U(VI) removal efficiency by the oxidation of Fe(II) under the only injection of O2 and co-injection of CO2 and O2

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Abstract. Batch experiments were carried out to investigate the U(VI) removal efficiency by the oxidation of Fe(II) under the only injection of O2 and co-injection of CO2 and O2. Experiment results show that under the only injection of O2, the synergistic effect of Fe(II) and O2 could effectively remove U(VI) from the solution. For the different initial concentrations of Fe(II) at 2, 5, 10, 25, 50, 100 mg/L, almost all the removal rates of U(VI) reach up to 90% in the neutral conditions. There is no inevitable correlation between the removal efficiency of U(VI) and the initial concentration of Fe(II), revealing that the coprecipitation of U(VI) with Fe-oxides plays a dominant role in the removal of U(VI) rather than the simple sorption to the surface of Fe-oxides. Under the co-injection of CO2 and O2, the generated carbonate ions have a significant effect on the removal efficiency of U(VI) by the synergistic effect of Fe(II) and O2. The removal efficiency of U(VI) increases with the initial concentration of Fe(II). In the presence of carbonate ions, U(VI) is easy to bind with HCO3- to form uranyl carbonate complexes such as UO2(CO3)20 and UO2(CO3)42-, which would hinder the process of sorption and co-precipitation of U(VI) with Fe-oxides.

1. Introduction
Uranium is a radioactive element with high chemical toxicity. It has two stable valence states of U(IV) and U(VI). In the oxidizing environments, uranium (VI) is most soluble and mobile in the hexavalent oxidation state. In the geological environment, which is often rich in Fe oxides, the process of reductive dissolution and re-oxidation of Fe-oxides has a significant effect on the transport and the biological availability of uranium [1, 2]. One process is the sorption of U(VI) to Fe-oxides minerals. Some studies [3-8] have shown that in the absence of high levels of complexing ligands, dissolved U can sorb to Fe-oxides minerals (such as hematite and goethite) over a wide range of solution pH conditions. Another potential process is the co-precipitation of U with Fe-oxides. This process is most likely to occur in aged U-contaminated geologic materials [1-3]. For the in-situ leaching of uranium ores [9], as the injection of the acidic leaching solution, an acidic and oxidizing environment of the groundwater is formed, which can greatly enhance the dissolution of Fe-oxides and Fe-sulfides and release a lot of ferrous ions into the groundwater. So the content of U(VI) and Fe(II) is quite high for the groundwater in the decommissioned mining area of in-situ leaching uranium. Since U could incorporate with the Fe oxides over long periods of time during the process of the reductive
dissolution and re-oxidation of Fe-oxides, it may be a potential way to remove U(VI) and Fe(II) simultaneously through the oxidation of Fe(II) and formation of the Fe-U co-precipitation. However, there is little study focusing on the U(VI) removal by the oxidation of Fe(II). In the present work, we aim at investigating the removal efficiency of U(VI) by the synergistic effect of Fe(II) and O$_2$ in the neutral conditions. In contrast to only inletting O$_2$ for illustrating the U(VI) removal efficiency, the bicarbonate effect on the removal efficiency of U(VI) also was discussed in this paper since the carbonate has a significant effect on the sorption of U(VI) on the Fe-oxides [10-12].

2. Materials and method

2.1. Experimental apparatus
JPB-607A Dissolved Oxygen Meter; PHS-3C acidometer; FB224 precision electronic autobalance; 101-3AB draught drying cabinet; T6 VIS spectrophotometer; THZ-82 Water-bathing Constant Temperature Vibrator.

2.2. Materials preparation
Preparation of ferrous ion standard stock solution: dissolve 0.7020g ammonium iron (II) sulphate ((NH$_4$)$_2$Fe(SO$_4$)$_2$) with 50mL of sulfuric acid in deionized water with the volume ratio of 1:1 and then diluted with deionized water to 1000mL. The concentration of ferrous ion standard stock solution was 100mg/L.

Preparation and calibration of vanadium ammonium nitrate solution [6]: mix 0.1 g ammonium vanadate (NH$_4$VO$_3$) with a small amount of distilled water into a paste and dissolved it with 250 mL uniform mixture of sulfuric acid and distilled water, then diluted to 1000 mL with distilled water after dissolving completely, placed for a week and setted them aside. Calibrating Vanadium ammonium nitrate solution with standard uranium solution, the titer of was 0.1051 mg/mL.

Preparation of diphenylamine sulfonic acid sodium: mix 0.20g diphenylamine sulfonic acid sodium (C$_{12}$H$_{10}$O$_3$N$_2$Na) with 0.20g sodium carbonate anhydrous (Na$_2$CO$_3$) and a small amount of distilled water into a paste and then dilute to 100 mL.

Preparation of U(VI) solution: 10 mL hydrochloric acid (HCl), 3 mL hydrogen peroxide (H$_2$O$_2$) and two drops of nitric acid (HNO$_3$) were added orderly into a 100 mL beaker with 10 g triuranium octaoxide (U$_3$O$_8$) in it and placed for 3 min, then began to shake it regularly until the intense reaction stopped and heated it on a sandbath until mixtures we completely dissolved, diluted to 1000 mL.

Preparation of iron (II) chloride solution: dissolve a certain amount of iron (II) chloride with distilled water to a 500 mL volumetric flask.

![Figure 1. Schematic diagram of the experimental apparatus.](image-url)
2.3. Experiment method
The desired amounts of deionized water, U(VI) (50 mg/L) and iron (II) chloride solution were respectively introduced into 6 conical flask of 500 mL with the final total volume of suspension of 400 mL and the Fe(II) concentration of 2mg/L, 5 mg/L, 10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L. Then adjusted the pH of all the solution to 7 with the error range of 0.10. The experiments were carried out with the experiment apparatus as shown in Figure 1 under the only injecting O2 and co-injection of CO2 and O2. The mixtures were horizontally oscillated at the speed of 150r/min in water-bathing constant temperature vibrator with the temperature at 30 °C and technical pure oxygen was continuously injected into each conical flask during the whole experiment. 30mL of solution were sampled with disposable syringes every 8 hours. The pH and Eh of the solution were measured in situ before sampling. The concentration of total iron and ferrous ion was determined by atomic absorption spectrophotometer. The concentration of U(VI) was determined by vanadium ammonium nitrate solution titration method.

3. Results

3.1. U(VI) removal by the oxidation of Fe(II) under the only injection of O2
As shown in Figure 2, the synergistic action of Fe(II) and O2 has significant effect on the decrease of U(VI) concentration. The U(VI) concentration of all solutions with the initial concentration of Fe(II) at 2mg/L, 5mg/L, 10mg/L, 25mg/L, 50mg/L and 100mg/L dropped to about 5 mg/L, with the removal efficiency of U(VI) up to about 90% (Figure 3). Obviously, there is no inevitable correlation between the removal efficiency of U(VI) and the initial dosage of Fe(II) in the neutral conditions.

Figure 2. U(VI) concentration change with time at different initial concentrations of Fe(II) under the only injection of O2.

Figure 3. U(VI) removal efficiency with time at different initial concentrations of Fe(II) under the only injection of O2.

Figure 4. pH change with time at different initial concentrations of Fe(II) under the injection of O2.

Figure 5. Eh change with time at different initial concentrations of Fe(II) under the injection of O2.
In addition, after 8 hours’ reaction, the pH value of the solution maintains at about 6 (Figure 4) and the redox potential of the solution stable between 250 ~ 300 mV (Figure 5). The formation of the pure phase Fe(OH)₃ is relatively little, at this pH and Eh condition. Therefore, it can be deduced that the decrease of U(VI) was not resulted from the single adsorption behaviour happening on the Fe-U interface but the incorporation of U(VI) into the iron oxides over reaction time, in other words, U(VI) may coprecipitate with the iron oxides. A previous study [1] has shown that U(VI) (with ionic radius of 0.72 to 0.8 Å, depending on the coordination environment) can be incorporated into iron oxides as uranate. In the previous studies [13-16] of nuclear waste treatment and U biogeochemistry, the uranium sorption and coprecipitation processes with Fe minerals have been discovered. As illustrated above, the removal efficiency of uranium by the synergy of Fe(II) and O₂ is remarkable. As for the groundwater in the decommissioning zone of in-situ leaching of uranium deposits, there exists elevated levels of Fe(II). Consequently, if O₂ is injected deep underground, it will have great significance on remediating the groundwater environment after in-situ leaching of uranium. In the natural environment, Fe(II) is prevalent, it can be a ideal materials for uranium remediation.

3.2. U(VI) removal by the oxidation of Fe(II) under the co-injection of CO₂ and O₂

As shown in Figure 6 and 7, the concentration of U(VI) decreased to 35mg/L, 30mg/L, 28mg/L, 25mg/L, 24mg/L and 15mg/L and the removal efficiency of U(VI) reached to 30%, 40%, 50%, 60%, 60% and 70% at the initial Fe(II) concentration of 2mg/L, 5mg/L, 10 mg/L, 25 mg/L, 50 mg/L and 100 mg/L, respectively. The U(VI) concentration decreased with the increase of initial Fe(II) concentration under the co-injection of CO₂ and O₂. A speculated reason on this result is that CO₂ dissolves into the water resulting the form of H₂CO₃ and the release of H⁺ and HCO₃⁻, and U(VI) binds with HCO₃⁻ to form uranyl carbonate complexes such as UO₂(CO₃)₂⁰ and UO₂(CO₃)₄²⁻ [10], which may significantly reduce the adsorption and co-precipitation of U(VI) during the process of the morphological transformation of iron[1].
The pH value of solutions rose rapidly first due to the oxidation of Fe$^{2+}$ to Fe$^{3+}$ by O$_2$ which consumes some acid, and then decreased owing to hydrolysis of Fe$^{3+}$ (Figure 8). The redox potential of solutions are stable between 100~300 mV (Figure 9). In addition, the result can also illustrate the low leaching concentration of U(VI) for the CO$_2$+O$_2$ in-situ leaching mine of uranium. During the leaching process, the oxidation of pyrite and the dissolution of Fe-oxides would release a lot of Fe$^{2+}$ which have significant effect on the leaching concentration and leaching rate of U(VI).

4. Discussion

4.1. Comparison on the transformation of Fe species between the injection of O$_2$ and co-injection of CO$_2$ and O$_2$

Here we compared the transformation of Fe species (including ferrous and ferric irons) under the injection of O$_2$ and co-injection of CO$_2$ and O$_2$. As discussed above, under the injection of O$_2$, the removal rate of U(VI) reached up to 90%; while under the co-injection of CO$_2$+O$_2$, the removal rate of U(VI) increases with the increase initial Fe(II) concentration, with the highest removal rate of 65%. However, as shown in Figure 10, the Fe(II) concentrations remained in solutions when the reaction was balanced were almost the same. Because there is few ferric hydroxide colloid, it can illustrate that a large number of U(VI) co-precipitated with Fe oxides. The reason why the removal rate of U(VI) under co-injection of CO$_2$+O$_2$ is lower than that under injection of O$_2$ is that CO$_2$ (dissolved HCO$_3^-$ or CO$_3^{2-}$) forms stable complexes with U(VI) and promote the dissolution of uranium in solution.

![Figure 10. Comparison of Fe transformation between the injection of O$_2$ and co-injection of CO$_2$+O$_2$.](image)
4.2. Discussion on the U(VI) removal mechanism by the oxidation of Fe(II)

Under the injection of O$_2$, most of U(VI) was removed within 8h. The results from these experiments indicates that there is no inevitable correlation between the decreases of U(VI) concentration and initial concentration of Fe(II) in the neutral conditions. The removal efficiency of U(VI) is remarkable influenced by synergistic effect of Fe(II) and O$_2$. A speculated reason on this result is that most U(VI) may incorporate with Fe oxides, rather than the only ordinary adsorption by ferric hydroxide colloid. A previous study [1] has indicated that Uranium could incorporate with the Fe oxides over long periods of time during the process that Fe(III) species transfer to more soluble Fe(II) species followed by the re-oxidation of Fe(II) to Fe(III) and the precipitation of Fe-oxide over reaction time.

![Figure 11. Molecular models of the association of U$^{6+}$ with distorted Fe octahedra from the hematite structure [1]](image)

As shown in Figure 11, a previous study [1] has indicated that U$^{6+}$(with ionic radius of 0.72 to 0.8Å, depending on the coordination environment) is incorporated in the Fe oxides as uranate. In the study of nuclear waste treatment and U bio-geochemistry, the processes that uranium is adsorbed and co-precipitate with Fe minerals have been discovered. The size of UO$_2$$^{2+}$ (1.80Å) is larger than that of Fe$^{3+}$(0.65Å), causing UO$_2$$^{2+}$ unlikely to be structurally incorporated into Fe oxides. However, its effective ionic radii is approximately 0.62 to 0.73Å (depending on coordination number), apparently allowing U(VI) incorporation into the structure.

In the presence of HCO$_3^-$, the removal efficiency of U(VI) is greatly affected. With its pH fairly stable at 6~7 and Eh shifting between +0.1V and +0.3V, most uranium exists in solution as UO$_2$(CO$_3$)$_2$$^{2-}$ and UO$_2$(CO$_3$)$_4$$^{4-}$, which has a larger ionic radius causing its high solubility and mobility. The results of this experiments is corresponding to the previous studies [8, 9, 12] that U(VI) binding with HCO$_3^-$ to form uranyl carbonate complexes such as UO$_2$(CO$_3$)$_2$$^{2-}$ and UO$_2$(CO$_3$)$_4$$^{4-}$ can significantly reduce the adsorption and co-precipitation of U(VI) during the process of the morphological transformation of iron, while which still have a significant effect on the concentration of U(VI), causing the decrease of leaching rate of U(VI) during CO$_2$+O$_2$ in-situ leaching of uranium.

5. Conclusions

In the present work, batch experiments were carried out to investigate the U(VI) removal efficiency under the oxidation of Fe(II) under the only injection of O$_2$ and co-injection of CO$_2$ and O$_2$. The main conclusions can be drawn as follows:

1) The synergistic effect of Fe(II) and O$_2$ could effectively remove the U(VI) from the solution. For the different initial concentrations of Fe(II) at 2, 5, 10, 25, 50, 100 mg/L, almost all the removal efficiencies of U(VI) are up to 90%. There is no inevitable correlation between the removal efficiency of U(VI) and the initial dosage of Fe(II) in the neutral conditions, revealing that the coprecipitation of U(VI) with Fe-oxide plays a dominant role in the removal of U(VI) rather than the sorption on the surface of Fe-oxide.

2) The carbonate present in the solution has a significant effect on the removal efficiency of U(VI) by the synergistic effect of Fe(II) and O$_2$. The removal efficiency of U(VI) increases with the increases of initial Fe(II) concentration. With the present of carbonate, U(VI) bind with HCO$_3^-$ to form uranyl
carbonate complexes such as $\text{UO}_2(\text{CO}_3)_3^{2-}$ and $\text{UO}_2(\text{CO}_3)_4^{2-}$, which would hinder the process of sorption and co-precipitation of U(VI) with Fe-oxide.

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