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White Paper: WIPP Chemistry-related Conceptual Models Compared to Natural Analogues

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INTRODUCTION

WIPP chemistry-related conceptual models use simplifying assumptions that are conservative in that their use under-estimates performance. The following are compared to natural analogues:

- No actinide (An) sorption in the disposal area (Section 1),
- Cellulose biodegradation to only CO_2 (Section 2),
- No organic ligand degradation (Section 3), and
- Solubility model-predicted actinide concentrations (Section 4).

Natural analogue evidence is used to enhance confidence in the safety case for nuclear waste repositories (NEA, 2012). Because natural analogues never exactly match specific repository processes, the goal here is to use natural analogues to identify analyses which could reduce uncertainty in the chemistry-related conceptual models. This should improve the chemistry-related conceptual models' ability to anticipate actinide mobility in disposal area fluids. The analysis below assumes large-scale mixing in the disposal area. Heterogeneity at the centimeter to meter scale might cause local variations in chemical behavior. Radiolysis in the disposal area is not considered.

SECTION 1. NO ACTINIDE SORPTION IN THE DISPOSAL AREA

Sorption is likely to control dissolved An levels at WIPP. Assuming no An sorption in the disposal area, DOE's present approach, means dissolved An concentrations are assumed to be controlled by solubility reactions that can can be measured, or predicted with an equilibrium thermodynamic model. WIPP uses model-predicted solubilities (DOE, 2019). When sorption is accounted for, actinide concentrations are predicted to be lower than predicted solubilities by factors of: 5 for Th; 90 for Pu; and 2400 for Am (Brady, 2024), which emphasizes that leaving out sorption is conservative. It also means that An solubility-controlling solids are unlikely to form at WIPP. This fits with measurements from radionuclide-contaminated environmental sites where dissolved An concentrations are typically lower than solubility limits because dissolved An concentrations are controlled by sorption reactions. The US Agency for Toxic Substances and Disease Registry (US ATSDR) states "*^{241}Am released into water from nuclear facilities will tend to stick to particles in the water or the sediment. ^{241}Am deposited on soil is so strongly attached to soil particles that it does not travel very far into the ground. Ultimately, most americium ends up in soil or sediment*" (US ATSDR, 2004); for plutonium, "*Once plutonium is deposited either on the land or surface water, sorption to soils or sediments is the primary environmental fate of plutonium*" (US ATSDR, 2010); for thorium, "*In most soil, thorium will remain strongly sorbed onto soil and the mobility will be very slow*" (US ATSDR, 2019). EPA states "*The adsorption of plutonium and americium is anticipated to be the predominant*

WIPP:4.4.2.2.1:PA:QA-L:574933

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mechanism controlling solid partitioning in ground-water systems" (Ford et al., 2010, Pg. 114), and "*thorium partitions strongly to essentially all mineral surfaces*" (Ford et al., 2010, Pg. 91). For example, mean sorption K_ds for americium, An(III), on sand, silt, clay, and organic soils range from 1900 to 119,000 mL/g; and for Th, An(IV), and the same substrates K_ds are 3200 – 89,000 mL/g (Thibault et al., 1990, Table 8). Measured K_ds for Am and Th sorption to marine sediments are, respectively, 1.5e5 – 1.8e5 mL/g (Vangenechten et al., 1986) and 1e5 to 1e7 mL/g (Cochran et al., 1986).

For reference, a K_d is the ratio of the concentration of a sorbed component (for example, in moles/mg) to its dissolved concentration (for example, moles/mL). A K_d greater than zero indicates sorption; the larger the K_d, the more sorption that occurs. K_ds are specific to the conditions under which they are measured. Site density is the number of available surface sites normalized to surface area or mass of a particular substrate in moles/M^2 or moles/g. Sorption capacity is the number of available surface sites in a given volume of substrate (moles). For K_ds to be most accurate, there must be more surface sites than there are sorbing species.

The previous analysis (Brady, 2024) identified Fe corrosion products, waste soil, and waste cement as important An sorbers at WIPP. Cellulosic sorption of Ans is examined below. Cellulosics makes up a large fraction of the WIPP waste, and are projected to persist to 10,000 years in a majority of PA calculations.

An Removal by Cellulosics

There are more reactive sites on WIPP cellulosic surfaces than there are Ans in the WIPP inventory. WIPP cellulosics include paper, cardboard, Kimwipes®, wood, cellophane, and cloth (DOE, 2016) which are made up of both true cellulose, a polysaccharide, and lignin. Cardboard is 10 % lignin; paper is 10 – 30 % lignin, the rest being cellulose. Cellulose surfaces primarily expose a carboxylate group (Sundman et al., 2008); lignin surfaces expose a phenolate group as well (e.g. Guo et al., 2008). The carboxylate surface site density of kraft pulp fiber, a widely used low-lignin ingredient of paper, is 4.3e-5 mol/g (Sundman et al., 2008). Lignin carboxylate and phenolate surface site densities are ~ 3.0e-4 and 6.0e-4 mol/g (Guo et al. 2008). The surface site density of the carboxylate + phenolate in the cellulose and lignin that make up wood is 1.1e-4 mol/g (Tiruta-Barna and Schiopu, 2011).

Assuming the WIPP cellulosic inventory to be 70 % cellulose, 20 % lignin, and 10 % wood, and using the cellulose, lignin, and wood site densities from above, predicts a WIPP cellulosic site density of 2.2e-4 mol/g. Multiplying the WIPP cellulosic site density by the WIPP cellulosic mass (g) and dividing by the minimum direct brine release (DBR) volume (3.38e4 M^3, King, 2021) indicates 45 moles of cellulosic sites per M^3 of brine. The minimum DBR volume is used to normalize concentrations to a M^3 of brine, because the latter is an easily conceived quantity.

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The cellulosic surface site density is over 5 times higher than the calculated total WIPP An inventory, Am + Pu + Th, in the minimum DBR, 8.0 mol/M^3. Am, Th, and Pu in the WIPP inventory are: 835, 5.9e4, and 2.1e5 moles (Reed, 2015 and National Academies Press, 2020).

Figure 1 compares the calculated sorption capacity of WIPP cellulosics to other prominent WIPP sorbents – Fe corrosion products, and waste soil and cement (Brady, 2024). The latter values were calculated by multiplying their respective masses by an assumed site density (2.3 sites/nm^2, Davis and Kent, 1990) and surface areas (from Brady, 2024), divided by the minimum DBR volume. Figure 1 suggests that An sorption to WIPP cellulosics will be a substantial sink for dissolved Ans at WIPP while they persist. If/when cellulosics are biodegraded to humic substances, a capacity for An sorption from immobile humics will still remain (Section 2).

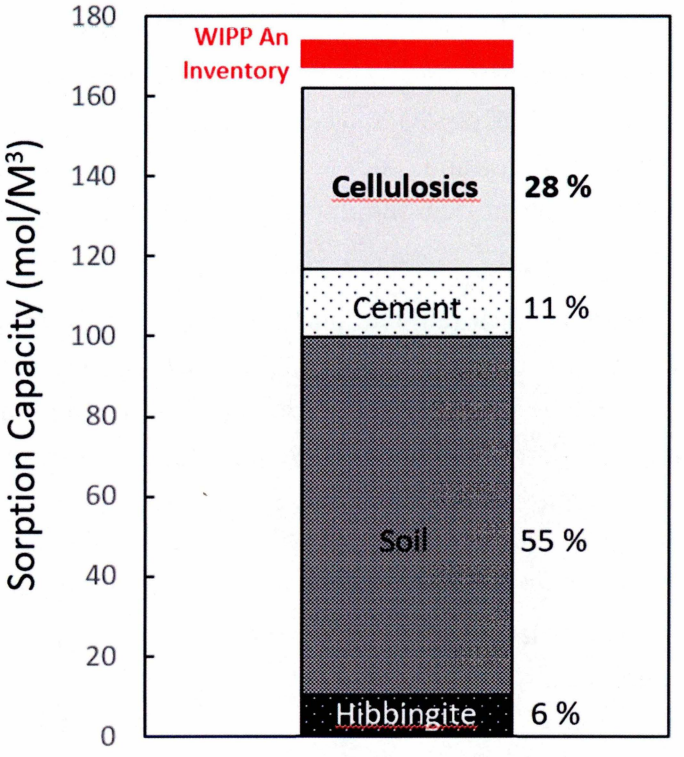


Figure 1. Sorption capacities of CH-waste packaging, and waste soil, cement, and cellulosics (normalized to the minimum DBR volume). Plastics and rubber are left out. 55 gal steel drums are assumed to be completely degraded to hibbingite.

Lastly, natural analogue and experimental measurements suggest the high salinity and Mg of WIPP brine should not decrease An sorption because: salinity does not significantly affect sorption of the Am analogue Eu to iron corrosion products (Morelova, 2020), Th sorption to γ-Al_2O_3 (Chen and Wang, 2007), or Th sorption to Al hydroxide (Hongxia et al., 2006); and Ans

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sorb strongly to marine sediments (e.g. McDonald et al., 2001) despite very high Mg/An solution ratios.

Uncertainty Reduction

Measure An K_ds in WIPP brine on WIPP sorbents - Fe corrosion products, waste soil and cement (Brady, 2024), and cellulose.

SECTION 2. CELLULOSE DEGRADATION TO CO_2

CPR at WIPP will probably degrade to produce humic substances, HSs, in addition to CO_2. DOE presently assumes that all waste CPR degrades to CO_2. Biodegradation of organic matter in soils and landfills produces humic substances (e.g. Castagnoli et al., 1990) as well. There is no reason to expect different at WIPP. This is important because HSs sorb Ans.

HSs are humic and fulvic acids, and humin. Each consists of a large number of compounds of varying stoichiometry each with their own solubility. The CCA recognized the possibility of HSs forming at WIPP noting (DOE, 1995, pg. SOTERM-58) "Probably more importantly, humic substances may form from condensation reactions between microbial metabolites (for example, carboxylic acids), cellulosic degradation products, and the extracellular polymers associated with microbes."

In the WIPP chemistry-related conceptual models HSs can only mobilize Ans. Natural analogue evidence from soils and sediments suggests that HSs will instead reduce concentrations of mobile Ans at WIPP. Immobile HSs dominate the total cation exchange capacity (CEC) of soils and sediments, and have a higher CEC than clays (Rashid, 1969). Because HS solubility measured in WIPP brine is 2 mg/L (DOE, 1996a, pg. SOTERM-59), most An-sorbing HSs will be immobile, thus able to remove Ans from solution. For example, while biodegradation of 1 % of the WIPP cellulosic C to HSs (0.82 g/L in the minimum DBR volume) would mean 2 mg/L of dissolved HSs available to mobilize Ans; it would also mean 818 mg/L of stationary HSs able to bind and immobilize roughly half the WIPP An inventory, assuming an HS site density of 5e-3 mol/g (Brady, 2024).

Although the bulk of HSs will be immobile, there will still be 2 mg/L of dissolved HSs. But because dissolved An concentrations will be lowered by binding with immobile HSs (and by sorption to other surfaces in the disposal area) the amount of HS-mobilized Ans will be substantially lower. This effect has been observed experimentally for the An(III) analogue Eu by Takahashi et al. (1998).

Uncertainty Reduction

Measure An binding to solubility-immobilized HSs in WIPP brine.

SECTION 3. NO ORGANIC LIGAND DEGRADATION

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EDTA will probably degrade before it becomes available for An transport at WIPP. For solubility predictions, WIPP assumes an inventory-limited EDTA concentration that conservatively ignores oxic biodegradation + sorption of EDTA before disposal, and biodegradation + sorption once disposed but before anoxic conditions prevail at WIPP (Brady, 2024). EDTA is the strongest An complexant of known WIPP organic ligands (e.g. Domski, 2023, Tables 8, 9, 12, and 13), and the most resistant to biodegradation (Swanson et al., 2013), particularly under anoxic conditions.

Yet EDTA is biodegraded rapidly under oxidizing conditions, having a biodegradation half-life of "weeks to months" (US EPA, 2006). Recent measurements of relatively rapid EDTA biodegradation support EPA's short biodegradation half-life. Wen et al. (2009) measured 14 % EDTA degradation in 20 days in Cd and Zn contaminated soil, and 30 % EDTA degradation in 20 days in uncontaminated soil. Guo et al. (2015) measured soil EDTA half-lives of 21 – 75 days.

Since EDTA in WIPP waste will have seen over a hundred years of non-anoxic conditions, above and below ground, natural analogue evidence suggests that EDTA persistence in the WIPP disposal area is unlikely.

Uncertainty Reduction

Examine the stability of EDTA in WIPP waste streams (Brady, 2024).

SECTION 4. ACTINIDE CONCENTRATIONS

There are no natural analogues for WIPP-predicted An solubilities. A natural analogue that might be relevant to WIPP is sediments in the Irish Sea exposed to decades of radioactive waste discharge from the British Nuclear Fuels Reprocessing facility at Sellafield, Cumbria, UK. But dissolved Pu and Am concentrations in the sediments off the Cumbrian coast are controlled by sorption reactions (e.g. McDonald et al. 2001) which the WIPP model conservatively leaves out.

In the CCA the DOE chose not to measure An solubilities directly, but to experimentally calibrate a Pitzer solubility model to predict solubilities because (DOE, 1996a, SOTERM-22; CCA text italicized, analysis follows):

1. *Waste intended for WIPP is heterogeneous.* Only 6 components have been added to the model since the CCA: EDTA, acetate, oxalate, citrate, Pb, and Fe. 28 years after the CCA the model remains unfinished. Experimental calibrations of Pitzer models take a long time. Direct experimental measurements of solubilities do not (Appendix). Measured An solubilities would be less uncertain, and might also be used to test the theoretical solubility model once the theoretical model is finished, and to determine both the deterministic and stochastic discrepancy between the two.

2. *A relatively wide range of chemical conditions would be possible in the repository without the MgO backfill.* MgO backfill has always been part of WIPP performance assessment (PA) calculations starting with the CCA. Moreover, WIPP presently needs only the compositions of

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GWB and ERDA-6 brines to bracket chemical conditions in the disposal area. This may be one brine too many, because baseline An solubilities calculated in GWB and ERDA-6 (King, 2023) are typically within ~ 10 % of each other.

3. *Measuring solubility directly in experiments using transuranic (TRU) waste and ensuring that the measurements reflect steady-state WIPP conditions would entail an extremely large number of measurements and considerable uncertainty*. Actual waste is not used to measure solubilities: solubilities are measured using An salts or pre-formed An solids (Appendix) and finished in relatively short times. Measurements should provide a more objective estimate of solubilities than a model prediction.

Maybe the CCA meant "measuring equilibrium An concentrations", not "measuring An solubilities". That would be a larger, yet very important, task (Appendix). But it is not the aim of a solubility measurement, or the solubility model predictions that PA has always used to calculate dissolved An concentrations at WIPP. Steady-state An concentrations could be experimentally measured with a limited number of experiments that would capture the most important An reactions in the disposal area including sorption (Appendix). WIPP originally planned to do such measurements in the Source Term Test Program (DOE, 1994).

In the absence of measured solubilities and concentrations, WIPP predicts disposal area An concentrations with an unfinished model using reactions that natural analogues suggest may not occur (An solubilities), and reactants (EDTA) that natural analogues suggest may not exist in the disposal area.

Uncertainty Reduction

Measure An solubilities and concentrations in WIPP brine (Appendix).

SUMMARY

The WIPP Dissolved Actinide Source Term and Gas Generation conceptual models are at odds with natural analogues in four areas because they conservatively assume:

1. No actinide (An) sorption in the disposal area (Section 1),

2. Cellulose biodegradation to only CO_2 (Section 2),

3. No organic ligand degradation (Section 3), and

4. Solubility model-predicted actinide concentrations (Section 4).

Assumptions 1, 3, and 4 are used in the Dissolved Actinide Source Term conceptual model. Assumption 2 is used in the Gas Generation conceptual model.

Sorption control over the environmental transport of Ans in WIPP-analogous systems, An-contaminated soils, groundwater, and sediments, is widely recognized by scientists and

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194 regulatory agencies (Section 1). Indeed, the assumption of no actinide sorption in the WIPP
195 disposal area was deemed "probably not valid" by the peer review of the CCA (DOE, 1996b, pg.
196 3-162).
197
198 The susceptibility of EDTA to biodegradation under oxidizing conditions has been well
199 documented (Section 3). A conservative aspect of WIPP's approach to HS mobilization of Ans is
200 that it ignores An sorption by immobilized HSs, and the cellulosics that preceded them (Sections
201 2). That there are no natural analogues for WIPP-predicted An solubilities (Section 4)
202 emphasizes the conservativeness of the WIPP approach.
203
204 The associated files for this paper are archived in the cvs directory
205 /data/cvs/CVSLIB/WIPP_EXTERNAL/conceptual_analogues2024.
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APPENDIX: Measurement of An Solubilities and An Concentrations

An solubility measurements would involve equilibrium between WIPP brine and An solids. An concentration measurements would involve equilibrium between An-containing WIPP brine and disposal area packaging solids, Fe corrosion products and cellulosics, and MgO. Detailed Test Plans for measurement of An solubilities and An concentrations would follow the broad features of the experiments outlined below.

An Solubilities

Nd and Th solubility could be measured at pH 9 in modified GWB (or ERDA-6) brine. 'Modified' here means pre-equilibrated with MgO, Fe and Pb corrosion products. The chosen brine might be spiked with EDTA if the long-term presence of EDTA in WIPP waste can be verified. Nd is an accepted analogue for the An(III)s, Am and Pu(III); Th is an accepted analogue for Pu(IV). Ans would be introduced as either An salts or pre-formed solids. The first would allow An measurement of solubility from over-saturation, the second would provide solubility measurement from under-saturation. If a pre-formed An solid is used it should be independently confirmed as the solubility-limiting phase for the particular An, presumably with experimental observations and/or thermodynamic calculations. Dissolved An levels would be measured over time from filtered extracts. The An solubility would be the measured equilibrium dissolved An level once dissolved levels no longer changed with time.

An Concentrations

As noted in Section 4, WIPP originally planned to measure An concentrations in the Source Term Test Program. Measured An concentrations would reflect a combination of 'dissolution/precipitation, adsorption/desorption, and colloid formation/destruction" (DOE, 1994, pg. 22). The simplest way to constrain An concentrations in the disposal area might be to focus on An equilibrium with CH-waste packaging. There is ≈ 4 times as much CH-waste + packaging as RH-waste + packaging. The RH-waste is presently disposed of in 16' horizontal shafts with Pb shielding and separated with a concrete plug from the rooms where the CH-waste is disposed.

All CH-waste will be in close contact with packaging, Fe corrosion products and cellulose, and MgO (Plastics and rubber are ignored in the analysis below). Because there is more mass in the CH-waste steel + cellulose packaging + MgO, 9.99e7 kg, than in the CH-waste, 6.98e7 kg, An concentration measurements measured in contact with packaging (no waste) + MgO, should give a first-order indication of waste + MgO controls over An concentrations. The measurement might therefore set an upper limit on An concentrations in a DBR while avoiding the experimental complexity of waste heterogeneity.

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Reaction vessels for the An concentration measurement would contain iron corrosion product hibbingite, cellulose, and MgO with GWB (or ERDA-6) brine in the proportions indicated by the WIPP inventory and the fluid/rock ratio expected in the collapsed disposal area. Each of the solids should be pre-aged in WIPP brine. Because the solid/liquid ratio in the reactors will be high, as it will be in the disposal area, the reactor must be physically stirred continually. Ans would be added stepwise to the stirred reactor as Nd and Th salts to their inventory limits over a matter of days to mimic An release from waste in the disposal area. Periodic solution extractions for An analyses would be done after allowing solids settling until An concentrations reached a steady-state. Solutions would be analyzed for major elements as well. After completion of the experiment solids would be analyzed to aid in constraining the primary reactions controlling An concentrations. Measured dissolved An concentrations might be used in place of solubility-predicted An concentrations for estimating DBR releases of Ans.

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Calculations for 'White Paper: The WIPP Chemistry Conceptual Model Compared to Natural Analogues' [Pat Brady]

CELLULOSE SITE DENSITIES

sundman 2008 kraft wood fiber-assumes no lignin			
	4.30E-05	mol/g cooh	[assumes sa = 100 m2/g]
tiruta 2015 wood		sa = 100 m2/g	
	1.10E-04	mol/g-cooh+phenol	
guo 2008 lignin	3.00E-04	mol/g-cooh	6.14E-02
	6.00E-04	mol/g-phenol	1.23E-01
WIPP	2.21E-04	mol/g cooh+phenol	
	4.53E-02	mol/l-dbr cooh+phenol	

WIPP AN INVENTORY

	moles	mol/l-dbr
Am	835	2.47E-05
Th	59000	1.75E-03
Pu	2.10E+05	6.21E-03
TOTAL		7.98E-03

NOT USED

CONVERTING HS-AN3 BINDING TO SORPTION KD

An3-HS/An	55
g/ml HS	2.00E-06
Kd	2.75E+07

WIPP CELLULOSE

6.92E+06	kg-cell-wipp
3.38E+07	l-dbr-vol
2.05E+02	g/l
8.19E+01	g-c/l
4.09E-01	sites/l

SORPTIVE SITE DENSITIES [FIGURE 1]

	mol-l-dbr		mol-M3-dbr
fe-cp	0.010	6	10.2356174
soil	0.090	55	89.6035503
cell+lig+wood	0.045	28	45.2666272
cement	0.017	11	17.0887574
TOTAL	0.162	100	162.194552

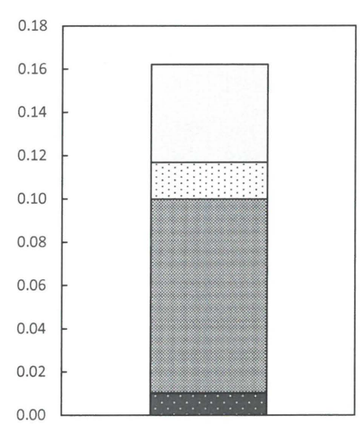
WIPP fe-cp-mass

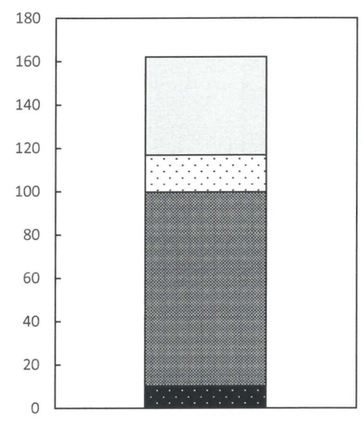
fe	3.92E+09	g
fe	7.02E+07	mol
hibb	3.51E+07	mol
hibb	6.95E+09	g

hibb = fe2[oh]3cl
mw = 198 g/mol

CONVERSION OF WIPP CELLULOSICS TO HUMICS

%HA/Ctot	HA-g-c/l	HA-sites eq/l
0	0.00	0
1	0.82	0.004095
2	1.64	0.008189
3	2.46	0.012284
5	4.09	0.020473
10	8.19	0.040947





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