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Sandia National Laboratories
Waste Isolation Pilot Plant

Calculation of Organic Ligand Concentrations for the WIPP Compliance Recertification Application

BOE 1.3.5.1.2

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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
DOE	(U.S.) Department of Energy
C	carbon
CCA	(WIPP) Compliance Certification Application
CRA	(WIPP) Compliance Recertification Application
EDTA	ethylenediaminetetraacetate or ethylenediaminetetraacetic acid
g	gram(s)
H	hydrogen
kg	kilogram(s)
L	liter(s)
M	molar
m	meter(s) or molal
mol	moles
N	nitrogen
Na	sodium
O	oxygen
PA	performance assessment
WIPP	(U.S. DOE) Waste Isolation Pilot Plant
wt	weight

2 INTRODUCTION

This report describes the calculation of revised concentrations of organic ligands in WIPP brines. We will use these ligand concentrations to calculate actinide solubilities for the performance assessment (PA) for the U.S. Department of Energy's (DOE's) first Waste Isolation Pilot Plant (WIPP) Compliance Recertification Application (CRA). These ligand concentrations will replace the concentrations calculated at the time of the Compliance Certification Application (CCA) PA, the concentrations currently in the WIPP Project's technical baseline (U.S. DOE, 1996a, Appendix B4; U.S. DOE, 1996b, Appendix SOTERM, SOTERM.5).

This work was carried out under the analysis plan for the CRA PA solubility calculations (Brush and Xiong, 2003, Subsection 7.2, Recalculation of the Concentrations of Organic Ligands).

3 OBJECTIVES

The objective of this work was to use new estimates of the total quantities of acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate in the contact- and remote-handled transuranic waste to be emplaced in the WIPP to calculate revised concentrations of these ligands in WIPP brines. In all other respects, the calculations described here are identical to those carried out at the time of the CCA PA.

4 ESTIMATES OF MASSES

Crawford (2003, Table 2, column labeled "Scaled Mass (kg)") provided estimates of the total masses of acetic acid, Na-acetate, citric acid, Na-citrate, Na-EDTA, oxalic acid, and Na-acetate to be emplaced in the WIPP. These estimates replace those provided by U.S. DOE (1996a, Appendix B4), the estimates available at the time of the CCA PA calculations (U.S. DOE, 1996b, Appendix SOTERM, SOTERM.5).

5 CALCULATION OF MOLECULAR WEIGHTS

We used the following atomic weights to calculate the molecular weights of acetic acid, Na-acetate, citric acid, Na-citrate, Na-EDTA, oxalic acid, and Na-acetate: 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 1 provides the formulas for these compounds.

Acetic acid, citric acid, EDTA, and oxalic acid contain one, three, four, and two protons, respectively, that can be substituted with Na (or other alkali or alkaline-earth metals). Crawford (2003) did not specify how many of these protons were replaced by Na in the Na-citrate, Na-EDTA, and Na-oxalate. Therefore, to calculate the molecular weights of Na-citrate, Na-EDTA, and Na-oxalate, we assumed that only one of the protons was substituted with Na. This assumption is "conservative;" in other words, it results in the highest molar quantities of the Na-bearing forms of these ligands.

We calculated the molecular weights of acetic acid, Na-acetate, citric acid, Na-citrate, EDTA, Na-EDTA, oxalic acid, and Na-oxalate as follows:

- Acetic acid: $(4 \times \text{mol wt H}) + (2 \times \text{mol wt C}) + (2 \times \text{mol wt O}) = (4 \times 1.00794 \text{ g/mol}) + (2 \times 12.0107 \text{ g/mol}) + 2 \times 15.9994 \text{ g/mol}) = (4.0318 + 24.0214 + 31.9988) \text{ g/mol} = 60.0520 \text{ g/mol}$.

- Na-acetate: (3 × mol wt H) + (2 × mol wt C) + (2 × mol wt O) = (3 × 1.00794 g/mol) + (2 × 12.0107 g/mol) + 2 × 15.9994 g/mol) + (1 × 22.989770 g/mol) = (3.0238 + 24.0214 + 31.9988 + 22.989770) g/mol = 82.0338 g/mol.

- Citric acid: (8 × mol wt H) + (6 × mol wt C) + (7 × mol wt 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.

- Na-citrate: (7 × mol wt H) + (6 × mol wt C) + (7 × mol wt O) + (1 × mol wt Na) = (7 × 1.00794 g/mol) + (6 × 12.0107 g/mol) + (7 × 15.9994 g/mol) + (1 × 22.989770 g/mol) = (7.0556 + 72.0642 + 111.9958 + 22.989770) g/mol = 214.1054 g/mol.

- EDTA: (16 × mol wt H) + (10 × mol wt C) + (2 × mol wt of N) + (8 × mol wt O) = (16 × 1.00794 g/mol) + (10 × 12.0107 g/mol) + (2 × 14.00674 g/mol) + (8 × 15.9994 g/mol) = (16.1270 + 120.1070 + 28.0135 + 127.9952) g/mol = 292.2427 g/mol.

- Na-EDTA: (15 × mol wt H) + (10 × mol wt C) + (2 × mol wt of N) + (8 × mol wt O) + (1 × mol wt Na)= (15 × 1.00794 g/mol) + (10 × 12.0107 g/mol) + (2 × 14.00674 g/mol) + (8 × 15.9994 g/mol) + (1 × 22.989770 g/mol) = (15.1191 + 120.1070 + 28.0135 + 127.9952 + 22.989770) g/mol = 314.2246 g/mol.

- Oxalic acid: (2 × mol wt H) + (2 × mol wt C) + (4 × mol wt 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.

- Na-oxalate: (1 × mol wt H) + (2 × mol wt C) + (4 × mol wt O) + (1 × mol wt Na) = (1 × 1.00794 g/mol) + (2 × 12.0107 g/mol) + 4 × 15.9994 g/mol) + (1 × 22.989770 g/mol) = (1.00794 + 24.0214 + 63.9976 + 22.989770) g/mol = 112.0167 g/mol.

Table 2 provides the results of these calculations.

6 CALCUALATION OF CONCENTRATIONS

We used a 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, 1996b), to calculate the dissolved concentrations of acetate, citrate, EDTA, and oxalate. This volume is conservative because any volume greater than 29,841 m^3 would result in lower concentrations of these ligands. A volume of 29,841 m^3 of brine is equivalent to 29,841,000 L of brine.

Table 2. Formulas and Molecular Weights of Compounds Containing Organic Ligands to Be Emplaced in the WIPP.

Compound	Formula	Mol Wt (g)
Acetic acid	CH_3CO_2H	60.0520
Na-acetate	CH_3CO_2Na	82.0338
Citric acid	$(CH_2CO_2H)_2C(OH)(CO_2H)$	192.1235
Na-citrate	$(CH_2CO_2H)_2C(OH)(CO_2Na)$	214.1054
EDTA	$(CH_2CO_2H)_2N(CH_2)_2N(CH_2CO_2H)_2$	292.2427
Na-EDTA	$(CH_2CO_2H)_2N(CH_2)_2N(CH_2CO_2H)(CH_2CO_2Na)$	314.2246
Oxalic acid	$(CO_2H)_2$	90.0349
Na-oxalate	$(CO_2H)(CO_2Na)$	112.0167

We calculated the concentrations of acetic acid, Na-acetate, citric acid, Na-citrate, Na-EDTA, oxalic acid, and Na-oxalate in units of mol/L (M) by multiplying the scaled masses of these compounds from Crawford (2003, Table 2, column labeled "Scaled Mass) by 1000 g/kg to convert Crawford's estimates to scaled masses in grams. Next, we divided these masses by the molecular weights of these compounds from Table 2 of this report, column labeled "Mol Wt (g)," which yielded the total quantities of these compounds to be emplaced in mol. We then divided these quantities by 29,841,000 L to obtain the concentrations of these compounds in M.

We calculated the concentrations of acetic acid, Na-acetate, citric acid, Na-citrate, Na-EDTA, oxalic acid, and Na-oxalate as follows:

- Acetic acid: $((2.01 \times 10^2 \text{ kg}) \times (1000 \text{ g/kg}) \div (60.0520 \text{ g/mol})) \div 2.9841 \times 10^7 \text{ L} = 1.12 \times 10^{-4} \text{ M}$.
- Na-acetate: $((1.21 \times 10^4 \text{ kg}) \times (1000 \text{ g/kg}) \div (82.0338 \text{ g/mol})) \div 2.9841 \times 10^7 \text{ L} = 4.94 \times 10^{-3} \text{ M}$.
- Citric acid: $((1.69 \times 10^3 \text{ kg}) \times (1000 \text{ g/kg}) \div (192.1235 \text{ g/mol})) \div 2.9841 \times 10^7 \text{ L} = 2.95 \times 10^{-4} \text{ M}$.

- Na-citrate: $((5.66 \times 10^2\ kg) \times (1000\ g/kg) \div (214.1054\ g/mol)) \div 2.9841 \times 10^7\ L = 8.86 \times 10^{-5}\ M$.

- Na-EDTA: $((3.63 \times 10^1\ kg) \times (1000\ g/kg) \div (314.2246\ g/mol)) \div 2.9841 \times 10^7\ L = 3.87 \times 10^{-6}\ M$.

- Oxalic acid: $((1.95 \times 10^4\ kg) \times (1000\ g/kg) \div (90.0349\ g/mol)) \div 2.9841 \times 10^7\ L = 7.26 \times 10^{-3}\ M$.

- Na-oxalate: $((4.81 \times 10^4\ kg) \times (1000\ g/kg) \div (112.0167\ g/mol)) \div 2.9841 \times 10^7\ L = 1.44 \times 10^{-2}\ M$.

Table 3 summarizes these calculations and provides the results.

We calculated the total dissolved concentrations of acetate, citrate, and oxalate by adding the concentrations of acetic acid and Na-acetate, citric acid and Na-citrate, and oxalic acid and Na-oxalate. The concentration of Na-EDTA is equal to the total concentration of EDTA because Crawford (2003) did not report any EDTA without Na. Table 4 provides the total dissolved concentrations of acetate, citrate, EDTA, and oxalate that we will use to calculate actinide solubilities for the CRA PA.

Table 3. Dissolved Concentrations of Compounds Containing Organic Ligands to Be Emplaced in the WIPP.

Compound	Scaled Mass (kg)[A]	Scaled Mass (g)	Scaled Quantity (mol)	Concentration (M)
Acetic acid	2.01×10^2	2.01×10^5	3.35×10^3	1.12×10^{-4}
Na-acetate	1.21×10^4	1.21×10^7	1.48×10^5	4.94×10^{-3}
Citric acid	1.69×10^3	1.69×10^6	8.80×10^3	2.95×10^{-4}
Na-citrate	5.66×10^2	5.66×10^5	2.64×10^3	8.86×10^{-5}
Na-EDTA	3.63×10^1	3.63×10^4	1.16×10^2	3.87×10^{-6}
Oxalic acid	1.95×10^4	1.95×10^7	2.17×10^5	7.26×10^{-3}
Na-oxalate	4.81×10^4	4.81×10^7	4.29×10^5	1.44×10^{-2}

A. From Crawford (2003, Table 2, column labeled “”Scaled mass (kg).”

Table 4. Concentrations of Ligands for the Solubility Calculations for the CRA PA.

Ligand	CRA Concentration (M)
Acetate	5.05×10^{-3}
Citrate	3.83×10^{-4}
EDTA	3.87×10^{-6}
Oxalate	2.16×10^{-2}

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