

Formation of surface mediated iron colloids during U(VI) and nZVI interaction

Youngho Sihn, Sungjun Bae and Woojin Lee*

Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

(Received May 31, 2013, Revised June 05, 2013, Accepted June 07, 2013)

Abstract. We investigated that removal of aqueous U(VI) by nano-sized Zero Valent Iron (nZVI) and Fe(II) bearing minerals (controls) in this study. Iron particles showed different U(VI) removal efficiencies (Mackinawite: 99%, green rust: 95%, nZVI: 91%, magnetite: 87%, pyrite: 59%) due to their different PZC (Point of Zero Charge) values and surface areas. In addition, noticeable amount of surface Fe(II) (181 μM) was released from nZVI suspension in 6 h and it increased to 384 μM in the presence of U(VI) due to ion-exchange of U(VI) with Fe(II) on nZVI surface. Analysis of Laser-Induced Breakdown Detection (LIBD) showed that breakdown probabilities in both filtrates by 20 and 200 nm sizes was almost 24% in nZVI suspension with U(VI), while 1% of the probabilities were observed in nZVI suspension without U(VI). It indicated that Fe(II) colloids in the range under 20 nm were generated during the interaction of U(VI) and nZVI. Our results suggest that Fe(II) colloids generated via ion-exchange process should be carefully concerned during long-term remediation site contaminated by U(VI) because U could be transported to remote area through the adsorption on Fe(II) colloids.

Keywords: uranium; nZVI; ion-exchange; Fe(II) colloids; LIBD

1. Introduction

Uranium (U) is a hazardous radioactive element that is limited by World Health Organization (WHO) at 0.015 mg/L for drinking water (WHO 2004). Recently, release of U through groundwater has been received an attention due to significant increase of industrial and military activities (e.g., U mining, handling and storage of radioactive waste) (Fiedor *et al.* 1998, Wazne *et al.* 2003, Noubactep *et al.* 2003). In the aquatic systems, U migration is strongly influenced by redox conditions in which U(VI) species are highly mobile while sparingly soluble U(IV) species have relatively low mobility. Therefore, reduction of U(VI) to U(IV) by abiotic and/or biotic reactions and maintaining U as U(IV) for long-term stabilization have been considered as a promising approach in remediation site contaminated by U.

Nano-sized zero-valent iron (nZVI) is a versatile material for remediation of soil and groundwater contaminated by U(VI) (Fiedor *et al.* 1998, Noubactep *et al.* 2006, Riba *et al.* 2008). It has been reported that nZVI particles are more reactive than commercial micro-sized ZVI due to higher surface area (Bae and Lee 2010, Amir and Lee 2011, Choi and Lee 2012). The structure of

*Corresponding author, Professor, E-mail: woojin_lee@kaist.ac.kr

nZVI has been well investigated by variety of spectroscopic and microscopic analysis tools (Sun *et al.* 2006, Li and Zhang 2006, Martin *et al.* 2008, Yan *et al.* 2010). Surface of nZVI near the water interface can be easily oxidized by air or oxygen in any case of synthesis methods. This surface oxidation has resulted in a formation of thin and oxide/hydroxide layer (i.e., Fe₂O₃, Fe₃O₄, and FeOOH) with typically 2-3 nm. The layer acts as adsorption sites for the variable contaminants, mostly heavy metals and radioactive elements, via inner and outer sphere binding and complexation with reactive surface ligands by electrostatic interaction. The electron transferring from core Fe(0) to the iron oxides/hydroxides layer can be occurred in nZVI structure leading to the degradation and reduction of contaminants.

Studies have shown that nZVI can effectively remove U(VI) from aqueous phase depending on the environmental conditions, e.g., pH, Eh, and CO₂ partial pressure etc (Fiedor *et al.* 1998, Noubactep *et al.* 2006, Riba *et al.* 2008, Dickinson and Scott 2010). Removal of U(VI) by the nZVI suspension may be attributed to competition of possible reactions following as: (1) U(VI) adsorption onto iron (hydr)oxide products on the outer sphere of nZVI surface; (2) reductive precipitation of U(VI) to insoluble U(IV) by structural Fe(II) at the outer-sphere and core Fe(0); (3) combination of sorption/reductive precipitation.

Recently, Hua and Deng (2008) and Hyun *et al.* (2012) have reported that the removal of U(VI) rapidly occurred by Fe^{II}S particles in aqueous phase accompanied by a simultaneous release of Fe(II) which indicates the aqueous U(VI) was removed by ion-exchange with Fe(II) on the Fe^{II}S surface. As aforementioned, one of the major constituent on nZVI surface is Fe(II) (hydr)oxides. Therefore, there is a possibility that aqueous U(VI) is removed by the ion-exchange with Fe(II) on the nZVI surface which can drive the simultaneous release of Fe(II) in aqueous phase. The released Fe(II) could be agglomerated as colloids by chemical reactions (e.g., hydrolysis and precipitation) (Ulrich *et al.* 2006) leading to the enhancement of U mobility by adsorption on the colloids. Indeed, Novikov *et al.* (2006) has shown that 70–90 mole fraction of Pu(VI) and U(VI) ions in groundwater were absorbed on the Fe (hydr)oxides colloids called actinide pseudo-colloids. The presence of actinide pseudo-colloids is responsible for the longer distance transport of U(VI) in the field due to their higher stability than that of pure U(VI) ions. The higher stability of Fe(II) colloid-associated U(VI) facilitates increase of U concentration in the groundwater by many orders of magnitude compared to the anticipated values from solubility calculation (Missana *et al.* 2003, Novikov *et al.* 2006). This result indicates that the formation of Fe(II) colloid should be carefully considered as a significant phenomenon for the long-term storage and management of radioactive wastes.

Because the permeable reactive barriers (PRB) holding nZVI is widely applied as effective in-situ technology for removal of U(VI) from groundwater plume, the abundant Fe colloids might be formed from ion-exchange between aqueous U(VI) and surface Fe(II) on nZVI during the remediation process. However, limited knowledge has been provided for the formation of Fe colloids during the interaction of nZVI and U(VI) to date. In this study, we focused on the investigation of ion-exchange and the formation of Fe colloids during U(VI) removal by nZVI suspension. Especially, Laser-Induced Breakdown Detection (LIBD) was used for monitoring of the colloids formation in aqueous phase.

2. Material and methods

2.1 Chemicals

All chemicals ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, NaBH_4 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NaHS} \cdot \text{H}_2\text{O}$, CS_2 , HNO_3 (60%), $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, NaOH , and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) used in the experiment were ACS grade or higher. Solutions were prepared using deaerated deionized water (DDW, resistivity $> 18.2 \text{ M}\Omega\text{cm}$) purged by N_2 for 4h. DDW was stored in an anaerobic chamber filled with 95% N_2 and 5% H_2 (Coy Laboratory Products Inc.). In order to remove any possible impurities in the solutions that could be detected as colloids, all solutions prepared for this study were centrifuged in ultra-centrifugal filter (Amicon Ultra-15, 10 K) for 40 min at 4000 g prior to their use. Buffer was prepared to maintain pH constant at pH 8.5 using 0.05 M trizma (tris, $\text{pK}_a = 8.06$) mixture of tris (hydroxymethyl) aminomethane (99.8%, Sigma) and trizma hydrochloride (99%, Sigma).

2.2 Synthesis of nZVI and Fe(II)-bearing minerals

nZVI was chemically synthesized by adding 0.9 M NaBH_4 solution into 0.11 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution (Wang and Zhang 1997). Precipitates formed in mixed solution were washed two times with DDW by centrifuge at 950 g for 10 min and followed with acetone. Synthesized nZVI was freeze-dried and stored in the anaerobic chamber. Fe(II)-bearing minerals such as magnetite (Fe_3O_4) (Bae and Lee 2010), green rust (GR- SO_4) (Srinivasan *et al.* 1996, Cho *et al.* 2012), mackinawite (FeS) (Amir and Lee 2012), and pyrite (FeS_2) (Han *et al.* 2012) were synthesized by following the procedure previously described. The synthesized Fe(II)-bearing minerals were used as controls to compare their Fe(II) release ability with that of nZVI during interaction with U(VI). The basic principles of the mineral synthesis methods are (1) reducing aqueous Fe(III) as Fe(II) particles by mixing with sulfide containing reductants under N_2 flow, (2) formation of Fe(II) particles from Fe(II) ions by pH titration using NaOH from acidic to neutral condition. Identification and purity of the synthesized minerals were checked by X-ray diffraction (XRD) patterns showing that all the synthesized minerals matched well with those in Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data files (JADE 9, Materials Data, Inc.) (data not shown).

2.3 Batch kinetic experiment for U(VI) removal by iron particles

All the batch experiments were conducted in the anaerobic chamber under N_2 atmosphere. An exact amounts of nZVI and Fe(II)-bearing minerals were transferred to 24 mL PTFE vials and 20 mL of Tris buffer (pH 8.5) was added to prepare the suspensions containing 4 mM of Fe(II). Reaction was initiated by adding 40 μL of U(VI) standard (0.01 M) into each vial to prepare the initial concentration of 20 μM U(VI) in the suspensions. Vials were tightly capped and transferred into sealed container filled with N_2 . The container mounted on an end-over-end rotator at 0.5 rpm. Periodically (1, 5, 20, and 60 min), the container was taken from the anaerobic chamber and sample was collected by plastic syringe (5 mL) and filtered through 0.2 μm filter (nylon syringe filter, Whatman). Three mL of filtrate was used for pH measurement and remained filtrate was used for the analysis of aqueous U concentration (1 mL), aqueous Fe(II)/Fe(III) concentration (5 mL), and confirmation of Fe colloids formation in aqueous phase (5 mL). As a subsequent step of aforementioned analysis, 2.5 mL of 0.2 μm filtrate was filtered again by a 0.02 μm filter (inorganic membrane filter, Whatman) to determine the size range of Fe colloids.

2.4 Analytical procedures

Inductively coupled plasma mass spectrometry (ICP-MS) and ferrozine method (Stookey

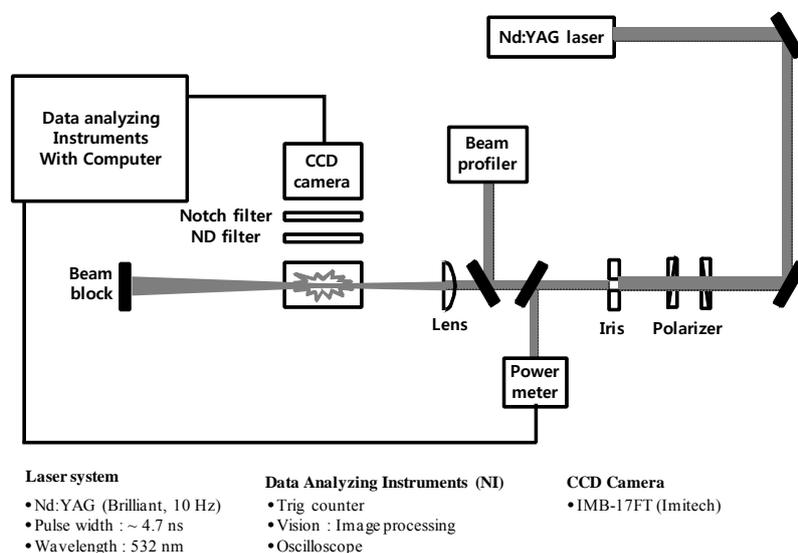


Fig. 1 Schematic diagram of LIBD system in this study (Kirana and Yun 2011)

1970) were used to measure the U and Fe concentrations in aqueous phase, respectively. The filtrates by 0.2 and 0.02 μm membranes were diluted 10 times with 8% HNO_3 to prepare acidic solutions prior to the measurement of aqueous U concentration by ICP-MS (Perkin-Elmer Elan 6000). Aqueous Fe(II)/Fe(III) concentrations were measured by UV-vis spectrophotometric analysis (HP-8452A diode array spectrophotometer) with its specific wave length at 562 nm.

To identify the formation of colloids during the interaction of nZVI and U, Nd-YAG laser (Brilliant, wavelength 532 nm, repetition rate 10 Hz) was used. The certain volume (2 mL) of 0.2 and 0.02 μm filtrates was decanted into 10 mm quartz cuvettes (Fisher) and mounted on the LIBD system (shown in Fig. 1). The laser beam was focused onto the sample and then the breakdown was optically measured by charge-coupled device camera for 2,000 laser shots. All samples were measured by LIBD in triplicate in this study.

3. Results and discussion

3.1 Monitoring of U(VI) removal kinetic and surface Fe(II) release

Fig. 2(a) illustrates aqueous U(VI) concentration in nZVI and Fe(II)-bearing mineral suspensions in 1 h. The aqueous U(VI) (82-89%) was rapidly removed by mackinawite, green rust, and nZVI suspensions in 5 min, while magnetite and pyrite suspensions showed 24-50% of removal. After 5 min, aqueous U(VI) concentration in all suspensions continuously but slowly decreased in 1 h. The highest removal efficiency was obtained from mackinawite suspension (99%) at 1 h, followed by green rust (95%), nZVI (91%), magnetite (87%), and pyrite (59%). This indicated that the type of Fe(II)-bearing minerals can differently affect the removal efficiency of U(VI). This may be attributed to different physical characteristics such as PZC and surface area. A number of studies have demonstrated that the adsorption of aqueous U(VI) on iron-(hydr)oxide

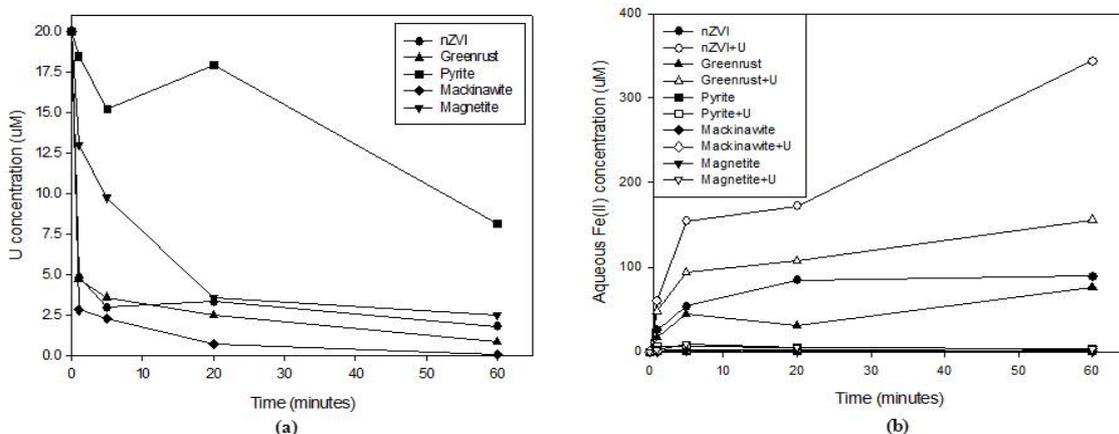


Fig. 2 (a) Removal of U(VI) and (b) increase of aqueous Fe(II) in suspensions of nZVI and Fe(II)-bearing minerals during interaction with U(VI)

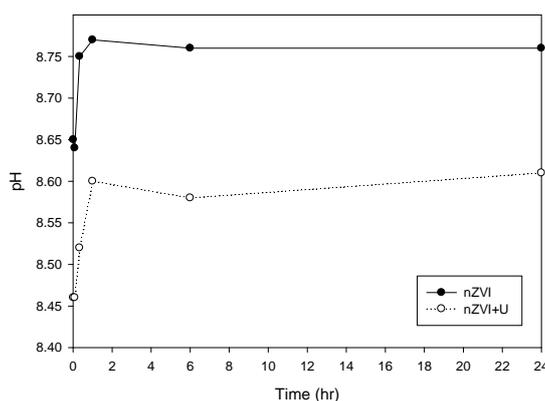


Fig. 3 pH variation in nZVI suspension with and without U(VI) in 24 h

Table 1 Physical properties of nZVI and Fe(II) bearing minerals

Mineral	Surface area (m ² /g)	PZC	Reference
nZVI	37.20	8.3	Kanel <i>et al.</i> (2005), Bae and Lee (2010)
Mackinawite	30.11	7.5	Amir and Lee (2012), Worthers <i>et al.</i> (2005)
Green rust	45.70	-	Elsner <i>et al.</i> (2004)
Magnetite	8.50	6.5	Missana <i>et al.</i> (2003), He and Traina (2005)
Pyrite	0.88	2.3	Matta <i>et al.</i> (2008), Kim and Batchelor (2009)

layers of iron-bearing mineral can be occurred in early stage in the mineral suspensions (Wersin *et al.* 1994, Fiedor *et al.* 1998, Charlet *et al.* 1998, Liger *et al.* 1999, O'Loughlin *et al.* 2003, Missana *et al.* 2003, Wazne *et al.* 2003, Noubactep *et al.* 2003, Scott *et al.* 2005, Rovira *et al.* 2007, Hua and Deng 2008, Riba *et al.* 2008, Dickinson and Scott 2010). It has been reported that the adsorption of aqueous U(VI) on iron particles was significantly influenced by electrostatic

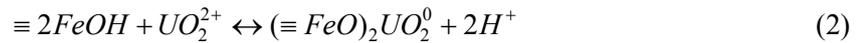
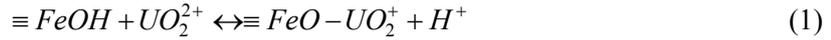
interaction between the surface of iron particles and U(VI) species. The surface layers, iron-(hydr)oxides, are chemically reactive with water, leading to dissociative chemisorptions of water called “protonation and deprotonation of surface functional groups” (Sparks 1995, Yanina and Rosso 2008). The surface can be positively ($> \text{OH}_2^+$) or negatively ($> \text{O}^-$) charged depending on the solution pH. PZC is a particular pH value of iron particle suspensions, when the fraction of positively charged sites is equal to the fraction of negatively charged sites on a surface. The surface can be positively charged under the condition with lower pH than PZC value, while it becomes the negatively charged surface under the condition with higher pH than PZC value. Therefore, all the used iron particles might have negatively charged surfaces with experimental condition (pH 8.5) in this study (Table 1). However, the amount of negatively charged sites considerably could differ from one surface type to another. Based on the PZC values for iron particles (Table 1), most pyrite surface (PZC = 2.3) might be negatively charged compared to the nZVI surface (PZC = 8.3) expected to be mainly neutral with small fraction of negatively charged at pH 8.5. Because neutral and anionic U species (i.e., $(\text{UO}_2(\text{OH})_2)$, $(\text{UO}_2(\text{OH})_3^-)$, and $(\text{UO}_2)_3(\text{OH})_7^-$) have been known as major aqueous U(VI) species under pH 8.5, (Moulin *et al.* 1998, Katsoyiannis *et al.* 2006, Riba *et al.* 2008, Hyun *et al.* 2012), electrostatic repulsion between anionic U(VI) species and iron particle surface could be increased as the number of negatively charged sites on surface increased. Therefore, anionic U(VI) species at pH 8.5 might have higher affinity for nZVI and mackinawite than those for magnetite and pyrite leading to the high removal efficiency of aqueous U(VI) in nZVI and mackinawite suspensions.

It is also generally accepted that the increase of surface area increases the density of adsorption sites on mineral surface. Indeed, mackinawite (30.11 m^2/g , Amir and Lee 2012), green rust (45.70 m^2/g , Elsner *et al.* 2004), and nZVI (37.20 m^2/g , Kanel *et al.* (2005)), synthesized by same methods with this study, have shown much greater surface area than those for magnetite (8.50 m^2/g , Missana *et al.* 2003) and pyrite (0.88 m^2/g , Matta *et al.* 2008) (Table 1). Even though the removal efficiency was not exactly controlled by the surface area (i.e., the highest removal efficiency was observed in mackinawite not green rust) in this study, our results may show the strong relationship between the U(VI) adsorption and surface area.

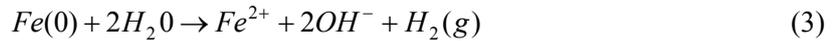
Interestingly, the addition of U(VI) into nZVI and green rust suspensions significantly enhanced the release of aqueous Fe(II). Especially, the aqueous Fe(II) concentration in nZVI suspension with U(VI) at 1 h was 4 times higher (350 μM) than that without U(VI) (80 μM). The results indicate that removal mechanism of aqueous U(VI) by nZVI and green rust suspensions at pH 8.5 was totally different from those by mackinawite, magnetite, and pyrite suspensions. The removal mechanism by nZVI and green rust could be explained by ion-exchange, resulting in the replacement of Fe(II) with aqueous U(VI) species on the surfaces. Recently, it has been reported that aqueous U(VI) can be removed by iron particles through ion-exchange (Hua and Deng 2008, Descostes *et al.* 2010). The uptake of aqueous U(VI) by mackinawite and PbS was accompanied by the noticeable amounts of Fe(II) and Pb(II) releases in aqueous phase (Hua and Deng 2008). Also, Descostes *et al.* (2010) observed that aqueous U(VI) was removed by pyrite with simultaneous release of Fe(II) into the solution. However, they reported that the removal efficiency of aqueous U(VI) and released Fe(II) concentration significantly decreased as pH increased. At pH higher than 8, released Fe(II) concentration was in the range of 0.01 - 10 μM , which is consistent with our experiment results showing no release of Fe(II) in mackinawite, magnetite, and pyrite suspensions with U(VI). Therefore, we could conclude that removal of U(VI) by nZVI suspension at pH 8.5 may be caused by the combination of adsorption and ion-exchange of U(VI), while the adsorption process may be a driving force for other Fe(II)-bearing minerals (i.e., mackinawite,

magnetite, and pyrite).

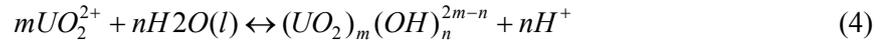
To investigate time period of the adsorption and ion-exchange of U(VI) on nZVI, pH variation was monitored in 24 h (Fig. 3). It has been known that adsorption and ion-exchange decreased the pH of Fe-bearing mineral suspensions due to proton generation by surface complexation process of Fe and U(VI) species (Eqs. (1) and (2)) (Bargar *et al.* 2000, Villalobos *et al.* 2001, Barnett *et al.* 2002, Wazne *et al.* 2003).



However, we observed that the initial pH (8.5) slightly increased in nZVI suspensions with (up to 8.77) and without (up to 8.60) U(VI) in 1 h and then kept constant the pHs for 24 h. The increase of pH in nZVI suspension may be induced by the higher production of hydroxide ions via anaerobic corrosion of nZVI (Eq. (3)) (Yan *et al.* 2010) than that of production of protons via surface complexation.



It should be noted that the increase of pH was slightly inhibited by addition of U(VI) in nZVI suspension. This may be caused by U(VI) hydrolysis that can produce proton in nZVI suspension (Eq. (4)) (Grenthe *et al.* 2003).



Intriguingly, pH change was almost terminated at 1 h in both nZVI suspensions with and without U(VI) which seems to be similar trend of U(VI) removal by nZVI (i.e., termination of U(VI) removal in 1 h) (Fig. 2(a)). This may indicate that the adsorption and ion exchange of U(VI) at the nZVI-water interface might be terminated within 1 h in this study. Then, the U(VI) on nZVI surface can be sequentially reacted by structural Fe(II) on nZVI surface, resulting in the reduction of U(VI) to U(IV) (Fiedor *et al.* 1998, Riba *et al.* 2008, Dickinson and Scott 2010).

3.2 Verification of Fe(II) colloids formation

Fig. 4(a) shows the aqueous Fe(II) concentration in 200 and 20 nm filtrates of nZVI suspensions with and without U(VI) in 24 h. Aqueous Fe(II) concentration rapidly increased until 1 h in both filtrates as similar to the previously observed in Fig. 2(b). The concentrations reached to the highest values (i.e., 200 nm filtrates: 181 (nZVI) and 384 μM (nZVI+U); 20 nm filtrates: 149 (nZVI) and 335 μM (nZVI+U)) at 6 h and slightly decreased in 24 h. As described in section 3.1, the released amounts of Fe(II) in nZVI suspension with U(VI) were 2-3 times higher than that without U(VI). Furthermore, aqueous Fe(II) concentration in both 200 and 20 nm filtrates was not significantly different in 24 h monitoring, indicating that Fe(II) colloids in less than 20 nm diameter could be generated in both nZVI suspensions with and without U(VI) in this study.

Fig. 4(b) represents aqueous U(VI) concentration in 200 and 20 nm filtrates during interaction of U(VI) with nZVI in 24 h. The most aqueous U(VI) in both filtrates were completely removed in 1 h. This indicates that colloids generated from nZVI suspension would be pure Fe(II) colloids, not pseudo U colloids. Previous studies reported that U(VI) has higher affinity toward colloidal particles than mineral phases due to higher charge and surface area of colloids (Alonso *et al.* 2006). However, adsorbed U(VI) on nZVI did not seem to be remobilized during the formation of Fe(II)

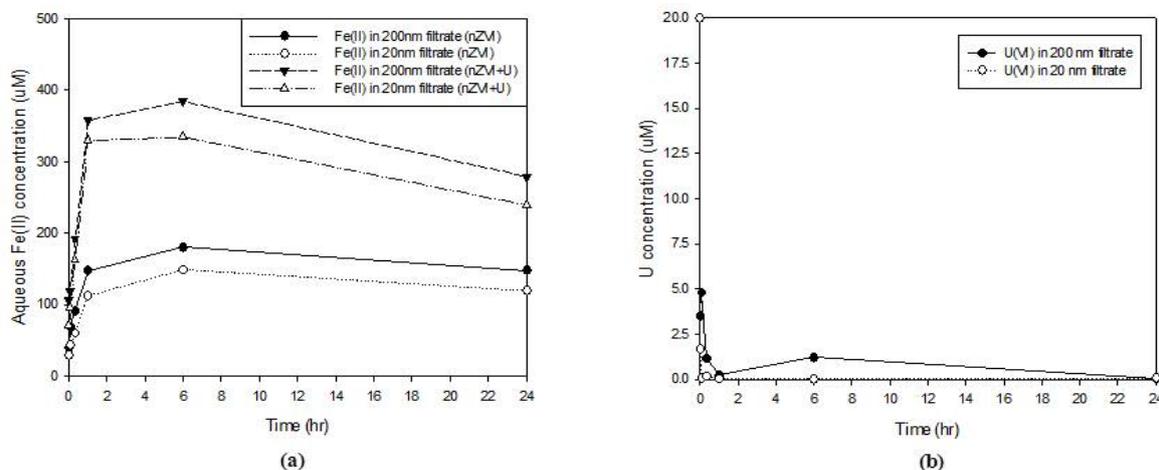


Fig. 4 Concentrations of (a) aqueous Fe(II) and (b) U(VI) in nZVI suspension with and without U(VI) after filtration by 20 and 200 nm membranes in 24 h

Table 2 Breakdown probability in 0.02 and 0.2 μm filtrates of nZVI suspensions with and without U(VI) (Reaction time: 20 min)

Sample	Breakdown Probability (0.2 μm filtrate)	Breakdown Probability (0.02 μm filtrate)
nZVI	0.73% \pm 0.11	1.2% \pm 0.17
nZVI+U	24.7% \pm 2.08	23.7% \pm 2.42

colloids in this study. It may be due to the strong electrostatic repulsive force between adsorbed U(VI) and Fe(II) colloid surfaces. A strong positively charged surface of Fe(II) colloids could be formed under our experimental condition (pH 8.5) due to the high PZC value (12) of Fe(II) colloids (Yoon *et al.* 1978). As shown in Eq. (1), U(VI) species on nZVI surface would be positively charged which are unfavorable to transport U(VI) from nZVI surface to Fe(II) colloid surface.

To investigate the presence of colloids in nZVI suspensions with and without U(VI), LIBD was used in this study. Recently, LIBD has been developed as a very sensitive technique for quantification of small aquatic colloids (diameter of > 1 nm). When light of high intensity which is pulsed laser beam interact with colloidal particles in aqueous phase, the generation of plasma (breakdown) occur as discrete-stochastic probability. The breakdown probability is the number of breakdown events divided by the number of laser shots. The threshold energy for breakdown of colloidal particle is much lower than those of pure liquid or gas, therefore, the breakdown of the colloidal particle can be selectively detected at appropriate pulse energy. The threshold energy in this study was fixed at the point of laser pulse energy where 1% of breakdown is generated for deionized water. As shown in Table 2, the breakdown probabilities were nearly 1% in the both filtrates of nZVI suspension without U(VI) (200 nm filtrate: 0.73%; 20 nm filtrate: 1.2%). However, the breakdown probabilities significantly increased to 24% (200 nm filtrate: 24.7%; 20 nm filtrate: 23.7%) in nZVI suspension with U(VI). The results of LIBD showed that released Fe(II) in nZVI suspension did not form Fe colloids in the absence of U(VI), while noticeable

amount of Fe(II) colloids were formed in nZVI suspension in the presence of U(VI). Moreover, the breakdown probabilities of 200 and 20 nm filtrates in nZVI suspension with U(VI) were very similar showing that Fe(II) colloids were in the range under 20 nm as previously concluded from the result of Fig. 4(a). Therefore, we can conclude that released Fe(II) from nZVI suspension without U(VI) was due probably to the anaerobic corrosion of nZVI, while it can be accelerated in the presence of U(VI) due mainly to the ion-exchange resulting in the formation of Fe(II) colloids in nZVI suspension.

4. Conclusions

We investigated the removal of aqueous U(VI) by nZVI suspension under reducing condition. Most studies have reported that aqueous U(VI) was removed by nZVI through the U(VI) adsorption onto nZVI surface (Fiedor *et al.* 1998, Gu *et al.* 1998, Riba *et al.* 2008, Dickinson and Scott 2010, Yan *et al.* 2010). However, we firstly propose the ion-exchange as the possible U(VI) removal mechanism by nZVI in this study. Furthermore, the ion-exchange caused by interaction of nZVI and U(VI) resulted in the formation of Fe(II) colloids (diameter < 20 nm). The formation of Fe(II) colloids in nZVI suspension with U(VI) should be seriously taken in the remediation of soil and groundwater contaminated by U(VI). Since the PRB holding nZVI has been widely applied as effective in-situ technology to remove U(VI) from groundwater plume, the abundant Fe colloids can be formed during the remediation process by ion exchange between aqueous U(VI) and nZVI. As a consequence of nZVI-PRB implementation on the sites, U(VI) in groundwater may be successfully removed and reduced as U(IV) by nZVI and surface Fe(II) is able to be simultaneously released into aqueous phase during several decades. However, once U remobilize by critical environmental change, U would be adsorbed on the pre-existing Fe colloids (actinide pseudo-colloids) formed by interaction of nZVI and U. This indicates that U could transport to the remote area from initial contaminated site. Therefore, not only the fate and transport of U but also those of Fe(II) colloids should be monitored in remediation site over a long period of time.

Acknowledgments

We thank Dr. Jong-il Yun and Ms. Kirana Y. Putri at Korea Advanced Institute of Science and Technology for analysis of LIBD and scientific discussion. The work was supported by the Korean Government (MEST) through the National Research Foundation of Korea Grant (NRF-2012-C1AAA001-M1A2A2026588).

References

- Alonso, U., Missana, T., Geckeis, H., Garcia-Gutierrez, M., Turrero, M., Mori, R., Schafer, T., Patelli, A. and Rigato, V. (2006), "Role of inorganic colloids generated in a high-level deep geological repository in the migration of radionuclides: Open questions", *J. Iberian Geol.*, **32**(1), 79-94.
- Amir, A. and Lee, W. (2011), "Enhanced reductive dechlorination of tetrachloroethene by nano-sized zerovalent iron with vitamin B12", *Chem. Eng. J.*, **170**(2-3), 492-497.
- Amir, A. and Lee, W. (2012), "Enhanced reductive dechlorination of tetrachloroethene during reduction of cobalamin (III) by nano-mackinawite", *J. Hazard. Mater.*, **235-236**, 359-366.
- Bae, S. and Lee, W. (2010), "Inhibition of nZVI reactivity by magnetite during the reductive degradation of

- 1,1,1-TCA in nZVI/magnetite suspension”, *Appl. Catal. B-Environ.*, **96**(1-2), 10-17.
- Bargar, J., Reitmeyer, R., Lenhart, J. and Davis, J. (2000), “Characterization of U(VI)-carbonato complexes on hematite: EXAFS and electrophoretic mobility measurements”, *Geochim. Cosmochim. Ac.*, **64**(16), 2737-2749.
- Barnett, M., Jardine, P. and Brooks, S. (2002), “U(VI) adsorption to heterogeneous subsurface media: Application of a surface complexation model”, *Environ. Sci. Technol.*, **36**(5), 937-942.
- Charlet, L., Liger, E. and Gerasimo, P. (1998), “Decontamination of TCE- and U-rich waters by granular iron: Role of sorbed Fe(II)”, *J. Environ. Eng.*, **124**(1), 25-30.
- Cho, C., Bae, S. and Lee, W. (2012), “Enhanced degradation of TNT and RDX by bio-reduced iron bearing soil minerals”, *Adv. Environ. Res., Int. J.*, **1**(1), 1-14.
- Choi, K. and Lee, W. (2012), “Enhanced degradation of trichloroethylene in nano-scale zero-valent iron Fenton system with Cu(II)”, *J. Hazard. Mater.*, **211-212**(15), 146-153.
- Descostes, M., Schlegel, M., Eglizaud, N., Descamps, F., Miserque, F. and Simoni, E. (2010), “Uptake of uranium and trace elements in pyrite (FeS₂) suspensions”, *Geochim. Cosmochim. Ac.*, **74**(5), 1551-1562.
- Dickinson, M. and Scott, T. (2010), “The application of zero-valent iron nanoparticles for the remediation of a uranium-contaminated waste effluent”, *J. Hazard. Mater.*, **178**(1-3), 171-179.
- Elsner, M., Schwarzenbach, R. and Haderlein, S. (2004), “Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants”, *Environ. Sci. Technol.*, **38**(3), 799-807.
- Fiedor, J.N., Bostick, W.D., Jarabek, R.J. and Farrell, J. (1998), “Understanding the mechanism of uranium removal from groundwater by zero-valent iron using X-ray photoelectron spectroscopy”, *J. Environ. Sci. Technol.*, **32**(10), 1466-1473.
- Grenthe, I., Fuger, J., Konings, R., Lemire, R., Muller, A., Nguyen-trung cregu, C., Wanner, H. and Forest, I. (2003), *Chemical Thermodynamics of Uranium*, OECD publication, Paris, France.
- Gu, B., Liang, L., Dickey, M., Yin, X. and Dai, S. (1998), “Cr(VI) reduction and immobilization by magnetite under alkaline pH conditions: The role of passivation”, *Environ. Sci. Technol.*, **39**(12), 3366-3373.
- Han, D., Batchelor, B. and Abdel-Wahab, A. (2012), “Sorption of selenium(IV) and selenium(VI) onto synthetic pyrite (FeS₂): Spectroscopic and microscopic analyses”, *J. Colloid. Interf. Sci.*, **368**(1), 496-504.
- He, Y. and Traina, S. (2005), “Cr(VI) reduction and immobilization by magnetite under alkaline pH conditions: The role of passivation”, *Environ. Sci. Technol.*, **39**(12), 4499-4504.
- Hua, B. and Deng, B. (2008), “Reductive immobilization of uranium(VI) by amorphous iron sulfide”, *Environ. Sci. Technol.*, **42**(23), 8703-8708.
- Hyun, S., Davis, J., Sun, K., and Hayes, K. (2012), “Uranium(VI) reduction by iron(II) monosulfide mackinawite”, *Environ. Sci. Technol.*, **46**(6), 3369-3376.
- Kanel, S., Manning, B., Charlet, L. and Choi, H. (2005), “Removal of arsenic(III) from groundwater by nanoscale zero-valent iron”, *Environ. Sci. Technol.*, **39**(5), 1291-1298.
- Katsoyiannis, I., Althoff, H., Bartel, H. and Jekel, M. (2006), “The effect of groundwater composition on uranium(VI) sorption onto bacteriogenic iron oxides”, *Water Res.*, **40**(19), 3646-3652.
- Kim, E. and Batchelor, B. (2009), “Macroscopic and X-ray photoelectron spectroscopic investigation of interactions of arsenic with synthesized pyrite”, *Environ. Sci. Technol.*, **43**(8), 2899-2904.
- Kirana, Y.P. and Yun, J. (2011), “Formation and stability of aluminosilicate colloids by coprecipitation”, Master’s Dissertation, Korea Advanced Institute of Science and Technology, Daejeon, Korea.
- Li, Z. and Zhang, W. (2006), “Iron nanoparticles: The core-shell structure and unique properties for Ni(II) sequestration”, *Langmuir.*, **22**(10), 4638-4642.
- Liger, E., Charlet L. and Van Cappellen, P. (1999), “Surface catalysis of uranium (VI) reduction by iron (II)”, *Geochim. Cosmochim. Acta.*, **63**(19-20), 2939-2955.
- Martin, J., Herzog, A., Yan, W., Li, X., Koel, B., Kiely, C. and Zhang, W. (2008), “Determination of the oxide layer thickness in core-shell zerovalent iron nanoparticles”, *Langmuir.*, **24**(8), 4329-4334.
- Matta, R., Hanna, K., Kone, T. and Chiron, S. (2008), “Oxidation of 2,4,6-trinitrotoluene in the presence of different iron-bearing minerals at neutral pH”, *Chem. Eng. J.*, **144**(3), 453-458.
- Missana, T., Garcia-Gutierrez, M. and Fernandez, V. (2003), “Uranium(VI) sorption on colloidal magnetite

- under anoxic environment: Experimental study and surface complexation modeling”, *Geochim. Cosmochim. Ac.*, **67**(14), 2543-2550.
- Missana, T., Maffiotte, C. and Garcia-Gutierrez, M. (2003), “Surface reaction kinetics between nanocrystalline magnetite and uranyl”, *J. Colloid Interf. Sci.*, **261**(1), 154-160.
- Moulin, C., Laszak, I., Moulin V. and Tondre, C. (1998), “Time-resolved laser induced fluorescence as a unique tool for low-level uranium speciation”, *Appl., Spectrosc.*, **52**(4), 528-535.
- Noubactep, C., Meinrath, G., Dietrich, P. and Merkel, B. (2003), “Mitigating uranium in groundwater: Prospects and limitations”, *Environ. Sci. Technol.*, **37**(18), 4304-4308.
- Noubactep, C., Schoner, A. and Meinrath, G. (2006), “Mechanism of uranium removal from the aqueous solution by elemental iron”, *J. Hazard. Mater.*, **32**(2-3), 202-212.
- Novikov, A.P., Kalmykov, S.N., Utsunomiya, S., Ewing, R.C., Horreard, F., Merkulov, A., Clark, S.B., Tkachev, V.V. and Myasoedov, B.F. (2006), “Colloid transport of plutonium in the far-field of the Mayak production association, Russia”, *Science*, **314**(5799), 638-641.
- O’Loughlin, E.J., Kelly, S.D., Cook, R.E., Csencsits, R. and Kemner, K.M. (2003), “Reduction of uranium (VI) by mixed iron(II)/iron(III) hydroxide (green rust): formation of UO₂ nanoparticles”, *Environ. Sci. Technol.*, **37**(4), 721-727.
- Riba, O., Scott, T.B., Ragnarsdottir, V. and Allen, G.C. (2008), “Reaction mechanism of uranyl in the presence of zero-valent iron nanoparticles”, *Geochim. Cosmochim. Ac.*, **72**(16), 4047-4057.
- Rovira, M., Aamrani, S., Duro, L., Gimenez, J., Pablo, J. and Bruno, J. (2007), “Interaction of uranium with in situ anoxically generated magnetite on steel”, *J. Hazard. Mater.*, **147**(3), 726-731.
- Scott, T.B., Allen, G.C., Heard, P.J. and Randell, M.G. (2005), “Reduction of U(VI) to U(IV) on the surface of magnetite”, *Geochim. Cosmochim. Ac.*, **69**(24), 5639-5646.
- Sparks, D. (1995), *Environmental Soil Chemistry*, Academic Press, San Diego, NY, USA.
- Srinivasan, R., Lin, R., Spicer, R.L. and Davis, B.H. (1996), “Structural features in the formation of the green rust intermediate and γ -FeOOH”, *Colloid. Surface. A.*, **113**(1-2), 97-105.
- Stookey, L.L. (1970), “Ferrozine – A new spectrophotometric reagent for iron”, *Anal. Chem.*, **42**(7), 779-781.
- Sun, Y., Li, X., Cao, J., Zhang, W. and Wang, H. (2006), “Characterization of zero-valent iron nanoparticles”, *Adv. Colloid. Interfac.*, **120**(1-3), 47-56
- Ulrich, K., Rossberg, A., Foerstendorf, H., Zanker, H. and Scheinost, A. (2006), “Molecular characterization of uranium(VI) sorption complexes on iron(III)-rich acid mine water colloids”, *Geochim. Cosmochim. Ac.*, **70**(22), 5469-5487.
- Villalobos, M., Trotz, M. and Leckie, J. (2001), “Surface complexation modeling of carbonate effects on the adsorption of Cr(VI), Pb(II), and U(VI) on goethite”, *Environ. Sci. Technol.*, **35**(19), 3849-3856.
- Wang, C.B. and Zhang, W.X. (1997), “Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs”, *Environ. Sci. Technol.*, **31**(7), 2154-2156.
- Wazne, M., Korfiatis, G.P. and Meng, X. (2003), “Carbonate effects on hexavalent uranium adsorption by iron oxyhydroxide”, *Environ. Sci. Technol.*, **37**(16), 3619-3624.
- Wersin, P., Hochella Jr, M.F., Persson, P., Redden, G., Leckie, J.O. and Harris, D.W. (1994), “Interaction between aqueous uranium (VI) and sulfide minerals: spectroscopy evidence for sorption and reduction”, *Geochim. Cosmochim. Acta.*, **58**(3), 2829-2843.
- Worthers, M., Charlet, L., Linde, P., Rickard, D. and Weijden, C. (2005), “Surface chemistry of disordered mackinawite (FeS)”, *Geochim. Cosmochim. Ac.*, **69**(14), 3469-3481.
- Yan, W., Herzing, A., Kiely, C. and Zhang, W. (2010), “Nanoscale zero-valent iron (nZVI): Aspects of the core-shell structure and reactions with inorganic species in water”, *J. Contam. Hydrol.*, **118**(3-4), 96-104.
- Yanina, S. and Rosso, K. (2008), “Linked reactivity at mineral-water interfaces through bulk crystal conduction”, *Science*, **320**(5873), 218-222.
- Yoon, R., Salman, T. and Donnay, G. (1978), “Predicting points of zero charge of oxides and hydroxides”, *J. Colloid. Interf. Sci.*, **70**(3), 483-493.