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Calculation of Organic-Ligand Concentrations for the Surplus Plutonium Disposition Performance Assessment

Author:	Paul Domski, 8882	10-15-18 Date
Technical Reviewer:	Sungtae Kim, 8881	10-15-18 Date
QA Reviewer:	Shelly Nielsen, 8880	SKN 10-15-18 10-15-18 Date
Management Reviewer:	Christi Leigh, 8880	10-15-18 Date

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1 ABBREVIATIONS, ACRONYMS, AND INITIALISMS

Table 1 defines the abbreviations, acronyms, and initialisms used in this report.

Table 1. Abbreviations, Acronyms, and Initialisms.

Abbreviation, Acronym, or Initialism	Definition
acetate	$CH_3CO_2^-$
acetic acid	CH_3CO_2H
AP	analysis plan
DOE	(U.S.) Department of Energy
C	carbon
CCA	(WIPP) Compliance Certification Application
citrate	$(CH_2CO_2H)_2C(OH)(CO_2)^-$
citric acid	$(CH_2CO_2H)_2C(OH)(CO_2H)$
CRA-2004	the first (WIPP) Compliance Recertification Application
DOE	(U.S.) Department of Energy
EDTA	ethylenediaminetetraacetate, $(CH_2CO_2H)_2N(CH_2)_2N(CH_2CO_2H)(CH_2CO_2)^-$; or ethylenediaminetetraacetic acid, $(CH_2CO_2H)_2N(CH_2)_2N(CH_2CO_2H)_2$
EPA	(U.S.) Environmental Protection Agency
g	gram(s)
H	hydrogen
kg	kilogram(s)
L	liter(s)
M	molar
m	meter(s) or molal
mol	moles
N	nitrogen
Na	sodium
Na acetate	CH_3CO_2Na
Na citrate	$(CH_2CO_2H)_2C(OH)(CO_2Na)$
Na EDTA	$(CH_2CO_2H)_2N(CH_2)_2N(CH_2CO_2H)(CH_2CO_2Na)$
Na oxalate	$(CO_2H)(CO_2Na)$
O	oxygen
oxalate	$(CO_2H)(CO_2)^-$
oxalic acid	$(CO_2H)_2$

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Table 1. Abbreviations, Acronyms, and Initialisms.

Abbreviation, Acronym, or Initialism	Definition
PA	(WIPP) performance assessment
PABC	(WIPP) Performance Assessment Baseline Calculation(s)
WIPP	(U.S. DOE) Waste Isolation Pilot Plant
wt	weight

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2 INTRODUCTION

This analysis report provides concentrations of acetate, citrate, ethylenediaminetetraacetic acid (EDTA), and oxalate (referred to hereafter as "organic ligands") in brines that could enter the U.S. Department of Energy's (DOE's) Waste Isolation Pilot Plant (WIPP) after closure of the repository. These concentrations will be used to calculate actinide solubilities for the WIPP Performance Assessment for the SPD (Surplus Plutonium Disposition) analysis (Zeitler, 2018).

This analysis report describes the calculation of organic-ligand concentrations based on the estimates of the masses of these organic ligands to be emplaced in the WIPP for surplus plutonium disposition (Van Soest, 2018), and the minimum brine volume (Clayton 2008) required for a direct brine release in performance assessment (PA) calculations.

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3 MASSES OF ORGANIC LIGANDS TO BE EMPLACED IN THE WIPP FOR THE POSSIBLE DISPOSION OF SURPLUS PLUTONIUM

The masses of organic ligands to be emplaced in the WIPP for the analysis of the possible disposition of surplus plutonium are from Van Soest (2018). The inventories of organic ligands are listed in Table 5-9 on Page 35 in the report of Van Soest (2018).

In Van Soest (2018), the masses for organic ligands were listed as those for acetic acid, acetate, citric acid, citrate, EDTA, oxalic acid and oxalate. Following the paradigm of Brush and Domski (2013) for calculations of organic ligand concentrations for the minimum brine volume, the ligands will be represented as acids for the purpose of calculating their molecular weight. In Brush and Domski (2013), they calculated the organic concentrations for multiple brine volumes (1x, 2x, 3x, 4x, and 5x) using the results from the minimum brine volume (17,400 m^3) as the basis.

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4 CALCULATION OF MOLECULAR WEIGHTS OF ORGANIC LIGANDS

The following atomic weights will be used to calculate the molecular weights of acetic acid, citric acid, EDTA, and oxalic acid: H, 1.00794 g/mol; C, 12.0107 g/mol; N, 14.00674 g/mol; O, 15.9994 g/mol, and Na, 22.989770 g/mol (Lide, 2002). Table 2 provides the formulas for these compounds.

Van Soest (2018) listed organic ligands as acetate, acetic acid, citrate, citric acid, EDTA, oxalate, and oxalic acid, however, for the purposes of this analysis the ligands will be considered in their acid form. The masses of acetate and acetic acid, citrate and citric acid, and oxalate and oxalic acid were combined and their concentrations calculated for this analysis.

The molecular weights of acetic acid, citric acid, EDTA (ethylenediaminetetraacetic acid, in this case), and oxalic acid, were calculated as follows:

- Acetic acid: (4 × atomic mass H) + (2 × atomic mass C) + (2 × atomic mass O) = (4 × 1.00794 g/mol) + (2 × 12.0107 g/mol) + 2 × 15.9994 g/mol) = (4.0318 + 24.0214 + 31.9988) g/mol = 60.0520 g/mol.

- Citric acid: (8 × atomic mass H) + (6 × atomic mass C) + (7 × atomic mass O) = (8 × 1.00794 g/mol) + (6 × 12.0107 g/mol) + (7 × 15.9994 g/mol) = (8.0635 + 72.0642 + 111.9958) g/mol = 192.1235 g/mol.

- EDTA: (16 × atomic mass H) + (10 × atomic mass C) + (2 × of N) + (8 × atomic mass O) = (16 × 1.00794 g/mol) + (10 × 12.0107 g/mol) + (2 × 14.00674 g/mol) + (8 × 15.9994 g/mol) = (16.12704 + 120.1070 + 28.0135 + 127.9952 + 22.989770) g/mol = 292.2427 g/mol.

- Oxalic acid: (2 × atomic mass H) + (2 × atomic mass C) + (4 × atomic mass O) = (2 × 1.00794 g/mol) + (2 × 12.0107 g/mol) + 4 × 15.9994 g/mol) = (2.0159 + 24.0214 + 63.9976) g/mol = 90.0349 g/mol.

Table 2 provides the molecular weights of these compounds.

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Table 2. Formulas and Molecular Weights of the Four Ligands That Could Be Emplaced in the WIPP.

Compound	Formula	Mol Wt (g)
Acetic acid	CH_3CO_2H	60.0520
Citric acid	$(CH_2CO_2H)_2C(OH)(CO_2H)$	192.1235
EDTA	$(CH_2CO_2H)_2N(CH_2)_2N(CH_2CO_2H)_2$	292.2427
Oxalic acid	$(CO_2H)_2$	90.0349

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5 CALCULATION OF ORGANIC-LIGAND CONCENTRATIONS

The method of Brush and Xiong (2009) was implemented to calculate organic ligand concentrations for the minimum brine volume. A minimum brine volume of 17,400 m^3 in the repository is required for a direct brine release (Clayton, 2008), to calculate the dissolved concentrations of acetate, citrate, EDTA, and oxalate in a homogeneous, 10-panel PA repository, for calculations of baseline actinide solubility for the performance assessment of the possible disposal of surplus plutonium in the WIPP. The organic ligand concentrations for other brine volumes, i.e., 2 × minimum brine volume, 3 × minimum brine volume, 4 × minimum brine volume, 5 × minimum brine volume, are calculated based on the organic ligand concentrations for the minimum brine volume by applying the dilution factors, similar to that in Brush and Domski (2013).

In the past, the value of 29,841 m^3 of brine, "the smallest quantity of brine required to be in the repository [for] transport away from the repository" (Larson, 1996; U.S. DOE, 1996), was used in CCA. A volume of 29,841 m^3 of brine was used by the U.S. DOE (1996, Appendix SOTERM, Section SOTERM.5), Brush and Xiong (2003a, 2003b), and the U.S. DOE (2004, Appendix PA, Attachment SOTERM, Section SOTERM-5.0) to calculate organic-ligand concentrations for the CCA and the CRA-2004 PA. Stein (2005) estimated a volume of 10,011 m^3 for CRA-2009 PA.

The concentrations of acetic acid, citric acid, EDTA, and oxalic acid were calculated by multiplying the total masses of these compounds in kg from Van Soest (2018, Table 5-9, column labeled "Total Mass") by 1000 g/kg to convert Van Soest's estimates to total masses in grams. Next, these masses were divided by the molecular weights of these compounds from Table 2 of this report, column labeled "Mol Wt (g/mol)," which yielded the total quantities of these compounds to be emplaced in moles. These quantities were then divided by 17,400,000 L to obtain the concentrations of these compounds in units of mol/L (M):

- Acetic acid: $((1.06 \times 10^4 + 1.57 \times 10^4\ \text{kg}) \times (1000\ \text{g/kg}) \div (60.0520\ \text{g/mol})) \div 1.7400 \times 10^7\ \text{L} = 2.52 \times 10^{-2}\ \text{M}$.

- Citric acid: $((2.59 \times 10^3 + 6.45 \times 10^3\ \text{kg}) \times (1000\ \text{g/kg}) \div (192.1235\ \text{g/mol})) \div 1.7400 \times 10^7\ \text{L} = 2.70 \times 10^{-3}\ \text{M}$.

- EDTA: $((1.64 \times 10^3\ \text{kg}) \times (1000\ \text{g/kg}) \div (292.2427\ \text{g/mol})) \div 1.7400 \times 10^7\ \text{L} = 3.23 \times 10^{-4}\ \text{M}$.

- Oxalic acid: $((1.89 \times 10^3 + 1.91 \times 10^4\ \text{kg}) \times (1000\ \text{g/kg}) \div (90.0349\ \text{g/mol})) \div 1.7400 \times 10^7\ \text{L} = 1.34 \times 10^{-2}\ \text{M}$.

Table 3 summarizes these calculations and provides the results (see page 11).

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Table 3. Dissolved Concentrations of the Four Ligands for a Homogeneous, 10-Panel Repository, Assuming a Brine Volume of 17,400 m^3.

Compound	Total Mass (kg)	Total Mass (g)	Total Quantity (mol)	Concentration (M)
Acetic acid	1.57×10^{4} [A]	1.57×10^{7}	2.61×10^{5}	2.52×10^{-2}
Acetate	1.06×10^{4} [A]	1.06×10^{7}	1.77×10^{5}	
Citric acid	6.45×10^{3} [A]	6.45×10^{6}	3.36×10^{4}	2.70×10^{-3}
Citrate	2.59×10^{3} [A]	2.59×10^{6}	1.35×10^{4}	
EDTA	1.64×10^{3} [A]	1.64×10^{6}	5.61×10^{3}	3.23×10^{-4}
Oxalic acid	1.91×10^{4} [A]	1.91×10^{7}	2.12×10^{5}	1.34×10^{-2}
Oxalate	1.89×10^{3} [A]	1.89×10^{6}	2.10×10^{4}	

A. From Van Soest (2018, Table 5-9, column labeled "Total Mass")

Table 4 provides the dissolved concentrations of organic ligands on a molar scale (M) in the minimum volume of brine required for a DBR and for volumes that are 2 times, 3 times, 4 times, and 5 times the minimum volume.

Table 5 provides the new total dissolved concentrations of acetate, citrate, EDTA, and oxalate for a homogeneous, 10-panel repository and compares them to the concentrations calculated by U.S. DOE (1996, Appendix SOTERM, Table SOTERM-4, column labeled "Organic Concentration (scaled),") for the CCA, Brush and Xiong (2003a) for the actinide-solubility calculations for the CRA-2004 PA, the corrected concentrations of Brush and Xiong (2003b), Brush and Xiong (2005) for CRA-2004 PABC and CRA-2009 PA, Brush and Xiong (2009) for CRA-2009 PABC, and Brush and Domski (2013) for CRA-2014 PA.

Table 4. Dissolved Concentrations of Organic Ligands (M) in the Minimum Volume of Brine Required for a DBR and for Volumes That Are 2 ×, 3 ×, 4 ×, and 5 × the Minimum Volume.

Organic Ligand	Minimum Required for a DBR	2 × Minimum	3 × Minimum	4 × Minimum	5 × Minimum
Acetate	2.52×10^{-2}	1.26×10^{-2}	8.39×10^{-3}	6.29×10^{-3}	5.03×10^{-3}

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Organic Ligand	Minimum Required for a DBR	2 × Minimum	3 × Minimum	4 × Minimum	5 × Minimum
Citrate	2.70×10^{-3}	1.35×10^{-3}	9.01×10^{-4}	6.76×10^{-4}	5.41×10^{-4}
EDTA	3.23×10^{-4}	1.61×10^{-4}	1.08×10^{-4}	8.06×10^{-5}	6.45×10^{-5}
Oxalate	1.34×10^{-2}	6.70×10^{-3}	4.47×10^{-3}	3.35×10^{-3}	2.68×10^{-3}

Table 5. Concentrations of Four Organic Ligands for a Homogeneous, 10-Panel Repository since CCA.

Organic Ligand	CCA[A] (m)	CRA-2004 PA[B] (M)	CRA-2004 PA, Corrected[C] (M)	SPD[D] (M)
Acetate	1.1×10^{-3}	5.05×10^{-3}	3.56×10^{-3}	2.52×10^{-2}
Citrate	7.4×10^{-3}	3.83×10^{-4}	2.71×10^{-4}	2.70×10^{-3}
EDTA	4.2×10^{-6}	3.87×10^{-6}	2.73×10^{-6}	3.23×10^{-4}
Oxalate	4.7×10^{-4}	2.16×10^{-2}	1.53×10^{-2}	1.34×10^{-2}

A. U.S. DOE (1996, Appendix SOTERM, Table SOTERM-4, column labeled "Organic Concentration (scaled)."
B. Brush and Xiong (2003a, Table 4, column labeled "CRA Concentration (M)").
C. Brush and Xiong (2003b, Table 4, column labeled "Corrected Concentration for a 10-Panel, Homogeneous Repository (M), This Report"). After the analysis written by Brush and Xiong (2003a), Crawford and Leigh (2003) and Leigh (2003) corrected Crawford's (2003) estimates of the total masses of organic ligands to be emplaced at time in the WIPP. In Brush and Xiong (2003b), they used the corrected total masses of organic ligands for calculation of concentrations of organic ligands.
D. This analysis report. Notice that this column is reproduced in the continued table for easy reading.

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Table 5. Concentrations of Four Organic Ligands for a Homogeneous, 10-Panel Repository since CCA (Continued).

Organic Ligand	CRA-2004 PABC[A], and CRA-2009 PA (M)	CRA-2009 PABC[B] (M)	CRA-2014 PA[C] (M)	SPD[D] (M)
Acetate	1.06×10^{-2}	1.94×10^{-2}	2.30×10^{-2}	2.52×10^{-2}
Citrate	8.06×10^{-4}	2.38×10^{-3}	2.33×10^{-3}	2.70×10^{-3}
EDTA	8.14×10^{-6}	6.47×10^{-5}	7.40×10^{-5}	3.23×10^{-4}
Oxalate	4.55×10^{-2}	1.73×10^{-2}	1.18×10^{-2}	1.34×10^{-2}

A. Brush and Xiong (2005, Table 4, column labeled "PABC (M)").
B. Brush and Xiong (2009, Table 5, column labeled "Concentration (M)").
C. Brush and Domski (2013). Notice that these organic concentrations were also used in CRA14_SEN4, and APCS.
D. This analysis report. This column is also reproduced in the table on the previous page for easy comparison.

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6 CONCLUSIONS

This analysis yielded the following organic-ligand concentrations for the minimum brine volume: (1) acetate: 2.52×10^{-2} M, (2) citrate: 2.70×10^{-3} M; (3) EDTA: 3.23×10^{-4} M; (4) oxalate: 1.34×10^{-2} M (see Table 4 above). Concentrations for the same organic ligand masses in brine volumes 2 times, 3 times, 4 times, and 5 times the minimum brine volume are also tabulated in Table 4. The organic-ligand concentrations in Table 4 will be used to calculate actinide solubilities for the SPD analysis.

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7 REFERENCES

Brush, L.H., and P.S. Domski. 2013. "Calculation of Organic Ligand Concentrations for the WIPP CRA-2014 PA." Analysis report, January 14, 2013. Carlsbad, NM: Sandia National Laboratories. ERMS 559005.

Brush, L.H., and Y.-L. Xiong. 2003a. "Calculation of Organic Ligand Concentrations for the WIPP Compliance Recertification Application." Analysis report, April 14, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 527567.

Brush, L.H., and Y.-L. Xiong. 2003b. "Calculation of Organic Ligand Concentrations for the WIPP Compliance Recertification Application and for Evaluating Assumptions of Homogeneity in WIPP PA." Analysis report, September 11, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 531488.

Brush, L.H., and Y. Xiong, 2005. "Calculation of Organic-Ligand Concentrations for the WIPP Performance-Assessment Baseline Calculations. Analysis report, May 4, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539635.

Brush, L.H., and Y.-L. Xiong. 2009. "Calculation of Organic Ligand Concentrations for the WIPP CRA-2009 PABC." Analysis report, June 15, 2009. Carlsbad, NM: Sandia National Laboratories. ERMS 551481.

Clayton, D.J. 2008. "Update to the Calculation of the Minimum Brine Volume for a Direct Brine Release." Memorandum to L.H. Brush, April 2, 2008. Carlsbad, NM: Sandia National Laboratories. ERMS 548522.

Crawford, B.A. 2003. "Updated Estimate of Complexing Agents in Transuranic Solidified Waste Forms Scheduled for Disposal and Emplaced at WIPP." Letter to C.D. Leigh, April 8, 2003. Carlsbad, NM: Los Alamos National Laboratory. ERMS 527409.

Crawford, B.A., and C.D. Leigh. 2003. "Estimate of Complexing Agents in TRU Waste for the Compliance Recertification Application." Analysis report, August 28, 2003. Carlsbad, NM: Los Alamos National Laboratory. ERMS 531107.

Larson, K.W. 1996. "Brine-Waste Contact Volumes for Scoping Analysis of Organic Ligand Concentration." Memorandum to R.V. Bynum, March 13, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS 236044.

Leigh, C.D. 2003. "New Estimates of the Total Masses of Complexing Agents in the WIPP Inventory for Use in the 2003 WIPP Performance Assessment." Memorandum to L.H. Brush, September 3, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 531319.

Information Only

Lide, D.R. 2002. *CRC Handbook of Chemistry and Physics*, 83rd edition. Boca Raton, FL: CRC Press.

Van Soest, G.D. 2018. "NNSA Surplus Plutonium Disposition Performance Assessment Inventory Report—2017." INV-SPD-17, Revision 1, February 14, 2018. Carlsbad, NM: Los Alamos National Laboratory.

Zeitler, T., 2018. Planning Document for the Surplus Plutonium Disposition Calculation. Albuquerque, NM: Sandia National Laboratories. ERMS 569299.

Stein, J.S. 2005. "Estimate of Volume of Brine in Repository That Leads to a Brine Release." Memorandum to L.H. Brush, April 19, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539372.

U.S. DOE. 1996. *Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Vol. 1-21.* DOE/CAO-1994-2184. Carlsbad, NM: U.S. Department of Energy Carlsbad Area Office.

U.S. DOE. 2004. Title 40 CFR Part 191 Compliance Recertification Application for the Waste Isolation Pilot Plant, Vol. 1-8. DOE/WIPP 2004-3231. Carlsbad, NM: U.S. Department of Energy Carlsbad Field Office.

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