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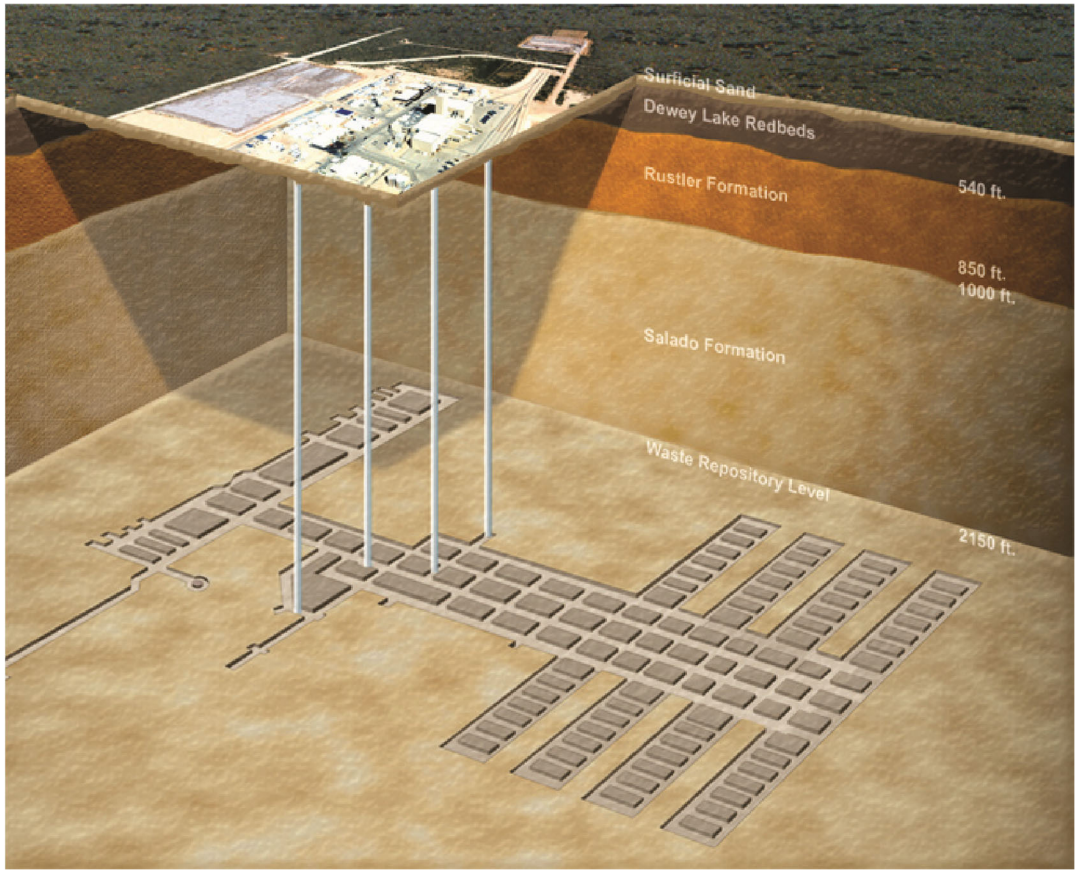
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Systematic Calculation of Pu Pourbaix Diagrams



WIPP Facility and Stratigraphic Sequence

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The funding for this document is provided by the Department of Energy, Carlsbad Area Office.

This report summarizes a modeling study performed by Amphos[21] in support of Los Alamos Actinide Chemistry and Repository Science Program that supports the WIPP project. It was issued as a Los Alamos LA-series report so that is can be referenced and disseminated.

About the cover: schematic of the Waste Isolation Pilot Plant (WIPP) repository, located near Carlsbad, New Mexico, that is being used for the permanent disposal of transuranic waste.

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Systematic Calculation of Pu Pourbaix Diagrams: Modelling Support for the LANL ACRSP team

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FOREWORD

The report enclosed entitled "Systematic Calculation of Pu Pourbaix Diagrams: Modelling Support of the LANL ACRSP Team" was prepared by Amphos[21] under contract to the Los Alamos National Laboratory Actinide Chemistry and Repository Science Program (ACRSP) team to support an enhanced understanding of the actinide and brine chemistry in the Waste Isolation Pilot Plant (WIPP) transuranic repository. In this report, the ThermoChimie chemistry model and database, with some slight modifications, were used to calculate Pourbaix diagrams to investigate the effects of ionic strength, organic complexation, and metal competition on the predominance diagrams for aqueous and solid plutonium species under the anoxic and reducing conditions expected in the repository. These diagrams were connected to iron chemistry phase diagrams since this iron chemistry is expected to define and control redox properties in the WIPP repository concept.

The WIPP salt repository, should inundation occur, is a high ionic-strength brine system ($I > 5$ M) that is appropriately modeled using the Pitzer formulation and approach. This remains the WIPP project position. In the WIPP model, plutonium solubility is modeled by analogy (Th for Pu(IV) and Am/Nd for Pu(III)). For this reason, there are no plutonium Pitzer data in this model. The speciation database in the WIPP model is also relatively small due to the lack of available Pitzer data. There continue to be ongoing efforts within the WIPP project, as well as internationally, to strengthen and further develop the Pitzer parameter database.

ThermoChimie is a model that supports a number of European nuclear waste programs. The basis of this model is the NEA-TDB peer-reviewed thermodynamic database with additional as-needed reactions added to account for relevant and identified repository-specific processes. The goal of using this model was to provide qualitative data, specific to plutonium speciation, to help assess some ongoing WIPP-specific issues as well as guide and prioritize the development of an expanded and more robust WIPP Pitzer model.

It is important to note that the ThermoChimie modeling results cannot be used, in a regulatory sense, to define the WIPP project position until confirmed by WIPP-specific Pitzer modeling and experimental results. There are two important reasons why this is true. First, it is well understood that extending the SIT approach to high ionic-strength systems ($I > 3$ M) is a non-standard approach that can introduce significant error to the modeled predictions for some reactions. This is especially true for highly charged species although some success is often observed for monovalent binary systems. The ThermoChimie model was used, despite this limitation, because it represents a much more complete and internally consistent, albeit low ionic-strength, database that includes plutonium reactions along with many key reactions that are also important to the WIPP case (e.g., iron and lead chemistry, organic/inorganic complexation, cation competition). Second, a WIPP-specific Quality Assurance qualification process is a necessary regulatory requirement to use modeling results as a basis for compliance decisions.

These ThermoChimie modeling results, given the qualifications just made, do however provide some very useful and interesting insights into the plutonium chemistry and associated issues in the WIPP repository. The most important of these are:

- The plutonium Pourbaix diagrams show that Pu(III) and Pu(IV) solid phases and aqueous species dominate the plutonium chemistry over the range of conditions predicted in the WIPP (low E_h, anoxic, pH 8-10, and high ionic-strength complex brines). This supports, in a more quantitative way, the current WIPP position.
- The iron phase that is predominant over a wide range of E_h and pH conditions in the WIPP is magnetite. This mixed oxidation Fe(II/III) phase exhibits high thermodynamic stability. Potential Fe(II) phases can be present but are never predominant and appear to be metastable or transitional. Understanding the chemistry associated with this phase is key to defining the upper E_h boundary in WIPP repository history.
- Higher ionic strength and the presence of highly complexing ligands lead to an expanded predominance field for reduced Pu(III) aqueous species. This provides a more quantitative view of the influence of these higher Pu(III) solubilities on the predominance diagrams under WIPP-relevant conditions.
- Competition with calcium, magnesium and iron completely mitigate the effects of EDTA, and more broadly organic ligand, complexation on plutonium solubility. This affirms the recent WIPP project decision to include these competitive reactions in the WIPP Pitzer model.
- Under WIPP-relevant conditions, the oxidation-state distribution is defined by the prevalence of the solubility-controlling phases in WIPP PA. From this perspective, there is only a very small region of the Pourbaix diagram where Pu(III) solid phases are predominant (> 50%). This region becomes diminishingly small at higher levels of predominance (e.g., > 90% Pu(III)). These results continue to support the predominance of Pu(IV) solids for reasonable redox assumptions under WIPP-relevant conditions.

As a whole, these qualitative ThermoChimie results continue to support the overall WIPP model and repository implementation but point to a number of areas where improved Pitzer modeling would greatly strengthen and better quantify the scientific basis of the contribution of plutonium to the mobile actinide source term and, more generally, the WIPP repository safety case.

Donald Reed



Team Leader, Actinide Chemistry and Repository Science Program
Repository Science and Operations
Los Alamos National Laboratory

AMPHOS 21
SCIENTIFIC AND STRATEGIC ENVIRONMENTAL CONSULTING

Systematic calculation of Pu Pourbaix diagrams

Modelling support for the LANL ACRSP team

E. Colàs, D. García, L. Duro

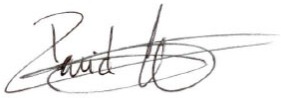


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1 Background and introduction

The Waste Isolation Pilot Plant (WIPP) is a transuranic waste repository initiated in 1999 and expected to operate beyond 2050. Its actinide/chemistry model is a key and critical aspect of supporting its safety case.

The solubility and speciation of multivalent actinides are often investigated with lanthanide and actinide analogs. In the WIPP modeling approach, it is common to use redox-invariant analogs (Nd(III)/Am(III) for for Pu(III) or Th(IV) for Pu(IV)), to determine oxidation-state-specific plutonium properties such as solubility or complexation (U.S. DOE 2019a). This analog approach has clear advantages as it simplifies some aspects of the experimental design; nevertheless, it also has some drawbacks, as detailed in U.S. DOE (2019a).

The purpose of the present report to evaluate Pu chemistry using the most current Specific ion Interaction Theory (SIT) model for ionic strength corrections, without using oxidation-state invariant analogues, under conditions relevant for WIPP. The calculations and figures provided are intended to provide support to the Los Alamos Actinide Chemistry and Repository Science Program (ACRSP) team in their objective to update the WIPP actinide/chemistry model to reflect recent scientific progress and lay a foundation for the development of an improved Pitzer-based modeling approach.

The following activities are defined within the task:

a) Review of thermodynamic data included in ThermoChimie v.10 for Pu.

b) Calculate Pu Pourbaix diagrams by extending SIT to I ~ 5-6 M typical of WIPP-relevant brine systems.

c) Investigate the effects of EDTA and other organics on Pu-Fe chemistry.

The main core of the report contains:

- A brief description of the conceptual model and calculation methodology (section 2), including a description of the groundwaters used in the calculations, the thermodynamic database used and the model setup.
- A brief summary of the main results for Pu chemistry in the absence (section 3) and presence (section 4) of organic ligands.
- Conclusions (section 5).

An appendix is also included that contains more extensive details on:

- Database modifications.
- Pu Pourbaix diagrams in the presence and absence of organic ligands, including calculations on NaCl, calculations in GWBrine and ERDA-6 and iron Pourbaix diagrams
- Calculations illustrating the effect of EDTA on Pu chemistry and how it is impacted by competition with calcium.

2 Conceptual model and calculation methodology

2.1 General description of the system

The Waste Isolation Pilot Plant (WIPP) repository is located at a depth of 800 m in the Permian Salado Formation. The Salado Formation is a relatively thick bedded salt, composed mainly of layers of impure halite (NaCl) with anhydrite, polyhalite, clay, and mudstone interbeds (U.S. DOE 2019b). The Salado Formation is underlaid by the Castile Formation, mainly composed of high-purity halite alternating with carbonate and anhydrite (U.S. DOE 2019b). The Salado and Castile brines are complex Na-Mg-Cl-K-SO_4^{2-}-borate high ionic-strength brines (I > 5 M).

The WIPP permanently disposes transuranic (TRU) waste. TRU waste consists of tools, rags, protective clothing, sludges, soil and other materials contaminated with radioactive elements, mostly plutonium. Organic materials are expected to be present among the waste; the organic chelating agents currently addressed by Performance Assessment are acetate, oxalate, citrate and ethylenediaminetetraacetic acid (EDTA) (U.S. DOE 2019a). The waste packaging materials and the waste itself also contain significant amounts of iron that is expected to define reducing/anoxic conditions in the repository.

Thus, the important points to consider in the evaluation of Pu chemistry will be:

- the influence of concentrated groundwaters in Pu chemistry,
- the role of iron in defining redox conditions, and
- the influence of organic ligands on the Pu chemistry

2.2 Groundwaters

2.2.1 Inorganic composition

The two standard WIPP brines used in the calculations in the present work are Generic Weep Brine (GWBrine) and Energy Research and Development Administration WIPP Well 6 (ERDA-6). GWBrine is a synthetic brine representative of the intergranular Salado Formation. ERDA-6 is a synthetic brine representative of the brine reservoirs in the Castile Formation. The composition of these groundwaters are reported in Domski and Sisk-Scott, (2019) and are summarized in Table 2-1 below.

Table 2-1: *GWBrine and ERDA-6 compositions used in the calculations in present work (from Domski and Sisk-Scott, 2019).*

Element or property	GWBrine Concentration (M)	ERDA-6 Concentration (M)	Comments (present work)
Na	4.69	4.66	
Mg	0.348	0.435	
K	0.663	0.499	
Ca	0.0109	0.0128	
S(VI)	0.232	0.224	Total S in calculations [a)]
Cl	5.40	5.22	
TIC	$2.50 \cdot 10^{-4}$	$2.50 \cdot 10^{-4}$	C(IV) [b)]
B	0.224	0.281	
Fe(II)	$2.61 \cdot 10^{-5}$	$2.67 \cdot 10^{-5}$	Total Fe in calculations [a)]
Br	0.0378	0.0566	
Pb	$1.90 \cdot 10^{-2}$	$1.88 \cdot 10^{-2}$	
pH	9.54	9.52	Varied from 4 to 12 [c)]
I [d)]	6.53	6.48	

a) Redox equilibrium S(VI)/S(-II) and Fe(III)/Fe(III) has been taken into account to draw the Pourbaix diagrams in present work.
b) Total inorganic carbon considered as total carbonate to draw the Pourbaix diagrams in present work.
c) pH is calculated in the presence of excess MgO for WIPP-relevant applications; in this modeling study pH is not a fixed parameter, but it is varied from 4 to 12 in the Pourbaix diagrams in present work.
d) Ionic strength reported in Domski and Sisk-Scott (2019), calculated with Data0.FM4 database and the Pitzer approach.

2.2.2 Organics

In addition to the brine data described in the previous section, the organic ligands acetate, citrate, EDTA (ethylenediaminetetraacetate) and oxalate are also included in some calculations. The concentrations used in the present work are summarized in Table 2-2.

Table 2-2: *Organic concentrations used in the calculations in the presence of organic ligands (from Domski and Sisk-Scott, 2019).*

Element or property	Concentration (M)
Acetate	$2.83 \cdot 10^{-2}$
Citrate	$2.30 \cdot 10^{-3}$
EDTA	$7.92 \cdot 10^{-5}$
Oxalate	$1.13 \cdot 10^{-2}$

2.3 Thermodynamic database

Calculations have been made with ThermoChimie version 10a (TC10a) (www.thermochimie-tdb.com, Giffaut et al. 2014, Grivé et al. 2015), with some modifications that are briefly summarized below and extensively described in the appendix (pages A5 to A24).

The ThermoChimie database uses SIT (Specific ion Interaction Theory) for activity corrections of the stability constants to the standard state. The SIT approach considers short-range non-electrostatic interactions by adding terms to the Debye-Hückel expression (Eq. 2-1):

$$\log(\gamma_i) = -z_i^2 \left(\frac{A\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}} \right) + \sum_k \varepsilon(i,k,I_m) m_k \qquad \textit{Eq. 2-1}$$

Eq. 2-1 accounts for the activity coefficient γ_i of an ion of charge Z_i in a solution of ionic strength I. A and B are empirical constants for a given temperature. The parameter a_i is the effective ion diameter, Z is the charge and $\varepsilon(i,k,I_m)$ is the ionic interaction coefficient ($Kg \cdot mol^{-1}$).

2.3.1 Database modifications

Several modifications have been made in TC10a in the light of new data appearing in the literature. The modified database will be referred to as TC10a-WIPP-2.

Pu inorganic data has been modified based on recent publications, specially the studies about solubility and redox behavior of hydrous Pu(IV) oxide published by Tasi et al. (2018). Using the data reported in this publication for the Pu-H_2O system results in a slightly higher stability of Pu(III) hydrolysis species and differences in Pu(VI) speciation (due to the inclusion of $PuO_2(OH)_3^-$ and $PuO_2(OH)_4^{2-}$) in comparison with the selection in ThermoChimie version 10a. These effectively

expand the stability field of Pu(III) aqueous/solid species and add Pu(VI) species to the Pourbaix diagrams. The effect of these database changes is illustrated in Figure 2-1 Further details are provided in the appendix, pages A6-A7 and A15-A16.

Ca-Pu(III)-OH and Ca-Pu(IV)-OH complexes reported in Altmaier et al. (2009) and Fellhauer et al. (2010) have also been included in TC10a-WIPP-2, but these are not formed at the pH and Ca concentrations used in the calculations, as seen in the appendix, pages A17-A18.

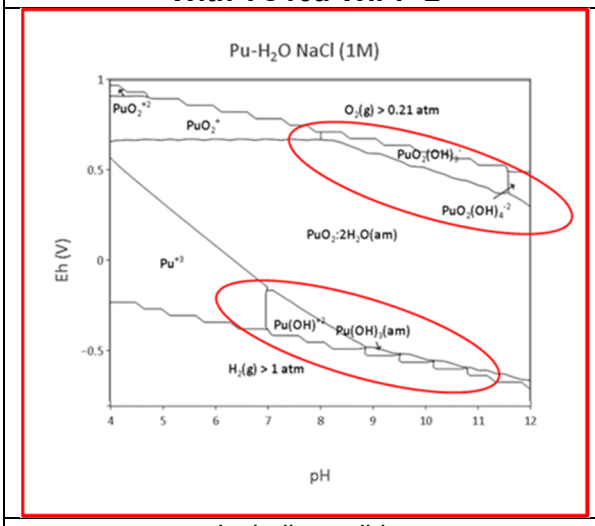
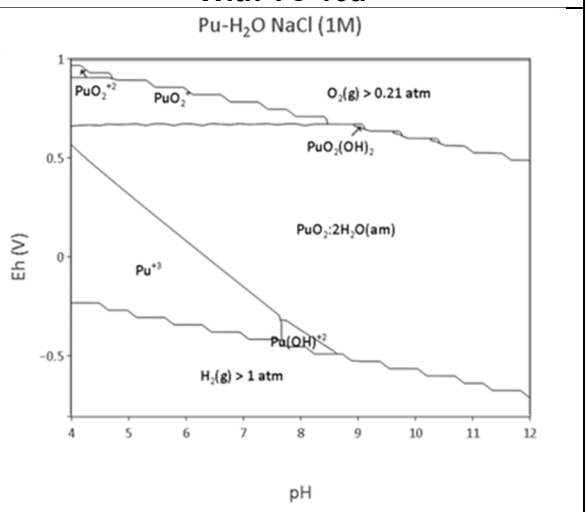
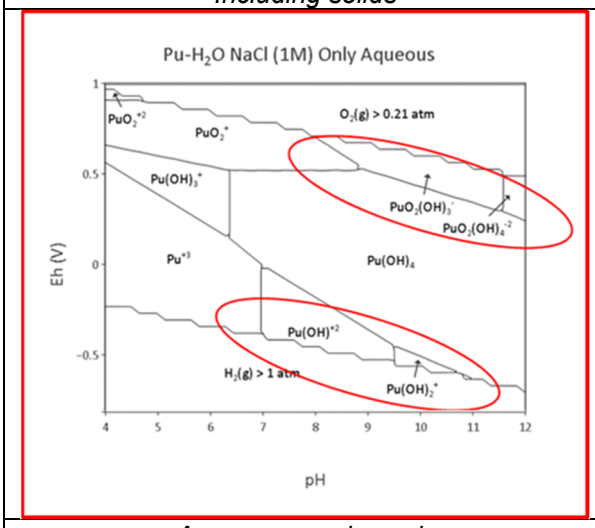
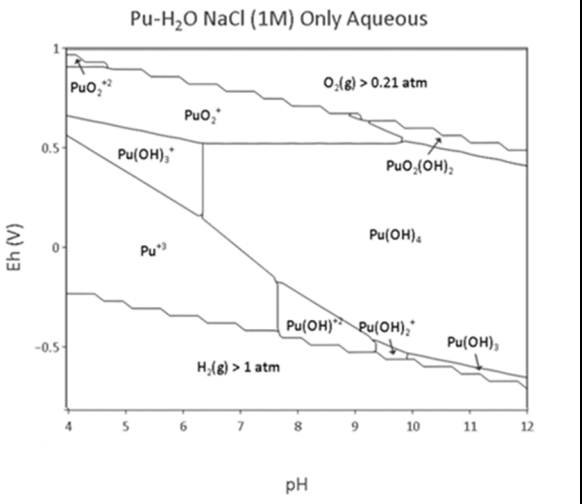
With TC10a-WIPP-2	With TC 10a
	
Including solids	*Including solids*
	
Aqueous species only	*Aqueous species only*

Figure 2-1: *Simplified Pourbaix diagrams (1M NaCl, $[Pu]_T=1\cdot10^{-8}$ M) that illustrate the effect of thermodynamic database changes in the Pu solid oxides and aqueous hydroxides.*

Data for Pb-EDTA, Pb-Oxalate and Pu-EDTA have been updated with the information reported in Colàs et al. (2017) (see appendix pages A8 to A11).

No ternary Pu(IV)-OH-EDTA complexes are included in ThermoChimie database. Rai et al. (2008) studied the solubility of PuO_2(am) at different pH values in the presence of EDTA and provided stability constants for $Pu(OH)EDTA^-$, $Pu(OH)_2EDTA^{2-}$ and $Pu(OH)_3EDTA^{3-}$ complexes. In the

present work, we have included in the calculations the data by Rai et al. (2008); the values are below the upper limit stability constants predicted by Hummel (1993).

Although the formation of these Pu(IV)-EDTA species increased Pu(IV) solubility, Rai et al. (2008) reported that, "*in the presence of $Fe(OH)_3(s)$ or at relatively low Ca concentrations, EDTA is primarily complexed with Fe(III) or Ca(II) and is unavailable for complexation with Pu(IV)*"; that is, competition with major ions will reduce the effect of EDTA in Pu mobility. This is also demonstrated in section 4.2.

As shown in Figure 2-2, the inclusion of Pu(IV)-OH-EDTA species affects the Pu(IV) calculated speciation in neutral to alkaline pH region.

Due to the lack of complete and reliable thermodynamic data, neither ThermoChimie nor the modified database TC10a-WIPP-2 include Pu-citrate complexes. This must be taken into account in order to evaluate the results obtained in the calculations with organic ligands.

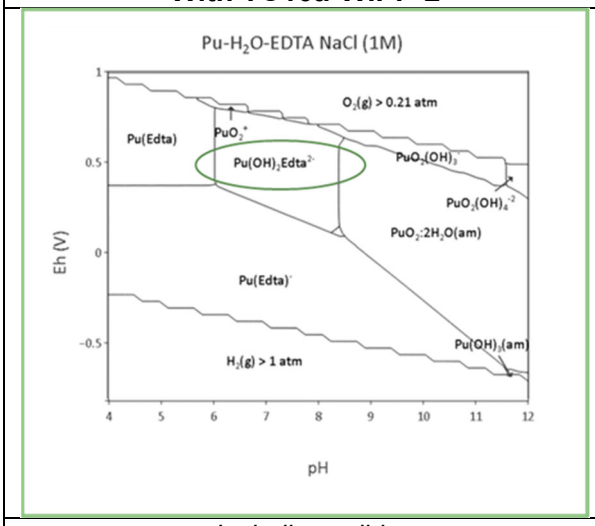
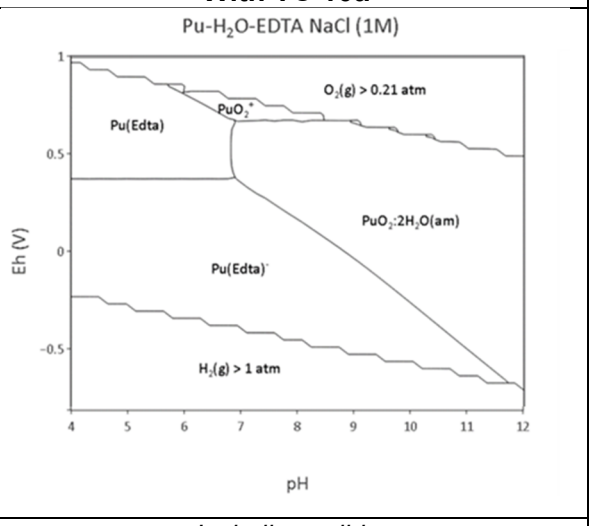
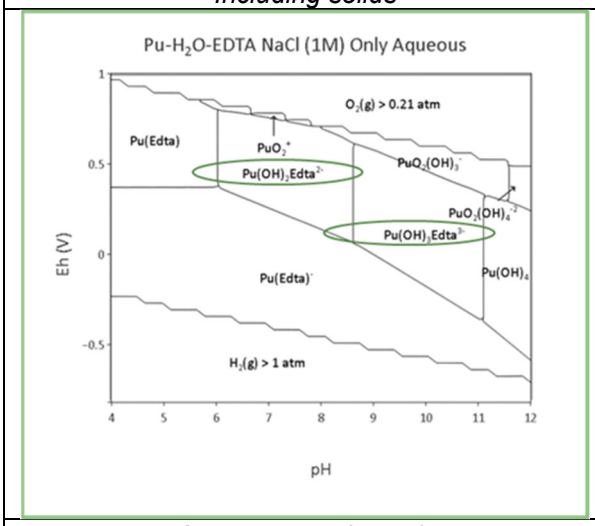
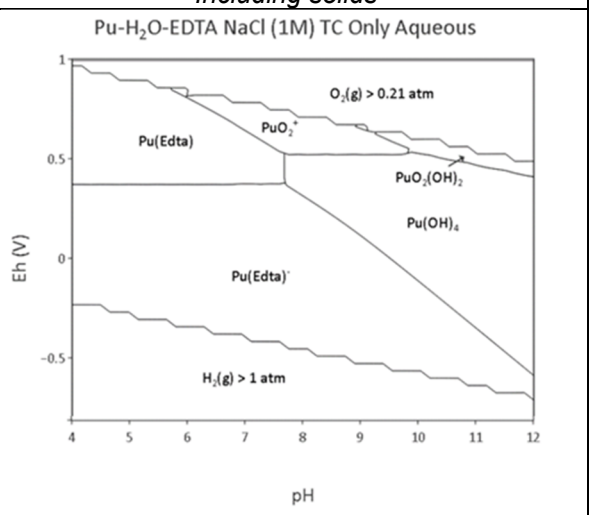
With TC10a-WIPP-2	With TC 10a
	
Including solids	*Including solids*
	
Aqueous species only	*Aqueous species only*

Figure 2-2: *Simplified Pourbaix diagrams (1M NaCl, $[Pu]_T=1\cdot10^{-8}$ M, $[EDTA]_T=7.9\cdot10^{-5}$ M) in order to illustrate the effect of thermodynamic database changes in Pu chemistry in the presence of EDTA.*

Some iron thermodynamic data have also been modified. Data for Fe(II)-Cl aqueous species have been updated following the suggestions in the NEA-TDB (Lemire et al. 2013). Data selection for Fe(III)-EDTA, Fe(II)-Citrate and Fe(III)-Citrate has been improved. Finally, metastable Fe(II)/Fe(III) solid phases known as Green Rusts have been included for scoping calculations in the present work. Extensive details are provided in the appendix, pages A12-A13 and A23.

In addition, $NaCO_3^-$ and $NaHCO_3$ complexes were eliminated from the database, following the approach used in the NEA-TDB. Only the SIT interaction coefficients $\varepsilon(Na^+, CO_3^{2-})$ and $\varepsilon(Na^+, HCO_3^-)$ are used to consider sodium/carbonate interactions.

2.4 Model setup

Most of the results are presented in terms of Pu Pourbaix (E_h versus pH diagrams). Besides the groundwater composition described in section 2.2, it is necessary to fix a concentration of Pu in order to draw those diagrams. The plutonium concentration has been set to $[Pu]_T=1\cdot10^{-8}$ M in most calculations; however, some additional calculations at $[Pu]_T=1\cdot10^{-6}$ M were also performed in order to evaluate the sensitivity to this parameter (results of the sensitivity analysis are provided in the appendix, pages A42 and A54).

Calculations include both aqueous species and some solid compounds. The selection of the solid compounds to be included (or not) in the calculations was mainly based on expert judgement, considering that:

a) solids with complex chemical composition are unlikely to form by direct precipitation from solution

b) the less crystalline phases are kinetically favored and consequently they constitute the initial solubility limiting solid phases (Ostwald's rule)

Taking this into account, the following solids are allowed to precipitate in the calculations when oversaturated:

- $PuO_2{:}2H_2O$ [1], $Pu(OH)_3$(am)
- Calcite, $CaCO_3$; magnesite, $MgCO_3$; brucite, $Mg(OH)_2$; gypsum, $CaSO_4{:}2H_2O$; mirabilite, $Na_2SO_4{:}10H_2O$
- Solids with organics, for example calcium oxalates

The following solids are excluded from calculations:

- Crystalline plutonium solids, PuO_2(s)

[1] This solid is written as $PuO_2{:}2H_2O$ in ThermoChimie. This nomenclature is maintained in the present report for practical reasons. However, it could be represented as PuO_2(am, hyd), as the number of waters present the formula is uncertain.

- Aragonite, $CaCO_3$; vaterite, $CaCO_3$; syngenite, $K_2Ca(SO4)_2$
- C(cr)

In the calculations, the different Pu oxidation states (Pu(VI), Pu(V), Pu(IV) and Pu(III)) are coupled. Furthermore, S(VI)/S(-II) and Fe(II)/Fe(III) are coupled; this is, sulphate is allowed to be reduced to sulfide and redox equilibria between Fe(II) and Fe(III) are included. This gave a more complete picture of the redox behavior of the different elements in the Pourbaix diagrams. Specific discussions related to microbial activity or the influence of radiolysis on the redox processes are out of the scope of present work.

The temperature for the calculations was 298.15 K (25°C).

The iron system, abundant due to the composition of the waste packages, is likely to control the redox state of the system. Given its relevance, and the variety of secondary corrosion products that iron may form, a discussion of the process and the implication on the control of the Pu system is included in section 3.2.

2.4.1 Geochemical codes

PhreeqC version 3.5.0 (Parkhurst and Appelo, 2013) was used to perform the calculations. In addition, GibbsStudio version 2 (Nardi and de Vries, 2017) and SPANA version 11-November-2018 (Puigdomènech, I. 2009) were used to support the graphical representation of the results. All codes are compatible with the use of TC10a-WIPP-2 database with the SIT approach.

3 Pu and Pu/Fe chemistry in the absence of organic ligands

Pu Pourbaix diagrams under GWBrine and ERDA-6 conditions in the absence of organic ligands are provided in the present section. A more detailed set of Pourbaix diagrams that show the speciation of plutonium and iron overlapped are presented in section 3.2; these results help provide insights on the E_h boundary conditions in the WIPP repository.

Extensive details are provided in the appendix (pages A35 to A56)

3.1 Pu chemistry in GWBrine and ERDA-6

Pu predominance diagrams in GWBrine and ERDA-6 in the absence of organic ligands (Table 2-1) are shown in Figure 3-1. Those results were calculated using the TC10a-WIPP-2 database with a total Plutonium concentration of $1 \cdot 10^{-8}$ M.

At pH ≈ 9.5 and E_h ≈ 0, the main aqueous plutonium species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can limit Pu aqueous concentrations. For the more reducing E_h conditions (E_h ≈ -0.5), $Pu(OH)^{2+}$ and $Pu(OH)_2^{+}$ are predicted to be the predominant Pu aqueous species and Pu(III) solid hydroxides may limit the Pu aqueous concentration.

Additional relevant Pourbaix diagrams in the absence of organics can be found in the appendix (pages A36 to A44 for GWBrine and A49 to A54 for ERDA-6).

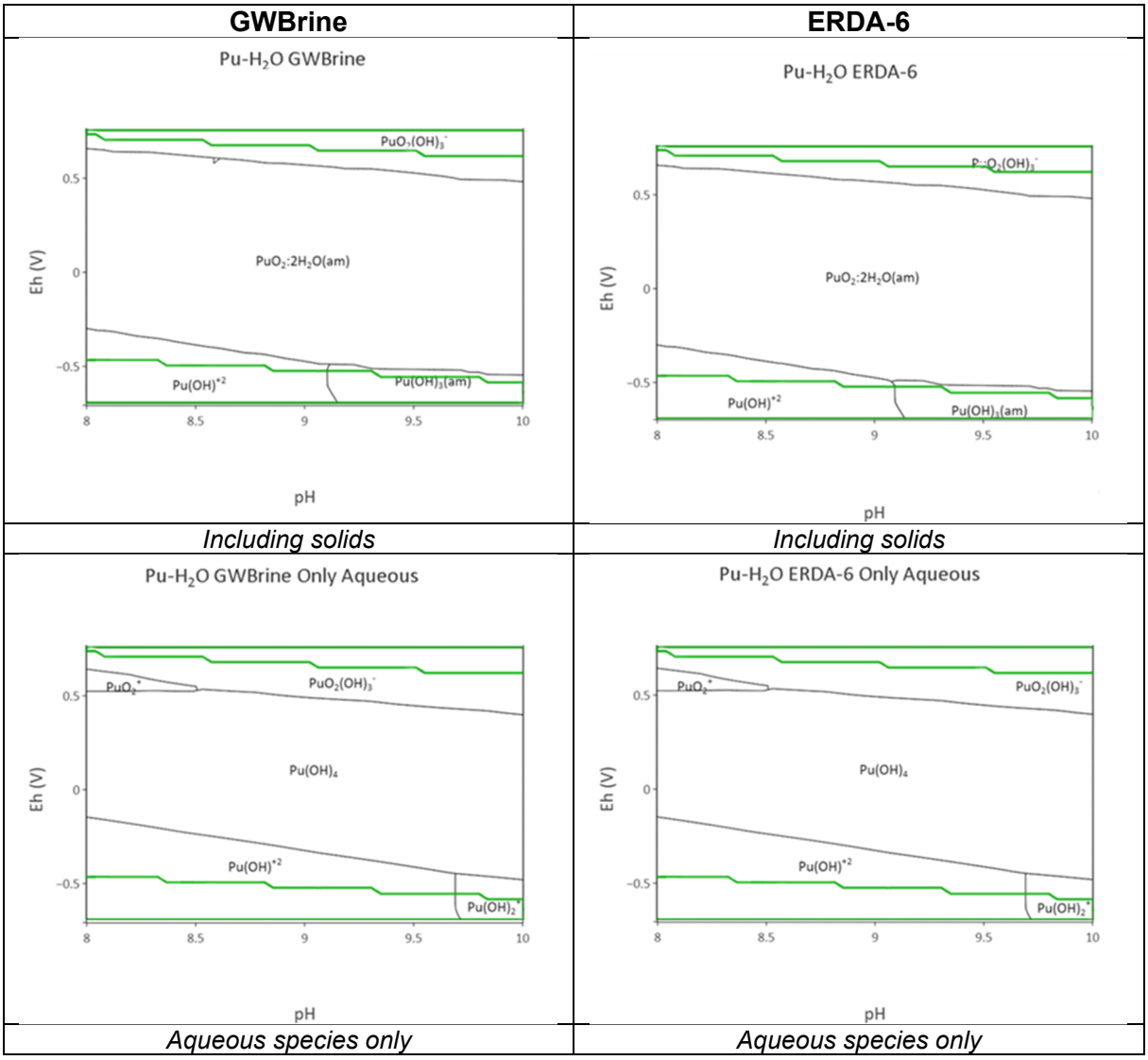


Figure 3-1: *Pu Pourbaix diagrams in GWBrine (left) and ERDA-6 (right) calculated with TC10a-WIPP-2 in the absence of organic ligands. $[Pu]_T=1\cdot10^{-8}$ M. Top: including solids. Bottom: aqueous species only. Green lines indicate the limits for water stability.*

Plutonium solubility (and the underlying aqueous speciation) are shown in Figure 3-2.

Figure 3-2 left shows the results of the calculation at Eh=0. At this E_h value and in the pH range 8-10, the plutonium solubility is expected to be very low, in the order of 10^{-11} M, and limited by PuO_2:$2H_2O$(am). The Pu aqueous chemistry is dominated by the Pu(IV) aqueous species $Pu(OH)_4$(aq).

In very reducing conditions (Eh=-0.5, Figure 3-2 right), the solubility may be controlled by Pu(III) solid hydroxides as $Pu(OH)_3$(am). The Pu aqueous chemistry is dominated by the Pu(III) species $Pu(OH)^{2+}$ and $Pu(OH)_2^{+}$ with contributions of Pu(IV) aqueous species $Pu(OH)_4$(aq).

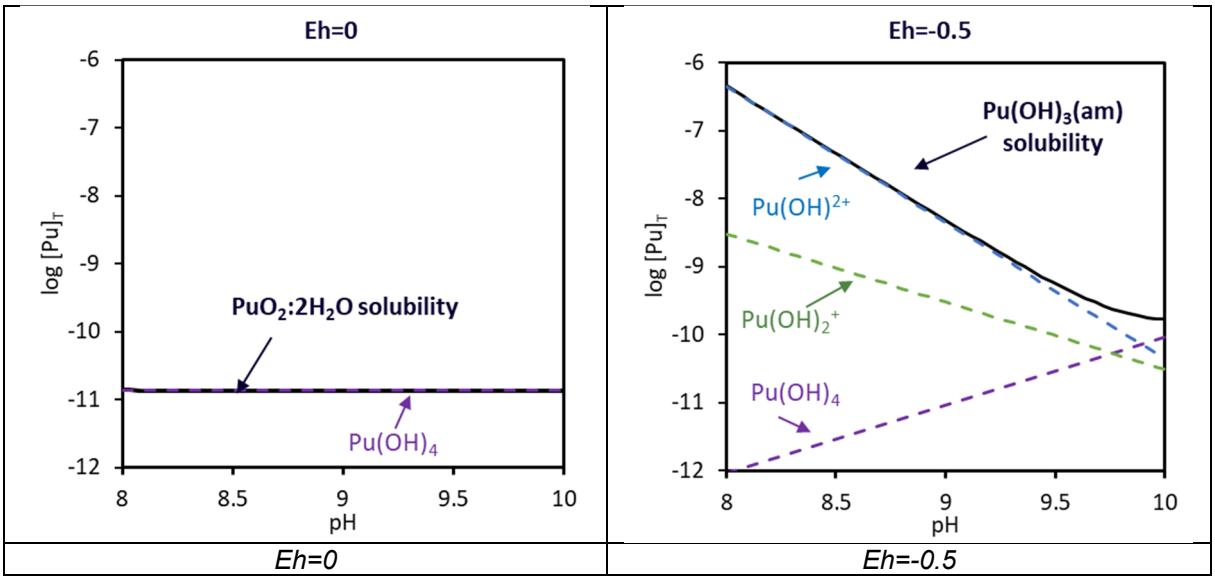


Figure 3-2: *Pu solubility in GWBrine calculated with TC10a-WIPP-2 in the absence of organic ligands. Left: at Eh=0. Right: at Eh=-0.5.*

A comparison between the calculated Pu(III) and Pu(IV) solubility with experimental data is provided in Figure 3-3; there is wide scatter and, at higher pH, some overlap in the experimental data for the oxidation-state specific solubilities. At pH ~ 9.5, the measured solubility of Pu(IV) and Pu(III) solid phases are essentially within experimental error of each other. Furthermore, there is a limited amount of $Pu(OH)_3$(am) experimental solubility data in the pH region 8-10. The Felmy et al. (1989) data shown in Figure 3-3 actually overestimates the Pu(III) solubility but these older data were developed to support the WIPP database and provide an upper bound to the solubility (see the discussion in Cho et al., 2016).

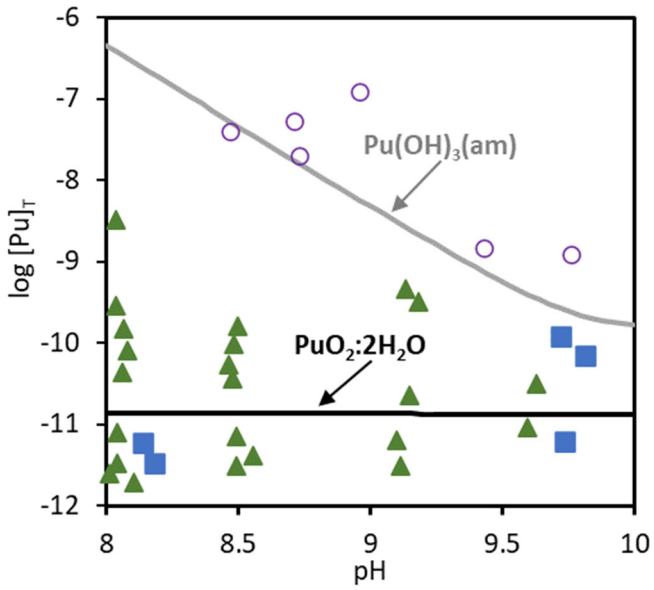


Figure 3-3: *Calculated $Pu(OH)_3(am)$ (grey line, Eh=-0.5V) or $PuO_2{:}2H_2O$ (black line, Eh=0V) solubility under GWBrine conditions. Empty symbols: experimental $Pu(OH)_3(am)$ solubility in PBB (Permian Bassin brines) from Felmy et al. (1989) (purple circles). Full symbols: Pu total concentration in solution at 0.1m NaCl in equilibrium with PuO_2(ncr, hyd) for systems buffered with hydroquinone (blue squares) and $SnCl_2$ (green triangles), from Tasi et al. (2018).*

3.2 The role of iron

Redox active metals such as iron are predicted to establish and maintain reducing conditions in WIPP. The phase relationships between the iron and plutonium system are illustrated in the overlapping Pu and Fe Pourbaix diagrams (Figure 3-4). These results help provide insights on the E_h boundary conditions in the WIPP repository.

Metallic iron is unstable in water. Its corrosion in oxic conditions may produce different type of Fe(III) solid phases, depending on the environment. Under the pH conditions prevalent in the

WIPP site, different Fe(III) oxides and hydroxides may form. Ferrihydrite[2], a poorly crystalline Fe(III) oxy-hydroxide, is commonly found in nature as it readily precipitates. More crystalline solid phases of Fe(III) can be formed with time under the conditions of the WIPP site, the most likely being Goethite (FeOOH) and Hematite (α-Fe_2O_3(s)).

Under anoxic conditions, the corrosion of metallic iron may lead to the formation of Fe(II) solid phases, such as $Fe(OH)_2$(s) and Fe(II) sulphides (amorphous FeS and pyrite) and also the so-called Green-Rusts, which contain different anions in their structure, such as Cl^-, SO_4^{2-} or NO_3^-. It is normally accepted that initially the corrosion of metallic iron (and that of iron present in steel) under anoxic conditions produces in the medium to long-term a mixed magnetite type Fe(II)-Fe(III) spinel. Magnetite (Fe_3O_4(s)) is therefore considered as the most likely solid phase to form and it is the anoxic corrosion product for steel and iron used in most assessments of the evolution of the redox conditions in underground repositories for radioactive waste (see for example Duro et al., 2013, Duro et al., 2014; Saheb et al., 2010, Schramke et al, 2020). Diagrams are provided in the appendix (A47, A48).

The uncertainty in the redox/pH field imposed by the iron system may arises from the different type of Fe(III) solid phases formed as well as from the sulphide solid phases formed (such as pyrite). This uncertainty can be captured by conducting several calculations assuming the different phases which may form (see appendix A47, A48).

The discussion in this work (see Figure 3-4) assumes that

- Ferrihydrite is the most likely Fe(III) corrosion product, which is metastable with respect to hematite and goethite and, therefore, able to prevail in the system for long-term periods
- Magnetite is the most likely Fe(III)-Fe(II) corrosion product under the conditions of the WIPP site, very relevant under anoxic conditions
- Pyrite (FeS_2) is the most likely solid phase to form if sulfide is present in the system; for example due to the reduction of sulphate catalyzed by microbial activity.

[2] Ferrihydrite is a Fe(III) solid with a low degree of crystallinity and a large amount of loosely associated water. Its exact solubility product will depend on the preparation and ageing procedures. The one solid used in the calculations in present work has a solubility product of Log Ks° = 2.54.

Other Fe(II) solid phases, such as siderite, are not predicted to form under the conditions of the repository. The complete set of calculations to help the discussion can be found in the appendix (A45-A48).

In Figure 3-4, the black arrow defines the E_h boundaries calculated taking into account the stability field of magnetite and the lower boundary of water stability defined by the H_2/H_2O reaction. Pu(IV) solid phase is expected to dominate the plutonium chemistry in most of this region, even in reducing conditions. As described in section 2.3.1, although the modifications in TC10a-WIPP-2 expand the $Pu(OH)_3$(am) and Pu(III) hydrolysis species stability field (in comparison with the original data in ThermoChimie version 10a), at pH values ≈ 9.5 Pu(III) only dominates plutonium chemistry in a small E_h region slightly above the lower boundary of water stability.

Additional details can be found in the appendix, pages A45-A47 and A54-A55.

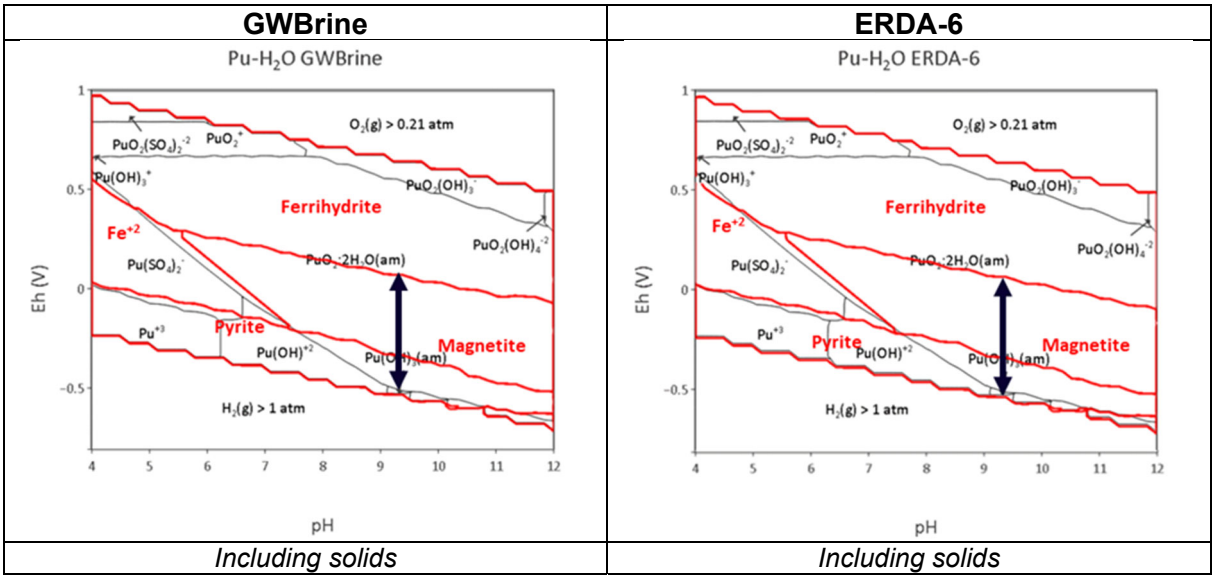


Figure 3-4: *Black lines: Pu Pourbaix diagrams in GWBrine (left) and ERDA-6 (right) calculated with TC10a-WIPP-2 in the absence of organic ligands, with* $[Pu]_T=1\cdot10^{-8}$ *M. Red lines represent the calculated Fe Pourbaix. Black arrow indicates the most representative* E_h *boundaries for WIPP calculations.*

4 Pu chemistry in the presence of organic ligands

An overview of key results on the effect of organic complexation on Pu chemistry are provided in section 4.1; details on calcium competition are provided in section 4.2. Extensive details are provided in the appendix (pages A57 to A81).

4.1 Pu chemistry in GWBrine and ERDA-6 in the presence of organic ligands

The current WIPP modelling approach requires an accounting for the impact of organic complexants, specifically acetate, oxalate, citrate and EDTA, on actinide speciation and solubility (U.S. DOE 2019a).

Pu predominance diagrams in GWBrine and ERDA-6 (Table 2-1) in the presence of organic ligands (Table 2-2) are shown in Figure 4-1. The results presented were calculated with TC10a-WIPP-2 database with a total Plutonium concentration of $1 \cdot 10^{-8}$ M. Notice that the role of citrate in Pu chemistry has not been evaluated due to the lack of reliable Pu-citrate thermodynamic data (no Pu-citrate complexes are included in the calculations). There also may be some missing high-pH species as this is an area still being evaluated.

At pH ≈ 9.5 and $E_h \approx 0$, the main aqueous plutonium species is predicted to be $Pu(OH)_4$. Pu(IV) is relatively unaffected by the presence of the organic ligands. For the more reducing E_h conditions (Eh≈-0.5), $Pu(EDTA)^-$ species may be formed that elevate the overall solubility .

The influence of EDTA (and other organics such as oxalate) on Pu speciation is limited in the presence of competing ions such as Ca. Specific details on the influence of calcium on EDTA are provided in next section.

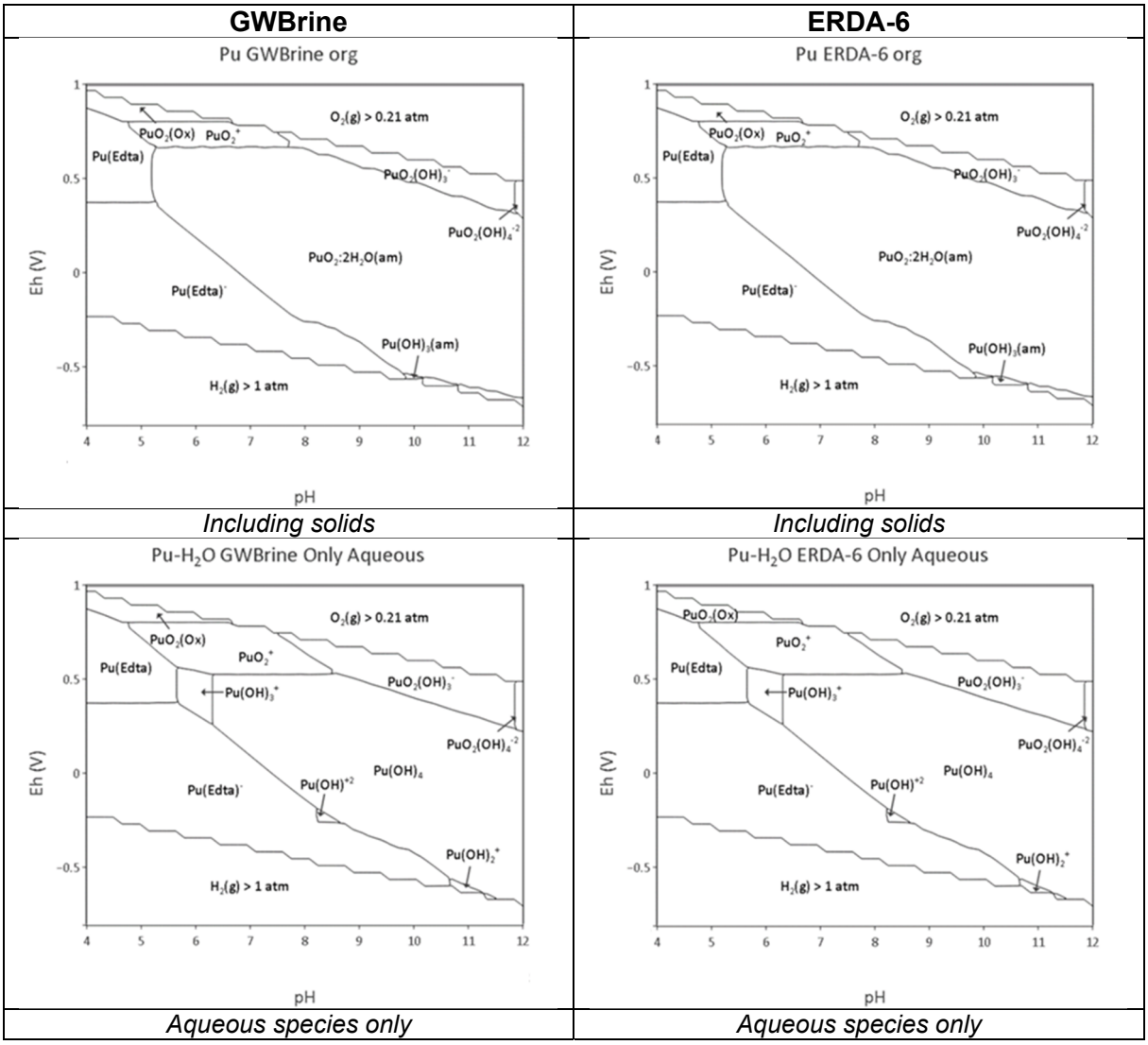


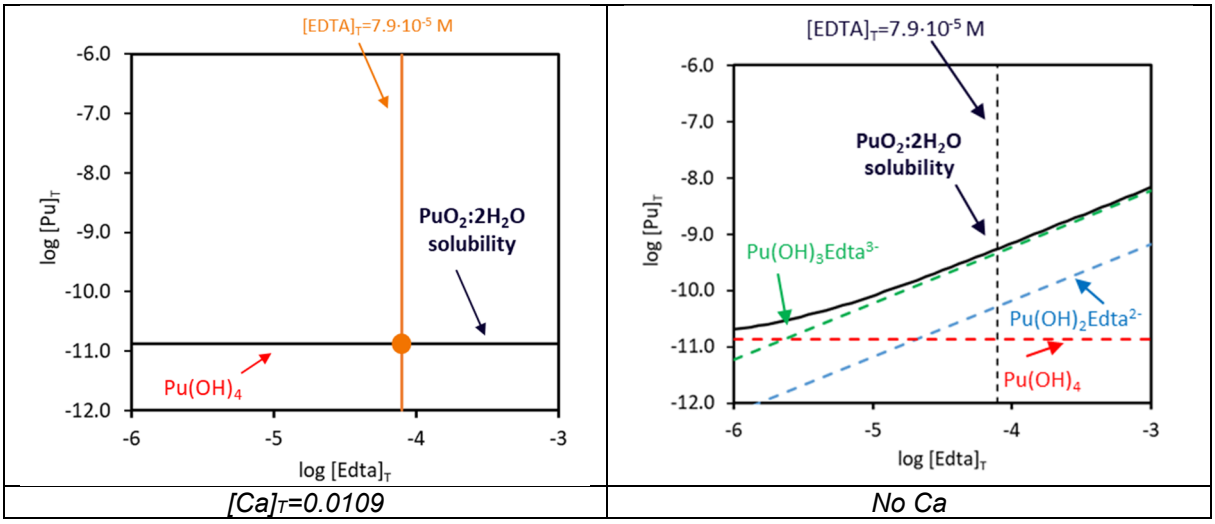
Figure 4-1: *Pu Pourbaix diagrams in GWBrine (left) and ERDA-6 (right) calculated with TC10a-WIPP-2 in the presence of organic ligands.* $[Pu]_T=1\cdot10^{-8}$ *M. Up: including solids. Down: Aqueous species only.*

4.2 Effect of EDTA on Pu chemistry: competition with calcium

Besides Pu, organic ligands are also expected to complex with other major elements present in the system, most importantly other actinides, calcium, magnesium, iron and lead. This can lead to a significant competition among the different elements.

This section provides additional supporting figures that illustrate the relevance of calcium in reducing the effect of organics (specifically EDTA) in Pu chemistry. The competition with Ca (and thus the formation of Ca-organic complexes and solids) were considered in the following calculations.

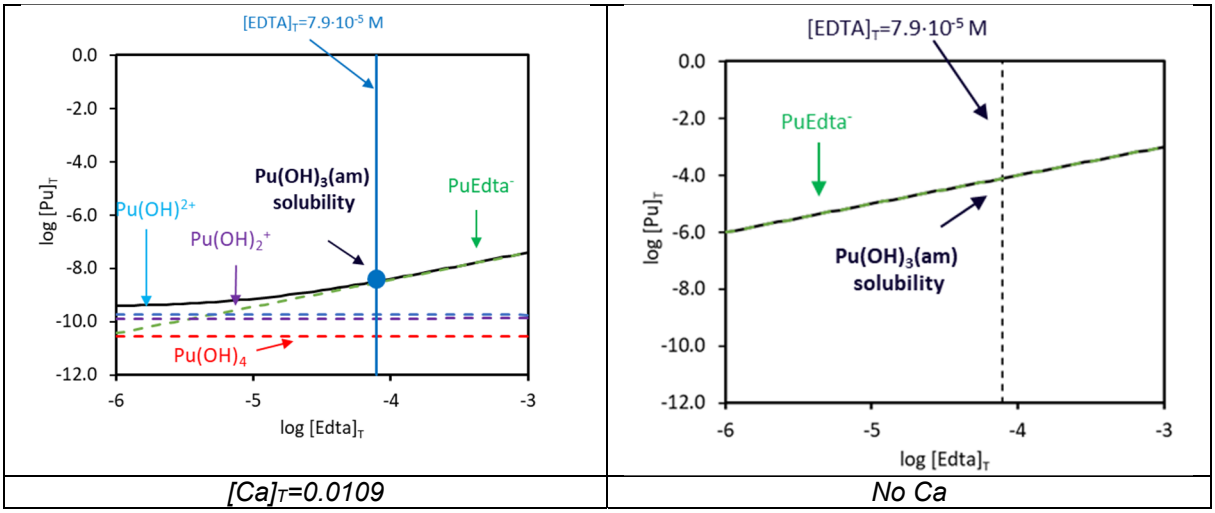
Figure 4-2 illustrates the role of calcium in Pu(IV)-EDTA chemistry by comparing PuO_2:$2H_2O$ solubility in the presence (left) and absence (right) of calcium. As seen in the figure, the presence of calcium in the repository significantly reduces the effect of EDTA in calculated Pu(IV) solubility.



[Ca]T=0.0109 | *No Ca*

Figure 4-2: *Calculated PuO_2:$2H_2O$ solubility in the presence of varying EDTA concentrations in the presence (left) and absence (right) of calcium. Vertical line indicates the assumed EDTA concentrations in the repository. 1 M NaCl, pH=9.5, E_h=0.*

Figure 4-3 illustrates the role of calcium in the Pu(III)-EDTA chemistry; here the presence of calcium also significantly reduces the effect of EDTA.



[Ca]T=0.0109	*No Ca*

Figure 4-3: *Calculated $Pu(OH)_3(am)$ solubility in the presence of varying EDTA concentrations in the presence (left) and absence (right) of calcium. Vertical line indicates the assumed EDTA concentrations in the repository. 1 M NaCl, pH=9.5, Eh=-0.5.*

5 Summary and conclusions

The purpose of the present report is the evaluation of Pu chemistry using Specific ion Interaction Theory (SIT) model for the ionic strength correction, without using oxidation state invariant analogues, under conditions relevant for WIPP. In this application, a more complete speciation model is being used relative to the current WIPP model although some error is introduced by not using a Pitzer-based modeling approach. These results are intended to provide support to the Los Alamos Actinide Chemistry and Repository Science Project (ACRSP) team in their objective to update the WIPP actinide/chemistry model.

Under the conditions defined by GWBrine or ERDA-6 compositions, the most relevant E_h range will be defined by magnetite/ferrihydrite boundary (upper limit) and by the lower limit for water stability (H_2/H_2O reaction).

At higher E_h values defined by this range (circle 1 in Figure 5-1), Pu(IV) solid hydroxides are the solubility-controlling phases and limit the Pu aqueous concentration. The solubility of plutonium remains low (typically around 10^{-11} M in the pH range 8-10) and the main aqueous Pu species is predicted to be $Pu(OH)_4$. The organic ligand influence on Pu(IV) speciation, primarily EDTA, leads to an increase of about an order of magnitude in solubility that is completely mitigated when the effects of competing ions such as Ca are taken into consideration. The same conclusions are true at the redox boundary between Magnetite and Pyrite (circle 3 in Figure 5-1).

At very reducing conditions (near the lower limit of water stability field (circle 2 in Figure 5-1), the Pu(III) amorphous solid hydroxides are the solubility controlling phase that defines the aqueous concentration. $Pu(OH)^{2+}$ and $Pu(OH)_2^{+}$ are the predominant Pu aqueous species in the absence of organic ligands. and the solubility is low (around 10^{-9} M at pH 9.5). $Pu(EDTA)^{-}$ is formed in the presence of EDTA, although calcium competition also greatly limits the effect of organics on the Pu(III) chemistry.

A simple scheme summarizing these conclusions is shown in Figure 5-1.

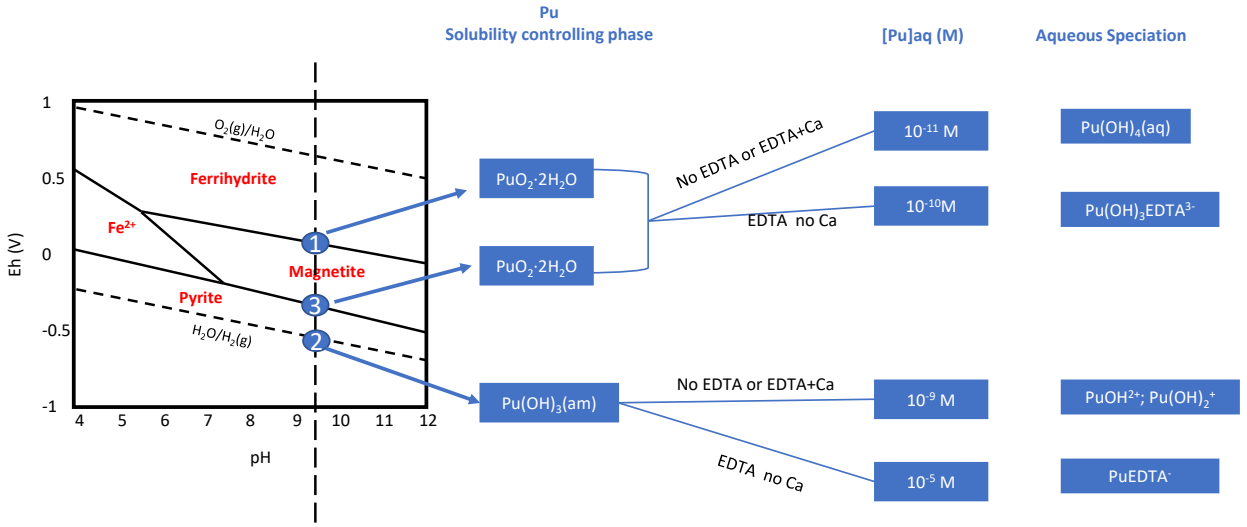


Figure 5-1. *Schematic view summarising the solubility controlling phases of Pu, its solubility and main speciation depending on the redox control exerted in the system.*

These data collectively show that the solubility of plutonium, when the effects of ions such as Ca competing for the complexation with organics are considered, is much lower (typically ~ two orders of magnitude) than those currently used in the WIPP performance assessment (based on analog data). This helps to reassess the degree of conservatism and provides additional confidence of the current WIPP strategy.

6 References

Altmaier, M., Neck, V., Lützenkirchen, J., & Fanghänel, T. 2009. Solubility of plutonium in $MgCl_2$ and $CaCl_2$ solutions in contact with metallic iron, Radiochimica Acta, 97(4-5), 187-192.

Cho, H. R., Youn, Y. S., Jung, E. C., & Cha, W. 2016. Hydrolysis of trivalent plutonium and solubility of $Pu(OH)_3(am)$ under electrolytic reducing conditions. Dalton Transactions, 45(48), 19449-19457.

Colàs, E., Grivé, M., Neall, F. 2017. Contractor Report to RWM: Review of thermodynamic data for radionuclides/non-radiological species and organics: Additional Data Selection. Version 1.

Domski, P. S., Sisk-Scott, C. 2019. Prediction of Baseline Actinide Solubilities for CRA 2019 with an updated EQ3/6 Pitzer thermodynamic database, DATA0.FM4.

Duro, L., Domènech, C., Grivé, M., Roman-Ross, G., Bruno, J., Källström, K. Assessment of the evolution of the redox conditions in the SKB ILW-LLW SFR-1 repository (Sweden) (2013) Materials Research Society Symposium Proceedings, 1518, pp. 211-216.

Duro, L., Domènech, C., Grivé, M., Roman-Ross, G., Bruno, J., & Källström, K. 2014. Assessment of the evolution of the redox conditions in a low and intermediate level nuclear waste repository (SFR1, Sweden). Applied Geochemistry, 49, 192-205.

Fellhauer, D., Neck, V., Altmaier, M., Lützenkirchen, J., & Fanghänel, T. 2010. Solubility of tetravalent actinides in alkaline CaCl2 solutions and formation of $Ca_4[An(OH)_8]^{4+}$ complexes: A study of Np(IV) and Pu(IV) under reducing conditions and the systematic trend in the An(IV) series, Radiochimica Acta, 98(9-11), 541-548.

Felmy, A. R., Rai, D., Schramke, J. A., & Ryan, J. L. 1989. The Solubility of Plutonium Hydroxide in Dilute Solution and in High-Ionic-Strength Chloride Brines, Radiochimica Acta, 48(1-2), 29-36.

Giffaut, E., Grivé, M., Blanc, P., Vieillard, P., Colàs, E., Gailhanou, H., Gaboreau, S., Marty, N., Madé, B., & Duro, L. 2014. Andra thermodynamic database for performance assessment: ThermoChimie. Applied Geochemistry, 49, 225–236.

Grivé, M., Duro, L., Colàs, E., & Giffaut, E. 2015. Thermodynamic data selection applied to radionuclides and chemotoxic elements: An overview of the ThermoChimie-TDB. Applied Geochemistry, 55, 85-94.

Hummel, W. 1993. Organic complexation of radionuclides in cement pore water: a case study. PSI report TM-41-93-03.

Lemire, R. J., Berner, U., Musikas, C., Palmer, D. A., Taylor, P., and Tochiyama, O. 2013. Chemical Thermodynamics of iron. Part I. OECD-NEA.

Nardi, A., de Vries, L.M., 2017. GibbsStudio. Barcelona Science Technologies SL, Barcelona, Spain. Retrieved from http://gibbsstudio.io

Parkhurst, D.L., Appelo, C.A.J., 2013. Description of input and examples for PHREEQC version 3 - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey. Retrieved from https://www.usgs.gov/software/phreeqc-version-3

Puigdomènech, I. 2009. Medusa: Make equilibrium diagrams using sophisticated algorithms. chemical equilibrium software. Retrieved from https://github.com/ignasi-p/eq-diagr/releases

Rai, D., Moore, D. A., Rosso, K. M., Felmy, A. R., and Bolton Jr, H. 2008. Environmental mobility of Pu(IV) in the presence of ethylenediaminetetraacetic Acid: Myth or Reality?. Journal of Solution Chemistry, 37(7), 957-986.

Saheb, M., Neff, D., Demory, J., Foy, E., Dillman, P., 2010. Characterisation of corrosion layers 32 formed on ferrous archaeological artefacts buried in anoxic media. Corros. Eng. Sci. Technol. 33 45, 381-387.

Schramke J.A., Santillan E.F.U., Peake R.T., 2020, Plutonium oxidation states in the Waste Isolation Pilot Plant repository, Applied Geochemistry, Volume 116, 2020, 104561, ISSN 0883-2927.

Tasi, A., Gaona, X., Fellhauer, D., Böttle, M., Rothe, J., Dardenne, K., Schild, D., Grivé, M., Colàs. E., Bruno, Källström, K., Altmaier, M., & Geckeis, H. 2018. Redox behavior and solubility of plutonium under alkaline, reducing conditions. Radiochimica Acta, 106(4), 259-279.

U.S. DOE. 2019a. Title 40 CFR Part 191, Subparts B and C. Compliance Recertification Application 2019 for the Waste Isolation Pilot Plant. Appendix SOTERM-2019. Actinide Chemistry Source Term. DOE/WIPP 2019. Carlsbad, NM; U.S. Department of Energy Carlsbad Field Office.

U.S. DOE. 2019b. Title 40 CFR Part 191, Subparts B and C. Compliance Recertification Application 2019 for the Waste Isolation Pilot Plant. Appendix GEOCHEM-2019. Implementation of Chemistry Conceptual Models. DOE/WIPP 2019. Carlsbad, NM; U.S. Department of Energy Carlsbad Field Office.

A1

AMPHOS 21

SCIENTIFIC AND STRATEGIC ENVIRONMENTAL CONSULTING



Appendix

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A2

Index

- Review of thermodynamic data in ThermoChimie version 10a
  - Modifications to thermodynamic data
  - Simplified Pourbaix diagrams: illustration of database changes
- Calculations of Pu Pourbaix diagrams – inorganic chemistry
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  - in GWB and ERDA brines
- Effect of EDTA (and other organics) on Pu chemistry: Calculation of Pourbaix diagrams
  - in NaCl
  - in GWB and ERDA brines
  - Effect of EDTA on Pu chemistry: competence with calcium
- Conclusions

- Appendix

Part I: Thermodynamic data

Part II: Inorganic calculations

Part III: Calculations including organics

A3

Part I: Thermodynamic data

- Review of thermodynamic data in ThermoChimie version 10a
  - Modifications to thermodynamic data
  - Simplified Pourbaix diagrams: illustration of database changes



A4

Thermodynamic data

Thermodynamic data (log K° values and SIT coefficients) used in the calculations

- Calculations have been made with ThermoChimie version 10a (TC10a) (www.thermochimie-tdb.com)
  - SPANA and PhreeqC database formats using the SIT approach
- Several modifications have been made in TC10a in the light of new data appearing in the literature. The modified database will be referred to as TC10a-WIPP-2.
- The following modifications have been implemented in TC10a-WIPP-2:
  - Following the approach used in the NEA-TDB, $NaCO_3^-$ and $NaHCO_3$ complexes have been eliminated from the database. SIT interaction coefficients $\varepsilon(Na^+, CO_3^{2-})$ and $\varepsilon(Na^+, HCO_3^-)$ are used to consider sodium/carbonate interactions
  - Pu inorganic data has been modified, considering latest publications
  - Data for Pb-EDTA, Pb-Ox and Pu-EDTA and Pu have been updated considering Colàs et al. (2017) (further details are provided in the appendix)
  - Following the suggestions in the NEA-TDB, data for Fe(II)-CI aqueous species have been modified
  - Data selection for Fe(III)-EDTA, Fe(II)-Citrate and Fe(III)-Citrate has been modified (further details are provided in the following slides)

Colàs et al. (2017): https://rwm.nda.gov.uk/publication/review-of-thermodynamic-data-for-radionuclides-non-radiological-species-and-organics-additional-data-selection/

A5

Part I: Thermodynamic data

- Review of thermodynamic data in ThermoChimie version 10a
  - Modifications to thermodynamic data
  - Simplified Pourbaix diagrams: illustration of database changes



Modifications to Pu thermodynamic data - INORGANIC

A6

The table summarizes modifications to TC 10a; other data remains unchanged

TC10a-WIPP-2

			log K° TC 10a	Reference TC 10a	log K° TC10a-WIPP-2	Reference TC10a-WIPP-2
Pu(III)	Aqueous	Pu(OH)+2	-6.90	01LEM/FUG	-6.20	16CHO/YOU, 19GAO/GRE
		Pu(OH)2+	-15.90	80ALL/KIP	-15.10	18TAS/GAO (analogy Am(III))
		Pu(OH)3(aq)	-25.30	80ALL/KIP	-26.20	18TAS/GAO (analogy Am(III))
		Pu(CO3)3-3	16.40	Estimation a)	15.20	Estimation b)
		Ca[Pu(OH)3]+2	not included	not included	-26.30	09ALT/NEC
		Ca2[Pu(OH)4]+3	not included	not included	-37.20	09ALT/NEC
		Ca3[Pu(OH)6]+3	not included	not included	-60.70	09ALT/NEC
		Pu(CO3)(OH)(s)	5.74	Estimation a)	6.27	Estimation b)
	Solids	Pu(OH)3(cr)	-15.80	01LEM/FUG	not included	
		Pu(OH)3(am)	not included	not included	-14.60	16CHO/YOU, 19GAO/GRE
Pu(IV)	Aqueous	Pu(CO3)2(OH)2-2	16.76	99RAI/HES	16.76	c)
		Pu(CO3)2(OH)3-3	not included	not included	not included	c)
		Ca4[Pu(OH)8]+4	not included	not included	-56.20	10FEL/NEC
Pu(V)	Aqueous	PuO2(OH)2-	not included	not included	-23.60	18TAS/GAO (analogy Np(V))
		PuO2CO3-	5.12	01LEM/FUG	4.95	09TOP/AUP
		PuO2(CO3)2-3	not included	not included	6.34	09TOP/AUP
		PuO2(CO3)3-5	5.03	01LEM/FUG	5.61	09TOP/AUP
Pu(VI)	Aqueous	PuO2(OH)3-	not included	not included	-20.30	18TAS/GAO (analogy U(VI))
		PuO2(OH)4-2	not included	not included	-32.40	18TAS/GAO (analogy U(VI))
		PuO2(CO3)	9.50	03GUI/FAN	9.34	18ALE/DAC
		PuO2(CO3)2-2	14.70	03GUI/FAN	14.99	18ALE/DAC
		PuO2(CO3)3-4	18.00	03GUI/FAN	17.94	18ALE/DAC

a) Estimation based on log K correlation with ionic radii
b) Updated estimation (also based on log K correlation with ionic radii)
c) According to Schepperle et al. (ABC-salt workshop 2019), the Pu(CO3)2(OH)3-3 (123 complex) should be predominant for the Pu(IV) system, but no log K data are available yet

- 16CHO/YOU: Cho et al. Dalton Trans. 2016; 6;45(48):19449
- 19GAO/GRE: Gaona et al. Migration2019 conference
- 09ALT/NEC: Altmaier et al. Radiochim. Acta 2009; 97(4-5): 187
- 18TAS/GAO: Tasi et al. Radiochim. Acta 2018; 106(4): 259
- 10FEL/NEC: Fellhauer et al. Radiochim. Acta 2010; 98(9-11): 541
- 09TOP/AUP: Topin et al. Electrophoresis 2009, 30, 1747
- 18ALE/DAC: Alexandre et al. Radiochim. Acta 2018; 106(10): 801–807

Modifications to Pu thermodynamic data – INTERACTION COEFFICIENTS

A7

The table summarizes modifications to TC 10a; other data remains unchanged

TC10a-WIPP-2

			Ɛ (i, j)	Reference	Ɛ (i, j)	Reference
	i	j	TC 10a	TC 10a	TC10a-WIPP-2	TC10a-WIPP-2
Pu(III)	Pu(OH)2+	Cl-	-0.29	Analogy Am(III)	-0.06	18TAS/GAO
Pu(IV)	Pu+4	Cl-	0.37	09RAN/FUG	0.4	18TAS/GAO
Pu(V)	PuO2+	Cl-	0.129	Estimation from ClO4-	0.09	18TAS/GAO
	PuO2(OH)2-	Na+	species not included	species not included	-0.01	18TAS/GAO
	PuO2(SO4)-	Na+	-0.74 b)	c)	-0.24	c)
Pu(VI)	PuO2+2	Cl-	0.223	Estimation from ClO4-	0.21	18TAS/GAO
	PuO2OH+	Cl-	-0.003	Analogy U(VI)	0.05	18TAS/GAO
	PuO2(OH)3-	Na+	species not included	species not included	-0.2	18TAS/GAO
	PuO2(OH)4-2	Na+	species not included	species not included	-0.12	18TAS/GAO
	(PuO2)2(OH)2+2	Cl-	-0.248	Analogy Np(VI)	0.69	18TAS/GAO
	PuO2(CO3)2-2	Na+	-0.7	01LEM/FUG	0.12	18ALE/DAC
	PuO2(CO3)3-4	Na+	-0.2	01LEM/FUG	0.14	18ALE/DAC

a) Ɛ(Na^+, $Pu(OH)_3(aq)$) reported in 18TAS/GAO is not included; interactions with neutral species not taken into account in the SPANA code.
b) Typing error in ThermoChimie 10a; the correct value is -0.24
c) Analogy with Np, calculated from ΔƐ value reported in Lemire et al. (2001)

- 18TAS/GAO: Tasi et al. Radiochim. Acta 2018; 106(4): 259
- 18ALE/DAC: Alexandre et al. Radiochim. Acta 2018; 106(10): 801–807

Modifications to ORGANIC thermodynamic data

A8

The table summarizes modifications to TC 10a; other data remains unchanged

TC10a-WIPP-2

			log K° TC 10a	Reference TC 10a	log K° TC10a-WIPP-2	Reference TC10a-WIPP-2
Pb(II)	Edta	Pb(H2Edta)	not included	not included	24.90	17COL/GRI
		Pb(HEdta)-	not included	not included	23.00	17COL/GRI
		Pb(Edta)-2	not included	not included	18.80	17COL/GRI
	Ox	Pb(Ox)	not included	not included	5.85	17COL/GRI
		Pb(Ox)2-2	not included	not included	8.05	17COL/GRI
		Pb(Ox)(cr)	not included	not included	11.13	17COL/GRI
Pu(IV)	Edta	Pu(OH)Edta-	not included	not included	24.44	17COL/GRI
		Pu(OH)2Edta-2	not included	not included	18.95	17COL/GRI
		Pu(OH)3Edta-3	not included	not included	9.33	17COL/GRI
Pu(III) Pu(IV) Pu(V) Pu(VI)	Citrate		not included	not included	not included	not included

No reliable data for Pu-citrate complexes are available in the literature.

- 17COL/GRI: Contractor Report to RWM: Review of thermodynamic data for radionuclides/non-radiological species and organics: Additional Data Selection https://rwm.nda.gov.uk/publication/review-of-thermodynamic-data-for-radionuclides-non-radiological-species-and-organics-additional-data-selection/

A9

Thermodynamic data for organics in TC10a-WIPP-2 (slide 1 of 3)

		Acetate	Citrate	EDTA	Oxalate
Acid/base	Aq.	Acetate- HAcetate	Cit-3 H(Cit)-2 H2(Cit)- H3(Cit)	Edta-4 H(Edta)-3 H2(Edta)-2 H3(Edta)- H4(Edta) H5(Edta)+ H6(Edta)+2	Ox-2 H(Ox)- H2(Ox)
	Solid		H3Cit:H2O(cr)	H4Edta(cr)	
Ca	Aq.	Ca(Acetate)+	Ca(Cit)- Ca(HCit) Ca(H2Cit)+	Ca(Edta)-2 Ca(HEdta)-	Ca(Ox) Ca(Ox)2-2
	Solid		Ca3(Cit)2:4H2O(s)		Ca(Ox):H2O(s) Ca(Ox):2H2O(s) Ca(Ox):3H2O(s)
Mg	Aq.		Mg(Cit)- Mg(HCit) Mg(H2Cit)+	Mg(Edta)-2 Mg(HEdta)-	Mg(Ox) Mg(Ox)2-2
	Solid				
Na	Aq.			Na(Edta)-3	
	Solid				
K	Aq.			K(Edta)-3	
	Solid				

In black: data already included in TC10a

In blue: data from Colàs et al. (2017) included in TC10a-WIPP-2



A10

Thermodynamic data for organics in TC10a-WIPP-2 (slide 2 of 3)

		Acetate	Citrate	EDTA	Oxalate
Fe(II)	Aq.		Fe(Cit)- Fe(H2Cit)+ Fe(HCit) Fe(OH)(Cit)-2	Fe(Edta)-2 Fe(HEdta)- Fe(OH)(Edta)-3 Fe(OH)2(Edta)-4	Fe(Ox) Fe(Ox)2-2 Fe(Ox)3-4
	Solid				
Fe(III)	Aq.		Fe(Cit) Fe(Cit)(OH)- Fe(Cit)2(OH)2-5 Fe(Cit)2-3 Fe(H2Cit)+2 Fe(HCit)(Cit)-2 Fe(HCit)+ Fe(HCit)2- Fe(OH)2(Cit)-2 Fe2(Cit)2(OH)2-2	Fe(Edta)- Fe(HEdta) Fe(OH)(Edta)-2 Fe(OH)2(Edta)-3 Fe(OH)3(Edta)-4 Fe2(OH)2(Edta)2-4	Fe(HOx)+2 Fe(Ox)+ Fe(Ox)2- Fe(Ox)3-3
	Solid				
Pb(II)	Aq.			Pb(H2Edta) (24.90) Pb(HEdta)- (23.00) Pb(Edta)-2 (18.80)	Pb(Ox) (5.85) Pb(Ox)2-2 (8.05)
	Solid				Pb(Ox)(cr) (11.13)

In black: data already included in TC10a
In blue: data from Colàs et al. (2017) included in TC10a-WIPP-2
In red: eliminated from the database

A11

Thermodynamic data for organics in TC10a-WIPP-2 (slide 3 of 3)

		Acetate	Citrate*	EDTA	Oxalate
Pu(III)	Aq.	Pu(Acetate)+2 Pu(Acetate)2+ Pu(Acetate)3		Pu(Edta)- Pu(HEdta)	PuOx+ Pu(Ox)2- Pu(Ox)3-3
	Solid				
Pu(IV)	Aq.	Pu(Acetate)+3 Pu(Acetate)2+2		Pu(Edta) Pu(OH)Edta- (24.44) Pu(OH)2Edta-2 (18.95) Pu(OH)3Edta-3 (9.33)	Pu(Ox)+2 Pu(Ox)2 Pu(Ox)3-2
	Solid				
Pu(V)	Aq.				
	Solid				
Pu(VI)	Aq.	PuO2(Acetate)+ PuO2(Acetate)2 PuO2(Acetate)3-			PuO2(Ox) PuO2(Ox)2-2
	Solid				PuO2(Ox):3H2O(s)

*No Pu-citrate species included in the calculations due to the lack of reliable data

In black: data already included in TC10a
In blue: data from Colàs et al. (2017) included in TC10a-WIPP-2



Modifications to Fe thermodynamic data - INORGANIC

A12

The table summarizes modifications to TC 10a; other data remains unchanged

TC10a-WIPP-2

		log K° TC 10a	Reference TC 10a	log K° TC10a-WIPP-2	Reference TC10a-WIPP-2
Fe(II)	FeCl+	0.14	91PEA/BER in 98CHI	-1.00 ± 0.80	a)
	FeCl2(aq)	-0.52	95CHI	-	Not included in the calculations b)
	FeCl3-	1.02	95CHI	-	Not included in the calculations b)
Fe(II)-Fe(III)	GR-Cl(s)	-	Not included	43.00	99BOU/TRO c)
	GR-CO3(s)	-	Not included	57.60	99BOU/TRO c)
	GR-SO4(s)	-	Not included	60.94	99BOU/TRO c)
Fe(III)	Ferrihydrite	-2.54±0.10	63SCH/MIC	-2.54±0.10	63SCH/MIC
	Ferrihydrite			-4.00	d)

			Ɛ (i, j)	Reference	Ɛ (i, j)	Reference
	i	j	TC 10a	TC 10a	TC10a-WIPP-2	TC10a-WIPP-2
Fe(II)	Fe+2	Cl-	-	Not included	0.17±0.01	a)
	FeCl+	Cl-	-	Not included	0.16±0.01	a)

a) Suggested but not selected in Lemire et al. (2013) (NEA-TDB review for iron).
b) No data suggested in Lemire et al. (2013) (NEA-TDB review for iron).
c) Green Rusts are metastable Fe(II)/Fe(III) solid phases for which exact formula and stability are difficult to stablish. The thermodynamic data in the table is used only for scooping calculations in present work.
d) Upper limit for ferrihydrite stability suggested but not selected in Lemire et al. (2013) (NEA-TDB review for iron). Used for sensitivity calculations in present work.

- 91PEA/BER: Pearson and Berner 1991. Nagra database.
- 98CHI: Chivot 1998. Andra report.
- 95CHI: Chivot 1995. Andra report.
- 99BOU/TRO: Bourrie et al. GCA 1999; 63: 3417
- 63SCH/MIC: Schindler et al. Helvetica Chimica Acta 1963; 46: 444

Modifications to Fe thermodynamic data - ORGANIC

A13

The table summarizes modifications to TC 10a; other data remains unchanged

TC10a-WIPP-2

		log K° TC 10a	Reference TC 10a	log K° TC10a-WIPP-2	Reference TC10a-WIPP-2
Fe(II)	**Fe(H2Cit)+**	24.70 a)	95AKR/BOU	13.64	91DUF/JOH in 00KON/KON
	Fe(OH)(Cit)-2	1.50±0.58	95AKR/BOU	-0.86	91DUF/JOH in 00KON/KON
Fe(III)	**Fe(H2Cit)+2**	30.40 a)	95AKR/BOU	13.20	82NAM/PAL in 00KON/KON
	Fe(Cit)2(OH)2-5	3.44±0.62	95AKR/BOU	-	Eliminated b)
	Fe(Edta)(OH)3-4	8.30±0.90 c)	51SCH/HEL in 95AKR/BOU	-2.24	51SCH/HEL

a) Data extracted from previous data compilations. According to 95AKR/BOU the value is uncertain as it is not possible to trace it to the original source or confront it to additional publications.
b) Eliminated, this species is not taken into account in other papers or data compilations.
c) The value reported in 95AKR/BOU is not correct; it is not in agreement with the one reported in the original source

- 95AKR/BOU: Akram and Bourbon 1995. Andra report.
- 91DUF/JOH: Duffield et al. Polyhedron 1991; 10: 1121
- 00KON/KON: Königsberger et al. J. Inorg. Biochem. 2000; 78:175
- 82NAM/PAL: Mamczák et al. Chem. zvesti 1982; 36:333
- 51SCH/HEL: Schwarzenbach et al. Helvetica Chimica Acta 1951; 34:576



A14

Part I: Thermodynamic data

- Review of thermodynamic data in ThermoChimie version 10a
  - Modifications to thermodynamic data
  - Simplified Pourbaix diagrams: illustration of database changes



Simplified Pu Pourbaix diagrams: database changes

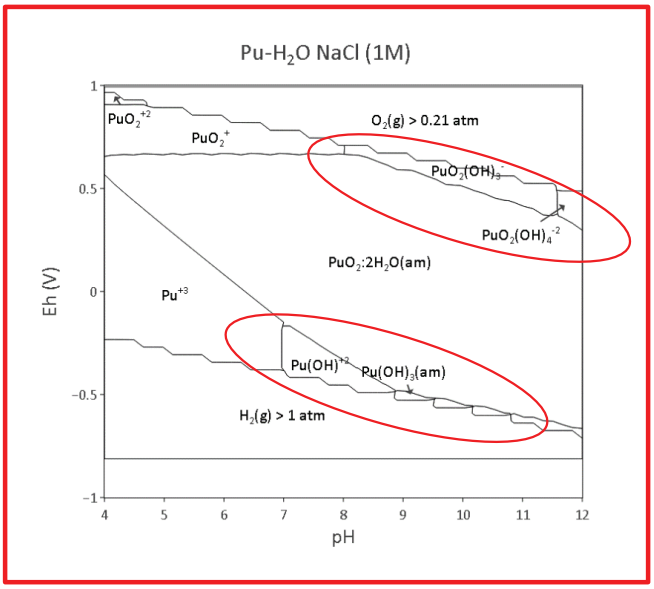
Effect of database changes in Pu solid oxides and aqueous hydroxides

1 M NaCl
$[Pu]_{(tot)}=10^{-8}$ M

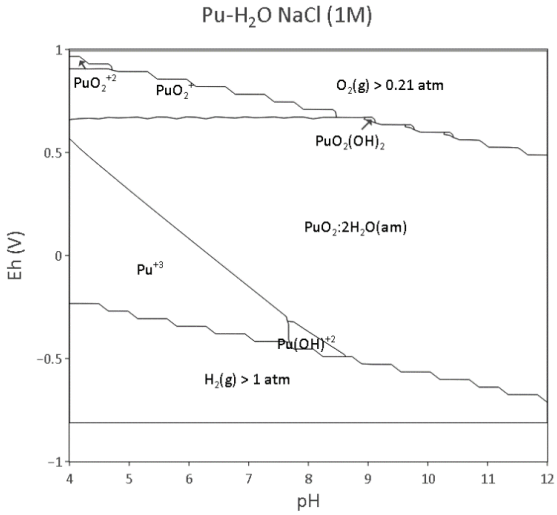
A15

*PuO_2(s) is not allowed to precipitate in the calculations

INCLUDING SOLIDS*



With TC10a-WIPP-2



With TC 10a

- Higher stability of Pu(III) species, slightly above the water stability field
- Differences in Pu(VI) speciation due to the inclusion of $PuO_2(OH)_3^-$ and $PuO_2(OH)_4^{2-}$

Simplified Pu Pourbaix diagrams: database changes

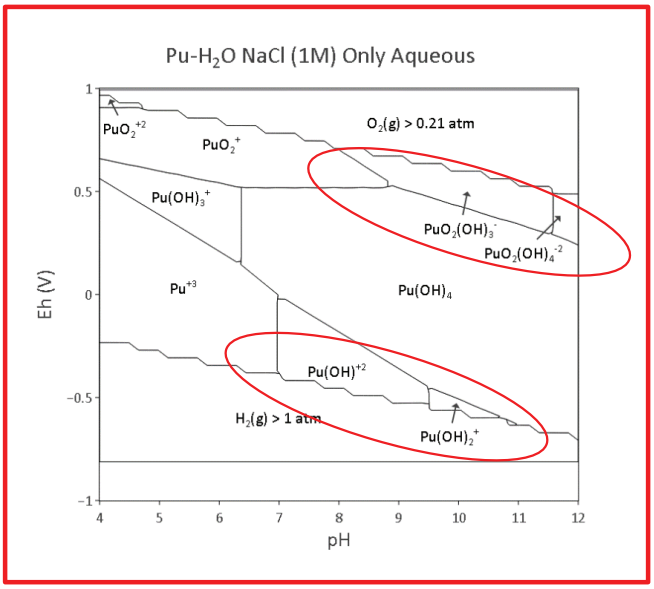
Effect of database changes in Pu aqueous hydroxides

1 M NaCl
$[Pu]_{(tot)}=10^{-8}$ M

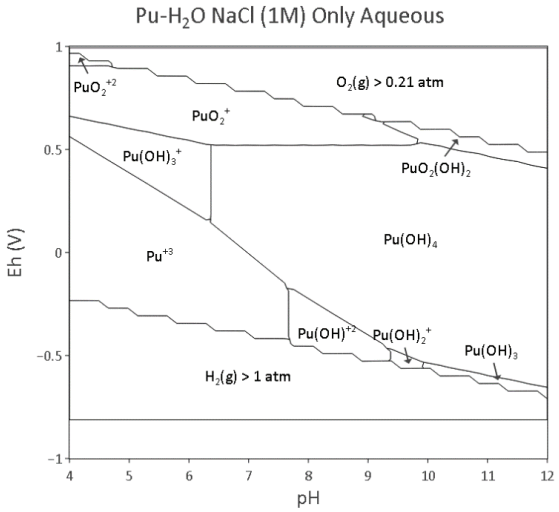
A16

*PuO_2(s) is not allowed to precipitate in the calculations

AQUEOUS SPECIES ONLY



With TC10a-WIPP-2



With TC 10a

- Higher stability of Pu(III) species, slightly above the water stability field
- Differences in Pu(VI) speciation due to the inclusion of $PuO_2(OH)_3^-$ and $PuO_2(OH)_4^{2-}$

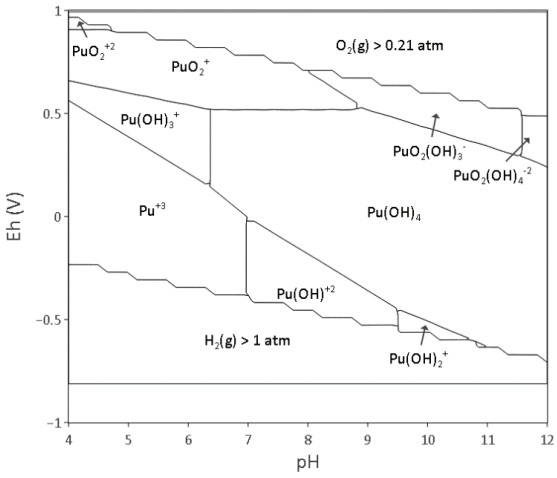
Simplified Pu Pourbaix diagrams: database changes

A17

Effect of Ca in Pu chemistry

AQUEOUS SPECIES ONLY

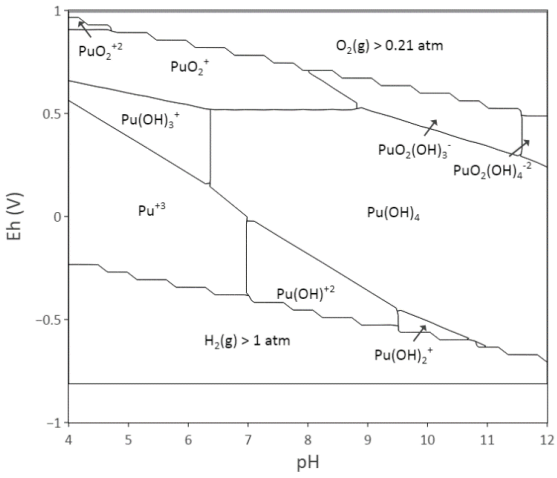
Pu-H_2O NaCl (1M) Only Aqueous



With TC10a-WIPP-2

1 M NaCl
No Ca
$[Pu]_{(tot)}=10^{-8}$ M

Pu-H_2O-Ca NaCl (1M) Only Aqueous



With TC10a-WIPP-2

1 M NaCl
[Ca]=0.0109 M *
$[Pu]_{(tot)}=10^{-8}$ M

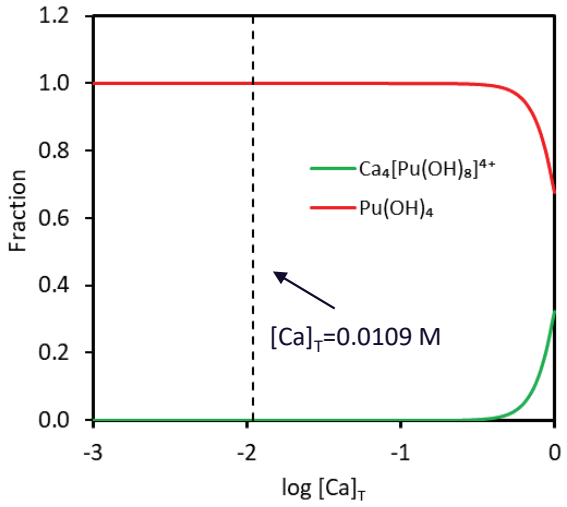
- Ca-Pu(III)-OH and Ca-Pu(IV)-OH complexes are not formed at the Ca concentrations used in the calculations (see next slide).

* Calcium concentration reported in "prediction of baseline Actinide solubilities for CRA 2019", table 6, GWBrine

Simplified Pu Pourbaix diagrams: database changes

A18

Effect of Ca in Pu chemistry



With TC10a-WIPP-2

1 M NaCl
pH=11.7
Eh=0
[Ca]=varied
$[Pu]_{(tot)}=10^{-11}$ M

Simplified Pu Pourbaix diagrams: database changes

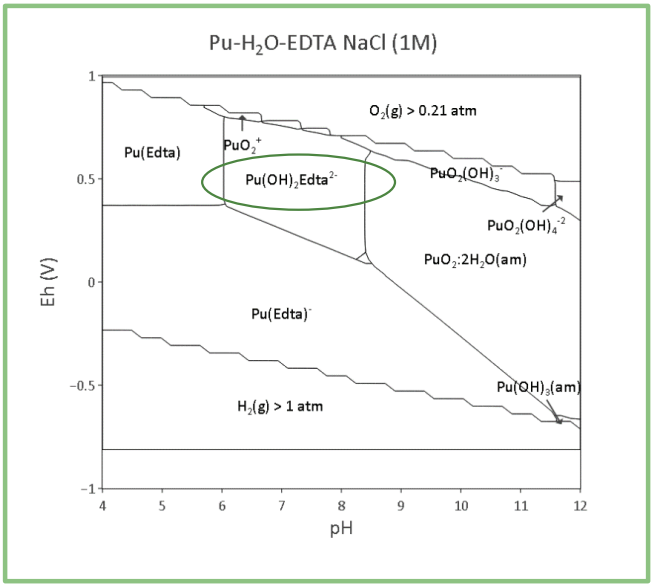
Effect of Edta in Pu chemistry

1 M NaCl
[Edta]=7.9·10^{-5} M *
[Pu]$_{(tot)}$=10^{-8} M

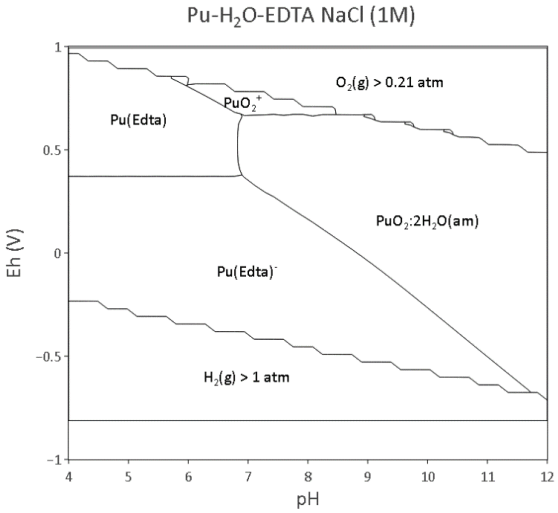
A19

INCLUDING SOLIDS*

*PuO_2(s) is not allowed to precipitate in the calculations



With TC10a-WIPP-2



With TC 10a

- The inclusion of Pu(IV)-OH-EDTA species affects Pu(IV) chemistry in neutral to alkaline pH region

* EDTA concentration reported in "prediction of baseline Actinide solubilities for CRA 2019", table 3, dissolved concentrations for organic ligands

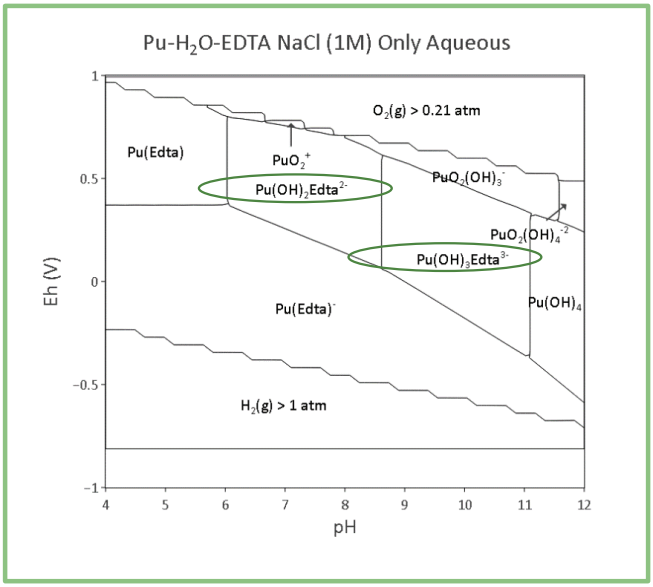
Simplified Pu Pourbaix diagrams: database changes

Effect of Edta in Pu chemistry

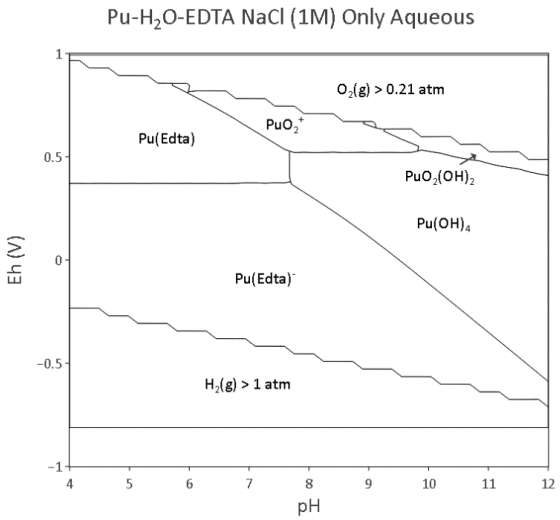
1 M NaCl
[Edta]=7.9·10^{-5} M *
[Pu]$_{(tot)}$=10^{-8} M

A20

AQUEOUS SPECIES ONLY



With TC10a-WIPP-2



With TC 10a

- The inclusion of Pu(IV)-OH-EDTA species affects Pu(IV) chemistry in neutral to alkaline pH region

* EDTA concentration reported in "prediction of baseline Actinide solubilities for CRA 2019", table 3, dissolved concentrations for organic ligands

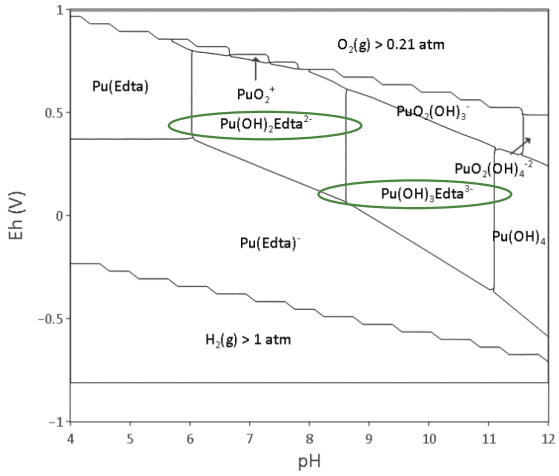
Simplified Pourbaix diagrams: database changes

A21

Effect of Ca and Edta in Pu chemistry

AQUEOUS SPECIES ONLY

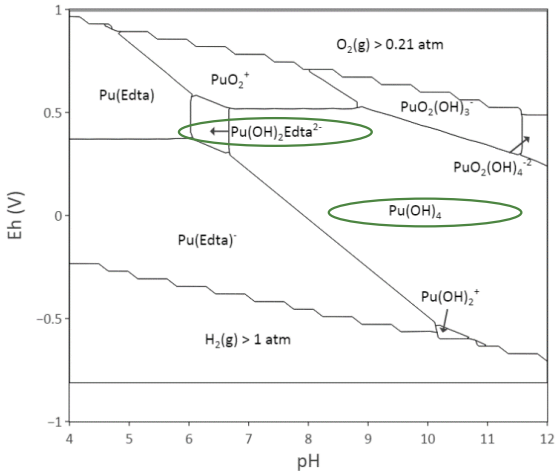
Pu-H_2O-EDTA NaCl (1M) Only Aqueous



With TC10a-WIPP-2

1 M NaCl
[Edta]=7.9·10^{-5} M
No Ca
$[Pu]_{(tot)}=10^{-8}$ M

Pu-H_2O-Ca-EDTA NaCl (1M) Only Aqueous



With TC10a-WIPP-2

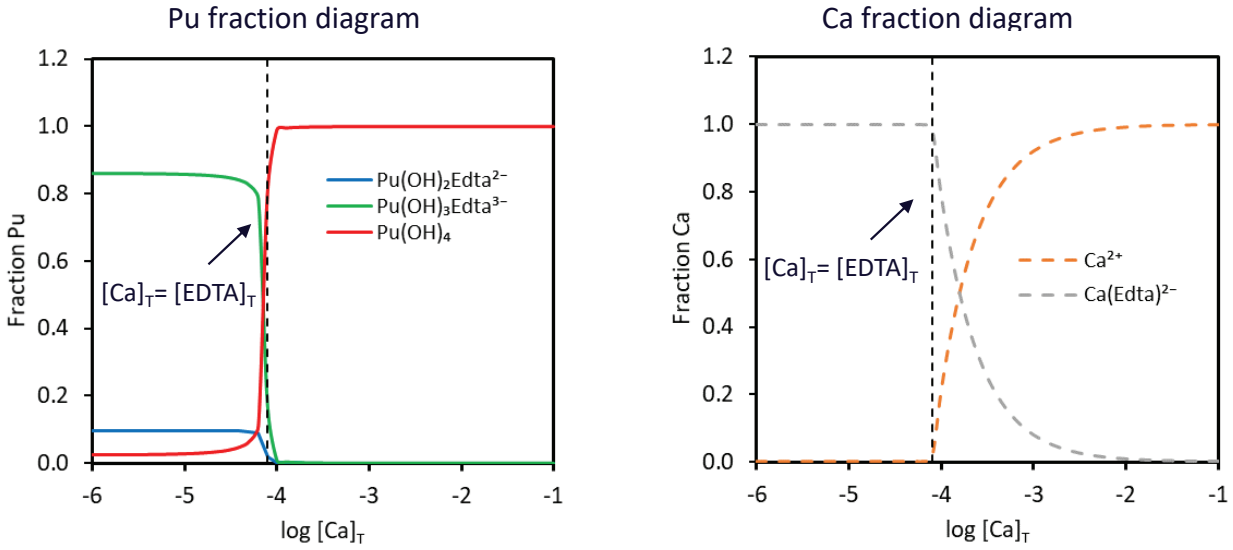
1 M NaCl
[Edta]=7.9·10^{-5} M
[Ca]=0.0109 M
$[Pu]_{(tot)}=10^{-8}$ M

- Ca competes with Pu(IV) for complexation with EDTA (see next slide).

Simplified Pourbaix diagrams: database changes

A22

Effect of Ca and Edta in Pu chemistry



With TC10a-WIPP-2

1 M NaCl
pH=9.5
Eh=0
[Edta]=7.9·10^{-5} M
[Ca]=varied
$[Pu]_{(tot)}=10^{-11}$ M

- Ca competes with Pu(IV) for complexation with EDTA.

Simplified Fe Pourbaix diagrams: database changes

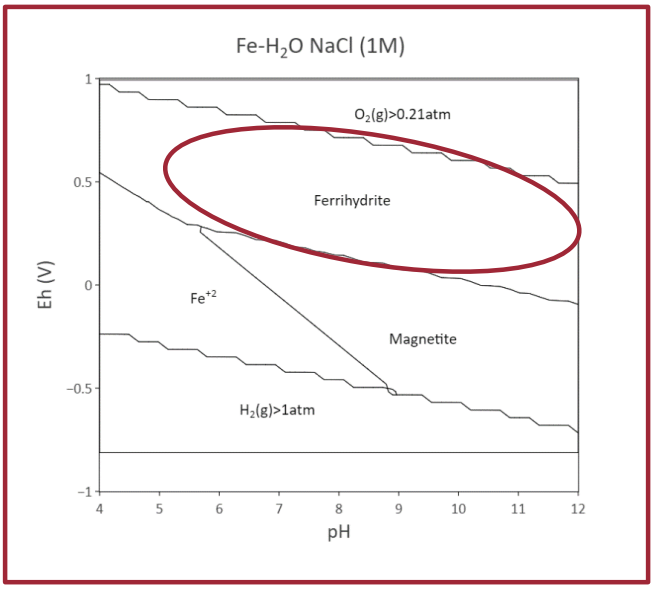
Ferrihydrite stability constant

1 M NaCl
$[Fe]_{(tot)}=2.61\cdot10^{-5}$ M

A23

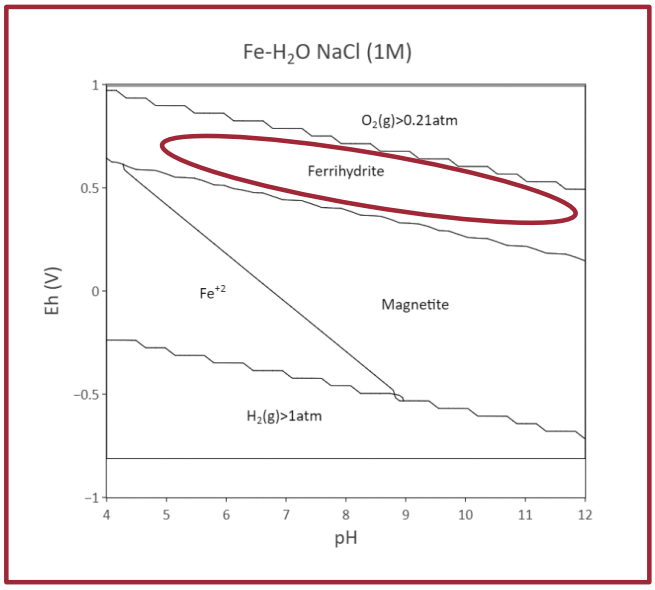
* Total Fe concentration used in calculations. Fe concentration reported in "prediction of baseline Actinide solubilities for CRA 2019", table 6

INCLUDING SOLIDS



With TC10a-WIPP-2

Ferrihydrite log K°=-2.54



With TC10a-WIPP-2

Ferrihydrite log K°=-4

- Changing the ferrihydrite stability modifies ferrihydrite/magnetite boundary
- Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

A24

Simplified Pourbaix diagrams: impact of database modifications

Pu

- Pu(III) aqueous speciation: the modification of Pu(III)-H_2O stability constants implies a higher stability of Pu(III) species, slightly above the water stability field.
- Pu(VI) aqueous speciation: differences due to the inclusion of $PuO_2(OH)_3^-$ and $PuO_2(OH)_4^{2-}$
- Ca-Pu(III)-OH and Ca-Pu(IV)-OH complexes are not formed at Ca concentrations used in the calculations.
- Pu(IV)-OH-EDTA species affects Pu(IV) stability and speciation in neutral to alkaline pH region.
- Ca competes with Pu(IV) for complexation with EDTA.
- Due to the lack of reliable data, no Pu-citrate complexes are included in the calculations.

Fe

- There is a lack of reliable thermodynamic data for Fe(II)-Cl system ; the aqueous Fe(II)-Cl speciation at high chloride concentrations is uncertain.
- Ferrihydrite stability depends on the crystallinity of the solid.



A25

Part II: Inorganic calculations

- Calculations of Pu Pourbaix diagrams – inorganic chemistry
  - in NaCl
  - in GWB and ERDA brines



Methodology

A26

Methodology for the calculations in the absence of organic ligands

- S(VI)/S(-II) and Fe(II)/Fe(III) are coupled in the calculations
- Not included in the calculations:
  - PuO_2(s)
  - Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations
  - Aragonite, vaterite, syngenite ($K_2Ca(SO_4)_2$)
  - CH_4(aq), CH_4(g), C(cr), CO(g)
- Solids allowed to precipitate if oversaturated:
  - $PuO_2:2H_2O$*, $Pu(OH)_3$(am)
  - Calcite, magnesite, brucite, gypsum, mirabilite
  - Ferrihydrite (log K°=2.54), Magnetite, Pyrite, $Fe(OH)_2$(cr)
  - Green Rust: GR-Cl(s), GR-CO_3(s), GR-SO_4(s)

*Although this solid is written as $PuO_2:2H_2O$ in ThermoChimie for practical reasons, it can also be written as PuO_2(am, hyd), as the number of waters present the formula is uncertain.



A27

Part II: Inorganic calculations

- Calculations of Pu Pourbaix diagrams – inorganic chemistry
  - in NaCl
  - in GWB and ERDA brines



NaCl

A28

Water composition used in the calculation of the
NaCl POURBAIX DIAGRAMS - INORGANIC

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	0	
Br	0	
Pb	0	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams

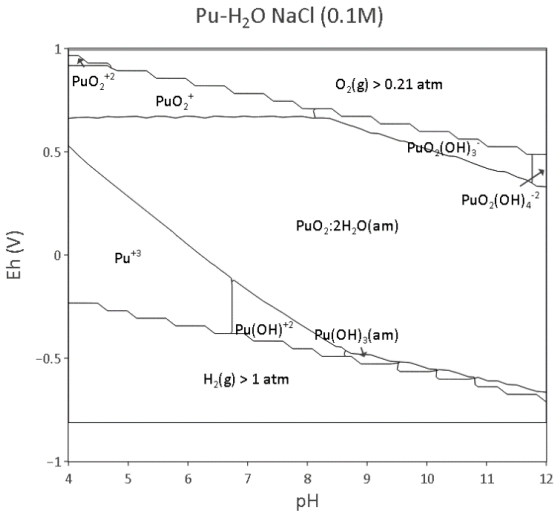
Results in NaCl

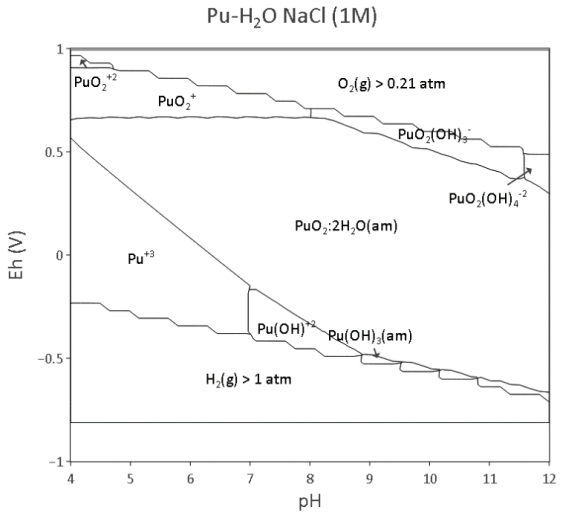
Pu predominance diagrams in NaCl – including solids

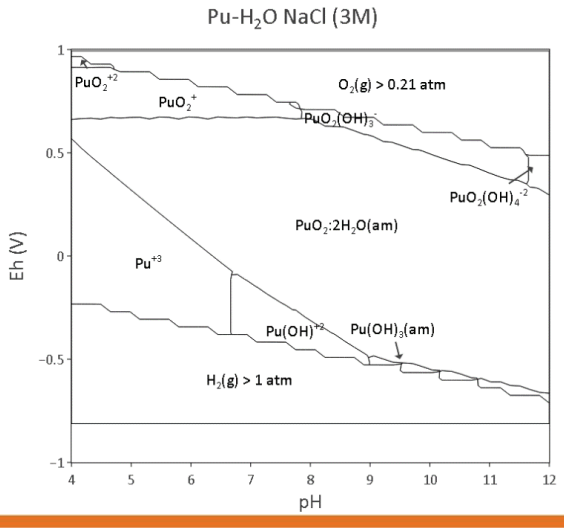
With TC10a-WIPP-2
0.1-1-3-5 M NaCl
$[Pu]_{(tot)}=10^{-8}$ M

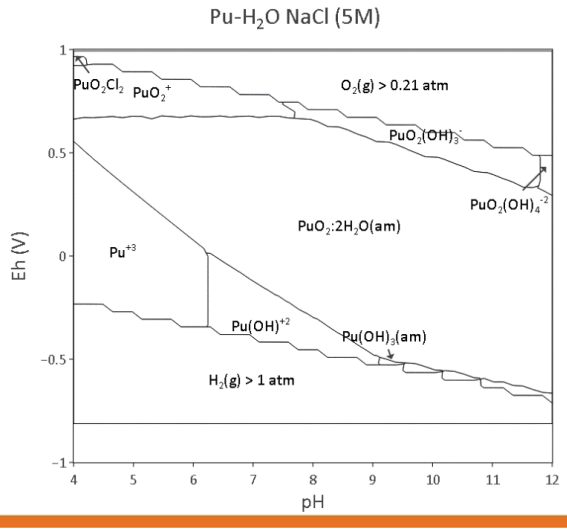
A29

INCLUDING SOLIDS









Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS - INORGANIC

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	0	
Br	0	
Pb	0	
pH		Varied from 4 to 12
Pu	$1\text{-}10^{-8}$	Pu concentration in Pourbaix diagrams

- At pH≈9.5 Pu(III) species are stable slightly above the water stability field

Results in NaCl

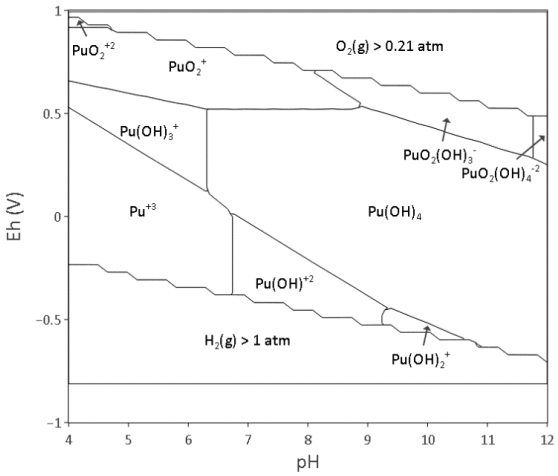
With TC10a-WIPP-2
0.1-1-3-5 M NaCl
$[Pu]_{(tot)}=10^{-8}$ M

A30

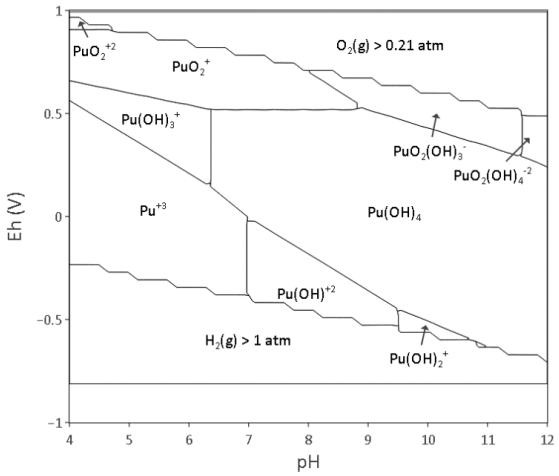
Pu predominance diagrams in NaCl – aqueous species only

AQUEOUS SPECIES ONLY

Pu-H_2O NaCl (0.1M) Only Aqueous



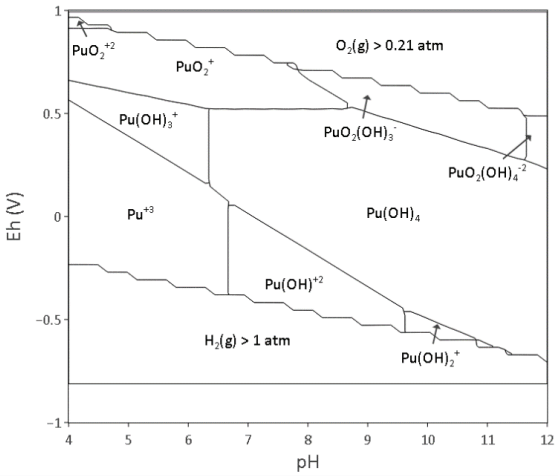
Pu-H_2O NaCl (1M) Only Aqueous



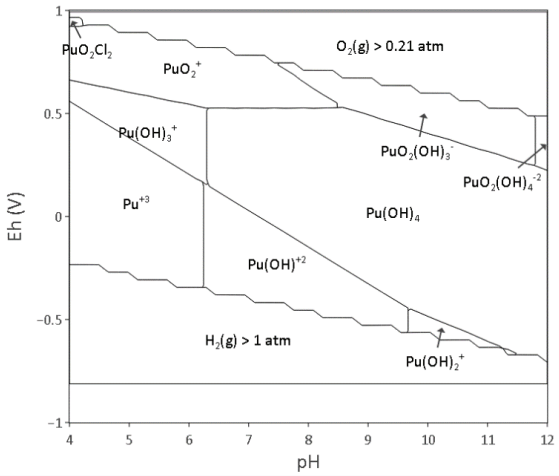
Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS - INORGANIC

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	0	
Br	0	
Pb	0	
pH		Varied from 4 to 12
Pu	$1\text{-}10^{-8}$	Pu concentration in Pourbaix diagrams

Pu-H_2O NaCl (3M) Only Aqueous



Pu-H_2O NaCl (5M) Only Aqueous



- At pH≈9.5 Pu(III) species are stable slightly above the water stability field
- Stability of charged species (e.g. Pu^{3+}) varies with ionic strength

A31

NaCl + Fe

Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS – INORGANIC INCLUDING IRON

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	$2.61 \cdot 10^{-5}$	As in GWBrine
Br	0	
Pb	0	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams

Overlapping Pu and Fe Pourbaix diagrams provides insights on expected boundaries for the Eh conditions.

- Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

Results in NaCl + Fe

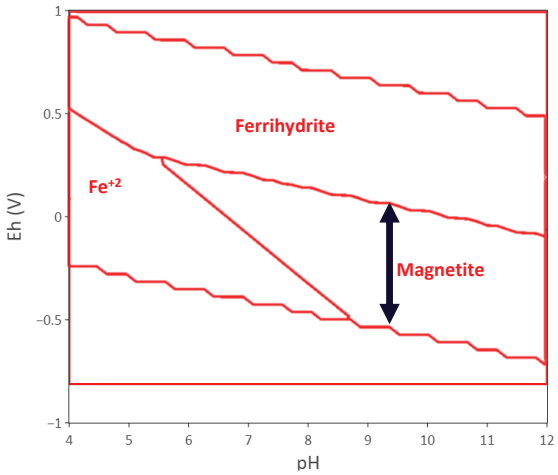
Fe predominance diagrams in NaCl – including solids

With TC10a-WIPP-2
0.1-1-3-5 M NaCl
$[Fe]_{(tot)}=2.61^{-5}$ M
$[Pu]_{(tot)}=10^{-8}$ M

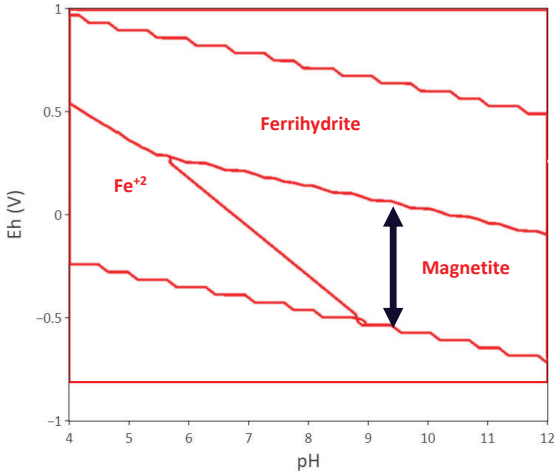
A32

INCLUDING SOLIDS

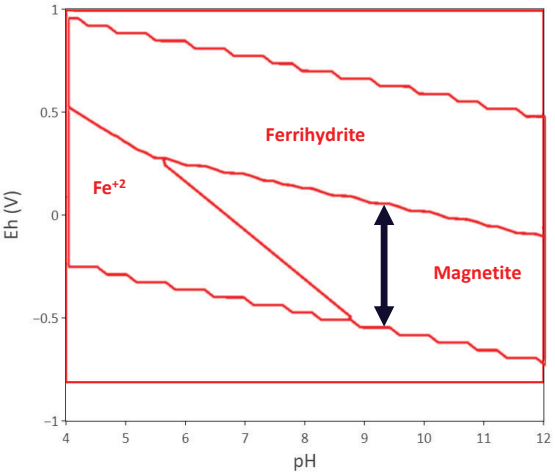
Fe-H_2O NaCl (0.1 M)



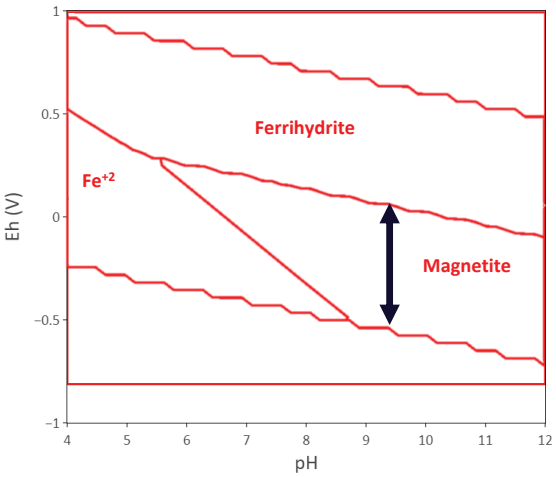
Fe-H_2O NaCl (1 M)



Fe-H_2O NaCl (3 M)



Fe-H_2O NaCl (5 M)



Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS – INORGANIC INCLUDING IRON

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	$2.61 \cdot 10^{-5}$	As in GWBrine
Br	0	
Pb	0	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams

- Magnetite is an Fe(II)-Fe(III) solid likely to dominate Fe chemistry under reducing equilibrium conditions.
- Most likely Eh boundaries will be defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)

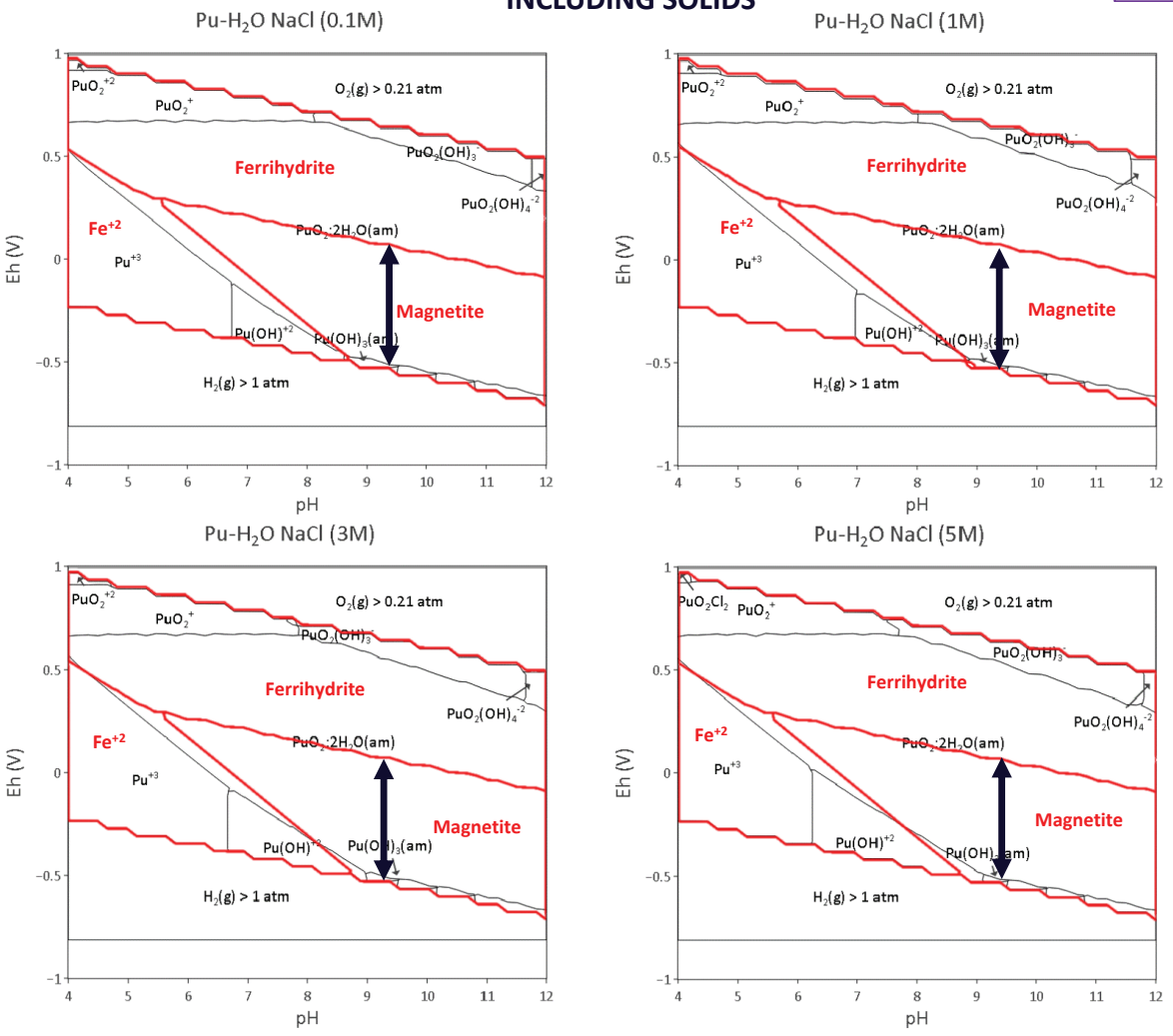
Results in NaCl + Fe

Pu and Fe predominance diagrams in NaCl – including solids

With TC10a-WIPP-2
0.1-1-3-5 M NaCl
$[Fe]_{(tot)}=2.61^{-5}$ M
$[Pu]_{(tot)}=10^{-8}$ M

A33

INCLUDING SOLIDS



Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS – INORGANIC INCLUDING IRON

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	$2.61 \cdot 10^{-5}$	As in GWBrine
Br	0	
Pb	0	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams

- Magnetite is an Fe(II)-Fe(III) solid likely to dominate Fe chemistry under reducing equilibrium conditions.
- Most likely Eh boundaries will be defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)

Results in NaCl + Fe

Effect of Ferrihydrite crystallinity on iron chemical behaviour

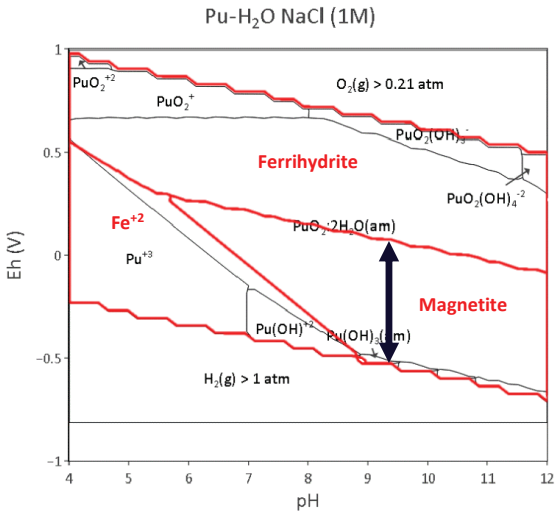
With TC10a-WIPP-2
1 M NaCl
$[Fe]_{(tot)}=2.61^{-5}$ M
$[Pu]_{(tot)}=10^{-8}$ M

A34

INCLUDING SOLIDS

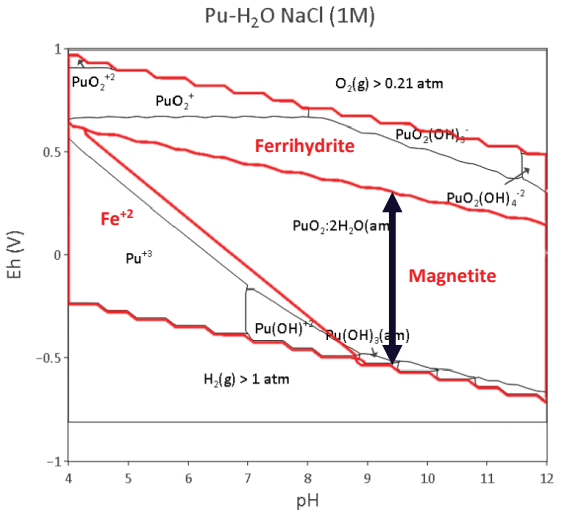
Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS – INORGANIC INCLUDING IRON

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	$2.61 \cdot 10^{-5}$	As in GWBrine
Br	0	
Pb	0	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams



With TC10a-WIPP-2

Ferrihydrite log K°=-2.54



With TC10a-WIPP-2

Ferrihydrite log K°=-4

- Changing the ferrihydrite stability modifies ferrihydrite/magnetite boundary
- Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

A35

Part II: Inorganic calculations

- Calculations of Pu Pourbaix diagrams – inorganic chemistry
  - in NaCl
  - in GWB and ERDA brines



Reacted GWBrine A36

GWBrine

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

Table 6. EQ3/6 Predictions of the Compositions and Solubilities of Th(IV), Np(V), and Am(III) in GWB (M Unless Otherwise Noted).

Element or Property	1 × Minimum[A]
B(III)(aq)	0.224
Na(I)(aq)	4.69
Mg(II)(aq)	0.348
K(I)(aq)	0.663
Ca(II)(aq)	0.0109
Fe(II)(aq)	2.61E-05
S(VI)(aq)	0.232
Cl(-I)(aq)	5.40
Br(-I)(aq)	0.0378
Pb(II)(aq)	1.90E-02
Th(IV)(aq)	5.45E-08
Np(V)(aq)	4.02E-07
Am(III)(aq)	1.63E-07
f_{CO_2} (atm)	2.02E-06
I	6.53
pH[B]	8.82
pcH	9.54
RH (%)[C]	0.732
TIC[D]	2.50E-04

GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

a) Total inorganic carbon considered as total carbonate in order to draw the Pourbaix diagrams
b) pH is not a fixed parameter but it is varied from 4 to 12 in the Pourbaix diagrams

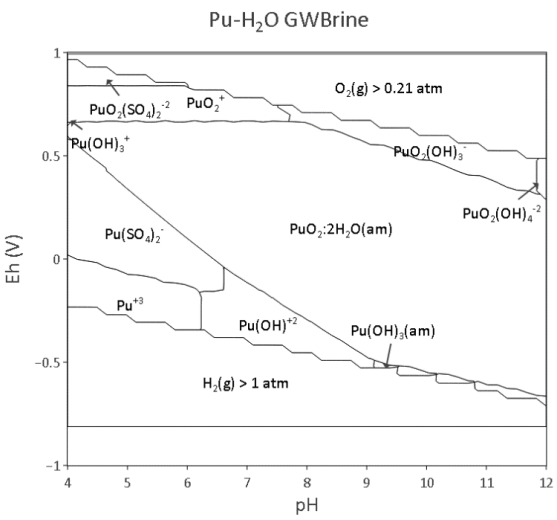
Results in GWBrine

Pu predominance diagrams in GWBrine – without organics

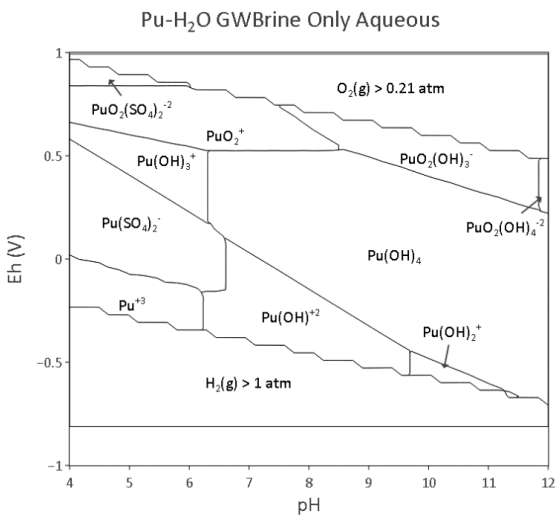
With TC10a-WIPP-2
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

A37

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

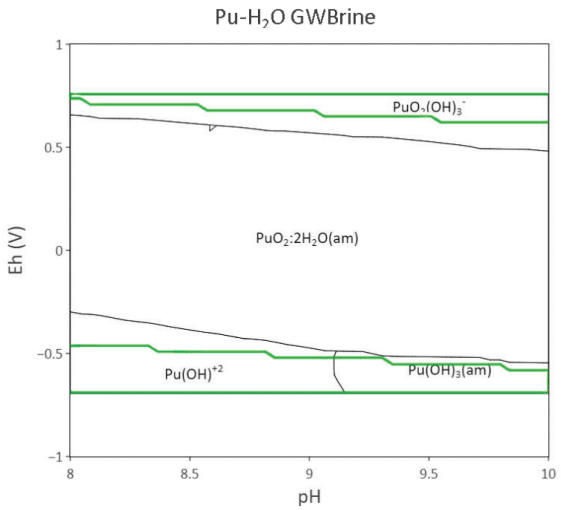
- At pH≈9.5, and Eh range -0.5 to 0.3:
  - At higher Eh values, main aqueous species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can limit Pu aqueous concentrations
  - In the more reducing Eh conditions, $Pu(OH)^{2+}$ and $Pu(OH)_2^+$ may be the predominant Pu aqueous species. Pu(III) solid hydroxides may limit Pu aqueous concentrations

Results in GWBrine

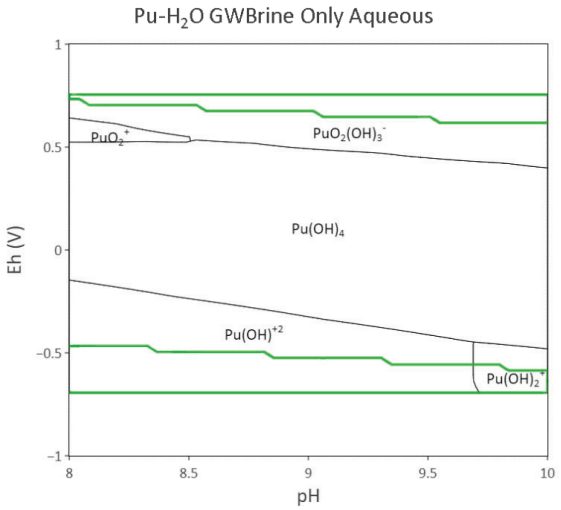
With TC10a-WIPP
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

A38

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-7}$	
pH		Varied from 4 to 12 b)

- Diagrams showing enlarged Pu regions beyond the pH-Eh stability field of water (represented by the region delimited by the green lines)

Results in GWBrine

With TC10a-WIPP
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

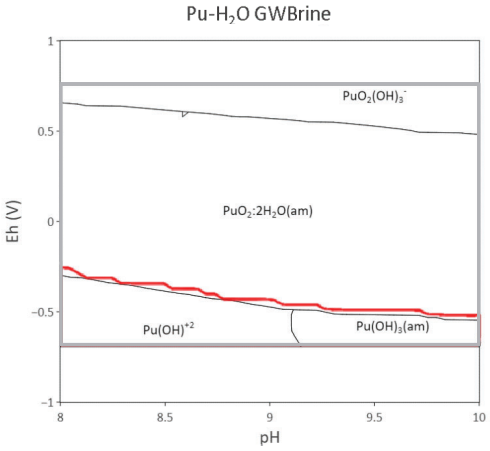
A39

GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

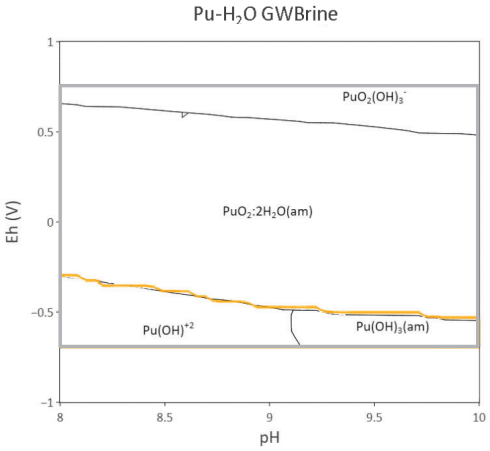
Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-7}$	
pH		Varied from 4 to 12 b)

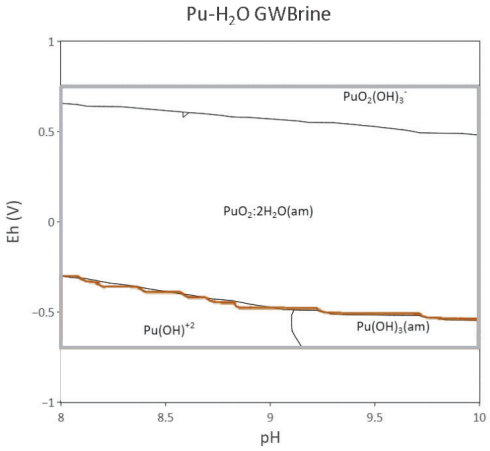
INCLUDING SOLIDS



- Red line indicates 50% Pu(III) and 50% Pu(IV) solid and aqueous species



- Orange line indicates 75% Pu(III) and 25% Pu(IV) solid and aqueous species



- Brown line indicates 90% Pu(III) and 10% Pu(IV) solid and aqueous species

Results in GWBrine

With TC10a-WIPP
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

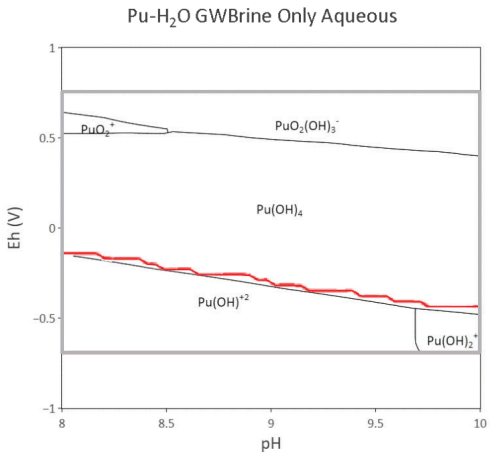
A40

AQUEOUS SPECIES ONLY

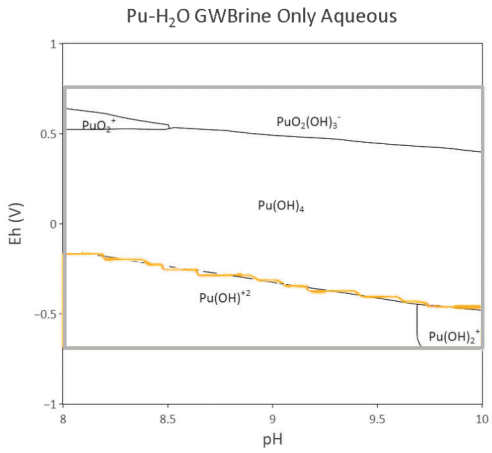
GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_1

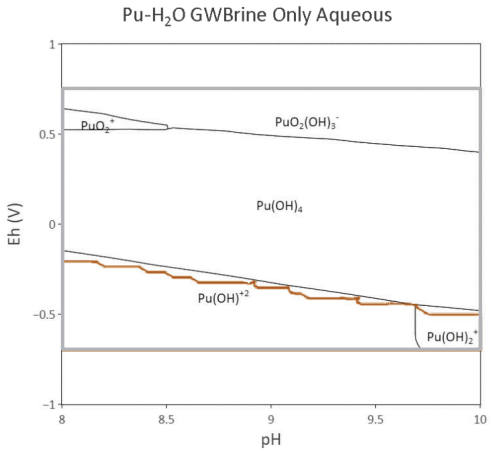
Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-7}$	
pH		Varied from 4 to 12 b)



- Red line indicates 50% Pu(III) and 50% Pu(IV) aqueous species



- Orange line indicates 75% Pu(III) and 25% Pu(IV) aqueous species



- Brown line indicates 90% Pu(III) and 10% Pu(IV) aqueous species

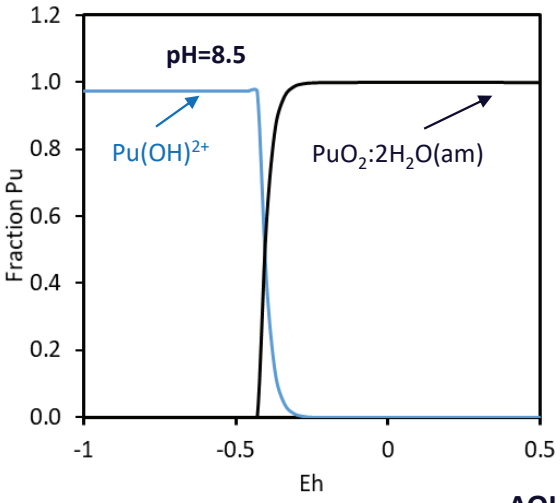
Results in GWBrine

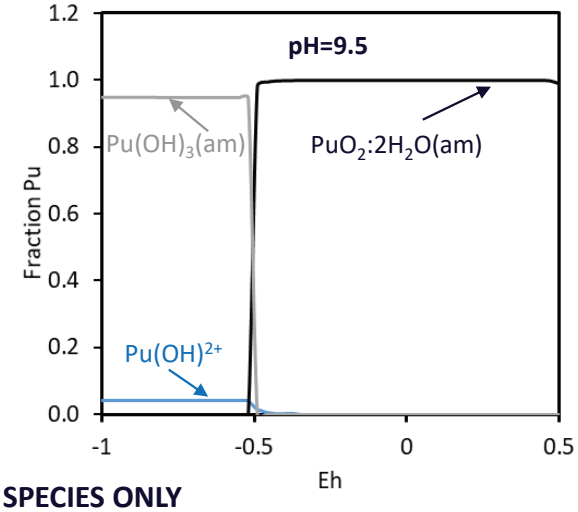
Fractions varying Eh

With TC10a-WIPP
Table GWBrine_1
$[Pu]_T=10^{-8}$ M

A41

INCLUDING SOLIDS



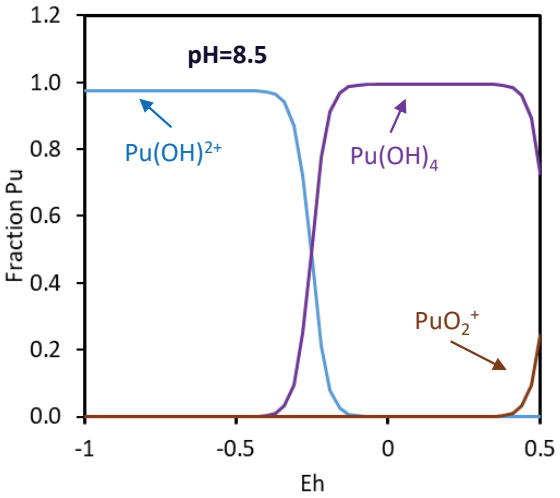


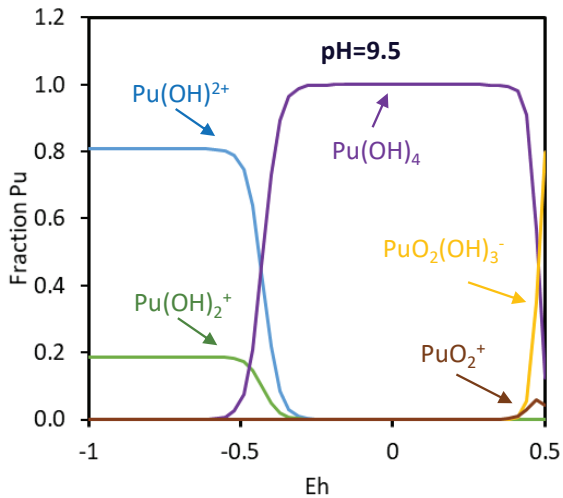
GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

AQUEOUS SPECIES ONLY





Results in GWBrine

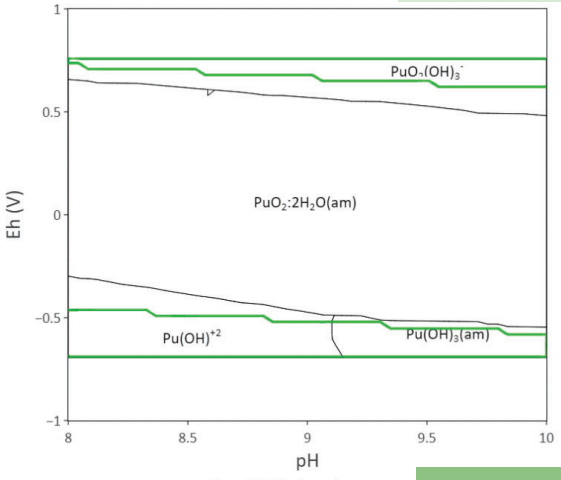
- Diagrams at two different Pu total concentrations: 10^{-8} M (up) and 10^{-6}M (down)

With TC10a-WIPP
Table GWBrine_1

A42

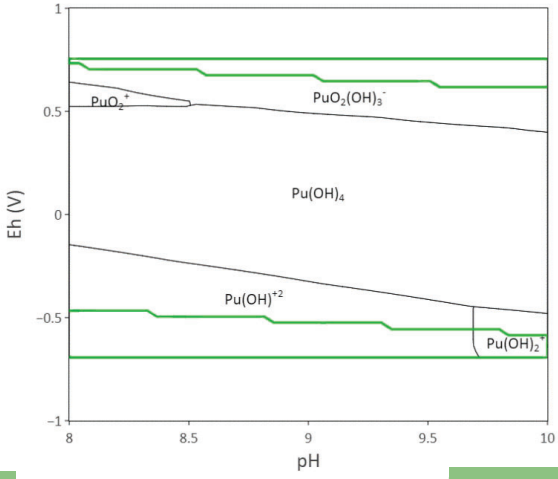
INCLUDING SOLIDS

Pu-H_2O GWBrine $[Pu]_T=10^{-8}$ M



AQUEOUS SPECIES ONLY

Pu-H_2O GWBrine Only Aqueous $[Pu]_T=10^{-8}$ M

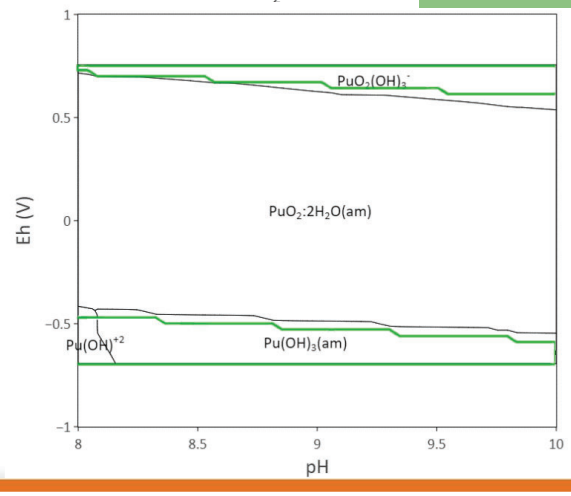


GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

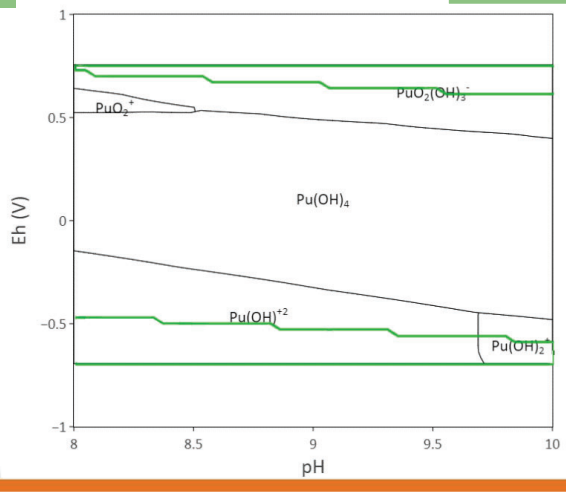
Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

Pu-H_2O GWBrine $[Pu]_T=10^{-6}$ M



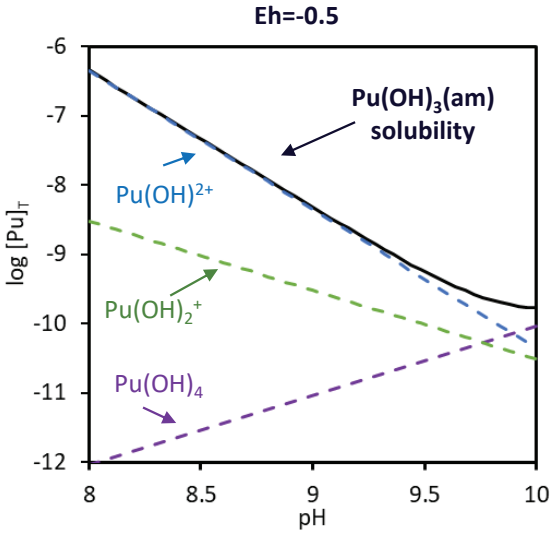
Pu-H_2O GWBrine Only Aqueous $[Pu]_T=10^{-6}$ M

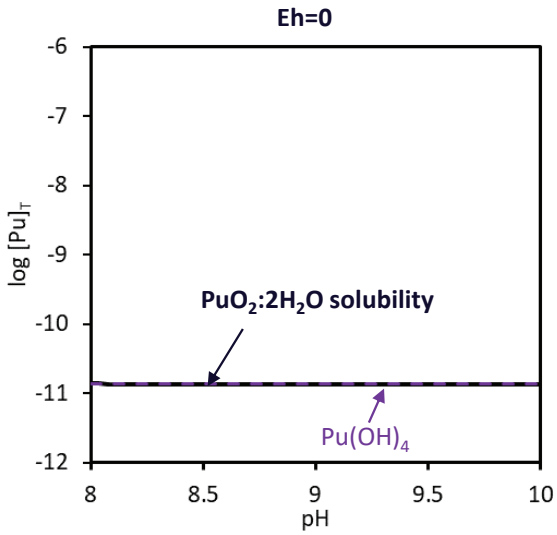


A43

Results in GWBrine

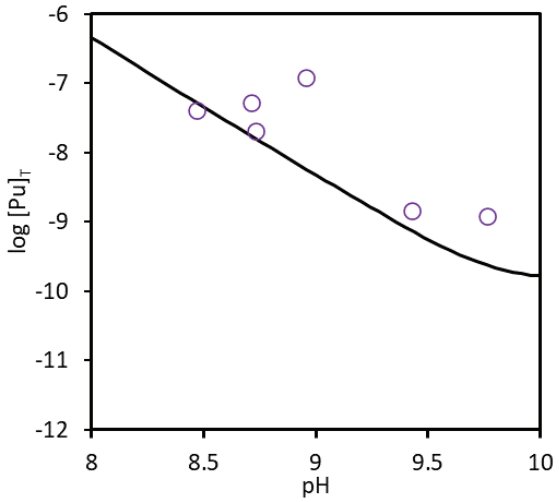
Solubility



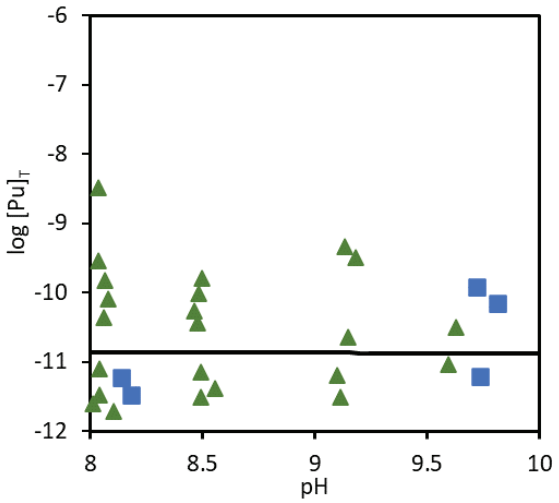


Comparison with available data

Solubility



- Black line: calculated $Pu(OH)_3$(am) solubility under GWBrine conditions, Eh=-0.5V. Pu(OH)3(am) solubility constant used in the calculations is the one selected in the NEA reviews (Guillaumont et al. 2005).
- Purple circles: experimental Pu(OH)3(am) solubility in PBB (Permian Bassin brines) from Felmy et al. (1989) (Radiochimica Acta 48: 29)



- Black line: calculated PuO_2:$2H_2O$ solubility solubility under GWBrine conditions, Eh=0V.PuO_2:$2H_2O$ solubility constant used in the calculations is the one selected in the NEA reviews (Guillaumont et al. 2005).
- Symbols: Pu total concentration in solution at 0.1m NaCl in equilibrium with PuO_2(ncr, hyd) for systems buffered with hydroquinone (blue squares) and $SnCl_2$ (green triangles) , from Tasi et al. (2018) (Radiochim. Acta 106: 259)

Results in GWBrine + Fe

Fe predominance diagrams in GWBrine – without organics

With TC10a-WIPP-2
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

A45

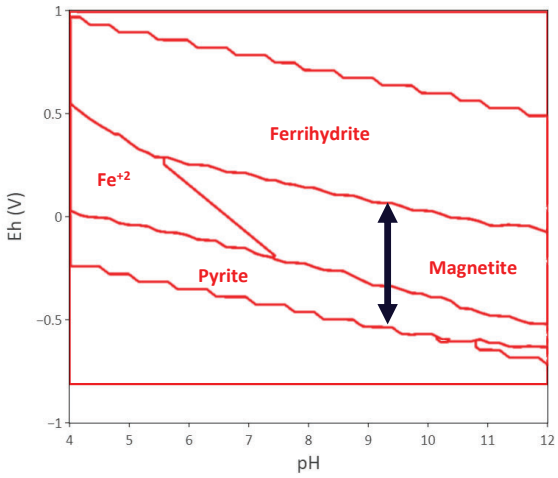
GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-7}$	
pH		Varied from 4 to 12 b)

INCLUDING SOLIDS

Fe-H_2O GWBrine



- Magnetite is an Fe(II)-Fe(III) solid likely to dominate Fe chemistry under reducing equilibrium conditions.
- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)

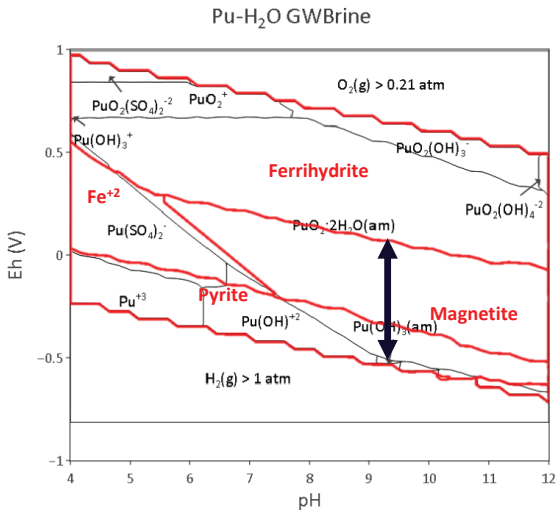
Results in GWBrine + Fe

Pu and Fe predominance diagrams in GWBrine – without organics

With TC10a-WIPP-2
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

A46

INCLUDING SOLIDS



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-7}$	
pH		Varied from 4 to 12 b)

- Magnetite is an Fe(II)-Fe(III) solid likely to dominate Fe chemistry under reducing equilibrium conditions.
- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)

Results in GWBrine + Fe

Fe predominance diagrams in GWBrine – without organics

A47

With TC10a-WIPP-2
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

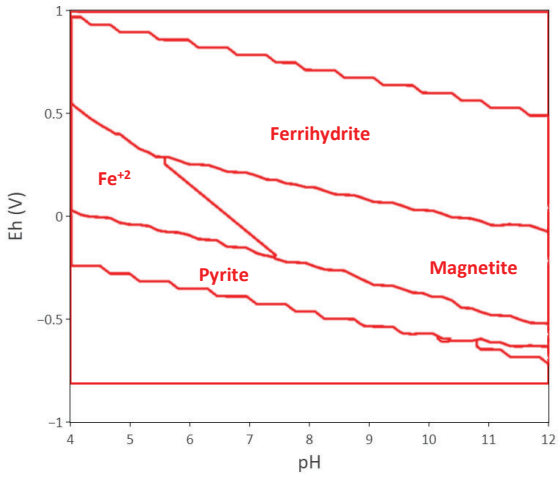
GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_1

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B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

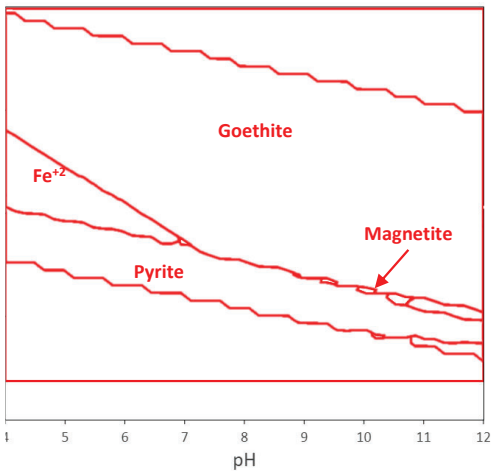
- Sensitivity analysis:
  - Comparison including Ferrihydrite, Goethite or Hematite in the calculations

Fe-H_2O GWBrine



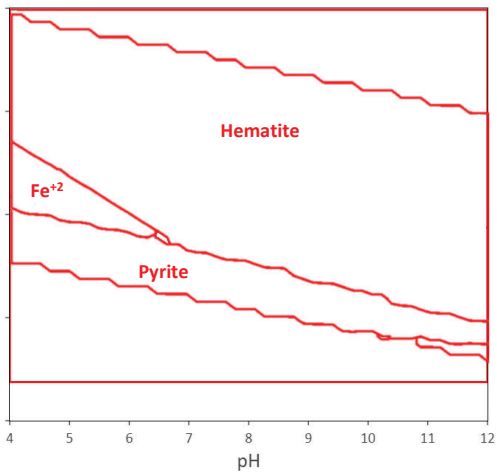
- Magnetite-Ferrihydrite

Fe-H_2O GWBrine



- Magnetite-Goethite

Fe-H_2O GWBrine



- Magnetite-Goethite

Hematite is the most thermodynamically stable Fe(III) oxide in the stability field of water. However, hydrous ferric oxides can prevail as metastable solid phases for long time periods as they have faster formation kinetics in corrosion processes.

Results in GWBrine + Fe

Fe predominance diagrams in GWBrine – without organics

With TC10a-WIPP-2
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

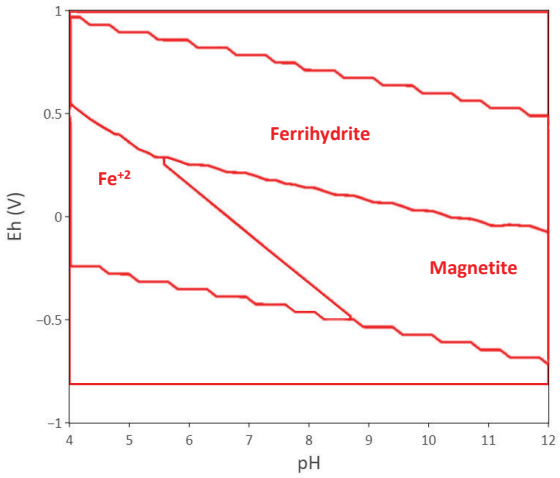
Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
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Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

A48

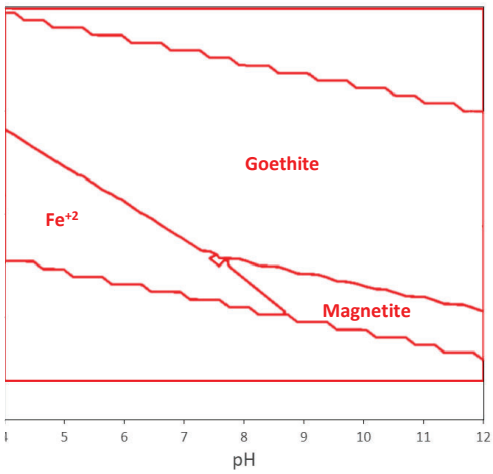
- Sensitivity analysis:
  - Calculations if S(VI) is not allowed to reduce to S(-II) (sulfate and sulfur are decoupled). Pyrite and aqueous iron sulfides are not allowed to form.

Fe-H_2O GWBrine



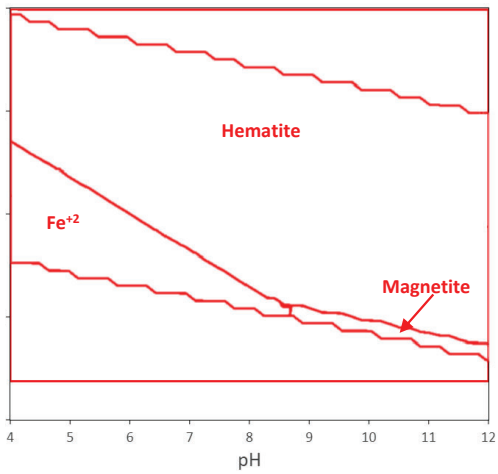
- Magnetite-Ferrihydrite
- S(VI) not allowed to reduce to S(-II)

Fe-H_2O GWBrine



- Magnetite-Goethite
- S(VI) not allowed to reduce to S(-II)

Fe-H_2O GWBrine



- Magnetite-Goethite
- S(VI) not allowed to reduce to S(-II)

Reacted ERDA-6 A49

ERDA-6

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

Table 7. EQ3/6 Predictions of the Compositions and Solubilities of Th(IV), Np(V), and Am(III) in ERDA-6 (M Unless Otherwise Noted).

Element or Property	1 × Minimum[A]
B(III)(aq)	0.281
Na(I)(aq)	4.66
Mg(II)(aq)	0.435
K(I)(aq)	0.499
Ca(II)(aq)	0.0128
Fe(II)(aq)	2.67E-05
S(VI)(aq)	0.224
Cl(-I)(aq)	5.22
Br(-I)(aq)	0.0566
Pb(II)(aq)	1.88E-02
Th(IV)(aq)	5.44E-08
Np(V)(aq)	1.20E-06
Am(III)(aq)	1.78E-07
f_{CO_2} (atm)	2.02E-06
I	6.48
pH[B]	8.82
pcH	9.52
RH (%)[C]	0.732
TIC[D]	2.50E-04

ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS

Table ERDA-6_1

Element or property	M	Comments
Na	4.66	
Mg	0.435	
K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

a) Total inorganic carbon considered as total carbonate in order to draw the Pourbaix diagrams
b) pH is not a fixed parameter but it is varied from 4 to 12 in the Pourbaix diagrams

Results in ERDA-6

Pu predominance diagrams in ERDA-6 – without organics

With TC10a-WIPP-2
Table ERDA-6_1
$[Pu]_{(tot)}=10^{-8}$ M

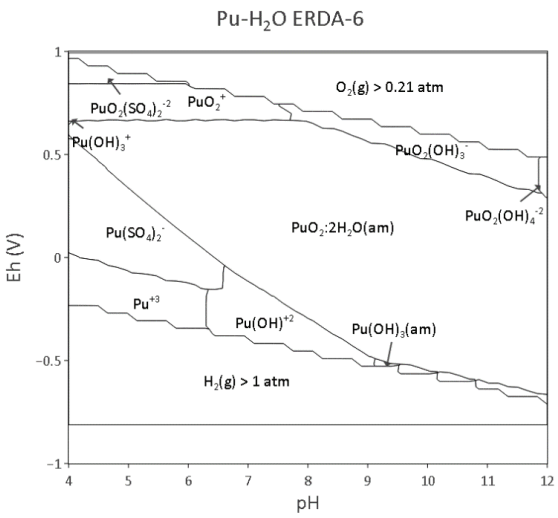
A50

ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS

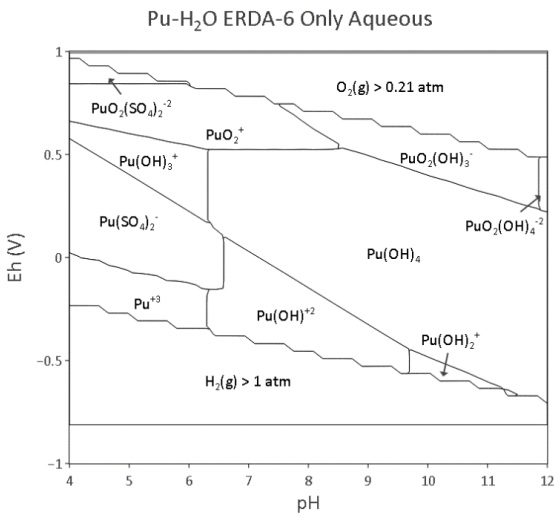
Table ERDA-6_1

Element or property	M	Comments
Na	4.66	
Mg	0.435	
K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



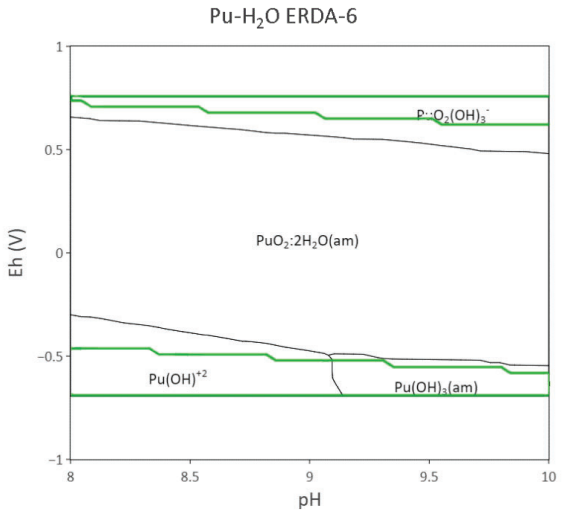
- At pH≈9.5, and Eh range -0.5 to 0.3:
  - At higher Eh values, main aqueous species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can limit Pu aqueous concentrations
  - In the more reducing Eh conditions, $Pu(OH)^{2+}$ and $Pu(OH)_2^{+}$ may be the predominant Pu aqueous species. Pu(III) solid hydroxides may limit Pu aqueous concentrations

Results in ERDA-6

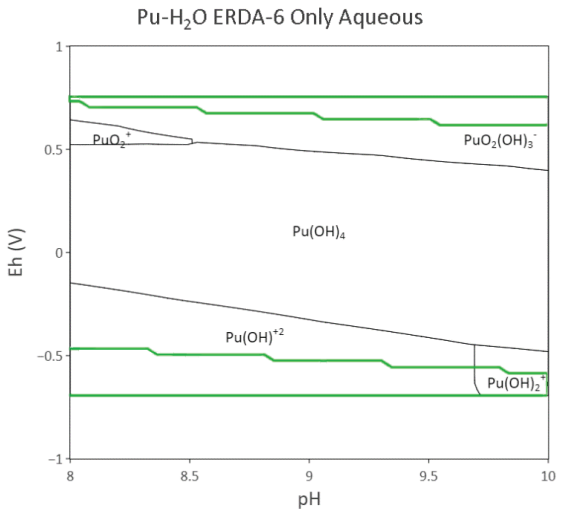
With TC10a-WIPP
Table ERDA-6_1
$[Pu]_{(tot)}=10^{-8}$ M

A51

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS

Table ERDA-6_1

Element or property	M	Comments
Na	4.66	
Mg	0.435	
K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

- Diagrams showing enlarged Pu regions beyond the pH-Eh stability field of water (represented by the region delimited by the green lines)

Results in ERDA-6

With TC10a-WIPP
Table ERDA-6_1
$[Pu]_{(tot)}=10^{-8}$ M

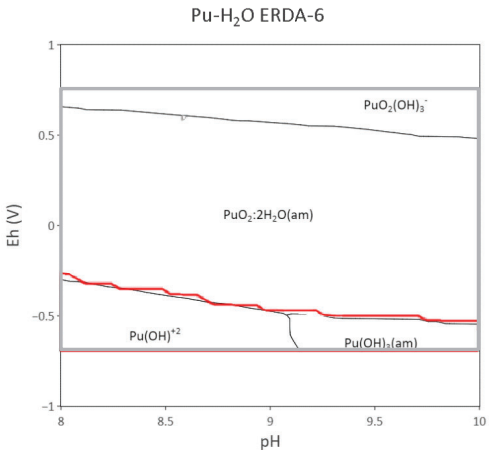
A52

INCLUDING SOLIDS

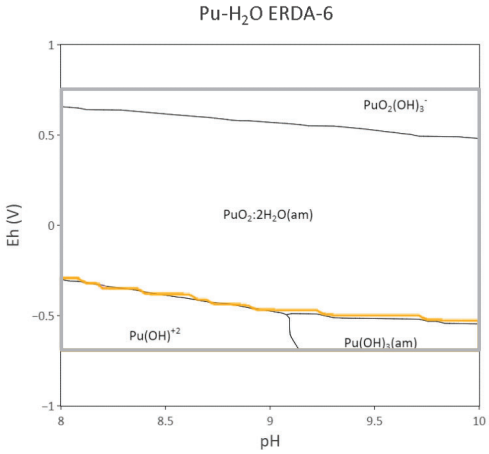
ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS

Table ERDA-6_1

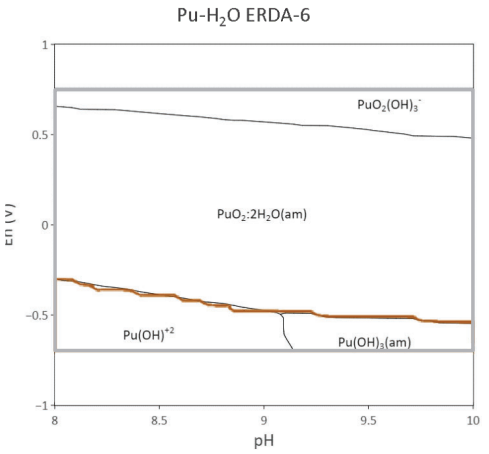
Element or property	M	Comments
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K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)



- Red line indicates 50% Pu(III) and 50% Pu(IV) solid and aqueous species



- Orange line indicates 75% Pu(III) and 25% Pu(IV) solid and aqueous species



- Brown line indicates 90% Pu(III) and 10% Pu(IV) solid and aqueous species

Results in ERDA-6

With TC10a-WIPP
Table ERDA-6_1
$[Pu]_{(tot)}=10^{-8}$ M

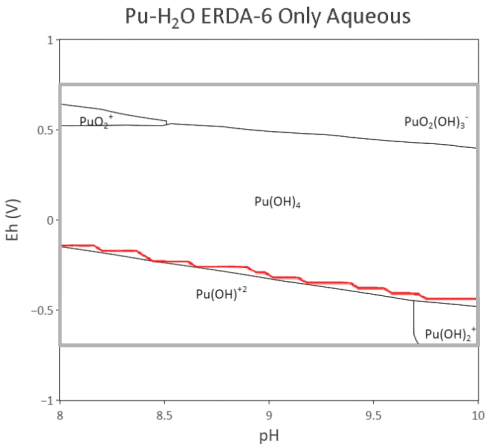
A53

AQUEOUS SPECIES ONLY

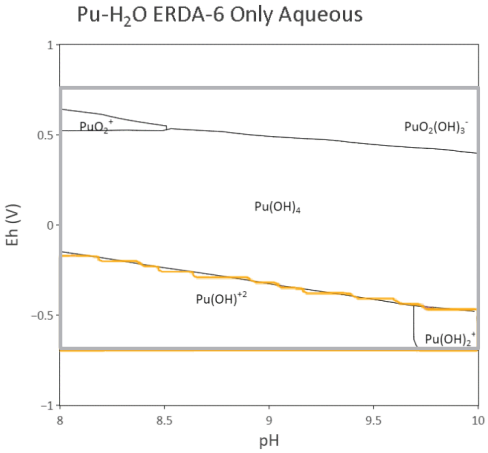
ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS

Table ERDA-6_1

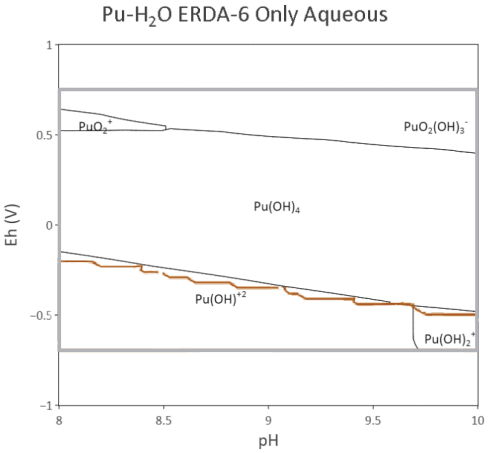
Element or property	M	Comments
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K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)



- Red line indicates 50% Pu(III) and 50% Pu(IV) aqueous species



- Orange line indicates 75% Pu(III) and 25% Pu(IV) aqueous species



- Brown line indicates 90% Pu(III) and 10% Pu(IV) aqueous species

Results in ERDA-6

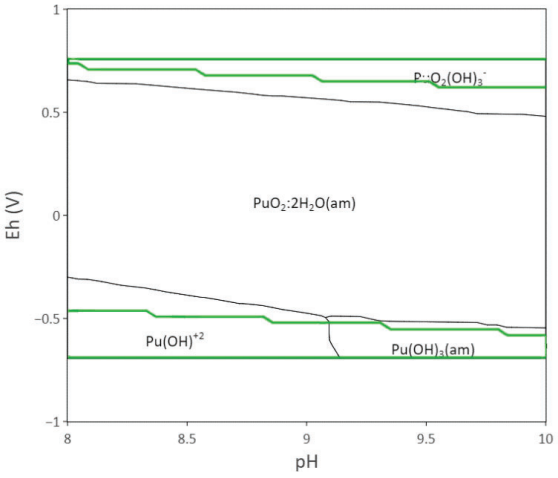
- Diagrams at two different Pu total concentrations: 10^{-8} M (up) and 10^{-6}M (down)

With TC10a-WIPP
Table ERDA-6_1

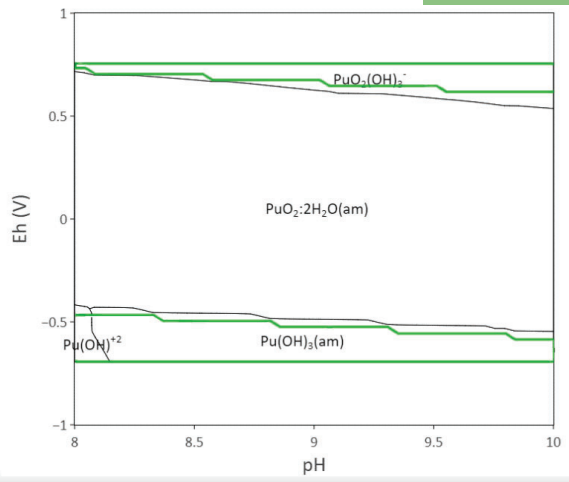
A54

INCLUDING SOLIDS

Pu-H_2O ERDA-6 $[Pu]_T=10^{-8}$ M

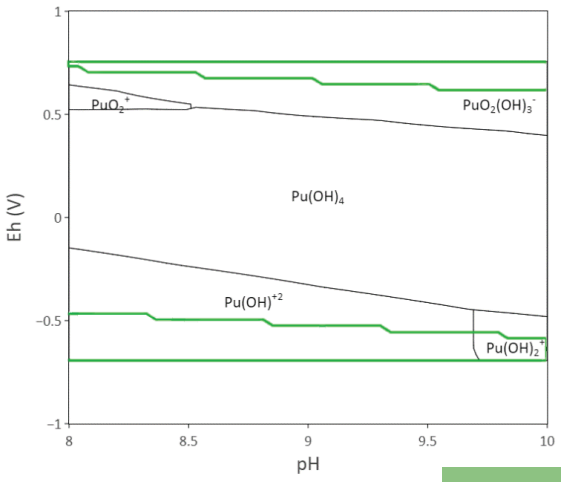


Pu-H_2O ERDA-6 $[Pu]_T=10^{-6}$ M

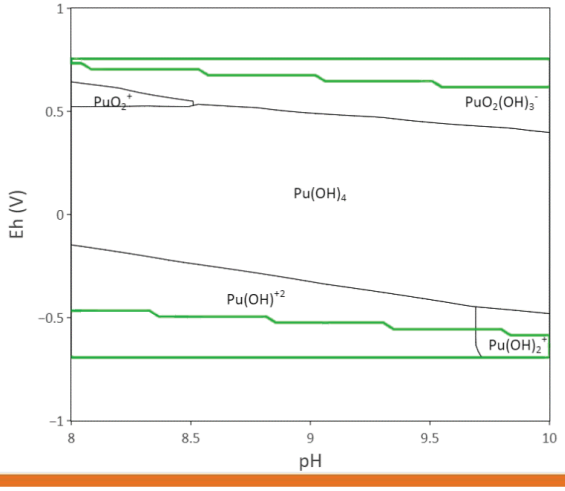


AQUEOUS SPECIES ONLY

Pu-H_2O ERDA-6 Only Aqueous $[Pu]_T=10^{-8}$ M



Pu-H_2O ERDA-6 Only Aqueous $[Pu]_T=10^{-6}$ M



ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS

Table ERDA-6_1

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Ca	0.0128	
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B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

Results in ERDA-6 + Fe

Fe predominance diagrams in ERDA-6 – without organics

With TC10a-WIPP-2
Table ERDA-6_1
$[Pu]_{(tot)}=10^{-8}$ M

A55

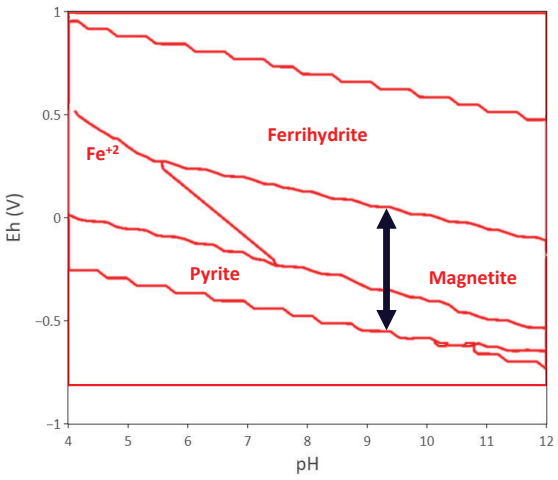
ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS

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TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

INCLUDING SOLIDS

Fe-H_2O ERDA-6



- Magnetite is an Fe(II)-Fe(III) solid likely to dominate Fe chemistry under reducing equilibrium conditions.
- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)

Results in ERDA-6 + Fe

Pu and Fe predominance diagrams in ERDA-6 – without organics

With TC10a-WIPP-2
Table ERDA-6_1
$[Pu]_{(tot)}=10^{-8}$ M

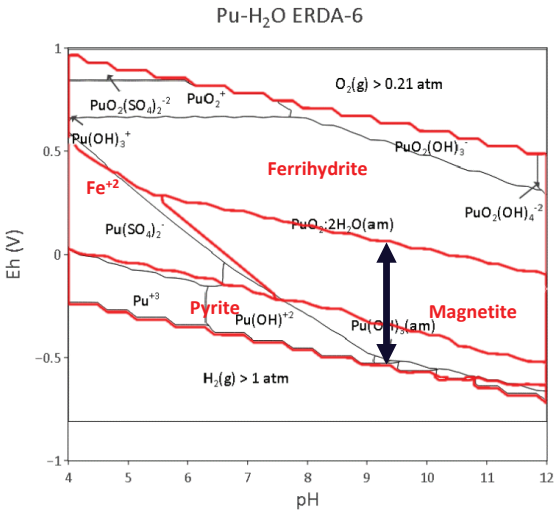
A56

ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS

Table ERDA-6_1

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Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

INCLUDING SOLIDS



- Magnetite is an Fe(II)-Fe(III) solid likely to dominate Fe chemistry under reducing equilibrium conditions.
- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)

A57

Part III: calculations including organics

- Effect of EDTA (and other organics) on Pu chemistry: Calculation of Pourbaix diagrams
  - in NaCl
  - in GWB and ERDA brines
  - Effect of EDTA on Pu chemistry: competence with calcium

Methodology

Methodology for the calculations in the presence of organic ligands

A58

- S(VI)/S(-II) and Fe(II)/Fe(III) are coupled in the calculations
- Not included in the calculations:
  - PuO_2(s)
  - Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations
  - Aragonite, vaterite, syngenite ($K_2Ca(SO_4)_2$)
  - CH_4(aq), CH_4(g), C(cr), CO(g)
- Solids allowed to precipitate if oversaturated:
  - PuO_2:$2H_2O$, $Pu(OH)_3$(am)
  - Calcite, magnesite, brucite, gypsum, mirabilite
  - Ferrihydrite (log K°=2.54), Magnetite, Pyrite, $Fe(OH)_2$(cr)
  - Green Rust: GR-Cl(s), GR-CO_3(s), GR-SO_4(s)
  - Solids with organics, for example Ca-oxalates



A59

Part III: calculations including organics

- Effect of EDTA (and other organics) on Pu chemistry: Calculation of Pourbaix diagrams
  - in NaCl
  - in GWB and ERDA brines
  - Effect of EDTA on Pu chemistry: competence with calcium



A60

NaCl + organics

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

Table 3. Dissolved Concentrations of Organic Ligands (M) in the Minimum Brine Volume Required for a DBR

Organic Ligand	Minimum Required for a DBR
Acetate	2.83×10^{-2}
Citrate	2.30×10^{-3}
EDTA	7.92×10^{-5}
Oxalate	1.13×10^{-2}

Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS - ORGANIC

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	0	
Br	0	
Pb	0	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams

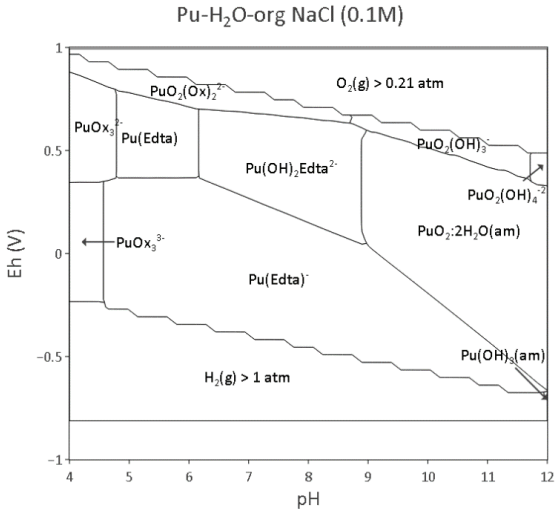
Results in NaCl + organics

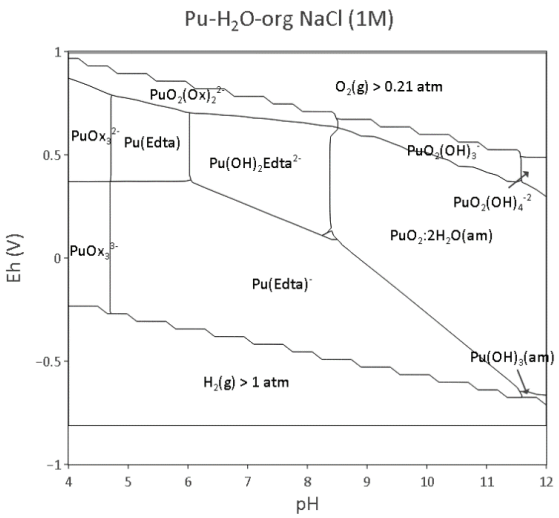
Pu predominance diagrams in NaCl and organics– including solids

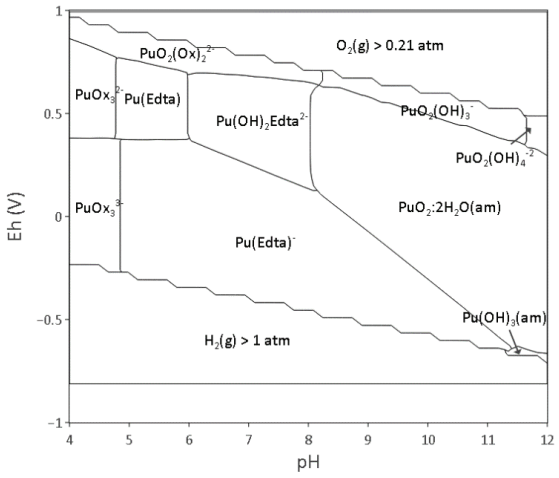
With TC10a-WIPP-2
0.1-1-3-5 M NaCl
Acetate, Cit*, Edta, Ox
$[Pu]_{(tot)}=10^{-8}$ M

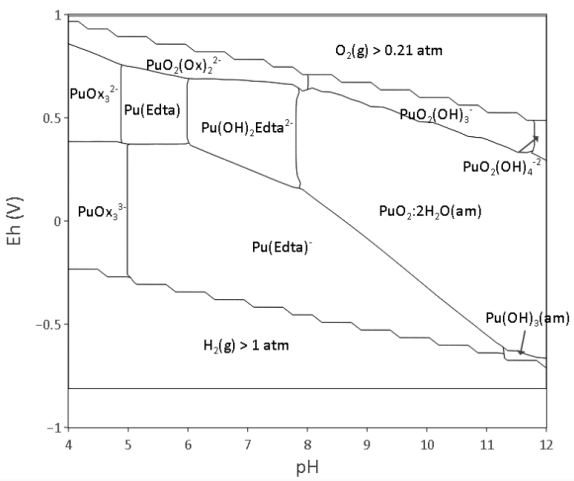
A61

INCLUDING SOLIDS









Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS - ORGANIC

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	0	
Br	0	
Pb	0	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-2}$	
EDTA	$7.92 \cdot 10^{-3}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams

*no Pu-citrate complexes are included in the calculations (see slide 9)

- In the absence of Ca, EDTA affects Pu chemistry.

Results in NaCl + organics

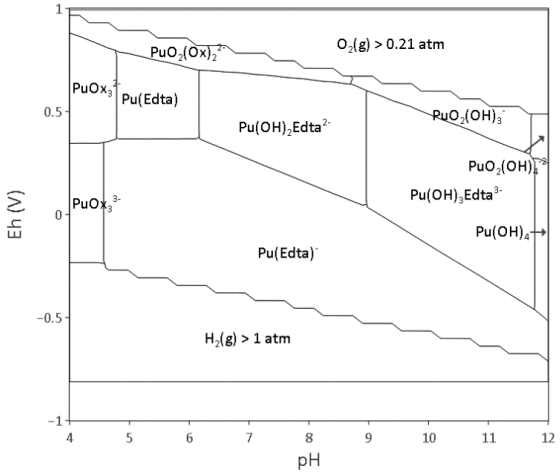
With TC10a-WIPP-2
0.1-1-3-5 M NaCl
Acetate, Cit*, Edta, Ox
$[Pu]_{(tot)}=10^{-8}$ M

A62

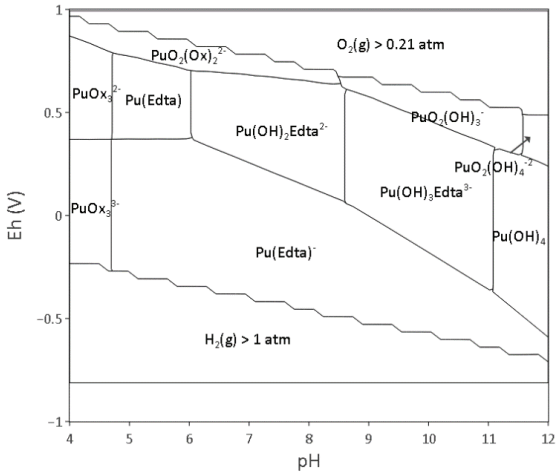
Pu predominance diagrams in NaCl and organics– aqueous species only

AQUEOUS SPECIES ONLY

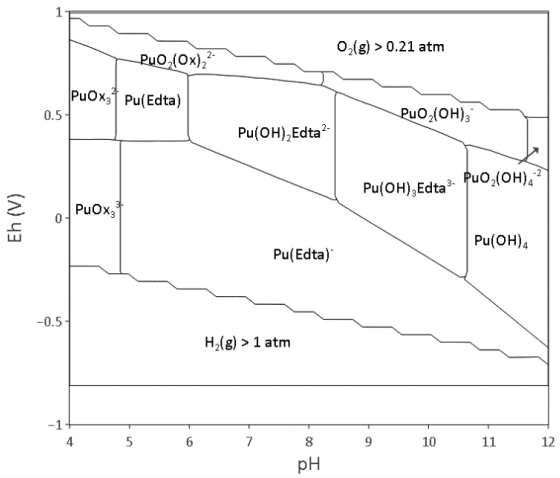
Pu-H_2O-org NaCl (0.1M) Only Aqueous



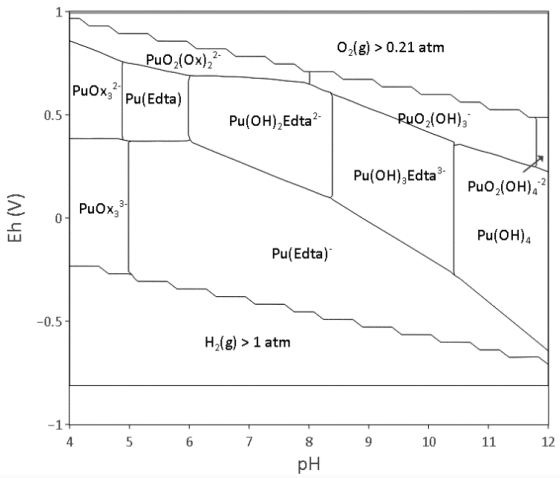
Pu-H_2O-org NaCl (1M) Only Aqueous



Pu-H_2O-org NaCl (3M) Only Aqueous



Pu-H_2O-org NaCl (5M) Only Aqueous



Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS - ORGANIC

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	0	
Br	0	
Pb	0	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-3}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams

*no Pu-citrate complexes are included in the calculations (see slide 9)

- In the absence of Ca, EDTA affects Pu chemistry.
- Stability of charged species (e.g. $Pu(OH)_3Edta^{3-}$) varies with ionic strength.

A63

NaCl + organics + Fe

Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS – ORGANIC INCLUDING IRON

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	$2.61 \cdot 10^{-5}$	As in GWBrine
Br	0	
Pb	0	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

Table 3. Dissolved Concentrations of Organic Ligands (M) in the Minimum Brine Volume Required for a DBR

Organic Ligand	Minimum Required for a DBR
Acetate	2.83×10^{-2}
Citrate	2.30×10^{-3}
EDTA	7.92×10^{-5}
Oxalate	1.13×10^{-2}

Overlapping Pu and Fe Pourbaix diagrams provides insights on expected boundaries for the Eh conditions.

- Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

Results in NaCl + organics + Fe

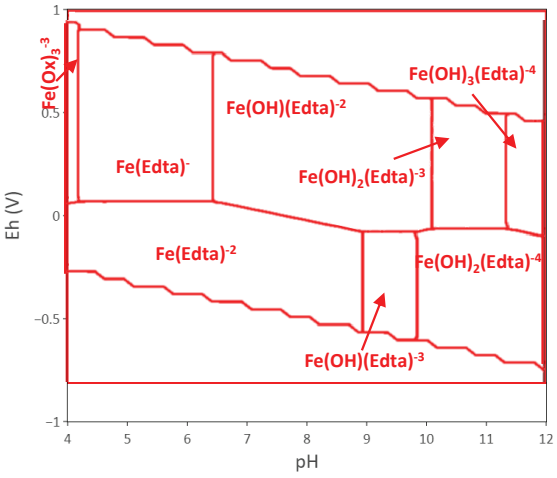
Fe predominance diagrams in NaCl and organics– including solids

With TC10a-WIPP-2
0.1-1-3-5 M NaCl
Acetate, Cit*, Edta, Ox
$[Fe]_{(tot)}=2.61\cdot10^{-5}$ M
$[Pu]_{(tot)}=10^{-8}$ M

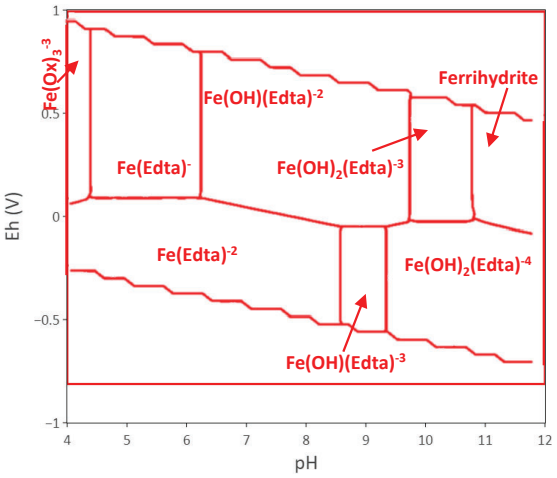
A64

INCLUDING SOLIDS

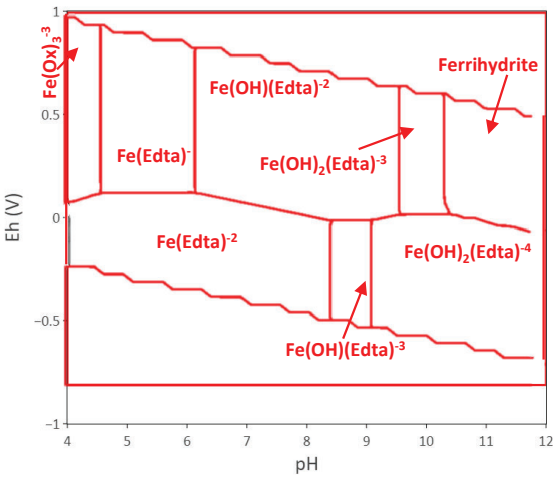
Fe-H_2O-org NaCl (0.1 M)



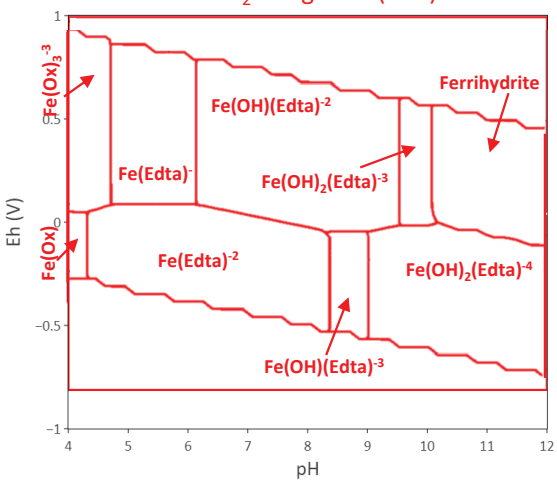
Fe-H_2O-org NaCl (1 M)



Fe-H_2O-org NaCl (3 M)



Fe-H_2O-org NaCl (5 M)



Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS – ORGANIC INCLUDING IRON

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	$2.61\cdot10^{-5}$	As in GWBrine
Br	0	
Pb	0	
Acetate	$2.83\cdot10^{-2}$	
Citrate	$2.30\cdot10^{-3}$	
EDTA	$7.92\cdot10^{-3}$	
Oxalate	$1.13\cdot10^{-2}$	
pH		Varied from 4 to 12
Pu	$1\cdot10^{-8}$	Pu concentration in Pourbaix diagrams

** Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

- In the absence of Ca, Fe-EDTA species dominate Fe aqueous chemistry.
- Stability of charged species (e.g. $Fe(OH)_2Edta^{3-}$) varies with ionic strength.

Results in NaCl + organics + Fe

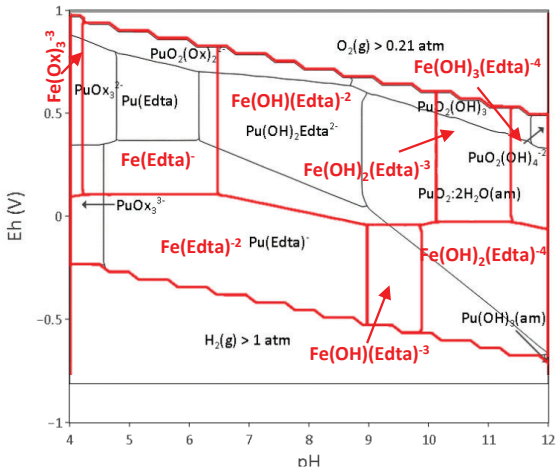
Pu and Fe predominance diagrams in NaCl and organics– including solids

With TC10a-WIPP-2
0.1-1-3-5 M NaCl
Acetate, Cit*, Edta, Ox
$[Fe]_{(tot)}=2.61\cdot10^{-5}$ M
$[Pu]_{(tot)}=10^{-8}$ M

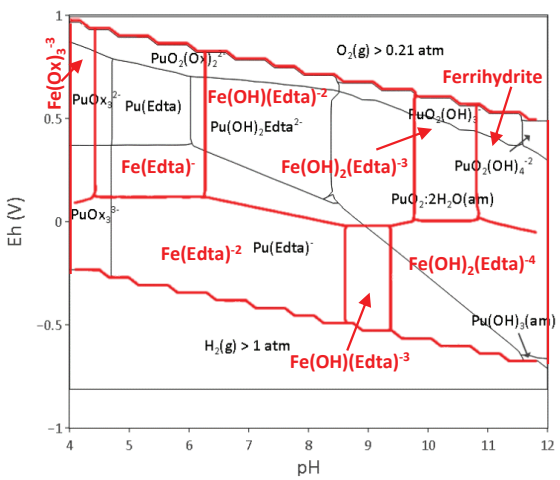
A65

INCLUDING SOLIDS

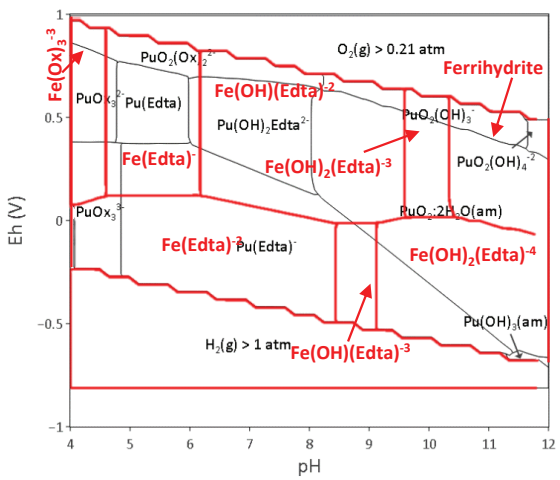
Pu-H_2O-org NaCl (0.1M)



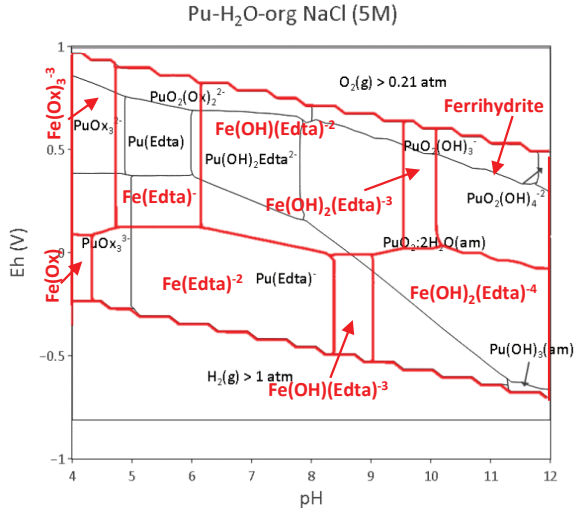
Pu-H_2O-org NaCl (1M)

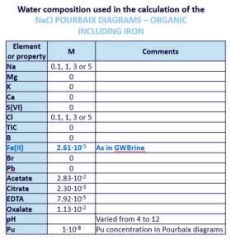


Pu-H_2O-org NaCl (3M)



Pu-H_2O-org NaCl (5M)





Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS – ORGANIC INCLUDING IRON

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	$2.61\cdot10^{-5}$	As in GWBrine
Br	0	
Pb	0	
Acetate	$2.83\cdot10^{-2}$	
Citrate	$2.30\cdot10^{-3}$	
EDTA	$7.92\cdot10^{-3}$	
Oxalate	$1.13\cdot10^{-2}$	
pH		Varied from 4 to 12
Pu	$1\cdot10^{-8}$	Pu concentration in Pourbaix diagrams

* No Pu-citrate complexes are included in the calculations

** Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

- In the absence of Ca, EDTA affects Pu and Fe chemistry.

A66

Part III: calculations including organics

- Effect of EDTA (and other organics) on Pu chemistry: Calculation of Pourbaix diagrams
  - in NaCl
  - in GWB and ERDA brines
  - Effect of EDTA on Pu chemistry: competence with calcium

Reacted GWBrine A67

GWBrine + organics

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

Table 6. EQ3/6 Predictions of the Compositions and Solubilities of Th(IV), Np(V), and Am(III) in GWB (M Unless Otherwise Noted).

Element or Property	1 × Minimum[A]
B(III)(aq)	0.224
Na(I)(aq)	4.69
Mg(II)(aq)	0.348
K(I)(aq)	0.663
Ca(II)(aq)	0.0109
Fe(II)(aq)	2.61E-05
S(VI)(aq)	0.232
Cl(-I)(aq)	5.40
Br(-I)(aq)	0.0378
Pb(II)(aq)	1.90E-02
Th(IV)(aq)	5.45E-08
Np(V)(aq)	4.02E-07
Am(III)(aq)	1.63E-07
f_{CO_2} (atm)	2.02E-06
I	6.53
pH[B]	8.82
pcH	9.54
RH (%)[C]	0.732
TIC[D]	2.50E-04

Table 3. Dissolved Concentrations of Organic Ligands (M) in the Minimum Brine Volume Required for a DBR

Organic Ligand	Minimum Required for a DBR
Acetate	2.83×10^{-2}
Citrate	2.30×10^{-3}
EDTA	7.92×10^{-5}
Oxalate	1.13×10^{-2}

GWBrine composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table GWBrine_1org

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

a) Total inorganic carbon considered as total carbonate in order to draw the Pourbaix diagrams
b) pH is not a fixed parameter but it is varied from 4 to 12 in the Pourbaix diagrams

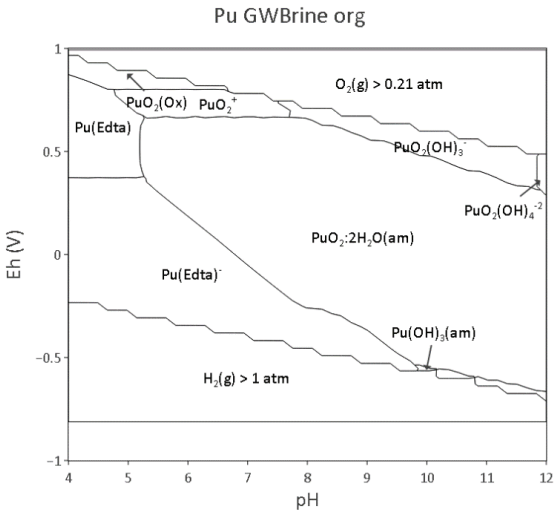
Results in GWBrine with org

Pu predominance diagrams in GWBrine - with organics

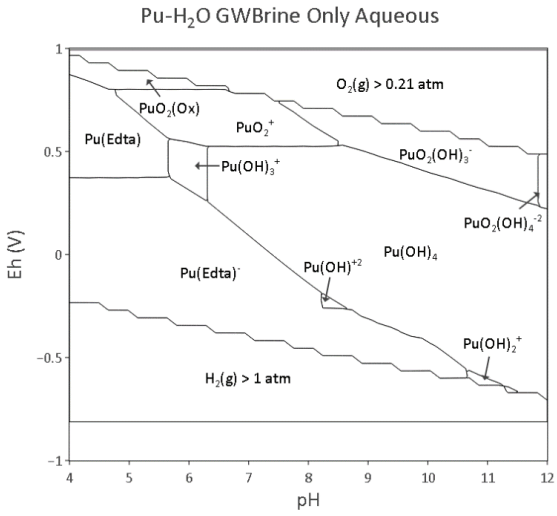
With TC10a-WIPP-2
Table GWBrine_1org
$[Pu]_{(tot)}=10^{-8}$ M

A68

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table GWBrine_1org

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) [a]
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 [b]

*no Pu-citrate complexes are included in the calculations (see slide 9)

- At pH≈9.5 and in the presence of organic ligands:
  - Main aqueous Pu(IV) species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can be formed. EDTA influence on Pu(IV) speciation is limited in the presence of competing ions such as Ca.
  - In the more reducing Eh conditions, $Pu(EDTA)^-$ species may be formed.

Results in GWBrine with org + Fe

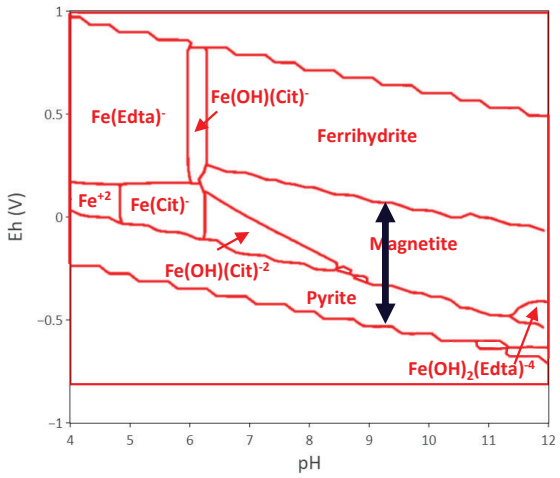
Fe predominance diagrams in GWBrine - with organics

With TC10a-WIPP-2
Table GWBrine_1org
$[Pu]_{(tot)}=10^{-8}$ M

A69

INCLUDING SOLIDS

Fe GWBrine org



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table GWBrine_1org

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) [a]
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 [b]

*no Pu-citrate complexes are included in the calculations (see slide 9)
** Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)
- At pH≈9.5 and in the presence of organic ligands:
  - EDTA influence on Fe(II) and Fe(III) is limited in the presence of competing ions such as Ca.

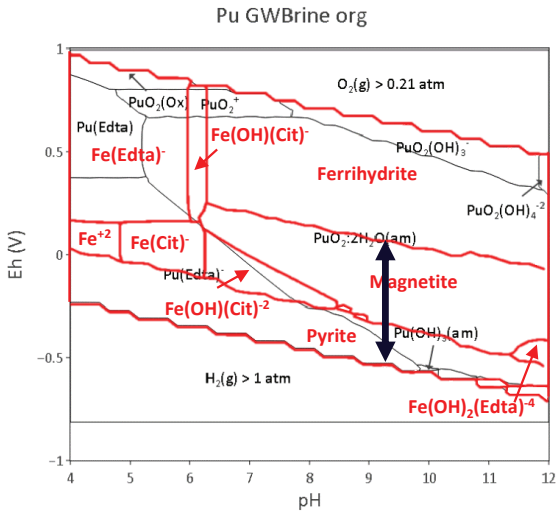
Results in GWBrine with org + Fe

Pu and Fe predominance diagrams in GWBrine - with organics

With TC10a-WIPP-2
Table GWBrine_1org
$[Pu]_{(tot)}=10^{-8}$ M

A70

INCLUDING SOLIDS



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table GWBrine_1org

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) [a]
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 [b]

*no Pu-citrate complexes are included in the calculations (see slide 9)
** Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)
- At pH≈9.5 and in the presence of organic ligands:
  - EDTA influence on Pu and Fe is limited in the presence of competing ions such as Ca.

Reacted ERDA-6 A71

ERDA-6 + organics

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

Table 7. EQ3/6 Predictions of the Compositions and Solubilities of Th(IV), Np(V), and Am(III) in ERDA-6 (M Unless Otherwise Noted).

Element or Property	1 × Minimum[A]
B(III)(aq)	0.281
Na(I)(aq)	4.66
Mg(II)(aq)	0.435
K(I)(aq)	0.499
Ca(II)(aq)	0.0128
Fe(II)(aq)	2.67E-05
S(VI)(aq)	0.224
Cl(-I)(aq)	5.22
Br(-I)(aq)	0.0566
Pb(II)(aq)	1.88E-02
Th(IV)(aq)	5.44E-08
Np(V)(aq)	1.20E-06
Am(III)(aq)	1.78E-07
f_{CO_2} (atm)	2.02E-06
I	6.48
pH[B]	8.82
pcH	9.52
RH (%)[C]	0.732
TIC[D]	2.50E-04

Table 3. Dissolved Concentrations of Organic Ligands (M) in the Minimum Brine Volume Required for a DBR

Organic Ligand	Minimum Required for a DBR
Acetate	2.83×10^{-2}
Citrate	2.30×10^{-3}
EDTA	7.92×10^{-5}
Oxalate	1.13×10^{-2}

ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table ERDA-6_1org

Element or property	M	Comments
Na	4.66	
Mg	0.435	
K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

a) Total inorganic carbon considered as total carbonate in order to draw the Pourbaix diagrams
b) pH is not a fixed parameter but it is varied from 4 to 12 in the Pourbaix diagrams

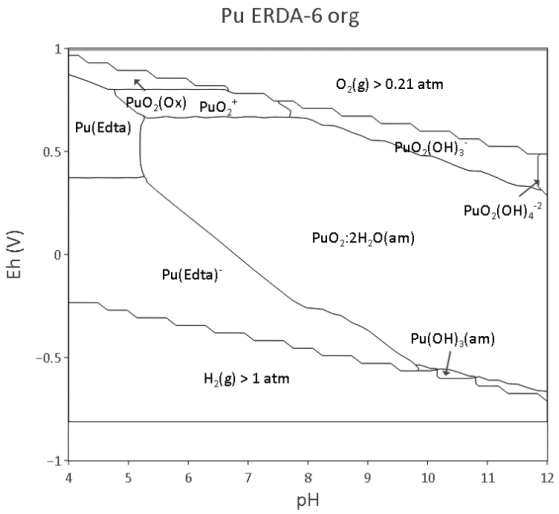
Results in ERDA-6 with org

Pu predominance diagrams in ERDA-6 - with organics

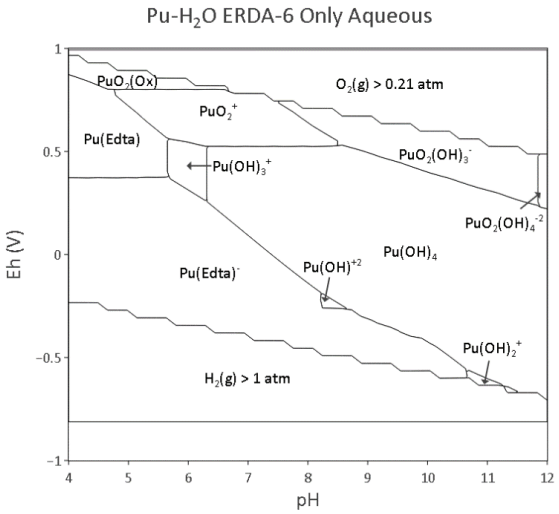
With TC10a-WIPP-2
Table ERDA-6_1org
$[Pu]_{(tot)}=10^{-8}$ M

A72

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table ERDA-6_1org

Element or property	M	Comments
Na	4.66	
Mg	0.435	
K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) [a]
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 [b]

*no Pu-citrate complexes are included in the calculations (see slide 9)

- At pH≈9.5 and in the presence of organic ligands:
  - Main aqueous Pu(IV) species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can be formed. EDTA influence on Pu(IV) speciation is limited in the presence of competing ions such as Ca.
  - In the more reducing Eh conditions, $Pu(EDTA)^-$ species may be formed.

Results in ERDA-6 with org + Fe

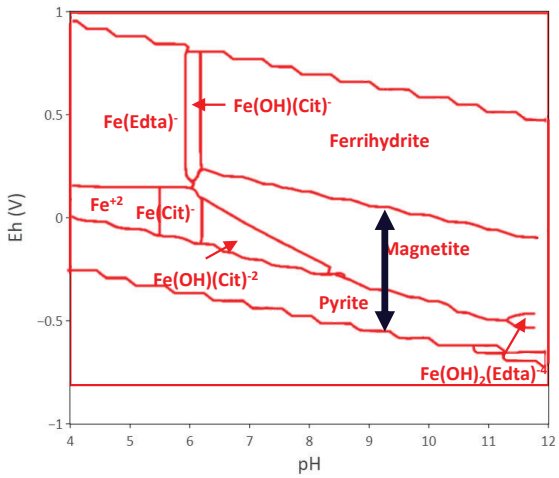
Fe predominance diagrams in ERDA-6 - with organics

With TC10a-WIPP-2
Table ERDA-6_1org
$[Pu]_{(tot)}=10^{-8}$ M

A73

INCLUDING SOLIDS

Fe ERDA-6 org



ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table ERDA-6_1org

Element or property	M	Comments
Na	4.66	
Mg	0.435	
K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) [a]
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 [b]

** Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)
- At pH≈9.5 and in the presence of organic ligands:
  - EDTA influence on Fe(II) and Fe(III) is limited in the presence of competing ions such as Ca.

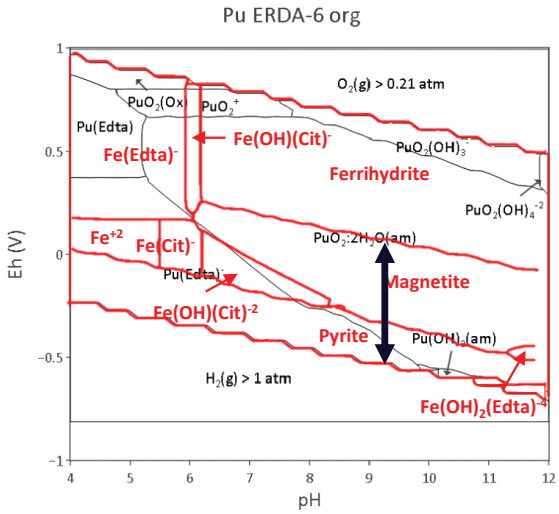
Results in ERDA-6 with org + Fe

Pu and Fe predominance diagrams in ERDA-6 - with organics

With TC10a-WIPP-2
Table ERDA-6_1org
$[Pu]_{(tot)}=10^{-8}$ M

A74

INCLUDING SOLIDS



ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table ERDA-6_1org

Element or property	M	Comments
Na	4.66	
Mg	0.435	
K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) [a]
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 [b]

*no Pu-citrate complexes are included in the calculations (see slide 9)
** Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)
- At pH≈9.5 and in the presence of organic ligands:
  - EDTA influence on Pu and Fe is limited in the presence of competing ions such as Ca.

A75

Part III: calculations including organics

- Effect of EDTA (and other organics) on Pu chemistry: Calculation of Pourbaix diagrams
  - in NaCl
  - in GWB and ERDA brines
  - Effect of EDTA on Pu chemistry: competence with calcium

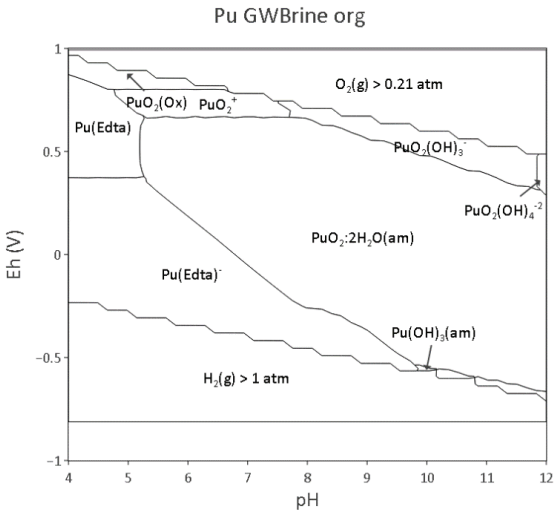
Results in GWBrine with org

Pu predominance diagrams in GWBrine - with organics

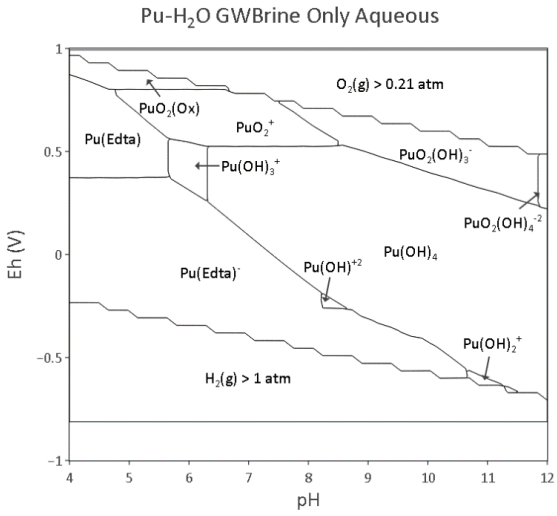
With TC10a-WIPP-2
Table GWBrine_1org
$[Pu]_{(tot)}=10^{-8}$ M

A76

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table GWBrine_1org

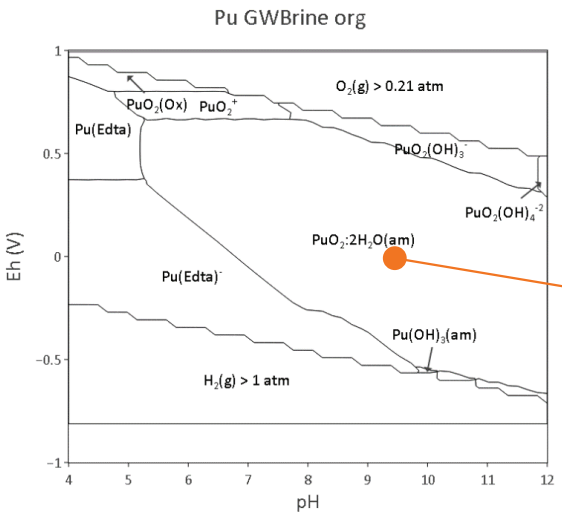
Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) [a]
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 [b]

*no Pu-citrate complexes are included in the calculations (see slide 9)

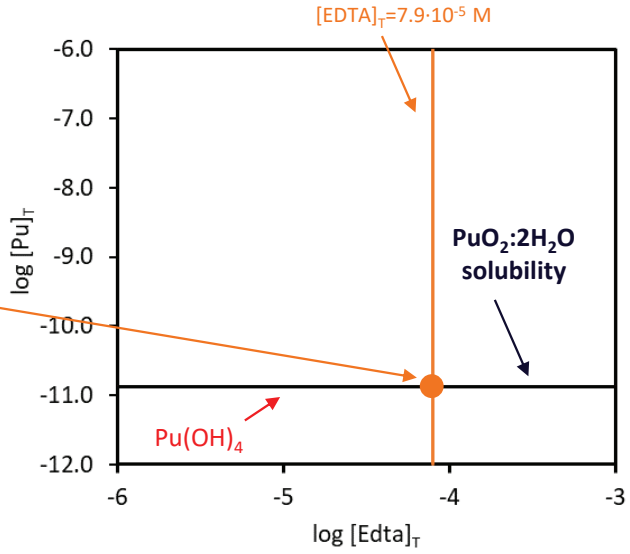
- At pH≈9.5 and in the presence of organic ligands:
  - Main aqueous Pu(IV) species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can be formed. EDTA influence on Pu(IV) speciation is limited in the presence of competing ions such as Ca.
  - In the more reducing Eh conditions, $Pu(EDTA)^-$ species may be formed.

Effect of Ca and Edta in Pu(IV) chemistry

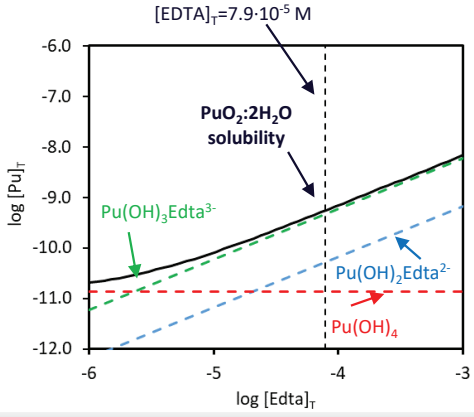
Eh=0; Pu(IV) A77



- **Ca competes with Pu(IV) for complexation with EDTA.**



1 M NaCl
pH=9.5
Eh=0
[Edta]=varied
[Ca]=0.0109
$PuO_2:2H_2O$ solubility



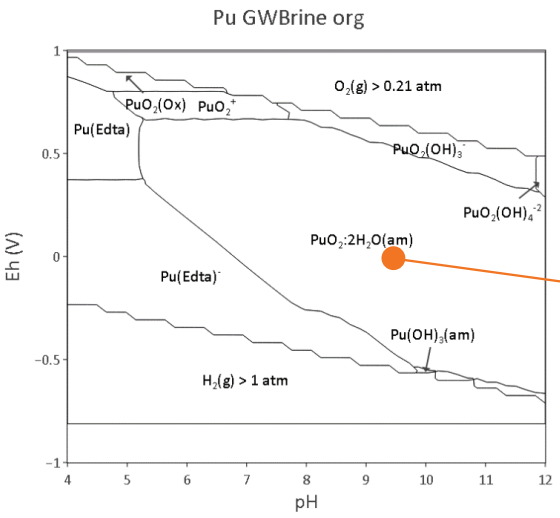
1 M NaCl
pH=9.5
Eh=0
[Edta]=varied
No Ca
$PuO_2:2H_2O$ solubility

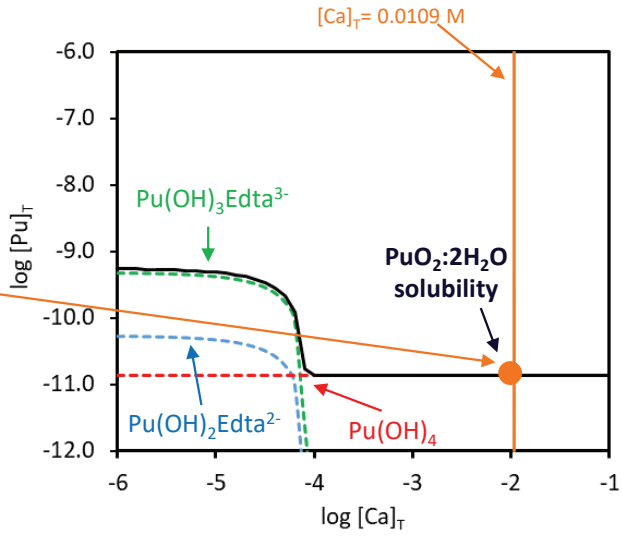
- In the absence of competing ions such as Ca, the Pu(IV) solubility would increase

Effect of Ca and Edta in Pu(IV) chemistry

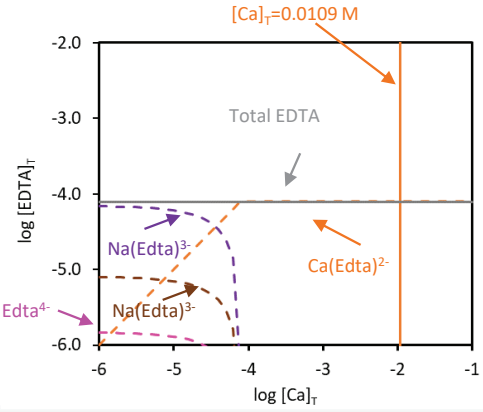
Eh=0; Pu(IV) A78

- **Ca competes with Pu(IV) for complexation with EDTA.**





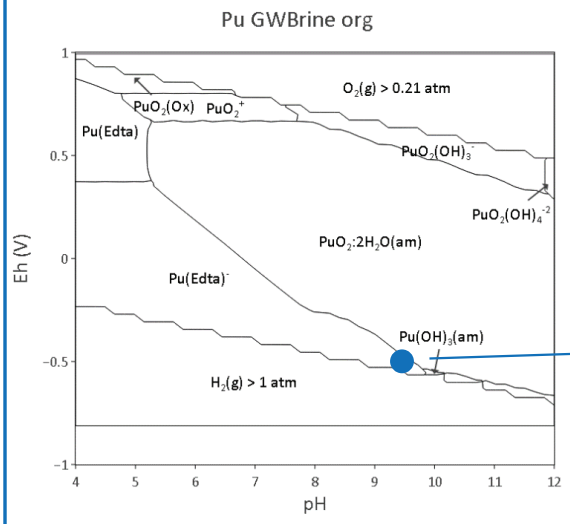
1 M NaCl
pH=9.5
Eh=0
[Edta]=7.9·10^{-5} M
[Ca]=varied
PuO_2:2H_2O solubility

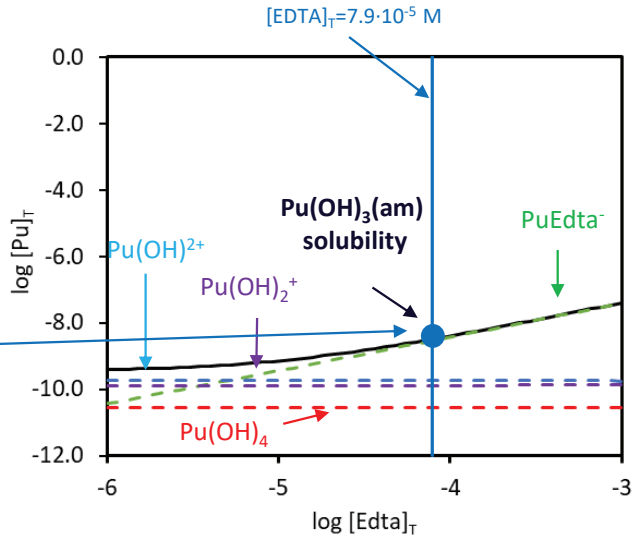


Effect of Ca and Edta in Pu(III) chemistry

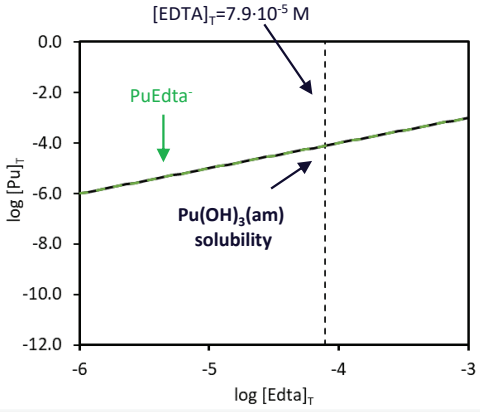
Eh=-0.5; Pu(III) A79

- **Ca competes with Pu(III) for complexation with EDTA.**
  The competence is not so strong as the one with Pu(IV)





1 M NaCl
pH=9.5
Eh=-0.5
[Edta]=varied
[Ca]=0.0109
$Pu(OH)_3(am)$ solubility



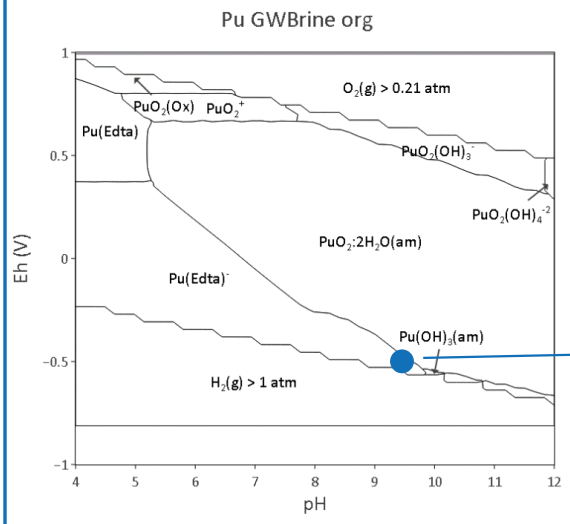
1 M NaCl
pH=9.5
Eh=-0.5
[Edta]=varied
No Ca
$Pu(OH)_3(am)$ solubility

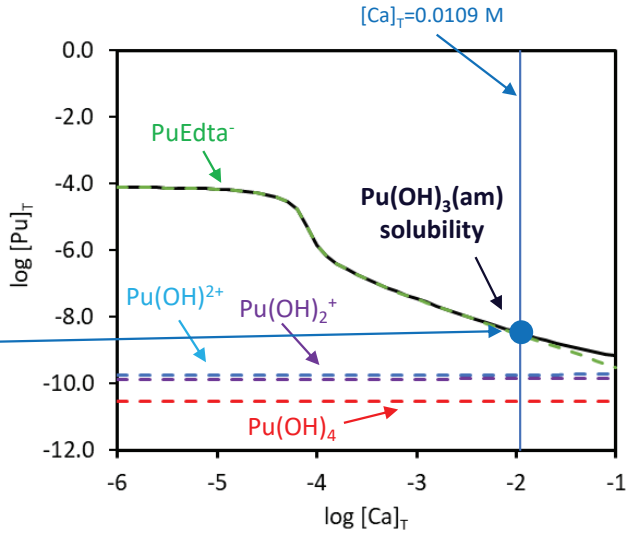
- In the absence of competing ions such as Ca, the Pu(III) solubility would increase significantly

Effect of Ca and Edta in Pu(III) chemistry

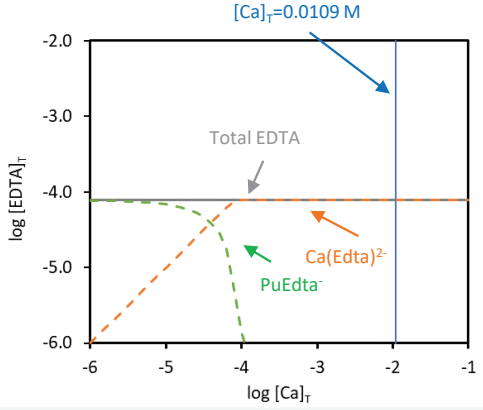
A80

- **Ca competes with Pu(III) for complexation with EDTA.**
  The competence is not so strong as the one with Pu(IV)





1 M NaCl
pH=9.5
Eh=-0.5
[Edta]=7.9·10^{-5} M
[Ca]=varied
Pu(OH)$_3$(am) solubility

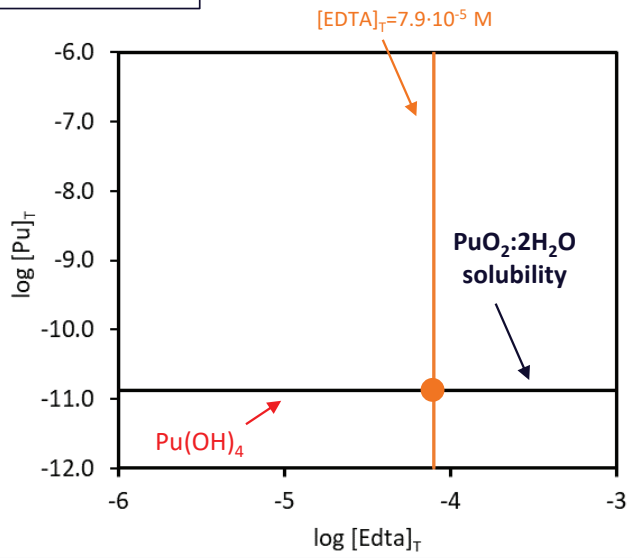


Effect of EDTA on Pu chemistry: conclusions

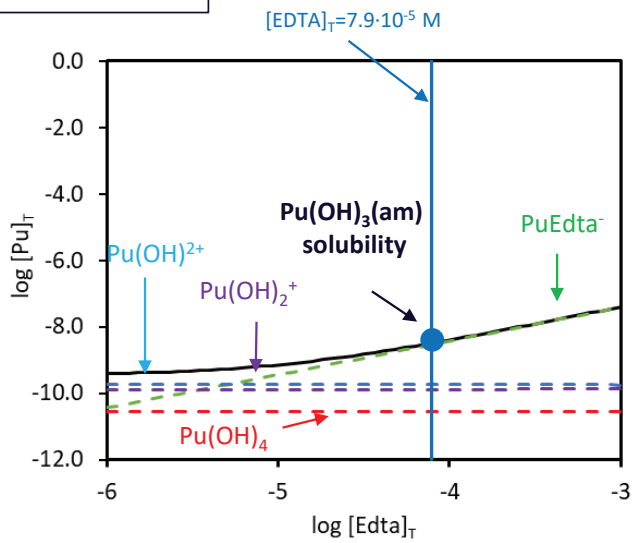
Effect of EDTA on Pu chemistry at 8<pH<10:

- At higher Eh values (Eh≈0), main aqueous species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can limit Pu aqueous concentration. In the presence of Ca, EDTA influence on Pu(IV) speciation is very limited.
- In the more reducing Eh conditions (Eh≈-0.5), $Pu(EDTA)^-$ species may be formed. EDTA influence on Pu(III) speciation is reduced due to the presence of Ca.

1 M NaCl
pH=9.5
Eh=0
[Edta]=varied
[Ca]=0.0109
PuO_2:$2H_2O$ solubility



1 M NaCl
pH=9.5
Eh=-0.5
[Edta]=varied
[Ca]=0.0109
$Pu(OH)_3$(am) solubility



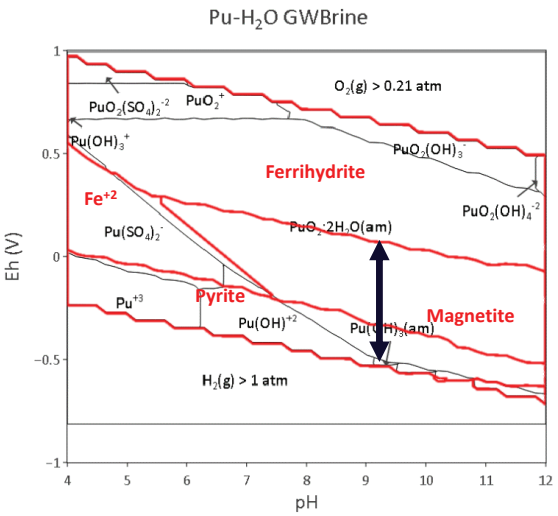
A82

Summary and conclusions



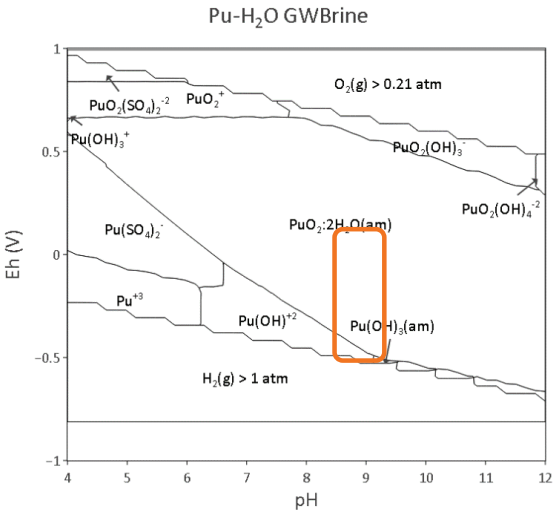
A83

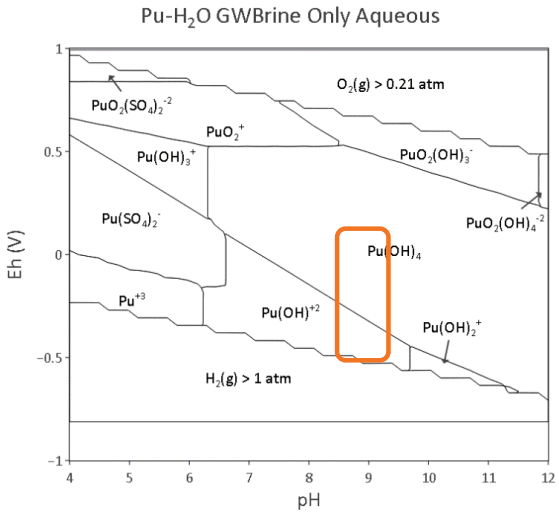
Summary and conclusions



Under the studied conditions (GWBrine, ERDA-6 compositions shown in the tables):

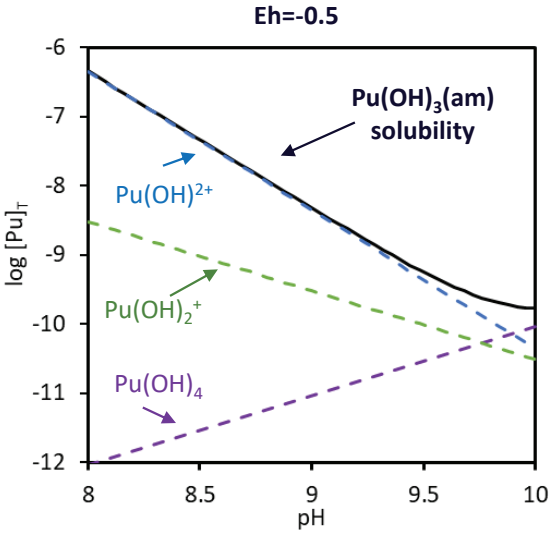
- At pH≈9.5, absence of organic ligands and Eh range defined by magnetite/ferrihydrite boundary:
  - At higher Eh values, main aqueous Pu species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can limit Pu aqueous concentration
  - In the more reducing Eh conditions, $Pu(OH)^{2+}$ and $Pu(OH)_2^{+}$ may be the predominant Pu aqueous species. Pu(III) solid hydroxides may limit Pu aqueous concentration

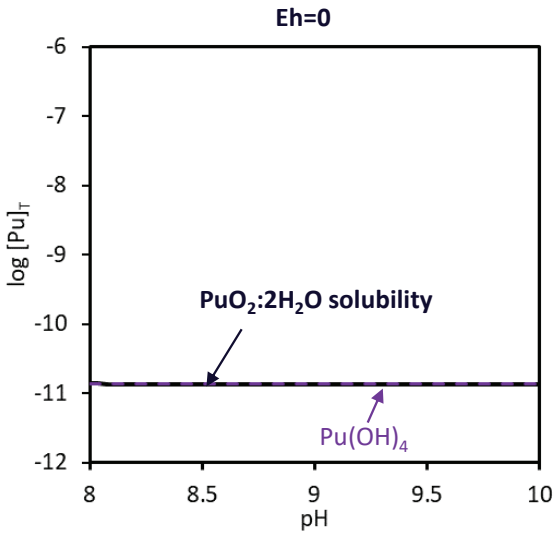




Summary and conclusions

- At 8<pH<10, absence of organic ligands :
  - Pu(III) species are stable slightly above the water stability field
  - At higher Eh values (Eh≈0), main aqueous Pu species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can limit Pu aqueous concentration.
  - In the more reducing Eh conditions (Eh≈-0.5), $Pu(OH)^{2+}$ and $Pu(OH)_2^{+}$ may be the predominant Pu aqueous species. Pu(III) solid hydroxides may limit Pu aqueous concentration.

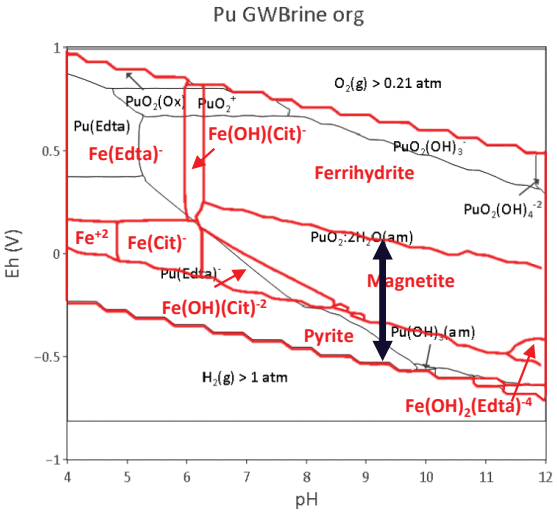


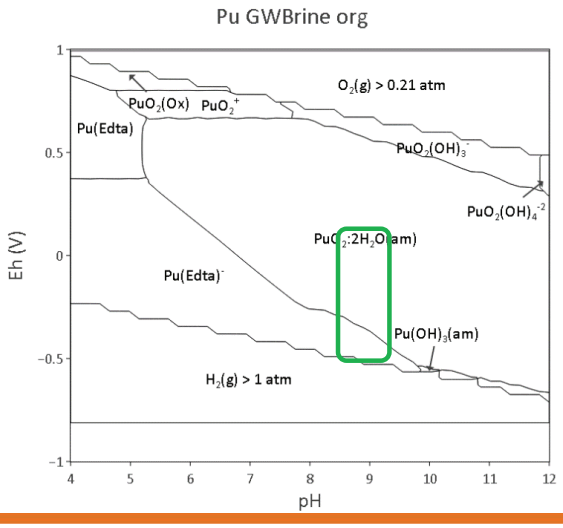


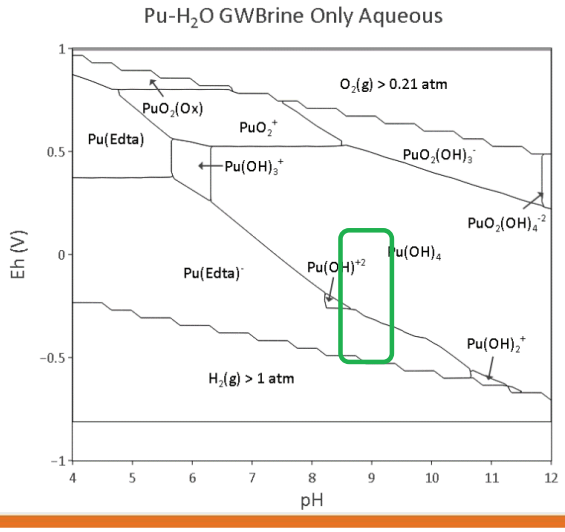
Summary and conclusions

Under the studied conditions (GWBrine, ERDA-6 compositions shown in the tables): A85

- At pH≈9.5, presence of organic ligands and Eh range defined by magnetite/ferrihydrite boundary:
  - The role of citrate in Pu chemistry has not been evaluated due to the lack of reliable Pu-citrate thermodynamic data (no Pu-citrate complexes are included in the calculations).
  - At higher Eh values, main aqueous species is predicted to be $Pu(OH)_4$. Pu(IV) solid hydroxides can limit Pu aqueous concentration. EDTA influence on Pu(IV) speciation is limited in the presence of competing ions such as Ca.
  - In the more reducing Eh conditions, $Pu(EDTA)^-$ species may be formed.







A86

Geochemical codes

- SPANA (version released 11-November-2018)
  - Puigdomènech, I. 2009. Medusa: Make equilibrium diagrams using sophisticated algorithms. chemical equilibrium software. Retrieved from https://github.com/ignasi-p/eq-diagr/releases
- PhreeqC version 3.5.0
  - Parkhurst, D.L., Appelo, C.A.J., 2013. Description of input and examples for PHREEQC version 3 - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey. Retrieved from https://www.usgs.gov/software/phreeqc-version-3
- GibbsStudio version 2
  - Nardi, A., de Vries, L.M., 2017. GibbsStudio. Barcelona Science Technologies SL, Barcelona, Spain. Retrieved from http://gibbsstudio.io





AMPHOS 21

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http://www.amphos21.com

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AENOR Gestión Ambiental UNE-EN ISO 14001 GA-2007/0174

EMAS GESTIÓ AMBIENTAL VERIFICADA ES-CAT-00266

25 YEARS 1994 2019

BREAKING THROUGH

A88

Additional calculations: Aqueous iron speciation diagrams

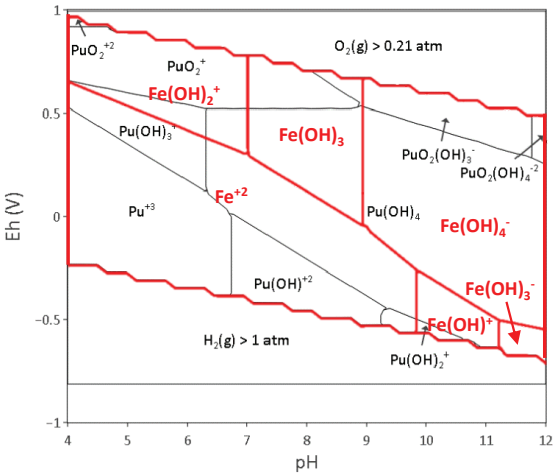
Results in NaCl + Fe

AQUEOUS SPECIES ONLY

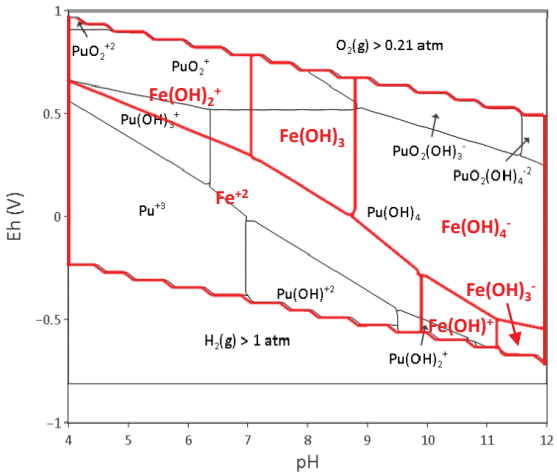
With TC10a-WIPP-2
0.1-1-3-5 M NaCl
$[Fe]_{(tot)}=2.61^{-5}$ M
$[Pu]_{(tot)}=10^{-8}$ M

A89

Pu-H_2O NaCl (0.1M) Only Aqueous



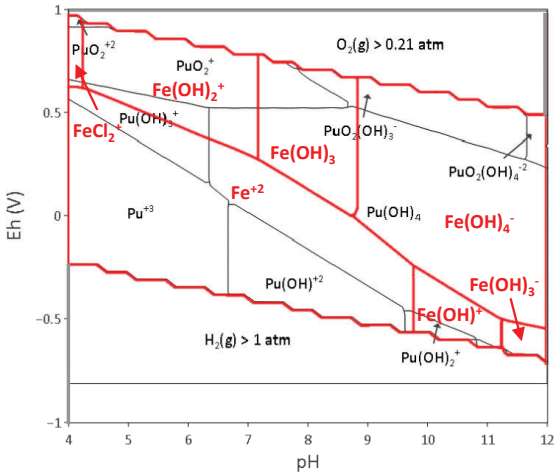
Pu-H_2O NaCl (1M) Only Aqueous



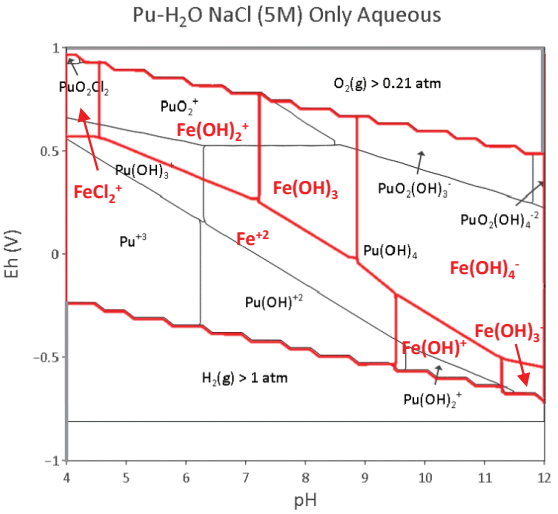
Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS – INORGANIC INCLUDING IRON

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	$2.61 \cdot 10^{-5}$	As in GWBrine
Br	0	
Pb	0	
pH		Varied from 4 to 12
Pu	$1 \cdot 10^{-8}$	Pu concentration in Pourbaix diagrams

Pu-H_2O NaCl (3M) Only Aqueous



Pu-H_2O NaCl (5M) Only Aqueous



Results in GWBrine + Fe

With TC10a-WIPP-2
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

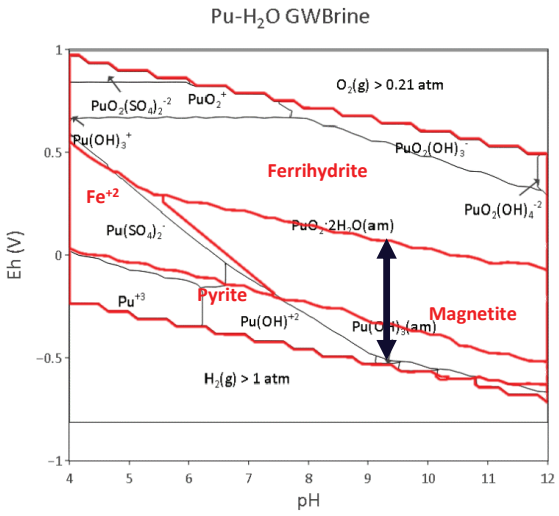
A90

GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

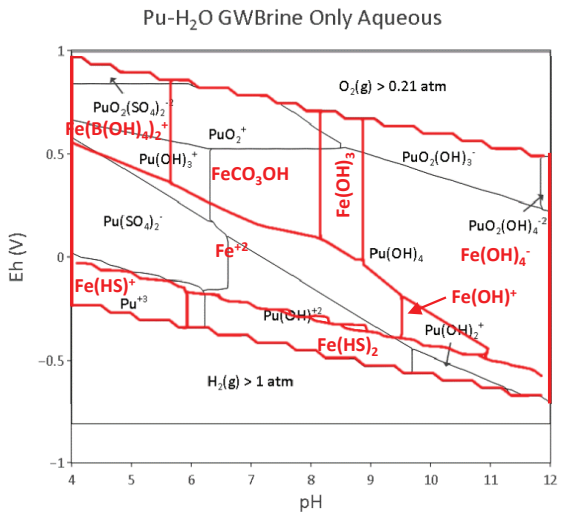
Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-7}$	
pH		Varied from 4 to 12 b)

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



- Magnetite is an Fe(II)-Fe(III) solid likely to dominate Fe chemistry under reducing equilibrium conditions.
- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)

Results in ERDA-6 + Fe

With TC10a-WIPP-2
Table ERDA-6_1
$[Pu]_{(tot)}=10^{-8}$ M

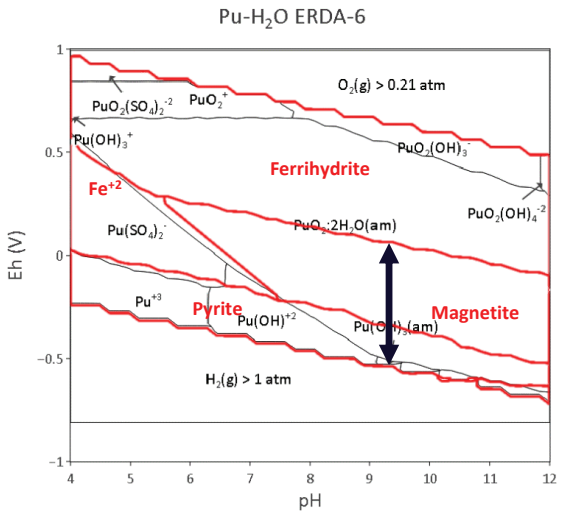
A91

ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS

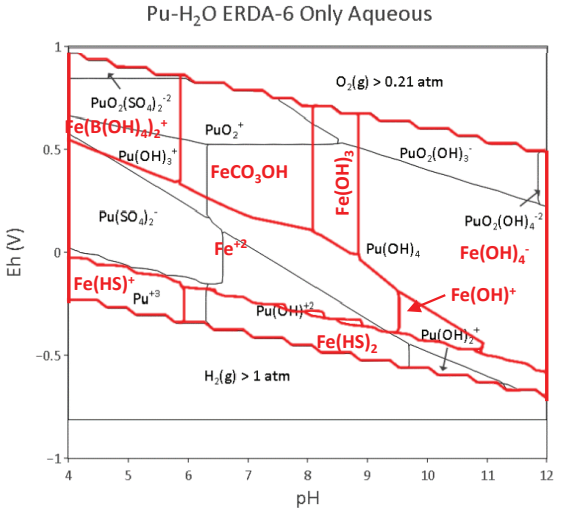
Table ERDA-6_1

Element or property	M	Comments
Na	4.66	
Mg	0.435	
K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



- Magnetite is an Fe(II)-Fe(III) solid likely to dominate Fe chemistry under reducing equilibrium conditions.
- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)

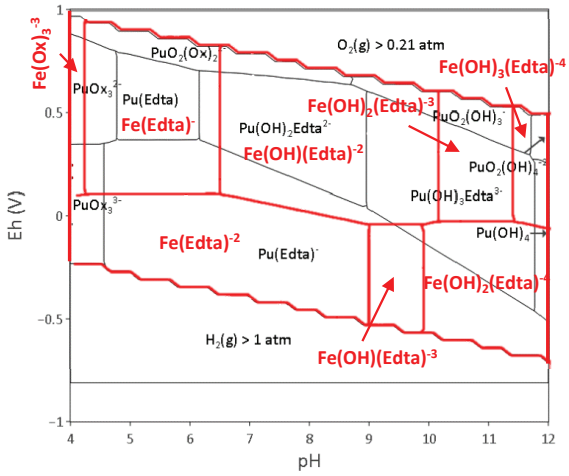
Results in NaCl + organics + Fe

AQUEOUS SPECIES ONLY

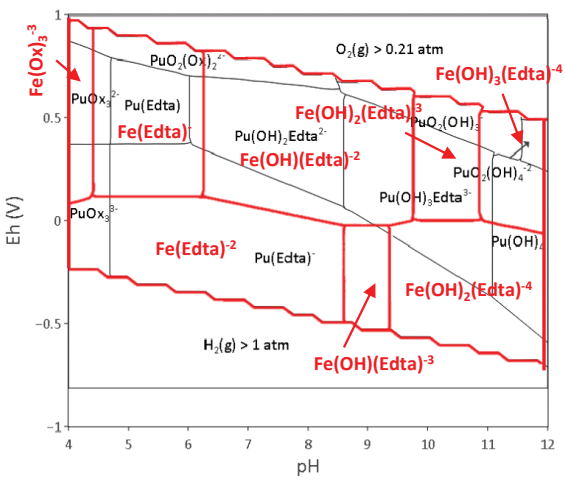
With TC10a-WIPP-2
0.1-1-3-5 M NaCl
Acetate, Cit*, Edta, Ox
$[Fe]_{(tot)}=2.61\cdot10^{-5}$ M
$[Pu]_{(tot)}=10^{-8}$ M

A92

Pu-H_2O-org NaCl (0.1M) Only Aqueous



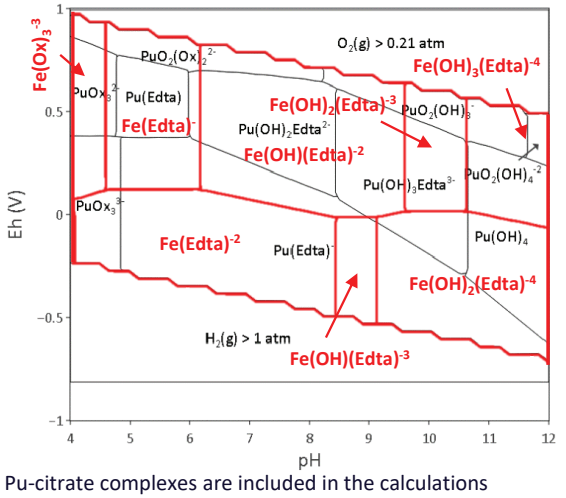
Pu-H_2O-org NaCl (1M) Only Aqueous



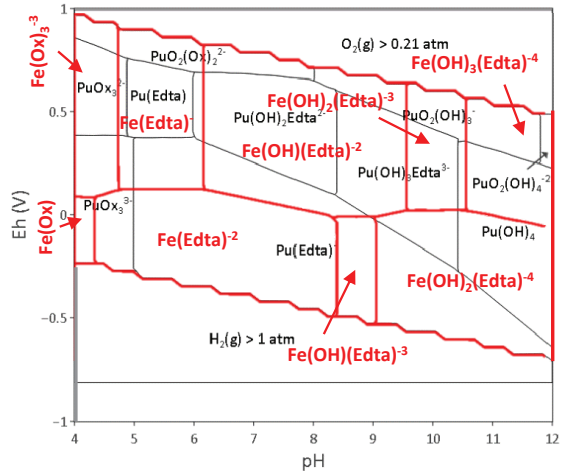
Water composition used in the calculation of the NaCl POURBAIX DIAGRAMS – ORGANIC INCLUDING IRON

Element or property	M	Comments
Na	0.1, 1, 3 or 5	
Mg	0	
K	0	
Ca	0	
S(VI)	0	
Cl	0.1, 1, 3 or 5	
TIC	0	
B	0	
Fe(II)	$2.61\cdot10^{-5}$	As in GWBrine
Br	0	
Pb	0	
Acetate	$2.83\cdot10^{-2}$	
Citrate	$2.30\cdot10^{-3}$	
EDTA	$7.92\cdot10^{-3}$	
Oxalate	$1.13\cdot10^{-2}$	
pH		Varied from 4 to 12
Pu	$1\cdot10^{-8}$	Pu concentration in Pourbaix diagrams

Pu-H_2O-org NaCl (3M) Only Aqueous



Pu-H_2O-org NaCl (5M) Only Aqueous



* No Pu-citrate complexes are included in the calculations

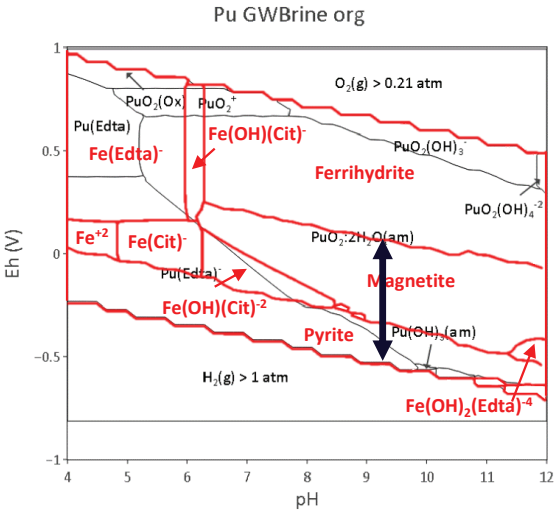
** Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

Results in GWBrine with org + Fe

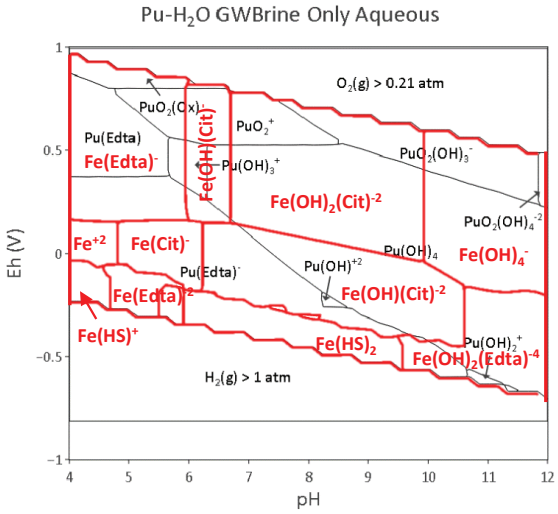
With TC10a-WIPP-2
Table GWBrine_1org
$[Pu]_{(tot)}=10^{-8}$ M

A93

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table GWBrine_1org

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50{\cdot}10^{-4}$	C(IV) [a]
B	0.224	
Fe(II)	$2.61{\cdot}10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90{\cdot}10^{-2}$	
Acetate	$2.83{\cdot}10^{-2}$	
Citrate	$2.30{\cdot}10^{-3}$	
EDTA	$7.92{\cdot}10^{-5}$	
Oxalate	$1.13{\cdot}10^{-2}$	
pH		Varied from 4 to 12 [b]

* No Pu-citrate complexes are included in the calculations

** Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

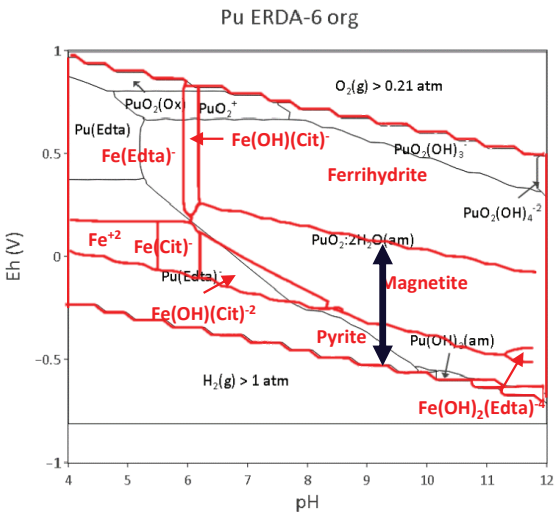
- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)
- At pH≈9.5 and in the presence of organic ligands:
  - EDTA influence on Fe(II) and Fe(III) is limited in the presence of competing ions such as Ca.

Results in ERDA-6 with org + Fe

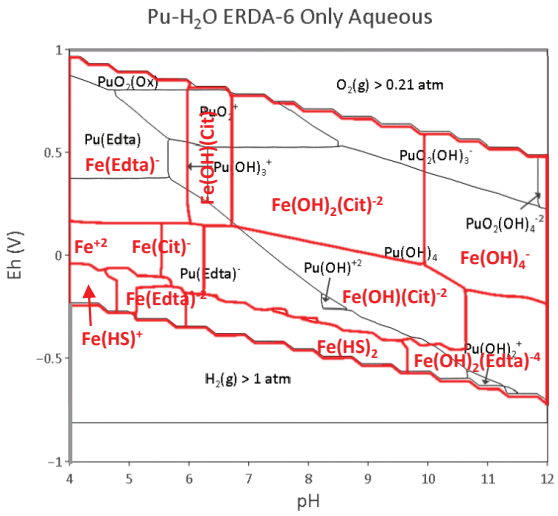
With TC10a-WIPP-2
Table ERDA-6_1org
$[Pu]_{(tot)}=10^{-8}$ M

A94

INCLUDING SOLIDS



AQUEOUS SPECIES ONLY



ERDA-6 composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table ERDA-6_1org

Element or property	M	Comments
Na	4.66	
Mg	0.435	
K	0.499	
Ca	0.0128	
S(VI)	0.224	Total S in calculations
Cl	5.22	
TIC	$2.50 \cdot 10^{-4}$	C(IV) [a]
B	0.281	
Fe(II)	$2.67 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0566	
Pb	$1.88 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 [b]

* No Pu-citrate complexes are included in the calculations

** Crystalline iron solids (hematite, goethite, lepidocrocite, maghemite, $CaFe_2O_4$) are excluded from calculations

- Most likely Eh boundaries will be then defined by H_2/H_2O reaction (lower Eh values) and Magnetite-Ferrihydrite boundary (upper Eh values)
- At pH≈9.5 and in the presence of organic ligands:
  - EDTA influence on Fe(II) and Fe(III) is limited in the presence of competing ions such as Ca.

A95

Additional calculations in GWBrine



GWBrine

Reacted GWBrine A96

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

Table 6. EQ3/6 Predictions of the Compositions and Solubilities of Th(IV), Np(V), and Am(III) in GWB (M Unless Otherwise Noted).

Element or Property	1 × Minimum[A]
B(III)(aq)	0.224
Na(I)(aq)	4.69
Mg(II)(aq)	0.348
K(I)(aq)	0.663
Ca(II)(aq)	0.0109
Fe(II)(aq)	2.61E-05
S(VI)(aq)	0.232
Cl(-I)(aq)	5.40
Br(-I)(aq)	0.0378
Pb(II)(aq)	1.90E-02
Th(IV)(aq)	5.45E-08
Np(V)(aq)	4.02E-07
Am(III)(aq)	1.63E-07
f_{CO_2} (atm)	2.02E-06
I	6.53
pH[B]	8.82
pcH	9.54
RH (%)[C]	0.732
TIC[D]	2.50E-04

GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

a) Total inorganic carbon considered as total carbonate in order to draw the Pourbaix diagrams
b) pH is not a fixed parameter but it is varied from 4 to 12 in the Pourbaix diagrams

Results in GWBrine

With TC10a-WIPP-2
Table GWBrine_1
$[Pu]_{(tot)}=10^{-8}$ M

A97

GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

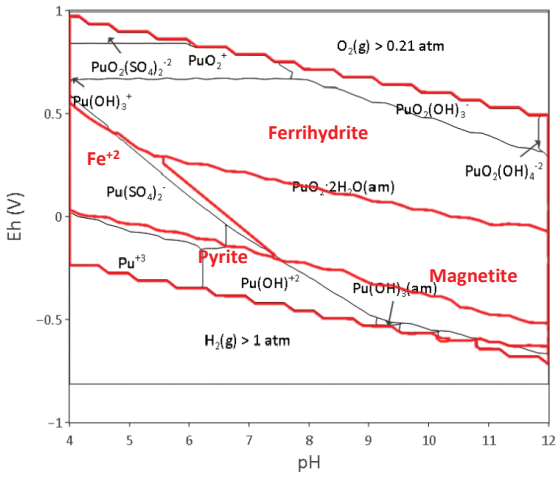
Table GWBrine_1

Element or property	M	Comments
Na	4.69	
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-7}$	
pH		Varied from 4 to 12 b)

INCLUDING SOLIDS

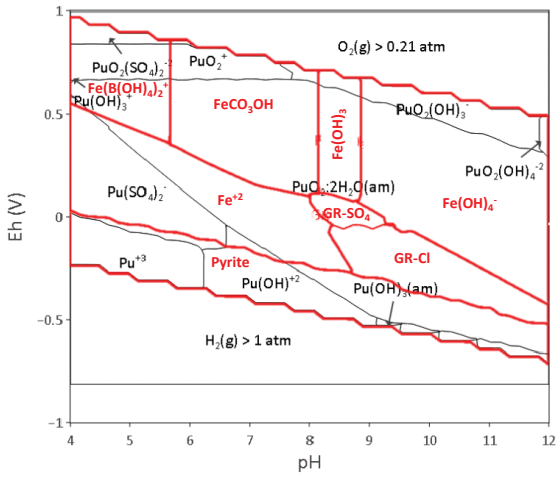
Magnetite and Ferrihydrite included in calculations

Pu-H_2O GWBrine



Magnetite and Ferrihydrite NOT included in calculations

Pu-H_2O GWBrine



- Metastable solids such as Green Rusts may be formed before equilibrium conditions are reached.

Reacted GWBrine A98

GWBrine

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

Table 6. EQ3/6 Predictions of the Compositions and Solubilities of Th(IV), Np(V), and Am(III) in Five Different Volumes of GWB (M Unless Otherwise Noted).

Element or Property	1 × Minimum[A]
B(III)(aq)	0.224
Na(I)(aq)	4.69
Mg(II)(aq)	0.348
K(I)(aq)	0.663
Ca(II)(aq)	0.0109
Fe(II)(aq)	2.61E-05
S(VI)(aq)	0.232
Cl(-I)(aq)	5.40
Br(-I)(aq)	0.0378
Pb(II)(aq)	1.90E-02
Th(IV)(aq)	5.45E-08
Np(V)(aq)	4.02E-07
Am(III)(aq)	1.63E-07
f_{CO_2} (atm)	2.02E-06
I	6.53
pH[B]	8.82
pcH	9.54
RH (%)[C]	0.732
TIC[D]	2.50E-04

GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_2

Element or property	M	Comments
Na	4.69	**Varied: 1 or 3 M**
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	**Varied: 1 or 3 M**
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

a) Total inorganic carbon considered as total carbonate in order to draw the Pourbaix diagrams
b) pH is not a fixed parameter but it is varied from 4 to 12 in the Pourbaix diagrams

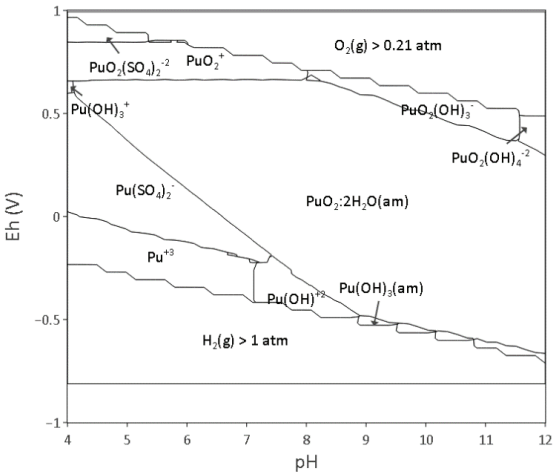
Results in 1-3 M NaCl and GWBrine

With TC10a-WIPP-2
Table GWBrine_2
1-3 M NaCl
$[Pu]_{(tot)}=10^{-8}$ M

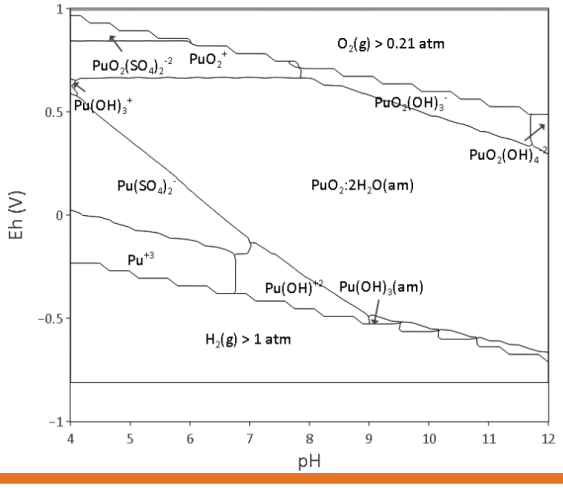
A99

INCLUDING SOLIDS

Pu-H_2O NaCl (1M)

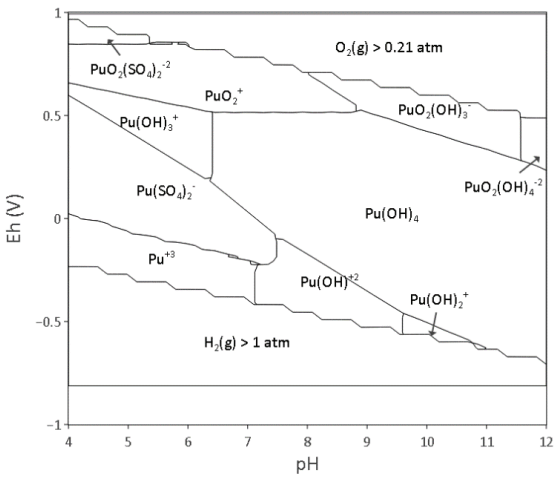


Pu-H_2O NaCl (3M)

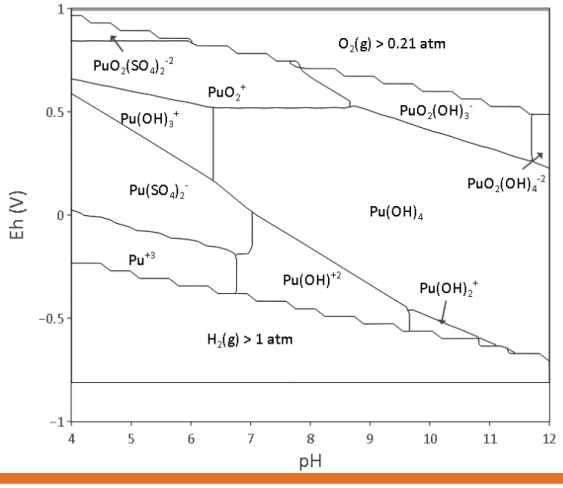


AQUEOUS SPECIES ONLY

Pu-H_2O NaCl (1M) Only Aqueous



Pu-H_2O NaCl (3M) Only Aqueous



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS

Table GWBrine_2

Element or property	M	Comments
Na	4.69	**Varied: 1 or 3 M**
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	**Varied: 1 or 3 M**
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

Reacted GWBrine A100

GWBrine

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

Table 6. EQ3/6 Predictions of the Compositions and Solubilities of Th(IV), Np(V), and Am(III) in GWB (M Unless Otherwise Noted).

Element or Property	1 × Minimum[A]
B(III)(aq)	0.224
Na(I)(aq)	4.69
Mg(II)(aq)	0.348
K(I)(aq)	0.663
Ca(II)(aq)	0.0109
Fe(II)(aq)	2.61E-05
S(VI)(aq)	0.232
Cl(-I)(aq)	5.40
Br(-I)(aq)	0.0378
Pb(II)(aq)	1.90E-02
Th(IV)(aq)	5.45E-08
Np(V)(aq)	4.02E-07
Am(III)(aq)	1.63E-07
f_{CO_2} (atm)	2.02E-06
I	6.53
pH[B]	8.82
pcH	9.54
RH (%)[C]	0.732
TIC[D]	2.50E-04

Table 3. Dissolved Concentrations of Organic Ligands (M) in the Minimum Brine Volume Required for a DBR

Organic Ligand	Minimum Required for a DBR
Acetate	2.83×10^{-2}
Citrate	2.30×10^{-3}
EDTA	7.92×10^{-5}
Oxalate	1.13×10^{-2}

GWBrine composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table GWBrine_2org

Element or property	M	Comments
Na	4.69	**Varied: 1 or 3 M**
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.40	**Varied: 1 or 3 M**
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-5}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-5}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

a) Total inorganic carbon considered as total carbonate in order to draw the Pourbaix diagrams
b) pH is not a fixed parameter but it is varied from 4 to 12 in the Pourbaix diagrams

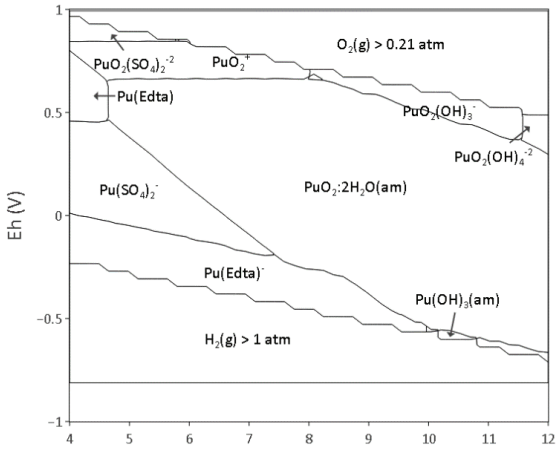
Results in 1-3 M NaCl and GWBrine with organics

With TC10a-WIPP-2
Table GWBrine_2org
1-3 M NaCl
$[Pu]_{(tot)}=10^{-8}$ M

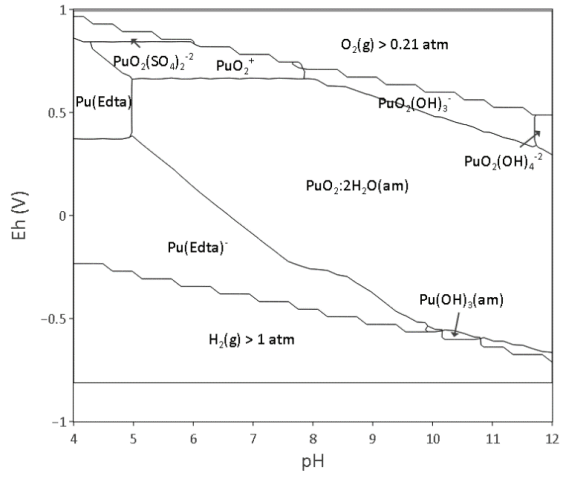
A101

INCLUDING SOLIDS

Pu-H_2O NaCl (1M)

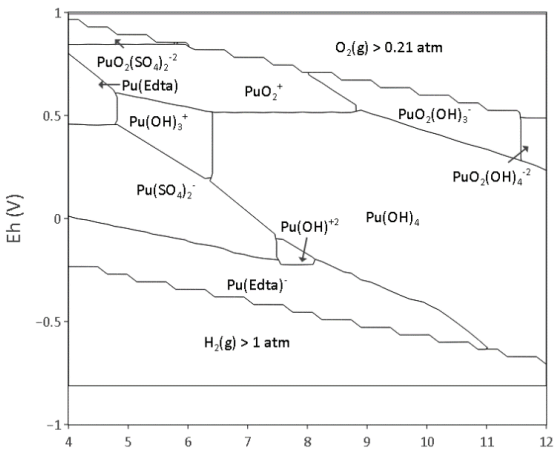


Pu-H_2O NaCl (3M)

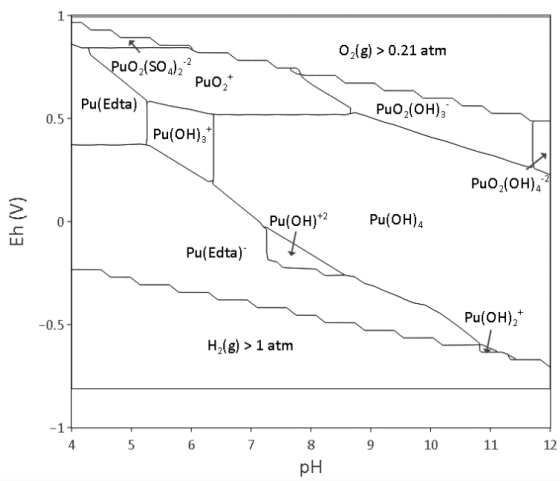


AQUEOUS SPECIES ONLY

Pu-H_2O NaCl (1M) Only Aqueous



Pu-H_2O NaCl (3M) Only Aqueous



GWBrine composition used in the calculation of the POURBAIX DIAGRAMS with organics

Table GWBrine_2org

Element or property	M	Comments
Na	4.00	Varied: 1 or 3 M
Mg	0.348	
K	0.663	
Ca	0.0109	
S(VI)	0.232	Total S in calculations
Cl	5.00	Varied: 1 or 3 M
TIC	$2.50 \cdot 10^{-4}$	C(IV) a)
B	0.224	
Fe(II)	$2.61 \cdot 10^{-3}$	Total Fe in calculations
Br	0.0378	
Pb	$1.90 \cdot 10^{-2}$	
Acetate	$2.83 \cdot 10^{-2}$	
Citrate	$2.30 \cdot 10^{-3}$	
EDTA	$7.92 \cdot 10^{-3}$	
Oxalate	$1.13 \cdot 10^{-2}$	
pH		Varied from 4 to 12 b)

*no Pu-citrate complexes are included in the calculations



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