

Article

Study on Mechanism of Oxygen Oxidation Leaching with Low Acid for High Acid Consumption Sandstone Uranium Deposit

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Abstract: In view of the problems of high acid consumption, the blockage of ore-bearing beds caused by iron ion precipitation and a low leaching rate in the conventional acid leaching of a sandstone-type uranium deposit, the author put forward “low-acid and oxygen leaching technology” research. In order to further clarify the mechanism of leaching sandstone-type uranium ore with low acid and oxygen, the oxidation mechanism of ferrous ion under acidic conditions, the influencing factors of ferrous ion oxidation process, the kinetic simulation of oxygen oxidizing uranium minerals, and the interaction of uranium and iron precipitation in acidic solution were analyzed and studied, and the mechanism of oxygen oxidizing uranium and uranium leaching under low acid conditions was explored. The results show that under the condition of low acidity, the kinetics that ferrous oxidized by oxygen is between the first-order and second-order reaction, which can reduce the iron ion precipitation and then reduce the influence of iron ion precipitation on uranium leaching, so as to improve the uranium leaching rate. This study confirmed the feasibility of the oxygen oxidation of uranium and uranium leaching under low acidity conditions, which has a good guiding significance for the effective leaching of uranium deposits with a high acid consumption.

Keywords: high acid consumption; in situ leaching of uranium; kinetics; coprecipitation



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1. Introduction

In the process of the in situ leaching of sandstone-type uranium deposit, in order to reduce the cost of acid and improve the efficiency of uranium leaching, it is necessary to use oxidants to directly or indirectly oxidize U(IV) in the ore to U(VI) [1–4]. At the same time, other minerals in the ore, such as pyrite, mica, chlorite, organic matter, and cemented minerals, are also oxidized and etched, resulting in the release of high valent iron ions in the leaching solution. In the process of a pregnant solution moving forward, the acidity gradually decreases, which easily leads to the precipitation of high valent iron. On the one hand, the precipitation of high valent iron may lead to the co-precipitation of uranium and iron or the adsorption of uranium by ferric hydroxide. On the other hand, the precipitation may lead to pore blockage and reduce the permeability of the ore bed [5,6].

Many sandstone-type uranium deposits in the Yili basin, Turpan Hami basin, and Ordos Basin in China are generally difficult to leach by the alkali method, low uranium concentration in pregnant solution, and serious blockage, which makes it difficult to economically extract such uranium deposits by in situ leaching. In view of the characteristics of this type of high acid consumption in situ leached sandstone uranium deposit, the previous study proposed to use sulfuric acid and oxygenation leaching technology under the condition of reducing the residual acid acidity (pH~2.0–4.0), using oxygen as an oxidant, which can reduce the use of sulfuric acid in the leaching process, reduce the dissolution of non-uranium minerals, and slow down the ore bed plugging phenomenon in the leaching process [7,8]. At present, the mechanism of low-acid and oxygen leaching, especially the

effect of iron precipitation, the oxidant of ferrous oxide, on uranium in the leaching process, is still unknown. This paper analyzes and studies the action mechanism of ferrous oxide, the factors and kinetics of oxidation, and the relationship between iron precipitation and uranium, and explores the mechanism of low-acid and oxygen leaching by comparing with conventional acid leaching, so as to provide theoretical and technical support for the low-acid and oxygen leaching test or production of high-acid consumption in situ leaching mines.

2. Theoretical Analysis of Ferrous Oxide

2.1. Thermodynamic Analysis of Oxidation Reaction

From the perspective of thermodynamics, the stability of iron in aqueous solution depends on the pH, potential, and its activity in solution. The thermodynamics of iron dissolution, oxidation–reduction, precipitation, and other reactions in the solution and process are displayed in Table 1 [9,10].

Table 1. Chemical reactions in solution (under normal temperature and pressure).

NO.	Chemical Reaction	φ -pH Calculation Formula
①	$\text{Fe}^{3+} + e = \text{Fe}^{2+}$	$\varphi = 0.7706 + 0.591 \log a_{\text{Fe}^{3+}} / a_{\text{Fe}^{2+}}$
②	$\text{Fe}(\text{OH})_3 + 3\text{H}^+ = \text{Fe}^{3+} + 3\text{H}_2\text{O}$	$\text{pH} = 1.617 - 1/3 \log a_{\text{Fe}^{3+}}$
③	$\text{Fe}^{2+} + 2e = \text{Fe}$	$\varphi = -0.44 + 0.0295 \log a_{\text{Fe}^{2+}}$
④	$\text{Fe}(\text{OH})_3 + 3\text{H}^+ + e = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	$\varphi = 1.057 - 0.1773 \text{pH} - 0.0591 \log a_{\text{Fe}^{2+}}$
⑤	$\text{Fe}(\text{OH})_3 + \text{H}^+ + e = \text{Fe}(\text{OH})_2 + \text{H}_2\text{O}$	$\varphi = 0.271 - 0.0591 \text{pH}$
⑥	$\text{Fe}(\text{OH})_2 + 2\text{H}^+ + e = \text{Fe} + 2\text{H}_2\text{O}$	$\varphi = -0.047 - 0.0591 \text{pH}$
A	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e = 2\text{H}_2\text{O}$	$\varphi = 1.776 - 0.0591 \text{pH}$
B	$\text{O}_2 + 4\text{H}^+ + 4e = 2\text{H}_2\text{O}$	$\varphi = 1.229 - 0.0591 \text{pH} + 0.0148 \log P(\text{O}_2)$
C	$2\text{H}^+ + 2e = \text{H}_2$	$\varphi = -0.0591 \text{pH}$

It can be seen from Figure 1 that compared with trivalent iron, the stability region of ferrous ion is wider. In the process of the in situ leaching of uranium by the acid method, the probability of an ore bed blockage caused by ferrous ion precipitation is small. Therefore, in the process of the in situ leaching of uranium by the low-acid and oxygen method, in order to prevent the blockage caused by ferrous precipitation, the iron in the system should be kept in the ferrous form. From the point of view of thermodynamic equilibrium, substances with equilibrium potential above line ① can be used as oxidants from ferrous to ferric. Therefore, hydrogen peroxide and oxygen can be used as oxidants.

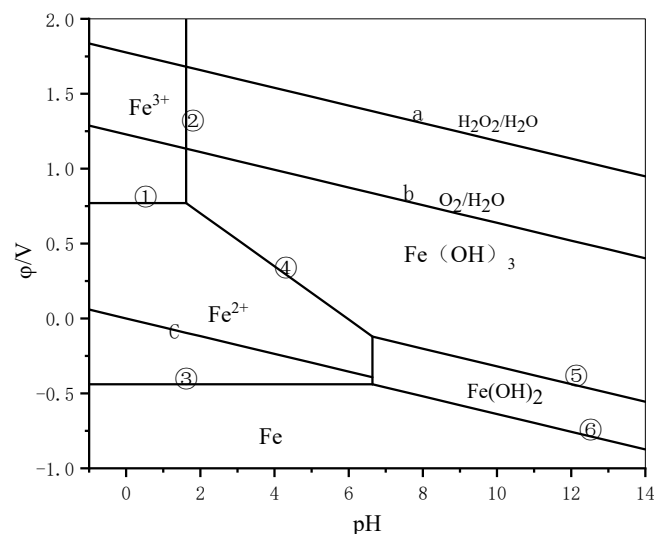
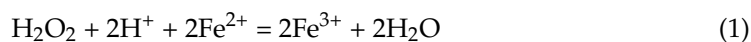


Figure 1. Fe-H₂O system φ -pH (normal temperature 25 °C).

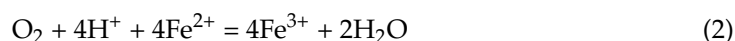
At the same time, the oxidant potential line and line ① distance can indicate the driving force of a redox reaction. The oxidation of ferrous oxide by hydrogen peroxide is:



$$\Delta\varphi = 1.00544 - 0.591\text{pH}$$

Generally, when hydrogen peroxide is used as an oxidant, ferrous oxide in the ore bed is relatively easy to be oxidized. In order to prevent precipitation, it is necessary to maintain the pH (leaching solution) < 2.

The oxidation of ferrous oxide by oxygen is:

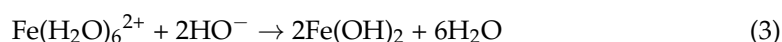


$$\Delta\varphi = 0.4584 - 0.591\text{pH} + 0.0148\log P(\text{O}_2)$$

Under the same pH condition, the distance between line a and line ① is larger, indicating that hydrogen peroxide as an oxidant has a greater driving force for the oxidation of ferrous oxide than oxygen. However, for high acid consuming deposits, in order to reduce acid consumption, on the one hand, it is necessary to maintain a low acidity and make the leaching solution $\text{pH} \geq 2$ to reduce the acid rock reaction rate; at the same time, it is also necessary to prevent iron from being oxidized in large quantities and precipitation.

2.2. Oxidation Reaction Kinetics

Generally, ferrous is easily oxidized by oxygen or air in an alkaline environment. As the pH value of the solution decreases, ferrous ions combine with water molecules to form hydrated iron ions. Ferrous ions are in the center of hydrated iron ions and are closely surrounded by water molecules [11]. These water molecules have a “masking effect” on the electron migration between oxygen molecules and ferrous ions. Therefore, the oxidation of ferrous ions by oxygen under acidic conditions is affected by oxygen solubility, the diffusion rate of dissolved oxygen in water molecules, and the redox reaction of dissolved oxygen. Therefore, compared with liquid oxidants such as hydrogen peroxide, the oxidation process is very slow. However, according to the mechanism of an oxidant, under acidic conditions, the process of ferrous oxide oxidation by oxygen lacks the autocatalytic mechanism similar to that of ferrous oxide oxidation by hydrogen peroxide [12–14]. With the increase in the pH value (i.e., the concentration of OH^- ion increases), OH^- ion can capture H^+ from the water molecules around $\text{Fe}(\text{II})$ ion, thus promoting the hydrolysis of ferrous hydrate ion. The hydrolysate of ferrous is separated due to the neutralization of the electric property of the central ion, which weakens its polarization ability to the coordination bound water molecules (so the hydrolysate of ferrous only contains free adsorbed water and does not contain crystalline water), so that the dissolved oxygen molecules in the solution can directly oxidize with $\text{Fe}(\text{II})$ ions due to the disappearance of the “masking effect” of coordination water. The chemical reaction formula is as follows:



The above is the influence of the OH^- ion concentration in the solution on the “shielding effect” of ferrous hydrate ion and the mechanism that oxygen can accelerate the oxidation rate of ferrous ion in aqueous solution with the increase in the pH value.

In contrast, the oxidation process of $\text{Fe}(\text{II})$ by H_2O_2 is mainly controlled by hydroxyl radicals, and the oxidation mechanism is as follows:





The reaction is a chain reaction initiated by H_2O_2 and Fe(II) in Formula (5); Formulas (6) and (7) are chain growth reactions, in which O_2 is released; Equation (8) is to terminate the chain reaction and generate HO^- . Compared with the oxidation of Fe(II) by oxygen, the activity is much greater. From the reaction process, it can be seen that when the concentration of iron ion is high, it is easy to form Fe(OH)_3 precipitation.

3. Experimental Study on Influencing Factors and Kinetics of Ferrous Oxide by Oxygen

3.1. Factors Affecting Ferrous Oxidation

In order to explore the influencing factors and degree of ferrous ion oxidation, the ferrous oxidation experimental research is carried out, and the basic data and technical basis for developing low-acid and oxygen leaching technology are provided. The experiment was carried out in a closed reactor, so the oxygen pressure mentioned in this article was achieved in it.

First, dilute sulfuric acid solution and analytical pure $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were prepared with Fe(II) concentrations of 1.0 g/L, 2.0 g/L, and 3.0 g/L, respectively, and concentrated sulfuric acid was used to adjust the pH of the solution. The adjusted pH values of the iron-containing solution were 2.0, 2.5, 3.0, and 3.5, respectively. The concentration changes in Eh, ΣFe , and Fe(II) were determined. The oxygen pressure during the experiment was set at 0.5 MPa and 1.0 MPa, respectively, and the oxidation of Fe(II) was compared with H_2O_2 as the oxidant. The oxygen used in this article was pure; its purity was 99.9%.

Under different pH conditions, the time-varying curves of the total iron and Fe(II) concentration in the solution are shown in Figure 2a,b. The time-varying curves of the total iron and Fe(II) concentrations in the solution under different oxygen pressures are shown in Figure 3a,b. Under different initial concentration of Fe(II) , the time-varying curves of the total iron and concentration of Fe(II) in the solution are shown in Figure 4.

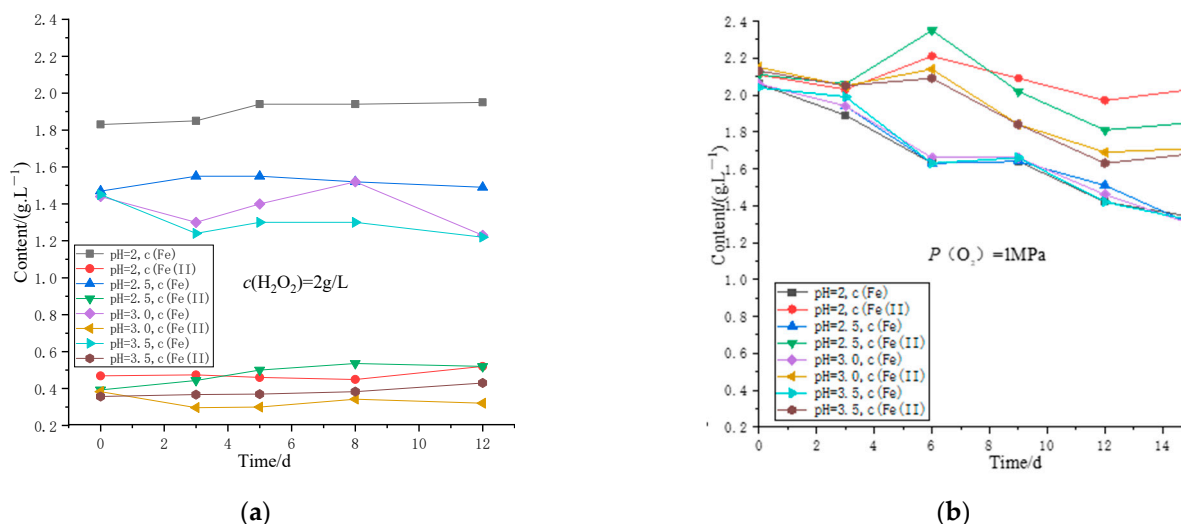


Figure 2. Oxidizing effect of oxidant on Fe(II) under different pH conditions. (a) shows the use of hydrogen peroxide. (b) shows the use of oxygen.

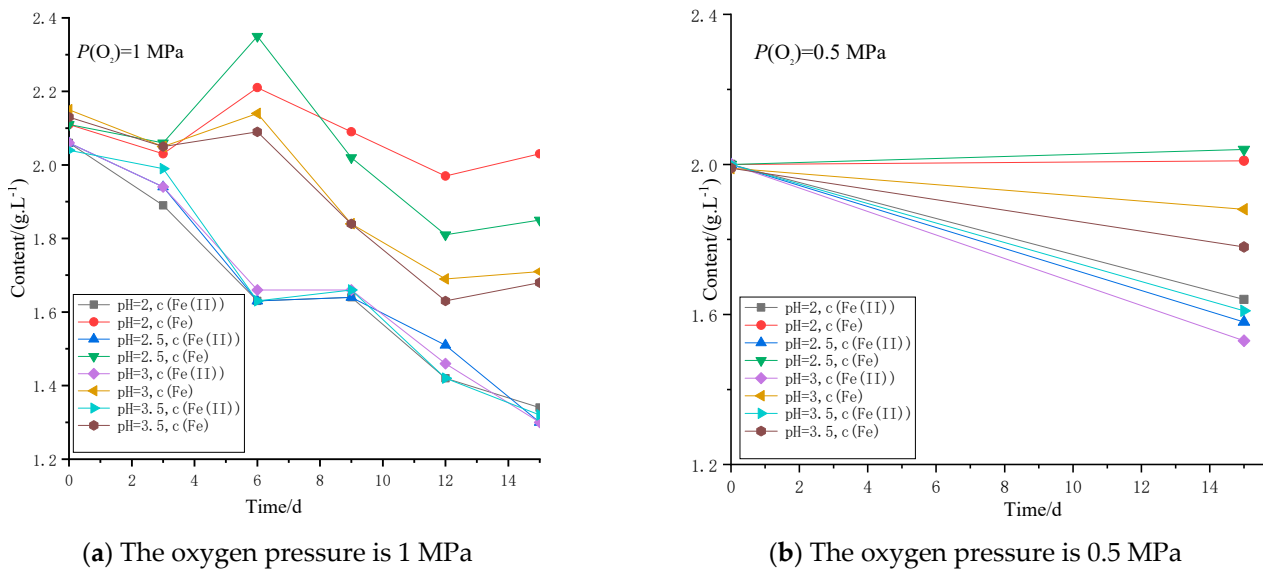


Figure 3. Oxidation of Fe(II) under different oxygen pressures.

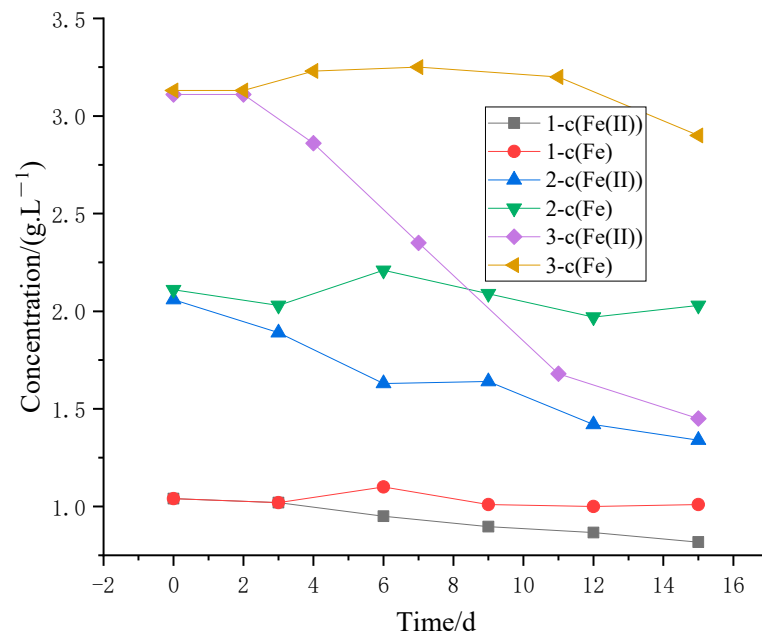


Figure 4. Variation in total iron and concentration of Fe(II) with time under different initial concentration of Fe(II) ($P(O_2) = 1.0 \text{ MPa}$, $\text{pH} = 2$).

It can be seen from Figure 2a that the concentration of Fe(II) in the solution decreased from 2.0 mg/L to about 3.3~0.5 mg/L when hydrogen peroxide was used as the oxidant for one day, indicating that hydrogen peroxide has a strong oxidation ability and can quickly oxidize Fe(II) to Fe(III). The total iron in the solution decreased from 2.0 mg/L to 1.5~1.8 mg/L. It can be inferred that Fe(III) precipitation occurred during the experiment. At the same time, the concentration of total iron and Fe(II) in the solution decreased with the increase in the pH. When oxygen was used as the oxidant (Figure 2b), the concentration of oxygen in the solution decreased from 2.0 mg/L to about 1.3 mg/L after 15 days of experiments. Compared with hydrogen peroxide, the oxidation capacity was weaker, and the oxidation speed was slower. The total iron in the solution decreased from 2.0 mg/L to 1.7~1.9 mg/L, and the Fe(III) precipitated phase was less than that when hydrogen peroxide was used as the oxidant. When oxygen is used as an oxidant, the effect of pH on the oxidation of Fe(II) to Fe(III) is not obvious.

It can be seen from Figure 3a,b that the oxygen pressure increased from 0.5 MPa to 1.0 MPa, and the concentration of Fe(II) in the solution decreased, but the decrease was not large. Taking pH = 3 as an example, the oxygen pressure increased from 0.5 MPa to 1.0 MPa, and the concentration of Fe(II) in the solution decreased from 1.5 mg/L to about 1.3 mg/L after 15 days of experiments; the total iron in the solution had little change.

It can be seen from Figure 4 that the greater the initial concentrations of Fe(II), the greater the change in the Fe(II) concentration in the solution with time. When the initial concentrations of Fe(II) is 1.0 g/L, the curve of the total iron and concentrations of Fe(II) is gentle, and the decrease in the Fe(II) concentration is small. When the initial concentrations of Fe(II) increases to 2.0 g/L, the decrease in the Fe(II) concentration increases, indicating that the proportion of Fe(II) oxidized to Fe³⁺ or precipitated increases. When the initial Fe(II) concentration increases to 3.0 g/L, the decrease in the Fe(II) concentration further increases. When the reaction time is 15 days, the Fe(II) concentration in the solution decreases to 1.45 g/L, with a decrease of more than 50%.

3.2. Study on Ferrous Oxidation Kinetics

3.2.1. Ferrous Oxidation Rate Analysis

The effects of pH, oxygen pressure, initial Fe(II) concentration, and other factors on the ferrous oxidation rate were studied, and further study on ferrous oxidation kinetics was carried out.

The experimental procedure is the same as in 3.1. During the experiment, the oxygen pressure was set to 0.5 MPa, 1.0 MPa, and the concentration of Fe(II) was set to 1.0 g/L, 2.0 g/L, and 3.0 g/L. The concentration changes in Eh, Σ Fe, and Fe(II) in the solution were measured, and the conversion of Fe(II) and the reduction in Σ Fe in the solution were calculated and compared with the oxidation of H₂O₂ as an oxidant.

The time-varying curves of the Fe(II) conversion under different pH and oxidant conditions are shown in Figure 5a,b. The time-varying curve of the Fe(II) conversion under different oxygen pressures is shown in Figure 6. Under different initial Fe(II) concentrations, the time-varying curve of the Fe(II) conversion is shown in Figure 7.

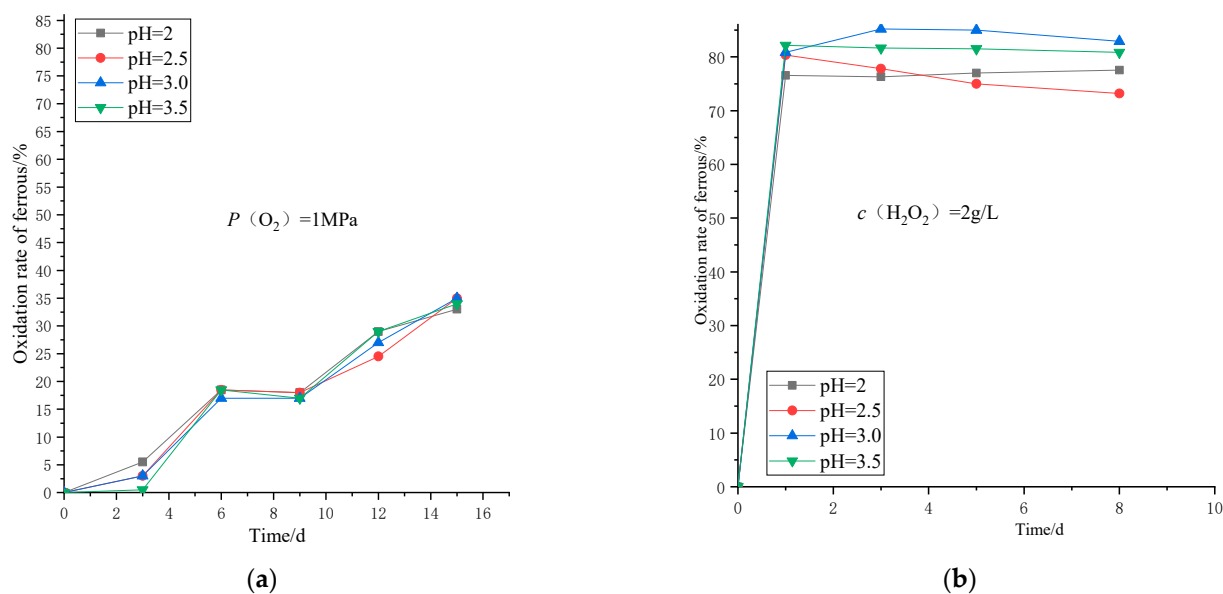


Figure 5. (a) Oxidation rate of Fe(II) under different pH with oxygen (b). Oxidation rate of Fe(II) under different pH with H₂O₂ (Fe(II) concentration is 2 g/L).

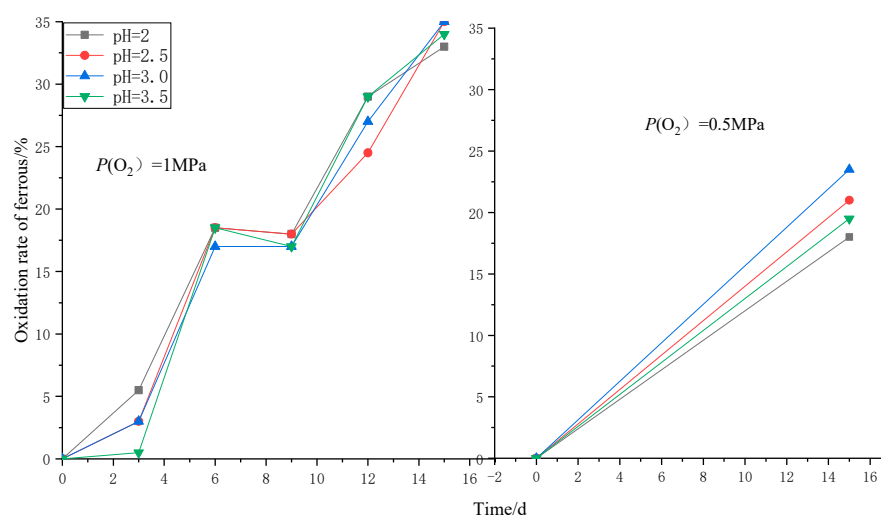


Figure 6. Oxidation rate of Fe(II) under different oxygen pressures ($c(\text{Fe(II)})$ is 2 g/L).

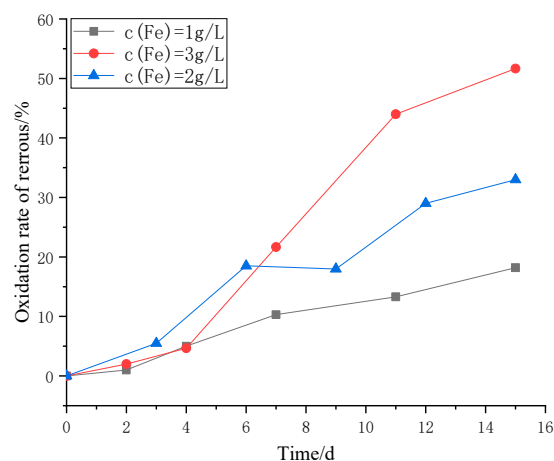


Figure 7. Oxidation rate under different initial concentrations of Fe(II) conditions ($P(\text{O}_2) = 1 \text{ MPa}$, $\text{pH} = 2$).

It can be seen from Figure 5b that when hydrogen peroxide is used as an oxidant and the reaction time is 1 day, the conversion rate of ferrous ion can reach more than 70% under 4 groups of pH conditions. In contrast, it can be seen from Figure 5a that when oxygen is used as an oxidant and the reaction time is 15 days, the conversion rate only increases to about 35%. Therefore, the reaction rate of hydrogen peroxide as an oxidant is much higher than that of oxygen as an oxidant, which also shows that the oxidation rate and degree of Fe(II) by oxygen are weak. Compared with the effect of pH on the oxidation reaction of ferrous oxide, it can be seen that in the first 2–3 days of the reaction, the oxidation rate decreases with the increase in the pH, and the reaction continues until the later stage, and the effect of pH on the reaction rate is not obvious.

It can be seen from Figure 6 that when the oxygen pressure increases from 0.5 MPa to 1 MPa and the reaction time is 15 days, the oxidation rate of iron increases from 25% to 35%, so increasing the oxygen pressure can improve the oxidation rate of Fe(II).

It can be seen from Figure 7 that the reduction in iron increases with the increase in pH, which is caused by the conversion of Fe(II) to Fe(III) and precipitation with the increase in pH. When the initial ferrous concentration increases from 1 g/L to 2 g/L, the reduction in iron further increases, indicating that increasing the initial ferrous concentration helps to increase the power of the Fe(II) conversion.

3.2.2. Redox Potential

The oxidation–reduction potential of oxygen and solution as an oxidant is shown in Figures 8 and 9.

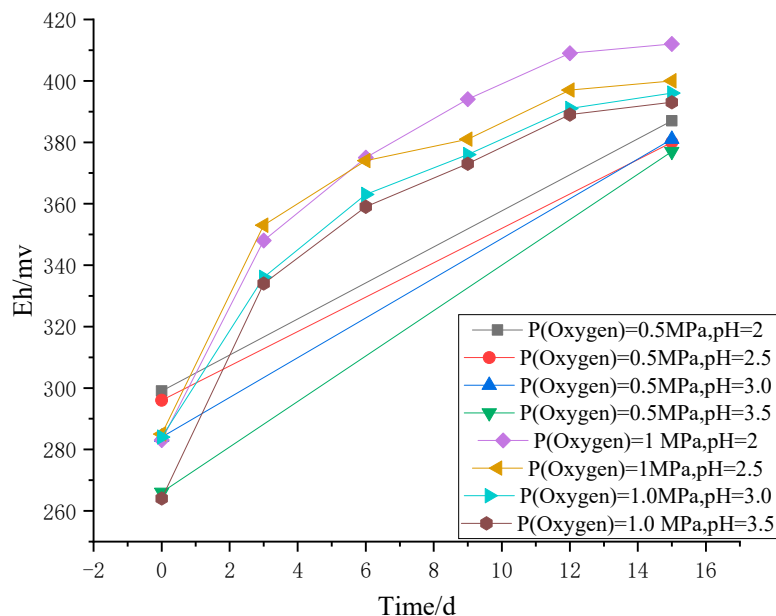


Figure 8. Variation in oxygen as oxidant Eh with time ($c(\text{Fe}(\text{II}))$ is 2 g/L).

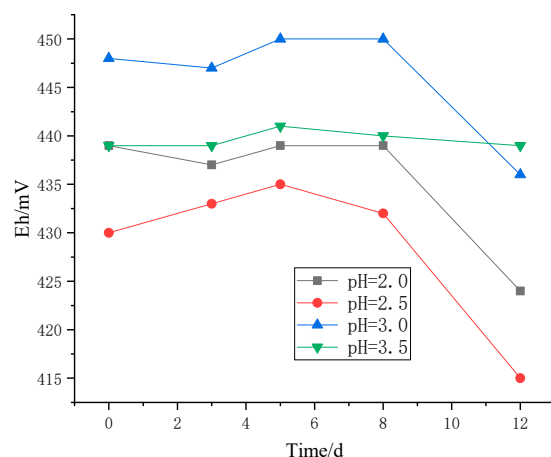


Figure 9. Variation in H_2O_2 as oxidant Eh with time ($c(\text{Fe}(\text{II}))$ is 2 g/L).

It can be seen from Figure 8 that the redox potential of the solution increases with the increase in the oxygen pressure. Taking $\text{pH} = 2$ as an example, when the oxygen pressure increases from 0.5 MPa to 1.0 MPa, the redox potential increases by about 40 mV. The comparison between Figures 8 and 9 shows that the oxidation–reduction potential of the solution is higher when hydrogen peroxide is used as the oxidant, indicating that its oxidation power is stronger than that of oxygen. In Figure 9, the oxidation–reduction potential of the solution decreased at the late stage of the reaction, further indicating that although hydrogen peroxide has a strong oxidation (resulting in a too fast release of $\text{Fe}(\text{III})$), it has the disadvantages of an easy decomposition and short action distance.

3.2.3. Ferrous Oxidation Kinetic Equation

In order to analyze the kinetics of ferrous oxide by oxygen, the following two simplified kinetic equations are used to simulate the experimental data ($\text{pH} = 2$, $P(\text{O}_2) = 1$ MPa) at different initial $\text{Fe}(\text{II})$ concentrations.

First-order reaction [10,15] kinetic:

$$\ln c_0(\text{Fe}^{2+})/c(\text{Fe}^{2+}) = k_1t \tag{9}$$

Second-order reaction [16–18] kinetic:

$$1/c(\text{Fe}^{2+}) - 1/c_0(\text{Fe}^{2+}) = k_2t \tag{10}$$

The kinetic fitting results of ferrous oxide by oxygen can be seen from Figures 10 and 11 and Table 2.

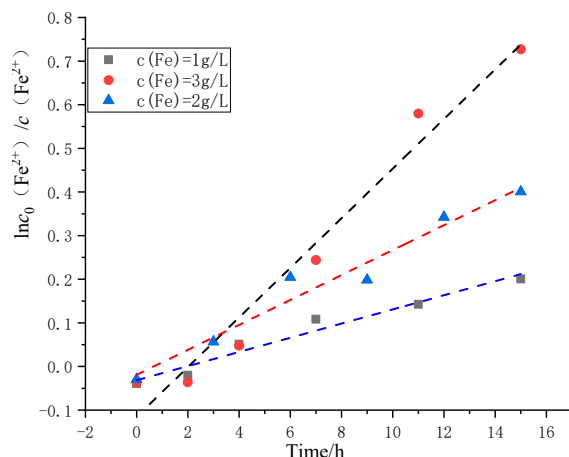


Figure 10. First-order kinetics fitting of ferrous oxidation reaction.

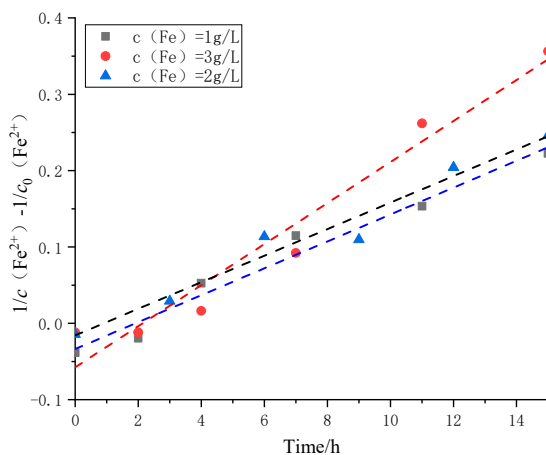


Figure 11. Second-order kinetics fitting of ferrous oxidation reaction.

Table 2. Kinetic equation and rate constant.

$c_0(\text{Fe(II)}) / (\text{g} \cdot \text{L}^{-1})$	First-Order Reaction Kinetics			Second-Order Reaction Kinetics		
	Regression Equation	R^2	k_1/d^{-1}	Regression Equation	R^2	k_1/d^{-1}
1	$Y = 0.0162x - 0.0314$	0.9625	0.0162	$Y = 0.0007x - 0.0336$	0.9716	0.0007
2	$Y = 0.0286x - 0.0189$	0.9631	0.0286	$Y = 0.0174x - 0.0157$	0.9643	0.0174
3	$Y = 0.0569x - 0.1153$	0.9666	0.0569	$Y = 0.0269x - 0.0576$	0.9554	0.0269

It can be seen from the results in Figures 10 and 11 that the linear fitting results of the three groups of simulations are good ($R^2 > 0.95$), and the kinetic equations and rate constants are shown in Table 2. Under the condition of low acid, the chemical reaction kinetics of ferrous oxide by oxygen is between the first-order and the second-order. The

first-order kinetic equation showed that the reaction rate constant was between 0.0162 and 0.0569; the second-order kinetic equation shows that the reaction rate constant is between 0.0007 and 0.0269.

4. Study on the Interaction between Uranium and Iron in Low-Acid and Oxygen System

4.1. Study on Iron Oxidation and Precipitation in Uranium-Containing Solution

4.1.1. Effect of Oxygen Pressure on Iron Oxidation and Precipitation in Uranium-Containing Solution

During the experiment, the oxygen pressure was set at 1.0 MPa and 2.0 MPa, respectively, and the concentration of Fe(II) was 2.0 g/L. The effect of oxygen pressure on iron precipitation was investigated. At the end of the experiment, the precipitate in the beaker was fully dissolved with 25 mL of H₂SO₄ solution with pH < 1 and shaken well. The concentrations of Σ Fe, Fe(II), and U in the solution were determined and compared with H₂O₂ as the oxidant. The experimental results are shown in Figure 12.

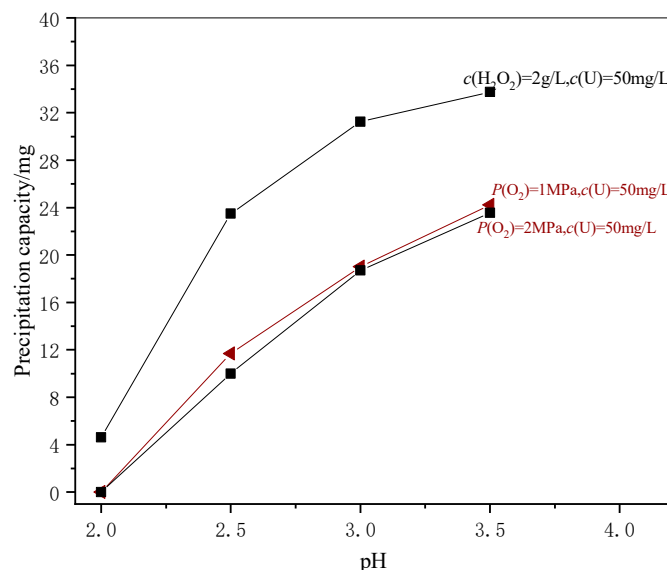


Figure 12. Precipitation amount of Fe(II) under different oxygen pressures ($c(\text{Fe(II)}) = 2.0 \text{ g/L}$).

It can be seen from Figure 12 that under different oxygen pressures, the amount of Fe precipitation increases with the increase in pH, and it reaches the maximum at pH = 3.5; compared with the effect of the oxygen pressure on the precipitation, the precipitation of Fe has little change when the oxygen pressure increases from 1 MPa to 2 MPa. According to the previous research on the influencing factors of ferrous oxidation, when the oxygen pressure is 0.5 MPa, the solution potential is low, and when the oxygen pressure increases, the potential increases little. It can be inferred that dissolved oxygen has a dual effect on the oxidation and precipitation of iron; that is, with the increase in the oxygen pressure, the oxidation capacity of ferrous oxide increases, increasing the trend of precipitation, but also enhancing the solubility of Fe³⁺ in solution, which leads to the decrease in the Fe precipitation under the increase in the oxygen pressure. Figure 12 also shows that the precipitation amount of hydrogen peroxide as an oxidant is higher than that of oxygen, which is consistent with the results of the influencing factors and the kinetic theory of ferrous oxidation.

4.1.2. Effect of Fe(II) and Uranium Concentration on Oxidation and Precipitation in Uranium-Containing Solution

Under the conditions of 1 MPa and 2 MPa oxygen pressure, the effects of Fe(II) concentrations of 0.5 g/L, 1 g/L, 2 g/L, and 3 g/L on the oxidation and precipitation of

Fe(II) were investigated. The concentrations of U in the solution were 0, 50 mg/L, and 90 mg/L, respectively. The experimental results are shown in Figure 13.

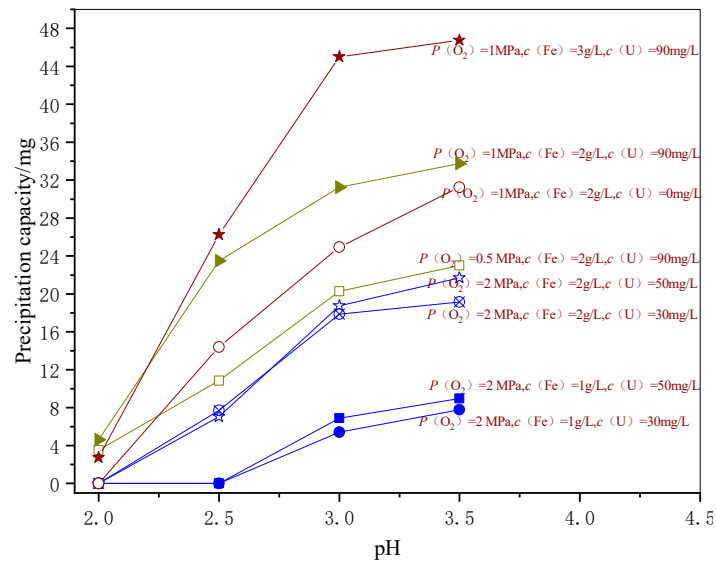


Figure 13. Effect of concentration and pH on iron precipitation.

It can be seen from Figure 13 that with the increase in the initial Fe(II) concentration in the solution, the precipitation amount of high valent iron after oxidation also increases exponentially. The precipitation amount increased from 2.6 mg to 48 mg with the increase in the Fe(II) concentration. The uranium concentration has little effect on iron oxidation and precipitation in solution. It fluctuates with the change in the uranium concentration, but it has no obvious regularity.

4.1.3. Effect Analysis of Fe-U Precipitation

By measuring the mass of Fe and U in the precipitation produced by the experiment under the conditions of different oxidants, the oxygen pressure, Fe(II) concentration, and uranium concentration, the relationship between them is analyzed, and the influence of iron precipitation on the stability of the uranium in the solution is further described. The results are shown in Figure 14.

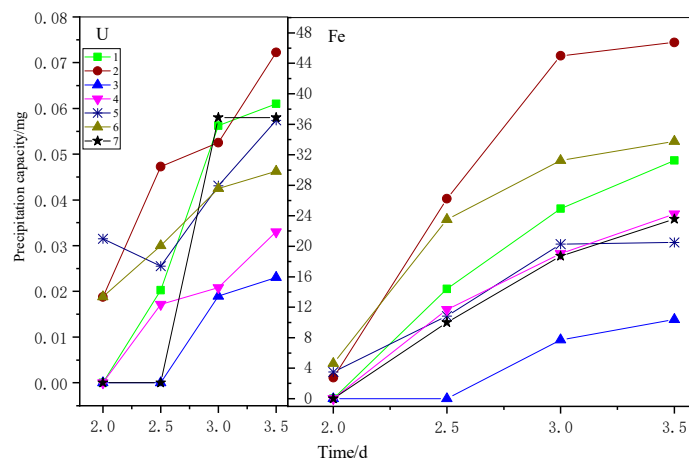


Figure 14. Corresponding relationship of U-Fe precipitation. [Line 1: $P(O_2) = 1 \text{ MPa}$, $c(Fe) = 2 \text{ g/L}$, $c(U) = 90 \text{ mg/L}$. Line 2: $P(O_2) = 1 \text{ MPa}$, $c(Fe) = 3 \text{ g/L}$, $c(U) = 90 \text{ mg/L}$. Line 3: $P(O_2) = 1 \text{ MPa}$, $c(Fe) = 1 \text{ g/L}$, $c(U) = 50 \text{ mg/L}$. Line 4: $P(O_2) = 1 \text{ MPa}$, $c(Fe) = 2 \text{ g/L}$, $c(U) = 50 \text{ mg/L}$. Line 5: $c(H_2O_2) = 1 \text{ g/L}$, $c(Fe) = 2 \text{ g/L}$, $c(U) = 50 \text{ mg/L}$. Line 6: $c(H_2O_2) = 2 \text{ g/L}$, $c(Fe) = 2 \text{ g/L}$, $c(U) = 50 \text{ mg/L}$. Line 7: $P(O_2) = 0.5 \text{ MPa}$, $c(Fe) = 2 \text{ g/L}$, $c(U) = 90 \text{ mg/L}$].

It can be seen from Figure 14 that the corresponding relationship between uranium and iron in the precipitation is obvious and has a positive correlation, indicating that there is co-precipitation or adsorption between iron precipitation and uranium.

4.2. Effect of Iron Precipitation in Low-Acid and Oxygen Leaching on Uranium Leaching

In order to further investigate the effect of iron precipitation on uranium leaching, the effect of low-acid and oxygen leaching was studied. In the experiment, the core samples were retrieved on site, and the chemical analysis results are shown in Table 3. The experimental results are shown in Figure 15.

Table 3. Chemical analysis data of ore sample.

Ingredient	ΣU	U (VI)	ΣFe	Fe (II)	Al	FeS ₂	Ca	Mg	ΣC	IC	Loss on Ignition
Content/%	0.050	0.037	1.39	0.48	5.26	0.13	0.15	0.42	1.26	0.001	4.4

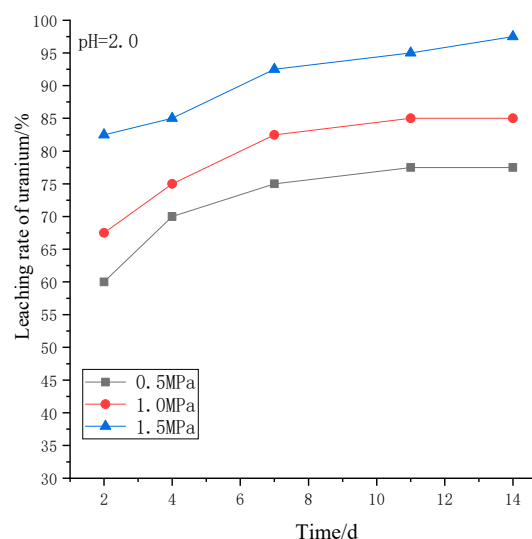


Figure 15. Variation in leaching rate with oxygen pressure (pH = 2.0).

From the relationship between the leaching rate and the oxygen pressure shown in Figure 15, it can be seen that the oxygen pressure can affect the uranium leaching rate of the ore. When the leachant's pH = 2.0, when the oxygen pressure increases from 1.0 MPa to 1.5 MPa, the leaching rate increases from 84% to 97%. When the oxygen pressure drop is 0.5 MPa, the leaching rate is only 77%. From the perspective of oxidation kinetics, it can be seen that with the increase in the oxygen pressure, the oxidation–reduction potential of the solution increases continuously, and the oxidation performance of dissolved oxygen increases, thus enhancing the solubility of Fe³⁺ in the solution, reducing the amount of precipitation and increasing the leaching rate of uranium. This conclusion is related to the corresponding relationship between iron–uranium precipitation and the actual situation in the process of in situ leaching uranium. When the leaching agent's pH = 3.0 (Figure 16), the leaching rate of uranium decreases significantly, but the leaching rate of uranium increases with the reaction. Both groups of tests did not show a decline in the leaching rate, indicating that the low-acid and oxygen leaching technology can achieve the oxidation leaching of uranium and improve the leaching rate of uranium under the condition of reducing iron precipitation.

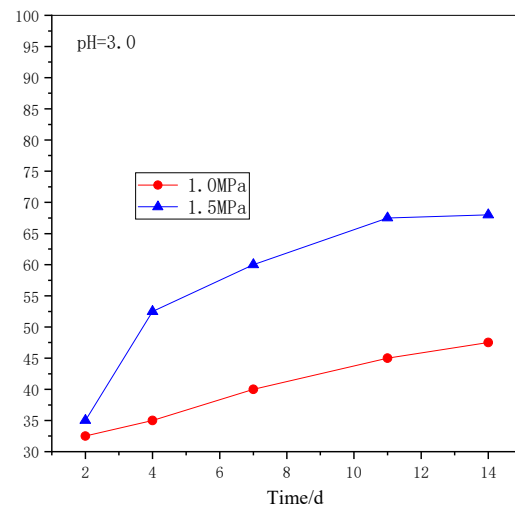


Figure 16. Variation in leaching rate with oxygen pressure (pH = 3.0).

5. Conclusions

- (1) The analysis of oxidation kinetics and thermodynamics of ferrous oxide by oxidant shows that the stability range of ferrous is wider than that of trivalent iron; compared with oxygen, hydrogen peroxide has a stronger oxidation power on ferrous iron. In order to avoid iron precipitation in the production process, the oxidation of ferrous to trivalent iron should be reduced. Therefore, it is theoretically feasible to use oxygen as an oxidant under acidic conditions to slow down the oxidation of ferrous iron and the precipitation of ferric iron.
- (2) The rate of ferrous oxidation is affected by the initial ferrous concentration, pH, oxygen pressure, and other factors, among which the initial ferrous concentration has the greatest impact. The kinetic analysis of ferrous in oxygen under the condition of low acid (pH~2.0–4.0) showed that the kinetic law was between the first-order reaction kinetics and the second-order reaction kinetics.
- (3) The study of the interaction between iron and uranium precipitation found that there is a positive correlation between them in the precipitation, which further verified that iron precipitation affects the stability of uranium in solution and reduces the leaching rate of uranium by coprecipitation or adsorption. The leaching test shows that compared with hydrogen peroxide as an oxidant leaching process, it is technically feasible to adopt low-acid and oxygen leaching technology to reduce iron precipitation in the system and improve the uranium leaching rate.
- (4) The research provides basic data and a theoretical basis for the application of low-acid and oxygen leaching technology. It is innovative in the field of sandstone leaching technology in uranium mining and metallurgy and has a good guiding significance for low-acid and oxygen leaching technology and the efficient development of sandstone uranium deposits with a high acid consumption.

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References

1. Hongfu, L.; Yiqun, X.; Yihan, Y. Research and application of in-situ leaching of uranium by O₂ oxidizing acid method. *Uranium Min. Metall.* **2022**, *41* (Suppl. S1), 43–49.
2. Ying, X.; Hong, C.; Wanliang, Z. Experimental study on enhanced leaching of uranium resources in the final mining area of an acid in-situ leaching mine. *China Min. Mag.* **2022**, *31*, 147–155.
3. Bing, W.; Yipeng, Z.; Tingjian, W. Acid leaching test of a uranium deposit in Xinjiang. *Nonferrous Met. (Extr. Metall.)* **2021**, *5*, 58–66.
4. Li, C.; Gongxin, C.; Wenfeng, W. Study on the synergistic leaching of metal ions and uranium in the process of bioleaching uranium from a uranium mine. *Nonferrous Met. (Extr. Metall.)* **2020**, *12*, 54–63.
5. Shen, N.; Li, J.; Guo, Y.; Li, X. Thermodynamic modeling of in situ leaching of sandstone-type uranium minerals. *J. Chem. Eng. Data* **2020**, *65*, 2017–2031. [[CrossRef](#)]
6. Tsai, A.-L.; Martin, E.; Berka, V.; Olson, J.S. How do heme-protein sensors exclude oxygen? Lessons learned from cytochrome *c'*, *Nostoc punctiforme* heme nitric oxide/oxygen-binding domain, and soluble guanylyl cyclase. *Antioxid. Redox Signal.* **2012**, *17*, 1246–1263. [[CrossRef](#)] [[PubMed](#)]
7. Liao, W.; Tan, Y.; Wang, L.; Li, J. Oxygen Used as an Oxidizer in Acid In-Situ Leach Uranium: From Theory to Practice[C]. In Proceedings of the International Conference on Nuclear Engineering, Charlotte, NC, USA, 26–30 June 2016; American Society of Mechanical Engineers: New York, NY, USA, 2016; Volume 50015, p. V001T02A010.
8. Limin, W.; Wensheng, L.; Yahui, T. Experimental study on low acid oxygen leaching of a sandstone uranium ore. *Uranium Min. Metall.* **2020**, *39*, 191–197.
9. Kaixuan, T.; Qingliang, W.; Hengshan, W. *Thermodynamics and Kinetics of Solution Mining*; Central South University Press: Changsha, China, 2002.
10. Sun, H.; Yao, Y.; Wei, F.; Zhao, Q.; Liu, B.; Zhang, L. Process optimization and mechanism study of acid red G degradation by electro-FentonFeox process as an in situ generation of H₂O₂. *Turk. J. Chem.* **2021**, *45*, 5–16. [[CrossRef](#)] [[PubMed](#)]
11. Gongdu, Z. *Inorganic Structural Chemistry*; Science Press: Beijing, China, 1982.
12. Hualin, Z. *Inorganic Reaction Mechanism*; Shanghai Science and Technology Press: Shanghai, China, 1988.
13. Khan, J.; Sayed, M.; Ali, F.; Khan, H.M. Removal of acid yellow 17 dye by Fenton oxidation process. *Z. Für Phys. Chem.* **2018**, *232*, 507–525. [[CrossRef](#)]
14. Lu, W.; Xunmin, Y.; Qingxin, L. Oxidation of Fe(II) by oxygen in air and its kinetics. *Pioneer. Sci. Technol. Mon.* **2009**, *22*, 154–155.
15. Wang, C.; Zhang, J.; Du, J.; Zhang, P.; Zhao, Z.; Shi, W.; Cui, F. Rapid degradation of norfloxacin by VUV/Fe²⁺/H₂O₂ over a wide initial pH: Process parameters, synergistic mechanism, and influencing factors. *J. Hazard. Mater.* **2021**, *416*, 125893. [[CrossRef](#)] [[PubMed](#)]
16. Yuanying, H.; Qian, W.; Qifeng, T. Reaction kinetics, adsorption equilibrium and influencing factors of cadmium removal from water by nano iron. *Ecol. Environ. Sci.* **2019**, *28*, 2053–2061.
17. Lirong, C.; Kailun, Y.; Zhenchao, G. Study on degradation of quinoline in water by UV/H₂O₂ enhanced by Fe²⁺. *Appl. Chem. Ind.* **2020**, *49*, 2808–2811.
18. Su, X.B.; Du, Z.M. Development and prospect of China uranium in-situ leaching technology. *China Min. Mag.* **2012**, *21*, 79–83.

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