Vapor – Aqueous Solution Partition Coefficients for Radionuclides Pertinent to High Level Waste Tank Closure

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Gas-liquid partitioning co-efficients equivalent to apparent inverse Henry's Law constants for several radionuclides pertinent to waste tank closure were estimated using The Geochemist's Workbench® (Bethke, 2005). Henry's Law for solutions is:

$$P_i = m_i H$$

where m_i is the molality (moles/kilogram) of constituent i in the aqueous phase, P_i is the partial pressure (atm) of constituent i in the gas phase, and H is the Henry's Law constant. Both the solution and the gas phase were assumed to behave ideally. Thus, the units of the Henry's Law constant are:

$$\frac{atm. \times kg}{moles}$$

Here, inverse Henry's Law constants with units of $moles/atm \times kg$ are reported so that a large value indicates the constituent partitions strongly into the liquid phase. These are also considered apparent inverse Henry's Law constants because most of these gases dissociate in solution to species other than the aqueous species of the gas. For example, CO_2 gas dissolved in water at a pH of 11 exists primarily as the carbonate ion CO_3^-.

The gases considered for each radionuclide, their reactions with their aqueous component, and the equilibrium constants for these reactions are shown in Table 1.

It is worth examining the stability of CO_2 under the reducing conditions, because if methane (CH_4) were the stable form of carbon, the apparent inverse Henry's Law constant for C-14 would likely be lower. This is because the solubility of methane under all but very acidic conditions is much lower than the solubility of carbon dioxide. Figure 1 shows the Eh-pH diagram for carbon. The compositions of Reducing Region II and Condition C plot just above the equal activity line for reduced and oxidized carbon, but within the oxidized carbon field.

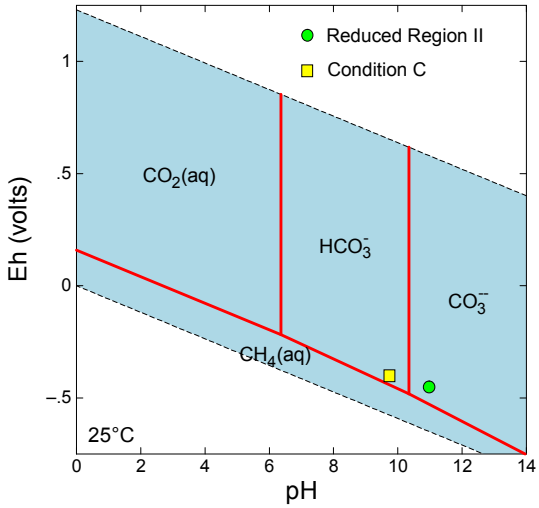

Figure 1: Eh-pH diagram for carbon showing compositions for Reduced Region II and Condition C.

Table 1: Gases considered for each radionuclide, their reaction with their aqueous component, and the equilibrium constants for each reaction used in The Geochemist's Workbench®.

Contaminant	Gas Species	Reaction	Log K (25°C)
C-14	CO_2	$CO_{2(g)} + H_2O = HCO_3^- + H^+$	-7.82
Cl-36	Cl_2	$Cl_{2(g)} + H_2O = 2Cl^- + 2H^+ + ½O_2$	3.03
Cl-36	$HClO_4$	$HClO_{4(g)} = Cl^- + 2O_2 + H^+$	33.38
Cl-36	HCl	$HCl_{(g)} = Cl^- + H^+$	6.31
H-3	H_2O	$H_2O_{(g)} = H_2O_{(l)}$	1.50
I-129	I_2	$I_{2(g)} + H_2O = 2I^- + ½O_2 + 2H^+$	-21.53
I-129	HI	$HI_{(g)} = I^- + H^+$	9.31
Sb-125, 126	$SbCl_3$	$SbCl_{3(g)} + 3H_2O = Sb(OH)_3^o + 3Cl^- + 3H^+$	4.83
Sb-125, 126	$SbCl_5$	$SbCl_{5(g)} + 4H_2O = Sb(OH)_3^o + 5Cl^- + ½O_2 + 5H^+$	2.74
Sb-125, 126	SbH_3	$SbH_{3(g)} + 3/2O_2 = Sb(OH)_3^o$	143.11
Se-79	H_2Se	$H_2Se_{(g)} + 3/2O_2 = SeO_3^{-2} + 2H^+$	71.83
Se-79	$SeCl_4$	$SeCl_{4(g)} + 3H_2O = SeO_3^{-2} + 4Cl^- + 6H^+$	13.78
Sn-121m, 126	$SnCl_4$	$SnCl_{4(g)} = Sn^{+4} + 4Cl^-$	15.85
Sn-121m, 126	SnH_4	$SnH_{4(g)} + 4H^+ = 4H_2 + Sn^{+4}$	20.10

The assumptions used in the calculations are based on calculated pore fluids for different waste tank scenarios and degradation states of the reducing grout. A description of these is available in Denham (2010). A summary table of the pore fluid compositions is shown in Table 2.

Table 2: Pore water compositions under different tank scenarios and reduced grout degradation states (Denham, 2010).

	pH	Eh (V)	Ca^{+2} (M)	Na^+ (M)	Cl^- (M)	HCO_3^- (M)	SO_4^{-2} (M)
Reduced Region II	11.12	-0.48	3.3E-3	4.3E-4	4.3E-4	3.5E-8	1.0E-5
Oxidized Region II	11.13	0.58	3.2E-3	4.3E-4	4.3E-4	3.5E-8	1.0E-5
Oxidized Region III	8.23	0.73	4.6E-4	4.3E-4	4.3E-4	1.7E-6	1.0E-5
Condition A	5.4	0.37	6.2E-5	4.4E-5	8.5E-5	9.8E-5	6.3E-6
Condition B	9.3	0.27	2.0E-4	4.3E-5	1.5E-4	2.4E-4	6.2E-6
Condition C	9.8	-0.38	2.1E-4	4.0E-5	2.7E-4	4.2E-5	4.2E-5
Condition E	9.8	0.62	2.1E-4	4.1E-5	2.6E-4	4.2E-5	6.5E-6

The calculations of gas-liquid partition coefficients were done using The Geochemist's Workbench® (Bethke, 2005) to obtain molalities of each dissolved radionuclide and fugacities of each radionuclide gas in pore water compositions of Table 2. The assumption of ideal behavior for the gas renders the fugacity equal to the partial pressure of the gas. The initial molality of each radionuclide was set to 1×10^{-8} and the program then calculated the equilibrium molalities and fugacities. In most cases the fugacity of one gas for each element was higher by several

orders of magnitude than the fugacity of the other gases. The highest fugacity was chosen for the estimate of the apparent inverse Henry's Law constant for a radionuclide.

Table 3 shows the estimated apparent inverse Henry's Law constants for partitioning the radionuclides of interest between pore water and the gas phase. Most of the apparent inverse Henry's Law constants are so high as to be essentially meaningless – all of the radionuclide can be assumed to be in the aqueous phase. The exceptions are tritium, C-14, and Se-79 under reducing conditions.

Table 3: Estimations of apparent inverse Henry's Law Constants ($moles/atm \times kg$) for the radionuclides of interest in the different pore water compositions shown in Table 2; the dominant gas for each is shown in parentheses.

	C-14	Cl-36	I-129	Sb-125	Se-79	Sn-126	H-3	Tc-99
Red. Region II	8E+4 (CO_2)	3E17 (HCl)	3.6E20 (HI)	1.8E35 (SbH_3)	1.8E6 (H_2Se)	1.3E61 (Sn)	2.1E3 (H_2O)	4.8E67 (Tc_2O_7)
Oxi. Region II	8.1E4 (CO_2)	3.2E17 (HCl)	1.1E33 (HI)	8.7E70 ($SbCl_3$)	2.5E101 (H_2Se)	1.8E71 ($SnCl_4$)	2.1E3 (H_2O)	5.7E51 (Tc_2O_7)
Oxi. Region III	2.8E0 (CO_2)	3.6E14 (HCl)	1.3E29 (I_2)	4.9E38 ($SbCl_3$)	3.8E87 ($SeCl_4$)	6.1E61 ($SnCl_4$)	2.1E3 (H_2O)	7.2E45 (Tc_2O_7
Condition A	3.8E-2 (CO_2)	5.2E11 (HCl)	6.3E14 (HI)	6.9E32 ($SbCl_3$)	2.8E25 (H_2Se)	9.6E53 ($SnCl_4$)	2.1E3 (H_2O)	1.5E40 (Tc_2O_7)
Condition B	3.6E1 (CO_2)	4.1E15 (HCl)	5.1E18 (HI)	4.3E44 ($SbCl_3$))	2.4E44 (H_2Se)	5.1E69 ($SnCl_4$)	2.1E3 (H_2O)	9.6E47 (Tc_2O_7
Condition C	1.6E2 (CO_2)	1.4E16 (HCl)	1.7E19 (HI)	3.5E34 ($SbCl_3$)	8.5E4 (H_2Se)	4.7E60 (Sn)	2.1E3 (H_2O)	2.1E68 (Tc_2O_7)
Condition D	1.6E2 (CO_2)	1.4E16 (HCl)	7.0E29 (I_2)	9.9E44 ($SbCl_3$)	1.6E96 (H_2Se)	4.8E98 ($SnCl_4$)	2.1E3 (H_2O)	!.2E49 (Tc_2O_7)

References

Bethke, C.M., 2005, The Geochemist's Workbench® (geochemical modeling software), Release 6.0, University of Illinois.

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