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Enhancement of reaction rate by microbubble generator in air oxidation of ferrous hydroxide suspension for crystal seed of iron oxide pigment

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Abstract
High productivity and energy saving become still challenges in the industrial scale production of crystal seed for iron oxide pigment today. To solve this problem, a new scheme of using a swirl type microbubble generator in the production of crystal seed by air oxidation of ferrous hydroxide suspension was proposed in this study. A conventional gas distributor and a swirl type microbubble generator were alternatively installed in the pilot-scale process for producing crystal seed. The aeration rate was constant at 30L/min and the liquid flow rate of the microbubble generator was varied in the range of 30-150L/min in all experiments. The experimental results indicate that if liquid flow rate is reasonably controlled, the microbubble generator is significant in enhancing productivity and saving energy compared to gas distributor. The oxygen transfer rate, which represents the productivity of crystal seed, is highest in 120L/min of liquid flow rate. And the oxygen transfer efficiency, which represents the energy consumption, is highest in 90L/min of liquid flow rate.

Keywords: Iron oxide pigment, crystal seed, microbubble, air oxidation, ferrous hydroxide

1. Introduction
Great interests have been paid to goethite nanoparticles, since they are widely used in environment and industry as eco-friendly material [1]. Especially, crystal seeds with goethite structure are added in order to ensure uniform growth of pigment in the production of iron oxide pigment [2]. Such seeds can be synthesized either from iron(III) salts such as nitrate or from iron(II) salts such as sulfate [3]. Among these methods, the latter is more economical and eco-friendly since it can use waste iron(II) salt from metallurgical plants as the starting material [4]. In this case, the goethite nanoparticles were formed by bubbling air to ferrous hydroxide suspension that are obtained by the reaction of iron(II) salts such as sulfate and alkaline such as sodium hydroxide through a gas distributor under certain conditions [1].
In order to enhance the productive capacity in the industrial scale production of iron oxide crystal seed with goethite structure, it is important to enhance oxygen mass transfer rate to ferrous hydroxide. And oxygen transfer rate generally depends on the gas distributor as well as aeration rate, rector geometry and stirring speed [5]. Hence, in order to ensure high oxygen mass transfer rate in the crystal seed production process, a new scheme, in which a swirl type microbubble generator is used for gas distribution, is proposed in this work. The swirl microbubble generators generate fine bubbles by intensive swirl flow of liquid and gas. And the liquid flow rate and aeration rate are main parameters that determine the liquid-gas mass transfer rate [6]. Hence, the effects of liquid flow rate and aeration rate of the microbubble generator on the oxygen mass transfer rate and the goethite size distribution have to be estimated in the production of crystal seed. In the case of conventional gas distributor, the effects of the process parameters such as pH, reactants concentration, aeration rate on the formation rate and size distribution of goethite were studied [3, 7]. However, to the best of our knowledge, research results relating to use of microbubble generator for efficiency air distribution in the production of crystal seed were not reported.

In this study, the air oxidation of ferrous hydroxide by a swirl microbubble generator according to liquid flow rate and aeration rate is compared with by a conventional gas distributor from the viewpoint of reaction rate and energy efficiency in detail.

2. Materials and Method

Ferrous hydroxide suspensions were prepared by using iron sulfate solution and ammonia water in all experiments. Ferrous solution and ammonia water used in the experiments were prepared with waste iron sulfate and 30% ammonia water purchased from a domestic company by purifying and diluting with deionized water to predetermined concentration. First, 170L of 180g/L $FeSO_4$ solution was poured in the cylindrical reactor (1)(400mm in diameter, 2400mm in height).

Then, predetermined amounts of 7% ammonia water was gradually poured in the reactor (1) while stirring the reaction solution so that reactant concentration ratio R([(OH)$^-$]/[Fe(II)]) equals to 0.72 at the end of mixing of reactants. At the beginning, white green precipitate was formed and the solution was gradually evolved to dark green suspension [8]. The rotation rate of the stirrer (2) was 500rpm.

The solution temperature in the reactor was constant at about 30℃ by the automatic temperature controller(6), and the temperature sensor electrode(5), and the heating bars(7). After each reaction, the samples were taken and washed by deionized water 5 times and then finally dried. The experimental setup of air oxidation of ferrous hydroxide for the formation of iron oxide crystal seed by a conventional gas distributor(a) and by a swirl microbubble generator(b) is shown in Fig. 1. Air compressor (9) provides air bubbles into suspension through the conventional gas distributor (13) with 500μm pore size and through the swirl microbubble generator (15) individually. The gas distributor (13) and the microbubble generator (15) were alternatively placed under the stirrer (2) impeller on the bottom of the reactor for comparison.

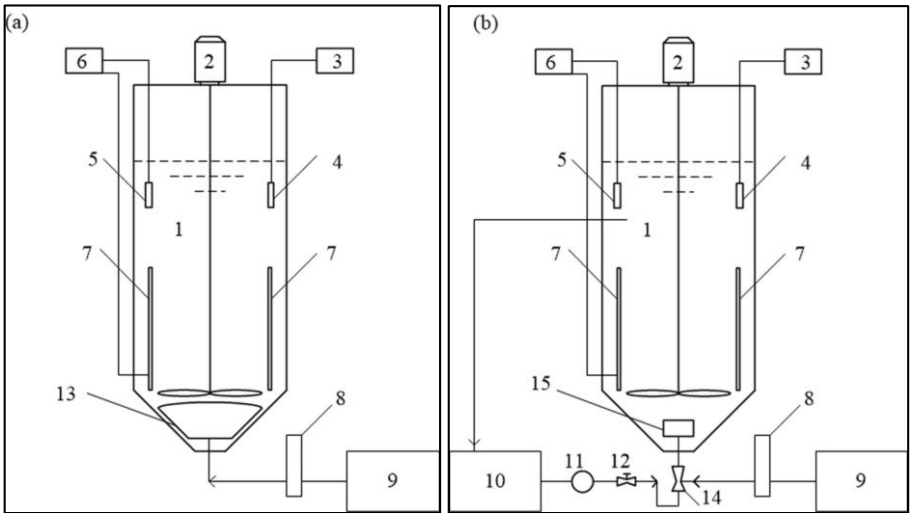

Fig 1: Experimental setup of air oxidation of ferrous hydroxide for the formation of iron oxide crystal seed by a conventional gas distributor(a) and by a swirl microbubble generator(b) (1-reactor, 2-stirrer, 3-ORP display, 4-ORP electrode, 5-temperature sensing electrode, 6-automatic temperature controller, 7-heating bars, 8-air flow meter with control valve, 9-air compressor, 10-variable frequency pump, 11-mass flow meter, 12-flow control valve, 13-conventional gas distributor, 14-venturi, 15-swirl microbubble generator)

Through the whole reaction, aeration rate was fixed at about 30L/min by using an air flow meter with control valve (8). The variable frequency pump with certain pressure head pumps suspension in the reactor to the microbubble generator (15). The liquid flow rate was measured with a mass flow meter (11) placed after the pump. Meanwhile, the reaction time was determined by sharp increase of ORP values [7]. SEM images were taken using a ULTRATM^{55} instrument to analyze the size distribution of goethite particles obtained. In order to evaluate the reaction rate in the air oxidation of ferrous hydroxide, the liquid-gas oxygen transfer rate, which is the rate determining for reaction step, have to be determined.

The goethite formation rate is of zero order, so the oxygen transfer rate also remains constant throughout the reaction [3]. The oxygen transfer rate r_{O2} ($mmol_{O2}$/min) can be calculated by Eq. (1) assuming that $Fe(OH)_2$ was completely converted to α-FeOOH in the solution after the end of the reaction in acidic regime characterized by R(=[(OH)$^-$]/[Fe(II)])<2.

$$r_{O2} = \frac{[(OH)^-]_0 \cdot V_{rct}}{8 \cdot t_{rct}} \quad (1)$$

where $[(OH)^-]_0$ is the initial concentration of NH_4OH, V_{rct} is the volume of the reaction solution, and t_{rct} is the reaction time. In this study the energy E(kWh) consumed during the reaction and the oxygen transfer efficiency *eff* (mol/kWh) are calculated in order to consider the oxygen mass transfer from the viewpoint of energy. The oxygen transfer efficiency is expressed as the oxygen transfer rate per unit energy.

$$eff = \frac{r_{O2}}{E} \quad (2)$$

$$E = \sum_i \int_0^t P_i dt \quad (3)$$

where E is the energy consumed for the formation of crystal seed, P_i is the power of the devices for the reaction.

In this work, only the energy consumed by the variable frequency pump and air compressor was considered, since the other devices were identically used in all experiments

3. Results and Discussion

Fig. 2 shows the oxygen transfer rate r_{O2}($mmol_{O2}$/min)

according to liquid flow rate q_L(L/min) in the air oxidation of ferrous hydroxide by the microbubble generator.

The aeration rate was constant at about 30L/min in all experiments.

As shown in Fig. 2, the oxygen transfer rate by the swirl microbubble generator is in the range of 20.1~104.4 $mmol_{O2}$/min, which is larger than 16.1$mmol_{O2}$/min by the conventional gas distributor. Nevertheless, despite constant aeration rates in all experiments, the oxygen transfer rate increases with increasing liquid flow rate in the range of 30-120 L/min, and then shows a decreased behavior at liquid flow rate of 150 L/min. According to the previous results [3, 7], the oxygen transfer rate is constant for a certain aeration rate in the case of gas distributors.

However, we found that the oxygen transfer rate varied with the liquid flow rate even when the aeration rate was fixed at 30 L/min. This may be due to the change in the size of the bubbles generated with the change in the liquid flow rate, although the aeration rate is constant when using a microbubble generator instead of a gas distributor.

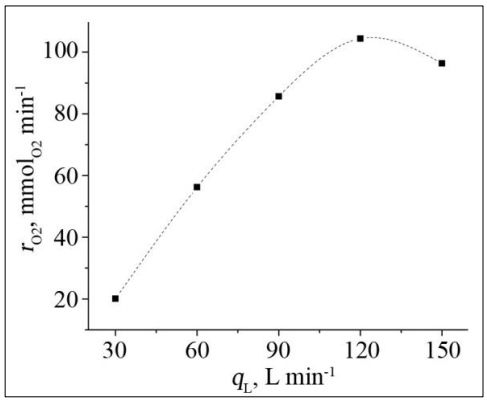

Fig 2: The oxygen transfer rate according to liquid flow rate q_L(L/min) in the air oxidation of ferrous hydroxide by the microbubble generator(aeration rate 30L/min, [$FeSO_4$]=0.98M, R(=[$(OH)^-$]/[Fe(II)])=0.72)

In the study by Mawarni *et al*. [9], it was reported that an increase in liquid flow rate lead to decreasing the average bubble size and increasing the number of bubbles in a swirl microbubble generator. Thus, it is expected that increasing the liquid flow rate leads to the generation of smaller bubbles, which increases the liquid-gas surface area and thus the oxygen transfer rate in the reaction solution. It is noted that, the oxygen transfer rate at 150 L/min of liquid flow rate is lower than that at 120 L/min. Thus, the oxygen transfer rate at 150 L/min was lower than that at 120 L/min, despite the larger total liquid-gas surface area due to smaller bubble size.

This may be due to the fact that gas-liquid mass transfer was reduced as a result of the shorter residence of bubbles in the solution in the reactor by the higher liquid flow rate at a liquid flow rate of 150 L/min. The result indicates that the microbubble generator requires reasonable adjustment of the liquid flow rate to increase the reaction rate. According to the results, at a liquid flow rate of 120 L/min, the oxygen transfer rate was 104 $mmol_{O2}$/min, which was the highest in the range of liquid flow rates in the experiment. The reaction rate for a given reaction is expressed as a function of the aeration rate [3].

$$\frac{d[FeOOH]}{dt} = 4 \cdot r_{O2} = 4 \cdot k \cdot A_{air} \quad (4)$$

where k is the coefficient related to the gas distributor and other process parameters, and A_{air} is the aeration rate. For the microbubble generator, k is $6.7 \cdot 10^{-7}$~$3.5 \cdot 10^{-6}$ mol_{O2}/ml_{air}, which is larger than $5.4 \cdot 10^{-8} mol_{O2}/ml_{air}$ for the gas distributor in this work and $3.6 \cdot 10^{-8} mol_{O2}$/mlair, $2.3 \cdot 10^{-7} mol_{O2}/ml_{air}$ for that in [3, 7]. This may be mainly due to large liquid-gas mass transfer rate, since the size of air bubbles generated by the microbubble generator is smaller than that generated by the gas distributors. It is expected that the use of microbubble generators for the production of crystal seed for iron oxide pigments will result in enhanced productivity.

As can be seen from Eq. (3), the energy consumption depends on the power required by the reaction system and the reaction time for aeration.

Fig. 3 shows the energy consumption E(kWh) and oxygen transfer efficiency eff(mol_{O2}/kWh) for the microbubble generator. For the gas distributor, the energy consumption and oxygen transfer efficiency were 9.35 kWh and 1.93 mol_{O2}/kWh respectively.

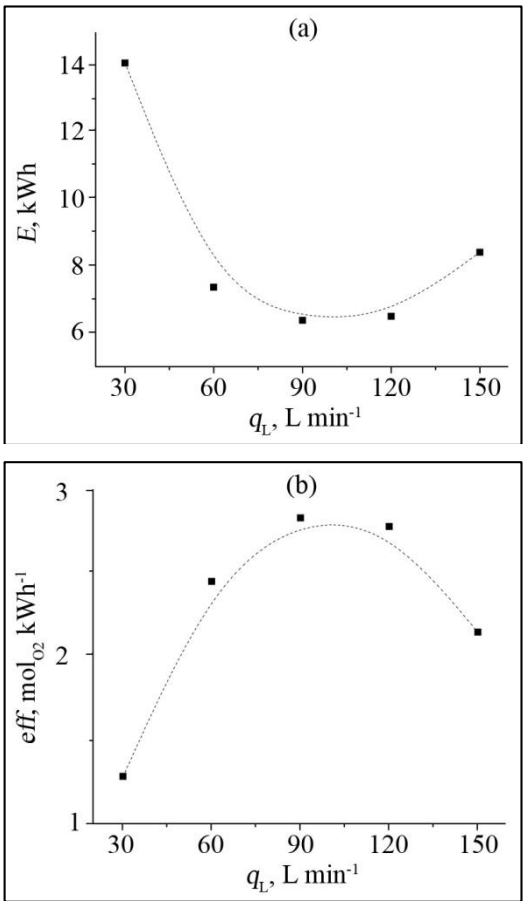

Fig 3: Energy consumption and oxygen transfer efficiency for the microbubble generator (aeration rate 30L/min, [$FeSO_4$]=0.98M, R(=[$(OH)^-$]/[Fe(II)])=0.72)

As shown in Fig. 3(a), the energy consumption decreases rapidly with increasing liquid flow rate, and then from 90L/min of liquid flow rate shows a trend of increasing again. This may be due to the fact that the power in Eq. (1) required by the system increases with increasing liquid flow rate, but the reaction time is shorter as the oxygen transfer rate increases, as shown in Fig. 2. It can be seen that the reasonably adjusted liquid flow rate can optimize not only the oxygen transfer rate mentioned above but also the energy consumption required for the reaction. The energy

consumption at 90 L/min was 6.3 kWh, which was lowest in our liquid flow rate range.

On the other hand, the oxygen transfer efficiency increases with increasing liquid flow rate, and then decreases again from the liquid flow rate of 90 L/min, as shown in Fig. 3 (b). It is due to the fact that the oxygen transfer efficiency is inversely proportional to the energy consumption, as can be seen from Eq. (2). The oxygen transfer rate at 90L/min was 2.82 mol_{O2}/kWh, which was highest in our liquid flow rate range

Fig. 4 shows the size distribution of goethite particles prepared using a microbubble generator.

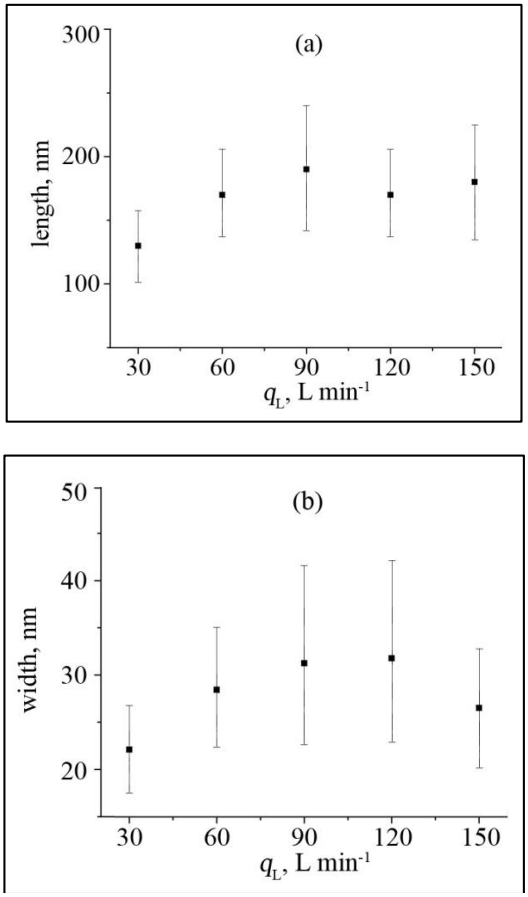

Fig 4: Length and width distribution of goethite particles prepared using a microbubble generator (aeration rate 30L/min, [$FeSO_4$]=0.98M, R(=[$(OH)^-$]/[Fe(II)])=0.72)

As shown in Fig. 4, the size of goethite nanoparticles produced by air oxidation of ferrous hydroxide suspension using microbubble generator is in the range of 100-250 nm in length and 15-40 nm in width, which is suitable as crystal seed for iron oxide pigment. The effect of liquid flow rate on the size of goethite nanoparticles was not clear. It is noteworthy that the size of goethite nanoparticles was particularly small at 30 L/min, the smallest liquid flow rate of the experiment. This may be due to the low oxygen transport rate at this liquid flow rate. We conducted six months of operation at 120 L/min of liquid flow rate and 30 L/min of aeration rate in the pilot-scale air oxidation process of ferrous hydroxide suspension for crystal seed production using the swirl microbubble generator. The operation results showed better crystal seed productivity and energy saving than the conventional gas distributor. Also, during the whole process operation, defect such as clogging of the pores in the gas distributor was not observed in the swirl microbubble generator. In the case of introducing swirl microbubble generation instead of gas distributor in the process for crystal seed production, the investment costs due to the addition of equipment devices such as pump and microbubble generator are high. However, the enhancement in the productivity of the crystal seed and the energy saving are expected to compensate the investment costs in a short time.

According to Hilman Syaeful Alam [10], an increase of aeration rate in a swirl microbubble generator was reported to increase the size of microbubbles and consequently affect the liquid-gas mass transfer.

Hence, in the future we are going to investigate comprehensively the combined effect of liquid flow rate and aeration rate when the microbubble generator is used for air oxidation of ferrous hydroxide suspension.

4. Conclusion

In this paper, the productivity enhancement and energy saving by swirl microbubble generator in the production of crystal seed for iron oxide pigment are described. The results shows that the appropriate control of the liquid flow rate in the microbubble generator results in both very high oxygen transfer rate and oxygen transfer efficiency, reflecting both productivity and energy efficiency, compared to the gas distributor at the same aeration rate. Also, the oxygen transfer rate in the case of microbubble generator was highest at 120 L/min in the range of liquid flow rate in this study. However, from the viewpoint of energy the oxygen transfer efficiency was highest at 90 L/min of liquid flow rate. Results indicate that when using of a swirl microbubble generator instead of a conventional gas distributor for air oxidation of ferrous hydroxide suspension for crystal seed, the liquid flow rate should be reasonably adjusted in order to both enhance productivity and save energy. In the future, we intend to investigate comprehensively the combined effect of liquid flow rate and aeration rate in microbubble generators on liquid-gas mass transfer in chemical processes such as air oxidation of ferrous hydroxide suspension. Our findings may be applicable to other chemical processes that require chemical reactions of liquid and gas, taking into account the process parameters reasonably.

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