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Redox Reactions Involving Chromium,  
Plutonium, and Manganese in Soils

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## Introduction

Certain findings from various NAEC studies suggest the presence of a more mobile, oxidized form of plutonium in some NTS soils. For example, Essington et al. (1976) have reported anomolous levels of Pu at depth in certain soil profiles from the NTS. It has been speculated that an oxidized, relatively mobile species of Pu such as  $\text{PuO}_2\text{CO}_3\text{OH}^-$  might be responsible for some of the vertical migration of Pu through the soil profile. Also, Romney et al. (1970) have reported the increased biological availability of Pu in pot studies over time. Perhaps this increased availability is due to the presence of a more mobile form of Pu. Therefore, it seems worthwhile to study possible Pu speciation in NTS soils. However, because of the complex behavior of Pu in soils at low levels, the investigator is beset with a myriad of problems. A worthwhile course of action is to study the speciation in soils of another element that might show certain similarities to Pu. With the discovery by Bartlett and James (1979) that soil manganese oxides can oxidize Cr(III) to Cr(VI), the selection of Cr as a model to study soil Pu seems logical, since it may be possible for soil manganese oxides to oxidize  $\text{PuO}_2$  to Pu(VI) species. In this paper, the similarities between Cr and Pu will be pointed out, a hypothesis concerning Pu speciation in NTS soils will be developed, and certain findings from Cr oxidation studies will be cited that may be relevant to the problem of Pu oxidation in soils.

### Similarities between the chemistries of Cr and Pu

Certain findings in the literature on Cr (Bartlett and Kimble, 1976; Bartlett and James, 1979) and on Pu (Rai and Serne, 1977; Bondietti and Sweeton, 1976; Bondietti and Reynolds, 1976; Cleveland, 1970; Francis, et al., 1976) lead to the following conclusions regarding the similarities between Cr and Pu behavior in aqueous environments:

- (1) Both elements can exist in multiple oxidation states in normal aqueous environments. Cr can exist in trivalent and hexavalent states, while Pu can exist in trivalent, quadrivalent, pentavalent, and hexavalent states.
- (2) Both elements can exist as cationic or anionic species in normal aqueous environments. Trivalent Cr exists as the cation,  $\text{Cr}^{3+}$ , and its hydrolysis products, or as the anion,  $\text{CrO}_2^-$ . Hexavalent Cr exists as the dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) or chromate ( $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ ) anions. Pu has cationic forms such as  $\text{Pu}^{3+}$  and  $\text{PuO}_2^+$  and anionic forms such as  $\text{PuO}_2\text{CO}_3\text{OH}^-$ .
- (3) Due to low solubility, Cr(III) and Pu(IV) are relatively "immobile" in normal aqueous environments. However, Cr(VI) and Pu(VI) are relatively "mobile."
- (4) Cr(VI) and Pu(VI) species are thermodynamically stable under approximately the same chemical environments in solution.
- (5) The oxidation of Cr(III) to Cr(VI) by soil manganese oxides is thermodynamically possible and has actually been observed in soils. This reaction occurs despite the presence of organic matter that would tend to keep Cr in the trivalent state. Pu(VI) species have been observed in natural waters, the oxidation of Pu(IV) by manganese oxide minerals is thermodynamically possible, and the oxidation of Pu(IV) by  $\text{MnO}_2$  has been observed.

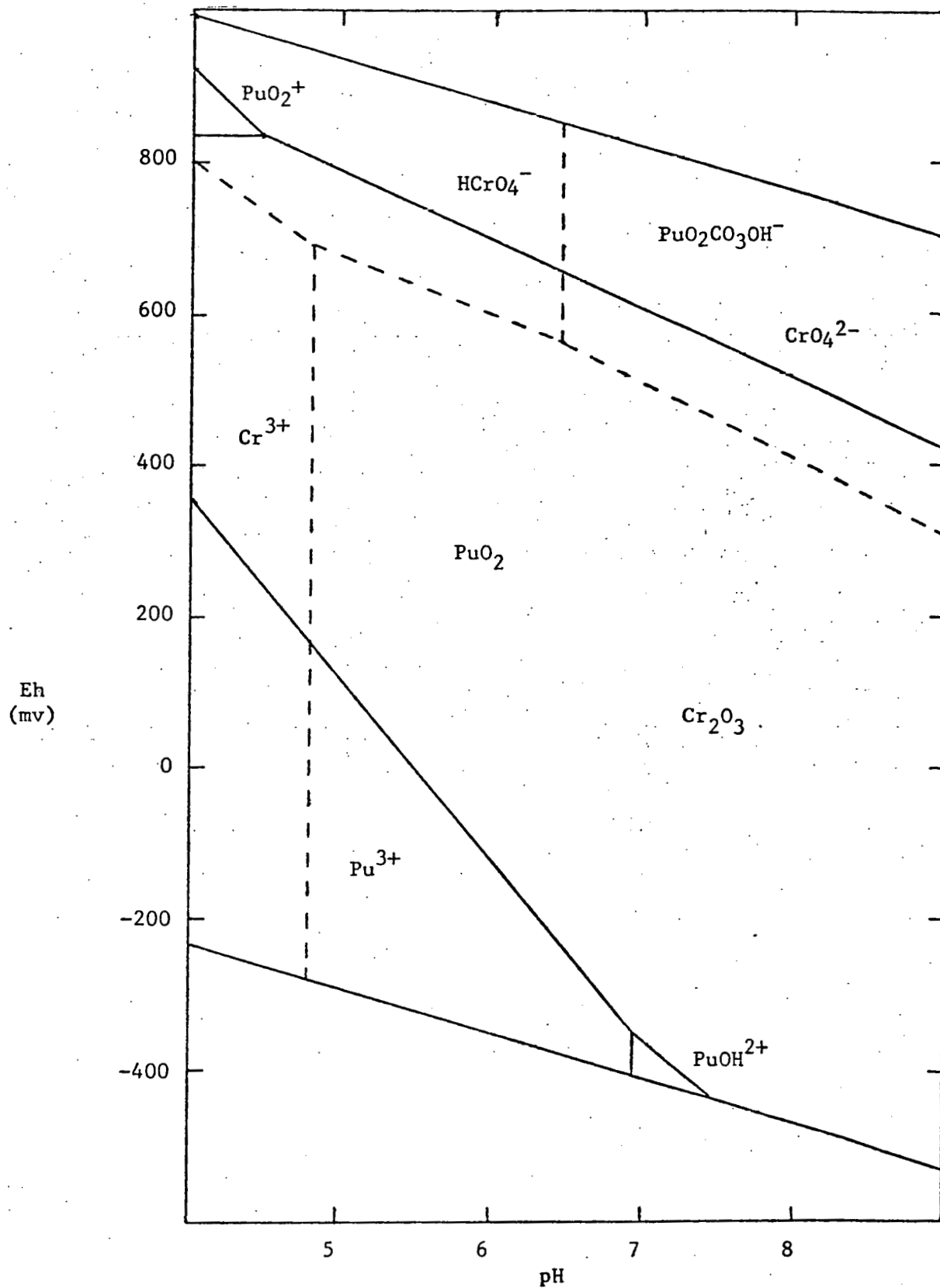
In pointing out the similarities between Cr and Pu behavior in aqueous environments, it must be remembered that there are also many differences between the two elements and analogies can only be pushed so far. Nevertheless, the similarities lead us to the following hypothesis: If low valence, colloidal Pu such as a  $\text{PuO}_2$  particle comes in contact with soil manganese oxides in a high Eh environment, then the Pu can be oxidized by the manganese oxides to a more mobile, higher valence species, thus the solubility of Pu is increased under these conditions. The question is whether this can occur in the soil environment found at NTS. Having pointed out the similarities between Cr and Pu and formulated a hypothesis concerning Pu oxidation in soils, it is now instructive to take a closer look at the thermodynamics of Pu and Cr reactions in normal soil environments.

Stability of Cr and Pu species in soil environments

Figure 1 shows the stability of  $\text{PuO}_2(\text{s})$  in a  $10^{-12}$  M Pu solution at  $25^\circ\text{C}$ ,  $\text{pCO}_2 = 3.5$ , and 1 atm pressure under a wide range of Eh and pH conditions. Superimposed over this is a stability diagram of  $\text{Cr}_2\text{O}_3(\text{s})$  in a  $10^{-6}$  M Cr solution under the same conditions. The thermodynamic data for the construction of the Pu stability diagram was taken from Rai and Serne (1977) and the data for the Cr stability diagram was taken from Garrels and Christ (1965). The Pu species stability fields are enclosed by solid lines, while the Cr species stability fields are enclosed by dotted lines.

The diagrams indicate that under low Eh-pH conditions the trivalent form of each element will be the most stable. Under high Eh conditions the hexavalent form of each element is the most stable. In the high Eh-pH environment of the NTS soils, it is expected that  $\text{PuO}_2\text{CO}_3\text{OH}^-$  will be the most stable soluble species. Thus, it appears that roughly under the same Eh-pH conditions both elements will shown approximately the same behavior with regard to oxidation state stability.

Figure 1. Stability of  $\text{PuO}_2$  and  $\text{Cr}_2\text{O}_3$  in  $10^{-12}$  M Pu and  $10^{-6}$  M Cr at  $25^\circ\text{C}$ ,  $p\text{CO}_2 = 3.5$ , and 1 atm.

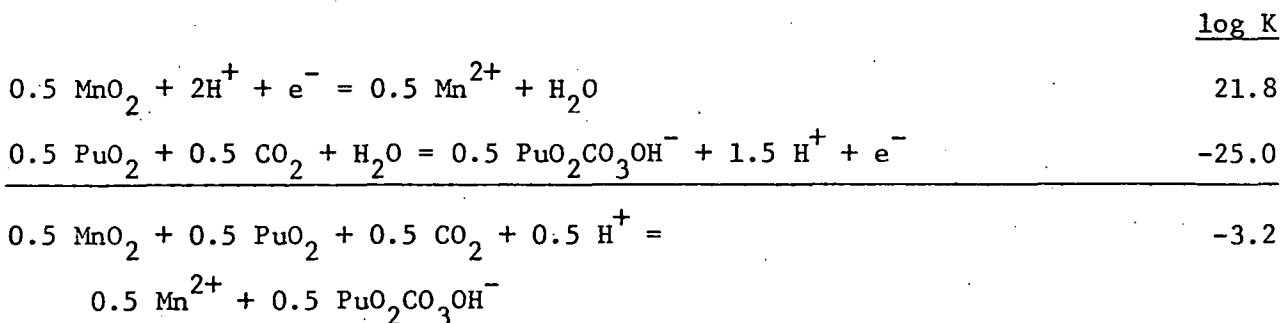




Thermodynamics of Cr and Pu oxidation by soil manganese oxides

Table 1 lists several oxidation and reduction half-reactions involving Cr, Pu, and Mn together with the log K values for the reactions. The log K values for the Pu oxidation reactions were calculated from data taken from Rai and Serne (1977). The log K values for the Cr and Mn half-reactions were taken from Bartlett and James (1979). The Cr oxidation reactions shown are for the oxidation of  $\text{Cr}_2\text{O}_3$ ,  $\text{Cr}(\text{OH})_3$ , and aqueous trivalent Cr to aqueous hexavalent Cr. The Mn reduction reactions shown are for the reduction of four common Mn(IV) oxide minerals to aqueous Mn(II). The Pu oxidation reactions shown are for the oxidation of  $\text{PuO}_2(\text{s})$  to the aqueous species indicated in the table.

If one combines one of the Cr or Pu oxidation half-reactions with one of the Mn mineral reduction half-reactions and adds the log K values for the two half-reactions, a net redox reaction and its equilibrium constant are obtained. By choosing appropriate reaction conditions, the equilibrium pH of the reaction can be calculated. Sample calculations reveal that the oxidation of Cr or Pu by manganese oxide minerals is thermodynamically possible at common soil pH values. As an example we will consider the oxidation of  $\text{PuO}_2(\text{s})$  to  $\text{PuO}_2\text{CO}_3\text{OH}^-$  by  $\text{MnO}_2(\text{s})$ . First, the two half-reactions and their log K values are added to obtain the net redox reaction and its log K value:



The equilibrium constant expression for this reaction is given by

$$\text{pK} = 0.5 \text{ pMn}^{2+} + 0.5 \text{ pPuO}_2\text{CO}_3\text{OH}^- - 0.5 \text{ pCO}_2 - 0.5 \text{ pH} = 3.2$$

Solving for pH leads to

$$\text{pH} = \text{pMn}^{2+} + \text{pPuO}_2\text{CO}_3\text{OH}^- - 0.5 \text{pCO}_2 - 6.4$$

By choosing reasonable values for  $\text{pMn}$ ,  $\text{pPuO}_2\text{CO}_3\text{OH}^-$ , and  $\text{pCO}_2$  the equilibrium pH can be calculated:

$$\text{pMn}^{2+} = 6$$

$$\text{pPuO}_2\text{CO}_3\text{OH}^- = 12$$

$$\text{pCO}_2 = 3.5$$

$$\text{pH} = 6 + 12 - 0.5(3.5) - 6.4 = 8.1$$

Since the soils of the NTS have pH values mostly between 7 and 8.5, this reaction could be in equilibrium in these soils. At higher  $\text{pCO}_2$  values the equilibrium will be shifted to higher pH values. If the pH of the soil solution is below the equilibrium pH, this indicates that the net reaction is thermodynamically spontaneous to the right. Non-ideality corrections were ignored in this calculation. If included the calculated pH would shift slightly.

Equilibrium pH values for the oxidation of  $\text{PuO}_2(\text{s})$  by three other common manganese oxide minerals are shown in Table 2 along with the result from the sample calculation. The calculated pH values seem to indicate that these oxidation reactions are possible in the alkaline soils found at the NTS provided such manganese oxide minerals exist in those soils.

Table 1. Oxidation or reduction half-reactions involving Cr, Mn, and Pu.

	$\log K_{25^\circ\text{C}}$
$0.17 \text{ Cr}_2\text{O}_3 + 0.67 \text{ H}_2\text{O} = 0.17 \text{ Cr}_2\text{O}_7^{2-} + 1.33 \text{ H}^+ + \text{e}^-$	-19.7
$0.17 \text{ Cr}_2\text{O}_3 + 0.83 \text{ H}_2\text{O} = 0.33 \text{ HCrO}_4^- + 1.33 \text{ H}^+ + \text{e}^-$	-20.0
$0.17 \text{ Cr}_2\text{O}_3 + 0.83 \text{ H}_2\text{O} = 0.33 \text{ CrO}_4^{2-} + 1.67 \text{ H}^+ + \text{e}^-$	-22.2
$0.33 \text{ Cr(OH)}_3 + 0.17 \text{ H}_2\text{O} = 0.17 \text{ Cr}_2\text{O}_7^{2-} + 1.33 \text{ H}^+ + \text{e}^-$	-18.6
$0.33 \text{ Cr(OH)}_3 + 0.33 \text{ H}_2\text{O} = 0.33 \text{ HCrO}_4^- + 1.33 \text{ H}^+ + \text{e}^-$	-18.9
$0.33 \text{ Cr(OH)}_3 + 0.33 \text{ H}_2\text{O} = 0.33 \text{ CrO}_4^{2-} + 1.67 \text{ H}^+ + \text{e}^-$	-21.0
$0.33 \text{ Cr}^{3+} + 1.17 \text{ H}_2\text{O} = 0.17 \text{ Cr}_2\text{O}_7^{2-} + 2.33 \text{ H}^+ + \text{e}^-$	-22.5
$0.33 \text{ Cr}^{3+} + 1.33 \text{ H}_2\text{O} + 0.33 \text{ HCrO}_4^- + 2.33 \text{ H}^+ + \text{e}^-$	-22.8
$0.33 \text{ Cr}^{3+} + 1.33 \text{ H}_2\text{O} = 0.33 \text{ CrO}_4^{2-} + 2.67 \text{ H}^+ + \text{e}^-$	-25.0
$0.33 \text{ CrO}_2^- + 0.78 \text{ H}_2\text{O} = 0.33 \text{ CrO}_4^{2-} + 1.33 \text{ H}^+ + \text{e}^-$	-15.2
$0.5 \text{ Mn}_3\text{O}_4 + 4 \text{ H}^+ + \text{e}^- = 1.5 \text{ Mn}^{2+} + 2\text{H}_2\text{O}$	30.7
$\text{MnOOH} + 3 \text{ H}^+ + \text{e}^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	26.1
$0.5 \text{ Mn}_2\text{O}_3 + 3 \text{ H}^+ + \text{e}^- = \text{Mn}^{2+} + 1.5 \text{ H}_2\text{O}$	24.4
$0.5 \text{ MnO}_2 + 2 \text{ H}^+ + \text{e}^- = 0.5 \text{ Mn}^{2+} + \text{H}_2\text{O}$	21.8
$\text{PuO}_2(\text{s}) = \text{PuO}_2^+ + \text{e}^-$	-26.0
$0.5 \text{ PuO}_2(\text{s}) = 0.5 \text{ PuO}_2^{2+} + \text{e}^-$	-20.8
$0.5 \text{ PuO}_2(\text{s}) + 0.5 \text{ CO}_2 + \text{H}_2\text{O} = 0.5 \text{ PuO}_2\text{CO}_3\text{OH}^- + 1.5 \text{ H}^+ + \text{e}^-$	-25.0

Table 2. Equilibrium pH values for the oxidation of  $\text{PuO}_2(\text{s})$  to  $\text{PuO}_2\text{CO}_3\text{OH}^-$  by manganese oxide minerals.

<u>Oxidation reaction</u> <u>(not balanced)</u>	<u>Reaction conditions</u>	<u>Oxidizing agent</u>	<u>Equilibrium pH</u>
$\text{PuO}_2(\text{s}) \longrightarrow$ $\text{PuO}_2\text{CO}_3\text{OH}^- (\text{aq})$	$[\text{PuO}_2\text{CO}_3\text{OH}^-] = 10^{-12} \text{ M}$	$\text{Mn}_3\text{O}_4$	7.58
	$[\text{Mn}^{2+}] = 10^{-6} \text{ M}$	$\text{MnOOH}$	7.56
	$\text{pCO}_2 = 3.5$	$\text{Mn}_2\text{O}_3$	6.43
	$25^\circ\text{C}$	$\text{MnO}_2$	8.10
	1 atm total P		

### Summary of Cr oxidation studies

Bartlett and James (1979) have studied the problem of Cr oxidation in soils. Chromium oxidation experiments are also being carried out in the authors' labs, but this data has not been published as yet. Certain findings from Bartlett's and the authors' experiments that may prove relevant to the problem of Pu oxidation in soils will be cited here:

- (1) Bartlett and James (1979) have found that when an unnamed series of Lithic Eutrochrepts was equilibrated with a  $10^{-6}$  M  $\text{CrCl}_3$  solution at a solution to soil ratio of 2000/1 and the pH adjusted with HCl and  $\text{KHCO}_3$ , virtually all of the added Cr(III) was oxidized at low pH, and the fraction of added Cr that was oxidized decreased with increasing pH. The amount of Cr(VI) that was adsorbed also decreased with increasing pH. The oxidation of Pu and sorption of oxidized Pu by soils is also expected to be affected by pH. However, since the soils at the NTS are alkaline, one only needs to consider the effect of pH on Pu oxidation over a narrow pH range (7 to 9).
- (2) The oxidation of Cr(III) to Cr(VI) in moist soils appears to be almost "instantaneous" once the Cr(III) species are in "contact" with the oxidizing agent in the soil. The rate limiting step appears to be the diffusion of Cr(III) species to the soil oxidizing agent. (Bartlett and James, 1979; Amacher and Baker, unpublished data).
- (3) The oxidation of Cr(III) solutions by moist soils occurs despite the presence of organic matter. Once the Cr(III) has been oxidized, it can be reduced, probably by the soil organic matter, and it can be re-oxidized (Bartlett and James, 1979).
- (4) The relatively insoluble  $\text{Cr}_2\text{O}_3$  can also be oxidized in moist soils, thus increasing its solubility (Amacher and Baker, unpublished data).

- (5) When Cr(III) has been oxidized by moist soil and the sample is then dried, no Cr(VI) can be extracted from the soil. Thus, the reaction appears reversible upon drying. If the soil is washed with ethanol or acetone after the Cr(III) is oxidized, some Cr(VI) can be extracted by the soil. Thus, the reaction is only partially reversible in this case and water appears to be a necessary component in the reaction (Amacher and Baker, unpublished data).
- (6) The ability of a moist soil to oxidize Cr(III) solutions can be exhausted by successive additions of Cr(III) to the soil (Amacher and Baker, unpublished data).
- (7) Oven-dry soils oxidize no added Cr(III) and air-dry soils oxidize very little Cr(III) (Bartlett and James, 1979; Amacher and Baker, unpublished data).
- (8) The amount of 1 N  $\text{CaCl}_2$  exchangeable Mn increases upon the oxidation of Cr(III) in moist soils and is also much higher in dry soils than in moist soils. Cr(III) oxidation does not occur in soils very low in Mn and the amount of Cr(III) that a moist soils can oxidize correlates well with the amount of Mn reducible by hydroquinone. Thus, it appears that Mn(IV) oxides in soils can oxidize Cr(III) and that some of the soil Mn(IV) oxides are reduced to yield exchangeable Mn(II) upon drying (Bartlett and James, 1979; Amacher and Baker, unpublished data).

Some of the above findings concerning Cr oxidation in soils may be observed for Pu oxidation in soils. Whether any of these discoveries prove applicable to the problem of Pu oxidation in soils remains to be seen.

Questions needing answered by future investigations

Despite the progress made thus far in studying the behavior of soil Pu at the NTS, the following questions still need to be answered:

- (1) In view of the findings regarding Cr and Pu oxidation by manganese oxides, can  $\text{PuO}_2$  be oxidized to Pu(VI) species by the manganese oxides in the soil environments at NTS?
- (2) If Pu(VI) species exist in NTS soils, how much do they contribute to the migration and plant uptake of Pu at the NTS?
- (3) Will clean-up operations at the NTS produce conditions favoring the formation of the more mobile Pu(VI) species?

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