Spectroscopic Speciation of Iron Using Complexing Agents

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

Dept. of Nuclear and Quantum Eng., KAIST, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea
[*]*Corresponding author: ps1000@kaist.ac.kr*

1. Introduction

Redox state is a highly influential chemical parameter for geologic waste disposal. Migration behaviors of radionuclides are strongly affected by their redox states. Iron, one of the most abundant elements in geosphere, may affect chemical behaviors of redox sensitive radioculides [1]. The chemical speciation of iron is important to investigate redox behaviors of iron.

In this work, we present the spectroscopic speciation of iron redox state as a function of pH and the iron concentration ratio of Fe(II)/Fe(III) by a combination of absorption spectroscopy and redox potential measurements.

2. Experimental

2.1 Fe(II)/Fe(III) sample

Ferrous ion solutions of 10ppb, 30ppb, 100ppb, 300ppb and 1ppm, and ferric iron solutions of [Fe(III)]=1ppm and [Fe(II)]:[Fe(III)]=1ppm:1ppm were prepared with highly pure $FeCl_2 \cdot 4H_2O$ (Sigma-Aldrich, 99.99%) and $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich, 99.99%) for the calibration of absorption spectroscopy. The pH of iron solutions was controlled with 1.0 M $HClO_4$ (Riedel-de Haen) and 1.0 M NaOH (Merck). $NaClO_4$ (Sigma-Aldrich, 98%) was used as ionic strength buffer. Ultra pure MQ water (18.2 MΩ cm, Millipore) was used for the dilution of all the solutions. The prepared solutions of iron were kept in an inert argon glove box at around 25^oC (O_2: 3~5 ppm). For the purpose of studying redox behaviors of Fe, iron samples were prepared at 1ppm:10ppb (100:1) and 10ppb:1ppm (1:100) in concentration ratio of Fe(II):Fe(III) in the pH range of 2 to 9. Redox potentials were measured by the Pt electrode against the Ag/AgCl reference electrode in 3M KCl electrolyte (Metrohm).

2.2 Absorption spectroscopy

Ferrozine and 1,10-phenanthroline monohydrate iron reagents are reagents complexed only with ferrous ions, Fe(II), and then the Fe(II) aqueous solutions are colored due to its complexation with Fe(II). The Fe(II) ion concentration is easily determined by absorption spectroscopy [2,3]. Furthermore, the concentration of ferric ion concentration can be also determined by reduction of Fe(III) to Fe(II) using a reducing reagent of $NH_2OH \cdot HCl$ (Sigma-Aldrich, 98%) and by difference of mass balance. The spectroscopic absorption follows the Beer-Lambert law:

$$A = \varepsilon cl \qquad (1)$$

where A is the absorbance, ε is the molar absorption coefficient ($M^{-1} \cdot cm^{-1}$), c is the concentration (M), and l is the absorption pathlength (cm). The UV-Vis diode-array absorption spectrometer (Scinco, S-4100) was used.

The redox potential is calculated on the basis of the concentration determination of each iron species using the Nernst equation. The hydrolysis constants and the solubility limit of iron must be taken into account for the calculation of redox potentials.

3. Results and Discussion

3.1 Absorption spectroscopic properties

When ferrous ions make a complexation with complexing agents, such as ferrozine and 1,10 phenanthroline monohydrate, their absorption spectrum appear at specific maximum wavelength of 562 nm and 511 nm, respectively, as shown in Fig.1. The absorbance varied linearly with the ferrous ion concentration. The molar absorption coefficient was determined to be 26251 ± 1069 M^{-1} cm^{-1} ($R^2 = 1.00$) for Fe(II)-ferrozine complexes, and 11128 ± 536.9 M^{-1} cm^{-1} ($R^2 = 1.00$) for Fe(II)-1,10-phenanthroline monohydrate compelxes (Figure 2). Based on the molar absorption coefficients resulted from these experiments, the limit of detection for ferrozine and 1,10-phenanthroline monohydrate was calculated to be 3.81×10^{-8} M and 8.99×10^{-8} M, respectively.
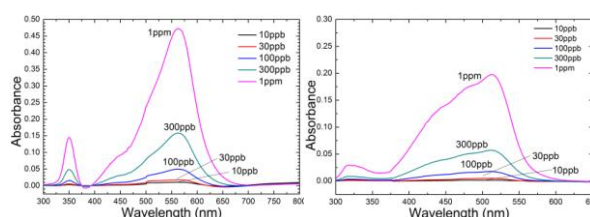

Fig. 1. Absorption curve of Fe(II)-ferrozine(left), Absorption curves of Fe(II)-1,10-phenanthroline monohydrate(right)
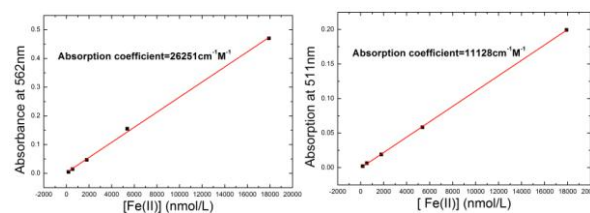

Fig. 2. Calibration curves for Fe(II)-ferrozine complexes at 562nm (left) and for Fe(II)-phenanthroline complexes at 562nm (right)

3.2 Speciation of Iron

Based on the analytical capability by using complexing reagents, we demonstrated the oxidation state speciation of iron metal ions in aqueous solutions. As ferrozine was added to the sample [Fe(III)]=1ppm, ferric ion did not complex with ferrozine or 1,10-phenanthroline monohydrate. First, the ferric iron solutions became colored, when Fe(III) is reduced to Fe(II) by adding the reducing reagent of $NH_2OH \cdot HCl$. The ion concentration of Fe(III) could be determined after reduction (Figure 3, left). As a mixture of iron samples with a concentration ratio of [Fe(II)]:[Fe(III)]=1ppm:1ppm was reduced, the absorbance equals the total Fe ion concentration in the solution. [Fe(III)] could be obtained from difference in absorbance between the original and the reduced iron solutions.

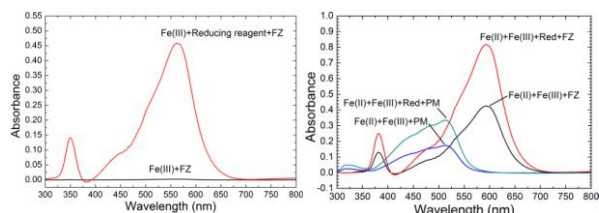Fig. 3. Absorption spectra of Fe(III)-FZ complexes of 1 ppm Fe(III) concentration and after reduction of Fe(III) to Fe(II) by adding $NH_2OH \cdot HCl$ (left) and absorption spectra of a mixture of Fe(II) and Fe(III) before and after reduction with $NH_2OH \cdot HCl$(right). The concentrations of each iron oxidation state are 1 ppm (1.791×10^{-5} M)

3.3 Comparison of redox potentials

Redox potential of iron was calculated based on the speciation and measured by E_h meter (see the paper by J. Y. Oh et al for the KNS Spring Meeting). The redox potential varied according to pH (Figure 4). The redox potential decreased as pH increased for both mixture ratios. All data were observed in the range of water stability [4].
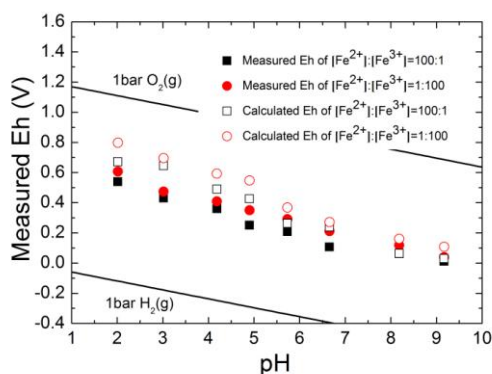

Fig. 4. The relationship between calculated Eh and measured Eh. The stability lines of water at pe+pH = 20.77 and pe+pH = 0 are shown for comparison.

4. Conclusions

We demonstrated spectroscopic speciation of iron using complexing agents. The absorption spectroscopy has been applied appropriately for the analysis of the oxidation state of iron. The relative measurement uncertainties using the Fe(II) selective complexing reagents such as ferrozine and 1,10-phenanthroline monohydrate have been evaluated to be smaller compared to other analytical tools. The LOD was sensitively enough to analyze the natural original state of iron metal ion in natural aquatic systems. Based on this work, redox potentials of natural groundwater could be calculated more sensitive and reliable from the chemical speciation of the Fe(II)/Fe(III) redox couple.

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