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Activity Estimates of Various Radionuclides in Saltstone Vapor Phase

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Activity Estimates of Various Radionuclides in Saltstone Vapor Phase

We were asked to estimate activities of various radionuclides in vapor phase associated with saltstone. Table 1 lists these radionuclides, as well as the estimated activity and concentration of each in the gas phase. Some of the activities are so low they should be considered zero. In particular, activity of the antimony and tin isotopes in the gas phase correspond to less than a molecule of gas per 340 m^3 of vapor volume. Equilibrium calculations of the partitioning of each radionuclide between vapor and dissolved phases were done using The Geochemist's Workbench® (release 4.0).

Table 1: List of radionuclides, their calculated ratios of moles in gas to moles in aqueous phase, calculated activities and concentrations in gas phase.

Constituent	**Gas/Aqueous Ratio**[1]	**Activity in Gas Phase (Ci)**	**Concentration in Gas Phase (Ci/Liter)**
C-14	3.4E-6	3.4E-6	1.0E-11
Cl-36	6.2E-18	6.2E-8	1.8E-23
H-3	2.5E-6	2.5E-6	7.4E-12
I-129	5.9E-16	5.9E-16	1.74e-21
Sb-125	8.4E-43	8.4E-43	2.5E-48
Sb-126	8.4E-43	8.4E-43	2.5E-48
Se-76	2.2E-8	2.2E-8	6.5E-14
Sn-121m	1.7E-64	1.7E-64	5.0E-70
Sn-126	1.7E-64	1.7E-64	5.0E-70

The conceptual model used was that 1 curie of each constituent was available to partition between vapor and dissolved phases. The overall assumption is that exposure would come from a single release of the vapor phase from a saltstone vault. Assumed conditions within the saltstone are listed in Table 2.

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[1] See memorandum text for explanation

Table 2: Assumed properties of saltstone vaults.

Property	Assumed value	Value used
Vault dimensions (meters)		
Length	180	180
Width	60	60
Depth	7.5	7.5
Total vault volume (m^3)	81000	81000
Saltstone porosity (fraction)	0.42	0.42
Residual moisture (fraction)	0.99	0.99
pH	12	10
Eh (volts)	-0.2 to - 0.4	-0.2 to -0.4
Na+ (moles/liter)	6	0.01
NO_3- (moles/liter)	6	0.01

In the model used to simulate partitioning, a lower pH and lower ionic strength were used. A pH of 10 is a more conservative case than a pH of 12 because most of the gases are less stable at high pH. The lower ionic strength was used to assure reliability of the calculations. Ion association models such as those used in these calculations are unreliable at ionic strengths exceeding about 0.5 molal. Models are available for higher ionic strengths, but no parameters exist for I, Sb, Se, or Sn. Thus, a lower ionic strength was used. The implications of this are discussed in the Uncertainty section below.

Figure 1 shows a generalized flow diagram of steps used in the simulations. For a given constituent, these begin with choosing the gases to consider. The criteria for these choices were sufficiently high vapor pressures at 25°C and availability of thermodynamic data. It was assumed that absence of thermodynamic data is an indication that a gas is not common enough to warrant consideration. Thermodynamic data for most of the gases selected for consideration were then entered into the database to be used by The Geochemist's Workbench®. Reactions for the gases and their equilibrium constants are shown in Table 3. In 11 of 14 reactions acid is produced by degradation of the gas of interest, suggesting that most of the gas species are favored at lower pH. Similar analyses were done to identify "worst case" scenarios for the master variables temperature, pH,

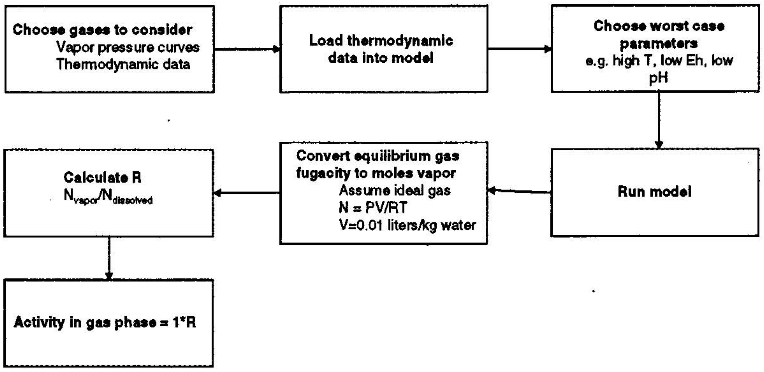

Figure 1: Flow diagram for gas/water partitioning calculations.

and Eh by generating curves of gas fugacity versus the variable. An example is shown in Figure 2. The simulation was then run using parameters discussed below. From the model output (see Appendix 1 for an example), the moles of contaminant in the gas phase (assuming an ideal gas) and in the dissolved phase were calculated. It is assumed that there is 1 curie of each radionuclide in the total pore space of a vault. Thus, the ratio of activity in the gas phase to activity in the aqueous phase was multiplied by 1 curie to give the activities in the gas phase. These represent the activities in 340 m^3 of vapor volume per vault.

Table 3: Contaminant gas species and reactions considered.

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	$Cl_{2(g)} + H_2O = 2Cl^- + 2H^+ + \frac{1}{2}O_2$	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	$I_{2(g)} + H_2O = 2I^- + \frac{1}{2}O_2 + 2H^+$	-21.53
I-129	HI	$HI_{(g)} = I^- + H^+$	9.31
Sb-125, 126	$SbCl_3$	$SbCl_{3(g)} + 3H_2O = Sb(OH)_3^{\circ} + 3Cl^- + 3H^+$	4.83
Sb-125, 126	$SbCl_5$	$SbCl_{5(g)} + 4H_2O = Sb(OH)_3^{\circ} + 5Cl^- + \frac{1}{2}O_2 + 5H^+$	2.74
Sb-125, 126	SbH_3	$SbH_{3(g)} + 3/2O_2 = Sb(OH)_3^{\circ}$	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

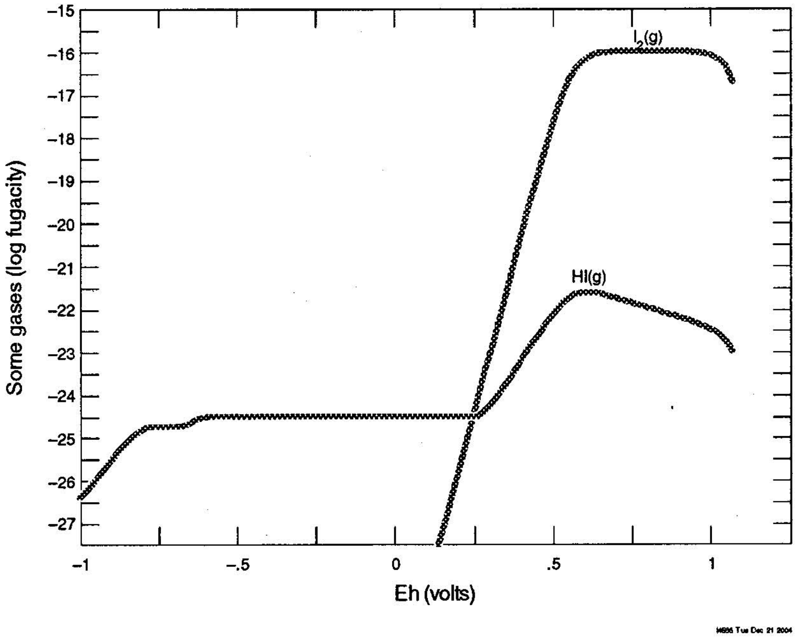

Figure 2: Curves used to indicate worst case Eh for modeling iodine gas generation.

The initial conditions for the simulations varied somewhat for different contaminants. For all contaminants it was assumed they were in a 0.01 mole/kg solution of sodium nitrate. Table 4 shows concentrations of constituents of interest used for the models. The concentrations of tin, antimony, and selenium were set to 10 ug/kg$_{H2O}$. These are much higher mass concentrations than calculated from 1 Ci dissolved in a vault's pore fluid. This accounts for the stable isotopes of these elements that might be in the saltstone pore water. For I-129, a concentration of 1000 ug/kg$_{H2O}$ was used to account for stable I-127 in the system. Bicarbonate and chloride for the C-14 and Cl-36 simulations were set at 100 mg/kg$_{H2O}$. For the C-14 simulation the system was assumed to be closed to carbon dioxide. This is a worst case scenario because a system open to atmosphere would have very high concentrations of dissolved carbon dioxide at a pH of 10. This would drive the ratio of C-14 in gas to C-14 in water to much lower values. For the tin and antimony simulations, a chloride concentration of 100 mg/kg$_{H2O}$ was used to provide the chloride necessary for generation of tin and antimony chloride gases.

With the exception of the Se-79 simulation, systems were considered open to nitrogen gas at a fugacity of 0.7 (near atmospheric) and redox potentials were controlled by the N_2/NO_3- couple. This is reasonable considering the high nitrate concentration in saltstone. However, it does result in a final redox potential that is higher than the Eh range expected for saltstone, 0.37 volts rather than -0.3 volts. This does not significantly affect any conclusions that may be drawn from this memorandum. In fact, it is conservative for Cl-36, I-129, and the tin isotopes. For selenium, H_2Se is the dominant gas, and thus, to simulate a worst case, redox potential was held constant at -0.4 volts and the system was closed with respect to N_2 gas.

The calculated ratios of moles of contaminant in the gas phase to moles of contaminant in the aqueous phase are shown in Table 1. The ratios were converted to activities by assuming that a total of 1 curie of each radionuclide was in the pore space of a saltstone vault. Concentrations were calculated using the volumes of vapor and water in the pore space, estimated from the dimensions of a vault, the porosity, and the residual moisture content.

Table 4: Concentrations of constituents used in simulations.

Constituent	**Concentration (moles/kg $_{H2O}$)**	**Comments**
C-14	1.6E-3	[HCO_3-] = 100 mg/kg $_{H2O}$
Cl-36	2.8E-3	
H-3	-	
I-129	7.9E-6	
Sb-125, Sb-126	8.2E-8	[Cl-] = 2.8E-3 moles/kg$_{H2O}$
Se-79	1.3E-7	Constant redox Eh = -0.4 volts
Sn-121m, Sn-126	8.4E-8	[Cl-] = 2.8E-3 moles/kg$_{H2O}$

Uncertainty

The primary uncertainty in these calculations is the use of lower ionic strengths in the modeling than those estimated for the saltstone pore fluids. This could lead to underestimation of the amount of a radionuclide in the gas phase for all constituents except tritium. For tritium, higher ionic strength lowers the vapor pressure of water at a given temperature, thus lowering the amount of tritium in the vapor phase. For other constituents, the high ionic strengths will likely result in higher activity coefficients than those at lower ionic strengths. As the activity coefficients increase the ratio of contaminant in the gas phase to contaminant in the aqueous phase will increase. This is illustrated by the reaction for $HI_{(g)}$,

$$HI_{(g)} = H^+ + I^-$$

$$K = \frac{a_{H+} \times \gamma_{I-} \times m_{I-}}{f_{HI}}$$

where K is the equilibrium constant, a_{H+} is the activity of hydrogen ion, γ_{I-} is the activity coefficient for the iodide ion, m_{I-} is the molality of the iodide ion, and f_{HI} is the fugacity of $HI_{(g)}$. If an ideal gas is assumed and the partial pressure is converted to moles/kilogram of gas (m_{HI}), the of m_{I-} to m_{HI} is the ratio of contaminant in the aqueous phase to that in the gas phase. The a_{H+} is defined by the pH selected for the simulation. Thus,

$$\frac{K}{a_{H+}} = \frac{\gamma_{I-}}{R}$$

where R is the ratio of contaminant in the gas phase to contaminant in the aqueous phase as reported in Table 4. Hence, as the activity coefficient of iodide increases R must increase as well to maintain a constant value on the left side of the equation. However, it is unlikely that the activity coefficients will increase by any more than a factor of 10. Such an increase would not significantly affect any conclusions based on this analysis. Furthermore, an increase in ionic strength would decrease the activity of water which will reduce the effect of increasing activity coefficients.

Uncertainty associated with the estimates in this memorandum could be minimized by performing sensitivity analyses of the results to variations in the major parameters.

Appendix 1

```
     Step #     0              Xi = 0.0000
          Temperature =  95.0 C     Pressure =  1.013 bars
          pH = 10.000               log fO2 =   -6.716
          Eh =   0.3659 volts       pe =   5.0098
          Ionic strength       =    0.018842
          Activity of water    =    0.999901
          Solvent mass         =    1.000000 kg
          Solution mass        =    1.001133 kg
          Solution density     =    0.959    g/cm3
          Chlorinity           =    0.002821 molal
          Dissolved solids     =       1132 mg/kg sol'n
          Rock mass            =    0.000000 kg

   No minerals in system.

   Aqueous species       molality    mg/kg sol'n    act. coef.    log
 act.
 ---------------------------------------------------------------------
-----
    Na+                   0.009974         229.0        0.8556     -2.0689
    NO3-                  0.009304         576.3        0.8500     -2.1019
    OH-                   0.005649         95.97        0.8529     -2.3171
    Cl-                   0.002808         99.44        0.8500     -2.6222
    Ca++                  0.002376         95.14        0.5577     -2.8777
    CaOH+                0.0004322         24.64        0.8556     -3.4321
    N2(aq)               0.0003478         9.732        1.0000     -3.4587
    NaOH                 2.382e-005       0.9516        1.0000     -4.6231
    CaCl+                1.080e-005       0.8149        0.8556     -5.0343
    NaCl                 1.931e-006       0.1127        1.0000     -5.7142
    Sb(OH)3(aq)          6.096e-008      0.01052        1.0000     -7.2150
    Sb(OH)4-             2.104e-008     0.003989        0.8556     -7.7446
     (only species > 1e-8 molal listed)

   Mineral saturation states
                      log Q/K                           log Q/K
 ------------------------------------------------------------
    Portlandite        -1.2326       Ca(OH)2(c)        -1.2326
     (only minerals with log Q/K > -3 listed)

   Gases                  fugacity     log fug.
 ----------------------------------------------
    Steam                   0.8309       -0.080
    N2(g)                   0.7000       -0.155
    O2(g)                1.921e-007      -6.716
    NO2(g)               1.213e-015     -14.916
    HCl(g)               5.275e-017     -16.278
    N2O(g)               7.002e-020     -19.155
    H2(g)                2.043e-029     -28.690
    Cl2(g)               6.100e-032     -31.215
    SbCl3(g)             2.085e-046     -45.681
    NH3(g)               1.587e-057     -56.799
    HClO4(g)             1.754e-060     -59.756
    SbCl5(g)             4.622e-075     -74.335
    SbH3(g)              1.469e-105    -104.833
```

```
                                    In fluid
 Original basis  total moles     moles       mg/kg
-----------------------------------------------------------------------
---------
   Ca++              0.002819     0.002819       112.9
   Cl-               0.002821     0.002821       99.89
   H+               -0.005410    -0.005410      -5.446
   H2O                  55.51        55.51  9.990e+005
   NO3-               0.01000      0.01000       619.3
   Na+                0.01000      0.01000       229.6
   O2(aq)          -0.0008695   -0.0008695      -27.79
   Sb(OH)3(aq)     8.200e-008   8.200e-008     0.01415

Elemental composition                     In fluid
                  total moles       moles       mg/kg
-----------------------------------------------------------------------
--------
   Antimony        8.200e-008   8.200e-008    0.009972
   Calcium           0.002819     0.002819       112.9
   Chlorine          0.002821     0.002821       99.89
   Hydrogen             111.0        111.0  1.118e+005
   Nitrogen           0.01000      0.01000       139.9
   Oxygen               55.54        55.54  8.876e+005
   Sodium             0.01000      0.01000       229.6
```

Appendix 2
Design Check Instructions to Kim Crapse

Specific instructions for this design check are as follows:

1) Check general technical approach.

2) Check calculations in the supporting spreadsheet.

3) Compare output generated for report using The Geochemist's Workbench to output generated using United States Geological Survey code PHREEQC.

Design Check by Kim Crapse

1) Check general technical approach.

The overall general approach is judged to be appropriate based on current assumptions regarding saltstone conditions and inventory. Uncertainties in the partitioning model are addressed and select sensitivity studies are described for several key parameters.

2) Check calculations in the supporting spreadsheet.

Checked calculations of fugacity to moles of gas in the vapor phase, R, and activities in the vapor and aqueous phases

3) Compare output generated for report using The Geochemist's Workbench to output generated using United States Geological Survey code PHREEQC.

Agreement between the output for the model output generated using The Geochemist's Workbench and PHREEQC provide a further validation of the approach.