Obtaining stable redox potential readings in gneiss groundwater and mine water: difficulties, meaningfulness, and potential improvement

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Abstract Natural samples were run in three parallel flow-through cells in the laboratory in order to study the difficulties of obtaining stable redox potential readings, especially in gneiss groundwater and mine water with little redox buffer capacity. Redox potentials were recorded every 2 min for up to 5 days. Measured redox potentials were compared to means of partial potentials, modeled based on species-selective determinations of the most predominant redox-sensitive elements iron and nitrogen. Redox potentials stabilized reproducibly within minutes for a synthetic redox buffer solution and two well-buffered acid mine water samples at pH 2.3 and 3.5. For waters in redox disequilibrium, species-selective analytics might still be the better alternative compared to measuring the redox potential as summary parameter for modeling species distribution. In cases where the redox potential is the only readily available parameter, filtration and possibly acidification is recommended for quicker stabilization of redox potential readings and less deviations between measured and modeled values. A minimum of 2% was achieved in the samples investigated, however, often after measuring significantly longer than the previously suggested 30 min. Final stabilization could take up to several hours in waters with low buffer capacity.

Résumé Afin d'étudier les difficultés à obtenir des lectures stables des potentiels redox, notamment sur les eaux souterraines présentes dans des gneiss et dans les mines, qui présentent un faible pouvoir tampon, des échantillons ont été prélevés régulièrement en laboratoire, dans trois cellules d'écoulement parallèles. Les potentiels redox ont été enregistrés toutes les deux minutes durant cinq jours. Ces potentiels redox mesurés ont été comparés aux moyennes des potentiels partiels, modélisés à partir des déterminations sélectives des espèces chimiques des éléments sensibles aux conditions redox les plus prédominants, le fer et l'azote. Les potentiels redox se sont systématiquement stabilisés en quelques minutes pour une solution tampon synthétique et pour deux échantillons d'eaux de mines acides bien tamponnées à pH 2.3 à 3.5. Pour les eaux en déséquilibre redox, des analyses sélectives des espèces chimiques seraient toujours la meilleure alternative aux mesures sommaires du potentiel redox, pour modéliser la distribution des espèces. Dans les cas où le potentiel redox est le seul paramètre directement disponible, une filtration et éventuellement une acidification sont recommandées pour obtenir une stabilisation plus rapide des lectures des potentiels redox, et pour réduire les écarts entre les valeurs mesurées et modélisées. Un minimum de 2% a été atteint parmi les échantillons étudiés, mais en prolongeant souvent les mesures au-delà des 30 minutes suggérées initialement. La stabilisation finale pourrait prendre jusqu'à plusieurs heures dans des eaux à faible pouvoir tampon.

Resumen Se han llevado a cabo experimentos en laboratorio sobre tres muestras naturales en tres células de flujo paralelas, para estudiar las dificultades en la obtención de medidas de potencial redox estables, especialmente en aguas subterráneas procedentes de gneisses y en agua de minas con capacidades tampón redox bajas. Los potenciales redox fueron medidos cada dos minutos durante más de cinco días. Los potenciales redox medidos fueron comparados con medias de potenciales parciales, modelizados en base a determinaciones selectivas de especies de hierro y nitrógeno, los elementos predominantes redox-sensitivos. Los potenciales redox se estabilizaron de forma reproducible en minutos en una solución redox tampón y dos muestras de agua ácida de pozos de mina a pH 2.3 y 3.5. Para aguas en desequilibrio redox los análisis selectivos por especies deberían ser todavía la mejor alternativa comparados con la medida del potencial redox como una suma de parámetros para

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modelizar la distribución de especies. En casos en los que el potencial redox sea el único parámetro fácilmente obtenible, se recomienda una filtración y una posible acidificación para una estabilización más rápida de las medidas de potencial redox y que haya menos desviaciones entre los valores medidos y los del modelo. En las muestras investigadas se consiguió un mínimo de un 2%, sin embargo, a menudo incluso después de medidas significativamente más largas que las previamente sugeridas de 30 minutos. La estabilización final tuvo lugar después de más de varias horas en aguas con capacidad tampón baja.

Keywords Redox potential · Electrochemistry · Equipment/field techniques · Hydrochemistry · Hydrochemical modeling

Introduction

Reduction–oxidation reactions (commonly referred to as redox) involve the transfer of electrons from one chemical species to another. The significance of such electron-transfer reactions manifests itself by exerting essential control on the reactivity, toxicity, bioavailability, and solubility (thus transport) of elements that exist in more than one oxidation state, so-called redox-sensitive elements. Ten out of the 16 inorganic elements for which the U.S. Environmental Protection Agency has specified a maximum contaminant level (MCL) are actually redox-sensitive. Theoretically, redox reactions are defined in terms of the free electron activity, which is, in fact, non-existent in aqueous solutions. The extent of these reactions is expressed by a potential that is a measure of the affinity of a chemical species for electrons.

Being an intensity factor, the redox potential (E_H) characterizes as a summary parameter the tendency, but not the capacity, of a system for oxidation or reduction. It is a direct potentiometric measurement of the equilibrium established between all oxidized and reduced species in solution, and is based on the Nernst equation (Eq. 1), which relates potential to the activities of electroactive species:

$$E_H = E^o - \frac{RT}{nF} In \frac{\{Red\}^{\mathrm{a}}}{\{Ox\}^{\mathrm{b}}} \tag{1}$$

Where R, T, n and F are the gas constant, temperature in Kelvin, number of electrons transferred in the process and the Faraday constant, respectively. The parameter E^0 is the standard electrode potential dependant on the standard hydrogen electrode (SHE) and the natural logarithm contains the ratio of the activity of the reduced to the activity of the oxidized species, with their stoichiometric coefficients a and b, respectively.

Although measured redox potentials are reported with respect to the SHE at standard state (1 bar gas pressure at 25°C, pH 0), secondary reference electrodes, such as Calomel or Ag/AgCl electrodes, with known potentials to the SHE are used for convenience in the field. In practice, redox values are determined by measuring the potential difference between an inert metal electrode (usually made of platinum) in contact with a solution and one of the above-mentioned secondary reference electrodes connected to the solution by a salt bridge. Electron exchange with the reduced and oxidized species takes place at the inert metal electrode. The measurement is done at zero net exchange current across metal-solution interface i.e., when electrochemical reversibility is maintained. This reversibility is attained when the individual exchange currents of electroactive redox ions exceed 10^{-7} amp×cm^{-2}, which corresponds to concentrations of about 10^{-5} molal (the number of moles of a solute per kilogram of solvent) and higher for both the donor and acceptor of electrons that form a redox couple (Morris and Stumm 1967).

One of the fundamental requirements for a meaningful redox potential measurement in a given time is the attainment of equilibrium between the different redox couples in a solution and the electrode surface, thus resulting in a stable redox reading. A number of earlier studies such as that carried out by Berner (1963) reported encouraging clarity of results. In his studies of hydrogen sulfides in marine sediments, he reported consistency between measured redox values and calculated values based on sulfur speciation. Thorstenson (1970) sampled several reducing environments and found consistency in measured and calculated redox potentials for sulfur and nitrogen redox couples. Nordstrom et al. (1979) reported redox consistency between measured and calculated redox potentials for iron complexes in acid mine drainage. In summary, it seems that reversible, thermodynamically meaningful redox potential measurements are possible in acid mine waters and iron-, manganese-, or sulfide-rich groundwaters or sediments (Langmuir 1997 and references herein).

In many natural systems, such as surface or waste waters with a predominance of the redox-sensitive elements carbon, nitrogen, oxygen, hydrogen, and sulfate (Langmuir 1997), however, electron transfer reactions are very slow, and redox couples thus generally far from equilibrium. Consequently, kinetics, apart from equilibrium thermodynamics, plays a very significant role. The measured redox potential, as summary parameter, can then differ significantly from the calculated potentials for each redox couple. Linder and Runnells (1984) concluded from their studies of groundwater redox reactions that neither measured E_H, nor any single calculated E_H, represents “a master redox value for the water”. For many natural systems, low exchange currents over the electrode interface render measurements unreliable (Hostettler 1984; Thorstenson 1984). Although a description on how redox potential measurements should be carried out is given in a U.S. Geological Survey (USGS) field manual, the USGS itself abstains from recommending this parameter for a routine determination and adds that if readings do not stabilize within 30 min, field measurements of redox potential should be abandoned (Nordstrom and Wilde 1998).

Regardless of the prevailing dissatisfaction about the reliability of redox potential measurements, the redox potential is used for a wide range of applications: as a monitoring parameter during sample collection (Puls and Barcelona 1996), for performance evaluation of pump-and-treat remediation, for evaluation of the stabilities of redox-sensitive elements in a given sample (Keely 1989), and as a master variable in all thermodynamic modeling. Both lab and field measurements are often based on poorly defined "steady-state readings" or the 30-min criterion found in field manuals such as that of the USGS (Nordstrom and Wilde 1998). Thus the redox potential is assigned either a mean value from single measurements that showed less than 10% relative standard deviation within 30 min or the measurement is aborted with the comment "no thermodynamic equilibrium reached within the time limit assigned". The second option is problematic since geochemical modeling programs such as PHREEQC (Parkhurst and Appelo 1999) require the definition of a redox potential in their input-files. A default value of pE=4 (pE or electrode potential is a dimensionless quantity defined as the negative common logarithm of electron activity. $pE \approx 16.9 \times E_H$ [V] at T=25°C) is assumed e.g., in PHREEQC if no redox potential is entered. Without measured pE, a default pE, or a certain redox couple from which a partial redox potential can be calculated, the calculation of species distribution for redox-sensitive elements is not possible. Geochemical codes that force redox equilibrium for all elements are grossly oversimplified and cannot be expected to reflect realistic redox conditions unless temperatures exceed 100°C (Nordstrom 2000).

The aim of this study was to understand the meaningfulness of the measured redox potential especially in natural systems in disequilibrium and the applicability of the 30 min −10% relative standard deviation (RSD) criterion. In a laboratory setup of three parallel flow-through cells, redox potentials were continuously recorded for 40−120 h in a redox buffer solution, gneiss groundwater, and mine water samples. The effects of filtration and acidification on stabilization of redox potential readings were investigated. To identify the redox reactions controlling the measured redox potential individual redox species were determined analytically and partial redox potentials were derived from geochemical modeling.

Materials and methods

Experimental setup

The initial experimental setup for continuous measurement consisted of three 1-L bottles, each connected to a separate flow-through cell via a pump that drove the water samples between bottles and flow-through cells in a loop, thus allowing continuous circulation between the bottles and the flow-through cells (Fig. 1). The amount of sample pumped was approximately 0.5 L/h to avoid build-up of a self-potential. Standard Tygon tubes and Teflon bottles with properties of low gas permeability and low sorption were chosen.

Each of the flow-through cells was provided with sensors from Sensortechnik Meinsberg GmbH for record-

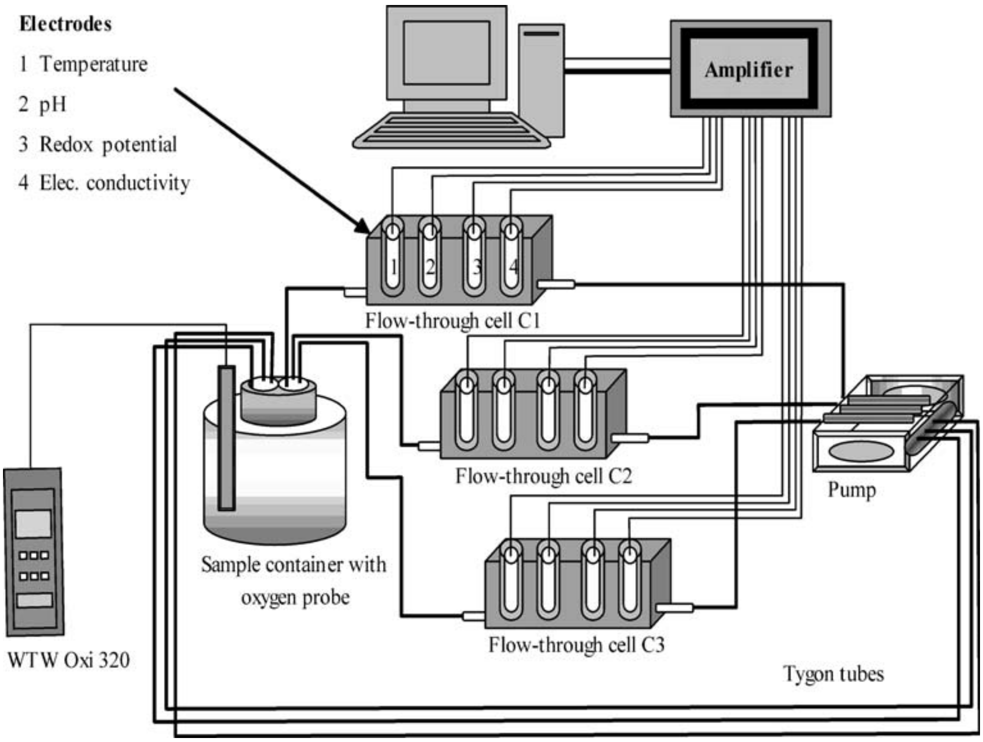

Fig. 1 Schematic presentation of the experimental setup

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ing temperature, pH, redox, and electrical conductivity. While one flow-through cell (C1) was equipped with a used redox potential electrode, C2 and C3 featured new electrodes. The platinum wire-tip of each Ag/AgCl redox electrode used was brushed carefully, cleaned with HCl, rinsed with distilled water, and then tested for functionality against a standard redox buffer solution prior to and at the end of each experiment. The electrodes were connected via an amplifier to a computer for continuous recording at a given time interval of every 2 min and the readings in millivolts were corrected for the difference between the standard potential of the reference electrode being used at the solution temperature (Eq. 2) and the SHE (Eq. 3).

$$E_{0\,25^\circ} = E_t - 0.198(t - 25) \tag{2}$$

$$E_H = E_{0\,25^\circ} + E_{ref} \tag{3}$$

where E_t is the potential measured by a secondary electrode such as a Ag/AgCl reference electrode at the sample temperature t, $E_{0\ 25^\circ}$ the standard potential, E_H the corrected oxidation-reduction potential against SHE, and E_{ref} the known literature potential-value of the secondary reference electrode versus SHE at the temperature t.

Since ensuring air-tightness was difficult, a modification of the setup was necessary. This led to reducing the number of sample containers from three to just one, as shown in Fig. 1. Further, the container was provided with an electrode to monitor the oxygen content hourly. With the help of a self-made glove box filled with nitrogen gas during each experiment, an oxygen-free environment surrounding the whole apparatus was provided. The primary objective was to prevent oxygen from entering the system through junctions or micro-perforations of the tubes and oxygen diffusion through the tubes. All parts that normally came into contact with air were cleaned thoroughly with ethanol, rinsed with distilled water, and dried at 70°C.

Samples for the redox potential laboratory experiments were collected in containers filled without headspace, closed tightly, and transported to the laboratory where they were connected to the setup shown in Fig. 1. Temperature, pH, dissolved oxygen, electrical conductivity as well as redox potential (in accordance with the 30-min criterion) were recorded with WTW sensors during sampling. Experiments were performed with unfiltered, filtered, and filtered-acidified samples. Filtration was performed using nitrogen gas and 0.2-µm cellulose acetate filters (Membrex). Filtration aimed at stabilizing redox kinetics by, at least partially, excluding micro-organisms. For acidification to a pH of about 2, ultrapur™ HCl was used.

For determination of the major cations and anions, the samples were cooled without preservation and analyzed by ion chromatography. Samples for arsenic determination with graphite furnace atomic absorption spectrometry (GF-AAS) and multi-trace element analysis by inductively coupled plasma mass spectrometry (ICP-MS) were filtered with 0.2-µm cellulose acetate filters (Membrex), preserved in 1% (v/v) 6 N ultrapur™ HCl, and 1% (v/v) concentrated ultrapur™ HNO_3, respectively, and cooled until analysis. The redox-sensitive elements Fe^{2+}, Fe^{3+}, NO_2^-, NO_3^- and NH_4^+ were determined photometrically at a maximum of 3 h after sampling and immediately at the end of each experiment.

Sampling locations

Field samples were collected from six sites within the fractured gneiss complex of a former mine area in Freiberg, Germany. One groundwater sample was collected from a well within the hydrogeological test field at the Technische Universität Bergakademie Freiberg tapping the Freiberg gneiss rock formation in 10 to 50 m depth. Five mine water samples were collected in the university´s research mine “Reiche Zeche-Alte Elisabeth”. The mine, which is an abandoned polymetallic sulfide mine with a maximum depth of 740 m, has been mined for more than 800 years (from 1168 to 1969) for silver, lead, copper, and zinc in sulfides such as galena, sphalerite, chalcopyrite, arsenopyrite, and pyrite (Siems 2004). In 1969, it was flooded up to a depth of about 225 m below the surface, which corresponds to the level of the deepest main adit, the so-called “Rothschönberger Stollen”. Water from the Reiche Zeche shaft discharges through this adit and mixes with other drainage waters before finally discharging into the Elbe River. The five sampling sites within the mine were the Reiche Zeche shaft, the Rothschönberger Stollen, seepage water from a shear zone, seepage water from a mined and backfilled ore vein (“Schwarzer Hirsch Stehender”), as well as a small pool of acid mine drainage water (AMD) close to “Schwarzer Hirsch Stehender”.

Results and discussion

An initial test in the experimental setup as shown in Fig. 1 was carried out with a redox buffer solution at pH 7 (commercially available e.g., from WTW as a mixture of 5.28 g/L potassium hexacyanoferrate(II), 4.11 g/L potassium hexacyanoferrate(III), 1.8 g/L potassium dihydrogen phosphate, and 3.9 g/L disodium hydrogen phosphate). Very low fluctuations and rapid attainment of stable readings were expected because of the high concentrations of electroactive species. The test served both to confirm the overall functionality of the experimental setup and each redox electrode as well as to establish criteria as to when a redox recording is to be regarded as “stable reading”. The experiment was run over 72 h in the three parallel flow-through cells and yielded mean values of 498±1.2 mV in the first flow-through cell C1, 482± 0.7 mV in C2, and 466±1.1 mV in C3. A mean for all three cells is shown in Fig. 2 (solid diamonds). Considering the first 30 min only, mean values were 487±1.6 mV

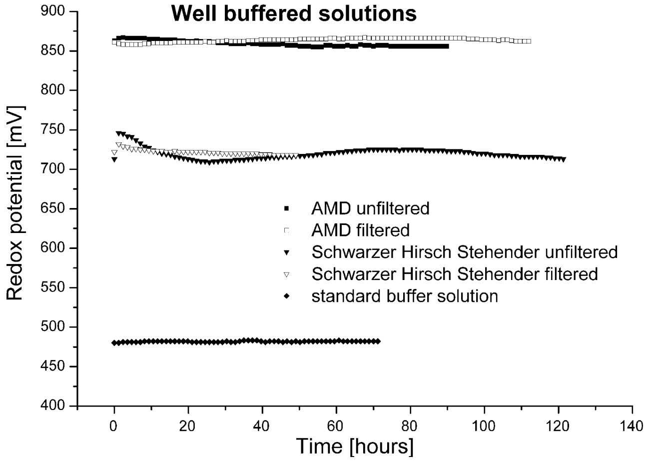

Fig. 2 Comparison of redox potentials measured for a standard buffer solution, filtered and unfiltered acid mine drainage (AMD) (pH 2.3) and a less acidic (pH 3.5) mine seepage water shows that rapid stabilization of recorded values characterizes these solutions

in C1, 480±0.5 mV in C2, and 464±1.0 mV in C3. As expected, the redox potential readings stabilized immediately and average relative standard deviations over the experimental run time of 72 h were 0.13%, over 30 min 0.22%. That is significantly less than the set criterion of a maximum of 10% RSD.

Chemical composition of the groundwater and mine water samples were determined before and after circulation in the flow-through cells (complete data can be found as Electronic supplementary material). Table 1 shows the concentrations for the redox species of iron and nitrogen which were determined individually by photometry.

The only natural sample in which stable readings were obtained as fast and with as little fluctuations as in the redox buffer solution, was, as expected, the acid mine drainage sample. Mean readings for the three flow-through cells were 858±0.6 mV (0.08% RSD) after 30 min and 861±2.4 mV (0.28% RSD) at the end of the experiment after 112 h (squares in Fig. 2). The AMD sample was taken from small acidic pools formed by seepage water from the low-grade ore at several localities in the horizontal shafts of the Freiberg research mine. It is characterized by low pH of 2.3, high electrical conductivity of 5 mS/cm, and high concentrations of iron (up to 840 mg/L) and arsenic (up to 7.8 mg/L). Low pH is known to retard redox processes, which is a reason for its application for the conservation of certain redox-sensitive elements such as iron and arsenic (McCleskey et al. 2004). The samples clearly showed the existence of redox buffering effects. As can be seen in Fig. 2, the difference between the unfiltered and filtered samples is negligible. The maximum standard deviations between C1, C2, and C3 were 6 mV and 8 mV for the unfiltered and filtered samples, respectively. Maximum deviations between initial and final potentials do not extend beyond 10 mV for all flow-through cells in both cases of unfiltered and filtered samples.

For a less acidic sample (pH 3.5) collected from seepage water in a mined and backfilled ore vein ("Schwarzer Hirsch Stehender") stable redox potential readings were also obtained within the 30 min-10% RSD criterion (triangles in Fig. 2). However, mean readings for the unfiltered sample (solid triangles) after 30 min (738± 18 mV) still showed larger fluctuations (2.4%) compared to those at the end of the experiment after 122 h (720± 7 mV, 1% RSD). Filtering the sample yielded both more overall stable readings and no differences in RSD after 30 min (722±3 mV, 0.3% RSD) compared to the end of the experiment (731±3 mV, 0.4% RSD) (open down triangles).

Significantly larger fluctuations in redox potential readings were observed for all other samples, namely the

Table 1 Iron and nitrogen redox species as analyzed by photometry for the groundwater and mine water samples (full chemical analysis can be found as Electronic supplementary material)

Samples	Start/end[a]	pH	Fe^{2+}	Fe^{3+}	NO$_3^-$	NO$_2^-$	NH$_4^+$
Hydrogeol. test field (unfiltered)	S	6.4	0.04	0.03	5	0.004	0.02
	E	5.9	0.003	0.003	4	0.003	0.003
Hydrogeol. test field (filtered)	S	6.3	0.07	0.01	4.7	0.009	0.01
	E	6.2	0.01	0.02	3.5	0.016	0.02
Hydrogeol. test field (pH 2)	S	6.4	0.08	0.01	5.2	0.004	0.003
	E	1.8	0.15	0.07	5.7	0.003	0.003
Rothschönberger Stollen (unfiltered)	S	6	0.003	0.02	1.7	0.032	0.01
	E	6.3	0.04	0.003	1.4	0.003	0.01
Rothschönberger Stollen (filtered)	S	6	0.05	0.003	4.4	0.004	0.03
	E	6.5	0.003	0.02	1.3	0.009	0.01
Rothschönberger Stollen (pH 2)	S	6.3	0.003	0.003	1.3	0.003	0.03
	E	2.0	0.02	0.31	1.1	0.004	0.01
Schwarzer Hirsch St. (unfiltered)	S	6	0.02	1.26	10.1	0.026	0.01
	E	3.4	0.01	0.22	10.8	0.004	0.01
Schwarzer Hirsch St. (filtered)	S	3.6	0.02	1.07	10.7	0.004	0.01
	E	3.5	0.02	0.55	12.3	0.018	0.02
AMD (unfiltered)	S	2.3	12.5	803	31	0.27	5
	E	2.1	53	787	32	0.88	0.32
AMD (filtered)	S	2.4	4.7	638	53	0.42	0.9
	E	2.2	10	690	37	0.38	0.6

[a] Start/end refers to analyses conducted before the beginning of the experiment and at the end of the experiment; concentrations are in mg/L

groundwater sample from the hydrogeological test field and three mine water samples (Reiche Zeche shaft, Rothschönberger Stollen, seepage water from a shear zone). All samples had near-neutral pH and relatively lower concentrations of redox-sensitive elements (Table 1). Generally, the redox potential readings in these samples showed an initial gradual decrease, as can be seen in Fig. 3a and b for the groundwater and the mine water Rothschönberger Stollen, respectively.

This initial decrease may be because the electrodes which were conserved at a potential of approximately 300 to 400 mV in 3 M KCl solution prior to experiments needed time to adjust to the potential of the sample of interest. How fast such an adjustment takes place depends upon the concentration of the electroactive redox species in the samples. Another aspect that can contribute to such a decrease in potential is the gradual poisoning of the electrodes as time elapses. Further evidence for the sensitivity of adjustments between redox couples and the electrode surface in solutions with low redox buffer potential are the differences in redox readings between the three flow-through cells. While in well-buffered solutions readings from the three cells were within 10–30 mV, the response of used electrode in C1 was rather sluggish compared to that of the two new electrodes (C2 and C3) for the groundwater and mine water samples with low buffer potential.

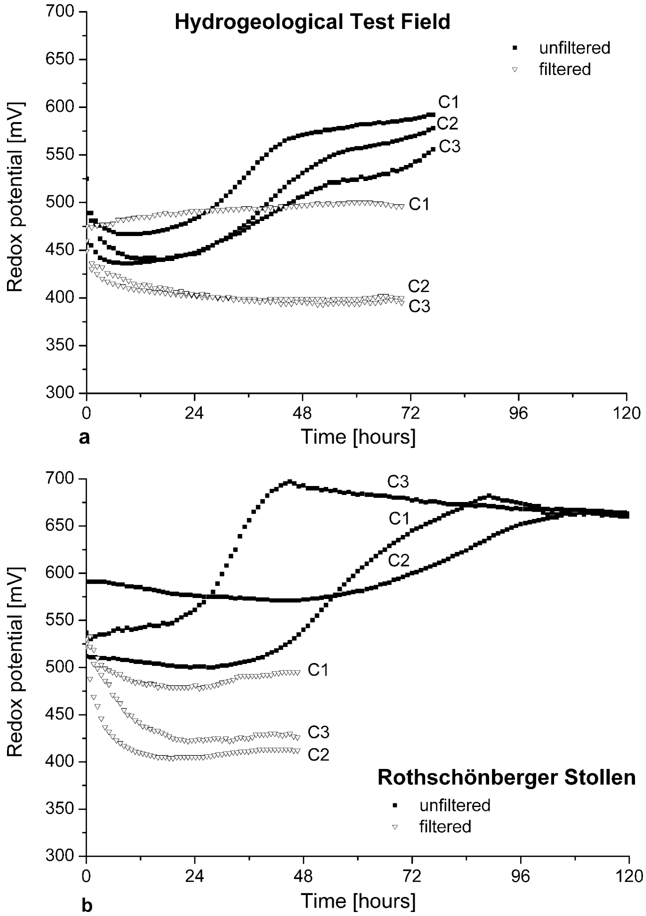

Fig. 3 Comparison of redox potential values measured in the three flow-through cells for the filtered (*open down triangles*) and unfiltered samples (*solid squares*) from **a** the hydrogeological test field and **b** the Rothschönberger Stollen

Another phenomenon observed among the unfiltered near-neutral pH samples was the attainment of stable readings at two or more different potential levels at different time intervals. Readings for the unfiltered groundwater sample (black solid squares in Fig. 3a) reached a first plateau after approximately 8–12 h at 440–470 mV. After 64 h the recordings level off at higher potentials between 520 to 600 mV. Similarly, a first plateau was reached for the unfiltered Rothschönberger Stollen mine water (black solid squares in Fig. 3b) after 8 h at 510–580 mV, while the final plateau after 96 h was at 650 mV. Between any two plateaus of stable redox potential readings a period of increasing or decreasing potential indicate a redox process taking place in the solution or changes at the electrodes surface. In filtered samples of the same sites, stable redox potential readings were obtained much faster and showed only one plateau, roughly 200 mV lower than the final plateau in unfiltered samples (open down triangles in Fig. 3).

As stated before, the redox potential readings stabilized quickly in the acid mine drainage sample since low pH slows down redox reactions. To examine if lowering the pH would also lead to rapid stabilization of redox potential readings in other samples, the samples from the hydrogeological test field and the Rothschönberger Stollen were filtered and then adjusted to about pH 2 with concentrated ultrapur™ HCl prior to measurements. To take into account the accompanying change in the Nernst voltage, the potentials so-obtained had to be corrected for the potential shift of −59.1 mV per unit pH-change (at 25°C) with respect to their natural pHs. This meant that the potentials of the hydrogeological test field (acidified from pH 6.4 to 1.8, ΔpH=4.4) and Rothschönberger Stollen (acidified from pH 6.3 to 2.0, ΔpH=4.3) had to be corrected by −272 mV and by −254 mV, respectively. Figure 4 presents the results obtained which show less fluctuations and rapid stabilization, however, at mean values 70 mV (unfiltered groundwater, Fig. 4a) and 55 mV (unfiltered mine water, Fig. 4b) higher than those of the filtered samples.

In summary, measuring redox potentials in solutions with low buffer potential shows high sensitivity to electrode performance including delayed response, significant fluctuations over time, various plateaus of “stable” readings at different potentials in unfiltered samples, and a difference between the “final, stable” readings for unfiltered, filtered and filtered/acidified samples. These observations inevitably lead to the search for the “true” redox potential value or the question whether there is any single redox potential at all to describe a system at disequilibrium.

The first reasoning might be that fluctuations in the redox potential were only observed because of an inapt experimental laboratory setup. However, the rapid and reproducible obtainment of stable readings for well-buffered solutions shows that there is no major drawback in the experimental design, like inorganic contamination

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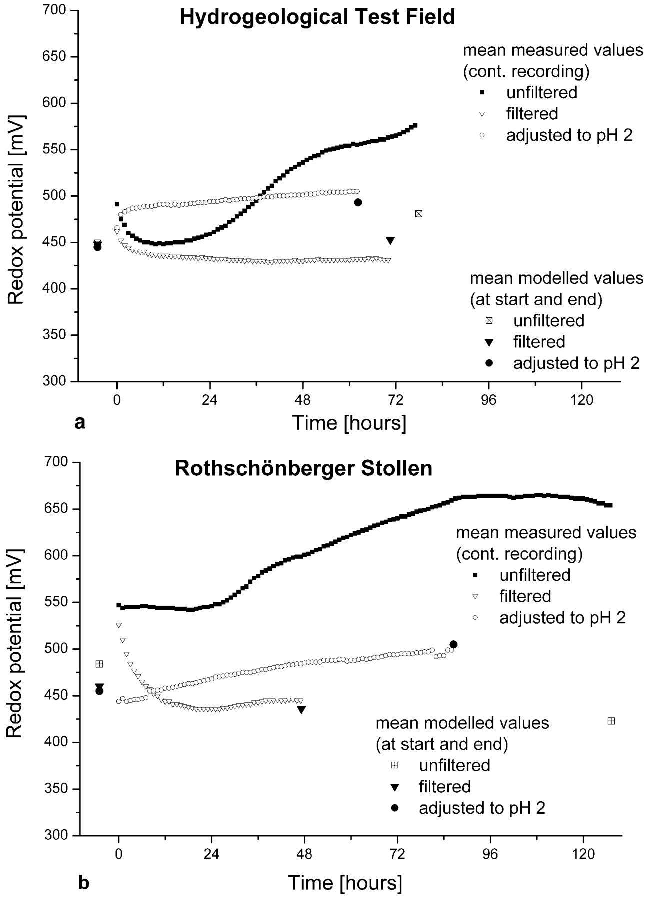

Fig. 4 Comparison of redox potentials for samples at natural pH (filtered as well as unfiltered) and samples adjusted to pH 2 for **a** the hydrogeological test field and **b** the Rothschönberger Stollen; values are averaged readings from all three flow-through cells (C1-C3). The single *symbols* at the beginning and end of each experiment show the modeled mean value of the partial potentials of the determined redox couples according to Table 2

during cycling, excess oxygen entry or significant microbiological processes. Solutions in disequilibrium are just extremely sensitive to even small changes at the electrode or in the solution, a problem that is not at all restricted only to lab experiments. Minor natural fluctuations of the water chemistry at any given sampling site, each penetration of the natural system for obtaining a sample (from the well design itself, to pump mode, flow rate, and design of percolation through flow-through cell), and minor changes to the electrode (from size, overall condition, and previous cleaning procedures to changes in performance even during sampling at the same site) will significantly affect any redox potential measurement in all systems at disequilibrium. An absolute “true” value is a mere theoretical construct.

The major reason for the demand of a single redox potential value is to handle the speciation of all redox-sensitive parameters by measuring one additional, supposedly readily available variable, the mean redox potential, instead of conducting time-consuming and expensive individual species analytics. The most important question, thus, is how well does that mean value represent the partial redox potentials of all redox-sensitive species in solution? To help address this question, partial potentials for the redox couples Fe(2)/Fe(3), N(−3)/N(3), N(−3)/N(5), and N(3)/N(5) were modeled with PHREEQC (Parkhurst and Appelo 1999) using the database WATEQ4F (Ball and Nordstrom 1991) at the beginning and at the end of each experiment (Table 2) based on the data given in Table 1. The modeling results could further be influenced by other redox couples such as Mn or As, which were however not determined individually in the present study.

Table 1 shows that some species conversions occurred during the experimental run, leading to both increases in oxidized and reduced species as well as, mainly for iron, to decreases in total concentrations probably due to precipitation (even though no visible precipitate was observed). High standard deviations between the partial potentials (Table 2) confirm that the systems were not at equilibrium, neither at the beginning nor at the end of the experiment. The results for the two acid mine water samples (AMD with pH 2.3 and Schwarzer Hirsch Stehender with pH 3.5) are included for comparison and show how little deviation (2 to a maximum of 10%) is observed between partial redox potentials in systems at equilibrium.

Figure 4 and Table 3 show that in unfiltered samples, average recordings over the first 30 min were 108% (groundwater from hydrogeological test field) and 113% (mine water from Rothschönberger Stollen) of the mean potentials predicted by modeling. For the groundwater sample, filtering helped to get the redox recording to 102% of the modeled value within the first 30 min. For the sample from Rothschönberger Stollen, the time to reach stable readings within a 2% limit of the modeled value was significantly longer with 6–12 h. The higher initial deviations and longer stabilization times could indicate a less buffered system, which is supported by the lower concentrations of the redox-sensitive elements investigated (iron and nitrogen) in the mine water compared to the groundwater samples. The latter also has low iron, but five times higher nitrogen concentrations (Table 1). On the other hand, the mine water contains a significant amount of manganese, which was not speciated in this study. Thus, the influence of partial potentials from the manganese redox couples on the mean modeled redox potential could not be considered.

As expected, since filtration is routinely used for stabilization of samples for species-selective analytics, all filtered samples showed less variations between modeled potentials from the beginning of the experiment to the end than unfiltered samples and good agreement of measured to predicted values over the whole run time of the experiments. For the unfiltered samples, the final “stable readings” differed significantly (120% for the groundwater, 155% for the mine water) from the predicted values (Table 3). These changes are most likely not only triggered by redox processes in the solution (which would be displayed by changes in the modeled values, too) but also by changes at the electrodes surface.

Table 2 Partial redox potentials of redox-sensitive iron and nitrogen species modeled with PHREEQC (for details see text) show relatively little difference for well-buffered solutions (such as the AMD), but higher relative standard deviations (STD) for samples obviously not in thermodynamic equilibrium (such as the hydrogeological test field and the Rothschönberger Stollen)

Samples	Start / end	Fe(2)/Fe(3) [mV]	N(−3)/N(3) [mV]	N(−3)/N(5) [mV]	N(3)/N(5) [mV]	Mean of all redox couples	STD	Rel. STD
Hydrogeol. test field unfiltered	S	378	403	445	570	449	74	16%
Hydrogeol. test field unfiltered	E	427	433	473	591	481	66	14%
Hydrogeol. test field filtered	S	352	419	456	566	448	78	17%
Hydrogeol. test field filtered	E	408	409	444	550	453	58	13%
Hydrogeol. test field pH 2[a]	S	338	415	454	573	445	85	19%
Hydrogeol. test field pH 2[a]	E	424	480	501	562	492	49	10%
Rothschönberger Stollen unfiltered	S	480	439	467	550	484	41	8%
Rothschönberger Stollen unfiltered	E	314	393	433	552	423	86	20%
Rothschönberger Stollen filtered	S	363	426	466	588	460	82	18%
Rothschönberger Stollen filtered	E	409	386	422	528	436	54	12%
Rothschönberger Stollen pH 2[a]	S	404	408	447	563	455	64	14%
Rothschönberger Stollen pH 2[a]	E	501	480	496	545	505	24	5%
Schwarzer Hirsch St. unfiltered	S	542	450	483	582	514	51	10%
Schwarzer Hirsch St. unfiltered	E	758	626	656	746	697	57	8%
Schwarzer Hirsch St. filtered	S	769	622	652	741	696	61	9%
Schwarzer Hirsch St. filtered	E	750	619	645	722	684	54	8%
AMD unfiltered	S	774	709	725	773	745	29	4%
AMD unfiltered	E	742	735	743	768	747	12	2%
AMD filtered	S	793	710	725	769	749	33	4%
AMD filtered	E	782	721	734	774	753	26	3%

[a] Redox potentials of filtered, acidified samples were corrected for a potential shift of −59.1 mV per unit pH-change (at 25°C) with respect to their natural pHs as discussed in the text

Table 3 Summary of redox potentials [mV] obtained for the hydrogeological test field and the Rothschönberger Stollen by measuring and modeling redox-sensitive species

Samples	Start/ end	Measured (unfiltered)	Modeled (unfiltered)	Measured (filtered)	Modeled (filtered)	Measured[a] (filtered, acidified)	Modeled[a] (filtered, acidified)
Hydrogeol. test field	S	483±19 108%[b]	449±74	457±16 102%	448±78	465±13 104%	445±85
	E	575±16 120%	481±66	437±47 96%	453±58	505±11 103%	492±49
Rothschön-berger Stollen	S	546±33 113%	484±41	522±14 113%	460±82	445±14 98%	455±64
	E	654±2 155%	423±86	445±36 102%	436±54	500±18 99%	505±24

Mean and standard deviations of measured potentials were calculated from the three different flow-through cells averaging the readings of the first 30 min for the “Start” value and of the last 30 min for the “End” value. Modeling was done with PHREEQC using the WATEQ4F database; partial redox potentials are shown in Table 2.

[a] Redox potentials of acidified samples were corrected for a potential shift of −59.1 mV per unit pH change (at 25°C) with respect to their natural pHs as discussed in the text

[b] The % values indicate the ratios of measured to modeled redox potentials

Acidifying filtered samples for redox potential measurements shows rapid stabilization and best overall agreements with predicted values both for the groundwater (104 and 103% for beginning and end of the experiment, respectively) and the mine water sample (98 and 99%, Table 3).

Conclusions

Obtaining meaningful redox potentials is straight-forward in solutions in equilibrium. As suggested in previous publications, readings stabilized quickly and reproducibly in well-buffered solutions, such as, in this study, the synthetic redox buffer solution and two acid mine waters with pH 2.3 and 3.5. The results suggest that in these cases, initial readings do not change significantly even within the first 30 min and fluctuations were significantly less than the reported 10% (on average below 1%, with a maximum of 3%).

The meaningfulness of one representative redox potential, however, becomes questionable when dealing with solutions in disequilibrium, like the investigated near-neutral pH groundwater and mine water samples of low buffer capacity. The only reliable alternative here is individual species analytics with the proper precautions taken to avoid species conversion during sampling, transport, and storage. If species-selective analytics is not feasible and the redox potential is to be used, it is recommended, based on the present study, that the current state-of-the-art measurement of redox potentials in untreated water samples should not be undertaken. State-of-the art, for general trace element preservation, is filtration and acidification. All values used for later speciation modeling originate from samples preserved in this way. Measuring the redox potential under comparable settings in a flow-through cell with an online filtration will greatly improve the agreement between mean partial redox potential and measured redox potential according to the experiments described here. Additional online acidification in a flow-through system will be more difficult to realize since it requires a flow injection system for maintaining constant pH throughout the measurement. In this case, it might be more feasible to take a sample in a gas-tight reaction vessel, preventing any exchange with atmospheric oxygen, acidify it and measure the redox potential without constant flow. In any case, the best agreement might only be achieved after significantly more than 30 min and could take up to several hours in waters with low buffer capacity.

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