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MEMORANDUM FOR: Timothy C. Johnson, Section Leader
Engineering Branch
Division of Waste Management

FROM: C. H. Peterson
Engineering Branch
Division of Waste Management

SUBJECT: THERMODYNAMIC RELATIONS IN THE MAGNETITE-HEMATITE-WATER
SYSTEM

Introduction

The DOE SCR for BWIP, November 1982¹, included a Section 11.4.1.4 on Eh and pH stating:

1. Eh and pH...control the stability and solubility of solid species and the form taken by aqueous species in solution.
2. Eh must be inferred from a pH-dependent model.
3. pH depends on temperature, water composition and water-to-solid ratio. Increased temperature and water-to-solid ratios decrease pH.

Equations were introduced for 1) pH as a function of temperature, 2) fugacity of oxygen as a function of temperature for each of two mineral buffers, and 3) Eh as a function of pH and oxygen fugacity. The latter is of the form:

$$Eh = A_0 + A_1 T \log f_{O_2} + A_2 TpH + A_3 (T-298).$$

Because of proposed applications of this equation, it is extremely important that the theoretical basis for this equation be firmly established and any assumptions or limitations be clearly identified. Our present understanding of the derivation of this equation is in Enclosure 1.

Discussion

Assuming we have reproduced the logic of the derivation, we note some serious deficiencies. First, and perhaps most important, while one can choose to isolate for examination a particular buffer system, we believe it is (a) incorrect to consider half of an electrochemical cell reaction in the analysis and (b) incomplete to limit the analysis to a single pair of reactions.

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Second, the pH equation in the SCR does not correspond to the graph representing it, and the graph is also plotted incorrectly. Third, the source of the oxygen taken up by the hematite was indicated as due to the electrochemical oxidation of water. We think that diffusion of air to the waste package and radiolysis of water are more likely sources before closure, and that after closure dissolved oxygen in the groundwater would be the major source. Fourth, the cell potential was evaluated without including the free energy change for the oxidation of magnetite. Fifth, the discussion in the SCR focussed on the effects of water. The oxidation of ferrous iron should therefore have been evaluated in the liquid phase. When this is done, one finds the free energy change shifts from -24251 calories/g-mole to +17762 (see Enclosure 2). This oxidation therefore does not proceed spontaneously in the liquid phase, illustrating how the choice of reactions can radically affect the conclusions. Sixth, the only reason why the calculated Ehs are of the order of -0.5 V is the extrapolation of the magnetite-hematite equilibrium calculation to vanishingly low concentrations of oxygen. No substantiation of the validity of this extrapolation was offered in the SCR. Seventh, the overall logic of equations 8 and 9, Enclosure 1, is incomplete if not faulty. The magnetite is introduced to pick up any oxygen molecules reaching the vicinity of the canister. Then a reaction is proposed to produce oxygen molecules, which, however, will not proceed as written spontaneously so it must be driven by some other reaction, which was not specified. This other reaction must involve a strong electron acceptor, something like chlorine or fluorine or the permanganate ion. If the reaction does proceed, it will lower the pH.

A revised derivation is given in Enclosure 2 to illustrate the effect of considering 1) other possible reactions and 2) a complete system. The overall conclusion is the same: 1) elemental iron placed in contact with water and oxygen spontaneously corrodes and 2) the derived equation does not account for some negative values reported for field measurements of Eh.

The situation actually is far more complex than either the SCR or the calculations given in the attached Enclosures indicate. While the overall oxidation of elemental iron (from the canister) to ferrous iron is accompanied by a large molar free energy change, the oxidation may proceed through many species of intermediate iron oxides, iron hydroxides, and hydrated oxides. There may also be iron silicates. Under certain conditions, protective layers may form. On the other hand, only exposed magnetite can serve as an oxygen sink and over geologic time all such magnetite has probably already been oxidized through contact with ground water and its dissolved oxygen.

Further, a review of over 100,000 analyses of ground waters by Lindberg and Runnels² which yielded 681 useful sets of Eh-pH data showed no correlation of

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Eh with molality of iron or manganese, or with saturation indices. Other conclusions were:

1. Observed Eh values measured in the field with a platinum electrode do not consistently correspond to the theoretical Eh computed from any one of ten analyzed redox couples reported in the 681 data sets.
2. The various couples possible were not in equilibrium with each other.
3. Investigation of redox chemistry should be through analyses for particular valence states of the elements under study.

We think the Lindberg and Runnels work refutes the SCR claim that Eh and pH control the stability and solubility of solid species and the form taken by aqueous species in solution. We note further that in fact paper studies of Eh proceed by calculating Eh from free energy changes. The Eh calculations do not, however, provide a basis for deciding which couples interact in an actual system, whereas the free energy calculations do as discussed below.

We think the revised derivation illustrates the problem involved in trying to choose which reactions to use. We therefore believe that another approach - geometric programming - is preferable. We do not propose to go through the theoretical basis: it is available in the literature³. Suffice it to say that for each molecular species possibly present at equilibrium, a free energy equation is written. There is also one material balance equation for each element plus the constraint that mole fractions sum to 1.0. A further constraint is that all mole fractions are positive. The method is implemented by assuming an initial set of mole fractions that satisfy the material balance and systematically adjusting them so as to minimize the total free energy of the system. With such an approach the problem mentioned above is completely avoided.

Conclusions/and Recommendations

We conclude that it is misleading to say that Eh and pH control the stability and solubility of solid species and the form taken by aqueous species in solution. It is more accurate to say, as suggested in Item 3 in the introduction, that these properties are controlled by composition, temperature and pressure. The only way one can change the Eh or pH in a system is to change composition, temperature, and/or pressure in the system.

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We think some valuable insights can be gained from this analysis. For one thing, the magnetite may be completely unnecessary. It may be more effective to minimize groundwater/canister contact. Second, we need reliable data on how fast the groundwater flows through the fractured basalt formation, for if it is slow, whether it is saturated with oxygen may not be important. Third, since thermodynamics only deals with equilibrium, we need kinetic data for the relevant reactions. Fourth, the corrosion data available should be reviewed in the context of the corrosion environment used to obtain those data versus that in the basalt repository. Fifth, an exploration of the equilibrium relationships over the temperature range of interest should be made from a free energy viewpoint using geometric programming rather than from an Eh viewpoint.



Charles H. Peterson
Engineering Branch
Division of Waste Management

Enclosures:
As stated

REFERENCES:

1. "Site Characterization Report for the Basalt Waste Isolation Project," November 1982, DOE/RL 82-3 Volume II, prepared by Rockwell Hanford Operations for the U.S. Department of Energy, Washington, D.C.
2. Lindberg, R. R. and D. D. Runnells, "Geohydrologic Exploration Using Equilibrium Modeling: A Critical Analysis of Eh and pH", presentation at Symposium of Assoc. Explor. Geochemists-International Assoc. Geochem. and Cosmochem., Helsinki, Finland, Aug. 1983.
3. White, W.B., S.M. Johnson, and G.B. Dantzig, "Chemical Equilibrium in Complex Mixtures," RAND Corporation, Santa Monica, CA, The Journal of Chemical Physics, Volume 28, Number 5, May, 1958, pp. 751-755.

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ENCLOSURE 1

Derivation of Eh Equation

A chemical reaction in general may be written as:



and the free energy change associated with it as:

$$2) \quad \Delta G - \Delta G^\circ = RT \ln \frac{a_R^r a_S^s \dots}{a_B^b a_C^c \dots}$$

where ΔG = the free energy change in general

ΔG° = the free energy change for an isothermal reaction with the products and reactants in their standard states of unit activity

and a_i^j = the activity of each participant species raised to a power given by its mole number in the reaction equation.

At equilibrium, $\Delta G = 0$ so

$$3) \quad -\Delta G^\circ = RT \ln K,$$

where K is the equilibrium constant.

Now if the system in which this chemical reaction occurs behaves as a galvanic cell, the relation between the free energy change and the emf generated is:

$$4) \quad -\Delta G = NFE$$

where E = cell electromotive force, volts

F = Faraday equivalent, 96487 coulombs/g-ion, the charge carried by a gram-ion of unit valency

and N = number of equivalents involved in the reaction.

N is measured by the number of electrons transferred. Thus, if iron is oxidized from elemental iron, Fe^0 , to ferrous iron, Fe^{2+} , $N=2$.

Similarly,

$$5) \quad -\Delta G^\circ = NFE^\circ$$

where E° is the standard full cell potential. Combining equations 2 to 5,

$$6) \quad NFE = NFE^\circ - RT \ln K$$

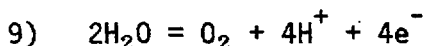
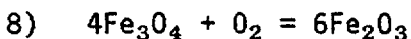
from which we get the Nernst equation:

$$7) \quad E = E^{\circ} - (RT/NF) \ln K$$

The system to which this equation was applied in the SCR is:

Magnetite (M)	Fe_3O_4 (s)
Hematite (H)	Fe_2O_3 (s)
Water (W)	H_2O (l)

for which the reactions were written as:



The equilibrium constant, K_2 , for Reaction 9 is

$$10) \quad K_2 = \frac{(a_{\text{O}_2})(a_{\text{H}^+})^4}{(a_{\text{H}_2\text{O}})^2}$$

while that for Reaction 8 is

$$11) \quad K_1 = \frac{(a_{\text{Fe}_2\text{O}_3})^6}{(a_{\text{Fe}_3\text{O}_4})^4 (a_{\text{O}_2})}$$

The activity is defined in thermodynamics as the ratio of f , the fugacity at conditions, to f° , the fugacity in a convenient standard state. For gases, this is often the state of unit fugacity, so $f^{\circ} = 1.0$ atmospheres. For solutions, activity is often related to mole fractions. For non-volatile solids, the standard state is usually the pure solid at 1.0 atm.

In the present case, for the low degree of ionization of water and for low concentrations of solutes, the fugacity of liquid water is essentially the same as that for the standard state. Hence $a_{\text{H}_2\text{O}} = 1.0$. Similarly, $a = 1.0$ for the two solids in equation 11. Then,

$$12) \quad K_2 = (a_{\text{O}_2})(a_{\text{H}^+})^4$$

$$13) \quad K_1 = (a_{\text{O}_2})^{-1}$$

Since the cell is to operate spontaneously, the net free energy change for the overall reaction involved must be negative. The value of $\Delta G^{\circ}_{298.15}$ for Reaction 8 as written is -97004 cal/g-mole, while that for Reaction 9 is +113,456 cal/g-mole.

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Thus the overall reaction would tend to go in the reverse direction. If we consider reversing only Reaction 9, the K value is the reciprocal of that in equation 12.

$$14) K_{2r} = (a_{O_2})^{-1} (a_{H^+})^{-4}$$

Substituting in equation 7,

$$15) E = E^{\circ} + (RT/NF) [\ln a_{O_2} + 4 \ln a_{H^+}]$$

If the assumption is made that M-H-W will act as a buffer in controlling the activity of oxygen, then the value of a_{O_2} determined from Equation 8 may be used in Equation 9.

$$16) a_{O_2} = f_{O_2}/f_{O_2}^{\circ} = f_{O_2} \text{ (atmospheres)}$$

$$17) E = E^{\circ} + (RT/NF) \ln f_{O_2} - (4RT/NF) \ln (1/a_{H^+})$$

The last term has been modified to facilitate comparison with pH, which is defined as:

$$18) pH = \log (1/H^+)$$

where H^+ is in g-equivalents/liter. Now the ionization of pure water at 298.15K is given by:

$$19) K_w = \frac{(a_{H^+})(a_{OH^-})}{a_{H_2O}} = (a_{H^+})(a_{OH^-})$$

At 298.15K, K_w is $1.0397E-14$ ¹, based on Robie free energy data² and $R = 1.98716$ cal/g mole-K. Assuming H^+ and OH^- ions are formed in equal numbers when considering Equation 19 only, each ion has then an activity of $1.02E-07$. For these low concentrations, the activity coefficients for each ion may be taken as unity, making the molalities of each $1.02E-07$ g moles/1000 g. Since this is numerically essentially the same as g moles/liter, we can write:

$$20) pH = \log (1/a_{H^+})$$

$$21) \ln (1/a_{H^+}) = (2.303) \log (1/a_{H^+}) = 2.303 pH$$

Combining 21) and 17) and inserting the value of N as 4 Faradays,

$$22) E = E^{\circ} + (2.303) (RT/4F) \log f_{O_2} - (2.303) (RT/F) (pH)$$

This is the form of Equation 11-18 in the SCR except for a small correction term derived from $(\partial E/\partial T)_p = S/NF$ to permit calculation of E at temperatures other than 298.15K.

¹Fortran exponential notation.

²Reference 1.

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To evaluate the constants, we first consider E° . The free energy change, ΔG° , is a function of temperature, so E° is also a function of temperature. At 298.15, the free energies of formation of the species in Reaction 9 are:

$$\begin{array}{lll} \Delta G^\circ_f (2 \text{ H}_2\text{O}, \text{ l}) & 2x (-237.141) & = -474.282 \text{ kJ} \\ \Delta G^\circ_f (\text{O}_2, \text{ g}) & 1x (0) & = 0 \\ \Delta G^\circ_f (4\text{H}^+, \text{ aq}) & 4x (0) & = 0 \end{array}$$

Hence, the free energy change for the reaction is -474.282 kJ and

$$23) \quad E^\circ = \frac{-474,282 \text{ volt-coulombs}}{(4 \text{ equivalents}) (96487 \text{ coulombs/equivalent})} = 1.229 \text{ volts}$$

which agrees with the value in the SCR.

The coefficient of $T \log f_{\text{O}_2}$ is $(2.303) (8.3147 \text{ J/mole-K}) / (4) (96487)$, or $4.961\text{E-}05$. This agrees with the SCR equation. Including T , the coefficient of f_{O_2} is $1.479\text{E-}02$. The coefficient of TpH is $4x$ that for $\log f_{\text{O}_2}$: $1.984\text{E-}04$ for the SCR equation and $5.916\text{E-}02$ when T is included. Hence, at 298.15K:

$$24) \quad E = 1.229 + (1.479\text{E-}02) \log f_{\text{O}_2} - (5.916\text{E-}02) (\text{pH})$$

This derivation, however, does not include the free energy change for the oxidation of magnetite that is supposed to be the control on oxygen concentration. Not including it is equivalent to saying the two reactions occur independently of each other, which is a contradiction of the assumption of a buffer action. Note that the electron transfers in equations 8 and 9 are independent. The four electrons transferred in the oxidation of magnetite come from the oxygen molecule in that reaction. The four electrons required in the reduction of oxygen (equation 9 reversed) have an unspecified donor.

To calculate E values for the M-H-W system, the SCR utilizes the equations:

$$25) \quad \log f_{\text{O}_2} = 13.96 - (25323/T), \text{ and}$$

$$26) \quad \text{pH} = (2640/T) + 1.64$$

The value of the fugacity of oxygen calculated from equation 26 is stated as being in pascals, but this is clearly in error, as the unit must be atmospheres. For reference, the SCR equation 11-18 is:

$$\begin{aligned} 27) \quad E_h = & 1.23 + (4.96\text{E-}05) T \log f_{\text{O}_2} - (1.984\text{E-}04) T \text{ pH} \\ & - (T-298)(1.7\text{E-}04) \end{aligned}$$

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Values calculated from equation 27 for three temperatures are in Table A. The three values shown are all negative and in the range -0.45 to -0.39V, which is within the range -0.54 to -0.37V stated in the SCR.

Also shown in Table A are values at the three temperatures for E° calculated by the SCR equation and from free energy data from Robie. The agreement appears good, although even small voltage differences may mean the system moves from one stability region to another on an Eh-pH diagram. The differences shown are attributed to the use of an average entropy change in the SCR temperature correction term. The changes in E° and Eh over the range 25 to 300°C are about 10%.

Table A. Eh Values for the M-H-W System
Calculated from SCR Equation

T, °C	25	51	300
T, K	298.15	324.15	573.15
pH	10.49	9.78	6.25
log f_{O_2}	-70.97	-64.16	-30.22
Eh, V	-0.442	-0.436	-0.387
E° , corrected for T	1.229	1.224	1.182
E° , from Robie	1.229	1.209	1.110
Eh, corrected for pH	-0.381	-0.387	-0.440
f_{O_2} , atm	1.06E-71	6.90E-65	6.00E-31

A further correction is necessary. Equation 26 does not plot as the line shown on SCR Figure 11-25. Both the pH and the temperature scales are arithmetic, and to get a straight line, the abscissa would have to be $1/T$. Without going back to the original Barnes and Sheetz data, we cannot say whether DOE plotted the data incorrectly or erred in fitting an equation to the data. Assuming the inverse temperature relationship is appropriate, different equations can be obtained, according to which two points are used. Using the extrapolated value of pH at 0° and the value at 350°C,

$$28) \text{ pH} = (1715/T) + 3.72$$

These values were merely convenient to read from the graph, so equation 28 is not necessarily the best fit to the data. The SCR concludes there is a correspondence between the Barnes and Sheetz data and the Smith and Martell data for silicic acid, and therefore the pH of groundwater at repository depths is controlled by the dissociation of silicic acid. This, however, seems to be in conflict with the role claimed for magnetite. The SCR reasons that water gets oxidized, producing oxygen, which is taken up by the magnetite. However, hydrogen ions are also produced which lower the pH.

The revised pH values are 9.47, 9.01, and 6.71, respectively; the corrected Eh values are in Table A. Despite the corrections, the conclusion appears to remain unchanged: Eh is negative over the indicated temperature range. When one examines why Eh is negative, one finds the cause to be the extremely low value for the fugacity of oxygen. At 1 atmosphere total pressure and 300°C,

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the fugacity of oxygen shown in Table A as $6.00\text{E-}31$ atmospheres corresponds to $3.61\text{E-}07$ molecules per mole of air, or 1 molecule of oxygen per 62030 m^3 of air. Given a sufficiently long reaction time, one might argue that all the oxygen molecules down to this concentration would eventually find the magnetite and react with it. By the same argument, however, these oxygen molecules would react with an iron canister.

The preceding analysis indicates a different perspective than that offered in the SCR statements quoted in the cover letter for this enclosure.

1. The role of pH in the SCR model is overshadowed by the role of vanishingly small concentrations of oxygen.
2. Eh does not control anything in the case of the galvanic cell: it is the result of the inherent potentials for reaction, whether they be thought of as chemical potentials, electrochemical potentials, or affinities. Eh, in fact, is calculated from the free energy changes and solute concentrations in the system. Eh may be useful as a descriptor. For control, one must adjust the composition of the system and perhaps other variables. In the present application, temperature but not pressure is susceptible to adjustment.

There is a further question as to the validity of predictions based on such low concentrations. Thermodynamic equilibrium is fundamentally a concept involving large enough numbers of each species so that fluctuations of system properties about mean values are negligible.

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References

1. Robie, R. A., B. S. Hemingway, and J. R. Fisher, "Thermodynamic Properties of Minerals and Related Substances at 298.15K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures," Geological Survey Bulletin 1452, U.S. Department of the Interior, U.S. Government Printing Office, Washington, DC, 1979.

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ENCLOSURE 2

Revised Derivation of the Eh Equation

The necessary first step in the analysis is a clear definition of the system being investigated. For this illustrative derivation, we consider a steel canister placed in a borehole with a backfill consisting of a 75% crushed basalt - 25% bentonite mixture. The basalt is assumed to contain 5% magnetite. The time period is after placement but before closure so that the total pressure is 1 atmosphere, neglecting the static head of 1000 m of air. (This pressure correction would be about 6.5% at 0°C.) Any temperature between 0 and 300°C may be used but we elected to use 25°C since free energy data are readily available in tables for this temperature. For this initial illustration, we assumed that any oxidation occurring would be due to dissolved oxygen in groundwater. We further assumed the groundwater would not contain any other dissolved substances.

Next we must establish initial amounts of potential reactants. Comparing the waste package dimensions as in Table 1, we note that per centimeter of canister length, the CHLW shows an intermediate value for the relative amount of canister iron to backfill magnetite: 191.5, on a molar basis. The basalt density used assumes the equivalent of 50% void volume. Also, rather than use as a basis one centimeter of canister length, we elected to use 1 mole Fe_3O_4 (1.590 cm length).

Table 1. Waste Package Dimensions^a

Type of Waste	DHLW	CHLW	SF-2
Overpack			
Outside diameter, cm	80.9	45.6	41.7
Inside diameter, cm	63.5	35.0	30.5
Wall volume, cm^3/cm	2512.6	854.4	635.1
Wall mass, $\text{g}/\text{cm}(\text{b})$	19774	6724	5001
Iron content, moles/cm	354.0	120.4	89.5
Backfill			
Outside diameter, cm	112.0	76.0	73.0
Inside diameter, cm	81.6	45.6	42.6
Volume, cm^3/cm	5885.4	3696.6	3514.2
Mass, $\text{g}/\text{cm}(\text{c})$	6178	3881	3690
Basalt @ 75%, g/cm	4635	2911	2767
Magnetite @ 5%, g/cm	231.8	145.6	138.4
Fe_3O_4 , moles/cm	1.009	0.629	0.598
Iron/ Fe_3O_4 ratio	353.8	191.5	149.8

^aReference 1.

^bDensity of iron taken as $7.87 \text{ g}/\text{cm}^3$.

^cDensity of basalt taken as $1.05 \text{ g}/\text{cm}^3$.

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As to oxygen supply, 0.25 moles O_2 are required to oxidize one mole magnetite. From literature data, the solubility of oxygen in water at 25°C is 0.0393 g/kg or 0.001228 g-mole/kg. Hence the 0.25 mole O_2 could be supplied by 203.6 kg saturated water (11,300 moles). We neglect the presence of other dissolved gases. In summary, the system contains the following molar quantities.

Component	Fe	O	H
Magnetite	3	4	-
Fe	191.5	-	-
Water	-	11300	22600
Dissolved oxygen	-	0.50	-
Total	194.5	11304.50	22600

The question is among what forms and to what extent will these constituents be distributed at equilibrium? We will indicate two approaches.

First, to parallel the treatment in the SCR, we may write (selected) reactions as follows:

	$\Delta G^\circ_{298.15}$ cal/g-mole
1) $Fe_3O_4, s + \frac{1}{4} O_2, g = 3/2 Fe_2O_3, s$	-24251
2) $H_2O, l = H^+, aq + OH^-, aq$	+19076
3) $\frac{1}{4} O_2, g + H^+, aq + e^- = \frac{1}{2} H_2O, l$	-28339
4) $\frac{1}{2} Fe^0, s = \frac{1}{2} Fe^{2+}, aq + e^-$	- 9425
5) $Fe^{2+}, aq = Fe^{3+}, aq + e^-$	+17751
6) $\frac{1}{4} O_2, g + \frac{1}{2} H_2O, l + e^- = OH^-, aq$	- 9175
7) $O_2, g = O_2, aq$	+ 3952

The main oxidation reaction is considered to occur in the liquid phase. The free energy data are based on Robie et al., 1979. The change for Reaction 7 is explained below in the text.

Reaction 1 represents one of the proposed buffering reactions. As indicated, if oxygen diffuses into the waste package environment, the magnetite is presumed to react with it to form hematite. On the other hand, if oxygen is depleted, the hematite will release O_2 . The action appears analogous to that of a pH buffer except that the system is buffered at an extremely low level of O_2 . The equilibrium value at 298.15K for the activity of oxygen is $7.83E-74$. For a total pressure of 1 atmosphere and a fugacity coefficient of 1.0, the oxygen partial pressure is $7.83E-74$ atmospheres. Unless there is some reason to want a finite oxygen level, it seems more appropriate to consider magnetite as an oxygen sink. It is of interest to note that at 100% utilization about 8mL of magnetite would have to contact each liter of $O_2(g)$. In the liquid

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phase, however, the solubility of air in water is about 0.0171 mL/mL water of which about 34% is oxygen (gas volumes are reduced to 0°C, 1 atm). The contact required when the oxygen is supplied from air rather than as pure oxygen is thus 1 mL magnetite per 21650 mL saturated water, or about 4.7x greater. The reaction capacity of the magnetite for oxygen is then zero. Reaction 1 is a redox equation and is written with fractional mole numbers to correspond to a transfer of one electron from magnetite to oxygen.

Reaction 2 represents the ionization of water which normally at 25°C leads to a pH of 7.0. Reactions 3 and 6 represent alternative fates for O₂. Both are reduction reactions. Both might occur but Reaction 3 is favored. To the extent that they occur, magnetite is conserved. Note that both tend to increase pH.

However, electrons can also be supplied by the oxidation of the canister as represented by 4) and 5), with 4) being favored over 5). Reaction 1 will preferentially consume oxygen relative to Reaction 4 because of its greater free energy change but kinetics and activation energies also must be considered.

Reaction 7 is an incidental reaction needed to make a correction to the free energy changes in the other reactions for liquid phase rather than gas phase reactions. The equilibrium constant for this reaction is:

$$8) \quad K = \frac{a_{O_2}(aq)}{a_{O_2}(g)}$$

For dilute solutions,

$$9) \quad a_{O_2}(aq) = m_{O_2} \text{ (molality)}$$

and in the case of oxygen,

$$10) \quad a_{O_2}(aq) = p_{O_2} \text{ (partial pressure, atm)}$$

Hence,

$$11) \quad K = 1/H,$$

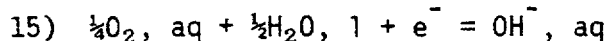
where H is the Henry's Law constant.

$$12) \quad \Delta G^\circ = -RT \ln K = RT \ln H$$

At 25°C, H is 7.89E+02 atm/unit molality so $\Delta G^\circ = +3952$ calories/mole. Adjusting Reactions 1, 3, and 6 by 7:

	$\Delta G^\circ_{298.15}$ cal/g mole
13) $Fe_3O_4, s + \frac{1}{4} O_2, aq = 3/2 Fe_2O_3, s$	-25239
14) $\frac{1}{4} O_2, aq + H^+ + e^- = \frac{1}{2} H_2O, l$	-29327

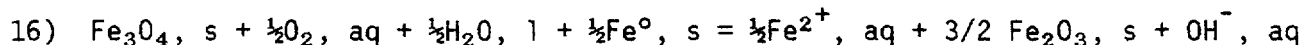
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-10163

There are obviously several other reactions whose impact on the equilibrium should be considered. If we assume that this set is adequate for one case in the real world, we may combine them in an appropriate linear combination.

For simplicity in this illustrative derivation, we elected to delete the oxidation of ferrous iron to ferric iron (Reaction 5) on the basis of its positive free energy change and also delete Reaction 6 in preference to Reaction 3.



The overall ΔG° is -44915 calories/g-mole. The redox aspect is balanced - the exchange is two electrons -, the electrical charge is balanced, and no additional ions are needed to make it electrically neutral. Note that the overall effect of the competing reactions is to increase the hydroxyl ion concentration, i.e., increase the pH. As an electrochemical cell, E° would be +0.974V.

Setting the activities of the three solid reactants and that for liquid water at unity, we can write Reaction 16 in the Nernst form as:

$$17) E = E^\circ - (RT/NF)[\ln(a_{OH^-,aq}) - \frac{1}{2} \ln(a_{O_2,aq}) + \frac{1}{2} \ln(a_{Fe^{2+},aq})],$$

in which $N = 2$.

By equation 19 in Enclosure 1,

$$18) \ln(a_{OH^-,aq}) = \ln K_w - 2.303 \text{ pH}$$

From equations 8, 10, and 11,

$$19) \ln(a_{O_2,aq}) = -\ln H + \ln p_{O_2}$$

Combining 17, 18, and 19.

$$20) E = E^\circ - (RT/NF) [\ln K_w - 2.303 \text{ pH}] + \frac{1}{2} (\ln H - \ln p_{O_2}) + \frac{1}{2} \ln(a_{Fe^{2+},aq})$$

Inserting numerical values ($E^\circ = 0.233V$, $K_w = 1.04E-14$, and $H = 7.89E+02$),

$$21) E = 0.975 + (9.921E-05)\text{pH} + (2.154E-05) \ln p_{O_2} - (2.154E-05) \ln(a_{Fe^{2+},aq})$$

By inspection, there are no practical values for the independent variables that can make E negative (i.e., favoring the formation of the reduced form of iron). Our interpretation is that for a system containing water, oxygen and iron, the spontaneous tendency is for the iron to go into solution (i.e., corrode). Experience supports this: elemental iron exposed to air and water is not found in nature.

Calculation of equilibrium concentrations for the set of equations 13, 14, 15, 2, 4, and 5 is best done by geometric programming methods. We can, however, examine subsets to permit some preliminary conclusions. The equilibrium constant for equation 16 is:

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$$22) \quad K = \frac{(a_{\text{Fe}^{2+}})^{\frac{1}{2}} (a_{\text{OH}^-})}{(a_{\text{O}_2})^{\frac{1}{2}}} = 8.388\text{E}-32,$$

using the value of ΔG° given above in conjunction with equation 3 of Enclosure 1. Letting x equal the moles of magnetite reacted, each of the variables in equation 22 can be expressed as a function of x and the initial molar quantities of reactants. Using the values in the description at the beginning of Enclosure 2 of the system under consideration, we find that at equilibrium, all but $2.7\text{E}-73$ moles of oxygen have reacted. Half of the magnetite and a quarter mole of the canister iron have reacted.

If we consider only reactions 4 and 15 (no magnetite present), we find all but $2.6\text{E}-70$ moles of oxygen have reacted and a half mole of canister iron has reacted.

Thus, magnetite does protect canister iron, but not in the way the DOE SCR implies. The SCR implies that no canister iron will be attacked until all the magnetite is consumed. The above illustrative calculations indicate a competition for oxygen exists among all oxidizable species. Further, while addition of magnetite to the waste package is directionally correct, it would appear more useful to minimize the contact of groundwater with the canister for two reasons: (1) to minimize the amount of dissolved oxygen introduced by the groundwater and (2) to minimize the production of oxidizing species by radiolysis of water. Such species should also include nitrogen oxides. Hydrogen peroxide formed radiolytically would also serve as an acceptor of electrons from iron undergoing oxidation.

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References

1. "Waste Package Conceptual Designs for a Nuclear Repository in Basalt," October 1982, RHO-BW-CR-136P/AESD-TME-3142, prepared for Rockwell Handford Operations, a prime contractor to the U.S. Department of Energy, by Westinghouse Electric Corporation Advanced Energy Systems Division.