

Development of SO₂–O₂ system as an oxidant at uranium leaching processes

A. B. Umanskii · A. M. Klyushnikov

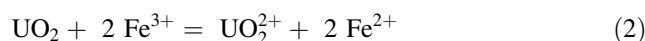
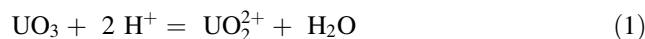
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Abstract The oxidation of Fe²⁺ in uranium leaching solutions with gaseous mixture of SO₂ and air has been studied. The variables studied include H₂SO₄ concentration, temperature, SO₂ concentration and time. The oxidation rate was founded to increase greatly with an increase in the solution temperature. The almost total oxidation of Fe²⁺ is readily achieved at 95 °C. By appropriately adjusting the temperature of solution and SO₂/O₂ in the gas, oxidation of ferrous ion and generation of sulphuric acid can be carried out. It was founded that solutions produced by such oxidation processing are very suitable for the uranium ore leaching.

Keywords Sulphur dioxide · Oxygen · Oxidation · Uranium leaching · Ferrous ion

Introduction

In the leaching of uranium ores with sulfuric acid, ferric ions are used [1]. Hexavalent uranium is rapidly solubilized from ores in an acidic medium as uranyl ion while the solubilization of tetravalent uranium requires a previous oxidation step to U(VI) with ferric ions:



That is to say, for a technique to be applied the Fe²⁺ produced in reaction above must be re-oxidized to Fe³⁺ and recycled.

At an industrial level, ferric ion regeneration is carried out by adding different chemical reagents which are strongly oxidizing and capable of maintaining the redox potential (Eh) between 400 and 500 mV. The most commonly used oxidants for this have been sodium chlorate, NaClO₃, and pyrolusite, MnO₂ [1]. However, these are expensive and represent a high percentage of the total costs of the process.

Another of the problems associated with this process is the environmental one, since the oxidants can release harmful impurities into the leaching circuit. Oxygen was proposed as cleaner and cheaper oxidant but its oxidation capacity appeared to be very low [2].

In the 1920s, air-sulfur dioxide mixture was used for oxidizing to produce ferric sulfate and sulfuric acid at the Bureau of Mines [3]. Leaver and Thurston used mixture with sulfur dioxide concentrations varied from 8 to 10 pct for ferrous ion oxidation. Oldright, Keyes, and Wartman produced ferric sulfate and sulfuric acid by treating ferrous sulfate solution with roaster gas [4].

McNally, Spedden, and Apps [5] reported that bisulfite ion would either oxidize or reduce iron in solution depending upon the oxygen concentration in the solution.

But an SO₂ application to oxidation processes in solutions that contains of about 1 g/L iron were not investigated in these works. All this works were done with solutions with high iron concentration (1–2 M FeSO₄) while the typical uranium leaching solution contains iron

A. B. Umanskii
Department of Radiochemistry and Applied Ecology,
Ural Federal University, Ekaterinburg, Russia
e-mail: pdwn1982@e1.ru

A. M. Klyushnikov (✉)
Department of Rare Metals, Ural Federal University,
Ekaterinburg, Russia
e-mail: kl-anton-mih@yamndex.ru

about as much as 1 g/L [1]. But an application of SO₂ to the ferrous ion oxidation at solutions with small amounts of iron is not much available in the literature.

That is why this paper mainly describes a study of the ferrous ion oxidation with O₂ + SO₂ mixture in typical sulfate uranium leaching solutions.

Experimental

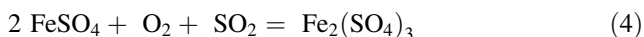
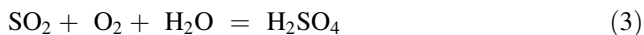
A 1.5 L, three necked, baffled spherical Pyrex flask was used as a reaction vessel. The central neck of the flask was equipped with a closed system glass stirrer. One of the side necks was fitted with a gaseous mixture bubbler submerged in the acidic ferrous sulfate solution, while the other side neck was fitted with a condenser and was also used to withdraw samples for analysis. The reaction vessel was placed in a thermostatic water bath.

Experiments were carried out using the typical uranium mining solution that contains 0.002 g/L U, 1.0 g/L Fe²⁺; 0.05 g/L Fe³⁺ and 4.1 g/L H₂SO₄.

The gas flow rate was constant in all experiments and its value was as much as 30 mL/min.

Results and discussion

In the presence of oxygen and ferrous ion the autocatalytic chemical processes is found to proceed quantitatively according to the stoichiometric reactions:



Experiments were conducted by means of solution contacting with the mixture of air and sulfuric oxide. A determining of Eh, concentration of ferric and ferrous ions as well as sulfuric acid concentration were used to detect whether the oxidation process is effective or not.

This parameters were determined as a function of sulfuric oxide and oxygen concentration, temperature and time.

Figures 1, 2 and 3 show results of this preliminary tests.

From Fig. 1 it is clear that for gas-saturated solutions, of about half of all ferrous ions are oxidized to ferric ions. Concentration of SO₂ at gaseous mixture of about 2–8% appeared to be the best for ferrous ions oxidation process.

The experimental results show that the aqueous oxidation of ferrous ion by O₂ in air is relatively slow (Fig. 1); however, a higher rate of oxidation occurred with an SO₂–O₂ mixture.

An increase in the oxidation rate with increasing SO₂ concentration in the gas phase indicates that that the oxidation process is controlled by the mass transfer of SO₂ from the gas to the liquid phase.

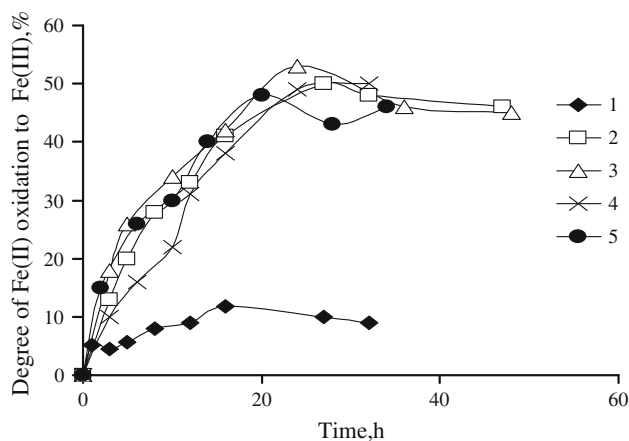


Fig. 1 Kinetic plots showing the ferrous ion oxidation in solution by gaseous mixture that contains various amounts of SO₂ and O₂. Percentage of SO₂ in gaseous phase, vol. %: 0(1), 2(2), 8(3), 16(4), 30(5)

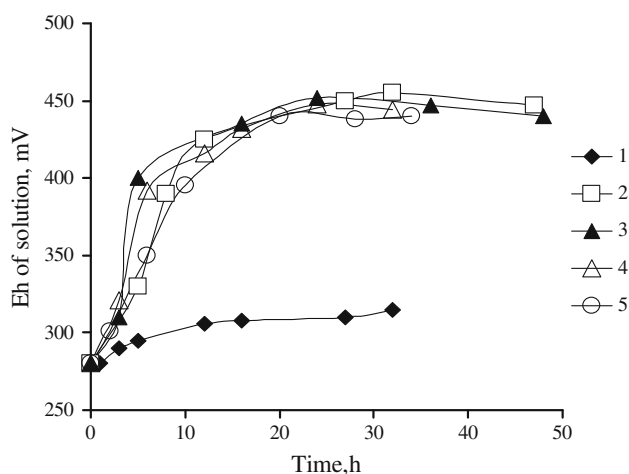


Fig. 2 Effect of SO₂ concentration on Eh at various percentage of SO₂ in gaseous phase, vol. %: 0(1), 2(2), 8(3), 16(4), 30(5)

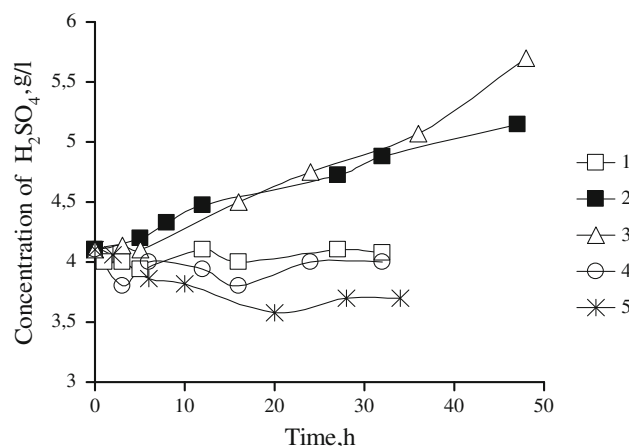


Fig. 3 Effect of SO₂ concentration on H₂SO₄ generation in solution at various percentage of SO₂ in gaseous phase, vol. %: 0(1), 2(2), 8(3), 16(4), 30(5)

It is worth noting that an increase of SO₂ percentage at mixture above 8% results in a decrease in the steady-state concentration of ferric ions.

It is apparent that the presence of SO₂ and air at proportions that mentioned before results in increase of Eh in solution up to 450 mV. Leaching solutions with such Eh are very appropriate to the process of uranium leaching.

At the same time Fig. 3 indicates that the presence of SO₂ at gaseous mixture at various proportions very slightly increased the amount of sulfuric acid in solution.

It is necessary also to know places of gaseous injection and starting H₂SO₄ concentration.

So experiments were made to learn answers for these questions. Figure 4 shows results of this experiment with temperature 20 °C and slow flow rate of gaseous mixture.

It was found that an increase in an acid concentration resulted in a decrease in the oxidation of Fe(II) and SO₂.

From Fig. 4 it is clear that the oxidation process may be devised better at two stages.

The oxidation of ferrous ions is to be performed at the first stage with subsequent generation of sulfuric acid at the second stage.

It was proposed that SO₂ oxidation is most dependent upon a temperature of the solution. So several experiments were conducted to investigate the effect of reaction temperature on the percentage of ferrous ions and SO₂ oxidized. The effect of reaction temperature of the solution on the percentage of SO₂ oxidation is shown in Fig. 5.

In order to investigate a temperature influence upon reaction it became necessary to rise flow rate of SO₂ as if the solution is heated by hot gas. That is why a flow rate of gaseous mixture was risen to ten times.

The additional heat required for heating the solution to the required temperature was administered by heating

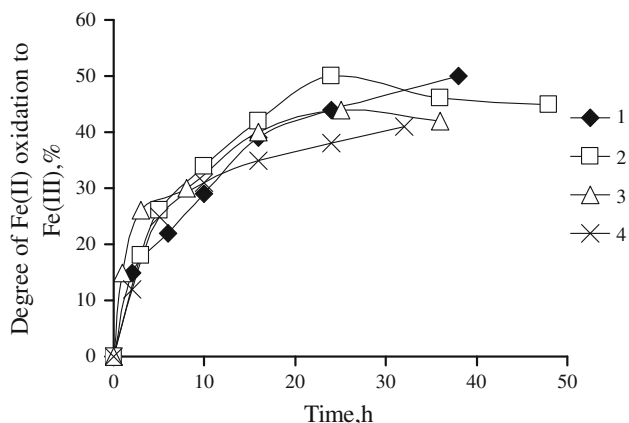


Fig. 4 Kinetic plots showing the ferrous ion oxidation in solution by SO₂ and air mixture that contains 8% (vol.) SO₂ at various concentration of H₂SO₄, g/L: 0.5(1); 4.1(2); 10 (3); 15(4)

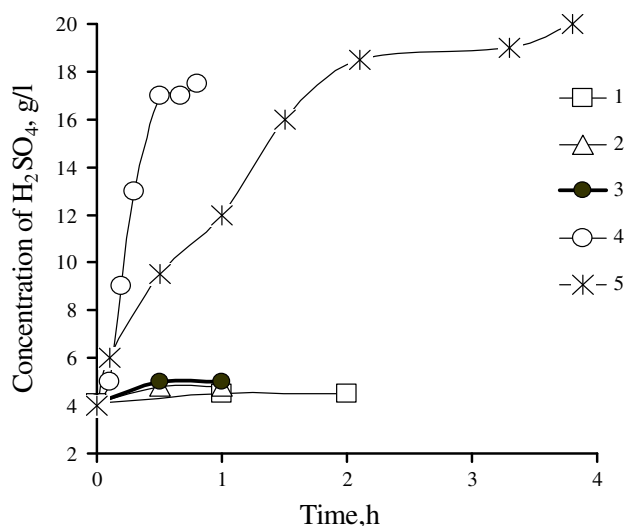


Fig. 5 Kinetic plots showing the H₂SO₄ generation in solution by SO₂ and air mixture that contains 8% (vol.) SO₂ at various temperatures of solution, °C: 20(1), 40(2), 50(3), 75(4), 95(5)

jacket, which was connected to a thermistor controller and voltage regulator.

The effect of reaction temperature of the solution on the percentage of Fe(II) oxidation is shown in Fig. 6.

The degrees of SO₂ and Fe(II) oxidation increased with increasing temperature up to 95 °C. It is clear that the temperature of solution ranging from 75 to 95 °C must be optimal for the process making the highest rate of SO₂ and Fe(II) oxidation.

Chemical mechanism of catalytic oxidation of ferrous ion by SO₂/O₂ mixture has been reported in the literature [6, 7] and can be used to explain results obtained in this

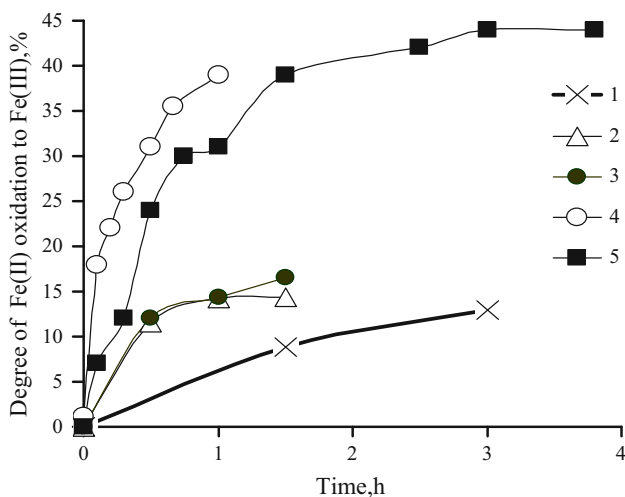
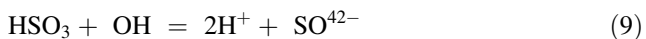
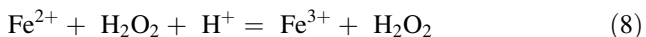
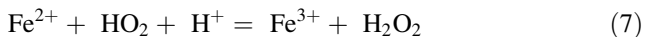
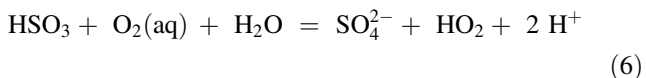
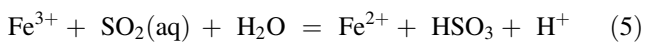
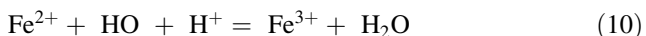


Fig. 6 Kinetic plots showing the ferrous ion oxidation in solution by SO₂ and air mixture that contains 8% (vol.) SO₂ at various temperatures of solution, °C: 20(1), 40(2), 50(3), 75(4), 95(5)

work. Karraker proposed [6] the following chemical mechanism of ferrous ion oxidation



Equation 10 instead of 9, can also be used with this mechanism to explain the oxidation of ferrous ion by SO_2/O_2 mixture.



The reversible nature of Eq. 5, which produces the HSO_3 radical, was proposed by Higginson and Marshall [13] to explain the oxidation of SO_2 to sulfuric acid. In the presence of the excess of O_2 in gaseous phase, the HSO_3 radical is partially oxidized by O_2 to produce sulfuric acid and HO_2 radical according to Eq. 6. Then HO_2 radical is supposed to oxidize ferrous ion rapidly by Eqs. 7, 8, 10.

Thus it can be seen from the aforesaid equations that two processes can be conducted together: oxidation of SO_2 to sulfuric acid accompanied by ferrous ion oxidation.

We can see from the Fig. 5 that by appropriately adjusting the temperature value and SO_2/O_2 ratio in the gas phase sulfuric acid and ferric ion may be favorably produced together. So it is clear that results of experimental work can readily confirm chemical mechanism of Eq.(5–10).

At the next stage laboratory batch uranium leaching test were performed using mining solution mentioned above that was preliminary contacted with SO_2 -air mixture. A known amount of SO_2 mixed with air was bubbled through this ferrous sulfate solution. Then solution was subjected to chemical analysis.

The chemical composition of the solution made by gaseous mixture contact became the following: 0.002 g/L U, 0.07 g/L Fe^{2+} ; 0.97 g/L Fe^{3+} and 15.0 g/L H_2SO_4 .

To make a comparison an additional leaching experiment was performed with leaching solution taken from the real uranium leaching plant.

Uranium ore used in such tests was taken from one of the uranium deposits in Ural state. Percentage of uranium in ore was analyzed to be 0.02%.

At the same time the chemical composition of leaching solution taken for experiment from uranium plant was as follows: 0.002 g/L U, 0.97 g/L Fe^{2+} ; 0.08 g/L Fe^{3+} and 15.0 g/L H_2SO_4 .

Batch leaching experiments were carried out in the same vessels during 4 h only without gaseous mixture bubbling. It was indicated that the gas-saturated solution utilization results in increase of uranium extraction up to 28% comparing with traditional leaching technology with traditional leaching solution. The results of experiments indicate that a promising process might be devised for treatment of leaching solutions of in situ leaching process. This process not only makes it possible to oxidize the total amount of ferrous ions in leaching solution but results in large amounts of additional sulfuric acid generated making an economy of acid consumption at uranium leaching plants.

Conclusions

1. Several experiments were performed to investigate Fe(II) oxidation in waste leaching solutions with gaseous SO_2 -air mixture as a function of H_2SO_4 concentration, temperature, SO_2 concentration and time. The concentration of H_2SO_4 in solutions was determined to increase by means of this oxidation process.
2. It was shown that the maximal degree of Fe^{2+} oxidation ranging up to 50% is readily achieved with the presence of gaseous SO_2 and air mixture containing 2–30% SO_2 in solutions containing 4 g/L H_2SO_4 .
3. Application of the SO_2 -air system uranium leaching appears to be promising alternative to the traditional technique of leaching.
4. It was shown that the process of leaching solution treatment with SO_2 -air mixture results in an increase of uranium leaching from ores.

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