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Compiled by:
Garth van der Kamp
Saskatchewan Research Council
Mika Madunicky
Alberta Research Council

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Validity of Redox Measurements
in Hydrogeologic Studies

Kevin A. Morin
Mines Pollution Control Branch
Saskatchewan Environment
P.O. Box 3003
Prince Albert, Saskatchewan S6V 6G1
Canada

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ABSTRACT

The redox condition of water is often measured either by a platinum electrode or through chemical analysis of redox couples. Eh measurements by the platinum electrode are subject to complications, such as formation of platinum compounds upon contact of water and electrode, and disagreement often occurs between measured platinum-based Eh values and Eh values calculated from concentrations of redox couples. Because of such problems, the current pessimistic view is that platinum-electrode measurements are generally meaningless. However, recent research and re-examination suggest the platinum electrode is more sensitive and reliable than often believed and many problems attributed to the platinum electrode are caused by other factors, such as aqueous speciation, depth-integrated sampling, chemical analysis of redox couples, and calculation of Eh from redox couples. In some cases, the platinum electrode provides the only method for estimating the redox state of water, as in high-iron neutral-pH water where the amount of ferric iron is below detection. The potential problems and shortcomings discussed in this paper can be condensed into a checklist to allow researchers to evaluate the validity of redox measurements on a site-specific basis.

1. INTRODUCTION

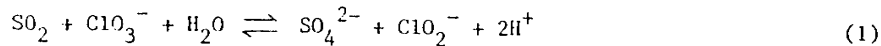
A common parameter addressed in many hydrogeologic studies is pH. A one-dimensional plot of pH from acidic to alkaline conditions would indicate the changes in complexation and concentrations that occur in a water sample as pH is varied. This view of aqueous geochemistry can be expanded to two dimensions through Eh (or pe), which indicates the redox state of a water sample. A two-dimensional plot of pH from acidic to alkaline conditions and of Eh from oxidized to reduced conditions would indicate the changes in redox species, complexation, and concentrations that occur in a sample as pH and Eh are varied.

In some studies, Eh passes beyond an interesting parameter and becomes essential for drawing valid conclusions. An example of this importance involves aqueous and chemically precipitated iron. High-iron groundwaters are normally reduced and the iron exists as ferrous iron (Fe^{2+}). At neutral pH, this high-iron water forms solid ferrous carbonate (siderite, FeCO_3). If a sample of the subsurface is collected and analyzed using common techniques, Fe^{2+} in the porewater will oxidize to Fe^{3+} and precipitate as $\text{Fe}(\text{OH})_3$, and siderite will oxidize to $\text{Fe}(\text{OH})_3$. Analytical results will then indicate there is little aqueous iron and most iron exists as solid $\text{Fe}(\text{OH})_3$. Surprisingly, this scenario regularly occurs in studies involving iron and this error has major implications on the predicted behavior of all aqueous and solid constituents and on the prediction of contaminant migration (Morin and Cherry, accepted; Morin, 1983).

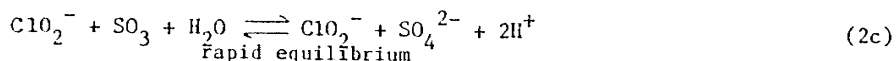
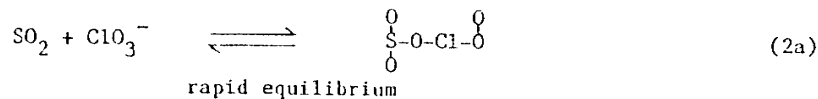
Because of this importance, Eh measurements have been conducted for decades. However, because of the complexities of theory and measurements, Eh measurements are not performed widely and regularly. Additionally, there is currently a pessimistic view on the validity of Eh measurements in general. This view is based primarily on limitations of the platinum electrode used for Eh measurements and on the common discrepancy between the measured Eh and Eh calculated from ratios of redox-active species. Through a detailed presentation of theory, recent experimental work, limitations, examples, and proper methods of measurement, this paper describes the conditions under which valid Eh and redox-species measurements can be made. Specific limitations apply to either measured Eh or redox species or both. In general, this presentation shows that platinum-electrode measurements are more reliable than generally believed.

2. THEORY

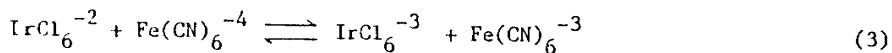
On an atomic scale, aqueous redox reactions involve exchanges of electrons and changes of ionic charge for the reactants. The exchange of electrons is more complex than the simple passing of electrons from one aqueous ion to another, because the stability of free hydrated electrons in the presence of water is low (Hart et al., 1966) and many electron transfers actually take place as atom transfers. For example,



where the intermediate reactions are (Taube, 1965):



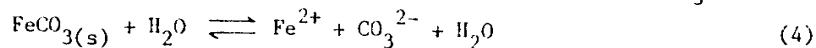
Reactions 2a and 2b indicate electron exchange is accomplished by the exchange of an un-ionized oxygen atom. This exchange is equivalent to an exchange of ionized O^- to SO_3 with $2e^-$ passing to ClO_3^- , and these two equivalent exchanges are operationally similar (Taube, 1965). In the above redox reactions, the exchanged oxygen is not derived from water; however, if ClO_3^- is not present, water could be a reactant. In reactions such as:



the exchange of atoms does not necessarily occur, but changes in the atomic shells and the hydration spheres of the ions affect the total energy change of the system. All the above points have a major impact on energy changes during reaction, thereby affecting equilibrium conditions, and suggest the necessity for examining redox systems instead of individual redox couples in hydrogeologic studies.

Hydrogeologic interest in redox reactions does not lie in the atom-level reactions but in the overall redox state of aqueous ions. However, as suggested above, the delineation of an overall state may in fact require a detailed examination of system-dependent reactions. Hydrogeologists and aqueous geochemists often bypass this examination by simply inserting a platinum-reference electrode assembly into a water sample and recording an Eh value. Before examining the behavior of the platinum electrode in water, the general behavior of an ideal redox-active water will first be described.

In the natural environment, pure water collects chemical constituents from contact with gases and minerals. As an example, pure water may come into contact with and dissolve siderite (FeCO_3):



A theoretical constraint on water and its aqueous constituents is electroneutrality. The addition of equal amounts of Fe^{2+} and CO_3^{2-} to pure water does not disrupt electroneutrality.

There are several inherent complications to Equation 4, however none of these complications disrupts the neutral state. First, a small fraction of water ionizes:



Second, in neutral-pH water (pure water has a pH of about 7 at 25°C), HCO_3^- will form from CO_3^{2-} and H^+ :



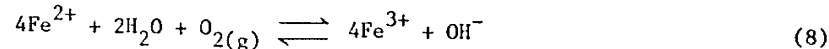
and pH will increase. Third, Fe^{2+} will form small quantities of aqueous complexes with HCO_3^- , CO_3^{2-} , and OH^- (e.g. Morin and Cherry, accepted). These interacting reactions form a complex, electroneutral system, and the equilibrium concentration of each ion and complex can be calculated (Morin, 1985a).

Fe^{2+} is one half of a redox couple:

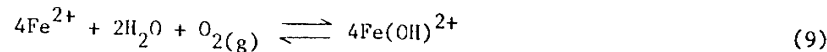


but in this siderite example there is no second couple to allow oxidation of Fe^{2+} to Fe^{3+} . This second couple is a necessity as free electrons essentially cannot exist in water. In reality, $\text{H}_2\text{O}-\text{H}_2$ and CO_3-CH_4 are possible redox couples through which H_2O and CO_3^{2-} may be reduced and Fe^{3+} created. A strict definition of "redox couple" is developed in Section 4.5.

Dissolved oxygen in water will allow iron oxidation:



At pH's greater than about 2.5, Fe^{3+} will combine with OH^- to predominately form $\text{Fe}(\text{OH})^{2+}$ up to pH 4.7 and other OH^- complexes such as $\text{Fe}(\text{OH})_2$ at higher pH. Also above pH 2.5, most Fe^{3+} will chemically precipitate from solution as a $\text{Fe}(\text{OH})_3$ compound. Therefore, Equations 7 and 8 are representative only of an iron-rich water below pH 2 and, in fact, many electrochemical reactions are measured at pH 0 to establish standard states and, in effect, to minimize complications such as complexing. At pH's between 2.5 and 4.7, the dominant redox reaction in the presence of oxygen is:



After adding a few additional redox couples to the above hypothetical system, it is obvious that a redox-active natural water is a complex system from a theoretical viewpoint. Additionally, there are several practical problems, which are discussed later in this paper, with theory, application, and measurement that discourage many researchers from examining the redox state of natural waters. Unfortunately, the theoretical and practical problems often justify the dismissal of redox measurements. However, if the problems can be addressed and resolved on a site-specific basis, valid redox information may be collected.

From the practical viewpoint, collection of redox data often begins with Eh measurements by a platinum electrode. The theory behind such Eh measurements is based on the detection of a voltage potential

at the platinum (or other inert) surface and the measurement of the difference between this potential and that of the standard hydrogen reference electrode. For the equation,



where A = the oxidized half of the couple

B = the reduced half

a, n, b = stoichiometric coefficients

k_f = forward reaction rate

k_r = reverse reaction rate

then the Eh is defined by:

$$E_h = E^0 - (RT/nF) \ln ([B]^b/[A]^a) \quad (11)$$

Where E^0 = experimentally measured standard redox (or "half-cell") potential relative to the standard hydrogen electrode

[A] and [B] = activities of the oxidized and reduced member of a couple

R, T, and F = gas constant, temperature and Faraday constant, respectively.

The "h" in "Eh" indicates the potential is relative to the standard hydrogen electrode. Because of difficulties with the hydrogen electrode (Kokholm, 1977; Linnet, 1970), the calomel or Ag/AgCl electrodes are commonly used as references. Therefore, to be true Eh measurements, most readings with the common references must be adjusted to the hydrogen reference by the addition of several hundred millivolts (Section 3.4).

Two theoretical conditions inherent in Equations 10 and 11 are that forward and reverse reaction rates are fast, i.e. chemical equilibrium is quickly attained and reversible, thereby justifying the use of thermodynamic principles in Equation 11, and that the activity of A and B generally deviate more from the concentrations of A and B as ionic strength increases. If equilibrium exists, a calculated Eh can be obtained using Equation 11 from the activities of A and B, obtained from full chemical analyses and subsequent speciation of analyses (Morin, 1985a), and this calculated Eh can be compared to, and should be equal to, the measured platinum-based Eh.

As indicated earlier in this section, an entire redox system should be considered instead of a series of individual couples. Returning to the example of pure water, this water now comes into contact with a large amount of siderite and a small amount of MnOOH. The solution will initially contain large amounts of Fe^{2+} and typically small amounts of Mn^{2+} . Some Fe^{2+} will oxidize to Fe^{3+} as Mn^{2+} reduces to Mn^{3+} ; the actual amount of oxidized iron will be limited by the commonly small amount of Mn^{2+} . Therefore, in this system, $Fe^{2+} = Fe^{3+}$

is the dominant redox couple by concentration while $Mn^{3+} - Mn^{2+}$ determines the maximum extent of redox reaction in the system. This effect of a dominant couple and a minor, limiting couple can be seen in the experimental data on the Fe-As and S-As systems in Cherry et al. (1979). Because the forward and reverse reaction rates for the Fe and Mn couples are relatively fast (e.g. Nordstrom et al, 1979; Hem, 1981), redox equilibrium is reached in a relatively short time. In other words, the cathodic and anodic currents generated by the couples through reaction rates produce a net current of zero and the potentials (Eh) produced by the couples are equal. If "standard-state" E^0 for the two couples were identical, then the activity ratios should be equal (Equation 11).

In the above Fe-Mn example if k_f for the Mn couple is slow, then little Mn^{2+} can form. This indicates 1) cathodic and anodic currents will be small and 2) the amount of oxidized Fe will be small. Therefore, the platinum electrode may detect a mixture of the more-negative Fe potential and less-negative Mn potential, commonly called "mixed potential". As equilibrium is slowly attained, a true Eh develops.

A final theoretical concept for redox reactions is pe:

$$pe = -\log [e^-] \quad (12)$$

which is analogous to $pH = -\log [H^+]$ where p represents the negative log of the activity of the subsequent symbol. Because free electrons are not stable in water, pe is strictly a theoretical concept. Whereas a pH electrode measures H_3O^+ activity, a platinum electrode measures a potential between charged ions. pe can be calculated in two ways. First is through Eh:

$$pe = (nF/2.303RT)E_h \quad (13a)$$

$$pe = 16.9 E_h \text{ when } T = 25^\circ\text{C, } n=1, \text{ and } E_h \text{ is in volts} \quad (13b)$$

Second is through the equilibrium constant for a redox couple:



$$K = [Fe^{3+}][e^-]/[Fe^{2+}] \quad (14a)$$

$$pe = \log [Fe^{3+}] - \log [Fe^{2+}] - \log K \quad (14b)$$

Combination of theory presented to this point leads to the creation of an Eh-pH (or pe-pH) diagram. A pe-pH diagram for iron is presented in Figure 1. The fields on the diagram are "stability fields", indicating the dominant form of Fe at a particular pH and pe. For example, at alkaline pH and high pe, most aqueous iron will precipitate from solution as $Fe(OH)_3$. However, pH-pe diagrams are based on assumptions which are not valid in all hydrogeologic studies (Morin, 1983; Morin and Cherry, accepted) and, thus, are site-specific.

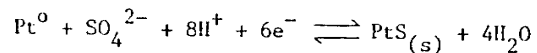
In summary, the theory of redox reactions and measurement in natural waters is complex. Much of the theory presented to this point can be handled and evaluated by computer programs (Nordstrom and Ball,

1984). The following sections of this paper present practical and additional theoretical problems for which knowledge is often insufficient or lacking. Where possible, procedures or suggestions are offered for evaluating the possible impact of a problem. Problems specific to the platinum-reference electrode assembly are discussed first, followed by problems with redox couples.

3. COMPLICATIONS WITH THE PLATINUM AND REFERENCE ELECTRODES

3.1 Formation of Platinum Compounds

The best known fault of the platinum electrode is that platinum is not inert, but is capable of forming oxides and sulfide compounds. Whitfield (1974), a common reference on this problem, defines the valid limits of platinum-based Eh measurements through thermodynamics and through a collection of Eh-pH measurements. Through thermodynamic data, Whitfield calculated the upper limit as the stability field of "Pt-O" and the lower limit as the stability field of PtS which result in "an oversimplified picture of the state of the platinum surface". In fact, for the calculation of the PtS field, a relatively high sulfate activity of 325 ppm was used and the following equation was employed.



A direct, rapid reduction of SO_4^{2-} to sulfide is highly unlikely without a strong catalyst (Section 4.3). Therefore, the PtS field can be eliminated as a lower limit for most platinum-based measurements, especially for measurements requiring less than 1 hour.

Whitfield (1974) noted that his upper limit of valid Eh measurement, the Pt-O stability line, is close to the H_2O_2 (peroxide) line. This agreement was considered coincidental, but Breck (1974) reviewed several studies which indicate H_2O_2 is an important intermediate redox species in the $\text{H}_2\text{O}-\text{O}_2$ system.

Whitfield (1974) presents over 4,000 Eh-pH measurements (his Figure 3) to support upper and lower Eh limits. On this figure, there is no clear evidence that PtS is a lower limit and the upper limit may well be a real chemical limit (H_2O_2) rather than an electrode artifact. Nevertheless, Whitfield collected and presented information that was available at that time and speculated where necessary. However, there is now experimental evidence for the valid limit of Eh measurements with a platinum electrode.

Vassiliev et al. (1984) performed detailed electrochemical experiments with platinum electrodes up to +3 volts and from pH 0 to 14, allowing the examination of Pt-O stability fields. Their results indicate that PtOH forms (reversibly) around +800 mV at about pH 2 and at around +450 mV at about pH 12.

Liu and Yu (1984) examined the reversible behavior of the platinum electrode in moist soil over several Eh ranges. Each test consisted of an initial anodic polarization and drift downwards (more negative)

towards equilibrium and an initial cathodic polarization and drift upwards towards equilibrium. Their tests indicated the platinum will respond reversibly over an Eh range of +710 to -200 mV and both upwards and downwards drifts generally converged within 15 minutes. Convergence time was sensitive to such factors as 1) electrode polarization time, 2) Eh and pH of the soil/water, 3) moisture content of the soil, 4) type of soil/water, and 5) aqueous iron concentration.

These recent studies indicate platinum electrodes are apparently capable of measuring Eh within 100 mV of the upper and lower stability limits for water (Figure 1).

3.2 Detection Limit of Potential and Formation of Other Compounds on the Platinum Electrode

If one member of a redox couple is present in a very low relative or absolute concentration, the current produced by the couple will be too low for the platinum electrode to detect a potential for the couple. In his review of redox potentials, Bohn (1971) indicates a reliable potential is obtainable if 1) the ratio of O_3 (presumably, the activity of) the couples (Equation 11) is between 10^{-3} and 10^{+3} and 2) concentrations are greater than 10^{-6} - 10^{-5} M, although concentrations of 10^{-8} M are sufficient for some couples (Cherry et al., 1979). However, as discussed in Section 2, an entire redox system should be examined in place of a redox couple. If other redox couples meet the above two restrictions, these redox couples will dominate the Eh potential, and the minor couple may well be in equilibrium with the solution Eh.

By examining the entire redox system, the problem of aqueous complexing on the above restrictions arise. As shown in the Fe example (Equations 8 and 9), the use of the $\text{Fe}^{2+} - \text{Fe}^{3+}$ couple above pH 2.5 may be invalid and the $\text{FeOH}^{2+} - \text{Fe}^{2+}$ couple instead should be evaluated in light of the restrictions. This is an important point for members of some redox couples which are highly complexed at neutral pH with the activity of the free ion orders of magnitude less than the activity of the dominant complex. Through equilibrium principles, the $\text{FeOH}^{2+} - \text{Fe}^{2+}$ couple should yield the identical Eh value as the $\text{Fe}^{2+} - \text{Fe}^{3+}$ couple. However, the discussion of Equations 1, 2, and 3 suggest that site specific complexing may indeed affect reaction rates and resulting redox equilibrium conditions. In addition, there is experimental evidence for alteration upon complexing of reaction rates (Section 4.5).

In the case of aqueous iron, moderately reduced neutral-pH groundwaters may have an undetectable amount of total ferric iron (Morin, 1983; Morin and Cherry, 1983, accepted). This can generally be seen on Figure 1 where Fe^{2+} and Fe^{3+} are at equal activities around pe=13 and the ratio $(\text{Fe}^{2+})/(\text{Fe}^{3+})$ increases one order of magnitude for each decrease of one pe unit. Fortunately, it is possible to obtain a representative low Eh in high-iron neutral-pH water through the artificial formation of FeOOH before measurement (Doyle, 1968). FeOOH can be formed by allowing the oxidation of an iron-rich solution on the platinum or exposing the wet electrode to the atmosphere before measurement. If a stable Eh reading is obtained within a few minutes, the Eh reading represents the border of the Fe^{2+} (or FeCO_3) and $\text{Fe}(\text{OH})_3$

stability field (Figure 1). If a slow downward drift is observed, the Eh is somewhat below the $\text{Fe}(\text{OH})_3$ field (Doyle, 1968). A rapid downward drift represents very reducing conditions, often including high sulfide concentrations. The same scenario no doubt applies to similar systems such as Mn^{2+} and MnOOH .

Formation of other, non-redox compounds on the platinum surface may prevent the measurement of a reliable Eh by the isolation of the platinum from the water sample and by the potential generated by the formation of the compound.

3.3 Drifting of Eh Readings With Time

Under ideal conditions, when k_f and k_r (Equation 10) are high and couple concentrations are high, a stable redox state will exist. When a foreign object like a platinum electrode assembly is inserted into a water sample, disequilibrium occurs in the water and electrode, and there is a gradual adjustment to equilibrium. In a balanced redox-active water, a reading within 50 mv of the equilibrium Eh can be obtained in a few minutes (Morin, 1983) to 30 minutes (Doyle, 1968; Liu and Yu, 1984). Up to one hour may be required to obtain the equilibrium Eh in active redox waters (Liu and Yu, 1984). If continuously fluctuating readings, alternating upwards and downwards, are obtained for over 15 minutes, a stable Eh probably does not exist in the sample.

One cause of drift is improper sampling procedures. If a reduced groundwater is exposed to the atmosphere and sunlight during Eh measurement, an upward drift in the reading may occur. Therefore, the sample should be isolated from the atmosphere with slow pumping of sample through the measuring cell. One such technique for Eh measurement is described in Morin and Cherry (1986).

3.4 Adjustment of Eh Readings to the Hydrogen Reference Electrode

As explained in Section 2, the "h" in "Eh" indicates the measured potential is relative to the potential of the hydrogen electrode. This fact is overlooked by some hydrogeologists, who use a meter reading as an Eh value. In practice the calomel or Ag/AgCl reference electrodes are used by hydrogeologists and, because there is a difference in potential between the hydrogen electrode and these other references, the reading must be adjusted by adding a temperature-dependent value. In addition, this correction is dependent on the normality of KCl in the calomel electrode.

There are two basic methods for adjusting the reading to the hydrogen reference. The preferable method is by obtaining an empirical correction through the use of a redox standard. For Zobell's solution (Nordstrom, 1977), the Eh is:

$$\text{Eh}(\text{volts}) = 0.43028 - 2.5157 \times 10^{-3}(t - 25) - 3.7979 \times 10^{-6}(t - 25)^2 \quad (16)$$

Thus, Zobell's solution has an Eh of 430.28 mV at 25°C. Other redox standards are described in Kokholm (1977).

After adjustment of the redox standard to the temperature of the sample, the platinum-reference electrodes are inserted into the standard and the stabilized reading is recorded. The correction value is obtained by subtracting the stabilized reading from the reported Eh (e.g. Equation 16) and this correction is added to subsequent sample readings to obtain Eh values. Occasional checks of the redox standard is suggested, although frequent checks may cause formation of compounds on the platinum and subsequent drifting (Section 3.3).

The second method for adjusting readings to the hydrogen reference is through theoretical calculations. Initially the millivolt meter must be short circuited by connecting the inputs for the platinum and reference electrodes. The resulting reading must then be adjusted to zero to eliminate the internal meter potential. The short circuit is removed, electrodes are attached and inserted into the sample, and the stabilized reading is recorded. Based on temperature and KCl normality in the reference electrode, the following mv corrections for the calomel electrode are added to the reading to obtain Eh (Reardon, 1980):

t(°C)	3N KCl	3.5N KCl	Saturated KCl
0	262 mV	-	260 mV
5	261	-	257
10	260	256	254
15	259	254	251
20	257	252	248
25	255	250	244
30	253	248	241

If an Ag/AgCl reference electrode is used, an additional correction is made: -40 mV from 0 to 15°C and -46 mV from 20 to 30°C. This additional correction is accurate to within 2 mV

3.5 Limitations of the Calomel and Ag/AgCl Reference Electrodes

The limitations of the platinum electrode are discussed in foregoing sections. This section addresses limitations of the other half of the electrode chain, the Ag/AgCl and calomel electrodes.

The stability of the Ag/AgCl electrode is disrupted by 1) light, 2) high levels of Cl^- , 3) oxygen at $\text{pH} < 1$, and 4) interfering aqueous ions (Linnet, 1970). The sensitivity of Ag to light indicates the electrode should be shielded from direct sunlight during measurements. High levels of Cl^- and $\text{pH} < 1$ rarely exist in natural water and, thus, are not often a concern. Interfering ions are trace amounts of Br and greater amounts of iodide, sulfide, and cyanide. In most cases, the disruptions will be no more than a few tens of millivolts.

The stability of the more common calomel electrode is disrupted by 1) temperature, 2) oxygen sensitivity at $\text{pH} < 1$, 3) extreme pH ranges, 4) high ionic strength, and 5) interfering aqueous ions (Linnet, 1970). In water, the calomel electrode is stable in the range of -11 to +70°C,

encompassing most natural waters. Upon a temperature change of 10°C , the electrode will require up to a few hours to stabilize. This indicates the electrodes should be stabilized at sample temperature before measurement (e.g. Morin and Cherry, 1986), although the error produced by small temperature changes is probably less than 20 mV. Extreme pH and high ionic strength affect the movement of K^+ and Cl^- from the electrode, i.e. liquid junction effect (Linnet, 1970). The only interfering ion that can significantly affect the calomel electrode is Br. The error produced by these ionic strength and interfering effects is not defined but may be as high as several tens of millivolts.

There are many other problems that may affect electrodes in general, such as plugging and electrostatic effects (Linnet, 1970; Nicholson, 1983). Field experience indicates many of these problems are often insignificant.

3.6 Mixed Potentials

As explained in Section 2, a well poised, active redox system is characterized by at least two couples having 1) concentrations greater than 10^{-8} - 10^{-6} M, 2) and activity ratio (Equation 11) between 10^{-3} and 10^3 , and 3) fast (reversible) redox reaction rates (Equation 10). If these conditions are not met, the measured Eh may represent a mixture of potentials. However, because these conditions carry implied assumptions, they cannot be simply applied to all redox systems.

Because a measured Eh does not implicitly indicate whether it is a true Eh or a mixed potential, the redox couples in a system must be evaluated for the possibility of creating mixed potentials. This detailed evaluation of couples is discussed in Section 4.

4. COMPLICATIONS OF REDOX-COUPLE MEASUREMENTS

In an attempt to evaluate the existence of mixed potentials, a few researchers have compared Eh calculated from chemical analyses of redox couples (Equation 11) and measured Eh. For many couples, calculated Eh did not agree well with measured Eh (Nicholson et al., 1983; Lindberg and Runnels, 1984). The surprising conclusion is that the discrepancy is often unquestioningly attributed to the platinum electrode. Section 2 shows that on the atomic level redox reactions are complex and variable. In light of this, Section 3, and the following arguments, redox couples also account for part of the discrepancy, thereby indicating the platinum electrode is more reliable than generally believed. The following complications can be collected into two general categories: 1) complication which affect the measurement of couples and the subsequent calculation of Eh by Equation 11 and 2) complications which affect the redox behaviour of couples. Some of these complications also affect platinum electrode measurements.

4.1 Sampling Procedures

The procedures for obtaining a representative, undisturbed water sample for analysis of redox couples are detailed, exhausting, and open to many problems. Sampling problems for groundwater begin with piezometer installation and end with delivery of the sample to a laboratory.

During drilling, the borehole is exposed to the atmosphere and oxygenated fluids. This no doubt alters the redox state surrounding the borehole. Afterwards a piezometer or water well is installed in the borehole. If the piezometer or well is metallic, the metal will be an electrochemically active site, possibly affecting redox stability, the metal will corrode and change redox conditions, and the iron system (Figure 1) may come to dominate the redox state if the piezometer is iron or steel.

If the well has a long screen or screens at various depths, typical of water-supply wells, samples will often be unacceptable for redox analysis. An extreme example of this screening problem is where one screen is across an FeS_2 -rich zone and a second screen is across a gypsum-hematite zone. The FeS_2 zone will yield water high in Fe^{2+} and S^{2-} , while the second zone will yield water with Fe^{3+} and SO_4^{2-} . The "redox state" of the Fe^{2+} - Fe^{3+} and S^{2-} - SO_4^{2-} couples (and also platinum-based Eh) in a sample from this well will depend on such factors as screen length, transmissivities of the zones, and reactions occurring upon mixing of the two waters. In any case, such wells, typical of water-supply wells, cannot be expected to yield worthwhile redox information through the couples or measured Eh.

After installation of a piezometer, an artificial sand or gravel pack is often placed around the screen to fill the open volume and to allow impermeable plugs to be placed above and below the screened interval. If this pack contains $\text{Fe}(\text{OH})_3$ or MnO_2 , for example, then groundwater passing through the pack into the piezometer may be thrown into disequilibrium or dominated by the Fe or Mn systems. Rarely is the mineralogy of a sand pack described in hydrogeologic studies.

To this point, only problems relating to the installation of the well or piezometer have been examined. All but two of the problems can be reduced or eliminated by withdrawing large amounts of groundwater while allowing several months for the redox state of the borehole and sandpack to equilibrate. Many times these conditions are not fulfilled before a sample is taken. The two problems that cannot be eliminated are metallic well materials and a long or segmented screen. If these problems are present, then valid redox data probably cannot be obtained. Unfortunately, many databases do not contain such details (Hart et al., 1985; Runnels, personal communication) and, thus, the reliability of redox data from a database is questionable. These problems may account for much of the discrepancy between calculated and measured Eh in studies such as Lindberg and Runnels (1984).

Upon sampling, water should initially be pumped and discarded. Then water should be pumped slowly at low head or minor vacuum out of the piezometer and through an isolated, temperature-equilibrated measuring cell containing the platinum and reference electrodes (Morin and Cherry, 1986). If a stable Eh is obtained, a sample isolated from sunlight, atmosphere and other bases should be immediately collected,

maintained at original temperature to eliminate temperature-dependent changes in couple activities, and analyzed quickly. Such techniques are rarely employed in the field and the iron system provides an example of the occasionally unobtainable degree of quality control required by the technique.

Experiments were performed under laboratory conditions in an attempt to stabilize an FeSO_4 solution in a sealed vessel (Buszka, personal communication). Bubbling high purity nitrogen through the solution allowed visible iron oxidation and precipitation, probably the result of the oxygen (0.01-0.1%) contained in high-purity nitrogen. Also, placing the solution under vacuum allowed visible iron oxidation and precipitation, possibly by the entry of air through the seals.

Under field conditions there are similar problems: high-iron, neutral-pH groundwaters, which are usually in equilibrium with siderite (Mogin and Cherry, accepted), contain about 10^{-1} M total Fe^{2+} and about 10^{-8} M total Fe^{3+} . A standard method for measuring Fe^{3+} is by measuring total Fe^{2+} and total aqueous iron, and subtracting to obtain total Fe^{3+} . Because total Fe^{3+} is about 10^{-8} M, it cannot be reliably detected because of detection limits and accuracy of both the above standard method (total Fe^{2+} and total Fe) and the direct measurement (Jasinski and Trachtenburg, 1973). Additionally, if 10^{-8} Fe^{3+} could be detected, within one minute of sampling (before the analysis could be performed) at least 10^{-7} M of Fe^{2+} can oxidize (e.g. Sung and Morgan, 1980) and, thus, alter the results by one order of magnitude. Therefore, in a well-poised redox system dominated by iron at neutral pH, the platinum-based Eh measurement using an isolated, flow-through technique with other details from Section 3.2 may often be the only method for obtaining representative redox information.

If the sample is taken to a laboratory, the above discussion on iron gives some idea of the changes that can occur in the redox couples. However, iron has relatively fast reaction rates and other couples may be stable for longer periods (Section 4.3 and Cherry et al., 1979).

To obtain indications of the presence of dissolved oxygen (D.O.) in a field sample before atmospheric contamination can occur, a D.O. meter or Winkler titration is used. Because the Winkler titration measures D.O. through a series of redox reactions, the presence of other couples will interfere with the results. In fact, if other couples dominate oxygen, the Winkler titration is unreliable. This may account for discrepancies between the $\text{O}_2 - \text{H}_2\text{O}$ calculated Eh and measured Eh. The occurrence of D.O. in deep groundwater (Winograd and Robertson, 1982) may be partially an artifact of the Winkler titration, although comparisons with results of a D.O. meter at one well suggest the Winkler results are valid.

The sampling procedures discussed in this section are difficult to implement. Other, invalid procedures, such as gas-lifting to obtain a sample, were probably used to collect some existing redox data. Like piezometer details, databases containing redox data do not usually include sampling procedures and, thus, such data is questionable.

4.2 Analytical Accuracy and Detection Limits

The discussion of on-site Fe^{3+} and D.O. analyses in the previous section highlights possible analytical problems with redox couples. Assuming the redox couples are stable during sampling, shipping, and preparation, the laboratory must then reliably analyze the members of the couples. Because concentrations or activities must be greater than $10^{-8} - 10^{-6}$ M, detection limits and accuracies for the analyses must be around 1 ppb. Detection limits and errors for analysis of natural waters have been decreasing with time in response to concerns over trace contaminants, and detection limits of 10 ppb are now routine. Past analytical errors were higher and, unfortunately, these errors are often not recorded with redox data. Also, current practical detection limits for water containing thousands of ppm TDS are as high as 1 ppm because of interferences and instability of some constituents during analysis (Morin, 1985b). Therefore, dominant redox couples can often be measured reliably in a laboratory environment, while minor couples may be questionable. Redox studies on calculated and measured Eh, such as Lindberg and Runnels (1984), often give no concentrations or accuracies.

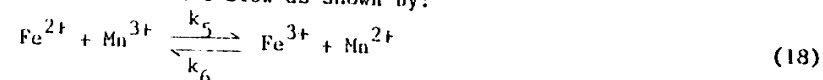
4.3 Kinetics and the Definition of Redox Couples

As discussed through Equation 10, the forward and reverse reaction rates for couples must be fast to provide a stable redox system. The only time frame examined to this point is up to a few hours for Eh measurement. A more general concept of time and redox reaction kinetics will now be examined, beginning with a hypothetical illustration.

In a water containing only Fe and Mn couples, the following half-cell reactions occur:



For this example, we assume k_3 is slow, thus reduction of Mn^{3+} and oxidation of Fe^{2+} are slow as shown by:



where k_5 is necessarily slow. Initially a mixed potential may be obtained by the platinum electrode with the value between the actual potential of the Fe and Mn couples. The value of the mixed potential will be a function of concentrations and activity ratios between all redox species in a system and this again highlights the importance of examining an entire system rather than the couples. With time,

equilibrium is reached and calculated Eh from both couples will equal measured Eh. For arsenic systems, this time for equilibrium is on the order of days (Cherry et al, 1979).

The time required to attain equilibrium is a function of reaction rates, concentrations, and activity ratios. If the couple with fast reaction rates dominate in concentration, a more rapid approach to equilibrium can be expected than with a dominant slow couple. Experimental evidence for this behavior apparently exists for the Fe-As and S-As systems in the data of Cherry et al. (1979). A simple field test to obtain this equilibrium time for shallow groundwater is surface resistivity methods which disturb the natural potential of the water. Pehme (1981; personal communications) found that the high-iron groundwater plume described by Morin (1983) and Dubrovsky et al. (1984) displayed a charging effect similar to a battery when using surface resistivity equipment and this charge decayed over a period of several hours. Equilibrium time obtained in this manner is representative of the in-situ water and is not valid for water exposed to the atmosphere or to temperature changes.

In a system where there are two couples with fast reaction rates and one couple with slow reaction rates, identification of the dominant couples is important. If the two fast couples dominate, the calculated Eh from the two couples will be equal while the slow couple may indicate disequilibrium. This example leads to a problem with terminology: if two or more dominant couples are in equilibrium, is the redox system in equilibrium? The resolution of this problem in turn depends on the precise definition of a redox couple.

A redox couple is properly defined as two ions of the same element that represent a relatively fast one-step change in oxidation state, usually by a value of one or two. A simple one-step change is the Fe couple (Equation 7), which accounts for its near ideal redox behavior. $S^{2-} - SO_4^{2-}$ is not a redox couple because sulfur changes from -2 to +6 and, thus, $S^{2-} - SO_4^{2-}$ actually represents several couples. The first couple is $S^{2-} - S_2^0$, but this couple is greatly complicated by the formation of polysulfide ions, S_n^{2-} where $n = 2$ to 5 (Giggenbach, 1972), and by the formation of solid-phase sulfur. For these reasons, the concentration of aqueous S^0 is below detection in most natural waters, indicating 1) this couple is often minor (e.g. Boulegue et al., 1979) and often has no effect on Eh and 2) the overall use of $S^{2-} - SO_4^{2-}$ for calculation of Eh is invalid. The second couple in the $S^{2-} - SO_4^{2-}$ system is $S^0 - S_2O_3^{2-}$. This couple is considered minor because of low S^0 concentrations, although Boulegue et al. found good agreement between calculated Eh from this couple and measured Eh in sulfide-rich waters. The remaining sulfur couples are $S_2O_4^{2-} - SO_3^{2-}$ and $SO_3^{2-} - SO_4^{2-}$. This same scenario applies to other "redox couples" such as $NH_4^+ - NO_3^-$, which has intermediate couples involving N_2 gas and NO_2^- , and $H_2O - O_2$ with H_2O_2 (Section 3.1), and $CH_4 - CO_2$. Caution over defining redox couples should also extend to the apparent one-step redox reactions on an atomic level. Equations 1 and 2 indicate there is actually an intermediate slow step in a reaction that appears to occur in one step.

In light of the previous paragraph, if a redox couple does not reach equilibrium with other couples, it is possible that the couple

has intermediate products. The discussion surrounding Equations 1 and 2 indicate the existence of intermediate products may be system-dependent. Because intermediate products are often not well known or described and often occur in relatively low concentrations, the very existence of intermediates indicates: 1) the overall "couple" will not have a significant impact on Eh and 2) "disequilibrium" in the overall "couple" can easily occur. If such disequilibrium occurs, it is possible an intermediate couple will reflect the measured Eh.

With the above strict definition of redox couples, the earlier discussion of redox equilibrium in a system becomes clearer. If at least two true redox couples exist in a water, redox equilibrium can be expected. Couples in disequilibrium may not be true couples in the system. With this approach in mind and considering the valid "redox window" (Cherry et al., 1979) for couples, in which the activity ratio is between 10^3 and 10^7 , disagreement of measured and calculated Eh's is no longer as disturbing and the validity of measured Eh is more acceptable. The following sections discuss additional factors which affect calculated Eh.

One process which has a major effect on kinetics and on the definition of system-dependent redox couples is catalysis by inorganic and organic constituents. Inorganic aqueous complexing can significantly affect redox reaction rates. Millerq. (1985) found that complexing of Fe^{2+} with Cl^- and SO_4^{2-} lowered Fe^{2+} oxidation rates. Redox rates are also affected by minerals in contact with water (White and Yee, 1985). The existence of microbes in the subsurface is well known (e.g. Wilson et al, 1983) and organic mediation of redox reactions are well documented (Horwarth and Teal, 1979; Jorgensen, 1977; Pugh et al., 1984; Nordstrom, 1982). In fact, organic mediation accelerates sulfate-sulfide redox rates to where $S^{2-} - SO_4^{2-}$ can be treated as a redox couple in some systems; the behavior of the sulfur intermediates in these accelerated systems are rarely examined. Other cases of properly behaved couples are compiled in Nordstrom et al. (1979).

Inorganic and organic alteration of redox rates may affect equilibrium states of the reactions. The effects are discussed in Section 4.5.

4.4 pH Factor

When calculating Eh from analytical concentrations of redox couples, the concentrations must be converted to activities by speciation of the entire water analysis (Morin, 1985a). Activities are then used in Equation 11 to calculate Eh. If a member of the couple is complexed with H^+ or OH^- and sometimes O_2^{2-} , the calculation of Eh must include pH. Paralleling Equations 10 and 11:



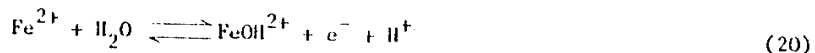
$$Eh = E^0 - (RT/nF) \ln ([B]/[A]) + (2.303 RT/nF)pH \quad (20)$$

4.5 Aqueous Complexing and Activities

The effect of aqueous complexing on redox reactions was discussed in Section 2 and 4.3. Relative to the iron system, the experimentally measured potential against the standard $\text{H}_2 - \text{H}^+$ couple (E^0) is based on free ions:



When pH is between 2.5 and 4.7 at about 25°C, the dominant redox reaction is:



In order to calculate the stability line for the $\text{Fe}^{2+} - \text{FeOH}^{2+}$ couple (Figure 1), the equilibrium constants for Equation 7 and the formation of FeOH^{2+} are combined to obtain an equation like Equation 20 or similar to Equation 14. The assumptions inherent in this common approach are: 1) e^- has a defined free energy of zero, 2) redox equilibrium is not altered from that of the $\text{Fe}^{2+} - \text{Fe}^{3+}$ couple beyond the thermodynamic effect of complexing, and 3) thermodynamic data are correct. Because e^- is not stable in water, other redox couples should be added to Equation 21 and, as previously discussed, the resulting redox equilibrium will be system dependent. For the second assumption, Section 4.3 points out the effect of complexing on redox reaction rates. Because equilibrium constants are the ratio of forward and reverse rates, the actual equilibrium constant for Equation 21 may be different from the thermodynamic-based constant using $\text{Fe}^{2+} - \text{Fe}^{3+}$ and FeOH^{2+} formation data. As discussed in Section 2, such a discrepancy can be expected by considering changes in atomic shells and hydration spheres upon complexing which can easily affect subsequent electrochemical reactions. However, detailed experimental work on this phenomenon is lacking. On the third assumption of accurate data, even the dissociation constant of HS^- has recently been found to be in error by up to two orders of magnitude (Uhler and Helz, 1984).

Aqueous complexing and associated factors such as ionic strength have a strong effect on the evaluation of activities of the couples from which Eh is calculated. As a result, calculations of activities must be done through speciation programs (Morin, 1985a; Nordstrom and Ball, 1984). The major problems with these models are: 1) full chemical analyses must be available for speciation, 2) chemical equilibrium is assumed, and 3) there are theoretical limitations especially with the calculation of activity coefficients and missing or unidentified complexes (e.g. Stipp, 1983). Interestingly, if the calculated Eh's from activities of several couples indicate redox disequilibrium in a system, the use of equilibrium principles to calculate the disequilibrium activities (speciation) and Eh (Equation 11) leads to a paradox, apparently ruling out the calculation (proof) of disequilibrium.

5. CONCLUSIONS AND RECOMMENDATIONS

This paper has discussed the validity of redox measurements in hydrogeologic studies. Based on theory and problems with implementation, the conditions under which Eh can be reliably measured

by a platinum electrode assembly were discussed. A thorough understanding of interactions of the platinum electrode with an aqueous redox system and recent experimental work indicate the platinum electrode is better behaved and more reliable than suggested by past studies. The calculation of Eh from activities of redox couples based on chemical analyses has been shown to be sensitive to an abundance of limitations and problems to the extent that many calculated Eh values are highly questionable. The common discrepancy between measured platinum-based Eh and calculated Eh from couples, which is often attributed to problems with measured Eh, should be attributed more often to the calculation of Eh. In some cases, such as in high-iron neutral-pH waters, a platinum-based Eh may be the only method of detecting the redox state of the water.

Before beginning a redox study, hydrogeologists should address formally or informally the points raised in this paper. One convenient method for addressing the points is through a checklist compiled from the section titles in this paper (Table 1).

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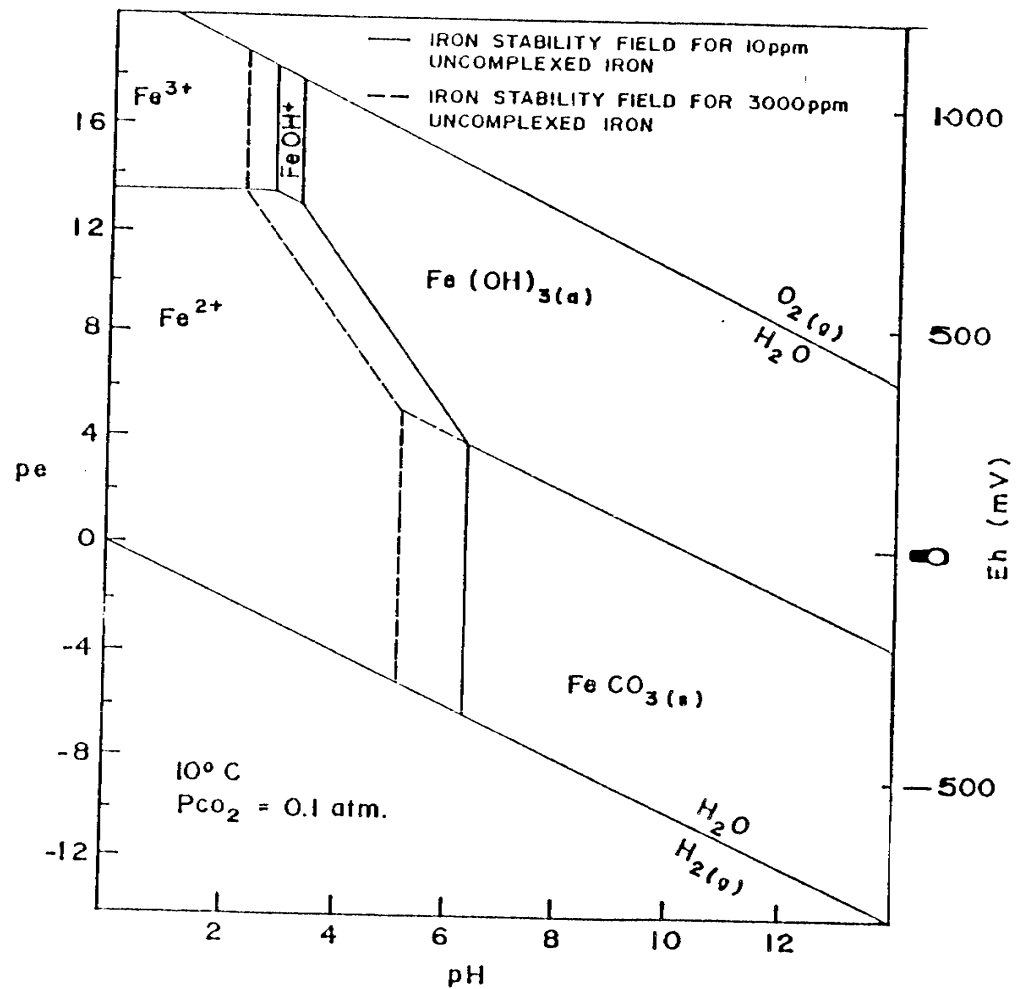


Figure 1. pH-pe-Fe Diagram.