Measuring the redox state of groundwaters: revisiting the use of the Platinum electrode in contaminated aquifers

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ABSTRACT
The measurement of the oxidation-reduction state of groundwater is often made using the combination Platinum (Pt) electrode. It is shown that when these electrode measurements are corrected to the standard hydrogen electrode, i.e., the Eh value, it is possible to infer the occurrence of sulphate and nitrate reduction that may be important in the attenuation of contaminants in the groundwater sample.

RÉSUMÉ
Il est necessaire à corriger les potentials mesurent aux champs avec une électrode de Platine à obtenir le potentiel redox – Eh – où le potentiel est se référé à l'électrode Hydrogène ('h'). Avec les eaux souterraines contaminées, il est possible à inférer l'occurrence de la réduction de sulfate et de nitrate au moyen des potentiels redox (Eh).

1. INTRODUCTION

Platinum (Pt) electrodes have been used since about 1950 to measure the reduction-oxidation (redox) state of groundwaters. Typically the Pt electrode used in the field is a combination electrode with a built-in Ag/AgCl reference (or calomel) electrode. Consequently the measured potential (E_{Pt}) must be referred to the hydrogen electrode ($½H_2(g) = H^+ + e^-$) in order to report the potential as an Eh value. Therefore a value for the reference electrode vs. the hydrogen electrode at the temperature of measurement is added to the measured Pt electrode potential to give the Eh value, i.e., $E_{Pt} + E_{ref} = Eh$. Nordstrom and Wilde (2005) list the reference electrode potentials for various reference solutions and provide guidance on measurement of Eh in the field.

The 'h' in Eh therefore refers the potential back to the hydrogen electrode. All too often in hydrogeological practice, a value of 'ORP' – oxygen-reduction potential – is reported and this step of referring the E_{Pt} to the hydrogen electrode to yield the Eh is neglected. Consequently, references to 'ORP' are usually confusing unless it is made clear that the additional potential (about 200 mV) has – or has not – been added to E_{Pt}..

Early field work by the US Geological Survey addressed the relationship between Eh and the concentrations of dissolved iron in groundwater (Back and Barnes, 1965). Edmunds (1973) of the British Geological Survey demonstrated that Eh values reflected changes in groundwater chemistry that could be related to the presence or absence of dissolved oxygen and sulphide. Edmunds introduced the term 'redox barrier' to describe the sudden drop in Eh that occurred in the Lincolnshire Limestone aquifer with the disappearance of dissolved oxygen. Champ et al. (1979) identified the reactions observed by both Back and Barnes and Edmunds were consistent with the aqueous thermodynamic model of Stumm and Morgan (1970) in which oxidised waters are mixed with an excess of reducing agents, e.g., dissolved organic carbon (DOC).

The purpose of this paper is to review the reported range of Eh measurements in a variety of aquifers when the following criteria are met (Champ et al., 1979):

- The Pt electrode surface is pre-treated prior to measurement to remove precipitates;
- Samples are measured in air-tight flow cells; and
- The electrode surface-groundwater interface in the flow cell has equilibrated.

If these conditions are satisfied then Champ et al. (1979) indicate that it is possible to measure Eh values "that provide a qualitative description of the redox state of ground waters" and are reproducible. Furthermore, in the words of Stumm (1967): "*natural media that contain large quantities of oxidizing agents certainly give measurements of high Eh values and those containing large quantities of reducing agents have low potential.*" Consequently, this paper seeks to provide some guidance on what values of Eh might be expected for particular redox conditions, such as nitrate or sulphate reduction.

2. REDOX SEQUENCES IN FLOW SYSTEMS

The concept that redox sequences develop in groundwater flow systems due to thermodynamic controls was proposed by Champ et al. (1979) after monitoring such changes in a fluvial sand aquifer at Chalk River Laboratories in the Ottawa Valley. The first such sequence had been reported earlier by Edmunds (1973) in his study of the Lincolnshire Limestone in England, although Back and Barnes (1965) had shown elements of a sequence in aquifers along the Maryland coastal plain. The sequence is presented in Figure 1.

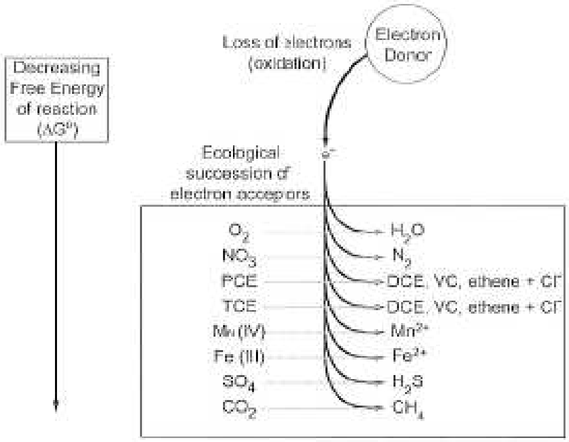

Figure 1: An ‘ecological succession’ or redox sequence that includes TCE and PCE (McMahon and Chapelle, 2008). Microbial processes facilitate the reduction of the oxidants listed on the left-hand column of this Figure into the reduced species on the right-hand column. The oxidants are known as ‘terminal electron acceptors’. The principal reducing agent causing the sequence to proceed is dissolved organic carbon (DOC). If DOC is present in sufficient quantities (e.g., 2-5 mg/L), the redox sequence will proceed through nitrate and then sulphate reduction to methane fermentation. The thermodynamic basis for the sequence was first identified by Stumm (1967) and is discussed in Stumm and Morgan (1970, 1981, 1996).

Studies of redox sequences in three uncontaminated English aquifers (sandstone, chalk and limestone) by Edmunds and colleagues (1984) indicated that the zone in which dissolved oxygen (DO) was present is given by Eh: > 300 mV. They point out that differences may exist due to the pH of the groundwaters because DO interacts with the Pt electrode to form a PtO or PtOH film that reflects the pH. At Chalk River Laboratories where the groundwater is quite acidic (pH ~ 5), the Eh was much higher in the oxygenated recharge area, i.e., Eh>400 mV.

The later stages of the redox sequence shown in Figure 1 reflect the presence of DOC that causes anoxic conditions to occur. These are most evident in groundwater in the presence of dissolved ferrous iron and sulphide in the form of HS$^-$ (aqueous). Edmunds (1973) was the first to measure dissolved sulphide (DS) in groundwater using the Ag/AgS electrode. He associated DS with low measured potentials, i.e., Eh < 100 mV.

Edmunds et al (1984) provided the field confirmation of Stumm’s earlier observation that high concentrations of oxidants (e.g., DO) cause a high potential to be measured, while high concentrations of reduced species (e.g., DS) cause a much lower potential to be measured. Our interest then can be phrased as: to what extent can we use this simple tool – the Pt electrode – to interpret redox reactions that may have implications for the natural attenuation of contaminants? Two examples will be used. The first is a Quaternary glacial outwash aquifer near Ottawa that is heavily contaminated with chlorinated solvents from waste disposal and hence has become anoxic. The second in the Permian sandstone of Prince Edward Island that is contaminated with nitrate from fertilization of the potato crop and which remains oxygenated for the most part.

3. GLOUCESTER LANDFILL, ONTARIO

The Federal Government used a “Special Waste Compound” at the Gloucester Landfill to dispose of chlorinated solvents from the laboratories and other facilities in nearby Ottawa. These were combusted in trenches dug into the sandy soils overlying the outwash aquifer which was initially protected by an aquitard that was probably punctured by excavation of various trenches during landfilling. The aquifer became heavily contaminated (Lesage et al., 1990) with dissolved trichloroethene (TCE) and its biotransformation products, e.g., 1,1-dichloroethene (DCE). In addition, the aquifer contained oxygenated solvents that had presumably dissolved from chlorinated solvents in which they were additives (see Jackson and Dwarakanath, 1999), as well as or chlorofluorocarbon solvents (“Freons”) that had been disposed in the trenches (Jackson et al., 1992).

Figure 2 shows the TCE plume in the aquifer as of May 1988 and the zone of suspected dense, non-aqueous phase liquid (DNAPL). Monitoring since 1988 has shown that this TCE plume appears to have reached a steady-state pattern, presumably due to natural attenuation by reductive dechlorination.

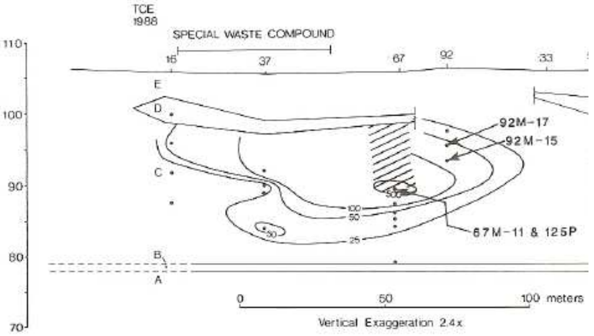

Figure 2: Cross-sectional view of the outwash aquifer beneath the Gloucester Landfill, near Ottawa, Ontario (from Jackson et al., 1992). The TCE plume is shown in May 1988 with multilevel monitors (e.g., 67M-11) and monitoring wells (125P) identified with concentration contours identified in µg TCE/L. The area shaded with hachure is the suspected DNAPL zone. Sulphide and Eh measurements were conducted on several multi-level ports of wells 67M and 37M (Gulens, 1985).

In the upgradient, uncontaminated recharge area to the left of Figure 2, DO was measured to be 2-6 mg/L, DOC = 1.3 and Eh = 550 mV. In the reduced plume shown in Figure 2, DS was measured to range from 5 µg/L to 1.1 mg/L, DO ≤ 0.3 mg/L, DOC: 1-21 mg/L and Eh = 40-70 mV. Lesage et al. (1990) reported that the pH and redox environment was stable for the previous 6 years. As is often the case, it is most likely that the measured DO reflects O_2 (gas) entrainment into flow lines and/or the flow cell during pumping and sampling.

The detection of numerous biotransformation products in the Gloucester aquifer, such as 11-DCE and the dechlorination products of CFC-113 (Lesage et al; 1990), indicates that biotransformation of dissolved chlorinated solvents was occurring in a sulphate-reducing environment with Eh < 100 mV. This is consistent with the Eh range measured in sulphate-reducing zones in the English aquifers by Edmunds et al. (1984) of < 100 mV.

Measurements of DS and Eh conducted in a shallow fluvial sand aquifer at Chalk River and reported by Jackson and Patterson (1982) were in a similar but slightly higher range as at the Gloucester Landfill: i.e., 10-120 µg/L and 50-200 mV, respectively.

4. SANDSTONE AQUIFER, PEI

The Upper Pennsylvanian – Permian sandstone of Prince Edward Island is the sole-source water supply for the Province. The dependence of PEI agriculture on the potato crop means that considerable amounts of nitrate fertilizer are applied to the fields above the aquifer that is not protected by the thin till. Studies in the 1980s by Environment Canada (Jackson et al., 1990; Mutch et al., 1992) were conducted to assess the fate of the pesticide Aldicarb in the aquifer, during which nitrate and redox parameters were carefully measured.

DO measurements in three instrumented field sites that included complete flow systems showed that the shallow groundwaters were highly oxygenated and of pH between 7.0 and 8.0. The mean DO for the three sites were 5.8, 7.5 and 6.8 mg/L and the respective mean Eh values were 417, 505 and 487 mV. Ammonia measurements indicated a mean value of 0.2 mg/L, which is probably at the limit of detection of this electrode, and there is no reason to suspect that denitrification was occurring in these groundwaters.

However, reducing conditions were observed in the flow system at Augustine Cove. See Figure 3. Piezometers 5 and 27 were found to have DO < 1 mg/L and Eh < 200 mV. Other geochemically similar wells that were installed adjacent to this cross section in the discharge area were also found to have Eh < 200 mV. In addition, DO concentrations in these wells were <1 mg/L which also exhibited relatively high concentrations of DOC (> 6 mg/L) and dissolved iron at concentrations of 1-11 mg/L. Thus, nitrate is absent in this flow system at Eh < 200 mV (see Figure 4). It appears that Eh values < 200 mV indicate denitrification as well as sulphate reduction.

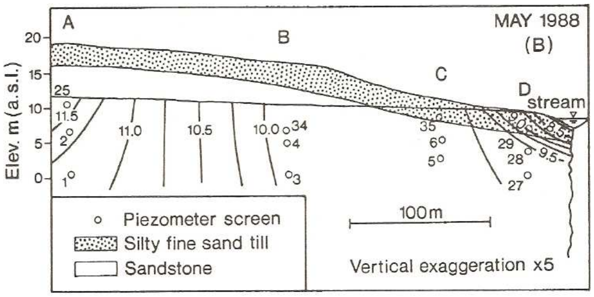

Figure 3: The groundwater flow system in fractured sandstone at Augustine Cove, PEI in May 1988. Piezometer numbers are shown next to the open circles. The contour intervals are equipotential lines in meters above mean sea level. From Mutch et al., 1992.

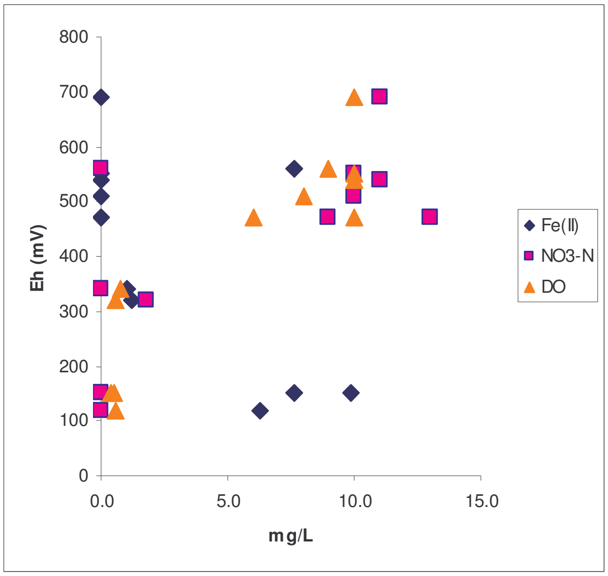

Figure 4: Relationship of dissolved iron, nitrate-nitrogen and oxygen to Eh, Augustine Cove, PEI.

5. OPERATIONAL LIMITATIONS OF GROUNDWATER Eh MEASUREMENTS

Whitfield (1974) pointed out that surface oxide and sulphide coatings on Pt electrodes could affect the measured potentials and thus indirectly reflect the presence of DO and DS. However, the formation of an oxide surface coating (Pt-O), Whitfield proposed, would lead to the Pt electrode responding to pH rather than any particular DO concentration, i.e., the measured potential (E) would be:

$$E = E^0(\text{Pt-O}) - 0.06\ \text{pH, where } E^0 = 0.88\text{V}$$

Whitfield postulated that "well aerated systems" would yield Eh values in the range +500 mV to +300 mV. Data from the groundwater flow systems at Chalk River and

Gloucester, Ontario and on Prince Edward Island are presented as functions of pH on Figure 5 and appear to confirm this prediction. These same data clearly do not indicate that a correlation exists between the measured DO values and pH, as is shown in Figure 6, nor between DO and Eh values as shown in Figure 7.

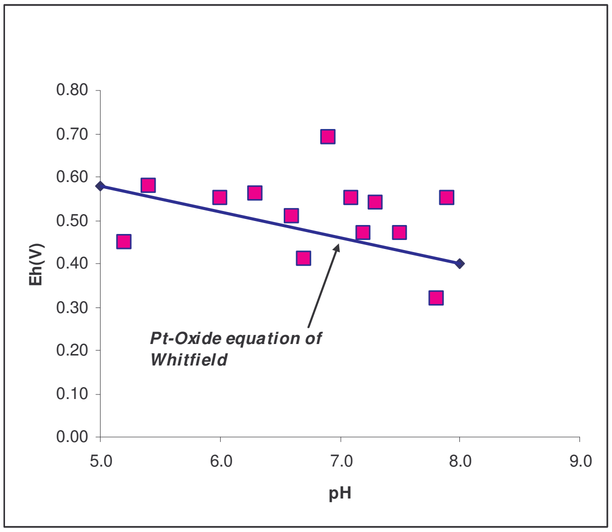

Figure 5: pH and Eh data from Gloucester, Chalk River and PEI studies apparently obeying the Pt-Oxide relation of Whitfield (1974).

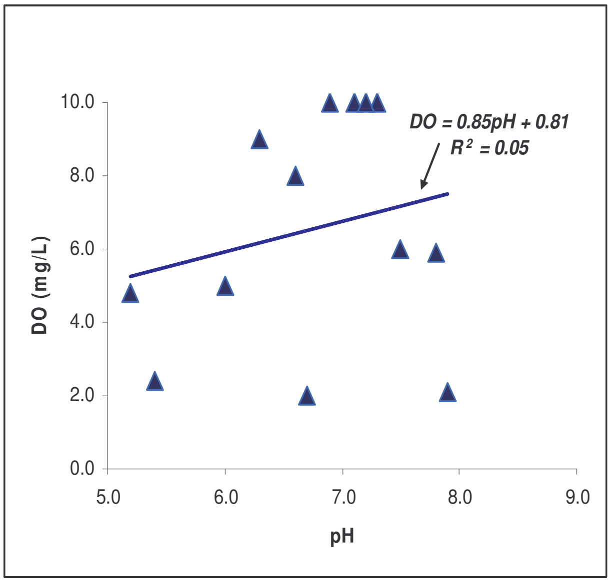

Figure 6: Absence of correlation between pH and DO. The squared correlation explains only 5% of the variance.

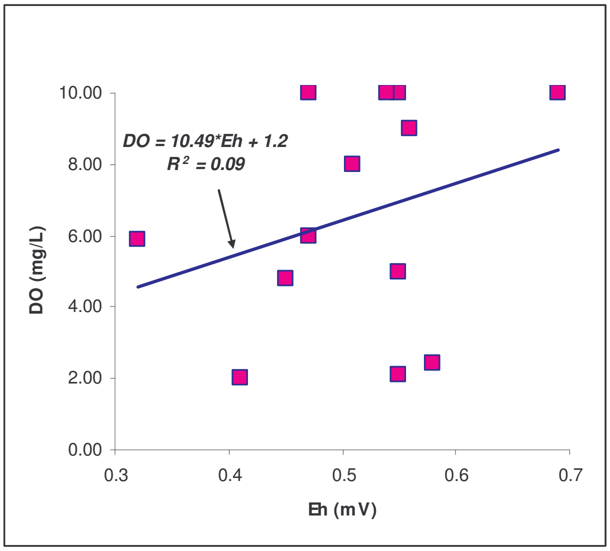

Figure 6: Absence of correlation between Eh and DO. The squared correlation explains only 9% of the variance.

In sulphate-reducing groundwaters, Whitfield proposed that the measured potential would be given by the relationship:

$$Pt^0 + S^{2-} = PtS + 2e^-$$

such that Eh = -0.96 +0.0295pS (Volts), where pS is the negative logarithm of the sulphide concentration.

Data from Chalk River and the Gloucester Landfill are shown in Figure 8, however the predicted Eh values for the measured pS values in the range 4.5 – 6.8 are very much lower than those measured in the field, i.e., 40-240 mV. Here it seems that the Pt-S interaction cannot explain the measured potentials and they are the result of mixed potentials as was earlier noted by Jackson and Paterson (1982).

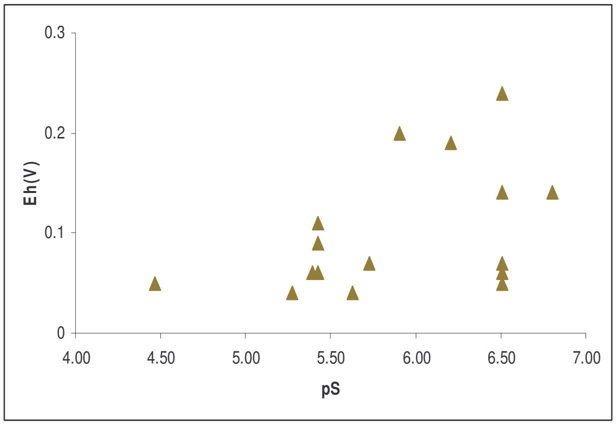

Figure 8: Absence of correlation between pS and Eh measurements at Chalk River and the Gloucester Landfill.

Another potential problem that occurs with groundwaters and Pt electrode measurements is that involving the presence of colloidal Fe(III)-oxide particles that are entrained in the pumped groundwater stream. This situation typically occurs with iron-stained sands and sandstones. These particles are often incorporated in the analysed sample because they are < 0.45 µm and thus are not filtered out but rather are dissolved during acid preservation and thus yield high Fe concentrations upon chemical analysis (Hem and Cropper, 1959; Edmunds et al., 1984; D.K. Nordstrom, USGS Boulder, Colorado, personal communication).

However, Fe(III)-oxide particles may also influence Pt electrode measurements in flow cells when the groundwater is reducing and the pH range of the sample is 5 – 8. Under these conditions, Fe(III)-oxide particles will dissolve and set up a system in which it is possible that the measured potential will reflect – in some manner – the Fe(II)-Fe(III) couple. Back and Barnes (1965) presented data in this pH range for a flow system in aquifers beneath the Maryland coastal plain. Figure 8 shows aqueous Fe(III) concentrations far in excess of the solubility of ferric oxides (~ 10 ppb in the pH range 5 – 8). Figure 9 presents the dissolved Fe(II) and Fe(III) concentrations for the samples contained within the box of Figure 8; very clearly Fe(II) is abundant and thus the groundwater is largely reducing in nature.

The data of Back and Barnes suggest that, when ferric oxide particles are entrained into a flow cell receiving reduced Fe(II)-containing groundwater of pH 5 – 8, it is reasonable to expect that the Pt electrode will yield a potential in the range 100 to 300 mV (see Figure 10).

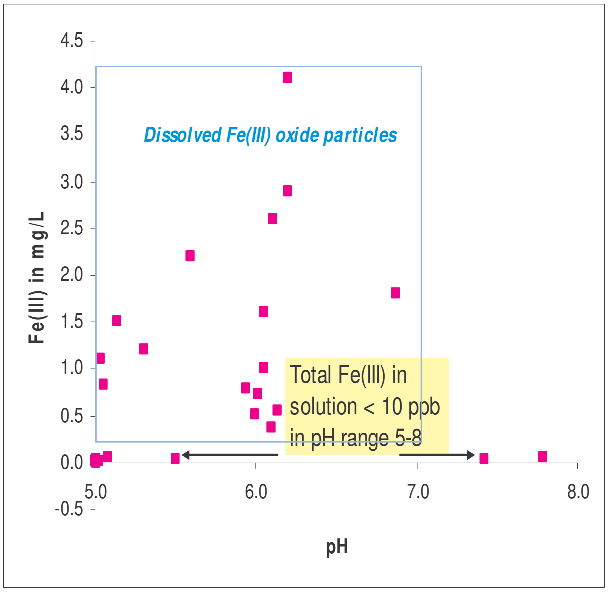

Figure 8: Dissolved ferric iron measured in samples collected by Back and Barnes (1965) at concentrations above the solubility of ferric oxides.

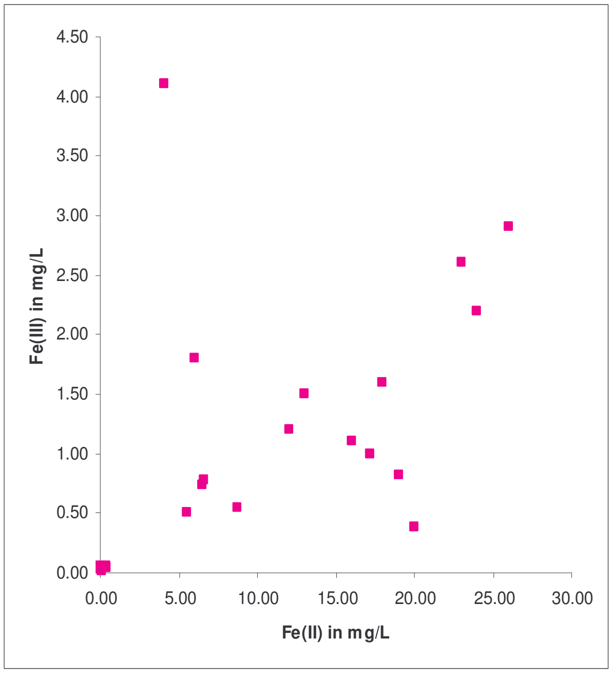

Figure 9: Measured ferrous and ferric iron concentrations for samples falling within the box shown in Figure 8. Most of these samples contain ferrous iron and so are anoxic, whereas the ferric iron is likely derived from the dissolution of Fe(III) oxides particles upon acidification.

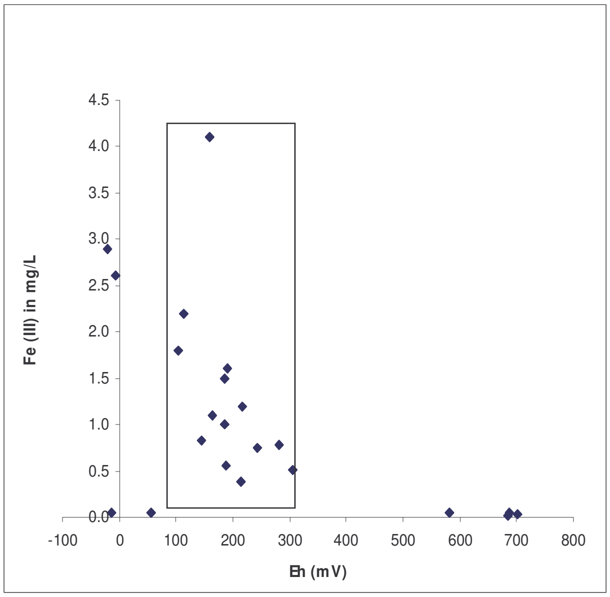

Figure 10: Relationship of dissolved ferric iron to measured Eh in reducing groundwaters for those samples falling within the box shown in Figure 8 (Back and Barnes, 1965). The apparent negative correlation between Fe(III) and Eh is not statistically significant, $R^2 = 0.28$.

Generally the data of Back and Barnes confirm the Pt-O relationship advanced by Whitfield (1974) in that in the absence of DO, the Eh recorded is < 300 mV. Although the concentrations of dissolved Fe(II) exceed 10^{-5}M, it appears that the colloidal Fe(III) does not dissolved to this concentration and therefore does not establish an electroactive couple (Stumm & Morgan, 1981, p. 491) that controls the Eh as in acid-drainage waters.

Therefore, Fe(III) particles suspended in anoxic groundwater may cause very small amounts of Fe(III) to dissolve in the flow cell, in which case the measured Eh may be expected to be in the range 100 – 300 mV. Their presence can be readily detected by testing the turbidity of the groundwater in the flow cell.

6. CONCLUSIONS

Despite years of guidance on the meaning and operational limitations of measured Platinum (Pt) electrode potentials – "oxidation-reduction potentials" – by Stumm and Morgan (*Aquatic Chemistry,* 1972, 1981, 1996) and others, there is continuing confusion among many geoscientists and engineers over the meaning and reporting of field measurements using this electrode. Similarly, excellent guidance on the field measurement and interpretation of the Pt electrode potential is given by Nordstrom and Wilde in the US Geological Survey's *National Field Manual for the Collection of Water-Quality Data* that may be downloaded from the USGS web site.

These documents establish that the Pt electrode potential cannot provide an unequivocal and quantitative measure of the redox state of typical groundwaters with near-neutral pHs due to the absence of high concentrations of electroactive species such as Fe(II) and Fe(III) or Mn(II) and Mn(IV). Because acid-mine drainage has sufficient quantities of Fe(II) and Fe(III), it is probably the only natural water that does provide meaningful estimates of the redox potential, Eh, when the field-measured Pt potential is corrected by adding the potential associated with that of the reference electrode (i.e., vs. the Hydrogen electrode, which is the 'h' in Eh).

What the measured Pt electrode potential does provide is a semi-quantitative measure of the redox state of a groundwater. When using a Pt electrode it is recommended that dissolved oxygen, iron and/or sulphide also are measured, whether by using either electrode or field colorimetric tools or both.

The 'redox barrier' cited by Edmunds et al. (1984) at approximately +300 mV in various English aquifers probably reflects the absence of DO in groundwater. As Edmunds et al. noted, the presence of DO would have caused the formation of an oxide film on the Pt electrode as hypothesized by Whitfield (1974). Such a Pt oxide control on Eh is supported by data from three Canadian aquifers, see Figure 5. Therefore, the Eh values for oxygenated groundwater are typically of the order +300 – +600 mV, depending on pH.

Below this range of Eh values, the Pt electrode appears to respond to mixed potentials involving undefined redox couples in groundwater. However, although the redox reactions affecting the measured Pt electrode below +300 mV may be obscure, it is clear that reduction of ferric iron, nitrate and sulphate are reflected *semi-quantitatively* in Pt electrode measurements of Eh provided that the electrode is pre-treated to remove precipitates and measured in an air-tight flow cell over a sufficient period of time to allow the electrode surface and groundwater to equilibrate, e.g., 10-30 minutes.

No correlation could be found for Eh with Pt-sulphide films in sulphide-containing groundwaters at Chalk River and the Gloucester Landfill. However, the lower that the measured Eh value is below +300 mV, nitrate and sulphate reduction become more likely; this is in accord with Stumm's (1967) observation that low Eh potentials can be associated with generally reducing conditions.

Thus, Eh values of <+200 mV are strong indicators of the likelihood of nitrate and sulphate reduction. This rule-of-thumb should be of assistance in identifying zones in groundwater flow systems where denitrification of dissolved fertilizer residues or reduction of dissolved chlorinated hydrocarbons such as TCE and PCE may be expected to occur.

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