

Pourbaix (pE-pH) diagrams for the aquatic environment (ECGEB No 6)

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Pourbaix diagrams (or eh-pH, or pE-pH diagrams) can help environmental workers to “predict” the physical and oxidation state of a chemical element in different aquatic environments. Pourbaix diagrams can explain and predict behaviour of contaminants in the environment but they should be used with caution and knowledge of their weaknesses.

The release of a potentially harmful chemical into the aquatic environment requires knowledge about the chemical released and any subsequent transformation of the chemical. Redox and acid-base reactions within the aquatic environment may cause a change to the oxidation state, molecular formula and physical state of the element and hence toxicity. A Pourbaix diagram (named after the Russian-born Belgian chemist Marcel Pourbaix) is a stability diagram (roughly similar to a phase diagram) and demonstrates which species predominates under different conditions of redox potential and pH. For example iron exists differently in the oxygen poor waters of ground water to that of acid mine drainage and that of an aerated stream.

Provided here is the briefest introduction to Pourbaix diagrams to show their potential use and common pitfalls. The author has found the use of Pourbaix diagrams useful in teaching and the explaining of concepts. Future *ECG Environmental Briefs* will show more advanced uses for the environmental professional, and an interested reader is referred to detailed texts, such as (1).

Introduction to the diagram

A Pourbaix diagram is typically electrode potential (relative to a standard hydrogen electrode potential) or pE plotted *versus* the pH of an aquatic media. pE is more common for environmental science and is similar to the definition of pH:

$$\text{pH} = -\log a(\text{H}^+_{(\text{aq})})$$

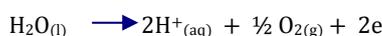
i.e. the logarithm of the activity of the hydrogen ion, and

$$\text{pE} = -\log a(\text{e}^-)$$

i.e. the logarithm of the hypothetical activity of electron.

Put simply, pE is a measure of the aquatic system to reduce or oxidise.

A typical Pourbaix diagrams for iron calculated using free software (2) is shown in **Figure 1**. The dashed lines bound the region where liquid water is stable; above the upper dashed line water is oxidised:



Below the lower dashed line water is reduced:



The lines on the graph enclose regions where different forms of iron may predominate. The lines are drawn where the activities of two neighbouring species are equal. The activity of solids in a Pourbaix diagram are explained in (3). Vertical lines represent acid-base reactions and horizontal lines represent redox reactions.

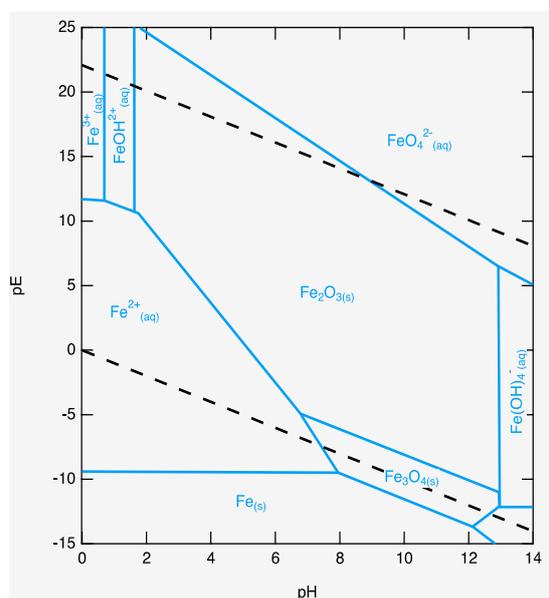


Figure 1. Pourbaix diagram calculated for iron at 10 °C and $[\text{Fe}^{3+}_{(\text{aq})}]_{\text{total}} = 1 \mu\text{M}$, using the Chemical Equilibration Diagram software (2). The graph is indicative and should not be considered accurate.

Consideration of **Figure 1** shows that a ground water (e.g. $pE < 0$ and $pH \sim 6.5-7.5$) may contain iron as $Fe^{2+}_{(aq)}$, surface waters (e.g. $pE > 0$ and $pH \sim 6.5-7.5$) will contain Iron as the solid Fe_2O_3 and extreme acid mine drainage water ($pE > 0$ and $pH < 3$) may contain Iron as $Fe^{3+}_{(aq)}$. pE-pH diagrams with typical values of pE and pH for natural water bodies can be found in Krauskopf and Bird (3) and Baird (4). These two sources have broadly similar diagrams but with some differences. It is difficult to measure the pE of natural waters as the water may not be at equilibrium or be in equilibrium with the probe measuring pE (5).

Figure 2 demonstrates that Pourbaix diagrams are very sensitive to the presence of other chemical species. Adding sulphur to previous system, **Figure 1**, demonstrates a new Pourbaix diagram, **Figure 2**, which may be used to explain the chemical speciation of iron occurring in natural waters containing sulphur or with a sulphur lithology.

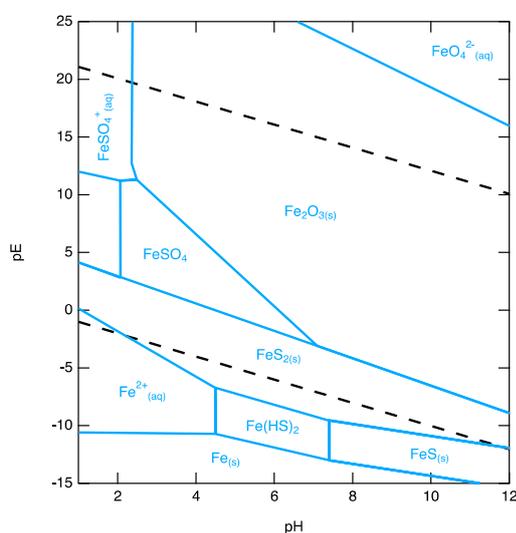


Figure 2. Pourbaix diagram calculated for iron at 10 °C with $[Fe^{3+}_{(aq)}]_{total} = 1 \mu M$ and $[SO_4^{2-}_{(aq)}]_{total} = 10 mM$, using the software in (2). The graph is indicative and should not be considered accurate.

Important caveats

There are many considerations with the interpretation of Pourbaix diagrams. Three caveats with Pourbaix diagrams are:

1. The diagrams represent thermodynamic equilibrium. They do not indicate how quickly the system will come to equilibrium and a water body may effectively never reach equilibrium. The kinetics of each situation must be assessed independently especially as many of the redox reactions are biologically mediated.

2. Pourbaix diagrams are constructed for the given conditions of temperature, pressure and activities of species present. Thus a general Pourbaix diagram is unlikely to be accurate for a specific situation.
3. Pourbaix diagrams display the dominating species. However, the systems are assumed to be at equilibrium thus other chemical species may be present at appreciable, but not dominant, concentrations.

Ideas for exploration or teaching

To further explore Pourbaix diagrams the chemical equilibrations software listed at the end of this article may be used to consider the following systems.

1. To complement a water quality field trip to Southern Florida looking at phosphate eutrophication of water bodies, students create Pourbaix diagrams of: (a) phosphorus, (b) phosphorus and aluminium, (c) phosphorus, aluminium, and iron, (d) phosphorus, aluminium, and calcium. With these diagrams they can explain why aqueous phosphate pollution can move through sandy soils to the water bodies.
2. Create Pourbaix diagrams for radionuclides of actinides, (a) with and without carbonate included, or (b) considering if artificial wetlands could be useful in trapping actinides from surface storm water from plants using radionuclides.

References

1. W. Stumm and J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, John Wiley, New York, 1996.
2. Free software for generating Pourbaix diagrams is coded by Ignasi Puigdomenech. (JAVA), see <https://sites.google.com/site/chemdiagr/home>
3. K. Krauskopf, and D. Bird, *Introduction to Geochemistry*, 3rd edn., McGraw-Hill, New York, 1995.
4. C. Baird, *Environmental Chemistry*, 2nd edn., W. H. Freeman, New York, 1998.
5. D. K. Nordstrom, F. D. Wilde, Reduction-oxidation potential (electrode method) (ver1.2): US Geological survey techniques of water resources investigations, book 9, chapter A6, Sec6.5. Accessed 28 May 2014 from <http://water.usgs.gov/owq/fieldmanual>.

The author is an ECG committee member and the *ECG Environmental Briefs* Commissioner.

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