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Solubility of Technetium Dioxides (TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$) in Reducing Cementitious Material Leachates: A Thermodynamic Calculation

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EXECUTIVE SUMMARY

Blast furnace slag is included in the formulation of cementitious waste forms, such as saltstone at the Saltstone Disposal Facility, to immobilize redox-sensitive radionuclides in low-level waste, primarily technetium. The objective of this study was to compare thermodynamic modeling results to recent laboratory measurements to provide best-estimates for technetium geochemical input values for transport modeling. Calculations were conducted to evaluate the various solid phases that may control Tc solubility, and therefore aqueous Tc concentrations under reducing conditions. In addition to evaluating likely solid phases, this study also evaluated different thermodynamic databases. The solubility of $TcO_2 \cdot 1.6H_2O$, $TcO_2 \cdot 2H_2O$ and $TcO_2(c)$ were calculated in (1) reducing saltstone leachates and (2) Portland cement leachates with the presence of pyrrohtite ($Fe_{1-x}S$ (x = 0-0.2); a mineral selected to simulate the reductant in blast furnace slag) using Geochemist's Workbench (GWB) React module. For the same Tc dioxide under the same environmental conditions (pH, Eh, leachate chemistry), the solubility values calculated using the databases of this work, Denham and Millings (2012) and Wang et al. (2009) were all very similar, whereas the solubility values calculated using the database of Cantrell and Williams (2012) were slightly higher (~2-5 times). This document has been revised to address the suggestions of an expert external panel that critically reviewed the original document. Their primary recommendations were (1) check the validity of GWB modeling for saltstone leachates of high ion strength; (2) check consistency between this and previous reports; (3) do editorial work. No issues were identified related to the proposed solubility values or the method by which they were obtained in the original document.

The three experimental Tc solubility values measured under reducing conditions with simulated saltstone samples were from: 1) a static single-pass flow-through batch experiment with leachate replenishing while sampling, in which the Tc solubility was 1.5×10^{-6} M in the sampled saltstone leachate on day 14 for which the measured pH was 12.66 and Eh was -0.38 V (Cantrell and Williams 2012), 2) a batch experiment, in which the Tc solubility was between 9×10^{-9} and 5×10^{-10} M in a pH of ~11.8 and Eh -0.44 V saltstone leachate (Estes et al. (2012; average after 319 days of contact with saltstone), and 3) a batch experiment in which the Tc solubility was 4.5×10^{-10} M at a pH of 10.9 and Eh -0.40 V saltstone leachate (Estes et al. 2012; average after 319 days of contact with reducing vault concrete). The thermodynamic calculations captured the data trends and the magnitude of the experimental data reasonably well. The calculations suggested that in the first two experiments, $TcO_2 \cdot 1.6H_2O$ (solubility is 6.3×10^{-7} M) or $TcO_2 \cdot 2H_2O$ (solubility is 9.5×10^{-7} M) were most likely controlling Tc concentrations in the reducing saltstone leachates, but not $TcO_2(c)$ (solubility is 6.0×10^{-11} M).

The solubility of hydrated $TcO_2 \cdot xH_2O$ (likely $TcO_2 \cdot 1.6H_2O$) controlled the Tc concentration in reducing saltstone leachates as long as the Eh remained < -0.38 V. However, as the Eh increased just above -0.35 V, the highly soluble Tc(VII) species, TcO_4^-, became the much more dominant species due to the re-oxidation of Tc(IV) in the aqueous and solid phases. Under the more oxidized environmental conditions, the TcO_4^-

concentration increased dramatically to millimolarity. The influence of pH on Tc solubility was evaluated because it is used to define the "age of the saltstone" in the PA; such that the saltstone is initially at pH 12 or larger, then as it ages, the evolving mineral assemblage of the saltstone and air and recharge water that contacts the saltstone buffer the pH to ~10.5. After extensive leaching/weathering, the saltstone is expected to degrade and eventually take on the pH of the background sediment at pH 5.5. Under reducing conditions (Eh < -0.38 V), the calculated Tc solubility decreased as the pH decreased. For example, when pH changed from 12.7 to 10.5 (the approximate pH decrease between the young and moderately-aged saltstone stages used in the PA) at a fixed Eh of -0.38 V, the calculated solubility of $TcO_2 \cdot 1.6H_2O$ is predicted to significantly decrease from 6.3×10^{-7} M to 5.2×10^{-9} M.

During the two early stages of cement aging, the modeling indicated that solubility of $TcO_2 \cdot xH_2O$ was the controlling process of aqueous Tc concentration of saltstone. However, once the system became oxidized, generally anticipated to occur during the 2nd stage of cement aging, then solubility no longer controlled aqueous Tc concentrations. Under oxidizing conditions, Tc adsorption to solid phases becomes the predominant mechanism controlling the concentration of Tc in pore water, and thus the Kd construct is appropriate to use for predicting Tc concentrations. Similarly, once sufficient pore water has leached through the saltstone to advance the modeling into the 3rd and final stage of aged cement, a Tc K_d for an oxidized system would be appropriate to use. These guidelines are summarized in the following table.

Cementitious Material	**Young Cement 1st Stage (pH ~12)**	**Moderately-aged Cement 2nd Stage (pH ~10.5)**	**Aged Cement 3rd Stage (pH ~5.5)**
Reduced	6×10^{-7} mol/L solubility[a]	1×10^{-8} mol/L solubility[a, d]	0.5 mL/g K_d[c]
Oxidized	0.8 mL/g K_d[b]	0.8 mL/g K_d[b, d]	0.5 mL/g K_d[b, d]

(a) This work
(b) Kaplan (2010)
(c) Assumed cement becomes oxidized
(d) Geochemical parameters most important to saltstone PA

This document is a revision of an earlier document (SRNL-STI-2012-00769, Rev. 0) that was sent out for external review to leading scientists actively conducting research in this subject matter. In addition to editorial comments, this revised document addressed the reviewers' request for additional information regarding the convention used to calculate activity coefficients, reduced Tc(IV)-sulfur aqueous species, and guidance for modelers on how to deal with uncertainty associated with the recommended input solubility and K_d values.

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LIST OF ABBREVIATIONS

DOE	Department of Energy
GWB	Geochemist's Workbench
NEA	Nuclear Energy Agency
NRC	Nuclear Regulatory Commission
PA	Performance Assessment
SI	Saturation Index
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TA	Total alkalinity

1. Introduction

Technetium-99 (^{99}Tc) is among the potential risk drivers for the saltstone Disposal Facility performance assessment (PA) due to its high solubility and low sorption potential (K_d < 1 mL/g) in oxidizing environments, long half-life (2.14×10^5 years), and moderate radiotoxicity (SRR 2009; Icenhower et al. 2008, 2010). The two most prominent oxidation states that technetium exists as are Tc(IV) and Tc(VII). In oxidizing environments technetium is manifested as the pertechnetate anion [$Tc(VII)O_4^-$]. In this form, technetium is mobile in the subsurface due to its poor sorption properties (Krupka and Serne 2002; Kaplan et al. 2008). Typical rock-forming minerals that make up the subsurface at circumneutral pH conditions possess an overall negative net charge on their surfaces, which repels the negatively-charged pertechnetate anion. The reduced form of technetium, Tc(IV), is relatively insoluble under circumneutral pH ($10^{-8.2}$ mol/L) (Meyer et al. 1991; Eriksen et al. 1992; Rard 2005; Warwick et al. 2007) and can precipitate into various solid phases, including $Tc(IV)O_2{\cdot}xH_2O$ (Allen et al. 1997; Lukens et al. 2002; Guillaumont et al. 2003; Liu et al. 2008).

Saltstone is a cementitious waste form developed to immobilize contaminants from low-level liquid waste, in which the highly reducing conditions cause the formation of the $Tc(IV)O_2{\cdot}xH_2O$ solid and/or TcS_2, Tc_2S_7 and Tc_3S_{10} (Lukens et al., 2005; Liu et al., 2007, 2009). Oxidation of Tc(IV) hydrous oxides or Tc(IV) sulfides to the highly soluble pertechnetate ion through exposure to oxygen is typically indicated as the mechanism responsible for technetium release from saltstone waste forms (Smith and Walton 1993; Kaplan et al. 2011). However, there still remains some uncertainty related to the Tc solid phases that control the Tc concentrations in reducing cement-based fluid chemistry, as demonstrated by available literature studies (Pickett et al. 2007). Much of the Tc experimental literature is concerned with leaching or sorption behavior and is, therefore, not directly applicable to solubility determination. Meanwhile, thermodynamic values for the solubility of hydrated TcO_2 solid are not well constrained (Johnson et al. 1991, Wolery 1992), and thermodynamic data for other aqueous species and solids containing Tc in its various valence states are limited. This limitation compromises the capability of thermodynamic calculation to evaluate the environmental behavior of reduced Tc species and the solubility of Tc solids with respect to pH, Eh and solution chemistry (Krupka et al. 2004).

The most recent experimental data using Savannah River Site (SRS) simulated saltstone indicated that the solubility of hydrated technetium dioxide is likely to control the Tc concentration under reducing cementitious leachate chemistry (Estes et al. 2012, Cantrell and Williams 2012). In addition, some of other measurements of Tc solubility in reducing cementitious material are presented in Table 1. In this cursory review of the literature, the Tc solubility values range from 10^{-6} to $<10^{-10}$ M with a median of $\sim10^{-9}$ M. More thermodynamic data from the Nuclear Energy Agency (NEA) for aqueous Tc species and minerals were recently made available for geochemistry modeling (Guillaumont et al. 2003; NEA 2012). The objective of this study was to compare the recent laboratory studies with thermodynamic estimates of the solubility of various Tc(IV) hydrated oxides to provide greater theoretical understanding and technical justification for the selection of input values for transport modeling. Three Tc dioxide phases (TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$) were evaluated using GWB and various thermodynamic datasets. More specifically, the objectives of this study were to: 1) benchmark GWB software and database with the latest NEA data for aqueous Tc species and minerals; 2) calculate the solubility of Tc dioxide phases in water of low ion strength to provide a simpler system for modeling; 3) calculate the solubility of Tc dioxide phases in saltstone leachates (Cantrell and Williams 2012); 4) calculate the solubility of Tc dioxide phases in Portland cement leachate with the presence of pyrrohtite (a surrogate for modeling the contribution of blast furnace slag) at 1 gram per liter. These calculations will permit evaluating the sensitivity of Tc solubility to different Tc dioxide phases to the sources of thermodynamic database, pH, Eh and solution chemistry.

Table 1. A literature summary on Tc solubility values and the expected solid phases controlling the solubility in reducing cement-based fluids

Systems	**Tc solids**	**pH**	**Eh (V)**	**Tc Solubility (M)**	**Method**	**References**
Concrete				$<10^{-10}$	Batch	Allard (1984)
Cement leachate	Hydrated TcO_2	8-13	-0.45	Consistently $\approx 10^{-7}$	Batch	Pilkington (1990)
Cement leachate	TcO_2 or $TcO_2 \cdot xH_2O$	12.3	-0.51	4×10^{-9} to 1×10^{-10}	Batch	Greenfield et al. (1998)
Highly alkaline solution	$TcO_2 \cdot xH_2O$			n/a	EXAFS	Lukens et al. (2002)
Hanford facility	$TcO_2 \cdot 2H_2O$	12 to 14	-0.35 to -0.50	10^{-7}	Model	Krupka et al. (2004)
Reducing grout	TcS_2, Tc_3S_{10}			n/a	EXAFS	Lukens et al. (2005)
Aqueous oxalate	$TcO_2 \cdot 2H_2O$	1.5-12	Ar atmosphere	10^{-3} to 10^{-8}	Batch, model	Hess et al. (2008)
Aged cement-water	n/a	11.9	-0.43	1.5×10^{-9}	Batch	Estes et al. (2012)
Saltstone Vault 2-water	n/a	10.9	-0.40	4.5×10^{-10}		
Saltstone TR547-water	n/a	11.9	-0.44	9×10^{-9}		
Saltstone TR545-water	n/a	12.1	-0.43	5×10^{-10}		
Saltstone with Tc in water-day 1	$TcO_2 \cdot xH_2O$	12.58	-0.11	3.5×10^{-6}	Static single-pass flow-through batch with leachate replenishing while sampling	Cantrell and Williams (2012)
Saltstone with Tc in water-day 7	$TcO_2 \cdot xH_2O$	12.59	-0.15	3.2×10^{-6}		
Saltstone with Tc in water-day 14	$TcO_2 \cdot xH_2O$	12.66	-0.38	1.4×10^{-6}		
Saltstone with Tc in water-day 84	$TcO_2 \cdot xH_2O$	12.62	-0.30	1.6×10^{-7}		

2. Software, Databases, and Benchmarking

2.1 Geochemist's Workbench Professional 8.0

Geochemist's Workbench (GWB) was developed by Craig Bethke at the University of Illinois at Urbana-Champaign (Bethke and Yeakel 1992; 2008; 2010a, 2010b, 2010c, and 2010d). The main programs in GWB Professional 8.0 are Rxn, Act2, React, Tact, SpecE8, X1t and X2t. These programs manipulate chemical reactions (Rxn), evaluate phase stability (Act2), calculate aqueous speciation, equilibrium conditions, and reaction pathways (React), evaluate temperature-activity relationships (Tact), and perform one-dimensional and two dimensional reactive transport calculations (X1t and X2t). Several thermodynamic databases (e.g., thermo.dat, thermo.com.v8.r6+.dat, thermo_phreeqc.dat, thermo_minteq.dat) are included in the GWB software package.

GWB has been used by many research institutes (e.g., Savannah River National Laboratory, Pacific Northwest National Laboratory, Southwest Research Institute, and The Belgian Nuclear Research Centre SCK•CEN) to provide technical assistance to the U.S. Nuclear Regulatory Commission (NRC), U.S. Department of Energy (DOE) and Nuclear Energy Agency (NEA) in their high-level waste programs. In this work, Act2 was used to evaluate phase stability of aqueous Tc species and Tc mineral phases; while React was used to calculate the solubility of TcO_2-c, $TcO_2{\cdot}1.6H_2O$ and $TcO_2{\cdot}2H_2O$ in several systems including (1) water of low ion strength, (2) reducing saltstone leachate solutions, and (3) Portland cement leachates with the presence of pyrrohtite as a reducing reactant.

2.2 Databases used in this work

No single database has all of the required thermodynamic data to complete the needed Tc calculations. As such, we elected, as previous modelers have done, to import missing constants from another data set into a baseline dataset. Three databases created in this manner were those of Cantrell and Williams (2012), Denham and Millings (2012), and Wang et al. (2009). We acquired these three Tc thermodynamic data sets through Dr. Kirk Cantrell (Pacific Northwest National Laboratory, Richland WA), Dr. Miles Denham (SRNL, Aiken, SC) and Dr. Lian Wang (SCK-CEN, Brussels, Belgium). These Tc databases have rather small differences and derived their data from similar laboratory experiments (Guillaumont et al. 2003; NEA 2012). The technetium thermodynamic data used in speciation and solubility calculations at 298.15 K, 0.1 Mpa are provided in Appendix I (Table A-1). However, it is noted that the data in Wang et al. (2009) are given at 12.5 °C (whereas the other databases were reported at 25°C); the thermodynamic reactions were also different from the other databases.

- In the database used in Cantrell and Williams (2012), the thermodynamic database thermo.com.V8.R6+.dat (that is the LLNL V8 R6 "combined" data set) was used (Bethke and Yeakel 2010a); augmented with data from Guillaumont et al. (2003). Like thermo.dat, thermo.com.v8.r6+.dat uses an extended form of the Debye-Huckel equation called the B-dot model (Helgeson 1969):

$$log\gamma_i = \frac{Az_i^2\sqrt{I}}{1 + \mathring{a}_i B\sqrt{I}} + \dot{B}I \qquad (1)$$

Coefficients A, B and B-dot vary with temperature, whereas the ion size parameter $\mathring{a}_i$ for each species remains constant. The B-dot model is parameterized from 0 °C to 300 ºC for solutions of up to 3 molal ion strength in which NaCl is the dominant solute. However, for the solutions of more complex solutes, it is valid up to 1 molal ion strength (Bethke 2008).

- The database of Denham and Millings (2012) used the thermo_phreeqc.data (Bethkel and Yeakel 2010a), augmented the database with data from Nuclear Energy Agency (Guillaumont et al. 2003; NEA 2012). When thermo_phreeqc.dat is loaded, GWB uses the same activity model originally used in PHREEQC, this is the Davies equation:

$$log\gamma_i = -Az_i^2\left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I\right) \qquad (2)$$

The Davies equation is reasonably accurate to an ionic strength of about 0.5 molal (Bethke 2008).

- The database used by Wang et al. (2009) was the thermo_phreeqc.dat database (Bethkel and Yeakel 2010a) and also augmented with data from Nuclear Energy Agency (NEA) (Guillaumont et al. 2003). The database was provided at 12.5 °C, whereas the other datasets were given at 25 °C.
- As mentioned, none of the above data sets had all of the constants of interest for TcO_2-c, $TcO_2·1.6H_2O$ and $TcO_2·2H_2O$. To permit all of these calculations we used the dataset reported by Denham and Millings (2012) and augmented the Tc data with those reported by Cantrell and Williams (2012). The dataset of Denham and Millings (2012) was used as a primary basis, because it has been used by SRNL scientists for PA calculations.

2.3 Benchmarking software

Benchmarking this software was conducted using three examples available from literature. The purpose of this was to evaluate whether the software used in this study (GWB, Version 8) would produce similar results to previous calculations in literature for two scenarios. For the first scenario, similar thermodynamic data inputs were used with a different software (examples 2 and 3). For the second one, the GWB version 8 we used was compared to the older versions of GWB (examples 1-3).

2.3.1 Tc speciation and solubility in water

The Eh-pH diagram for aqueous technetium species is shown in Figure 1 (left). The solubility of $TcO_2·1.6H_2O$ at Eh = -0.4 V as a function of pH is also presented in Figure 1 (right), where speciation and solubility were produced with GWB ACT2 module and the modified thermodynamic data in this work. These results are identical to graphs calculated at the identical environmental conditions by Wang et al. (2009; see Figures 75 and 76 in this reference).

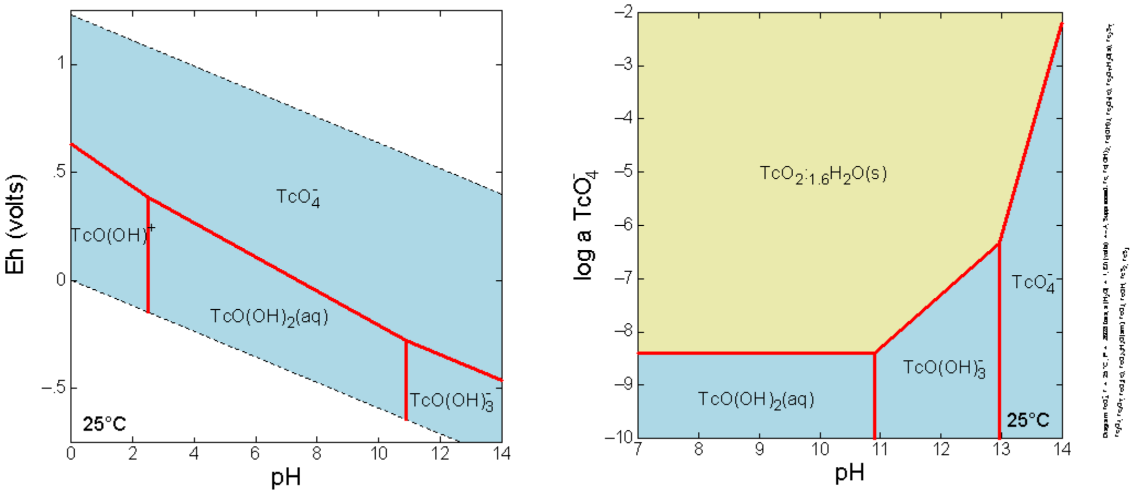

Figure 1. Left: Eh-pH diagram of aqueous Tc species (Tc activity 10^{-8} M, all minerals are suppressed) and Right: solubility of $TcO_2{\cdot}1.6H_2O$ as a function of pH (Eh = -0.4 V, all other Tc minerals are suppressed)

2.3.2 Solubility of barite in pure water and seawater

The solubility of barite ($BaSO_4$) in pure water and seawater was calculated using the Pabalan and Sabido (2007) input data files and GWB Professional 8.0 and the database of this work. The results are given in Table 2. Our calculated solubility of barite was identical to that calculated by Pabalan and Sabido (2007) who used an earlier version of the GWB 6.0, and the results were also similar to those calculated with PHREEQC 2.12.5 software (Pabalan and Sabido 2007). This calculation was originally designed to describe experimental data (Richardson and McSween 1989; Blount 1977).

Table 2. Solubility of barite in pure water and seawater

	Ba^{2+} (M)	SO_4^{2-} (M)	Activity coefficient of Ba^{2+}	Activity coefficient SO_4^{2-}
In pure water				
GWB Pro 8.0 (this work)	**1.067×10^{-5}**	**1.067×10^{-5}**	**0.9701**	**0.9701**
GWB 6.0 (Pabalan and Sabido 2007)	1.067×10^{-5}	1.067×10^{-5}	0.9701	0.9701
PHREEQC 2.12.5 (Pabalan & Sabido 2007)	1.055×10^{-5}	1.055×10^{-5}	0.9701	0.9701
Richardson & McSween (1989)	1.051×10^{-5}	1.051×10^{-5}	0.9704	0.9704
Blount (1977)	1.060×10^{-5}	1.060×10^{-5}	N/A	N/A
In seawater				
GWB Pro 8.0 (this work)	**3.981×10^{-5}**	**3.080×10^{-5}**	**0.2982**	**0.2928**
GWB 6.0 (Pabalan and Sabido 2007)	3.981×10^{-5}	3.080×10^{-5}	0.2982	0.2928
PHREEQC 2.12.5 (Pabalan & Sabido 2007)	3.937×10^{-5}	3.047×10^{-5}	0.2982	0.2927
Richardson & McSween (1989)	3.611×10^{-5}	3.611×10^{-5}	0.2987	0.2671
Blount (1977)	3.700×10^{-5}	3.700×10^{-5}	N/A	N/A
N/A: not available				

2.3.3 Effects of temperature on saturation index of gypsum and anhydrite in water

The saturation indices (SI) of gypsum ($CaSO_4{\cdot}2H_2O$) and anhydrite ($CaSO_4$) in pure water as a function of temperature were calculated using the Pabalan and Sabido (2007) input data files and GWB Professional 8.0 and our database, the results are given in Table 3. Our calculated data are identical to those calculated using GWB 6.0 (Pabalan and Sabido 2007), and similar to those calculated using PHREEQC 2.12.5 software (Pabalan and Sabido 2007, Parkhurst and Appelo 1999).

Table 3. Saturation index of gypsum and anhydrite in water as a function of temperature

T (°C)	**This work**		Pabalan and Sabido (2007)			
	GWB Pro 8.0		GWB 6.0		PHREEQC Version 2.12.5	
	SI (Anhy)	**SI (Gyp)**	SI (Anhy)	SI (Gyp)	SI (Anhy)	SI (Gyp)
25	**-0.2178**	**0**	-0.2178	0	-0.2197	0
30	**-0.1978**	**0**	-0.1978	0	-0.1977	0
35	**-0.1713**	**0**	-0.1713	0	-0.1713	0
40	**-0.1407**	**0**	-0.1407	0	-0.1404	0
45	**-0.1060**	**0**	-0.1060	0	-0.1060	0
50	**-0.0678**	**0**	-0.0678	0	-0.0678	0
55	**-0.0261**	**0**	-0.0261	0	-0.0261	0
60	**0**	**-0.0188**	0	-0.0188	0	-0.0187
65	**0**	**-0.0666**	0	-0.0666	0	-0.0665
70	**0**	**-0.1172**	0	-0.1172	0	-0.1171
75	**0**	**-0.1704**	0	-0.1704	0	-0.1704
SI = saturation index; Anhy = anhydrite; Gyp = gypsum						

3. Results

A set of Tc speciation and solubility calculations of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ as a function of pH were conducted. The first calculation was at fixed pH 8.0 and Eh -0.40 V in pure water using our database to provide a measure of sensitivity to the database of interest (Section 3.1). The second and third calculations were for young cement at fixed pH of 12.66 and for moderately aged cement at a fixed pH of 10.5, both at the Eh -0.38 V (Section 3.2). The fourth calculation was conducted in Portland cement leachate with the presence of pyrrohtite as reducing reactant (section 3.3). The speciation and solubility calculations were conducted using GWB React module.

3.1 Solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in pure water

The speciation and solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in pure water are given in Table 4, and more detailed figures are presented in Appendix II. The solubility of TcO_2-c is lower by four orders of magnitude compared to those of $TcO_2 \cdot 1.6H_2O$ and

$TcO_2 \cdot 2H_2O$. The solubility of $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ are similar, the more hydrated $TcO_2 \cdot 2H_2O$ has slightly higher solubility than $TcO_2 \cdot 1.6H_2O$.

Table 4. Solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in pure water

	TcO_2-c	**$TcO_2 \cdot 1.6H_2O$**	**$TcO_2 \cdot 2H_2O$**
Database	this work	this work	this work
pH	8	8	8
Eh (V)	-0.4	-0.4	-0.4
$TcO(OH)_2(aq)$, M	4.04E-13	3.98E-09	5.86E-09
$TcO(OH)_3^-$, M	5.09E-16	5.02E-12	7.39E-12
Total species (solubility), M	4.04E-13	3.98E-09	5.86E-09

3.2 Solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in reducing saltstone leachates

The speciation and solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in saltstone leachates were calculated using GWB React module. The modified database was used in the solubility calculations. The results were compared with similar calculations using the databases of Cantrell and Williams (2012), Denham and Millings (2012) and Wang et al. (2009). Early stage saltstone fluids are of higher ionic strength, higher than what is probably valid for computing activity coefficient (Debye-Huckel, Davis equation or B-dot method) used in these thermodynamic databases, which might be a source of uncertainty in the calculated solubility values. However, because saltstone is expected to have such a high ionic strength environment for only a very short period during the Young Cement Stage, it is expected that the error associated with activity coefficient during this time will have little effect on predicted long-term geochemistry. Ionic strength is not an issue for calculating activity coefficients in the moderately aged saltstone leachates (e.g., the 84 day saltstone leachate) and the Portland cement leachate, in which the ionic strengths were well below 0.5 molal, and both of the activity coefficient models should allow fairly accurate calculation.

The basic leachate chemistry of saltstone used in the solubility calculation was taken from Cantrell and Williams (2012) and provided in Table 5. Cantrell and Williams (2012) demonstrated that technetium release from crushed (size range <2 mm) saltstone in contact with 0.005 M calcium hydroxide at a solid to solution ratio of ~1 under anoxic conditions is controlled by the solubility of $TcO_2 \cdot xH_2O$ (likely $TcO_2 \cdot 1.6H_2O$), the equilibrium solubility appeared to have reached within two weeks at a Tc concentration of approximately 1.5×10^{-6} M. The saltstone leachate chemistries under reducing conditions of reactor #3 after 14 days and 84 days in the static single-pass flow-through batch experiments were chosen for the Tc dioxide solubility calculation.

Table 5. The chemistry of saltstone leachates and Portland cement leachate

	Saltstone leachates		**Portland cement leachate**
	14 day static batch	**84 day static batch**	
CO_3^{2-} (mg/L)	4344**	2685**	
Al^{3+} (µg/L)	61500	76500	
H_3BO_3 (µg/L)	22019	(14735)*	
Ca^{2+} (µg/L)	11000	(2428)*	765000
Fe^{2+} (µg/L)	2360	6440	
Li^+ (µg/L)	4780	3640	
MoO_4^{2-} (µg/L)	7166	747)*	
K^+ (µg/L)	2.42E+6	371000	247000
H_4SiO_4 (µg/L)	134437	245955	
Na^+ (µg/L)	3.89E+7	6130000	150800
SO_4^{2-} (mg/L)	4790	345	
NO_3^- (mg/L)	77900	9030	
PO_4^{3-} (µg/L)	6834	(5660)*	
pH	12.66	12.74	12.3
Eh (V)	-0.38	-0.30	N/A
References	Cantrell and Williams (2012) * Values given in the parenthesis are estimated and below the estimated quantification limit as indicated in this reference. ** The CO_3^{2-} concentrations were calculated using the reported total alkalinity (TA) values according to the formula, where K_2 is equal to $10^{-10.3}$: $[HCO_3^-] = \frac{2TA - 10^{-14+pH}}{1 + 2K_2 \times 10^{pH}}$ $[CO_3^{2-}] = \frac{K_2 \times [HCO_3^-]}{[H^+]}$		Li et al. (2011)

The speciation and solubility (more specifically the concentrations of dominant Tc aqueous species) of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ are provided in Tables 6, 7 and 8, respectively, assuming that they are in equilibrium with the saltstone leachate chemistry which were obtained after 14 days in the static batch experiments. The speciation and solubility of the Tc dioxides in the saltstone leachate were also calculated assuming pH values 11.8, 11.0 and 10.5 using different databases to evaluate how the calculated solubility is sensitive to different database and pH values. The speciation and solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in the saltstone leachate after 84 days in the static single-pass flow-through batch experiments are presented in Table 9. More detailed figures that demonstrated how the speciation and solubility of these technetium dioxides varied with the database used, Eh and pH of the saltstone leachate are presented in Appendix III.

For the same Tc oxide at the same conditions (pH, Eh, leachate chemistry), the solubility calculated using the database of this work, Denham and Millings (2012) and Wang et al (2009) are very similar, whereas the solubility values calculated using the database of Cantrell and Williams (2012) are slightly higher (~2-5 times) than those calculated from the other three datasets (Tables 6, 7 and 8). In reducing saltstone leachate at pH 12.66 and Eh -0.38 V, the solubility of $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ supports the calculated total Tc solution concentrations of 6.3×10^{-7} and 9.5×10^{-7} M, respectively, while the solubility of $TcO_2(c)$ supports the calculated total solution concentration of 6.0×10^{-11} M. Compared with the experimentally derived values of Tc concentrations of 1.5×10^{-6} M in pH 12.66 and Eh -0.38 V saltstone leachates (Cantrell and Williams 2012) and $9 \times 10^{-9} \sim 5 \times 10^{-10}$ M in the pH ~11.8 and Eh -0.44 V saltstone leachates (Estes et al. 2012), these data suggest that the solubility of hydrated $TcO_2 \cdot xH_2O$ (likely $TcO_2 \cdot 1.6H_2O$) controlled the aqueous Tc concentration in a reducing saltstone leachate environment (Eh < -0.38 V). However, as the Eh increases just above -0.35 V, the TcO_4^- concentration increased dramatically to millimolarity due to the re-oxidation of the Tc(IV) solid phases to the more soluble Tc(VII) species (Table 9). Also, as long as Eh remains at < -0.38 V in the pore fluids of saltstone waste forms, the solubility of Tc oxide phases decreases with deceasing pH in the saltstone leachate (Table 7). For example, when pH decreases from 12.7 to 10.5, the solubility of $TcO_2 \cdot 1.6H_2O$ decreases from 6.3×10^{-7} M to 5.2×10^{-9} M (Table 7).

Table 6. Speciation and solubility of TcO_2-c in reducing (Eh = -0.38 V) saltstone leachate

	TcO_2-c					
Database	this work	Denham	Wang	this work	this work	this work
pH	12.66	12.66	12.66	11.8	11	10.5
Eh (V)	-0.38	-0.38	-0.38	-0.38	-0.38	-0.38
All other Tc minerals	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed
Charge balance	off	off	off	off	off	off
$TcO(OH)_2(aq)$, M	3.03E-13	3.03E-13	2.97E-13	3.05E-13	3.06E-13	3.06E-13
$TcO(OH)_3^-$, M	2.66E-11	2.66E-11	2.57E-11	3.69E-12	5.86E-13	1.85E-13
TcO_4^-, M	3.28E-11	3.28E-11	3.70E-11	1.20E-14	7.58E-18	7.58E-20
Total Tc species (solubility), M	5.97E-11	5.97E-11	6.30E-11	4.01E-12	8.92E-13	4.91E-13

Table 7. Speciation and solubility of $TcO_2·1.6H_2O$ in reducing (Eh = -0.38 V) saltstone leachate

	$TcO_2·1.6H_2O$									
Database	this work	Cantrell	Denham	Wang	this work	Cantrell	this work	Cantrell	this work	Cantrell
pH	12.66	12.66	12.66	12.66	11.8	11.8	11	11	10.5	10.5
Eh (V)	-0.38	-0.38	-0.38	-0.38	-0.38	-0.38	-0.38	-0.38	-0.38	-0.38
Other Tc minerals	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed
Charge balance	off	off	off	off	off	off	off	off	off	off
$TcO(OH)_2$ (aq), M	3.22E-09	6.96E-09	3.22E-09	3.22E-09	3.24E-09	6.96E-09	3.24E-09	6.96E-09	3.24E-09	6.96E-09
$TcO(OH)_3^-$ M	2.82E-07	6.67E-07	2.82E-07	2.87E-07	3.91E-08	9.20E-08	6.21E-09	1.46E-08	1.96E-09	4.61E-09
TcO_4^-, M	3.48E-07	5.14E-07	3.48E-07	4.00E-07	1.27E-10	1.87E-10	8.03E-14	1.18E-13	8.03E-14	1.18E-13
Total Tc species (solubility) M	6.33E-07	1.19E-06	6.33E-07	6.90E-07	4.24E-08	9.92E-08	9.45E-09	2.16E-08	5.20E-09	1.16E-08

Table 8. Speciation and solubility of $TcO_2 \cdot 2H_2O$ in reducing (Eh = -0.38 V) saltstone leachate

	$TcO_2 \cdot 2H_2O$							
Database	this work	Cantrell	this work	Cantrell	this work	Cantrell	this work	Cantrell
pH	12.66	12.66	11.8	11.8	11	11	10.5	10.5
Eh (V)	-0.38	-0.38	-0.38	-0.38	-0.38	-0.38	-0.38	-0.38
All other Tc minerals	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed	suppressed
Charge balance	off	off	off	off	off	off	off	off
$TcO(OH)_2$(aq), M	4.83E-09	2.79E-08	4.85E-09	2.79E-08	4.86E-09	5.86E-08	4.86E-09	2.79E-08
$TcO(OH)_3^-$, M	4.23E-07	2.68E-06	5.87E-08	3.70E-07	9.31E-09	2.79E-08	2.94E-09	1.85E-08
TcO_4^-, M	5.23E-07	2.06E-06	1.91E-10	7.49E-10	1.20E-13	4.73E-13	1.21E-15	4.73E-15
Total Tc species (solubility), M	9.51E-07	4.77E-06	6.37E-08	4.05E-07	1.42E-08	8.65E-08	7.80E-09	4.64E-08

Table 9. Speciation and solubility of TcO_2-c, $TcO_2·1.6H_2O$ and $TcO_2·2H_2O$ in less reducing (Eh = -0.30 V) saltstone leachate

	TcO_2-c	**$TcO_2·1.6H_2O$**		**$TcO_2·2H_2O$**	
Database	this work	this work	Cantrell	this work	Cantrell
pH	12.74	12.74	12.74	12.74	12.74
Eh (V)	-0.3	-0.3	-0.3	-0.3	-0.3
All other Tc minerals	suppressed	suppressed	suppressed	suppressed	suppressed
Charge balance	off	off	off	off	off
$TcO(OH)_2(aq)$, M	3.81E-13	2.64E-09	3.81E-09	2.53E-09	3.64E-09
$TcO(OH)_3^-$, M	3.71E-11	2.57E-07	4.22E-07	2.46E-07	4.03E-07
TcO_4^-, M	9.08E-07	6.30E-03	6.30E-03	6.02E-03	6.02E-03
Total Tc species (solubility), M	9.08E-07	6.30E-03	6.30E-03	6.02E-03	6.02E-03

Table 10. Speciation and solubility of TcO_2-c, $TcO_2·1.6H_2O$ and $TcO_2·2H_2O$ in Portland cement leachate with the presence of pyrrohtite ($Fe_{1-x}S$ (x = 0-0.2)) as a reducing agent

	TcO_2-c	**$TcO_2·1.6H_2O$**		**$TcO_2·2H_2O$**	
Database	this work	this work	Cantrell	this work	Cantrell
pH	12.3	12.3	12.3	12.3	12.3
Eh (V), starting	-0.38	-0.38	-0.38	-0.38	-0.38
Eh (V), ending	-0.69	-0.69	-0.64	-0.69	-0.64
All other Tc minerals	suppressed	suppressed	suppressed	suppressed	suppressed
Charge balance	off	off	off	off	off
$TcO(OH)_2(aq)$, M	3.98E-13	3.93E-09	6.96E-09	5.79E-09	2.79E-08
$TcO(OH)_3^-$, M	1.24E-11	1.23E-07	2.22E-07	1.81E-07	8.92E-07
TcO_4^-, M	1.89E-28	1.86E-24	1.39E-21	2.74E-24	5.61E-21
Total Tc species (solubility), M	1.28E-11	1.27E-07	2.29E-07	1.87E-07	9.20E-07

3.3 Solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in Portland cement leachate with the presence of pyrrohtite ($Fe_{1-x}S$ (x = 0-0.2)) as a reducing agent

Portland cement was mixed with DI water at the water to cement radio of 0.6:1 for hydration and cured for 30 days. The cured cement was crushed to pass a #12 sieve, <1.68 mm. 200 gram of the crushed cement was mixed with 2000 ml DI water, which was equilibrated on a shaker for 7 days. 0.45 μm filter (Type HA) and vacuum pump were used for filtration to get Portland cement leachate. Its pH value was 12.3, and the chemical compositions analyzed using ICP-OES were Na 150.8 mg/L, K 247 mg/L and Ca 765 mg/L (Table 5).

The speciation and solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in the Portland cement leachate with the presence of pyrrohtite as a reducing reactant were calculated (Table 10), and supporting figures are presented in Appendix IV. At fixed pH 12.3 and Eh -0.38 V, the calculated solubility of $TcO_2 \cdot 1.6H_2O$, $TcO_2 \cdot 2H_2O$ and TcO_2(c) are 1.3×10^{-7} M, 1.9×10^{-7} M, and 1.3×10^{-11} M, respectively, in Portland cement leachate with the presence of pyrrohtite (one gram per one liter leachate solution).

4. Conclusions

The solubility of $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in water of low ionic strength at pH 8 and Eh -0.4 V supports total Tc solution concentration of 4.0×10^{-9} and 5.9×10^{-9} M, respectively, while that of TcO_2(c) supports a total Tc solution concentration of 4.0×10^{-13} M (Table 4).

For the same Tc dioxide at the same conditions (pH, Eh, leachate chemistry), the solubility calculated using the database from this work, Denham and Millings (2012) and Wang et al. (2009) are very similar, whereas the solubility calculated using the database of Cantrell and Williams (2012) was slightly higher (2-5 times).

In reducing saltstone leachate at pH 12.7 and Eh -0.38 V, the solubility of $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ are 6.3×10^{-7} and 9.5×10^{-7} M, respectively, while the solubility of TcO_2(c) is 6.0×10^{-11} M. Similarly, in Portland cement leachate with the presence of pyrrohtite as a reducing agent at pH 12.3 and Eh -0.38 V, the solubility values of $TcO_2 \cdot 1.6H_2O$, $TcO_2 \cdot 2H_2O$ and TcO_2(c) are 1.3×10^{-7} M, 1.9×10^{-7} M, and 1.3×10^{-11} M, respectively. These results are in good agreement with experimentally measured Tc solubility of simulated saltstone waste forms in contact with water: 1.5×10^{-6} M in the pH 12.66 and Eh -0.38 V saltstone pore fluids (Cantrell and Williams 2012) and 9×10^{-9} ~ 5×10^{-10} M in the pH ~11.8 and Eh -0.44 V saltstone leachates (Estes et al. 2012). The solubility of hydrated $TcO_2 \cdot xH_2O$ (likely $TcO_2 \cdot 1.6H_2O$) controls the Tc concentration in reducing Tc saltstone nuclear waste forms in contact with water as long as the Eh remained < -0.38 V, the dominant Tc species are $TcO(OH)_{3-}$, TcO_{4-} and lesser $TcO(OH)_2$(aq). However, as the Eh increased just above -0.35 V, the TcO_4^- become much more dominant than the others due to the re-oxidation of Tc(IV) species and/or solid phases, and the TcO_4^- concentration would increase dramatically to millimolarity.

In the reducing leachate of saltstone waste forms (Eh remains < -0.38 V), the solubility of Tc dioxide phases decreases with deceasing pH values. For example, when pH decreased from 12.7 to 11.8, the solubility of $TcO_2 \cdot 1.6H_2O$ decreased from 6.3×10^{-7} to 4.2×10^{-8} M. Similarly, when the pH decreased from 11.0 to 10.5, the solubility values decreased from 9.4×10^{-9} M to 5.2×10^{-9} M.

During the two early stages of cement aging, the modeling indicates that solubility of $TcO_2 \cdot xH_2O$ is the controlling process of aqueous Tc concentration of saltstone at the pH and Eh values that exist at these stages. The calculated solubility values of $TcO_2 \cdot xH_2O$ tended to vary by less than an order of magnitude, irrespective of which database was used to model a given scenario. However, once the system becomes oxidized, generally anticipated to occur during the 2nd stage of cement aging, then solubility no longer controls aqueous Tc concentrations and adsorption to solid phases becomes the predominant mechanism, and thus the K_d construct is appropriate to use (Estes et al. 2012; Kaplan et al. 2011). Similarly, once sufficient pore water has leached through the saltstone to advance the modeling into the 3rd and final stage of aged cement, a Tc K_d for an oxidized system would be appropriate to use. These guidelines are summarized in Table 11. Uncertainty associated with stochastic modeling using the cement geochemistry constants described in Table 11 should be estimated by the equations provided by Almond et al. (2012), which recommended using a lognormal distribution and the range set at 0.25^*K_d and 1.75^*K_d.

Table 11. Guidelines for the selection of parameters in PA modeling

Cementitious Material	**Young Cement 1st Stage (pH ~12)**	**Moderately-aged Cement 2nd Stage (pH ~10.5)**	**Aged Cement 3rd Stage (pH ~5.5)**
Reduced	6 x 10^{-7} mol/L solubility[a]	1 x 10^{-8} mol/L solubility[e, d]	0.5 mL/g K_d[c]
Oxidized	0.8 mL/g K_d[b]	0.8 mL/g K_d[b, d]	0.5 mL/g K_d[b, d]

[a] Based on experimental (Cantrell and Williams (2012) and modeling consideration described in this document. Experimentally derived solubility of Tc leached from a simulated saltstone sample was 1.5×10^{-6} M and $TcO_2 \cdot 1.6H_2O$ was estimated to be controlling Tc concentration under reducing conditions. It is noted that their static single-pas flow-through batch systems were not in steady states. Estes et al. (2012) studied the solubility of a saltstone using batch experiments and measured a solubility of 9×10^{-9} M in pH 11.9 and Eh -0.44 V saltstone leachate. The modeling indicated that the solubility of $TcO_2 \cdot 1.6H_2O$ is 6.32×10^{-7} M (our database) or 1.19×10^{-6} M (Cantrell's database) in pH 12.66 and Eh -0.38 V saltstone leachates.

[b] Unchanged (Kaplan 2010)

[c] Assumed cement becomes oxidized

[d] Geochemical parameters most important to saltstone PA

[e] Based on experimental (Estes et al. 2012) and modeling considerations described in this document. Experimentally derived solubility of Tc leached from a simulated saltstone sample was 4.5×10^{-10} M in a pH 10.9 and Eh -0.40 V saltstone leachate solution. The measured value may have been lower than calculated 5.2×10^{-9} M ($TcO_2 \cdot xH_2O$ at pH 10.5 and Eh -0.38 V) because it was a closed system that did change the aqueous solution, promoting increased ion concentrations with respect to a flow-through system.

5. Acknowledgements

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7. Appendix

Appendix I

Technetium thermodynamic data used in speciation and solubility calculations

Table A-1. **Technetium thermodynamic data used in speciation and solubility calculations (298.15 K, 0.1 Mpa)**

	Log K° (I=0)			
	Cantrell & Williams (2012)	**Denham & Millings (2012)**	**Wang et al. (2009)***	**This work**
$TcO_4^- + 3H^+ = \mathbf{TcO^{2+}} + 0.75O_2(aq) + 1.5H_2O$	–31.5090	-31.0434	-31.0595	-31.0434
$TcO^{2+} + 2H_2O = \mathbf{TcO(OH)_2(aq)} + 2H^+$	–3.3221	-4.0000		-4.0000
$TcO_4^- + H^+ + 0.5H_2O = \mathbf{TcO(OH)_2(aq)} + 0.75O_2(aq)$			-35.0595	
$TcO^{2+} + 3H_2O = \mathbf{TcO(OH)_3^-} + 3H^+$	–14.2221	-14.8999		-14.8999
$TcO_4^- + 1.5H_2O = \mathbf{TcO(OH)_3^-} + 0.75O_2(aq)$			-45.9595	
$TcO^{2+} + HCO_3^- + H_2O = \mathbf{TcCO_3(OH)_2(aq)} + H^+$	5.5915			
$TcO^{2+} + CO_3^{--} + H_2O = \mathbf{TcCO_3(OH)_2(aq)}$		-15.2522		-15.2522
$TcO_4^- + HCO_3^- + 2H^+ = \mathbf{TcCO_3(OH)_2(aq)} + 0.5H_2O + 0.75O_2(aq)$			-26.1340	
$TcO^{2+} + HCO_3^- + 2H_2O = \mathbf{TcCO_3(OH)_3^-} + H^+$	–2.7085			
$TcO^{2+} + CO_3^{--} + 2H_2O = \mathbf{TcCO_3(OH)_3^-} + H^+$		6.9518		6.9518
$TcO_4^- + HCO_3^- + H^+ = \mathbf{TcCO_3(OH)_2(aq)} + 0.5H_2O + 0.75O_2(aq)$			-34.4341	
$TcO^{2+} + H_2O = \mathbf{TcO_2(s)} + 2H^+$	N/A	8.3936		8.3936
$TcO_4^- + H^+ = \mathbf{TcO_2(s)} + 0.5H_2O + 0.75O_2(aq)$			-22.6659	
$TcO^{2+} + 2.6H_2O = \mathbf{TcO_2{\cdot}1.6H_2O(s)} + 2H^+$	4.8356	4.4001		4.4001
$TcO_4^- + H^+ + 1.1H_2O = \mathbf{TcO_2{\cdot}1.6H_2O(s)} + 0.75O_2(aq)$			-26.6594	
$TcO^{2+} + 3H_2O = \mathbf{TcO_2{\cdot}2H_2O(am)} + 2H^+$	4.2319	N/A	N/A	4.2319
$TcO^{2+} + 2HS^- = \mathbf{TcS_2(s)_2} + H_2O$	65.9742	N/A	N/A	65.9742
$2TcO_4^- + 7HS^- + 9H^+ = \mathbf{Tc_2S_7(s)} + 8H_2O$	230.2410	N/A	N/A	230.2410
N/A: not available; * Wang's data were given at 12.5 ºC.				

Appendix II

Solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in water

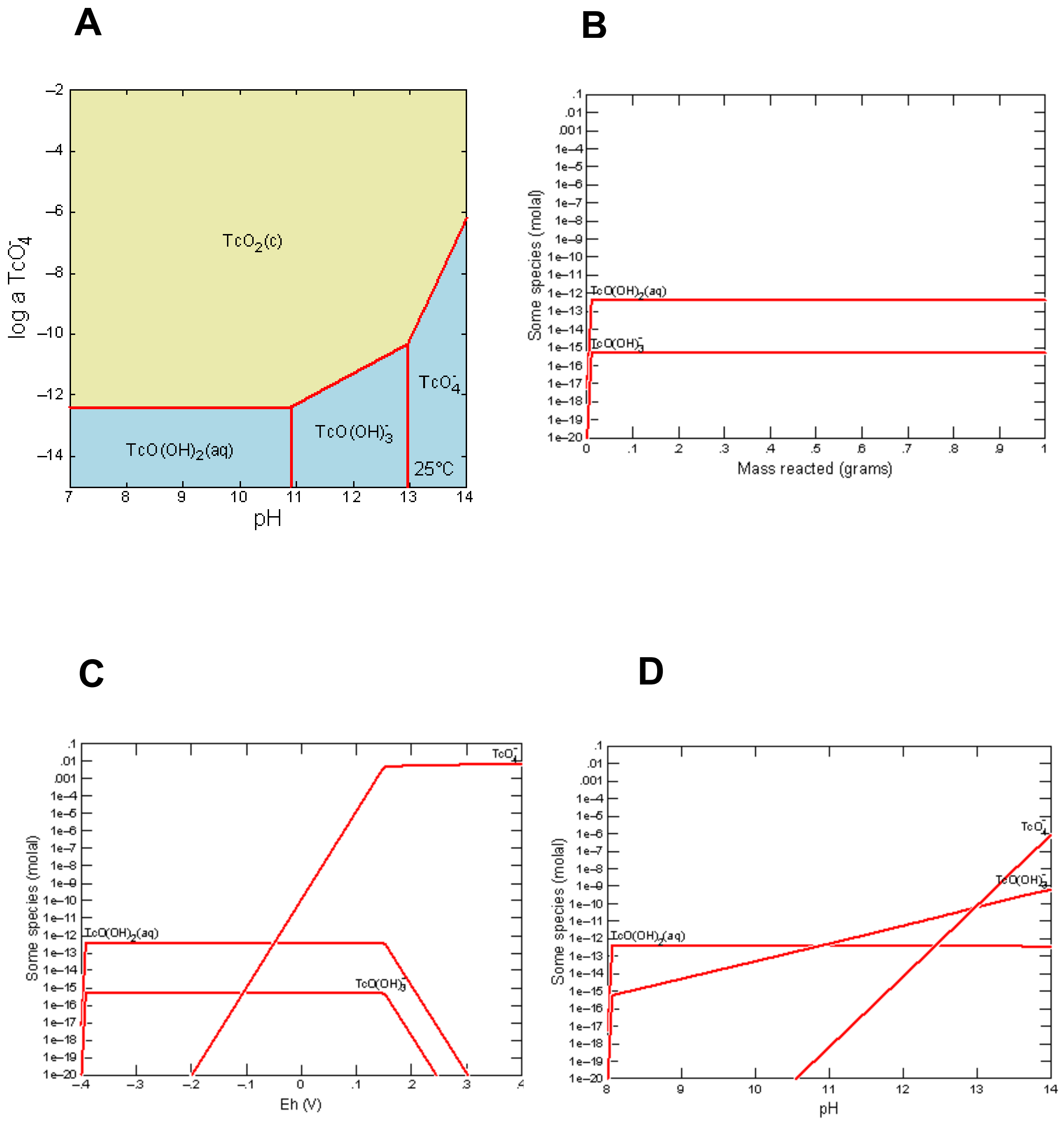

Figure A-1. Speciation and solubility of TcO_2-c in water (Eh = -0.38 V, pH 8.0, our database, all other Tc minerals are suppressed).

A. Phase diagram as a function of pH **B. As a function of TcO_2-c reacted**

C. As a function of Eh **D. As a function of pH**

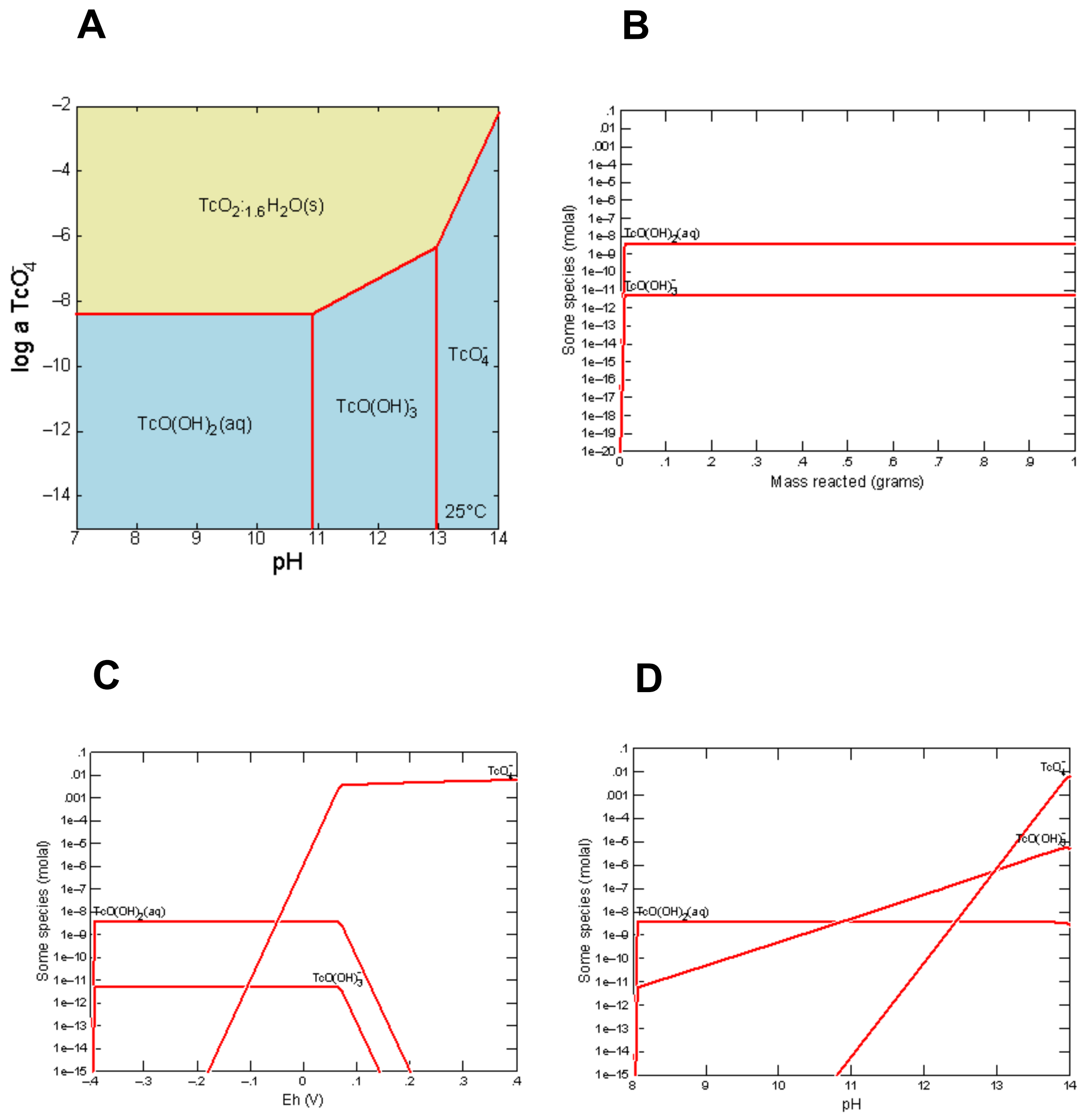

Figure A-2. Figure A-1 Speciation and solubility of $TcO_2 \cdot 1.6H_2O$ in water (Eh = -0.38 V, pH 8.0, our database, all other Tc minerals are suppressed).

A. Phase diagram as a function of pH **B. As a function of $TcO_2 \cdot 1.6H_2O$ reacted**

C. As a function of Eh **D. As a function of pH**

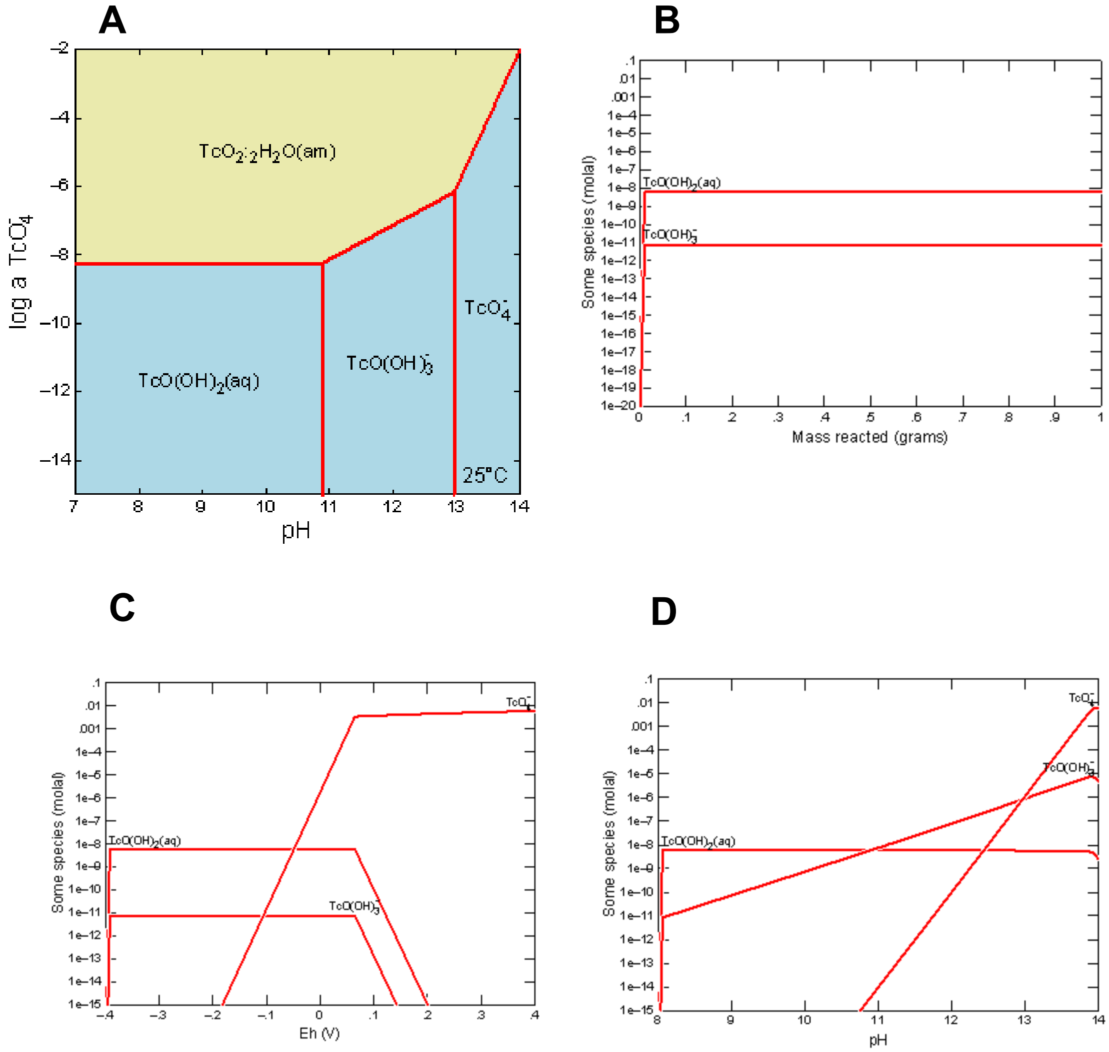

Figure A-3. Speciation and solubility of $TcO_2 \cdot 2H_2O$ in water (Eh = -0.38 V, pH 8.0, our database, all other Tc minerals are suppressed).

A. Phase diagram as a function of pH

B. As a function of $TcO_2 \cdot 2H_2O$ reacted

C. As a function of Eh

D. As a function of pH

Appendix III

Solubility of TcO_2-c, $TcO_2\cdot1.6H_2O$ and $TcO_2\cdot2H_2O$ in reducing saltstone leachates

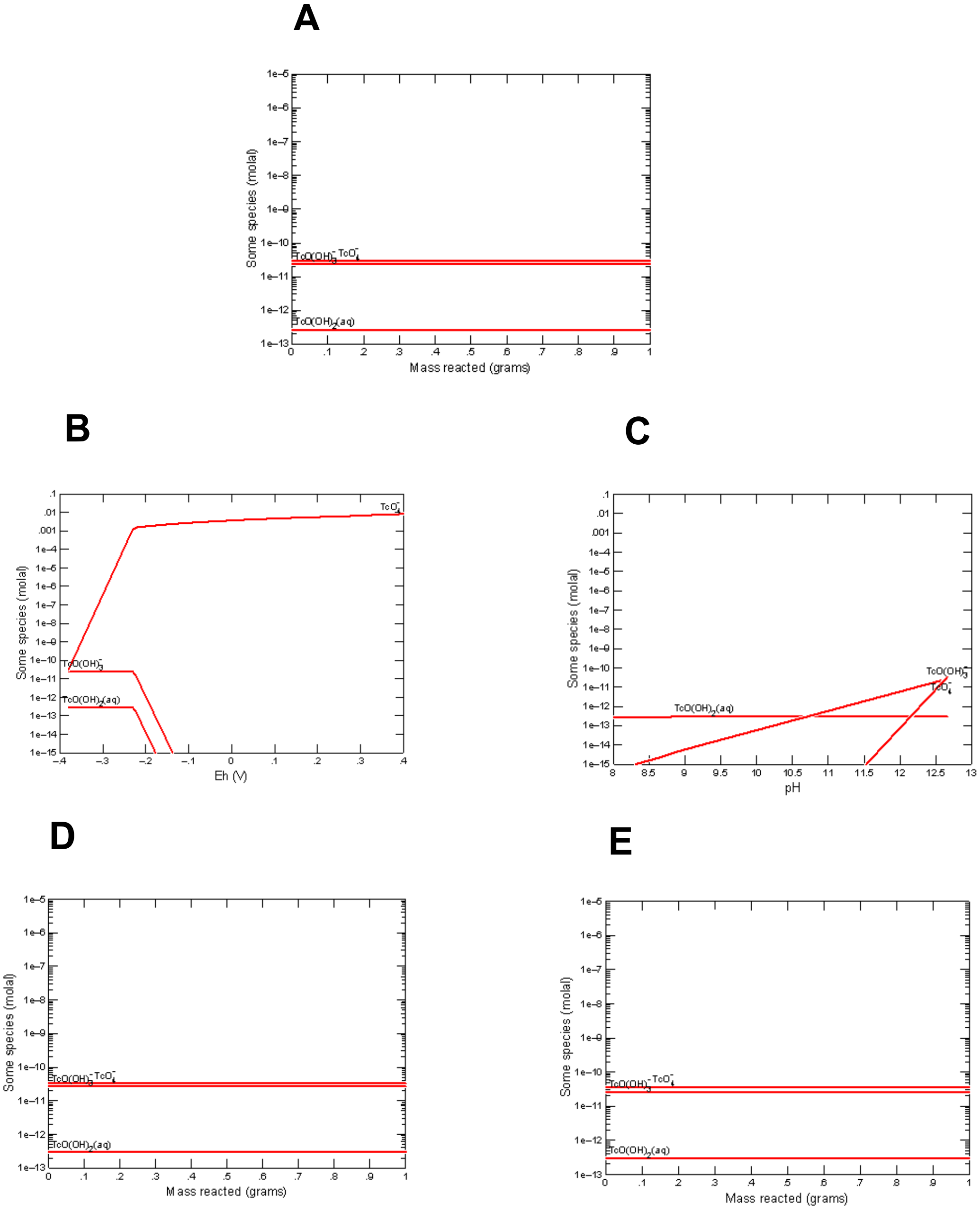

Figure A-4. Speciation and solubility of TcO_2-c in reducing saltstone leachates (Eh = -0.38 V, pH = 12.66, all other Tc minerals are suppressed, charge balance off).

A. As a function of TcO_2-c reacted, the database of this work
B. As a function of Eh, the database of this work
C. As a function of pH, the database of this work
D. As a function of TcO_2-c reacted, the database of Denham and Millings (2012)
E. As a function of TcO_2-c reacted, the database of Wang et al. (2009)

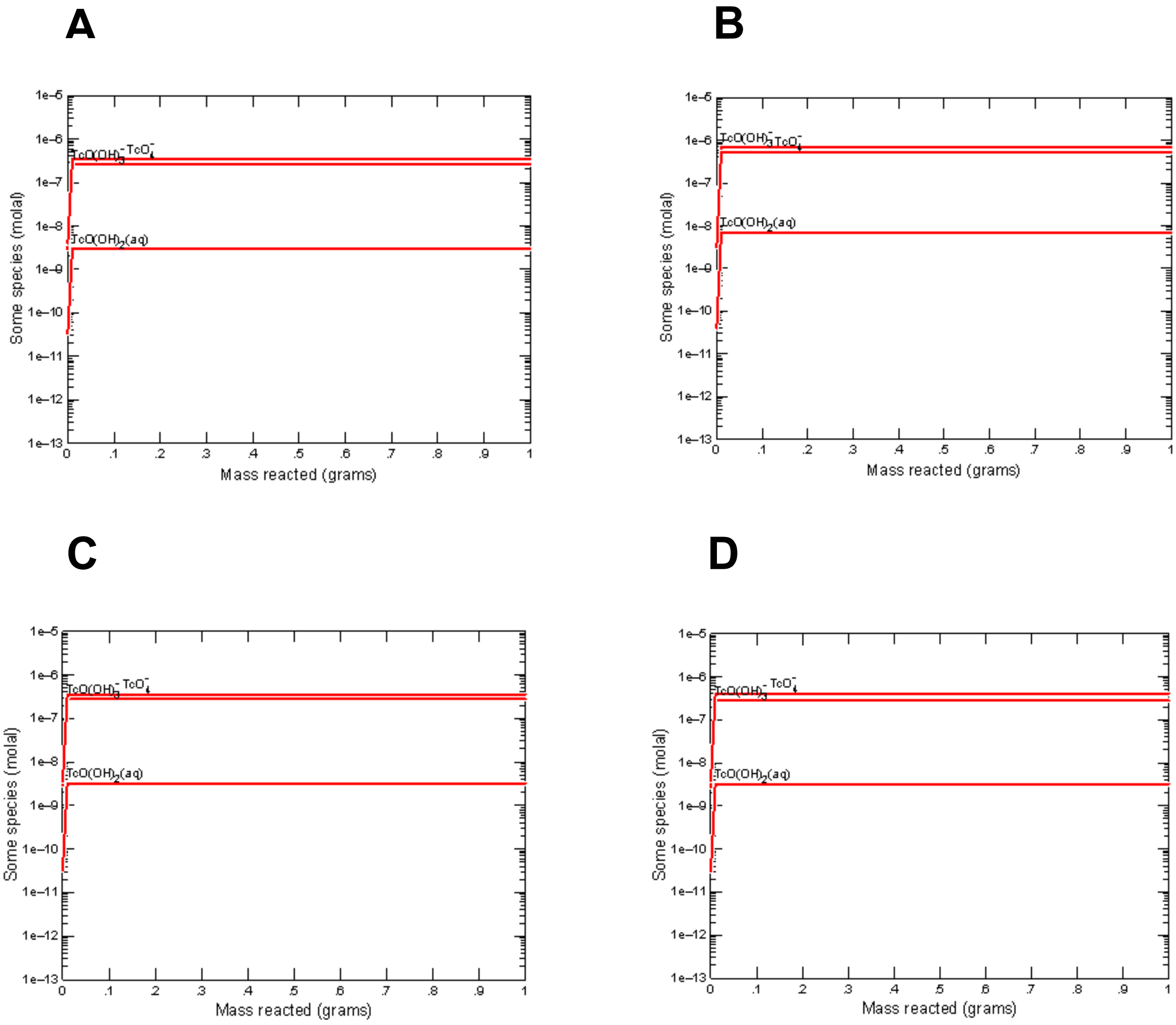

Figure A-5. Speciation and solubility of $TcO_2{\cdot}1.6H_2O$ in reducing saltstone leachates (Eh = -0.38 V, pH = 12.66, all other Tc minerals are suppressed, charge balance off) as a function of $TcO_2{\cdot}1.6H_2O$ reacted.

A. The database of this work
B. The database of Cantrell and Williams (2012)
C. The database of Denham and Millings (2012)
D. The database of Wang et al. (2009)

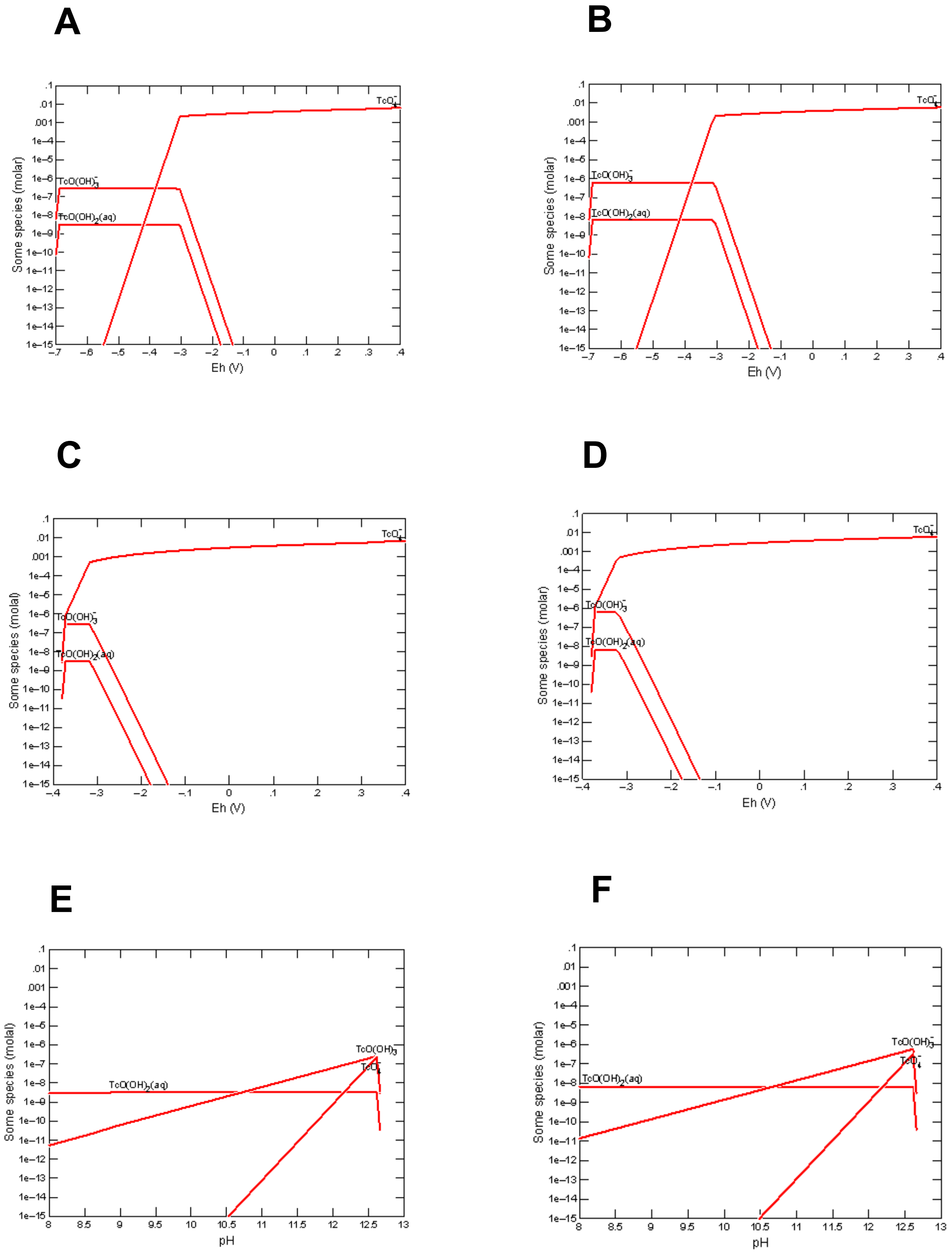

Figure A-6. Speciation and solubility of $TcO_2\cdot 1.6H_2O$ in reducing saltstone leachates (Eh = -0.38 V, pH = 12.66, all other Tc minerals are suppressed, charge balance off) as a function of pH and Eh.

A. As a function of Eh, starting from -0.7 V, the database of this work
B. As a function of Eh, starting from -0.7 V, the database of Cantrell and Williams (2012)
C. As a function of Eh, starting from -0.38 V, the database of this work
D. As a function of Eh, starting from -0.38 V, the database of Cantrell and Williams (2012)
E. As a function of pH, the database of this work
F. As a function of pH, the database of Cantrell and Williams (2012)

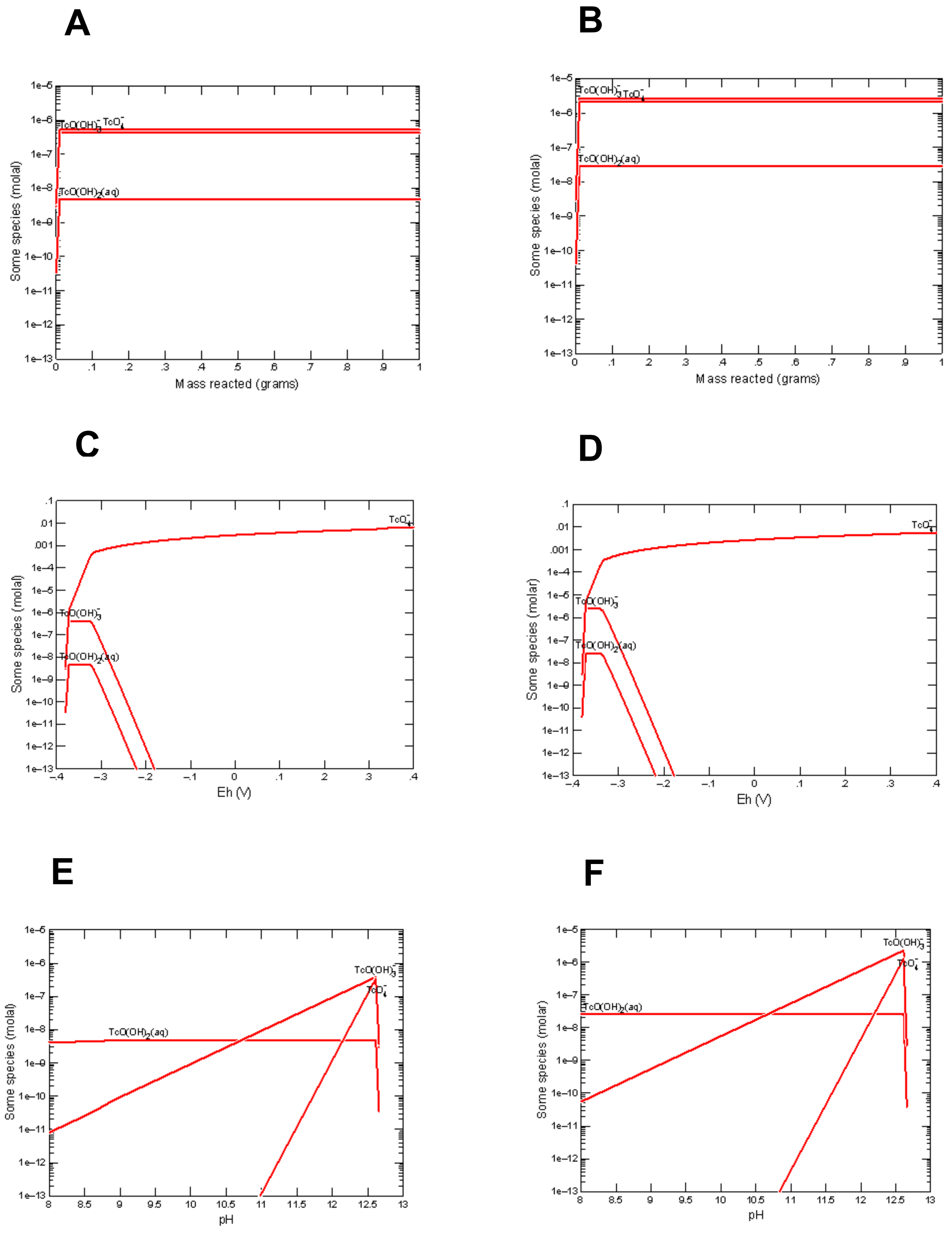

Figure A-7. Speciation and solubility of $TcO_2{\cdot}2H_2O$ in reducing saltstone leachates (Eh = -0.38 V, pH = 12.66, all other Tc minerals are suppressed, charge balance off).

- **A. As a function of $TcO_2{\cdot}2H_2O$ reacted, the database of this work**
- **B. As a function of $TcO_2{\cdot}2H_2O$ reacted, the database of Cantrell and Williams (2012)**
- **C. As a function of Eh, the database of this work**
- **D. As a function of Eh, the database of Cantrell and Williams (2012)**
- **E. As a function of pH, the database of this work**
- **F. As a function of pH, the database of Cantrell and Williams (2012)**

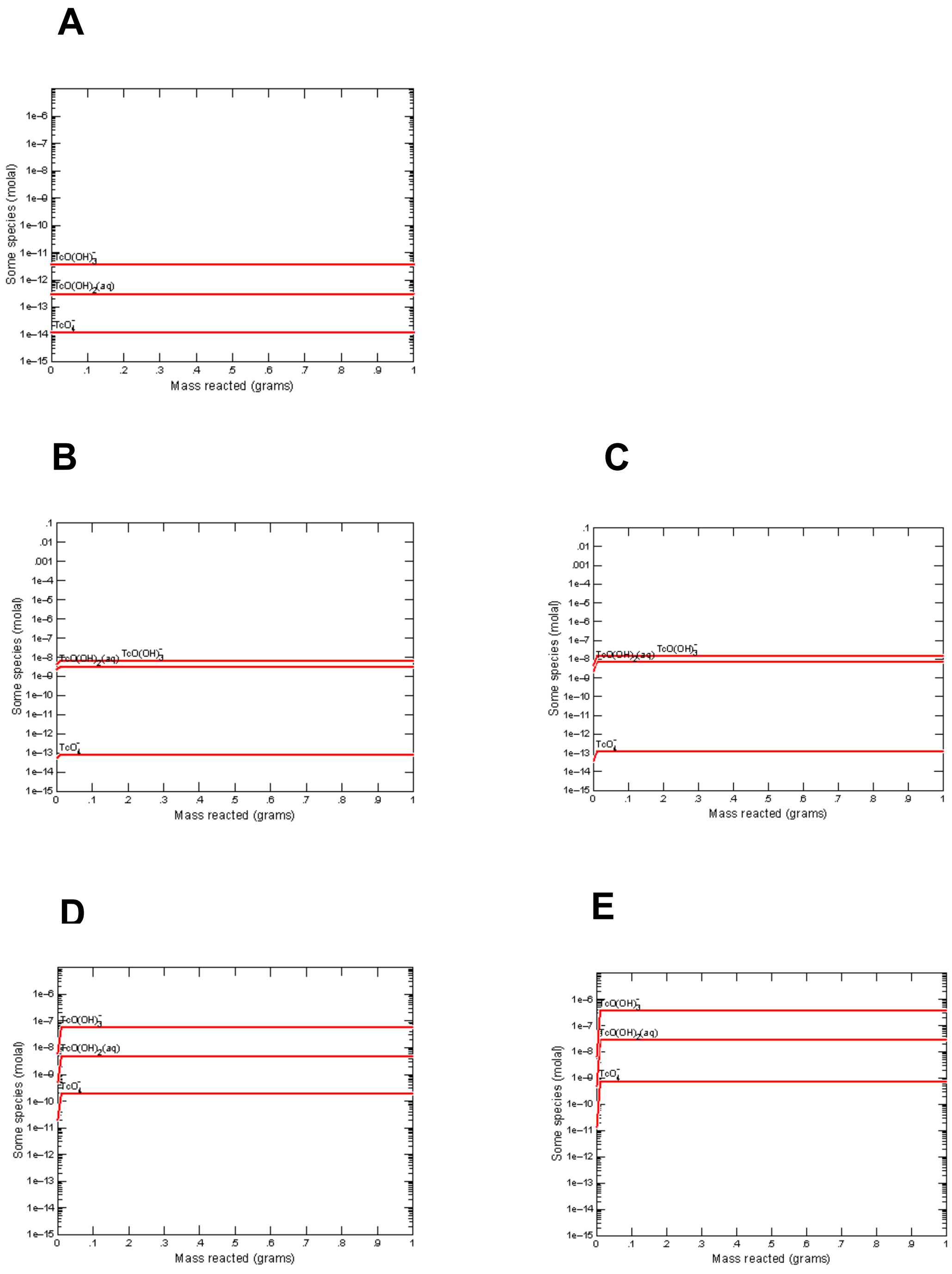

Figure A-8. Speciation and solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$, $TcO_2 \cdot 2H_2O$ in pH 11.8 reducing saltstone leachates (Eh = -0.38 V, all other Tc minerals are suppressed, charge balance off).

A. TcO_2-c, the database of this work
B. $TcO_2 \cdot 1.6H_2O$, the database of this work
C. $TcO_2 \cdot 1.6H_2O$, the database of Cantrell and Williams (2012)
D. $TcO_2 \cdot 2H_2O$, the database of this work
E. $TcO_2 \cdot 2H_2O$, the database of Cantrell and Williams (2012)

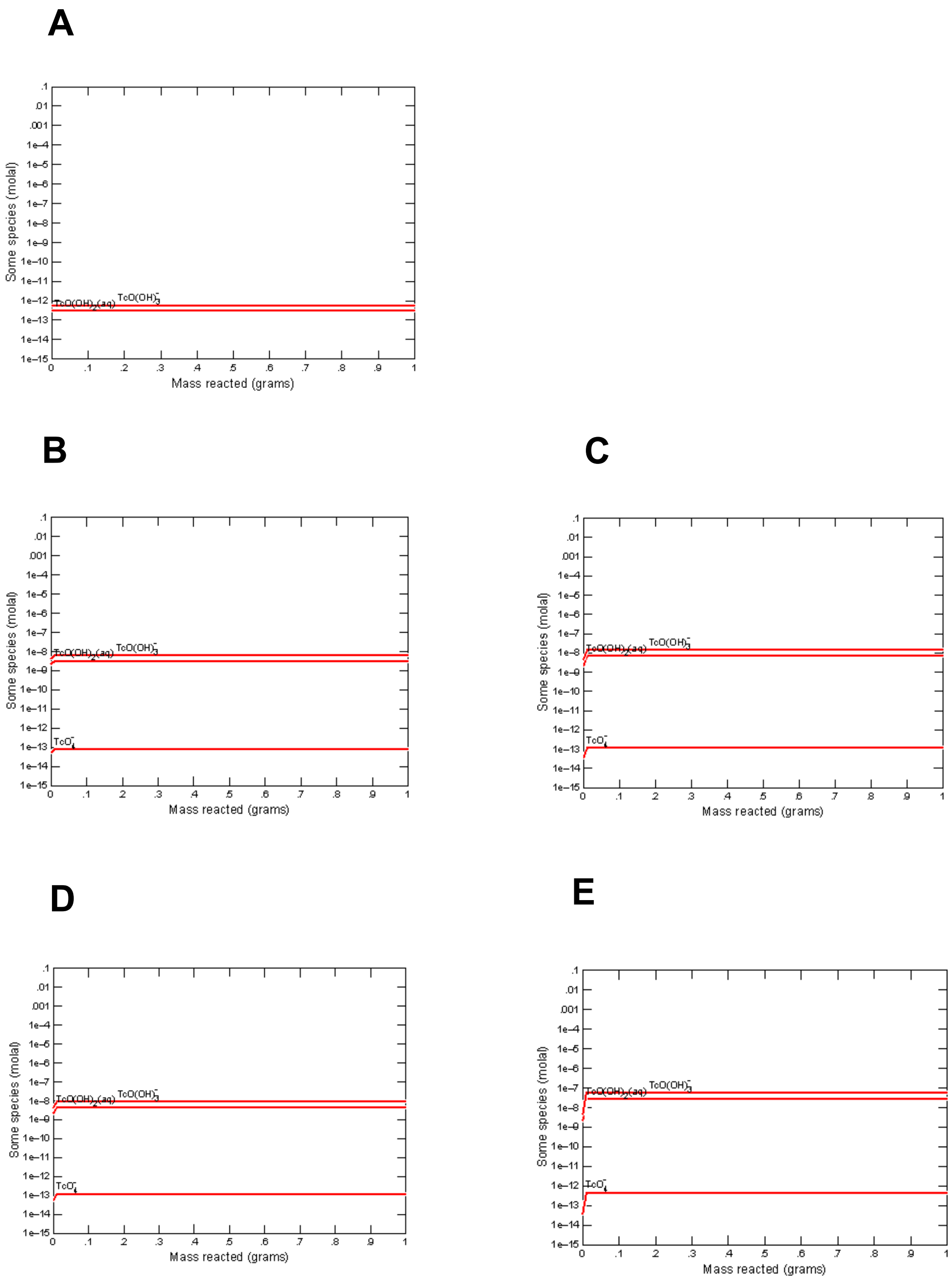

Figure A-9. Speciation and solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$, $TcO_2 \cdot 2H_2O$ in pH 11.0 reducing saltstone leachates (Eh = -0.38 V, all other Tc minerals are suppressed, charge balance off).

A. TcO_2-c, the database of this work
B. $TcO_2 \cdot 1.6H_2O$, the database of this work
C. $TcO_2 \cdot 1.6H_2O$, the database of Cantrell and Williams (2012)
D. $TcO_2 \cdot 2H_2O$, the database of this work
E. $TcO_2 \cdot 2H_2O$, the database of Cantrell and Williams (2012)

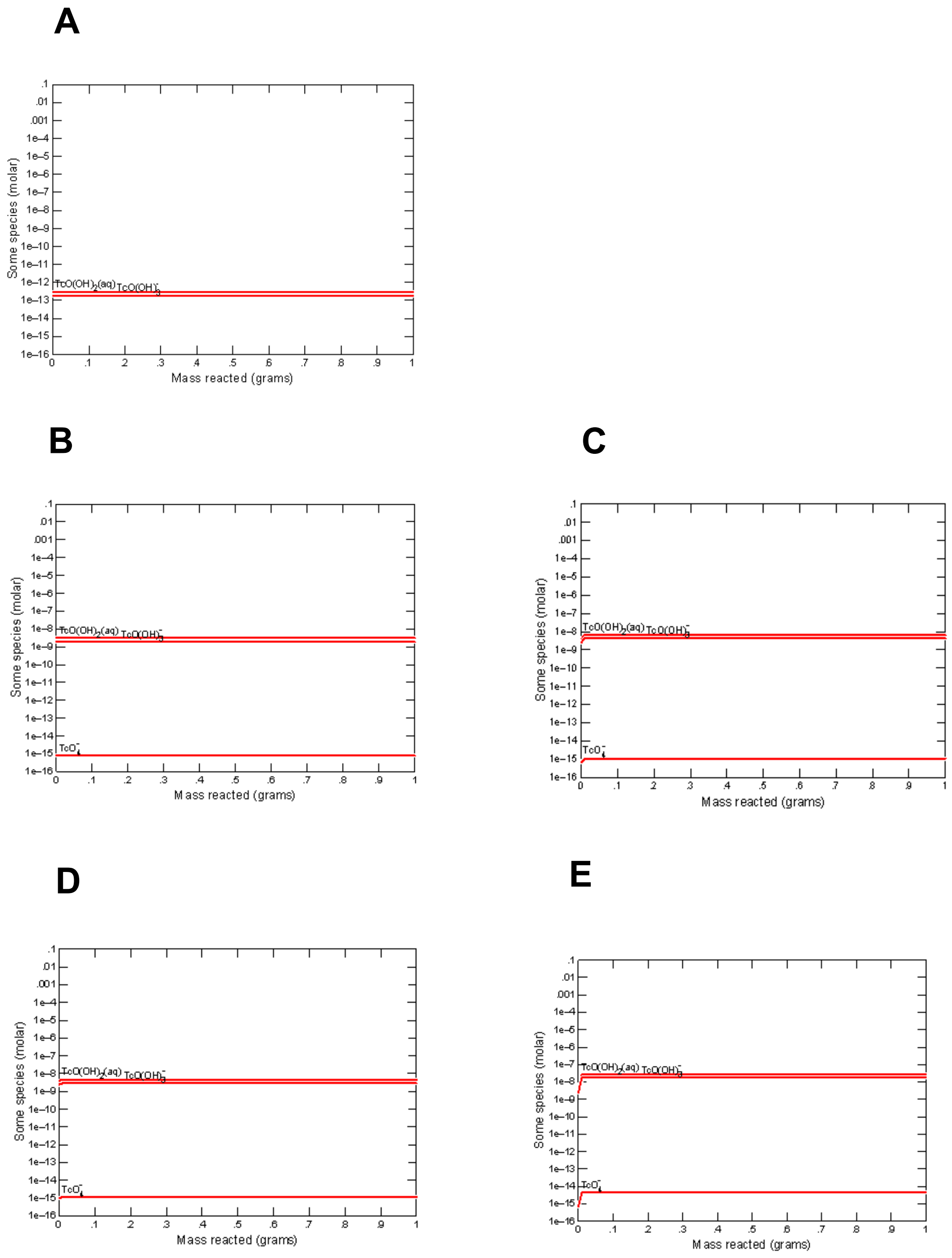

Figure A-10. Speciation and solubility of TcO_2-c, $TcO_2{\cdot}1.6H_2O$, $TcO_2{\cdot}2H_2O$ in pH 10.5 reducing saltstone leachates (Eh = -0.38 V, all other Tc minerals are suppressed, charge balance off).

- **A. TcO_2-c, the database of this work**
- **B. $TcO_2{\cdot}1.6H_2O$, the database of this work**
- **C. $TcO_2{\cdot}1.6H_2O$, the database of Cantrell and Williams (2012)**
- **D. $TcO_2{\cdot}2H_2O$, the database of this work**
- **E. $TcO_2{\cdot}2H_2O$, the database of Cantrell and Williams (2012)**

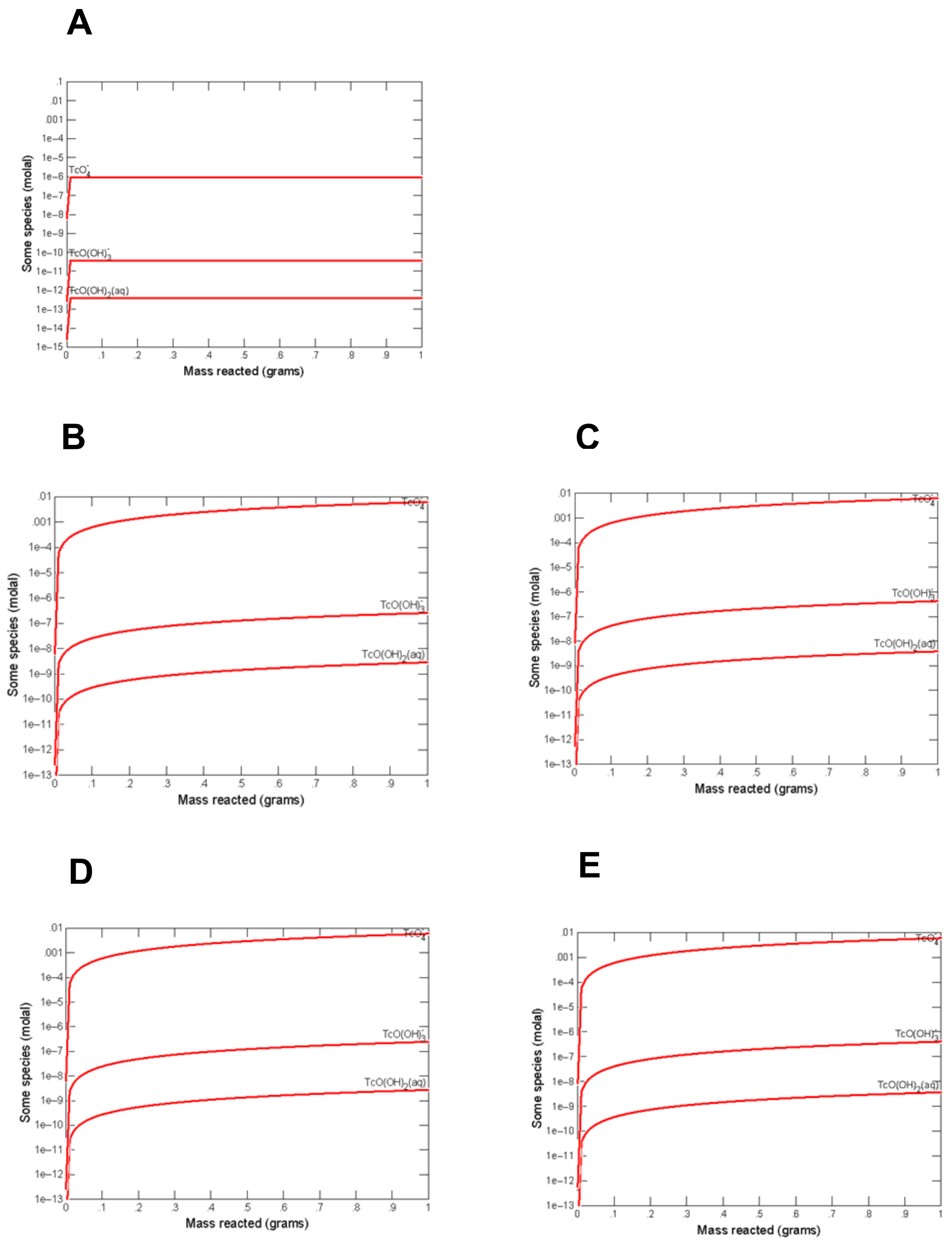

Figure A-11. Speciation and solubility of TcO_2-c, $TcO_2{\cdot}1.6H_2O$, $TcO_2{\cdot}2H_2O$ in less reducing saltstone leachates (Eh = -0.30 V, pH 12.74, all other Tc minerals are suppressed, charge balance off).

A. TcO_2-c, the database of this work
B. $TcO_2{\cdot}1.6H_2O$, the database of this work
C. $TcO_2{\cdot}1.6H_2O$, the database of Cantrell and Williams (2012)
D. $TcO_2{\cdot}2H_2O$, the database of this work
E. $TcO_2{\cdot}2H_2O$, the database of Cantrell and Williams (2012)

Appendix IV

Solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$ and $TcO_2 \cdot 2H_2O$ in Portland cement leachate with the presence of pyrrohtite ($Fe_{1-x}S$ (x = 0-0.2)) as a reducing agent

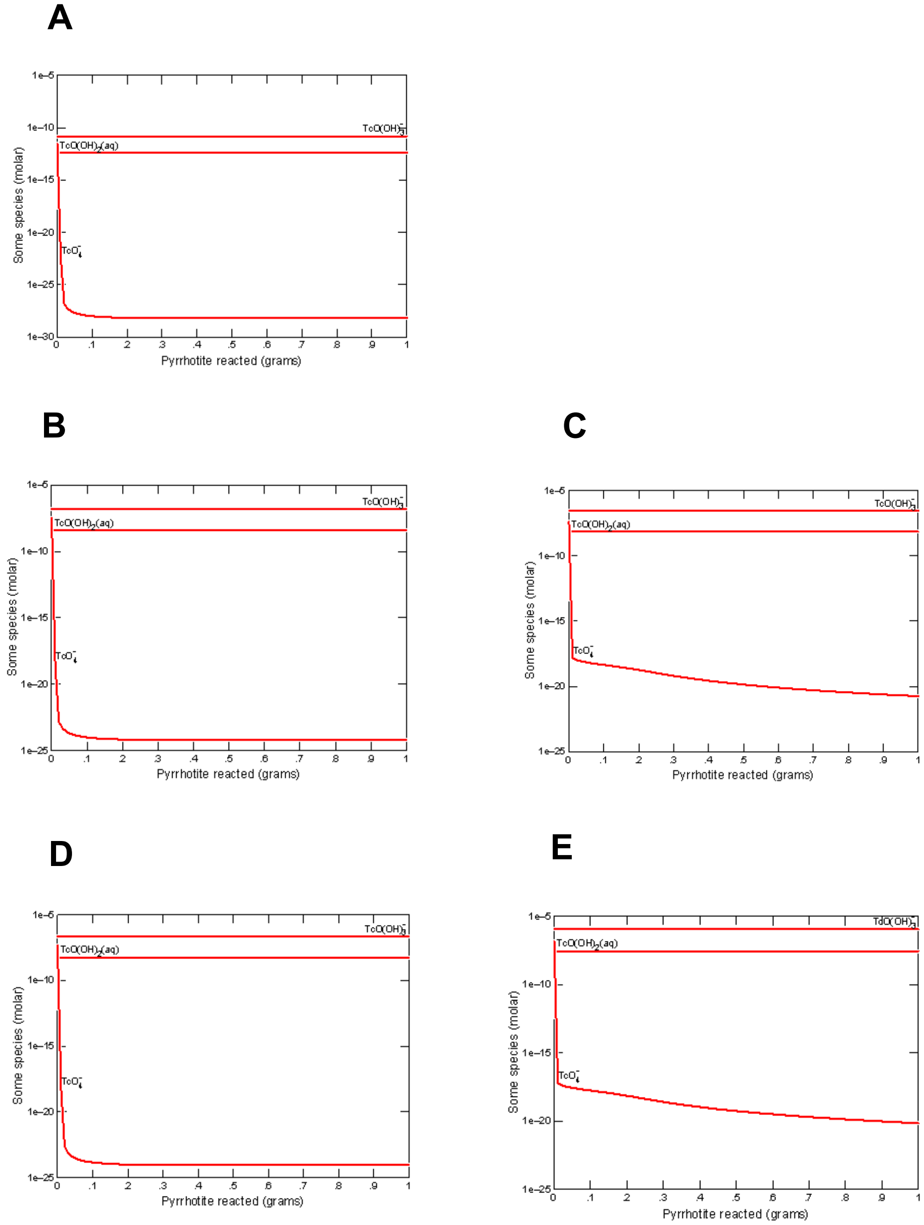

Figure A-12. Speciation and solubility of TcO_2-c, $TcO_2 \cdot 1.6H_2O$, $TcO_2 \cdot 2H_2O$ in Portland cement leachate with the presence of pyrrohtite as a reducing agent (Eh = -0.38 V, pH 12.3, all other Tc minerals are suppressed, charge balance off).

A. TcO_2-c, the database of this work
B. $TcO_2 \cdot 1.6H_2O$, the database of this work
C. $TcO_2 \cdot 1.6H_2O$, the database of Cantrell and Williams (2012)
D. $TcO_2 \cdot 2H_2O$, the database of this work
E. $TcO_2 \cdot 2H_2O$, the database of Cantrell and Williams (2012)

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