# Redox Behavior of $Fe^{2+}$/$Fe^{3+}$ Redox Couple by Absorption Spectroscopy and Measurement

J. Y. Oh[*], S. Park, J.-I. Yun

*Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea*
[*]*Corresponding author : onlymywill@kaist.ac.kr*

## 1. Introduction

Redox behavior has influences on speciation and other geochemical reactions of radionuclides such as sorption, solubility, and colloid formation, etc. It is one of the factors for evaluation of long-term safety assessment under high-level radioactive waste (HLW) disposal conditions. Accordingly, redox potential (Eh) measurement in aquatic system is important to investigate the redox conditions. Eh is usually measured with redox active electrodes (Pt, Au, glassy carbon, etc.). Nevertheless, Eh measurements by general methods using electrodes provide low accuracy and high uncertainty problem. Therefore, Eh calculated from the concentration of redox active elements with a proper complexing reagent by using UV-Vis absorption spectroscopy is progressed.

Iron exists mostly as spent nuclear waste container material and in hydro-geologic minerals. In this system, iron controls the redox condition in near-field area and influences chemical behavior and speciation of radionuclides including redox sensitive actinides such as U, Np, and Pu [1]. In the present work, we present the investigation on redox phenomena of iron in aquatic system by a combination of absorption spectroscopy and redox potential measurements.

## 2. Experimental

### 2.1 $Fe^{2+}$/$Fe^{3+}$ redox couple sample

$Fe^{2+}$/$Fe^{3+}$ redox couple is used for investigating iron redox behavior due to its simplicity and strong influence in near-field system. In this work, $FeCl_2 \cdot 4H_2O$ (Sigma-Aldrich, 99.999%) is used as $Fe^{2+}$ compound and $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich, 99.99%) as $Fe^{3+}$ compound. The samples were prepared in a relatively wide pH coverage from 2 to 9 (2.014, 3.015, 4.186, 4.900, 5.731, 6.654, 8.183, 9.167), and the pH was controlled by $HClO_4$ (Rieden-de Haen) and NaOH (Merck) in 0.1 M $NaClO_4$ (Sigma-Aldrich, 98%). 5 different concentration ratios of $Fe^{2+}$/$Fe^{3+}$ redox samples were made with a variation of 3 different total iron concentrations. ([$Fe^{2+}$]:[$Fe^{3+}$] = 100:1 and 1:100 at the total iron concentration of $1.809 \times 10^{-5}$ M; 10:1 and 1:10 at $1.970 \times 10^{-6}$ M; 1:1 at $3.582 \times 10^{-7}$ M)

### 2.2 Eh measurement

Eh of each sample was measured with a Pt-Ag/AgCl electrode in 3M KCl electrolyte (Metrohm), when the equilibrium was reached. To avoid carbonate effect and oxidization, all the experimental procedures are conducted in a glovebox under argon inert gas ([$O_2$] = 3 ~ 4ppm).

### 2.3 Absorption spectroscopy

UV-Vis diode-array absorption spectrometer (Scinco, S-4100) was used to determine the iron ion concentrations. For measuring the absorbance of Fe(II), ferrozine (Merck) was employed as Fe(II) complexing reagent. Ferric iron, Fe(III), was reduced to ferrous iron, Fe(II), by using a reducing agent, $NH_2OH \cdot HCl$. The detection limit for Fe(II) was determined to be $3.4 \times 10^{-8}$ M, based on its molar absorption coefficient of 26,476 $M^{-1} \cdot cm^{-1}$ from the experiments.

## 3. Results and Discussion

### 3.1 Eh measurements

Fig.1. shows the measured Eh values as a function of pH. As expected, Eh decreased with increasing pH. Nevertheless, the measured Eh values are not related to the initial concentration ratios of [$Fe^{3+}$]/[$Fe^{2+}$] except for the sample set of [$Fe^{3+}$]/[$Fe^{2+}$] = 1, which has slightly lower Eh values. It is noted that [$Fe^{3+}$]/[$Fe^{2+}$] ratio was steadily changed over reaction time, until the redox equilibrium was reached.
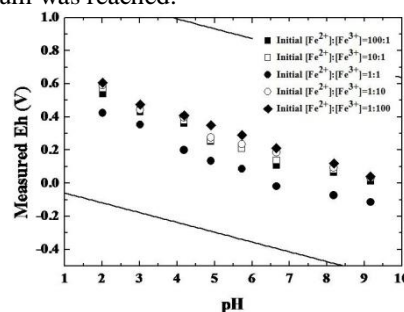


Fig. 1. Measured Eh values as a function of pH and the concentration ratios of [$Fe^{3+}$]/[$Fe^{2+}$].

### 3.2 Calculated Eh based on absorption spectroscopy

Fe(II)-ferrozine complex is purple-colored and presents the absorption peak at 562 nm. The absorbance is linearly dependent on the Fe(II) concentration. Beer-Lambert law is used to calculate the ferrous iron concentration. (Eq. (1))

$$A = \varepsilon c l \qquad (1)$$

where A is absorbance, $\varepsilon$ is the molar absorption coefficient of sample, c is the concentration of sample, l is the absorption pathlength.

Using absorption spectroscopy, the Fe(II) concentrations can be determined because of the only formation of the Fe(II)-ferrozine complex, whereas there is no Fe(III)-ferrozine complex. Furthermore, the hydrolysis reactions of Fe(II) and Fe(III) have to be considered for the calculation of the free ion concentration of each iron oxidation state, [$Fe^{2+}$] and [$Fe^{3+}$].

As shown in Fig. 2, the distribution of the hydrolyzed species fraction of Fe(II) and Fe(III) are presented with the well-known formation constants for the hydrolysis reactions. By taking the fraction of the hydrolyzed species concentration into account, the concentrations of $[Fe^{2+}]$ and $[Fe^{3+}]$ were calculated (see the paper by S. Park et al for the KNS spring meeting 2010). Eh was calculation by $[Fe^{3+}]/[Fe^{2+}]$ concentration ratios according to the following reactions:

$$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}, \quad log\,K = 13.02 \;[\,2\,] \quad (2)$$
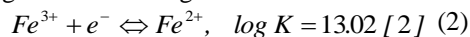
$$pe = 13.02 + \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad (3)$$

$$pe = 16.9 \cdot Eh \; [V] \quad (4)$$

In addition, it is necessary to consider the solubility limit of Fe(II) and Fe(III) for the Eh calculation. Solubility limit curves of Fe(II) and Fe(III) are presented in Fig. 3.
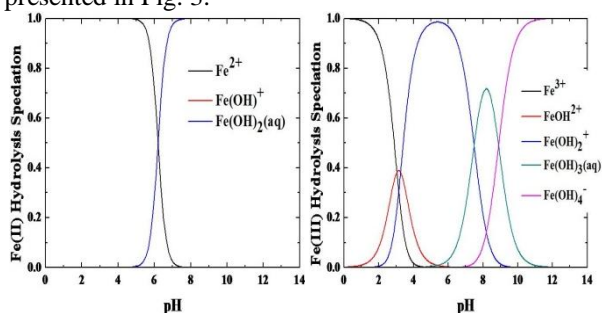


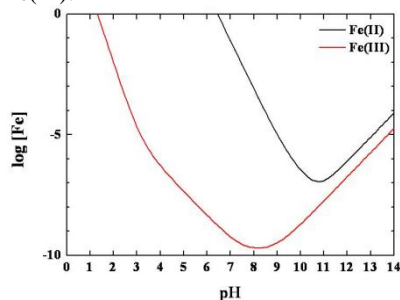Fig. 2. The distribution of the hydrolyzed species fraction of Fe(II) and Fe(III).



Fig. 3. Solubility limit curves for Fe(II) and Fe(III) in 0.1M NaClO$_4$ media.

In the experimental conditions of high pHs, Fe(III) may precipitate as a solid phase such as hematite ($Fe_2O_3$) or $Fe(OH)_3(s)$ and can be adsorbed on the surface of the Eh electrode, when the solubility is exceeded. To investigate the accuracy and reliability of Eh values, we compared the Eh values measured by the Eh electrode with the calculated values by absorption spectroscopy, as shown in Fig. 4. Differences of both Eh values were relatively large, and the measured Eh values were mostly lower than the calculated Eh values by around 200 mV. In the range of pH 6~9, the Eh difference is little changed due to the decrease of calculated Eh above pH 5.731. The difference between measured and calculated Eh of $[Fe^{2+}]:[Fe^{3+}] = 1:1$ ratio sample set (Total iron concentration $= 3.582\times10^{-7}$ M) is quite larger than the difference of other samples ($1.809\times10^{-5}$ M and $1.970\times10^{-6}$ M). It is noted that total soluble iron concentration influences on differences between measured and calculated Eh. The difference of measured and calculated redox potentials becomes large with decreasing the total iron concentration. As a result, it can be presumed that a minimum amount of iron is needed for the reliable performance of Eh measurements by electrodes. This experimental observation agrees well with literature [3]. Additionally, the complicated phenomenon may be related with a precipitation of Fe(III) as hematite or iron hydroxide solids. The solid phase of Fe(III) being predominantly formed in this pH range can be easily adsorbed on the surface of Eh electrode. Additionally, the mixed redox couples of $Fe^{2+}/Fe^{3+}$ and $Fe^{2+}/Fe_2O_3(s)$ are formed under the conditions.
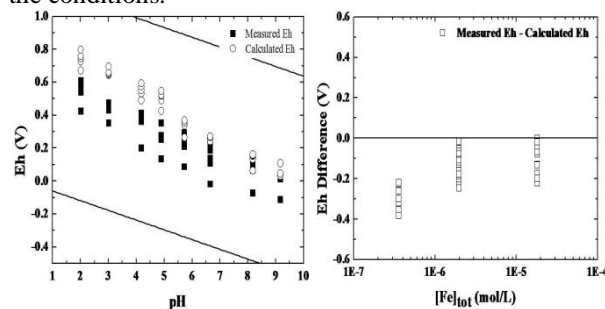


Fig. 4. Comparison between measured Eh values and calculated Eh values (left figure) and the differences between both values as a function of the total iron concentration (right figure).

## 5. Conclusions

We investigated the redox behaviors of iron by a combination of redox potential measurements and absorption spectroscopy. There is still a relatively large discrepancy between the measured and calculated Eh values, even though the qualitative tendencies are more or less consistent. Measured Eh can be affected by the formation of mixed redox potentials and adsorption of metal ions and/or precipitates onto the electrode surface. At higher than $10^{-6}$ M iron concentration, the measured Eh values are close to those calculated. Presumably, measuring the Eh values becomes insensitive to the very low redox couple concentrations. For a better prediction of the chemical behaviors of radionuclides including actinides in geosphere, accurate and reliable redox measurements are highly necessary and desirable. Our investigation is in progress.

## REFERENCES

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