Froth Separation of Ferrihydrite Slurry Using Microbubbles with Ultrasonic Irradiation

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Here we show the newly developed process of microbubble froth separation enhanced by ultrasonic irradiation for colloidal slurry. In this study, microbubbles were applied to the froth separation of dilute ferrihydrite colloidal suspension. Furthermore, enhancement of the microbubbles froth separation by controlling the motion, aggregation and clustering of microbubbles using the “Bjerknes force” in ultrasonic acoustic fields was investigated. The rate of microbubble froth separation of ferrihydrite colloidal slurry was increased by the ultrasonic irradiation and was more efficient than settling separation. Adjustment of the ultrasonic frequency is important for the microbubble froth separation. With a frequency of 38kHz producing stronger primary and secondary Bjerknes forces, the motion and clustering of microbubbles are too extreme; the microbubbles abruptly aggregated to form clusters and rose rapidly without carrying the ferrihydrite colloidal particles. However, with ultrasonic irradiation at a frequency of 430kHz, the motion of microbubbles was moderate and they aggregated widely. In this case, the clear froth separation of ferrihydrite colloidal slurry progressed rapidly, and its rate was increased with increasing output power of ultrasonic irradiation. [doi:10.2320/matertrans.M-MER2008815]

(Received November 26, 2007; Accepted April 14, 2008; Published June 18, 2008)

Keywords: microbubble, ultrasonic, froth separation, ferrihydrite, colloidal slurry

1. Introduction

It is difficult to efficiently precipitate dilute colloidal particles in waste water as a solid-liquid separation process, even though the main treatment steps for the solid-liquid separation of sewage and industrial waste water are settling and filtration. In such cases, additional treatments for the enhancement of precipitation, such as the addition of flocculants and heating to bring about their crystallization, cause an increase in sludge amount and high treatment costs.

Iron hydroxides such as ferrihydrite are some of the typical colloidal particles that are difficult to precipitate. They have a large surface area, strong adsorptive effects, high adsorption capacity, and low cost for preparation, thus they are recognized as an attractive material for treatment of wastewater from various industries.1–5 Adsorption/coprecipitation with ferrihydrite is a feasible process for the removal of trace elements such as heavy metals and arsenic from wastewater of various industries including plating shops, non-ferrous metallurgy and power plants. However, the ferrihydrite has very low crystallinity, is hydrophobic and has weak-aggregation of nanoparticles. Consequently, it is difficult to separate the ferrihydrite colloidal particles from aqueous phase in the wastewater treatment. In some cases, because it takes a long time to precipitate ferrihydrite colloidal particles, the colloidal slurry is heated at over 80°C in order to transform the ferrihydrite to a crystallized iron oxide such as hematite for precipitation.1

The main purpose of this study is to develop a new method of microbubble froth separation enhanced by ultrasonic irradiation for ferrihydrite colloidal slurry. Froth separation is one of the traditional treatments for ore dressing in the mining. It is also applied in other industries for the solid-liquid separation of suspensions of waste water, in which solid particles are difficult to precipitate. The applications of microbubbles in the froth separation of oil from soil and also that of sewage sludge are examples that have been recently investigated.6

“Microbubbles” are the small bubbles, ten to several tens of micrometers in size. Recently, their application has attracted attention and become varied, such as water purification and the supplying of dissolved oxygen to lakes and dam reservoirs.7 Microbubbles have various features due to their small size, such as large specific surface area, high dispersivity in an aqueous medium, enhancement of chemical reactions, physical adsorption and diffusivity. Due to their characteristics, it is reasonable to use microbubbles for the solid-liquid froth separation of dilute colloidal suspensions. However, the very low rising velocity of the microbubble, (about 1mm/s for a bubble sized 50μm in diameter), becomes much lower with the adsorption of colloidal particles on its surface. This low rising velocity makes efficient froth separations difficult.

Usage of microbubbles under ultrasonic irradiation is applied in medical and chemical technologies. Most of these applications use the properties of the secondary sound source effect and the collapse of bubbles. And, the controlling the motion of microbubbles by the action of the “Bjerknes force” on a bubble in an ultrasonic acoustic field was investigated.8–13 A bubble placed in a field with a pressure gradient receives a force, the so called primary Bjerknes force, that is in proportion to its volume and pushes the microbubble from higher pressure to lower pressure. If the bubble is small and oscillates in the ultrasonic standing wave, it moves toward the pressure antinode. A large bubble, which cannot follow the pressure changes of ultrasound because of larger inertia, oscillates out of phase and moves toward the pressure node. The secondary Bjerknes force, an attractive force between the bubbles, is also important for the bubble motion. If two bubbles are oscillating in phase, they attract one another and this force governs the aggregation and clustering of bubbles.12,13 The aggregated and clustered bubbles caused by the secondary Bjerknes force are rapidly rising by their own buoyancy and the effect of the primary Bjerknes force.

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In this study, microbubbles were applied to the froth separation of dilute ferrihydrite colloidal suspension. Furthermore, enhancement of the microbubble froth separation by controlling the motion, aggregation and clustering of microbubbles using the “Bjerknes force” in ultrasonic acoustic fields was investigated.

2. Experimental Method

The hand agitated solution technique of utilizing two syringes joined with a glass column (φ10 mm × 150 mm) via a three-way check valve was used to generate microbubbles dispersing in colloidal suspension or water. The glass column was immersed in an acrylic water bath (420 × 300 × 500 mm). Ultrasound was irradiated in the water bath from an ultrasonic oscillator (Kaijo, model 64103 and 67101) positioned at the base of the bath, thus the ultrasonic standing wave field was formed in the water bath. Ultrasound was applied at frequencies of 38 kHz and 430 kHz and with an output power from 0 to 600 W (38 kHz: 0–1 W/cm², 430 kHz: 0–3.9 W/cm²). Froth separation of the slurry using microbubbles and microbubble motion were observed using a digital video camera (Sony, DCR-SR100) and high-speed video camera (Photoron, FASTCAM-512 PCI) equipped with a long-length microscope with a 10x magnification (Nikon, CM-5A). The glass column was illuminated by a 100 W halogen lamp (Mejiro Precision, PHL-100) through a light guide. The temperature of the water bath was maintained at 25°C by heating and/or cooling devices. The schematic diagram of the experimental apparatus is shown in Fig. 1.

In the froth separation experiments, 20 mL of ferrihydrite colloidal slurry with 10 ppm of Triton X-100 added as surfactant was loaded into a syringe with 8 mL of air. Two syringes were moved alternately 10 strokes (about one stroke per second) to generate microbubbles, and then the glass column was filled with ferrihydrite colloidal slurry in which microbubbles were uniformly dispersed. The slurry with microbubbles was then kept for 20 seconds to stop liquid flow and to eject the large bubbles from the column. Ultrasound was irradiated to the column and the microbubble froth separation behavior of the colloidal slurry was observed by the high-speed video camera and digital video camera. The slurry was concentrated and separated from the clarified water during the froth separation, thus we could observe and measure the position of their boundary in the column. The volume of concentrated and separated ferrihydrite slurry from the clarified water was evaluated from their boundary position and the column diameter. When the microbubbles motion without colloidal ferrihydrite was observed, 20 mL of water with 10 ppm of Triton X-100 was loaded in a syringe with 8 mL of air for the experiment.

A ferrihydrite colloidal particles were synthesized following the procedure of Majzlan et al. The ferrihydrite sample was synthesized by titrating 50 mL of 0.1 mol/L Fe(NO₃)₃ aqueous solution with 120 mL of 0.125 mol/L NaOH aqueous solution. The rate of titration was kept constant at 1 mL/min, using a peristaltic pump. The NaOH solution was pumped into the Fe(NO₃)₃ solution via Teflon tubing. The Fe(NO₃)₃ solution was titrated with vigorous stirring to pH = 7. Figure 2 shows the X-ray diffraction (XRD; Cu Kα radiation) pattern of the dried ferrihydrite powder. The dried powder was prepared by freeze-drying of the slurry at –50°C. The XRD pattern shows two very broad peaks at 2θ = 35° and 62°, and is thus called as 2-line ferrihydrite. The broad peaks of the synthesized ferrihydrite indicate its low crystallinity and/or aggregations of nanosized particles.

3. Results and Discussion

The rate of froth separation of ferrihydrite colloidal slurry using microbubbles was significantly increased by ultrasonic irradiation at a frequency of 430 kHz. The microbubbles dispersing in the colloidal slurry aggregated and then rose up, carrying the particles of ferrihydrite adsorbing on the surface of microbubbles. In Fig. 3, the microbubble froth separation with ultrasound at 430 kHz of 600 W was compared with settling without microbubbles and microbubble froth separation without ultrasound. Without ultrasonic irradiation, the ferrihydrite particles were hardly separated after 1 min, and consequently the boundary between the clarified water and slurry could not be observed in this time. On the other hand, with ultrasonic irradiation for 1 min at 600 W, the ferrihydrite particles were separated and concentrated to about 1/3 of the height of the column, however a quite small amount of particles were dropped into the clarified water, as shown in Fig. 3. In this experimental condition, the settling separation without microbubbles took about 120 min to separate and concentrate the slurry to the level achieved by the microbubble froth separation with ultrasound in 5 min.
The froth separation of the colloidal slurry using microbubbles was also observed at output powers of 100, 300 and 600 W at 430 kHz. Figure 4 shows the volume changes of concentrated slurries with time for each output power at 430 kHz. In this figure, the results of settling separation and microbubble froth separation without ultrasound are shown for comparisons. Comparing 100, 300 and 600 W, it can be seen the froth separation was accelerated by increasing the ultrasonic output power. It is obvious that ultrasonic irradiation can increase the rate of froth separation, and the rate is remarkably faster than for settling separation without microbubbles.

However, with ultrasonic irradiation of 38 kHz, microbubbles dispersing in the colloidal slurry abruptly rose up within 1 second, and the motion of microbubbles was too fast to keep the adsorption of the ferrihydrite particles on the surface of the bubbles. Figure 5 shows the video images of the motion of microbubbles in water under ultrasonic irradiation at 38 kHz of 600 W. In this observation, the ferrihydrite colloidal particles were not added to the aqueous media to take a clear image of the microbubble motion. For the ferrihydrite slurry, the colloidal particles remained dispersing in the aqueous phase during the abrupt clustering and the rising of clustered microbubbles. That is, with the ultrasonic irradiation at 38 kHz, the ferrihydrite colloidal slurry cannot be separated and concentrated by microbubble froth separation. The difference in separation behaviors between 38 kHz and 430 kHz can be explained by the primary and secondary Bjerknes forces on the microbubble motion in an ultrasonic acoustic field. The primary Bjerknes force is proportional to bubble volume and pushes up the bubbles from higher pressure to lower pressure in the sound field. The secondary Bjerknes force is an attractive force between bubbles that causes clustering and aggregation. The primary and secondary Bjerknes forces decreases with increasing ultrasonic frequency, with the secondary Bjerknes force decreasing more than the primary and being approximately inversely proportional to the fourth power of ultrasonic frequency. At 38 kHz in this study, it was supposed that the primary and secondary Bjerknes forces strongly
acting on the microbubbles in the slurry caused the abrupt clustering and raising of the bubbles leaving the colloidal particles in the aqueous medium.

Figure 6 shows photo images of microbubble motion in water at a frequency of 38 kHz and output power of 600 W observed using the high-speed video camera. The ultrasonic irradiation time of photo images are from 0 to 160 milliseconds. In this observation, the ferrihydrite colloidal particles were not added in the aqueous medium to take a clear image of microbubble motion. As shown in Fig. 6, the diameter of microbubbles dispersed in the slurries using two syringes was in the range of about 10 to 60 \( \mu \text{m} \) (a radius of 5 to 30 \( \mu \text{m} \)). The microbubbles moved extremely quickly and formed clusters of about 300 \( \mu \text{m} \) in size within 20 milliseconds. The cluster balls rose up rapidly and then all microbubbles in the water disappeared within one second.

Figure 7 shows the photo images of microbubble motion in water at a frequency of 430 kHz and an output power of 600 W. The microbubble motion at 430 kHz was much
Fig. 7 High-speed camera images of the motion of microbubbles in water under ultrasonic irradiation at a frequency of 430 kHz and output power of 600 W.

Microbubbles Without Ultrasonic

Fig. 8 Video images of the glass column during the froth separation of ferrihydrite colloidal slurry using microbubbles without ultrasonic irradiation.

Ultrasonic 430kHz / 600W

Fig. 9 Video images of the glass column during the froth separation of ferrihydrite colloidal slurry using microbubbles with ultrasonic irradiation at a frequency of 430 kHz and output power of 600 W.
slower than that at 38 kHz. Microbubbles aggregated loosely over wide distances and rose up slowly. The wide and loose aggregation of microbubbles causing their slow rising enables the froth separation of ferrihydrite colloidal particles adsorbing on the surface of microbubbles. They may be due to much weaker Bjerknes forces compared with those at 38 kHz.

For the primary Bjerknes force, when a bubble oscillates sinusoidally and its radius is smaller than the resonant radius corresponding to the irradiating ultrasonic frequency, it moves to the antinode of the sound pressure where the pressure amplitude is large. The detailed explanations and equations of “Bjerknes force” have been shown in literatures.\(^8\)\(^{-13}\) If there is only a single bubble, it is trapped in the antinode, then oscillated.\(^17\)\(^,\)\(^18\) On the other hand, if the bubble is larger than the resonant radius, it moves to a node of sound pressure distribution where the bubble does not strongly oscillate because of the lower amplitude of the sound pressure. The resonant radius \(R_s\) (m) of the bubble for an ultrasonic frequency \(f\) (Hz) is given by

\[
R_s = \frac{1}{2\pi f} \sqrt{\frac{3\kappa P}{\rho}}
\]

where \(\kappa\) (\(\text{J/kg}\cdot\text{K}\)) is the specific heat ratio of the bubble, \(P\) (Pa) is the hydrostatic pressure in the liquid and \(\rho\) (kg/m\(^3\)) is the liquid density. For an air bubble in water, \(\kappa = 1.4\) (\(\text{J/kg}\cdot\text{K}\)), \(P\) is approximated to be atmospheric pressure (10\(^5\) Pa) and \(\rho\) is 10\(^3\) kg/m\(^3\). From eq. (1), the resonant radii of an air bubble are 85.8 \(\mu\text{m}\) at 38 kHz and 7.6 \(\mu\text{m}\) at 430 kHz.

In the experiments, the diameters of microbubbles dispersed in the slurries using two syringes were in the range of about 10 to 60 \(\mu\text{m}\) (a radius of 5 to 30 \(\mu\text{m}\)). They were much smaller than the resonant radius at 38 kHz and the microbubbles moved to the pressure antinode. The microbubbles were clustered with sizes about 300 \(\mu\text{m}\) by the stronger secondary Bjerknes force which is approximately inversely proportional to the fourth power of ultrasonic frequency. The clusters were oscillated and rose up by their own buoyancy and the primary Bjerknes force strongly pushing up them from the pressure antinodes to nodes. The clusters avoided the pressure antinodes during their rapid rising because clusters sized around 300 \(\mu\text{m}\) are larger than the resonant radius at 38 kHz.\(^{12}\) On the other hand, at a frequency of 430 kHz, the sizes of microbubbles in the experiments were mostly larger than the resonant radius. The microbubbles moved to the pressure node where aggregations are much slow and loose due to weaker secondary Bjerknes forces than that at 38 kHz, enabling the carrying and separation of the ferrihydrite particles. The aggregated bubbles also avoided the pressure antinodes during their rising because their aggregated sizes were much larger than the resonant radius. The aggregated bubbles were slowly rising with ferrihydrite particles by their own buoyancy and weaker primary Bjerknes force pushing up them from the pressure antinodes to nodes.

Figures 8 and 9 show photo images of the glass column during the froth separation of ferrihydrite colloidal slurry using microbubbles without ultrasound and with ultrasound, respectively. The ultrasonic irradiation used in Fig. 9 was at 430 kHz and 600 W. In the photo images, the microbubbles dispersing in the ferrihydrite slurry were brightly contrasted to the darkened water. As seen in Fig. 8, without ultrasonic irradiation, the microbubbles slowly rose up maintaining their dispersion without remarkable aggregation. With the ultrasonic irradiation at 430 kHz and 600 W in Fig. 9, a pattern of microbubble aggregations can be observed during their rising. The microbubbles tend to gather at the pressure node and avoid the pressure antinode of the sinusoidal ultrasonic standing wave, causing the dense-weak pattern of the aggregation. The approximate distances between the dense and weak positions of aggregated bubbles were 3–4 \(\text{mm}\). They roughly correspond to the wavelength (3.6 \(\text{mm}\)) at 430 kHz calculated using the speed of sound in water (1540 m/s). In Fig. 9, it can be seen that the dense-weak patterns of the bubbles become blurred in the upper part of the column by ultrasonic attenuation. Even with ultrasonic attenuation, the rising of bubbles proceeded by a vertical buoyancy force of their aggregation.

4. Conclusions

The rate of froth separation of ferrihydrite colloidal slurry using microbubbles was increased by the application of Bjerknes forces with ultrasonic irradiation. The microbubble froth separation with ultrasonic irradiation was far more efficient compared with settling separation in this experimental setting. Adjustment of the ultrasonic frequency is important for the froth separation using microbubbles; when the frequency is 38 kHz, the motion and clustering of microbubbles is too extreme due to the stronger primary and secondary Bjerknes forces. They abruptly aggregated to form clusters and rose up rapidly without carrying the ferrihydride colloidal particles. However, for an ultrasonic frequency of 430 kHz, the motion of microbubbles was moderate and they aggregated widely. In this case, the clear froth separation of ferrihydrite colloidal slurry progressed rapidly, and its rate was increased with increasing ultrasonic irradiation output power.

Acknowledgment

This work was financially supported by a Grant-in-Aid for Exploratory Research from the Ministry of Education, Culture, Sports, Science and Technology (No. 18656265). The authors would like to thank Prof. H. Fukuyama for lending us the high-speed camera and valuable discussions.

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