(\text{H}_2\text{O}) = 0.05$ atm and $p(\text{O}_2) = 0.10$ atm, the $\text{HCl}(\text{g})$ pressure is 4.7×10^{-5} atm. Thus, at pressures of $\text{HCl}(\text{g})$ greater than 4.7×10^{-5} atm, $\text{Na}_2\text{UO}_4(\text{s})$ will no longer be stable but $\text{U}_3\text{O}_8(\text{s})$ will be the stable form. For plutonium, we take the stable form to be $\text{PuO}_2(\text{s})$, and for americium, we take a 200 ppm solid solution of AmO_2 in $\text{PuO}_2(\text{s})$.

Thermodynamic data are not available for americium oxychloride gaseous species. We will assume the species to be $\text{AmO}_2\text{Cl}_2(\text{g})$ and the free energy of vaporization of $\text{AmO}_2\text{Cl}_2(\text{g})$ from $\text{AmO}_2(\text{s})$ to be the same as for $\text{PuO}_2\text{Cl}_2(\text{g})$ from $\text{PuO}_2(\text{s})$. Further assuming AmO_2 to be present as an ideal solution in $\text{PuO}_2(\text{s})$, the

$\text{AmO}_2\text{Cl}_2(\text{g})$ volatilities will be in proportion to the $\text{PuO}_2\text{Cl}_2(\text{g})$ volatilities according to the AmO_2 content in $\text{PuO}_2(\text{s})$. Making similar assumptions, we take the volatilities of $\text{AmO}_3(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ to be in proportion to $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ volatilities according to the AmO_2 content in $\text{PuO}_2(\text{s})$.

We now proceed to calculate the volatilities of the actinide oxide, actinide oxyhydroxide, and actinide oxychloride species under the RFP Fluidized Bed Incinerator conditions and summarize the results in Table 5. Four different conditions of $\text{HCl}(\text{g})$ pressures ranging from 10^{-4} to 10^{-1} atm are assumed for the calculations. Thermodynamic data for these calculations are from our previous report [1] for $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$, for $\text{UO}_2\text{Cl}_2(\text{g})$ and all of the Pu species as discussed above, and for the Am species, according to the approximations indicated above. Auxiliary thermodynamic data are from our previous report [1] and from the JANAF tables [3]. The volatilization reactions are summarized as follows.

We find that the actinide oxychloride species dominate over the oxide and oxyhydroxide species in all cases for the $\text{HCl}(\text{g})$ pressures that we have chosen. We will illustrate the annual amount of volatilized actinides evolved in the offgas for the case where $p(\text{HCl})$ is 10^{-2} atm for the RFP Fluidized Bed Incinerator. Taking the conditions given in Table 5 with an offgas flow rate of 40 kmol/h and an operational time of 6000 h/y, volatilization rates of 1.5 g/y U, 22 $\mu\text{g/y}$ Pu, and 4.4 ng/y Am are obtained. These are very low values, and are reduced even further through the use of HEPA filters for removal of the actinide condensates on fine flyash particulates.

Table 5. Calculated pressures in atm of actinide vapor species at 823 K as a function of $p(\text{HCl})$ where $p(\text{O}_2)$ and $p(\text{CO}_2)$ are taken as 0.10 atm and $p(\text{H}_2\text{O})$ is taken as 0.05 atm. U is taken to be present as $\text{U}_3\text{O}_8(\text{s})$, Pu as $\text{PuO}_2(\text{s})$ and Am as 200 ppm AmO_2 in $\text{PuO}_2(\text{s})$.

$p(\text{HCl})$	1.0×10^{-4} (atm)	1.0×10^{-3} (atm)	1.0×10^{-2} (atm)	0.10 (atm)
$p(\text{UO}_3)$	1.8×10^{-17}	1.8×10^{-17}	1.8×10^{-17}	1.8×10^{-17}
$p(\text{UO}_2(\text{OH})_2)$	5.8×10^{-16}	5.8×10^{-16}	5.8×10^{-16}	5.8×10^{-16}
$p(\text{UO}_2\text{Cl}_2)$	2.6×10^{-15}	2.6×10^{-13}	2.6×10^{-11}	2.6×10^{-9}
$p(\text{PuO}_3)$	4.5×10^{-25}	4.5×10^{-25}	4.5×10^{-25}	4.5×10^{-25}
$p(\text{PuO}_2(\text{OH})_2)$	5.4×10^{-21}	5.4×10^{-21}	5.4×10^{-21}	5.4×10^{-21}
$p(\text{PuO}_2\text{Cl}_2)$	3.9×10^{-20}	3.9×10^{-18}	3.9×10^{-16}	3.9×10^{-14}
$p(\text{AmO}_3)$	9.0×10^{-29}	9.0×10^{-29}	9.0×10^{-29}	9.0×10^{-29}
$p(\text{AmO}_2(\text{OH})_2)$	1.1×10^{-24}	1.1×10^{-24}	1.1×10^{-24}	1.1×10^{-24}
$p(\text{AmO}_2\text{Cl}_2)$	7.8×10^{-24}	7.8×10^{-22}	7.8×10^{-20}	7.8×10^{-18}

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