

## KINETICS OF CHEMICAL OXIDATION OF FERROUS IRON BY OXYGEN IN ACID SULFATE SOLUTIONS

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## KINETIKA CHEMICKÉJ OXIDÁCIE DVOJMOCNÉHO ŽELEZA KYSLÍKOM V KYSLÝCH SÍRANOVÝCH ROZTOKOCH

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### Abstrakt

Roztoky železitých solí sú vďaka silným oxidačným schopnostiam  $\text{Fe}^{3+}$  iónu často používaným reagentom v hydrometalurgii. Pri reakcii so sulfidickými minerálmi dochádza k redukcii  $\text{Fe}^{3+}$  na  $\text{Fe}^{2+}$ . Predpokladom úspešného lúhovacieho procesu je možnosť regenerácie a recyklácie oxidačného činidla. Re-oxidácia dvojmocného železa na trojmocné v prítomnosti molekulárneho kyslíka v kyslom prostredí prebieha podľa rovnice č.1. Oxidácia  $\text{Fe}^{2+}$  je dôležitou reakciou aj v procesoch zvetrávania minerálov a pri tvorbe kyslých banských vôd. Kinetika tejto oxidačnej reakcie je silne závislá od chemického zloženia roztoku. Ide hlavne o hodnotu pH a charakter prítomných aniónov. V prítomnosti chloridových, alebo síranových aniónov pri hodnotách  $\text{pH} < 2$  je rýchlosť chemickej oxidácie  $\text{Fe}^{2+}$  pomalá, prvého poriadku vo vzťahu k parciálnemu tlaku kyslíka  $P_{\text{O}_2}$  a druhého poriadku vzhľadom ku koncentrácii  $\text{Fe}^{2+}$ . Existuje viacero spôsobov na zvýšenie oxidačnej rýchlosti  $\text{Fe}^{2+}$ , napr. tlaková oxidácia, alebo použitie fyzikálnych a chemických katalyzátorov. Veľmi atraktívnou metódou je použitie železo oxidujúcich baktérií. Kinetická rovnica bola vypočítaná z dielčích rýchlostných konštánt  $k_1$  prvého poriadku zo záznamu kyslíkovej elektródy počas reakcie v uzavretej banke (Obr.1, rovnice 4 a 5) a závislosti týchto konštánt na ďalších premenných- koncentrácii  $\text{Fe}^{2+}$  a teplote. Lineárny priebeh Arrheniovoho grafu a hodnota aktivačnej energie poukazujú na kinetický režim.

Rýchlostná rovnica č. 8  $d\text{Fe}^{2+}/dt = 1,26 \times 10^7 [\text{Fe}^{2+}]^2 P_{\text{O}_2} \exp(-72000/RT)$  je platná pre výpočet rýchlosti oxidácie v koncentračnom rozsahu  $\text{Fe}^{2+}$  0,08-0,64 M v rozmedzí teplôt 288-323 K (15-50°C) pri pH 2.

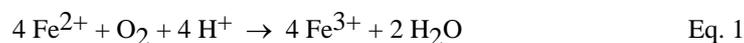
## Abstract

Ferric sulfate is one of the most important reagent used in hydrometallurgy for dissolution of metal sulphides. The leaching of minerals depends upon the re-oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and recycling of the reagent. The oxidation of ferrous iron plays an important role in either commercial leaching operations or natural weathering of sulphide minerals. Iron oxidation rates observed in natural acid mine drainage highly exceed the rates found in experiments performed under sterile conditions in laboratory. This is due to the catalytic action of iron oxidizing bacteria which are usually present in such natural environments. This work presents the kinetic study of chemical (abiotic) oxidation of ferrous sulfate to ferric sulfate with molecular oxygen. For an initial ferrous iron concentration in the range of 0.08-0.64 M, temperatures in the range of 288-323 K and  $\text{pH} \approx 2$ , the  $\text{Fe}^{2+}$  oxidation rate was found to be well described by the rate expression  $-\text{dFe}^{2+}/\text{dt} = 1.26 \times 10^7 [\text{Fe}^{2+}]^2 P_{\text{O}_2} \exp(-72000/RT)$ .

**Key words:** Fe, oxidation, ferrous, ferric, sulfate, kinetics, oxygen, acid solutions, acid mine drainage

## 1. Introduction

The leaching of metal sulfides by ferric iron is a fundamentally important process in hydrometallurgy. However, during the reaction, ferric becomes reduced to ferrous ion and has to be re-oxidized back into its higher oxidation state. The regenerating step can be usually achieved with oxygen in acid solution according to Eq. 1.



The rate of oxidation of ferrous ion by molecular oxygen in acid solutions is very dependent upon the nature of the anions present. The oxidation rate increases as the complexing affinity of the anion for ferric ion increases. Thus, at a given pH, the rate was found to decrease in the series pyrophosphate, phosphate, chloride, sulfate and perchlorate [1]. The rate law is  $-\text{dFe}^{2+}/\text{dt} = k[\text{Fe}^{2+}] P_{\text{O}_2}$  for the first three anions listed above and  $-\text{dFe}^{2+}/\text{dt} = k[\text{Fe}^{2+}]^2 P_{\text{O}_2}$  for the second two [1,2,3].

To increase the slow rate of the reaction, high oxygen pressures at higher temperatures [4,5,6],  $\text{SO}_2/\text{O}_2$  mixtures [7] and some kind of surface catalyst, such as platinum black and activated carbon [2,8] have been used. Another method to increase the rate of oxidation of ferrous iron is to use appropriate acidophilic bacteria which possess the iron oxidizing ability [9]. These bacteria regenerate the oxidizing agents and enhance the degradation of sulphide minerals either in natural weathering processes or commercial bioleaching operations. This work presents the kinetics study of the chemical (abiotic) iron oxidation rate as a function of  $\text{Fe}^{2+}$  concentration, partial oxygen pressure,  $P_{\text{O}_2}$ , and temperature.

## 2. Experimental

The experiments were performed in a jacketed reaction cell tempered by circulating water. Reaction mixture in a volume of 20 ml was stirred at 200 rpm with magnetic stirrer.

$\text{Fe}^{2+}$  concentration was determined by a modified *o*-phenanthroline spectrophotometric method [10], and  $\text{Fe}^{3+}$  concentration by UV-spectrophotometric method at 300 nm [11]. The oxygen consumption rate was measured by polarographic Clark-type oxygen sensor in a closed system.

### 3. Discussion of results

According to the stoichiometry, (Eq. 1), the reaction rate can be determined either as a decrease of the  $\text{Fe}^{2+}$  or increase of  $\text{Fe}^{3+}$  concentration as a function of time, or as the oxygen consumption rate.

Eq. 2

To determine the kinetic equation, following overall relationship was chosen:

Eq. 3

where: parameters  $a$ , and  $b$  are particular reaction orders

$E_a$  is the Arrhenius activation energy [ $\text{J mol}^{-1}$ ],

$R$  is universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and

$T$  is absolute temperature [K].

To calculate parameters of the kinetic equation, a series of experiments was carried out in order to obtain the relations between the rate constant and reactants activity. The effect of temperature was studied in the range of 288-323 K. Measurements with the oxygen electrode lasted only a few minutes and gave records with a sufficient amount of data points, allowing a reliable calculation of the first order rate constant for particular reactions with respect to oxygen partial pressure. The change in  $\text{Fe}^{2+}$  concentration during this period was negligible.  $[\text{Fe}^{2+}]$  in the course of one measurement was considered to be constant.

Fig.1 Decrease of the oxygen partial pressure with time during abiotic  $\text{Fe}^{2+}$  oxidation in a closed reaction cell.

Initial  $[\text{Fe}^{2+}] = 0.64 \text{ M}$ ,  $\text{pH} = 2.2$ , temperature = 303.15 K

Measurements of the abiotic  $\text{Fe}^{2+}$  oxidation with oxygen electrode in a closed reaction cell, showed exponential decrease of the oxygen partial pressure with time (Fig.1).

Eq. 4

Differential form of the Eq. 4 indicates that the reaction rate is proportional to the  $P_{O_2}$ . Reaction kinetics is of the first order with respect to oxygen partial pressure.

(at fixed  $[Fe^{2+}]$ ,  $[H^+]$  and temperature) Eq. 5

Rate constant  $k_1$ ,  $[s^{-1}]$  equals the reaction rate of the particular reaction at  $P_{O_2} = 1$  kPa. The parameter  $b$  in Eq. 3 is equal to 1.

The rate of  $P_{O_2}$  change can be expressed as oxygen consumption rate (in  $\mu\text{moles l}^{-1} \text{ s}^{-1}$ ) according to Eq. 6 and subsequently as  $Fe^{2+}$  oxidation rate using Eq. 2.

Eq. 6

where:  $C_{O_2}^*$  is the dissolved oxygen concentration  $[\mu\text{mol l}^{-1}]$  in equilibrium with oxygen partial pressure ( $P_{O_2}$ ) in the gas phase [kPa] at given temperature.

A series of measurements of the initial rate of  $Fe^{2+}$  oxidation has been performed in solutions with different  $Fe^{2+}$  concentration. Fig.2 shows dependence of the reaction rate on  $Fe^{2+}$  concentration. The rate increased proportionally to square of  $Fe^{2+}$  concentration. Exponent  $a$  in the kinetic Eq. 3 is  $\approx 2$ . Reaction kinetics is of the second order with respect to  $[Fe^{2+}]$ .

Fig.2 Reaction rate as a function of  $Fe^{2+}$  concentration at partial pressure of oxygen 101.325 kPa (1 atm) at 303.15 K and pH = 2.2

Rate constants obtained for different temperatures in the range 288-323 K were used to construct the Arrhenius plot (Fig.3) by linearization of the Arrhenius equation

$\Rightarrow$  Eq. 7

Fig.3 The Arrhenius plot of  $\ln k$  vs.  $1/T$  for oxidation of ferrous iron with oxygen measured in the temperature range 288-323 K,  $P_{O_2} = 101.325$  kPa

The activation energy involved has been found to be equal to  $72 \text{ kJ mol}^{-1}$  ( $17 \text{ kcal mol}^{-1}$ ) and the frequency factor found was  $K = 1.26 \times 10^7$ . The linear behaviour of Arrhenius plot and the value activation energy indicate the kinetic regime of the reaction in observed region of temperature. Finally, the following kinetic equation has been evaluated for the studied reaction at  $P_{\text{O}_2} = 101.325 \text{ kPa}$  (1 atm) at pH 1.5.

$$[\text{M s}^{-1}] \quad \text{Eq. 8}$$

#### 4. Conclusions

The principal features of the kinetics of ferrous iron oxidation in acid sulfate solutions are that the rate constant is directly proportional to the oxygen partial pressure and is of the second order with respect to ferrous iron concentration. The kinetic expression Eq. 8 derived from our measurement and calculated activation energy of  $72 \text{ kJ mol}^{-1}$  are in a good agreement with values reported for the sulfate media by other workers [13]. While the oxidation of ferrous iron is desirable reaction from hydrometallurgical point of view it is of great importance to pay attention to the biocatalytic action of *thiobacilli* in acid mine drainage which can enhance the iron oxidation rate and consequently mineral destruction and metal mobilization. The kinetics experiments on bacterial ferrous iron oxidation are commonly performed at low  $\text{FeSO}_4$  concentrations, where chemical oxidation can be neglected because the bacterial Fe-oxidation rate is up to one million times faster than the abiotic one. In experiments with growing cultures, where the initial  $\text{Fe}^{2+}$  concentrations are as high as  $0.2\text{-}0.3 \text{ mol l}^{-1}$ , and the bacterial activity in the lag period is low, it is important to pay attention to the contribution of chemical oxidation to the overall Fe-oxidation rate [14].

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