Plutonium Chemistry in the WIPP: Update and Path Forward

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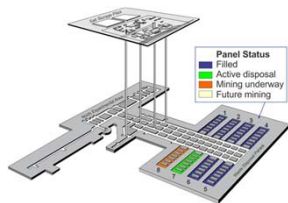## Waste Isolation Pilot Plant (WIPP) Repository: Status and Path Forward

The Waste Isolation Pilot Plant (WIPP) transuranic (TRU) repository remains a cornerstone of the U.S. Department of Energy's (DOE) nuclear waste management effort. At this time, the WIPP is shutdown due to two operational incidents in February 2014. Although shutdown, the WIPP remains certified to operate and is in the process of being recertified for continued operation by the EPA. Parallel efforts to maintain the WIPP license and implement a WIPP recovery plan are underway.

WIPP recovery planning and implementation continues with the expectation that full recovery will be completed in late 2021 to early 2022. This will be done in a series of steps (see figures on the right) that will likely invoke design changes in the WIPP underground, revised acceptance criteria for TRU waste shipments, and a strengthened safety case.

The operational issues at the WIPP have not impacted the long-term safety case for TRU waste containment. Documentation to support a third recertification was submitted in March 2014 and is still under review. A completeness determination by the EPA (WIPP regulator) is expected by the end of 2016, with recertification expected in mid-late 2017.
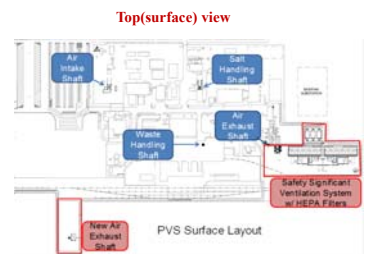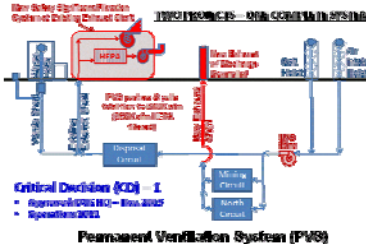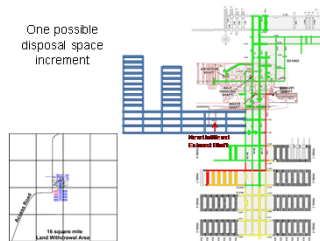

WIPP Surface Facilities

Current Emplacement Status

Path Forward for the WIPP Project

Top(surface) view

PVS Surface Layout

Permanent Ventilation System (PVS)

Underground View

One possible disposal space increment
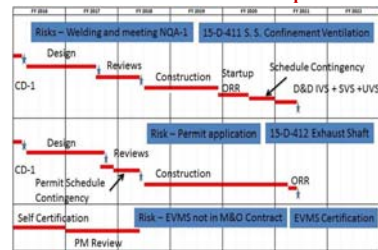
Tentative Schedule FY 2018 - FY 2022 CBFO Request

PLUTONIUM CONTAINMENT IN THE WIPP

Plutonium, especially in the longer term, continues to be the actinide of most concern with respect to release in the WIPP repository concept. The oxidation state distribution and solubility/ speciation of plutonium, in this context, only become important in the low-probability of brine inundation due to human intrusion scenarios. In this context, long-term studies to evaluate the impacts of reduced iron on the likely oxidation state distribution of plutonium and its solubility/speciation using redox-invariant analogs for Pu(III) and Pu(IV) are ongoing [1-5]. The results of these experiments to date continue to support the current conceptualization of plutonium in the WIPP safety case.

The core safety case for the containment of plutonium in the WIPP is the self-sealing property of the bedded salt formation[5]. This self-sealing is relatively rapid (a few hundred years or less) and will permanently isolate the TRU waste. Under this scenario, geologic isolation is achieved since the repository will not likely saturate leading to essentially no significant release of TRU. However, low-probability human intrusion scenarios could lead to brine saturation of the waste in the repository and the formation of a mobile actinide concentration and subsequently release actinides to the accessible environment.

The approach used to model plutonium behavior, should brine-inundation occur, was established for the initial license application and has been reviewed/accepted by the EPA regulator three times (initial license and two recertification reviews). The key features of this approach are:

o Once self-sealing occurs, the repository will rapidly become anoxic and the reduced iron phases will establish a strongly reducing brine chemistry environment. This is augmented by microbial processes that also remove oxygen and may reduce metals/actinides directly.

o Pu(V) and Pu(VI) do not persist in the WIPP due to these reducing conditions. It is, however, recognized that they may be present as transients due to radiolytically-induced localized oxidizing zones.

o The oxidation-state distribution of plutonium is fixed, by expert opinion, to be Pu(III) in ~50% and Pu(IV) in ~50% of the PA vectors. This is considered to be a conservative assumption because Pu(IV) should predominate and Pu(III) is ~ 10 times more soluble.

o The concentration of mobile plutonium species is determined as the solubility of Pu(III) and Pu(IV) phases and the corresponding colloidal species that are associated with each oxidation state.

o Th(IV) is used as an oxidation-state invariant analog for Pu(IV). Am/Nd(III) are used as the oxidation-state invariant analog for the solubility of Pu(III). In both cases, the Pitzer model is used to calculate solubility and these model calculations are confirmed by site-specific solubility measurements.

In the WIPP safety case, the reliance is on the site geology, and not the survivability/integrity of the container, to attain TRU waste isolation. The container is to aid shipping and emplacement.

Calculated Actinide Solubility: Historical Trends

Actinide Oxidation State, and Brine	CRA-2004 PABC (M)	CRA-2009 PABC (M)	CRA-2014 PA (M)
III, GWB	3.87×10^{-7}	1.66×10^{-6}	2.59×10^{-6}
III, ERDA-6	2.88×10^{-7}	1.51×10^{-6}	1.48×10^{-6}
IV, GWB	5.64×10^{-8}	5.63×10^{-8}	6.05×10^{-8}
IV, ERDA-6	6.79×10^{-8}	6.98×10^{-8}	7.02×10^{-8}
V, GWB	3.55×10^{-7}	3.90×10^{-7}	2.77×10^{-7}
V, ERDA-6	8.24×10^{-7}	8.75×10^{-7}	8.76×10^{-7}

Pu Isotopes in WIPP and key waste components emplaced

Plutonium Isotope	Activity in Ci (% of Total)	Mass in Kg (% of Total)
^{238}Pu	6.01×10^{5} (29.7)	34.7 (0.29)
^{239}Pu	5.74×10^{5} (28.4)	9.13×10^{3} (76.3)
^{240}Pu	1.75×10^{5} (8.6)	762 (6.4)
^{241}Pu	6.63×10^{5} (32.8)	6.38 (~0)
^{242}Pu	8.09×10^{3} (0.40)	2.04×10^{3} (17.0)
^{244}Pu	0.0101 (~0)	0.567 (~0)

Waste Material	Total Mass (Kg)
Iron-Based metals/alloys	4.91×10^{7}
CPR (Cellulosic/Plastic/Rubber)	1.54×10^{7}
MgO (Engineered Barrier)	5.14×10^{7}
Organic Ligands (Citrate)	7.78×10^{3}
Organic Ligands (EDTA)	3.76×10^{2}

Total Pu as f(time)

Repository time	2033 (0 years)	2133 (100 years)	3033 (1000 years)	12033 (10,000 years)
Pu — Ci	2.02×10^{6}	1.03×10^{6}	7.24×10^{5}	5.00×10^{3}
Pu — Kg	1.20×10^{4}	1.19×10^{4}	1.16×10^{4}	9.12×10^{3}
% of Actinide Activity	74%	62%	83%	99.8%

Plutonium Redox Chemistry in the WIPP

Plutonium, for most of the duration of repository performance (10,000 y), is the most important actinide with respect to potential release as well as public perception and concern. Overall, the ranking of actinides is:

$$Pu \approx Am \gg U > Th \gg Np \approx Cm$$
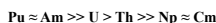
From the point of view of oxidation state, rather than nuclide, the ranking with respect to release is:

$$An(III) > An(IV) \gg An(VI) \gg An(V)$$

Under the expected conditions in the WIPP, a range in the redox environment is considered in PA where plutonium is predicted to exist predominantly as Pu(III) and/or Pu(IV) species. This is captured in PA by assuming that Pu(IV) exists in all "oxidized" vectors (50% of the time) and Pu(III) exists in all "reduced" vectors (also 50% of the time).
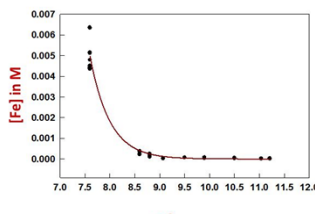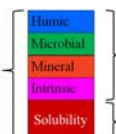
The predominant redox pathway that will sustain lower plutonium oxidation states in the WIPP in the event of brine inundation is the reduction of higher-valent plutonium by reduced iron (Fe(0) or Fe(II)). In the presence of reduced iron, we have shown that reduction of Pu(V/VI) occurs under all anoxic conditions that have been investigated. Measured E_h values between -100 mV and -250 mV are observed. Plutonium (IV) and Pu(III) are observed in both the solids present (XANES) and the aqueous phase (TTA extraction). Currently our data show that in the presence of organics and/or Pu-239 we see predominantly Pu(IV); with mixed Fe(II/III) oxides we see both Pu(III) and Pu(IV); and for Pu-242 (lower radiolysis) w/o organics we see only Pu(III) in both the solid and aqueous phase.

~ 6-10 year data obtained cryogenically at SLAC showing Pu(III) in Fe(0) and Pu(IV) when magnetite was the predominant iron phase

Pu(V/VI) → **Rapid** → Pu(IV) → **Slow** → Pu(III/IV)
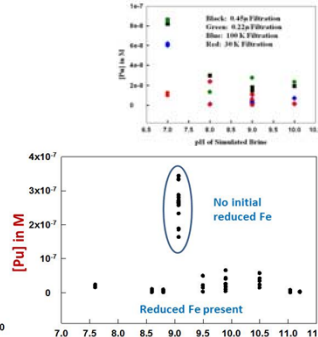
~3-month Analyses

~4-year Analyses
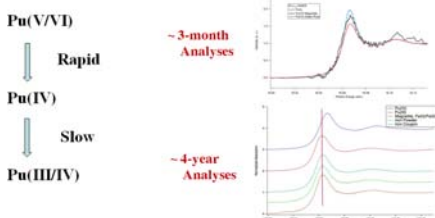
Plutonium Solubility and Speciation in the WIPP

The solubility of plutonium is modeled using a combination of Am(III)/Nd(III) data and Th(IV) data as analogs. Current WIPP-specific calculations are shown above. The speciation of Pu(III) will be dominated by EDTA/Citrate complexation and the assumed concentration of these organic complexants defines the current predicted solubilities. This is confirmed experimentally in our Nd^{3+} studies. The solubility of thorium(IV) is not significantly affected by pH and the range of carbonate and organic complexants expected in the WIPP. Plutonium concentrations expected are however 100 to 1000 times lower in Fe dominated systems. Plutonium studies are underway to further evaluate oxidation-state distribution trends, colloidal contributions to solubility, and overall solubility as a function of brine and ionic strength.

Size distribution of plutonium in long-term solubility studies (colloidal Fe is present)

Mobile actinide concentration (actinide source term): Humic, Microbial, Mineral, Intrinsic, Solubility

Actinide concentration added due to colloidal species

solubility of the actinide that reflects pH, inorganic/organic complexation

~ 10 year Pu-Fe data showing that Fe(0, II) are key to establishing low Pu solubilities and Pu(III/IV) oxidation state predominance. A higher amount of colloidal species is observed in the pH regime where borate and carbonate speciation predominates (pC$_{H+}$ 8.5 – 11).

References

[1] J. F. Lucchini, M. Borkowski, M. K. Richmann, and D. T. Reed, "Solubility of Nd^{3+} and UO$_2$$^{2+}$ in WIPP brine as oxidation-state invariant analogs for plutonium," Journal of Alloys and Compounds, Volumes 444-445 (2007) 506-511.
[2] M. Borkowski, M. Richmann, D.T. Reed and Y. Xiong, "Complexation of Nd(III) with Tetraborate Ion and Its Effect on Actinide(III) Solubility in WIPP Brine", Radiochim. Acta, 98, 1-6 (2010).
[3] M. Borkowski, J-F. Lucchini, M. Richmann, D.T. Reed. Actinide (III) Solubility in WIPP Brine: Data Summary and Recommendations. Report LA-14360. Los Alamos. September 2009. LA-UR 09-03222
[4] D. T. Reed, J. F. Lucchini, S. B. Aase, and A. J. Kropf, "Reduction of Plutonium (VI) in Brine under Subsurface Conditions," Radiochim Acta, 94 (2006) 591-597.
[5] Appendix SOTERM-2014, Actinide Chemistry Source Term. Title 40 CFR Part 191Subparts B and C Compliance Recertification Application 2014. for the Waste Isolation Pilot Plant; and Van Soest, G. 2012. *Performance Assessment Inventory Report – 2012* (PAIR 2012). INV-PA-12, LANL-CO\Inventory Report, Los Alamos, NM: Los Alamos National Laboratory (2013).