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| UNIVERSITY OF PRETORIA |
| Use of Eh-pH diagrams in groundwater geochemistry |
| Department of Geology |
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| **Muravha Sedzani Elia** |
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Student: 28234422

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| Abstract An Eh-pH diagram is a diagram that illustrates the equilibrium occurrence of minerals and dissolved species as a function of Eh and pH. This paper will give a brief discussion on redox potential and pH. The main focus of the paper is on the applications of Eh-pH diagrams in groundwater geochemistry and a case study will be used as a common example for application of Eh-pH diagrams. The construction of Eh-pH diagrams and the effect of temperature and pressure on the Eh-pH diagrams are thus important in geochemistry. |

Contaminant transport report (GTX 719)

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1. Introduction

The Eh-pH diagrams have been useful in many scientific studies for the past decades and are still used today. An Eh-pH diagram is a diagram that illustrates the equilibrium occurrence of minerals or ions as domains relative to Eh or pE and pH. The Eh-pH diagrams are commonly constructed in two-dimension, where pH and Eh are the axes. Redox potential is the energy gained through the transfer of one mole of electrons from an oxidant to hydrogen and pH is a negative log base of 10 molar activity of H+ in aqueous solution. The Eh-pH diagrams are constructed through the use of Nernst equation and they depend on pressure and temperature of the reactions. This paper will discuss the applications of Eh-pH diagrams in geochemistry and will also provide a case study for a marine geochemical problem.

1. What is redox potential?

Redox potential is a complex parameter of aqueous sample that involves many separate redox reactions (Henke 2009). Eh or redox potential or oxidation potential, oxidation-reduction potential is the energy gained through the transfer of one mole of electrons from an oxidant to hydrogen (Poehls and Smith 2009). In the abbreviation Eh; the E represents the electromotive force and h symbolises that the potential is on the hydrogen scale (Poehls and Smith 2009). Nernst equation is an equation which mathematically defines oxidation potential, Eh and is given by:

Where:

* Eh is the oxidation potential expressed in volts and millivolts are commonly used
* Eh0 is the standard or reference condition at which all substances have a unity activity concentration and is commonly measured for many reactions at 250C and 1 atm (Poehls and Smith 2009).
* The factor 2.3 was developed when converting “In” to “log” (Merkel and Planner-Friedrich 2005).

Redox potential readily measures the field electrodes potentials as voltage and if the reaction is oxidising the sign of the potential is positive and if reaction is reducing the potential is negative (Poehls and Smith 2009). Understanding of the oxidation potential provides information on how compounds such as uranium, iron-sulphur and other minerals are transported in aqueous system (Collins 1975). The solubility of some other minerals or elements and compounds is dependent on the pH and the redox potential in their environment (Collins 1975). Knowledge of the redox potential helps in determining how to treat water before injecting or infiltrating it into the subsurface formation, for example, if the water is exposed to the atmosphere; the Eh of water will be oxidising, but if the water is kept under a closed system in an oil-production operation; the Eh cannot be easily changed as it is brought to the surface (Collins 1975).

1. What is pH?

The pH is a negative log base of 10 molar activity of H+ in aqueous solution and its measurements is done with electrodes, with accuracy tolerance of ±10 units (Henke 2009). When water undergoes equilibrium dissolution; then from the law of mass action, the following equations are defined (Poehls and Smith 2009):

Where the activity of pure water is unity at 250C and 1 bar and water has equal H+ and OH- activities and pH 7 is given by (H+)-(OH-)-10x10-7 (Poehls and Smith 2009).

1. Eh-pH diagrams

An Eh-pH diagram is a diagram that illustrates the equilibrium occurrence of minerals or ions as domains relative to Eh or pE and pH (Poehls and Smith 2009). Eh-pH diagrams help in understanding of different processes that control the mobility and occurrence of minor and traces of elements (Poehls and Smith 2009). The thermodynamically preferred species are commonly shown in two-dimensional diagram where pH and Eh are the axes and most redox reactions depend on pH and the electrical potential (Crittenden *et al.* 2005). When constructing the Eh-pH diagrams; stability field or equilibrium conditions of dissolved ions or minerals in the aqueous solution are important (Poehls and Smith 2009). The establishment of conditions at which water is stable would be an appropriate step when constructing an Eh-pH diagram (Poehls and Smith 2009).

1. Constructing the Eh-pH diagrams

The stability of water is given as a function of hydrogen and oxygen partial pressure by determining the equilibrium constant for the reaction below (Garrels and Christ 1965).

Determination of upper stability limit of water is done when water and oxygen are at equilibrium with 1 atmospheric pressure and the equation is given by (Garrels and Christ 1965):

……………………………………………………………………………….(a)

And …………………………………………………………………………(b)

Where the activities of liquid water and oxygen are unity, then the Eh equation is given by:

…………………………………………………………………………………..(c)

When substituting –pH for [H+] at the equation above, we get:

…………………………………………………………………………………………(d)

Equation (d) shows that the equilibrium of water and oxygen is given as a function of a straight line with a slope of -0.059 volt per pH unit at partial pressure of 1 atmosphere and temperature of 250C in an Eh-pH diagram and has an interception of E0 (Garrels and Christ 1965). The standard free energy for the reaction is determined numerically by the equation:

Where:

* E0 is a voltage of the reaction at unity substance
* ∆For is the standard free energy change
* f is the Faraday constant
* n is the number of electrons

From equation “(a)”

0 + (4x0) – (2x -56.69) = +113.4kcal

Then

The final equation is given by:



**Figure 1** Stability limits of water as a function of Eh-pH at 250C and 1 atm (Garrels and Christ 1965).

In the figure above; the straight diagonal lines represent the partial pressures of oxygen and hydrogen at intermediate oxidation potential (Garrels and Christ 1965). The equation “(b)” can be rewritten as:

The equation above can be used to plot a line on an Eh-pH diagram at any chosen pressure of oxygen, but when the partial pressure of oxygen is 1 atm; the term PO2 disappears (Garrels and Christ 1965). Every line on the diagram represents activities of products and reactants with consideration of reactions to be at equilibrium where the reaction is 50% complete (Marsden and House 2006).

1. The effect of pressure and temperature on the Eh-pH diagrams

The Eh-pH diagrams are dependent on the temperature and pressure. Using the data derived from different conditions where the temperature is not 250C and pressure is not 1 atm the Eh-pH diagram slightly differs, for example, the Eh-pH boundary between magnetite and hematite is given by the equation (Garrels and Christ 1965):

At temperature of 250C the Eh equation is given by:

And at greater temperature of 350C the equation is given by:

The effect of slight change in the temperature doesn’t alter the diagram more than the width of the line indicating the phase boundaries (Garrels and Christ 1965). On the other hand if the partial pressure of the reacting gasses is small; then the net pressure increase of some tens of atmospheres can be safely neglected, but if the reaction fugacity is large it can be calculated relative to the corresponding equilibrium partial pressure through the activity coefficient of gas (Garrels and Christ 1965).

1. Applications of Eh-pH diagrams

In general; the Eh-pH diagrams are used to illustrate the stability fields of solids and dissolved species in the solution depending on the redox potential and pH (Brookins 1988). They are also applied in explanation of mineral paragenesis, in predicting species in a solution, in alteration products of ores and in hydrothermal systems (Brookins 1988). The Eh-pH diagrams are also used to illustrate equilibrium relationship between dissolved and precipitated species (Hu *et al.* 2009). Examples of different applications of Eh-pH diagrams:

1. Eh-pH diagrams are used to determine the stability of native iron oxides e.g. magnetite and hematite.

The stability reaction is obtained as a function of oxygen partial pressure and is then expressed as a function of Eh-pH by adding the water dissociation half-cell to the reaction expression as shown in the reaction below (Garrels and Christ 1965).

The reaction between iron and magnetite is given by a straight line plot on the Eh-pH diagram and the slope of the line is similar to the water stability limit boundary line (Garrels and Christ 1965). The iron-magnetite boundary line is given by the equation:

The oxidation of magnetite to hematite is given by the equation Eh = 0.221 – 0.059pH with the same slope as iron-magnetite and parallel boundary (Garrels and Christ 1965).



**Figure 2** Boundaries of iron-magnetite and magnetite-hematite as a function of Eh-pH at 250C and 1 atm (Garrels and Christ 1965).

The figure above shows the reactions of iron-magnetite, magnetite-hematite and water stability limits (Garrels and Christ 1965). The boundary of iron-magnetite is below the lower stability limit of water, therefore the reaction is metastable (Garrels and Christ 1965). The reaction between iron and magnetite cannot take place stably in the presence of water because it lies below the lower limit of water stability (Garrels and Christ 1965). Beneath the potential line at which water dissociates to release hydrogen; magnetite exist stably (Garrels and Christ 1965). If the equilibrium is not maintained; the stability of iron cannot be reached in the presence of water (Garrels and Christ 1965).

1. Eh-pH diagrams can be used to determine activities of ions in equilibrium with iron oxides.

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**Figure 3** illustrates the stability relations of iron oxides and water as a function of Eh-pH and will be used for determining the ionic activities (Garrels and Christ 1965).

The figure above shows that the reaction necessary to illustrate the activities of dissolved species is an expression of a reaction between magnetite and hematite (Garrels and Christ 1965). Reaction with involvement of hematite and any dissolved species containing ferric and ferrous iron is Eh dependent (Garrels and Christ 1965). The activities of all dissolved species in equilibrium with hematite and magnetite are calculated and activity contours are constructed (Garrels and Christ 1965). After all the contours have been drawn, they are then superimposed to develop a composite diagram which shows all information about dissolved species for which the data is available (Garrels and Christ 1965).



**Figure 4** Composite diagram showing stability fields of hematite and magnetite in water (Garrels and Christ 1965).

In the composite diagram above; the stability field limit of a given solid is arbitrarily drawn where net activities of ions at equilibrium with solid exceed the chosen value (10-6) (Garrels and Christ 1965). If the net activity of dissolved known species at equilibrium with solids is less than 10-6, then the solid will be an immobile constituent in its environment (Garrels and Christ 1965). The contour which represents the sum or net activity ions is equal to 10-4 and is drawn to illustrate the slope of solubility as a function of Eh and pH, example in the figure below (Garrels and Christ 1965).



**Figure 5** Activity of Fe(OH)++ion in equilibrium with magnetite and hematite at 250C and 1 atm within the stability field of water (Garrels and Christ 1965).

1. The effect of CO2 on iron-water-oxygen

The Eh-pH diagrams can be utilised to determine the stability fields of iron forms as a function of CO2 influence through the consideration of reaction of hematite first; then siderite and magnetite (Garrels and Christ 1965).



**Figure 6** illustrates the stability of hematite, magnetite and siderite as a function of Eh, pH and Pco2 at 250C and 1 atmosphere total pressure (Garrels and Christ 1965).

Figure 6 is a three dimensional Eh-pH stability diagram as a function of CO2; commonly used to illustrate the net reactions in the system (Garrels and Christ 1965). In the figure above; the stabilities of hematite, magnetite and siderite are illustrated as a function of Eh, pH and Pco2 at 250C and 1 atm (Garrels and Christ 1965). Pco2 is plotted as a third dimensional unit with magnetite-hematite boundaries independent of Pco2 (Garrels and Christ 1965). A point given by logPco2 in the figure at 10-3.5 Pco2 atmosphere resembles the partial pressure of CO2 in the earth’s atmosphere where siderite has a small stability field (Garrels and Christ 1965). When Pco2 reaches 10-1.4 atmosphere, magnetite becomes completely displaced by siderite (Garrels and Christ 1965).

1. The effect of sulphur on the iron-water-oxygen reactions

Three dimensional Eh-pH diagrams as a function of sulphur can provide useful information on pyrite and pyrrhotite (Garrels and Christ 1965).

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**Figure 7** illustrates the stability of hematite, magnetite, pyrite and pyrrhotite as a function of Eh, pH and log Ps2 at 250C and 1 atmosphere total pressure in the presence of water (Garrels and Christ 1965).

The boundary between pyrite and pyrrhotite is given the reaction:

The reaction takes place at a fixed Ps2.

The figure above illustrates the stability relations of magnetite, hematite, pyrite and pyrrhotite as a function of Eh, pH and logPs2 at 250C and 1 atm (Garrels and Christ 1965).

1. Case study

In the case study; Eh-pH diagrams were constructed to illustrate the stability of Mn, Fe, Co, Cu and As in the bottom waters of the Angola Basin (Glasby and Schulz 1999).

8.1 Aim

The aim of the case study is to see if there are any significant differences between the Eh-pH diagrams constructed by Brookins (1988) and the new diagrams for study of specific problems in marine geochemistry, and if there are differences; their geochemical implications will be assessed (Glasby and Schulz 1999).

8.2 Methods

The calculations of Eh-pH diagrams were produced through a computer program known as PHREEQE. The Eh-pH diagrams were simplified by representing separate fields for aqueous species and the solid phase stability with a pressure of 1 bar, temperature of 20C (Glasby and Schulz 1999). The calculations of two separate diagrams were done because where several minerals are present, the degree of super-saturation is greater and less space is available to represent the distribution of aqueous species and the diagram will be too complex (Glasby and Schulz 1999). In the solid phase calculations; oxides, hydroxides, sulphides and carbonates were considered (Glasby and Schulz 1999). The part of the diagram where the pH is greater than 9 or less than 4 was considered to be meaningless for the case study and the Eh of +0.4V and pH of 8 were assumed for seawater (Glasby and Schulz 1999). When many minerals in the part of the diagram are super-saturated, it doesn’t necessarily indicate their precipitations but it shows the possibility of minerals to precipitate (Glasby and Schulz 1999). The diagrams calculated were dependent of the thermodynamic dataset used; in this case recent vision of PHREEQC was used (Glasby and Schulz 1999).

8.3 Results

Figures 8-13 represent the calculated Eh-pH diagrams for Mn, Fe, Co, Ni, Cu and As with significant difference from those represented by Brookins (1988).

*The distribution of aqueous Mn species and mineral stability 20C (Glasby and Schulz 1999).*



**Figure 8** The Eh-pH diagrams which illustrate aqueous species and solid phases of Mn calculated for the Angola deep-seawater condition basin (Glasby and Schulz 1999).

The solid phases in the diagram are:

* γ- MnO2 is nsutite
* is birnessite
* β-MnO2 is pyrolusite
* α-Mn2O3 is bixbyte
* Mn3O4 is hausmannite
* γ-MnOOH is manganite

Brookins (1988) stated that; Mn2+ is a principal aqueous species of Mn in the seawater, which predominates at pH values >9.1 and at this pH, MnCl+ speciation of Mn is never a predominant species. Case study results showed that various MnO2 and MnOOH solid phases appeared to be stable, which contradicts with Brookins (1988) findings where the main solid phases were MnO2, MnO and Mn3O4.δMnO2 (Glasby and Schulz 1999). It was found that the stability boundary of δMnO2 had similar gradient as the boundaries of γ-MnO2 and β-MnO2 and was situated between these boundaries (Glasby and Schulz 1999). In deep-sea conditions; solid Mn oxyhyroxide phases are thermodynamically unstable and precipitation of MnS requires high activities of dissolved sulphide and Mn coupled with low Fe activity (Glasby and Schulz 1999).

*The distribution of aqueous Fe species and mineral stability 20C (Glasby and Schulz 1999).*



**Figure 9** The Eh-pH diagrams which illustrate aqueous species and solid phases of Fe calculated for the Angola deep-seawater condition basin (Glasby and Schulz 1999).

The solid phases in the diagram are:

* α-FeOOH is goethite
* α-Fe2O3 is hematite
* Fe3O4 is magnetite
* γ-Fe2O3 is maghemite
* FeS2 is pyrite

The major principal aqueous speciation of iron in the seawater is Fe(OH)30 and other preferred forms are FeCl2+, FeSO4+, FeF2+, Fe(OH)4- with Fe2+ in divalent state (Glasby and Schulz 1999). In the case study results; the observed speciation of iron in the seawater were Fe(OH)30, Fe(OH)2+ and Fe2+ with an exception of FeCl+ (Glasby and Schulz 1999). Aqueous speciation stable under reducing conditions were Fe(HS)20 and Fe(HS)3- (Glasby and Schulz 1999). The stable solid phases observed were goethite, maghemite and magnetite under deep-sea conditions with pyrite stable under reducing conditions, but siderite appeared to be undersaturated (Glasby and Schulz 1999).

*The distribution of aqueous Co species and mineral stability 20C (Glasby and Schulz 1999).*



**Figure 10** The Eh-pH diagrams which illustrate aqueous species and solid phases of Co calculated for the Angola deep-seawater condition basin (Glasby and Schulz 1999).

The solid phases in the diagram are:

* CoS is cattierite
* Co3S4 is linnacite
* Co3O4 is Co-Spinel

The major principal Co aqueous speciation in seawater is Co2+ with lesser amounts of CoSO40 and CoCl+ as stated by Cosovic *et al.* (1982). Cosovic *et al*. (1982) also stated that the minor amounts of CoOH+, Co(OH)20 and CoCO30 are less dominant species in seawater. In the solid phase; CoFe2O4 appeared to be a stable solid phase under seawater which contradicts with Brookins (1988), where Co3O4 was a stable solid phase (Glasby and Schulz 1999).

*The distribution of aqueous Ni species and mineral stability 20C (Glasby and Schulz 1999).*



**Figure 11** The Eh-pH diagrams which illustrate aqueous species and solid phases of Ni calculated for the Angola deep-seawater condition basin (Glasby and Schulz 1999).

The solid phases in the diagram are:

* NiS is millerite

Bruland (1983) and Brookins (1988) illustrated that Ni2+ was a principal aqueous species of Ni in the seawater which contradicts with the results from the case study, where NiCO30 is a principal aqueous species (Glasby and Schulz 1999). All solid Ni phases appeared to be undersaturated and NiCl+ is not predominant (Glasby and Schulz 1999).

*The distribution of aqueous Cu species and mineral stability 20C (Glasby and Schulz 1999).*



**Figure 12** The Eh-pH diagrams which illustrate aqueous species and solid phases of Cu calculated for the Angola deep-seawater condition basin (Glasby and Schulz 1999).

The solid phases in the diagram are:

* CuFe2O4 is cupric ferrite
* CuFeO2 is cuprous ferrite
* CuFeS2 is Chalcopyrite
* Cu2S is chalcocite
* CuS is covellite
* Cu2O is cuprite

In the aqueous speciation of Cu; CuCl32- and Cu(OH)2 appeared to be the principal species in the seawater and Cu2+ appeared as a dominant species at Eh>+0.48V (Glasby and Schulz 1999). Bruland (1983) found that the principal forms of Cu in seawater were CuCO3-, CuOH+ and Cu2+. In the solid phase; it was found that CuFe2O4 and CuFeO were undersaturated with sulphides occurring under reducing conditions (Glasby and Schulz 1999). Brookins (1988) ignored CuCl32- as an aquatic species of Cu and showed that CuO is a stable solid phase of Cu.

*The distribution of aqueous As species and mineral stability 20C (Glasby and Schulz 1999).*



**Figure 13** The Eh-pH diagrams which illustrate aqueous species and solid phases of As calculated for the Angola deep-seawater condition basin (Glasby and Schulz 1999).

The solid phases in the diagram are:

* AsS is realgar
* As2S3 is orpiment

In the aqueous speciation of As; HAsO42- was found to be the principal species in the seawater with H3AsO30 stable under reducing conditions (Glasby and Schulz 1999). The dominant stable solid phase of As under deep-sea conditions was Ba3(AsO4)20 (Glasby and Schulz 1999).

8.4 Case study conclusion

The calculated Eh-pH diagrams determined different speciation of trace elements in the Angola deep-seawater basin and provided the insight understanding in the marine geochemistry of the case study. It was concluded that; Fe, Co, Cu and As in the solid phase demonstrates supersaturated solids. On the other hand; Mn and Ni were thermodynamically stable in the aqueous phases which demonstrate that the solid phases are undersaturated.

1. Conclusion

An Eh-pH diagram is a diagram that illustrates the equilibrium occurrence of minerals and dissolved species as a function of Eh and pH. These stability diagrams are commonly used to illustrate the stability fields of solids and dissolved species in the solution depending on the redox potential and pH. They are also applied in explanation of mineral paragenesis, in predicting species in a solution, in alteration products of ores and in hydrothermal systems. The Eh-pH diagrams are also used to illustrate equilibrium relationship between dissolved and precipitated species. Drawn Eh-pH diagrams from the case study determined different speciation of trace elements in the Angola deep-seawater basin and provided the insight understanding in the marine geochemistry of the case study.

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