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Redox Chemistry of Mine Waters – Still Misunderstood

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Abstract

Redox processes are critical to understanding nutrient and contaminant mobility and fate in natural waters. Solubility and toxicity of such species as Fe(II,III), As(III/V), Cr(III/VI) and Se(IV/VI) depend substantially on the dominant redox species. Unfortunately, the concept of aquatic reduction-oxidation processes is often misunderstood and misapplied. Because natural waters and mine waters contain redox species that oxidize or reduce at different rates and do not reach equilibrium, no analogy exists between pH and pE (or Eh), and a redox potential of a natural water is not meaningful. What IS meaningful is to obtain the concentrations of redox species by analysis.

Keywords: Redox species, redox processes, redox applications

Introduction

Processes of reduction-oxidation, or redox, are critical to understanding the solubility, speciation, mobility, and toxicity of redox-sensitive contaminants. Unfortunately, descriptions of redox chemistry are still burdened with decades old misconceptions when applied to natural waters. This paper reviews our knowledge of redox processes in general and some examples with acid mine drainage.

Examples of several redox-sensitive elements and their relative solubilities and toxicities are shown in Table 1. These can be useful as a qualitative guide to redox chemistry. Additional complications arise from the fact that some elements methylate or form complexes with inorganic or organic ligands which can greatly change their solubility and toxicity. The classic example is with mercury. Methylmercury is much more toxic than elemental mercury. Consequently, determining the total dissolved concentration of a redox-sensitive elements is insufficient for characterizing its solubility and toxicity. These complications are magnified when attempting to model redox transformations in natural waters because many redox processes are not amenable to equilibrium assumptions. In the absence of any direct knowledge of redox changes (by chemical analysis) at a particular site, modelling must depend on analogous studies elsewhere which has limitations because every location tends to have site-specific characteristics. It is possible to model redox chemistry using rate constants, however, the assumptions that must be made when applying simple experimental lab data to complex field situations are rarely warranted.

Table 1 *Relative solubilities and toxicities of redox species found in natural waters.*

Element	Reduced Form	Oxidized Form
Fe	Fe(II), soluble	Fe(III), insoluble
Mn	Mn(II), soluble	Mn(IV), insoluble
As	As(III), soluble, more toxic	As(V), less soluble, less toxic
Sb	Sb(III), soluble, more toxic	Sb(V), less soluble, less toxic
Se	Se(IV), less soluble, less toxic	Se(VI), more soluble, more toxic
U	U(IV), insoluble	U(VI), soluble, more toxic
Cr	Cr(III), insoluble	Cr(VI), soluble, much more toxic

This paper begins the clarification of redox by describing "redox potential," and its lack of relationship to redox couples. Examples will follow of redox species in natural waters, including mine drainage and the controlling factors.

Redox potential

The redox chemistry of an aqueous solution has often equated with the "Eh" or "pE." That mistake has been largely influenced by the adoption of the Pourbaix (or Eh-pH) diagrams by Garrels and Christ (1965) and subsequently taught in geochemistry courses for decades. I am in full agreement with the use of Eh-pH diagrams as a valuable heuristic device and should continue to be introduced in geochemistry courses. However, it has been emphasized appropriately by Hostetler (1984); Langmuir (1971, 1997); Nordstrom and Munoz (1994); Stumm and Morgan (1996); Thorstenson (1984) and Appelo and Postma (2005) that pE is not analogous to pH, that pE or Eh refers to the equilibrium between a redox couple and a conductive electrode and not a redox potential of the water, and that different redox couples do not come to equilibrium with each other. There can be a pH of an aqueous solution, but not a redox potential of an aqueous solution. There is a redox chemistry of an aqueous solution, and it can be determined analytically by measuring the redox species. Furthermore, measuring the redox species tells us far more about the redox conditions of a water than measuring the EMF (electromotive force, often mislabelled the ORP) from which the Eh (or pE) is calculated. It should be noted that Eh is best used when speaking of field measurements and pE is more appropriate for pE-pH diagrams (Truesdell 1968).

There are two situations in which the conductive electrode behaves in a Nernstian equilibrium manner. One situation is acid mine drainage (with limitations as shown below) and the other is porewaters or groundwaters undergoing sulfate reduction. In the former case, Fe(II) and Fe(III) are "electroactive" and in the latter case, sulfide (as H2S or HS-), is electroactive such that the electrode responds as if it were a sulfide ion-selective electrode (Berner 1963; Morris and Stumm 1967). In all other cases that we know about, other redox couples are not sufficiently electroactive in natural waters to give a quantitative Nernstian response.

Methods

Fe(II/III)

The sample can be filtered and acidified in the field with redistilled HCl except for waters containing sulfide which may cause some sorption or precipitation as iron sulfide. Adding 1% (v/v) to a 125 mL sample will bring the pH down to <2 and stabilize the Fe(II/III) ratio for months in the absence of nitrate.

Many "ferroin" reagents that determine Fe(II) and total Fe are quite sensitive to these species such as 1,10-phenanthroline, PTDS, TPTZ, and FerroZine. One of the most common ferroins is FerroZine because of it low cost, sensitivity and availability (Stookey 1970; Gibbs 1976). These colorimetric reagents are of similar molecular structure. FerroZine is more sensitive than 1,10-phenanthroline because of a higher absorption coefficient and a stronger ligand complex. Detection limit with FerroZine is 1−2 µg/L using a 1 cm cell. Lower detection limits are possible with a 5 or 10 cm cell. Total dissolved Fe is measured by reducing the solution with a reagent such as hydroxylamine at a buffered pH and remeasuring. The Fe(III) concentration is determined by difference and has a different detection limit of ≤ 3% of the total Fe. Because there is a need to measure Fe(III) at lower concentrations than this, a method was developed to determine Fe(III) directly (To *et al.* 1999).

As(III/V)

As with Fe(II/III), the sample can be filtered and acidified with redistilled HCl for months (McCleskey *et al.* 2004). When sulfide is present, then thioarsenites and thioarsenates can be present and the sample must be flash frozen in the field and kept frozen while transported to the laboratory. At the lab, the sample must be thawed in an oxygen-free glove box and run on an oxygen-free HPLC-ICP-MS instrument to determine thioarsenates and thioarsenates along with As(III/V) (Planer-Friedrich *et al.* 2007).

The redox species of arsenic can be determined by hydride-generation atomic absorption spectroscopy (HGAAS), ion chromatography (IC), HPLC-ICP-MS, anion-exchange chromatography ICP-MS (AEC-ICP-MS), or field separation using ion exchange columns and eluted in the lab and run on AAS, ICP-MS, or colorimetry.

Sb(III/V), Se(IV/VI)

Antimony, selenium, and other hydride-forming elements can be effectively determined by HGAAS (or hydride combined with ICP-MS). These elements also can form thio-complexes in the presence of sulfide (Planer-Friedrich and Scheinost 2011).

Cr(III/VI)

Although Cr(III) is rather insoluble as a hydroxide, these redox species can be determined in water samples by an EPA method that requires transport of sample to a laboratory within 24 hours and determination on an IC with an absorbance detector. Another common method is a colorimetric determination using diphenylcarbazone (DPC) but the sensitivity is not as good as the EPA method. Both methods are described in the third method that uses cation-exchange in the field to separate the Cr(III) on the column and Cr(VI) comes out in the eluent (Ball and McCleskey 2003). Any technique with sufficient sensitivity can be used to determine the separated Cr. With this method, the redox species are stable for several weeks and with better sensitivity than the DPC.

Mn(II, III, IV), U(IV/VI)

These aqueous redox species have rarely been determined for natural waters and could use further research. Uranium speciation has been reviewed by (Smedley and Kinniburgh 2023) and Mn(II) has been determined electrochemically with various types of voltammetry (Crapnell and Banks 2022).

N(-III, 0, I, IV, VI)

Ammonia, nitrogen gas, nitrite and nitrate are the main redox species of nitrogen and their determination by IC and gas chromatography (GC) for nitrogen gas are routine and well-established in Standard Methods and EPA methods.

Examples

One of the best examples of redox disequilibria of different redox couples in the same groundwater was demonstrated by (Lindberg and Runnells 1984). They compiled measured redox species for Fe, N, S, O, C, and the Eh and showed that they were generally out of equilibrium with each other on a plot of measured vs. calculated Eh. The calculated Eh values were, however, clustered around the standard electrode potential for each couple whereas the field measurements were spread over a large range of about 500-700 mV for any given couple. A simple example is shown from my Ph.D. thesis (Nordstrom 1977) (See Table 2).

In this example, I had measured the dissolved oxygen and calculated the Eh based on the O2/H2O redox couple and showed it bore no relation to the measured Eh. These surface waters were mountainous streams which were close to equilibrium with respect to oxygen in the atmosphere. If a measured Eh bears no relation to a calculated Eh, what does it mean to speak of a redox potential of a water? You can choose one value over the other and try to justify it, but it makes little sense. What does make sense is to ask what

Table 2 *Comparison of measured Eh values with those calculated from dissolved oxygen (D.O.) and the O_2/H_2O redox couple. Data are from Nordstrom (1977).*

Location	Spring Creek(H)	Boulder Creek(C)	Boulder Creek(G)	Spring Creek(J)
pH	6.40	3.02	1.85	2.32
D.O. (mg/L)	10.3	10.5	11.0	11.8
Eh, measured, V	0.380	0.694	0.625	0.640
Eh, calculated from D.O., V	0.948	1.156	1.227	1.197

is in the water that is "electroactive." This adjective refers to a Nernstian response at the electrode interface. For a redox couple to be electroactive the redox species must be present at high enough concentrations, and they must be able to transfer electrons rapidly across the solution/electrode interface so that equilibrium can be attained. Concentrations need to be about 10^{-5} molar or higher. Anions like arsenate, selenate, and antimonate consist of a central metalloid atom strongly covalently bonded to oxygen atoms that inhibit the transfer of electrons. These species have been shown to be insufficiently electroactive in aqueous solution, for example Runnells and Lindberg (1990).

For acid mine waters, dissolved Fe is electroactive and Nernstian equilibrium is observed. About 1510 analyses of waters contaminated with acid mine drainage from the western USA (Nordstrom 2011) were speciated to demonstrate this equilibrium. These samples were selected using several criteria: (1)the water analyses were complete for major ions with good charge balances and documented QA/QC, (2)they included analyses for Fe(II/III), and (3)they had Eh values based on field-measured EMF values that were converted to Eh based on the half-cell potential of the reference electrode (Garrels and Christ 1965; Langmuir 1971). The results for measured vs. calculated Eh based on Fe(II/III) and appropriately speciated for activities are shown in Fig. 1a below. A cluster of values at high Eh correlated quite well but at lower Eh values very few values correlated well. Detection limits for Fe(II) (<10-5 molar), Fe(III) (<3% of total dissolved iron), and for the redox electrode (Morris and Stumm 1967) were applied and used to delete any data that were below detection limits. The resulting plot is shown in Fig. 1b.

Another valuable result is that when the data from Fig. 1a is used to plot saturation indices (SIs) of freshly precipitating hydrous ferric oxides such as ferrihydrite or schwertmannite, many of the SI values are greatly supersaturated as shown in Fig. 2a. By removing data points below detection limits from the plot, the supersaturation disappears (Fig. 2b, Nordstrom 2011). The reason is that the conductive electrode only responds to dissolved Fe(II/III) and not to colloidal Fe(III) which typically is only nanometers to tens of nanometers in particle size when freshly precipitating and easily goes through the pores of filters that are usually 0.45 micrometers in pore size. Those iron colloids dissolve in the acid preservative and added to the total dissolved iron even though it is not truly dissolved. This supersaturation effect has been noted for some time by many authors and the data from Nordstrom (2011) reproduced here shows that it is caused by a filtration artifact.

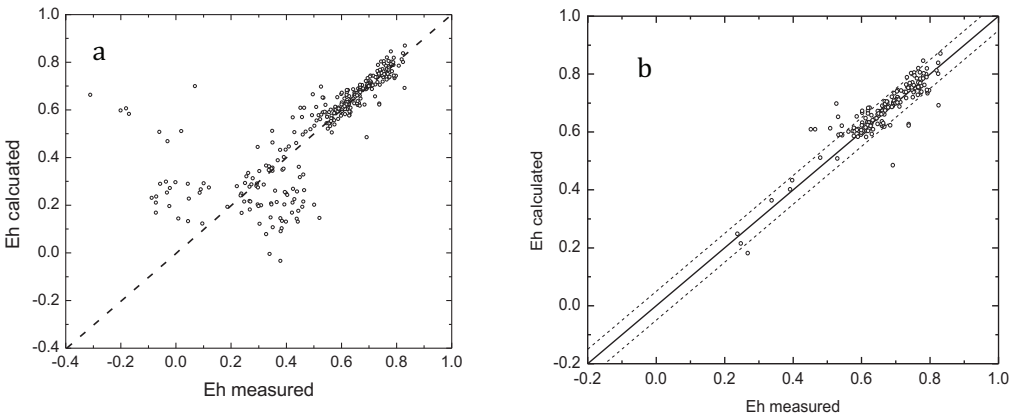

Figure 1 *(a) Eh calculated from Fe(II/III) determinations and speciated from the PHREEQC code using the wateq4f.dat database. Dashed line is the 1:1 correlation. (b) Same plot as in (a) after removing data points that were below detection with respect to Fe(II), Fe(III), and electrode potential measurements (see text). Solid line is the 1:1 correlation and the dotted lines are a ±30 mV envelope of uncertainty.*

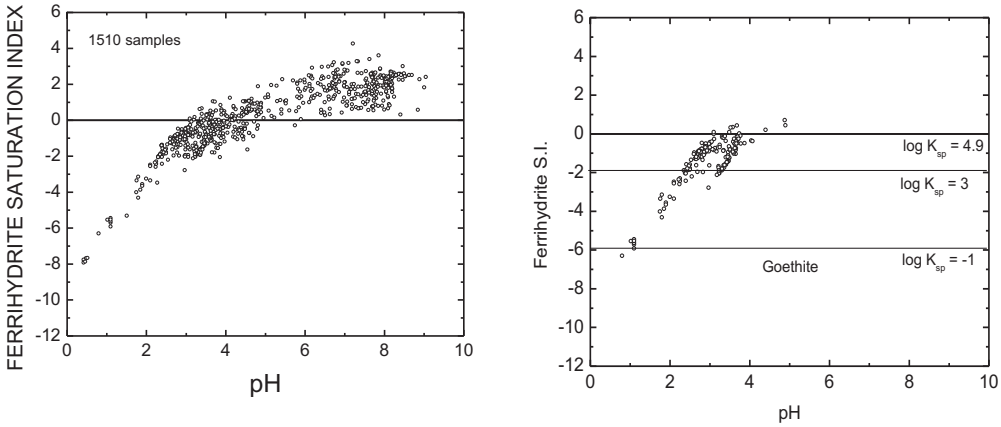

Figure 2 a. Saturation indices for freshly precipitating hydrous ferric oxides showing orders of magnitude supersaturation. b. When points based on data that are below detection limits are removed, the supersaturation disappears.

Geochemical modelling

Codes used for geochemical model computations usually allow the Eh calculations for different redox couples to be independent from each other. This would be the appropriate way of inputting and controlling redox data. Codes also allow for an input Eh or pE to determine the redox speciation for a redox element. This method is not meaningful and should not be used because it assumes redox equilibrium exists for an aqueous solution when it does not exist. Hence, modelling that assumes equilibrium between different redox couples will be incorrect.

Conclusions

These results demonstrate several important points.

1. There is no such thing as a single equilibrium redox potential of a natural water (or aqueous solution).
2. The Nernst equation applies to the equilibrium of an electroactive redox couple or species at an inert conductive electrode surface.
3. You can discuss redox chemistry of a natural water if you have measured the individual redox species, BUT disequilibrium is the rule.
4. Redox potential measurements often do not reach a stable reading because of mixed potentials, kinetic barriers, and electroactive species are too low in concentration.
5. There is no practical analogy between pE and pH (Truesdell, 1968).
6. Analytical measurements of redox species tells you far more about redox conditions of the water than any Eh measurement.
7. Redox determinations of Fe, O_2, N, S, As, Sb, Se, and Cr have been done by labs for many decades and are not very expensive; so why not determine them?
8. **Please do not plot water analyses of redox species on a pE-pH diagram** when we have much better methods (speciation and saturation index calculations). The pE-pH diagram is useful for teaching, but they are limited to one temperature, usually do not include multi-component speciation, and omit ionic strength and complexing effects.

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