U(VI) removal efficiency by natural pyrite under the oxygen-rich conditions with/without bicarbonate present

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Abstract. Natural pyrite, as an ubiquitous mineral in the reducing environments, shows great potential on the treatment of wastewater polluted by heavy metals. In the present work, a dynamic leaching experiment was carried out to investigate the removal efficiency of U(VI) by natural pyrite under the oxygen rich conditions with/without bicarbonate ions. Experimental results shows that pyrite oxidation can significantly remove U(VI) from the solution under the oxygen rich conditions with/without bicarbonate ions. With the absence of bicarbonate ions, U(VI) concentration decreases from 50 mg/L to 20 mg/L with the removal rate up to 60%; with the presence of bicarbonate ions, U(VI) concentration decreases from 50 mg/L to 30 mg/L with the removal rate up to 40%, indicating that natural pyrite can be an effective material to treat high-uranium groundwater under the oxygen-rich conditions with bicarbonate present or not.

1. Introduction
The increasing mining and refinement of uranium mines have resulted in widespread environmental pollution[1]. U(VI) is a particularly dangerous contamination as its inherent toxicity, radioactivity, mobility and bioaccumulation[2]. Numerous technologies for U(VI) removal have been investigated. Adsorption of uranium by various inert materials such as titanate, silicate minerals (e.g. sericite), phosphate rock apatite, and iron minerals[3-4]; reducing U(VI) to a less soluble and mobile oxidation states (U3O8, U4O9, UO2)[5-6]; incorporating uranium into stable mineral structure (e.g. iron oxides, hematite, goethite, magnetic)[7-8]; bio-remediating soluble U(VI) by microorganism secretions, such as enzymes and extracellular polymeric substances[9]. Uranium can be effectively removed by adsorption and reduction, however, which may experience desorption, reoxidation and remobilization when geochemical conditions change[41]. There are some studies, in recent years, reported that the structure incorporation of U(VI) into iron mineral structure is more stable and effective, providing possibility of in situ remediation.

Natural pyrite (FeS2), the most abundant sulfide mineral, is an ubiquitous component in reduced environments[10]. Many researchers have confirmed that natural pyrite have favorable effects on removal of heavy metal ions, such as Cr(VI), Cd(II), Pb(II), As(III/V), pertechnetate, mercury(II) et al.[11-14]. The immobilization of U(VI) by natural pyrite have also been widely observed. Yao P.P. et al.[20] researched U(VI) adsorption behavior on pyrite and stated the important influence of pH on it. Wang Z.Q. et al[21] proved that pyrite, under anaerobic conditions, can decrease the redox potential of mineral-solution interface to about -250 mV and reduce U(VI) to U(IV). However, literature examining the interactions between iron, released by pyrite oxidation, and uranium with the present
of bicarbonate is scarce, and the authentic reason for U(VI) removal by nature pyrite is still unclear. In this study, we conducted a dynamic leaching experiment to investigate the U(VI) removal efficiency under aerobic conditions with or without CO₂ and the fate of uranium during the pyrite oxidation.

2. Materials and methods

2.1 Materials preparation

Natural pyrite used in this study was sieved through a 200-mesh screen. Table 1 shows the elementary composition of natural pyrite based on XRF. The content of S and Fe is up to 98% in the natural pyrite. There are also some microelements such as Rb, Th, Pb, As, Zn, Cu, Co, Mn, Ca.

| Elements | Content, % (wt.) |
|----------|-----------------|
| Rb       | 0.0018±0.0008   |
| Pb       | 0.0484±0.0060   |
| Zn       | 0.1786±0.0126   |
| Co       | 0.2679±0.1603   |
| Mn       | 0.1327±0.0468   |
| S        | 30.4266±2.5296  |

Preparation of U(VI) solution: add 10 mL hydrochloric acid (HCl), 3 mL hydrogen peroxide (H₂O₂) and two drops of nitric acid (HNO₃) orderly into a 100 mL beaker with 1.1792g uranouranic oxide (U₃O₈) and place for 3 min, and then shake it regularly until the intense reaction stops. Heat it on a sandbath until mixtures are completely dissolved. Shift the cooling solution into 1000 mL volumetric flask and dilute to the scale line with deionized water.

Preparation and calibration of vanadium ammonium nitrate solution: Mix 0.1 g ammonium vanadate (NH₄VO₃) with a small amount of distilled water into a paste and dissolve it with 250 mL uniform mixture of sulfuric acid and distilled water, then dilute to 1000 mL with distilled water after dissolving completely and place for a week.

Preparation of diphenylamine sulfonic acid sodium: Mix 0.20g diphenylamine sulfonic acid sodium (C₁₂H₁₀O₃NSNa) with 0.20g sodium carbonate anhydrous (Na₂CO₃) and a small amount of distilled water into a paste and then dilute to 1000 mL.

2.2 Experiment method

Figure 1 shows the schematic diagram of the experimental setup. The desired amounts of natural pyrite(25mg/L), deionized water and 20 mL Uranium Standard Solution were sequentially introduced into a 500 mL conical flask with the final total volume of suspension of 400 mL. O₂ and CO₂ were co-injected into the first three conical flask while O₂ were injected into the last three conical flask, representing the bicarbonate-rich and no bicarbonate conditions, respectively. The reaction devices were stirred by magnetic stirrer. solutions were sampled and filtered to measure its pH values, redox potential and concentrations of U(VI) and Fe every five days, data are averaged.

pH values and redox potential of solutions were measured by HS-3C pH meter. U(VI) concentrations were determined by titrimetry with reduction of titanium trichloride. Concentrations of total Fe and Fe(II) were determined by phenanthroline spectrophotometric method of Chinese Environmental Protection Industry Standard (HJ/T345-2007) (Beijing Purkinje General Instrument Co., Ltd., China).
3. Results and discussion

3.1 Results

Here we first analyze the change of U(VI) concentrations with time caused by pyrite oxidation under the oxygen-rich conditions with or without the bicarbonate ions present. As shown in figure 2, whether the bicarbonate present or not, U(VI) concentration dramatically decreases and reaches equilibrium after about 40 days. With the absence of bicarbonate ions, U(VI) concentration decreases from the initial 50mg/L to the equilibrated 20mg/L with the removal rate up to 60%. With the presence of bicarbonate ions, U(VI) concentration decreases from the initial 50mg/L to the equilibrated 30mg/L with the removal rate up to 40%. Obviously, natural pyrite can act as an effective material to remove U(VI) from solutions under the oxygen-rich conditions with/without the bicarbonate present. It is indicates that the bicarbonate-rich conditions are less favorable for the removal of U(VI) compared to the bicarbonate-absent conditions.

Figure 3 shows that the change trends of pH values are probably consistent under oxygen-rich conditions with or without bicarbonate present both of which experience a slight increase and then decline slowly. The pH value keeps steady at about 3.2 under the only injection of O₂ and about 3.0 under the co-injection of CO₂ and O₂. Redox potential of solutions under the co-injection CO₂ and O₂ changes between 320 mV ~ 375 mV, which is higher than that under the only injection of O₂, changing between 315 mV ~ 345 mV (figure 4). The higher redox potential and lower pH values under the co-injection of CO₂ and O₂ may result from the higher U(VI) concentrations in bicarbonate-rich aqueous. High U(VI) concentrations would enhance the redox potential of solutions, leading to more thoroughly oxidation of pyrite which would increase the acidity of the system...
Concentration of ferric iron released by pyrite oxidation appears a sudden increase in the initial phase and then shows a rapid downward trend for the next 5 to 30 days and then followed by a mild increase (figure 5). Lastly, iron concentration of solutions under the only injection of O₂ keeps stable at around 100 mg/L, which is lower than that under the co-injection of CO₂ and O₂, keeping stable at about 170 mg/L. The final concentrations of iron and U(VI) of solutions with bicarbonate present are higher than that without bicarbonate present.

3.2 Discussion
In recent years, the mechanism of pyrite oxidation and its influence factors have been studied extensively. The reactions of pyrite oxidation in aqueous have been defined as follows [22-23]:

$$2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2(\text{aq}) \rightarrow 2\text{Fe}^{3+} + 4\text{SO}_4^{2-} + 4\text{H}^+$$  \(1)$$

$$4\text{Fe}^{2+} + \text{O}_2(\text{aq}) + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$$  \(2)$$

$$\text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$  \(3)$$

Based on the previous studies, UO$_2^{2+}$ can be reduced to UO$_{2(\text{cr})}$ by pyrite [24]. Under acidic conditions, the first step for U(VI) reduction by pyrite can be represented by the following reactions [25]:

$$\text{UO}_2^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) = \text{UO}_{2(\text{cr})} + 2\text{Fe}^{3+}(\text{aq}) \Delta_G^o = 69.22 \text{kJ/mol}$$  \(4)$$

$$\text{UO}_2(\text{OH})_2^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) = \text{UO}_{2(\text{cr})} + 2\text{Fe}^{3+}(\text{aq}) + \text{OH}^{-}(\text{aq}) \Delta_G^o = 119.17 \text{kJ/mol}$$  \(5)$$

Therefore, due to the positive $\Delta_G^o$, reactions 4 and 5 are thermodynamically feasible when Fe$^{2+}$ and U(VI) species are of high concentrations. In addition, U(VI) could be adsorbed on the surface of iron oxides or have co-precipitation with them, leading to the removal of U(VI) in aqueous [24, 26].
Studies of U(VI) interaction with Fe(II)-bearing phases, such as magnetite, also indicate that U(VI) can be adsorbed and subsequently reduced to U(IV), precipitating as hyperstoichiometric $\text{UO}_2^{2+}$[27-28].

As shown in figure 3 and 5, under the only injection of $\text{O}_2$, U(VI) concentration decreases from 50mg/L to 20mg/L with the removal rate up to 60% and irons concentration decreases by about 240mg/L; under the co-injection of $\text{CO}_2$ and $\text{O}_2$, U(VI) concentration decreases from 50mg/L to 30m/L with the removal rate up to 40% and irons concentration decreases by about 120mg/L. Concentrations of ferric ions and U(VI) both decrease rapidly in 30 days, and the final value of which are both higher under bicarbonate-rich condition. It illustrates that natural pyrite can be an effective material to treat high-uranium groundwater under the oxygen-rich conditions with bicarbonate present or not and the removal of U(VI) have a lot to do with iron. U(VI) removal may results from the reduction of Fe$^{2+}$, the sorption of iron oxide or the co-precipitation of uranium with iron oxides. Moreover, $\text{UO}_2\,(\text{OH})_2$ sediment and U(VI) is easy to bind with $\text{HCO}_3^-$ to form soluble uranyl carbonate complexes, such as $\text{UO}_2\,(\text{CO}_3)_2^0$, $\text{UO}_2\,(\text{CO}_3)_2^-$ and $\text{UO}_2\,(\text{CO}_3)_4^{2-}$ under bicarbonate-rich aqueous[29-30], which is corresponding to this experience that U(VI) removal efficiency is lower under oxygen and bicarbonate-rich conditions. It indicates that bicarbonates have a negative effect on U(VI) removal by nature pyrite in acidic and aerobic conditions.

As shown in figure 5, the sudden increase of ferric iron on account of the initial oxidation phase of pyrite. Then, a series of intermediate oxide (including elemental sulfur, iron-depleted sulfide Fe$_{1-x}$S$_2$, polysulfide Fe$_x$S$_n$ and iron oxide, etc)[31], covering on the surface of pyrite and forming passive films, slow down the oxidation rate of pyrite. Meanwhile, large number of iron have a co-precipitation with U(VI), resulting the aqueous iron and U(VI) concentrations show a rapid downward trend during around 5-30 days. Finally, the passive films are further oxidized to soluble $\text{SO}_4^{2-}$, resulting a mild increase of aqueous iron concentrations.

4. Conclusion
Pyrite oxidation has remarkable effect on U(VI) removal efficiency under the oxygen rich conditions with/without bicarbonate ions. With the absence of bicarbonate ions, U(VI) concentration decreases from 50 mg/L to 20 mg/L with the removal rate up to 60%; with the presence of bicarbonate ions, U(VI) concentration decreases from 50 mg/L to 30 mL with the removal rate up to 40%, indicating that natural pyrite can be an effective material to treat high-uranium groundwater under the oxygen-rich conditions with bicarbonate present or not, and bicarbonates have a negative effect on U(VI) removal by nature pyrite in aerobic conditions.

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