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Field Measurements of Geochemical Redox
Parameters
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Field measurements of geochemical redox parameters.

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MANAGEMENT PERSPECTIVE

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Restoration of contaminated groundwater is frequently required at hazardous waste sites. Restoration efforts can involve active and passive techniques, including advanced pump-and-treat systems, in situ injection techniques to promote chemical or biochemical breakdown or stabilization of contaminants, and passive technique such as monitored natural attenuation and permeable reactive barriers. Most techniques for groundwater restoration involve monitoring changes in the groundwater chemistry, including changes in oxidation-reduction processes. This publication is a chapter in a US EPA document which summarizes recommendations by a team of experts on procedures and approaches for monitoring oxidation-reduction processes in groundwater. The specific chapter summarizes group consensus of techniques that are recommended for field measurement of redox sensitive parameters. The volume is geared toward scientists and engineers working at contaminated sites.

Field measurement techniques will continue to be improved for application to hazardous waste sites, with the long-term goal of improving restoration techniques and the quality of groundwater in the vicinity of hazardous waste sites.

Mesures sur le terrain de paramètres géochimiques redox

Wilkin, R.T. et C.J. Ptacek

SOMMAIRE À L'INTENTION DE LA DIRECTION

Ce travail appuie les activités de la DGSE sur la conservation des écosystèmes au Canada et le secteur d'activités de la Nature.

Dans les sites de déchets dangereux, il faut souvent dépolluer les eaux souterraines. Pour ce faire, on peut appliquer des méthodes actives telles que des systèmes perfectionnés de pompage et de traitement, des techniques d'injection *in situ* pour accélérer la dégradation chimique ou biochimique ou la stabilisation de contaminants, et des méthodes passives comme la surveillance de l'atténuation naturelle et de barrières réactives perméables. La plupart des techniques de dépollution des eaux souterraines nécessitent la surveillance de changements relatifs à la chimie des eaux souterraines, dont des changements dans les processus redox. La présente publication constitue un chapitre d'un document de l'USEPA qui présente une synthèse des recommandations d'une équipe de spécialistes au sujet des méthodes de surveillance des processus redox dans les eaux souterraines. On y résume les techniques recommandées par le groupe de spécialistes pour les mesures sur le terrain de paramètres redox sensibles. Le document s'adresse aux scientifiques et aux ingénieurs qui étudient des sites contaminés.

On continuera à perfectionner les techniques de mesures sur le terrain dans le but de les utiliser dans des sites de déchets dangereux et, à long terme, d'améliorer les méthodes de dépollution et la qualité des eaux souterraines près de ces sites.

Session 4 Summary:
Field Measurement of Geochemical Redox Parameters

Richard T. Wilkin and Carol J. Ptacek

4.1 Introduction

Conceptual models of contaminant transport and fate in ground water critically depend on geochemical measurements and their interpretation. Transport and fate processes are often dependent on redox processes because in many cases oxidation-reduction reactions cause changes in speciation that have a marked effect on contaminant mobility and toxicity. The importance of reliable field characterization is especially significant when evaluating redox-sensitive speciation because of the potential for sample alteration (oxidation) during sample collection and handling.

This group considered methods used by environmental scientists to characterize the redox chemistry of ground water in support of site characterization and remedial performance monitoring. The group recognized that a wide variety of analytical techniques are available to quantitate redox-sensitive elements (e.g., Fe, S, N). Selection of the appropriate technique for a given parameter will depend on specific project objectives. It was recognized that project objectives and principal data uses collected in monitoring programs change with time as more site-specific information is obtained and conceptual models evolve. Although a wide variety of techniques are available for redox characterization (see Appendix A), members of this group agreed that standards for improved field practices are needed (see, for example, U.S. Geological Survey, 1997). Methods of analysis identified during the group discussion are briefly reviewed in this chapter, and include Eh, dissolved oxygen, iron speciation, sulfur speciation, nitrogen speciation, and alkalinity.

4.2 Sampling and Measurement Objectives

Sample collection programs are designed around goals associated with specific project objectives. Data Quality Objectives (DQOs) define the types, quality, and quantity of data that are required by the various aspects of a project. With DQOs in place, appropriate sampling methodologies, analytical protocols, and specific methods may be considered and selected. For example, DQOs may be different if project goals put emphasis on detection and monitoring of contaminant concentrations or whether geochemical speciation and the development of site conceptual models are targeted goals.

The principal objective of geochemical characterization in site assessment and remedial performance monitoring is to obtain water quality information, with no alteration of water chemistry, from a chosen sampling point. Such uncompromised data are critical in developing accurate conceptual and quantitative models of contaminant transport and fate. There was strong agreement among the group that sample collection practices and measurement techniques are among the greatest challenges to developing reliable site conceptual models. Several categories of ground-water sampling methods were recognized: accumulation or diffusion samplers, purge techniques with flow-through cells, and bailing. The generally recommended and most commonly practiced method is low-flow, minimal draw-down purging and sampling. Low-flow methods minimize chemical and hydrological disturbances in and around the well. In some situations, multiple-tube bundle piezometers or diffusion samplers may provide the best method for collecting ground-water samples without chemical alteration. Bailing techniques were not recommended for purposes of redox characterization because of the likelihood of changing water chemistry by unavoidable reaction with air.

Measurements of geochemical parameters can be divided into three categories: laboratory, in situ, and purging or field measurements. Laboratory analyses are carried out on preserved samples for characterization of total or selected metals, anions, and organic constituents. In some cases redox integrity of dissolved components can be

preserved by acidification (e.g., for NO_3^-/NH_4^+) because oxidation rates generally decrease substantially with decreasing pH. In situ measurements such as down hole probes or contained sampling devices are desirable for the measurement of unstable parameters that are ideally made at well conditions. In-situ measurements are potentially advantageous for the determination of dissolved oxygen, temperature, and oxidation-reduction potential. Project objectives may or may not require the extra cost and effort required to collect data using in-situ techniques.

Measurements carried out in the field include electrode measurements of DO, pH, specific conductance, Eh, and other ions using ion-selective electrodes. Field-deployable techniques for ions also include UV-Vis spectrometry and ion chromatography. Field analyses are made to gather information in the field to guide activities and/or because the measured parameters are considered to be too unstable to transport samples without compromising their chemical integrity. There was general agreement that unstable parameters, best measured in the field at the time of sample collection, include pH, turbidity, DO, ferrous iron, alkalinity, sulfide, and oxidation-reduction potential. Measurements of these parameters are ideally made during well purging. Members of the group reported a variety of demonstrated techniques for preserving the redox integrity of samples pumped to the surface, such as: minimizing tubing length, use of high-quality tubing with low oxygen diffusion coefficients, use of syringes with luer-lok fittings, preventing direct exposure of tubing and all electronic equipment to sunlight, and ensuring air-tight seals. Specific methods are discussed below for the measurement of Eh, DO, and speciation of iron, sulfur, and nitrogen (Table 4.1).

Table 4.1 Redox Parameters and their Common Methods of Measurement

Parameter	Common Field Methods	Standards for Performance Assessments	References
Oxidation-Reduction Potential (ORP)	Combination Platinum electrode with Ag/AgCl reference electrode; KCl filling solution	Zobell's solution; Light's solution	Langmuir (1971) Nordstrom (1977) Standard Methods for the Examination of Water and Wastewater (1999)
Dissolved Oxygen (DO)	Membrane-covered electrode Colorimetric (high range, indigo carmine) Colorimetric (low range, rhodazine D) Modified Winkler titration	Air-saturated water	Hitchman (1978) Gilbert et al. (1982) White et al. (1990) Standard Methods for the Examination of Water and Wastewater (1999)
Iron Speciation	Ferrous iron colorimetric indicators (1,10 phenanthroline; ferrozine)	Prepared ferrous solutions	Tamura et al. (1974) Stookey (1970)
Sulfur Speciation	Sulfate (turbidimetric); Sulfide (methylene blue colorimetric method)	Prepared sulfate and sulfide solutions	Standard Methods for the Examination of Water and Wastewater (1999) Cline (1969)
Nitrogen Speciation	Nitrate+Nitrite (cadmium reduction) Ammonia (Nessler method; Salicylate method)	Prepared nitrate, nitrite, or ammonia solutions	Standard Methods for the Examination of Water and Wastewater (1999)
Alkalinity	Acid titration	Prepared bicarbonate or carbonate solutions	Standard Methods for the Examination of Water and Wastewater (1999)

4.3 Geochemical Parameters

Eh

The Eh measurement is the most commonly used technique to characterize the oxidation-reduction state of ground water. Eh is the measured potential of a platinum electrode corrected to the Standard Hydrogen Electrode (SHE). Eh is not the same as the oxidation-reduction potential (ORP), which is the direct, uncorrected potential reading of the reference electrode. It was recognized during the group discussion that although measured Eh values usually do not correspond to Eh values calculated using the Nernst Equation with measured concentrations of aqueous redox pairs, e.g., N(V)/N(-III) or S(-II)/S(VI), there is benefit to measuring this parameter in the field. Eh measurements are a relatively easy approach for determining overall redox conditions. Eh measurements should be thought of as qualitative indicators of the state of oxidation or reduction of a natural system (Langmuir, 1971). In rare situations, such as acid-mine waters, high activities of both $Fe(III)$ and $Fe(II)$ provide a dominant and reversible couple that poises Eh measurements (Nordstrom et al., 1979). Many ground waters are not well poised and speciation calculations for ground waters have shown that redox couples typically exist in a state of disequilibrium (e.g., Stumm, 1966; Lindberg and Runnells, 1984). Such systems in disequilibrium yield mixed potentials that may or may not represent the redox distribution of any specific redox couple. The reasons for this include disequilibria in low-temperature ground water (Lindberg and Runnells, 1984; Thorstenson, 1984), poisoning or coating of Pt electrodes (Jackson and Patterson, 1982; Whitfield, 1974), potential measurements reflect mixed potentials with little thermodynamic significance (Morris and Stumm, 1967).

The recommended procedure for measurement of Eh involves the use of a small-volume flow-through cell into which a temperature and Eh electrode is inserted. The type of electrode recommended for ease of use is a high-quality combination Pt electrode typically with a Ag/AgCl reference electrode. After purging the flow-through cell with several volumes of ground-water, Eh readings are recorded until they stabilize or a minimum value is obtained. Often 30 minutes or longer is required for electrode stabilization, but the group generally agreed that waiting >30 minutes for electrode stabilization was not a time-effective practice. Proper preparation and maintenance of the Pt electrode is required, including frequent polishing of the electrode surface, changing of the internal filling solution, and frequent checks with standard solutions that are maintained at ground-water temperature (American Public Health Association et al., 1999). The most common standard solution for reference checks is Zobell's solution (Nordstrom, 1977). Additional check solutions include Light's solution (Light, 1972), and others recommended by electrode manufacturers (i.e., Orion ORP standard). The importance of correcting field measurements of ORP to reference the values to the Standard Hydrogen Electrode was emphasized. To properly reference measured values, correction factors must be available as a function of temperature for the specific type of reference electrode and reference solution used in the measurement assembly. To determine Eh of a sample relative to the Standard Hydrogen Electrode, measure the ORP of both sample and standard solution (at the same temperature). Eh of the sample may then be calculated:

$$Eh = ORP \ (mV) - ORP_{reference \ solution} \ (mV) + Eh_{reference \ solution} \ (mV) \qquad [1]$$

The group discussed the limitations on the use of corrected Eh readings. It was recommended that the readings be used in three ways: 1) as a general guide to interpret other redox data, 2) for speciation of $Fe(II)$ and $Fe(III)$ in acidic mine drainage waters, and 3) for geochemical speciation calculations to determine mineral stability for selected Fe and Mn phases that are stable under intermediate Eh conditions. Views from the session participants varied, but it was recognized that in the absence of a field Eh reading, there was no widely available method of calculating saturation indices for phases such as Fe(oxy)hydroxides, Mn oxides, and Mn and Fe carbonates. It was further recommended that Eh values should not be used to determine saturation indices for phases such as FeS, which incorporate species (HS$^-$) that are not generally responsive to measurement by Pt electrodes (Whitfield, 1974; Walton-Day et al., 1990).

Dissolved Oxygen

Dissolved oxygen (DO) is often the principal oxidizing chemical component in ground water; consequently, DO can be a key parameter governing the mobility of redox-sensitive contaminants, including organic compounds, transition metals, and transuranic metals. DO is also important in governing the nature and level of microbial activity. It is therefore directly tied to the fate of dissolved nutrients and organic contaminants consumed through metabolic processes (e.g., Baedecker and Back, 1979). The concentration of DO in ground water is controlled by local inputs of oxygen-rich meteoric water, microbial respiration, biodegradation of organic matter, and reaction with reduced mineral phases in the aquifer (Champ et al., 1979; White et al., 1990).

The group recognized four major methods for determining DO concentrations: 1) the Winkler titrimetric method, 2) the membrane-covered electrode method, 3) the indigo carmine colorimetric method, and 4) the rhodazine D colorimetric method. Of these methods, the Winkler method (and its modifications) was regarded as the most accurate and precise technique for determining DO. This method has served as a benchmark for laboratory comparisons and calibration of the electrochemical and colorimetric techniques (e.g., Reynolds, 1969; Hitchman, 1978; Gilbert et al., 1982). From the field perspective, the Winkler method is cumbersome and it uses reagents that can be hazardous to manage in the field. Seven different Winkler modifications exist and selection of the appropriate modification requires prior knowledge of a sample that is often not available during field investigations.

Because of the difficulties associated with carrying out Winkler titrations in the field, alternative methods such as membrane-covered polarographic electrodes are widely used (Hitchman, 1978). Membrane-covered electrodes are simple to use and calibration checks are usually limited to determining oxygen concentrations in water-saturated air (American Society for Testing Materials, 1992). Electrodes are ideally suited for in-situ measurements of DO concentrations and for continuous monitoring of oxygen levels. Dissolved oxygen electrodes do not function at temperatures greater than about 50 °C, which is not a limitation for most ground waters. Membrane fouling can be a common cause of difficulty, and electrode measurements can be inaccurate without any indication that poor results are being obtained. Hydrogen sulfide, thio-organic, and other organic compounds are the most problematic to continued reliable electrode performance. These species react irreversibly at the electrode surface and detrimentally affect electrode response and accuracy.

Several colorimetric methods have been developed for the measurement of DO. The indigo carmine (blue) and rhodazine D (reddish violet) methods are the most prominently used techniques (Gilbert et al., 1982; White et al., 1990; American Society for Testing Materials, 1995a). These colorimetric procedures provide quick and convenient methods for accurate field measurements of dissolved oxygen. Colorimetric reagents utilize oxidation-reduction indicators that upon reaction with dissolved oxygen in water transform from reduced, colorless forms to oxidized, colored forms. The extent of color formation is proportional to the concentration of dissolved oxygen and can be measured by visual comparison to sets of liquid color standards or with a spectrophotometer. Color development by reaction with dissolved oxygen is independent of salinity so that a wide range of sample types from seawater to fresh water can be analyzed with these methods without correction (Gilbert et al., 1982).

Because the colorimetric reagents involve oxidation-reduction reactions to indicate the concentration of DO, other redox species in ground water can influence the result of colorimetric determinations (Gilbert et al., 1982). Concentrations of the easily reduced species Fe(III), Cr(VI), and Cu(II) can lead to erroneously high DO values when rhodazine D is used (White et al., 1990). A potential cause of false-positive readings using the rhodazine-D reagent in ground-water studies may be the presence of very fine-grained ferric hydroxide colloids. Both Fe(II) and Fe(III) as well as nitrite were shown to lead to inaccurate determinations of DO using the indigo carmine reagent (Gilbert et al., 1982). Hydrogen sulfide does not interfere with either colorimetric technique. The effects of dissolved organic carbon (DOC) on the use of the rhodazine D and indigo carmine reagents are incompletely understood.

Winkler, electrode, and colorimetric methods for determining DO have different strengths and weaknesses. For projects requiring the highest available quality (in terms of accuracy and precision over a wide range of DO concentrations), the extra effort associated with the Winkler methods is warranted. Where data quality objectives are not as strict, both electrode and colorimetric methods are acceptable. Electrodes are generally reliable at DO levels above 1 mg/L, but are less accurate at levels below 1 mg/L. Multiple methods are preferred if high quality data are required to meet project objectives (Wilkin et al., 2001). Figure 4.1 shows a decision tree discussed by the group that may be useful for selecting an appropriate method or methods for DO determination.

The most common and convenient quality check for field measurements of DO is air-saturated water. Air-saturation is achieved using an aerator or through manual agitation. Members of the group pointed out that using such methods can cause water to become supersaturated with respect to air. Air-saturated DO values are mainly dependent on temperature and less so on salinity (Figure 4.2). Thus, when quality check values are reported the temperature must be specified for the check to be meaningful.

Iron Speciation

Iron is present in ground water as dissolved ferrous iron (Fe(II)), colloidal particles containing either ferric or ferrous iron, and as dissolved ferric iron (Fe(III)). The relative and absolute abundances of these iron forms vary widely depending mainly on pH and redox state of ground water. Dissolved forms may be unassociated or
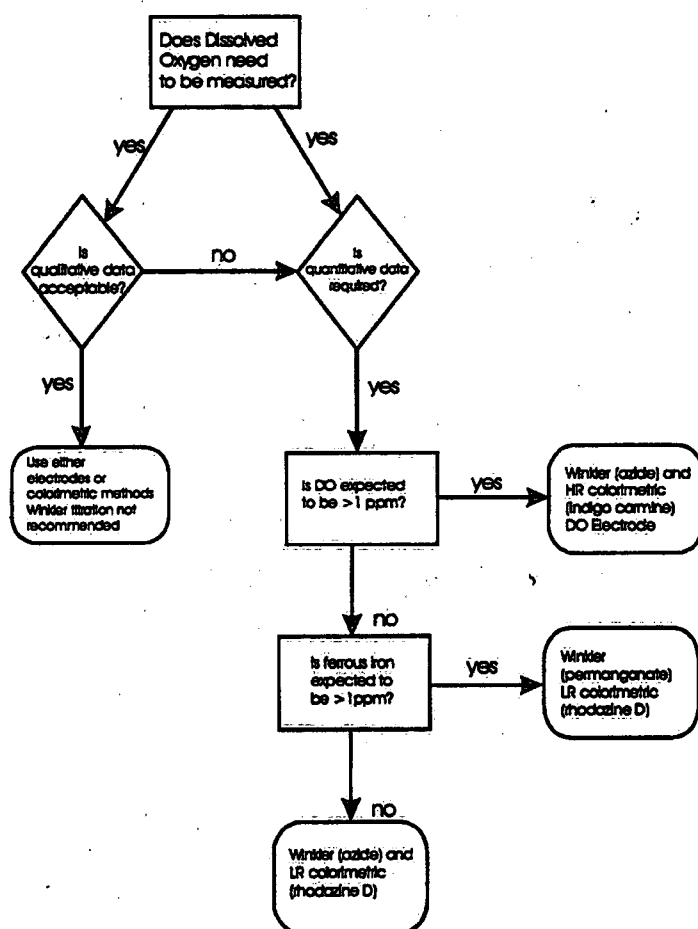
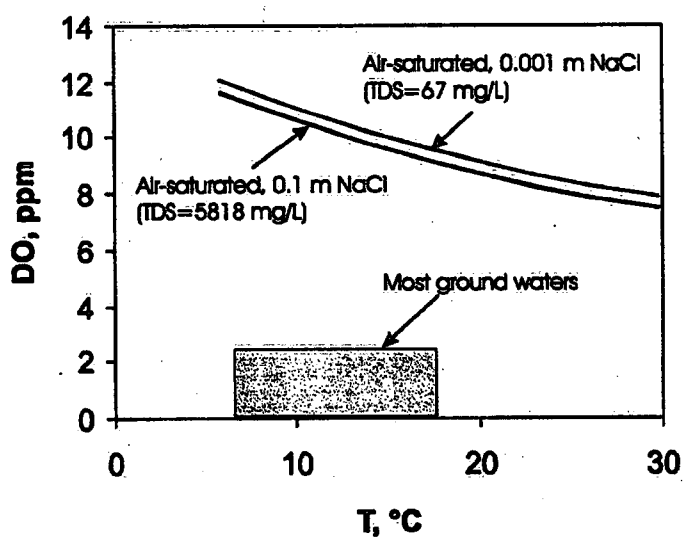**Figure 4.1** Decision tree for selecting method for determining concentration of DO.

Figure 4.2 Air-saturated DO concentration in water.

complexed with organic or inorganic ligands. Dissolved iron is generally considered to be that fraction passing through a 0.45 μm filter paper, however, water filtered in this way may still contain colloidal iron that will dissolve upon addition of an acid.

Ground waters containing dissolved oxygen at concentrations above 1 mg/L will seldom contain concentrations of dissolved iron above 1 mg/L. Exceptions to this general rule are more acidic ground waters (pH<4) in which the solubility of ferric oxyhydroxides is sufficiently high to be detected using standard methods of analysis. The solubility of ferrous iron increases under reducing conditions, where oxygen is depleted and Eh values are low (<0 mV). In zones of intense iron reduction, concentrations of ferrous iron may reach levels as high as several hundred mg/L.

Dissolved Fe(II) concentrations in ground waters are commonly measured using colorimetric techniques with complexing reagents, such as 1,10 phenanthroline (Tamura et al., 1974), ferrozine (Stookey, 1970 as modified by Gibbs, 1976; To et al., 1999), and bipyridine (e.g., Baedecker and Cozzarelli, 1992). There was general agreement among the group that ferrous iron measurements using colorimetric reagents should be completed soon after sample collection. Minimizing the amount of time between sample collection and Fe(II) measurement is necessary because of the relatively fast oxidation rate of ferrous iron at near-neutral pH. Ferrous iron oxidizes following the overall reaction

$$Fe^{2+} + 5/2H_2O + 1/4O_2 = Fe(OH)_3 + 2H^+$$

The abiotic rate of ferrous iron oxidation is principally controlled by the partial pressure of O_2, pH, and alkalinity. At pH<3.5, the oxidation rate of ferrous iron is slow and independent of pH. At pH below about 5, however, iron-oxidizing bacteria greatly increase the rate of iron oxidation. For purposes of sample preservation biotic ferrous iron oxidation is avoided by filtration and acidification. At pH>3.5, a pH-dependent rate equation is given by Eary and Schramke (1990):

$$-d[Fe^{2+}]/dt = k[Fe^{2+}]P O_2[OH^-]^2$$

Figure 4.3 shows the rate of ferrous iron consumption via oxidation as a function of pH (6-8) and $P O_2$ (0.02 and 0.2 bars) estimated using this equation. Note that at pH 7, ferrous iron concentrations will decrease by a factor of two in < 15 minutes at air-saturated conditions. A sample recovered from a well and brought to the surface does not necessarily experience the full atmospheric $P O_2$ of 0.2 bars unless it is continuously agitated. A more realistic value of $P O_2$ = 0.02 bars still imparts a fast loss of Fe(II), especially at pH > 7 (Figure 4.3). These calculations illustrate the importance of carrying out Fe(II) measurements immediately after sample collection.

A common practice for estimating Fe(III) is to measure total iron (ΣFe) on filtered and acidified samples and subtract from that quantity the concentration of ferrous iron from measurements made in the field. The group agreed that no assumptions should be made about the speciation of the iron fraction represented by ΣFe-Fe(II). At near-neutral pH and in the absence of significant concentrations of DOC there should be reasonable agreement between total iron and Fe(II). However, ΣFe on filtered samples should not be assumed to be equal to Fe(II) due to the potential formation of soluble Fe(III) - DOC complexes. Measurement of total iron can in many instances be a useful quality check for Fe(II) measurements made in the field.

Acid mine drainage represents a special case with respect to iron measurements because at low pH the solubility of Fe(III) increases significantly. An accurate determination of the abundances of Fe(II) and Fe(III) is especially important because such waters are typically rich in iron and charge balance calculations strongly depend on the Fe(II)/Fe(III) ratio (see To et al., 1999). When dealing with low pH waters it is desirable to directly measure Fe(III) concentrations (To et al., 1999).

Field quality checks can be carried out using purchased or prepared iron solutions. Mohr's salt (ferrous ammonium sulfate) can be used as a standard ferrous solution. Standard solutions should be prepared daily and ideally should be made from deoxygenated water, prepared by purging with nitrogen gas.

Sulfur Speciation

Dissolved sulfur may be present in ground water as sulfate (most oxidized form), sulfide (most reduced form), or as species with oxidation states intermediate between sulfate and sulfide including polysulfides, sulfite, and thiosulfate. Concentrations of the intermediate sulfur species are typically low in ground water and their occurrence is believed to be restricted to redox interfaces that separate reducing hydrogen sulfide-bearing waters from oxygenated waters. Such interfaces can occur within aquifers or in mixing zones between ground and surface waters. Sampling techniques and methods for determining the concentration of intermediate sulfoxyanions can be
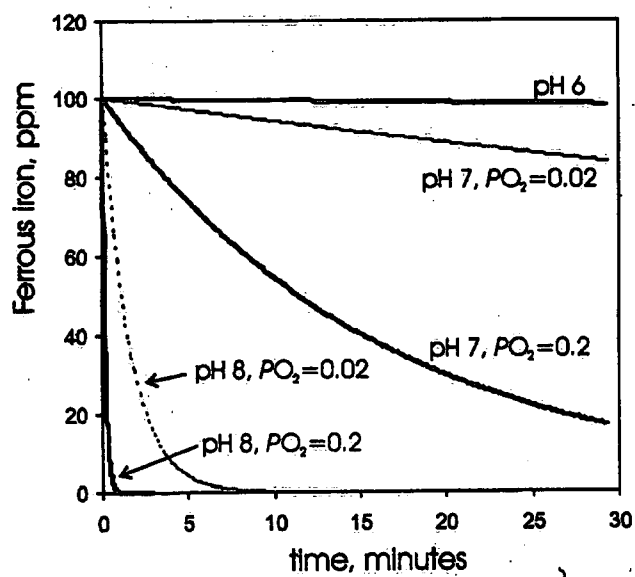
Figure 4.3 Ferrous iron oxidation kinetics at pH 6-8 and PO_2 at 0.02 and 0.2 bars.
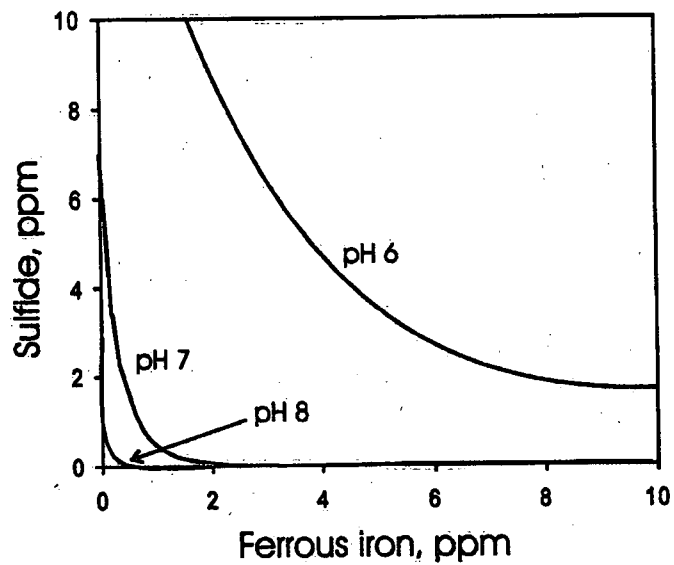

Figure 4.4 Iron monosulfide solubility at pH 6-8 (Ionic strength = 0.0).

found in Moses et al. (1984). Sulfate concentrations in ground water vary widely from below 1 to several thousand milligrams per liter. The highest concentrations of sulfate are typically found associated with acidic surface drainage produced from the oxidative weathering of metal sulfides. Sulfate concentrations in ground water are measured using gravimetric methods (precipitation as barium sulfate), the barium dichloride turbidimetric method, or using laboratory techniques such as ion chromatography or capillary electrophoresis. Preservation is generally not a problem for sulfate unless samples are especially rich in DOC that can be respired by sulfate reducing bacteria. Because samples collected for anions are typically not acidified, ferrous iron-rich samples may be problematic if sulfate becomes incorporated into iron hydroxide precipitates that form prior to sample analysis.

Hydrogen sulfide is produced in anoxic systems through the bacterial reduction of sulfate. Measurements of total sulfide in ground water include $H_2S(aq)$, HS^-, and acid-soluble metal sulfides present in colloidal suspended materials. These species can react rapidly in the presence of oxygen so samples must be collected with a minimum of aeration. Methods for determining hydrogen sulfide concentrations include electrode, gravimetric, iodometric, and colorimetric techniques.

The handling and storage methods are critical for water samples containing concentrations of dissolved sulfide. Ideally, measurements are carried out immediately after sample collection. Preservation of samples will otherwise be necessary to prevent losses through volatilization or oxidation. At pH less than ~6, volatilization of H_2S can be a problem, i.e., $H_2S(aq) \rightarrow H_2S(gas)$. Sulfide anti-oxidant buffers (SAOB) are alkaline solutions that contain complexing agents such as EDTA and a reductant such as ascorbate. Hydrogen sulfide is then released from the alkaline solutions by acidification and purging with an inert gas such as nitrogen or argon.

The most commonly used methods for determining dissolved sulfide concentrations are modifications of the methylene blue technique described by Cline (1969). In this method, reduced sulfur species (H_2S, HS^-, S^{2-}) react with diamine (N,N-dimethylphenyl-1,4-diamine) in the presence of ferric chloride to form a blue complex that is measured spectrophotometrically at a wavelength of 670 nm. Visual colorimetric comparison kits are also available. Detection limits down to 0.01 ppm sulfide are obtainable. Standard solutions can be prepared by dissolving into deoxygenated water quantities of sodium sulfide ($Na_2S \times 9H_2O$). The concentration of sulfide is then measured by adding excess iodine and back-titrating with thiosulfate. To minimize oxidation of sulfide species, reagents should be added to samples immediately after sample collection followed by spectrophotometric measurement.

Sulfide electrodes that use silver sulfide as the sensing element are generally not used in field studies. Specific ion electrodes are better suited for laboratory studies conducted under controlled conditions. Long response times and poisoning of the reference electrode by sulfide have limited the use of sulfide-selective electrodes (Lawrence et al., 2000). Gravimetric determinations of sulfide concentrations are appropriate in situations where concentrations of dissolved sulfide are > 5 mg/L. Solutions can be directly collected into bottles containing quantities of Zn acetate or Cd acetate solutions. A 1 L sample of solution containing 5 mg/L dissolved sulfide will produce a mass of 15.2 mg or 22.5 mg of ZnS or CdS precipitate, respectively.

In ground-water systems containing dissolved sulfide, dissolved oxygen concentrations will be generally 0 or < 1 mg/L. If hydrogen sulfide is present in ground water above 1 mg/L, concentrations of ferrous iron will generally be negligible. The concentrations of ferrous iron and hydrogen sulfide in surface and subsurface environments are generally governed by the solubility of iron monosulfide minerals, such as mackinawite, i.e.,

$$FeS + H^+ = Fe^{2+} + HS^-$$
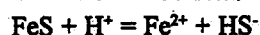
The equilibrium constant (K_{sp}) for this reaction is $10^{-3.1}$ where FeS is taken to be crystalline mackinawite (Davison, 1991). In Figure 4.4 the solubility curves of mackinawite are plotted at three pH values from 6 to 8. Note that solubility decreases as pH rises, and that when concentrations of either iron or sulfide are low the other is necessarily high.

Nitrogen Speciation

The common nitrogen species present in ground water include nitrate (NO_3^-), nitrite (NO_2^-), and ammonia (NH_3). At near-neutral pH typical of most ground water, ammonia is present predominantly as the ammonium ion (NH_4^+). Although colorimetric methods are available to quantitate nitrate, nitrite, and ammonia, field determination using these methods is not generally needed as long as laboratory measurements can be made within specified holding times.

The cadmium-reduction method can be used to determine the amount of nitrate+nitrite in ground water. In this method, cadmium metal is used to reduce nitrate to nitrite. The nitrite ions then react with sulfanilic acid and gentistic acid to form an amber-colored compound (American Society for Testing Materials, 1995b). Strong oxidizing and reducing substances are possible interfering components; ferric iron, in particular, will cause high results.

Ammonia is produced during the microbiological decay of organic matter. Two colorimetric methods for ammonia are the Nessler method and the Salicylate method. The Nessler method is probably the most commonly used method and develops a yellow color proportional to the concentration of ammonia. High concentrations of calcium and magnesium may cause interferences. Ferrous iron and dissolved sulfide can also interfere with ammonia determinations using this method.

Samples collected for nitrogen speciation should be preserved by keeping cold (4°C) and measured within specified holding times, generally < 48 h. Longer holding times are possible by acidifying samples with sulfuric acid and keeping them cold. Before analysis the samples should be brought back to room temperature and neutralized by adding base.

Alkalinity

Alkalinity is a measure of the acid neutralizing capacity of dissolved solutes in a water sample and is reported as equivalents per liter or as mg/L of $CaCO_3$. Alkalinity is not typically included as a redox parameter. The group included this parameter because alkalinity production often accompanies oxidation-reduction reactions, e.g., in sulfate or iron reduction. The alkalinity concentration consists of the sum of titratable carbonate and titratable non-carbonate species in a water sample, including proton-accepting organic compounds. Proton-accepting species include CO_3^{2-}, HCO_3^-, OH^- (and metal-OH complexes), HS^-, PO_4^{3-}, ammonium, silicate, and borate. The alkalinity measurement is important for evaluating charge balance of a solution and is a critical component of modeling approaches using geochemical speciation computer packages. Because particulate materials can be an important sink for acid, alkalinity determinations should be made in filtered or low-turbidity waters (turbidity < 5 NTU).

The most accurate determinations of alkalinity are made in the field at the time of sample collection. Fixed end-point titrations to pH 4.3 are suitable for ground waters with negligible concentrations of dissolved organic matter or titratable species other than inorganic carbon. For more complex ground waters, especially those rich in dissolved organic material, fixed end-point titrations will give inaccurate results (see Hemond, 1990). Total alkalinity should then be determined by measuring pH as a function of titrated acid to a pH of 3.0. Using this method, alkalinity is calculated from the volume of acid added to reach the end-point pH. The end-point is determined graphically by plotting pH as a function of titrant volume and locating the inflection point. The importance of protecting the sample from oxidation was also discussed. In high Fe(II) waters, the oxidation of Fe(II) to Fe(III) can produce sufficient acid to bias the titration, resulting in an underestimation of actual alkalinity. Rapid analysis is recommended, and protection of the sample from aeration is needed for accurate measurements of alkalinity in iron-rich water.

4.4 Summary

A variety of measurement options are available for monitoring the most important redox parameters in ground water. The core list of parameters identified by this group was Eh, dissolved oxygen, iron speciation, sulfur speciation, and nitrogen speciation. Selection of the appropriate technique for a given parameter will depend on specific project objectives. It was recognized that project objectives and principal data uses collected in monitoring programs change with time as more site-specific information is obtained and conceptual models evolve. There was general agreement that there exists a need for improved standards for routine field practices. There was strong agreement among the group that sample collection practices and measurement techniques are among the greatest challenges to developing reliable site conceptual models.

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