



Air Oxidation of Ferrous Iron in Water[#]

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Abstract: Air oxidation of ferrous iron in water was studied. It was worked at three different values of pH and concentration. Oxidation was firstly carried out at stationary atmosphere. Thereafter, the experiment was successively repeated by blowing air to the solution without and with inert packing. Lastly, the catalytic effect of ferric hydroxide was investigated. While the maximum yield of 86 % is catalytically achieved by blowing air at a neutral medium, the oxidation was almost completed in an alkaline solution even at stationary atmosphere. The reaction was first order with respect to Fe²⁺.

Keywords: Iron, water pollution, oxidation

Introduction

Oxygenated water will have only low levels of iron. The problem is most likely to develop in water from wells with high carbonate and low oxygen. Iron carbonates in an oxygen poor environment are relatively soluble and can cause high levels of dissolved iron (<http://www.ext.nodak.edu>). In addition to groundwater supplies, acidic mine waters are often characterised by elevated concentrations of metal ions such as Fe²⁺ and Mn²⁺ (Banks *et al.*, 1997). On the other hand, alkaline mine discharges are generally not that polluting in terms of metal toxicity, but can be highly ferruginous (Younger & Banwart, 1999).

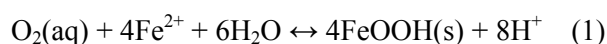
Iron in water does not present a health hazard. However, its presence may cause taste, staining and accumulation problems. The treatment can be performed by various techniques. Chemical oxidation followed by filtration is the accepted method for treatment of iron when its concentration is greater than 10 ppm (<http://www.ext.nodak.edu>).

Oxidation of iron is achieved by addition of chemical oxidants. However, it can be easily and low cost carried out by contact with air (Wong, 1984). During oxidation of Fe²⁺ salt aqueous solutions, poor soluble compounds including Fe³⁺ oxides are formed (Domingo *et al.*, 1994). The composition of precipitate formed depends on numerous parameters such as temperature, pH, concentration, feed rate and anion nature (Das & Anand, 1995; Tolchev *et al.*, 2002).

For acidic discharges, lime dosing is often used to raise the pH. In this way, the rate of oxidation and the subsequent precipitation of Fe²⁺ oxide minerals are increased. Aeration will also assist O₂ transfer for the oxidation of Fe²⁺ to Fe³⁺ and the subsequent removal by precipitation (Burke & Banwart, 2002). Additionally, the reaction is catalyzed by the reaction product ferric hydroxide (Sarıkaya, 1990). In this work, air oxidation of Fe²⁺ ions in water is studied. Firstly, oxidation is performed at stationary atmosphere. Thereafter, the experiment is repeated by blowing air to the solution without and with packing. Additionally, the reaction is tried to catalyze by ferric hydroxide. Effects of concentration and pH on oxidation are investigated.

Experimental

The oxidation kinetics of Fe(II)(aq) species has been previously reviewed by many workers (Wehrli, 1990; Zhang *et al.*, 1992). The stoichiometry for the overall oxidation of Fe²⁺ ions by O₂ is given by Eq. (1) (Burke & Banwart, 2002).



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[#]This study has been presented at BIES'08, Giresun-Turkey

Eq. (2) gives the most commonly verified rate law for the oxidation of Fe(II) (Davison & Seed, 1983; Tamura et al., 1976). It has been, however, reported that the oxidation kinetics appear to change depending on pH, acidic compounds and ions in solution (Miles & Brezonik, 1981; Millero, 1985; Sung & Morgan, 1980), and oxygenation is greatly accelerated in the presence of surfaces (Barry et al., 1994).

$$-d[\text{Fe(II)}]/dt = k[\text{Fe(II)}][\text{OH}^-]^2[\text{O}_2] \quad (2)$$

In the light of this, it may be thought that the oxygenation is affected by numerous factors, e.g. solution pH, ferrous ion and oxygen concentrations, and catalyzed by solid surfaces.

In experiment, it was tried to study these effects. For this purpose, it was conducted at three different values of pH and concentrations of Fe^{2+} (Table 1). The oxidant was air. Aqueous solutions of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were prepared as an initial reagent and the required pH value was achieved by adding NH_3 or H_2SO_4 . The distilled water used to prepare solutions was saturated to air by resting at open atmosphere for a long time prior to use.

Oxidation was carried out in a batch system was used for oxidation. The experiment was firstly made at stationary atmosphere and the solution of 100 mL was rested at 20°C in a thermostatic bath for 15 minutes. The second part of experiment was also performed as similar to the first one. Differently, it was worked at 35°C in order to study the effect of temperature. The third part experiment was conducted by blowing air to the centre of the solution in order to support the transfer of O_2 . Air flow rate was determined as 20.3 mL/s with a flow meter. To increase the gas-liquid contact efficiency and catalyze the reaction, last studies were completed in a solution with inert packing (8 mm spherical glass bead) and $\text{Fe}(\text{OH})_3$ respectively.

For each case, variations happened on oxidation of Fe^{2+} were observed. Amounts of unoxidized Fe^{2+} in the solution were measured with bipyridine method (Fresenius, 1988). Oxidation yields were calculated by using initial and final concentrations of ferrous ion in the solution. The results were discussed from several points of view.

Result and Discussion

Reaction order can be calculated from experimental results. If concentrations of OH^- ion and oxygen are kept constant, the oxidation rate changes only depending on the concentration of Fe^{2+} in the solution according to the equation 2. If a logarithmic graph is drawn as oxidized amount versus concentration of Fe^{2+} , the slope of obtained line gives the reaction order with respect to Fe^{2+} .

An example graph drawn for this purpose has been shown in Fig. 1. This graph can also be formed for different conditions (Table 2). The slope of line can be calculated as 1.0 from Fig.1. The values obtained from other graphs ranges from 0.9 to 1.1 by which the mean value can be found as 1.0, i.e. air oxidation of ferrous ion in water is first order with respect to Fe^{2+} .

Table 1: Experimental Conditions

System	Batch
Initial reagent	$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
Solution volume, m^3	0.1
Initial concentration of Fe^{2+} , kg m^{-3}	0.025, 0.050, 0.075
pH	3, 7, 9
pH adjuster	NH_3 or H_2SO_4
Temperature of solution, °C	20, 35
Oxidant	Air
Operation time, sec	900
Air flow rate, $\text{m}^3 \text{s}^{-1}$	0.0000203
Inert packing	Spherical glass
Diameter of inert packing, m	0.008
Catalyst	$\text{Fe}(\text{OH})_3$
Determination method of Fe^{2+}	Bipyridine

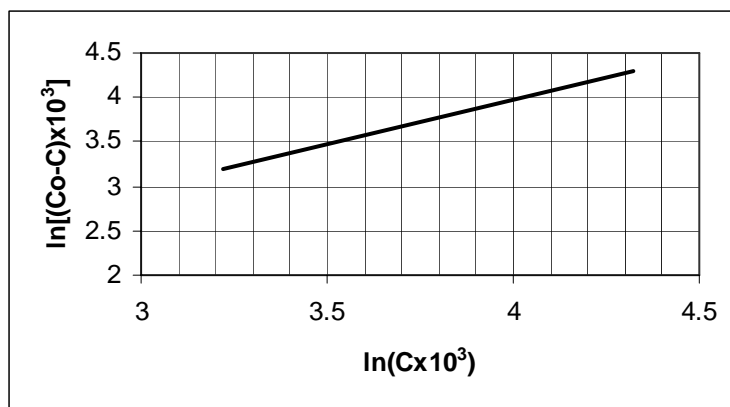


Figure 1: An example graph drawn to calculate the reaction order (pH=9, stationary atmosphere, 20°C, 15 minutes resting)

Figures 2 to 5 show oxidation yields in different cases. As seen from Fig. 2, in the case of resting in stationary atmosphere for 15 minutes, the minimum conversion of Fe^{2+} to Fe^{3+} is 96 % in basic solution while the yield is maximally 88 % in acidic medium. The yields obtained in neutral medium are around 30 % only. This result is agreed to those in the literature (Eroğlu, 1984; Lorenz et al., 1988; Stauffer, 1987).

Table 2. Line slopes calculated from graphs

Ventilation	pH	Line slope
Stationary atmosphere	3	1.1
Stationary atmosphere	7	0.9
Stationary atmosphere	9	1.0
Air blowing	3	1.1
Air blowing	7	0.9
Glass packing + Air blowing	3	1.0
Glass packing + Air blowing	7	1.0

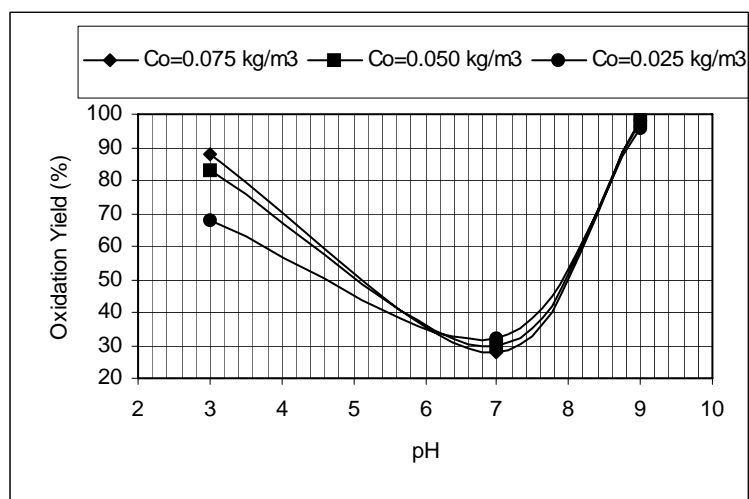


Figure 2. Oxidation yields (20°C, solution without packing, stationary atmosphere, 15 minutes resting)

As seen, it is enough for oxidation of Fe^{2+} in basic medium to rest the solution at open atmosphere. It may be shown as a reason to this that $\text{Fe}(\text{OH})_3$ formed after oxidation easily precipitates in basic medium and catalyzes the reaction. The solution has to be more effectively ventilated in nonbasic medium, especially at neutral one.

Similar operations were repeated at 35°C by changing temperature only. As shown in Fig. 3, the values observed are approximately equal to those at 20°C, i.e. increasing of the temperature does not affect the conversion remarkably. This result is perhaps sourced from two different effects of temperature. Increasing of temperature accelerates the reaction and depending on this, the conversion percent in a certain time increases. However, the solubility of oxygen in water decreases with increase in temperature (Tchobanoglous & Schroeder, 1987). This decrease results in decreasing of the conversion percent. Which one of these two effects dominates will change depending on the conditions. In this study, a change on the oxidation yield has not been observed when temperature is increased. The effect of temperature is neglected because of discussions above and subsequent studies are conducted at 20°C only.

The yields observed in basic medium are very high even at stationary atmosphere. Therefore, latter parts of experiment are performed in nonbasic solutions only. In this stage, the mass transfer of oxygen was supported by blowing air to the solution and it was tried to raise the contact efficiency of oxygen with the solution. The results obtained in acidic and neutral mediums as comparing to previous ones are shown in Fig. 4.

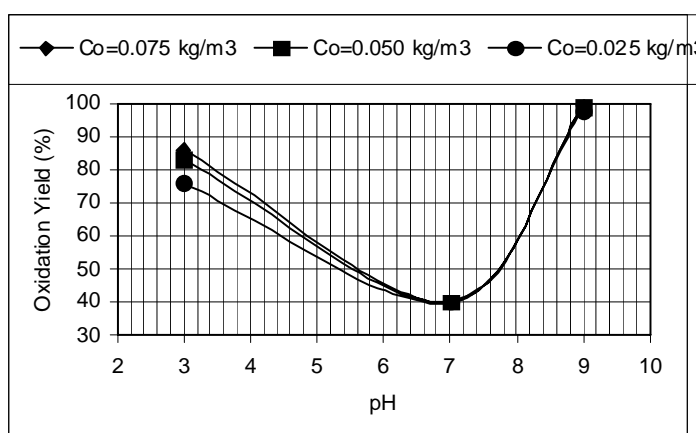


Figure 3: Oxidation yields (35°C, solution without packing, stationary atmosphere, 15 minutes resting)

As seen from the figure, the yields in neutral medium are low still. However, in the case of air blowing, an important increase reaching to the 12 % has been observed as comparing to the stationary atmosphere. The increase in gas-liquid contact efficiency by air-blowing may be shown as a reason of this increase in yield.

In addition to air blowing, the gas-liquid contact can also be improved by solid surfaces in the solution. The results obtained from experiments performed in this manner have been shown in Fig. 5 as comparing to the previous ones.

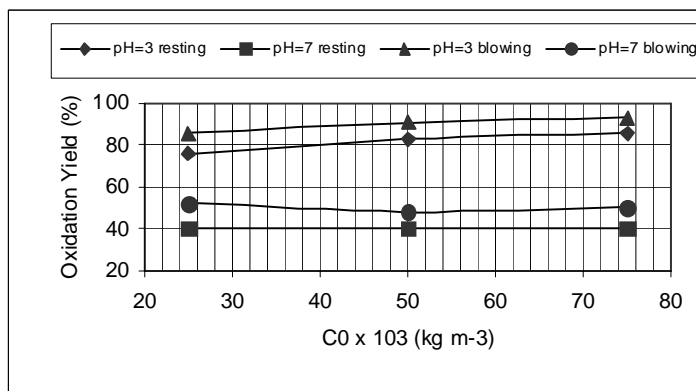


Figure 4: Oxidation yields (20°C, solution without packing, 15 minutes operation)

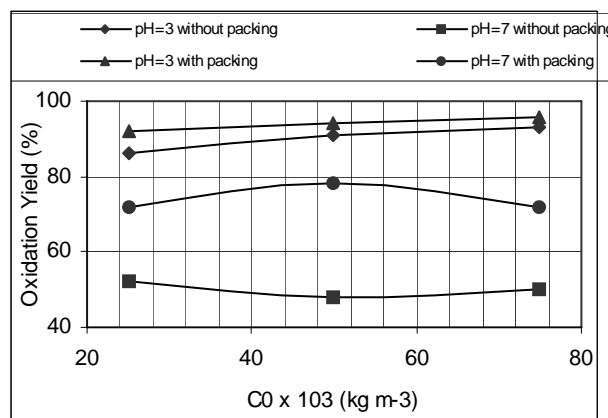


Figure 5: Oxidation yields (20°C, 15 minutes air blowing)

It is seen from the figure that in the solution with glass packing, especially at neutral medium, an improvement in yield of 24 % has been observed as comparing to that without packing. It is clear that this increase in yield results from the increase obtained in gas-liquid contact by using of packing (Alicilar et al., 1994). This increase although less has been observed in acidic medium too. Although the increases in oxidation yield for acidic solutions are recorded as 4 % mean, the yield in this case is minimally 92 % and reaches to 96 % for the solution with high concentration. Hence, the last part of experiment has been carried out at neutral medium only and the catalytic effect of $\text{Fe}(\text{OH})_3$ has been investigated. The results obtained are shown in Table 3.

Table 3. The oxidation yields at catalytical conditions (pH=7, 20°C, solution with glass bead/ $\text{Fe}(\text{OH})_3$, 15 minutes air blowing)

Concentration, kg m ⁻³	Yield, %
0.025	84
0.050	86
0.075	84

The yield increases in the range of 8 to 12 % as comparing to that without $\text{Fe}(\text{OH})_3$. This result can be explained so that $\text{Fe}(\text{OH})_3$ catalyzes the air oxidation of Fe^{2+} , which is agreed to the literature (Hafsi, 2001; Tamura et al., 1976). It has been stated that $\text{Fe}(\text{OH})_2(\text{aq})$ and the $\text{Fe}(\text{II})$ species adsorbed on the $\text{Fe}(\text{III})$ oxide mineral surface are significantly more reactive than Fe^{2+} [9] and iron oxygenation is greatly accelerated in the presence of surfaces [19]. Similar discussions are also made by other researchers and it is offered that the oxidation of $\text{Fe}(\text{II})$ by molecular O_2 is a result of adsorption and surface catalyzed auto-oxidation (Burke & Banwart, 2002; Tamura et al., 1976; Hafsi, 2001).

Conclusion

It can be conclusively said that Fe^{+2} ions in basic solution can be easily oxidized even at stationary air. Different techniques must be tried in acidic medium to contact gas and liquid phases more effectively. Support operations such as air blowing, packing usage may be applied for this purpose. High conversion in neutral medium can be catalytically achieved and catalysts different from $\text{Fe}(\text{OH})_3$ may be studied. Nevertheless, if water hardness is low, a basic medium can be easily and low cost formed by dosing lime, where the yield for air oxidation of Fe^{2+} is minimally 96% even at stationary atmosphere.

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