Reverse Column Flotation of Ultrafine Magnetite Mixture with Fine Glass Beads Enhanced by Fine Bubbles

N. N. Rulyov 1,2, L. O. Filippov 3,* , D. Y. Sadovskyi 1,2, V. V. Lukianova 2,4 and I. V. Filippova 3

Abstract: Magnetite ores are among the most important sources of iron, which is in high demand in the global economy. Metallurgical properties of the magnetite concentrate significantly depend on impurities of silicon- and aluminum-bearing minerals. These impurities have to be separated from ore by magnetic separation and flotation techniques. Reverse column flotation is one of the methods applied for reducing the content of impurities in magnetite concentrate. This method allows recovering impurities from ore in the froth product (flotation tailings). However, the efficiency of this method significantly decreases with the decrease in particle size. As previously demonstrated, the effectiveness of fine particle column flotation can be increased if, before feeding the pulp into a column, fine bubbles are introduced into the pulp and the pulp is then passed through a tubular reactor. The major purpose of this study was to define the effectiveness of the reverse column flotation performance of ultrafine magnetite from the mixture with fine glass beads (ballotini) when, before the pulp is fed into the flotation column, it is mixed with fine air-in-water dispersion, and the mixture is then passed through a tubular flotation reactor (TFR). The obtained experimental findings allowed the definition of the optimal conditions of the mixture treatment in TFR that ensured high concentrate grade and iron recovery for the initial iron content in the mixture of 63.76%. These conditions were defined as follows: treatment time of the mixture in the TFR—7.5 s; average flow shear rate inside the TFR—1000 s −1; volume dosage of fine bubbles per solid mass unit—0.032 or 0.21 mL/g. At the fine bubble dosage of 0.032 mL/g, the iron recovery and the concentrate grade were, respectively, 88.1% and 68.3% Fe, and at the dosage of 0.21 mL/g, the iron recovery reached 89.4% for the concentrate grade of 68.7% Fe.

Keywords: magnetite; glass beads; fine bubbles; column flotation; tubular reactor

1. Introduction

Magnetite is among the most common and valuable economic iron-bearing minerals [1]. Metallurgical properties of this product essentially depend on impurities of silicon- and aluminum-bearing minerals, and in ore treatment the major part of these impurities is separated from ore by magnetic separation [2]. Nevertheless, when the particle size of impurities falls below 20 µm, magnetic separation is not an effective method for decreasing the content of impurities to a desirable level. Thus, additional approaches are needed to upgrade magnetite to a required concentrate grade. The routine method of reducing the content of impurities in magnetite concentrate involves flotation [3], particularly, reverse cationic flotation using amines as a collector for the silicates [4,5]. In the recent decades, alongside the pneumatic flotation of iron ore, reverse column flotation has found wider applications [6], particularly for the flotation of iron ore slimes [7–9]. This technology offers a number of economic advantages, but also entails the challenge of fine particle...
flotation [10]. The problem becomes even more complex in the beneficiation of ores where the liberation of valuable components requires fine grinding. It is generally known [11,12] that the capture efficiency of particles by bubbles is in direct relationship with the second degree of the ratio of the particle size to the bubble size. Hence, we can assume that there must be two ways to increase the flotation effectiveness of fine particles: either by increasing the size of floated particles through their flocculation (coagulation), or by using fine bubbles in combination with coarse ones [13,14].

The first of the above options was explored in [15], who reported that preliminary dispersion and selective flocculation followed by reverse flotation of silicate is the only proven method to efficiently process fine-grained (<25 µm) hematite ores. The second method, called combined microflotation [13], is based on the application of fine bubbles as flotation carriers that collect fine particles on their surface, and also form with them sufficiently large hetero-aggregates comprising multiple fine bubbles [16]; this significantly increases their floatability by coarse bubbles.

The case of the reverse pneumatic flotation of finely dispersed magnetite (<10 µm) from the mixture with glass beads (ballotini) explored in [17] demonstrated that the use of fine bubbles in combination with conventional coarse bubbles produced a notable enhancement in the efficiency of magnetite beneficiation.

The example of ballotini flotation discussed in [18] showed that the efficiency of column flotation of fine particles can be significantly improved by applying fine bubbles, when prior to feeding pulp into a flotation column, fine bubbles under certain conditions are allowed to interact with the particles. Such conditioning can be conveniently implemented by passing pulp comprising fine bubbles for several seconds at a certain predefined turbulence level through a tubular flotation reactor (TFR). During this time, sufficiently coarse hetero-aggregates of particles and fine bubbles may form. Once these enter a column, these fine bubbles can be more effectively floated by coarse bubbles and entrained in the froth. At the same time, it would be erroneous to assume that the effectiveness of the flotation process would be higher for greater volume dosages of fine bubbles per unit weight of floated particles. As shown in [18], even in monomineral flotation, the maximum recovery has been observed at the dosage of fine bubbles of around 0.3 mL per gram of solid. A further increase in the fine bubble dosage does not necessarily lead to a noticeable increase in the recovery. According to the theory elaborated in the same work, this effect can be explained by the fact that the increase in the volume concentration of fine bubbles promotes the increase in the rate of their coarsening due to coalescence, and thus can lead to a significant decrease in their efficiency of capturing fine particles.

In the work [19] it was shown that the maximum share of fine particles that are able to attach to the surface of fine bubbles in the process of pulp movement in a turbulent flow can be described by the formula

\[ R_{\text{max}} = 1 - \exp \left[ -\frac{\left( \frac{3}{2} + \frac{\Delta \rho}{\rho_w} \right) \pi g E_{\text{att}} d_0^2}{16 G \alpha_b \phi_b} \right] \]  

(1)

and the characteristic time of the particle collection by bubbles can be estimated by the relation

\[ t_c = \frac{3\pi}{4G \alpha_b \phi_b} \]  

(2)

where \( E_{\text{att}} \) is the bubble–particle attachment efficiency; \( G \) is the mean shear rate of the medium; \( d_0 \) is the initial bubble size; \( d_{p0} \) is the particle size; \( g \) is acceleration due to gravity; \( \phi_b \) the volumetric bubble concentration in pulp; \( \alpha_b \) is the bubble coalescence (aggregation) efficiency; \( \rho_w \) is water density; \( \Delta \rho \) is the density difference of water and particles; \( \nu \) is the kinematic viscosity of medium.

The numerical analysis of Relations (1) and (2) shows that, by varying such parameters as the initial bubble size \( d_0 \), bubble concentration \( \phi_b \), and the bubble coalescence effectiveness \( \alpha_b \), and also the mean shear rate of the flow \( G \), it is possible to achieve the factor of
particle collection by bubbles of around 80–90% within one minute of treating the pulp in a turbulent flow. From Relation (2), it is obvious that the required treatment time of the mixture in TFR can be significantly reduced by increasing the $G G \alpha b \phi b$ product. According to Relation (1), the increase in the mean flow shear rate $G$ or bubble coalescence efficiency $\alpha b$ leads to the decrease in the maximum share of particles that can attach to a bubble’s surface. The most suitable option to decrease the characteristic time of the particle collection on a fine bubble’s surface is increasing the volumetric bubble concentration $\phi b$, the suppression, and, to a certain extent, the effectiveness of coalescence $\alpha b$ using frothers having a low critical coalescence concentration (CCC). It should be noted that fine bubbles, and bubbles having fine particles attached to their surface in particular, significantly increase the water recovery of the froth. This effect boosts the entrainment of fine particles [20] and significantly reduces the recovery of the valuable mineral in reverse flotation [16].

The above considerations suggest that efficient use of fine bubbles in the combined selective flotation of finely dispersed minerals requires thorough and careful adjustment of the dosage of fine bubbles, and controlling the treatment time and mode of pulp flow in a TFR.

This work aimed at defining how the effectiveness of the reverse column flotation of ultrafine magnetite from a mixture with fine ballotini depends on the dosage of microbubbles and also on the time of pulp treatment in TFR before feeding the pulp into the flotation column. Glass beads were selected as model impurities of the magnetite concentrate because their surface features are quite similar to those of oxidized mineral impurities (in particular, to quartz), based on the fact that their flotation characteristics were thoroughly studied previously [17,18].

2. Materials and Chemicals

In all test runs, the suspension of the mixture of practically pure magnetite (Fe 72.4%) and ballotini with respective concentrations of components 220 and 30 g/L in tap water was used as the magnetite concentrate model, in which the iron content in the solid phase was 63.8%. Processing of fine-grained magnetite ore routinely includes the stage of ore regrinding to produce particles below 33 $\mu$m, and is performed after the magnetic separation but before flotation [5]. However, practical experience shows that in, actual mineral mixtures, the maximum size of iron oxide particles is around three times smaller than the maximum size of impurity particles [21]. Considering that the particle size plays a critical role in flotation, to ensure the model mixture closely matched actual ore, in test runs we used samples of magnetite and ballotini having particle sizes of <10 and <35 $\mu$m, respectively.

Cetyltrimethylammonium bromide (CTAB) was used as the ballotini collector; the consumption of this reagent amounted to 20 or 24 g/t, and its concentration in the pulp was 5 or 6 mg/L. Corn dextrin was used as the depressant for magnetite, and in all test runs its dosage was 800 g/t. BASF test product PPG-600 (HO(C$_3$H$_6$O)$_{10}$H, CCC—3 mg/L [22], served as the frother, and its concentration in the pulp was maintained at the value of 50 mg/L. Pulp pH was adjusted to 8.4 $\pm$ 0.1 using NaOH solution.

In order to eliminate the effects of water quality variations with time on test results, before use, 500 L of water was kept in a plastic container at the temperature of 20–22 $^\circ$C until stabilization of water conductivity and pH.

3. Equipment

All tests were conducted on the experimental plant shown in detail in Figures 1 and 2. Flotation was performed in a $9 \times 10$ cm$^2$ rectangular cross-section stainless-steel column, for which the vertical dimensions are shown in Figure 1. At the bottom part of the column, an air sparger made of sintered glass powder was placed. The sparger was powered by the peristaltic pump P4. In all test runs, the airflow rate in the column was maintained at 4.2 L/min (0.78 cm/s).
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Figure 1. Laboratory rig layout for studying the process of the column flotation.

PVC tubes having an inner diameter of 4 or 6 mm served as the TFR, and the tube length was adjusted accordingly to the set treatment time: 2.5, 5.0, 7.5, and 10 s. The pump P3 fed the pulp from the container through the TFR into a column. In all tests, the feed flow rate was 21 ± 0.3 L/h to ensure that the flow shear rates in the tubes of 4 and 6 mm diameter were at values 1000 ± 20 and 500 ± 10 s⁻¹, respectively.

Fine bubbles were produced by an MBGen-0.001 laboratory-scale generator of air-in-water dispersion, developed by TURBOLOTSERVICE Company (Kyiv, Ukraine); the generator supplied the air and a frother solution with the help of dosing pumps P1 and P2. In all tests, the frother solution consumption was 1 ± 0.01 L/h, and its concentration amounted to 1 g/L, which, upon mixing with the pulp at the inlet to the TFR, produced a frother concentration of 50 mg/L. By adjusting the airflow rate in the MBGen-0.001, it was possible to change the microbubble dosage in the range from 0 to 0.334 mL/g.
4. Experimental Methods

The test procedure included the following steps—before the start of a test run, 1 L of suspension containing 220 g of magnetite and 30 g of ballotini at pH 8.4 ± 0.1 was placed in a mixer, then 800 g/t (200 mg/L) of corn dextrin solution was added into a mixer followed by 7 min mixing. Then, CTAB solution was added to the suspension calculated on the basis of 20 or 24 g/t (5 or 6 mg/L), and after that the suspension was stirred for 3 min. Simultaneously, water was supplied to the flotation column, and dextrin, CTAB, and the frother were added to it in concentrations of 200, 5 (or 6), and 50 mg/L, respectively, and pH was adjusted to 8.4 ± 0.1. In addition, during the tests for generating air-in-water dispersion, PPG-600 frother solution of the concentration of 1 g/L and pH—9.1 ± 0.1 was used.
At the start of the test, pump P4 was turned on to supply air into a flotation column in the form of coarse bubbles having the size below 1.5 mm. Once the froth edge in the column reached the spillover level, the MBGen-0.001 generator and dosing pumps P1, P2, and P3 were turned on to feed, through the TFR, the mixture of pulp and fine bubbles into the flotation column. Flotation tailings in the form of the froth product were collected for 3.5 min, which was roughly by 0.5 min longer than the pumping time of 1 L of a suspension sample. Collected tailings were weighed, dried, and weighed again to define the iron content in the solid phase, and the amount of recovered water. Knowing the iron content and the weight of the initial sample, it was possible to define the concentrate grade $G$ and iron recovery $R$ by the formulae

$$G = \frac{m_0c_0 - m_tc_t}{m_0 - m_t}$$ (3)

$$R = \frac{m_0c_0 - m_tc_t}{m_0c_0} \times 100\%$$ (4)

where $m_0$ and $m_t$ are the mass of the initial sample and tailings, respectively, and $c_0$ and $c_t$ are the percentage content of iron in them. All experiments were repeated three times, which allowed definition of the root-mean square scatter of values at the level below 0.5%.

Obviously, the data obtained in this way would not fully depict the process of continuous column flotation, considering that 3.5 min is too short a duration to achieve the steady state conditions of the mixture components in the column. However, such experiments provide the alternative to assess the effects of factors such as the dosage of fine bubbles, and the duration and the mode of the hydrodynamic treatment of the mixture in the TFR, on flotation performance.

5. Results and Discussion

Figure 3 shows the cumulative volumetric distribution functions of ballotini and fine bubbles calculated by computer processing of micrographs. The obtained results demonstrated that 80% of ballotini mass fell within the range 20–37 $\mu$m, with a median size 25 $\mu$m, whereas 80% of the volume of fine bubbles were in the range 150–210 $\mu$m, with a median size 180 $\mu$m. The size of coarse bubbles produced in the tested flotation column was around 1500 $\mu$m, as reported previously [18]. Based on the account of the above-mentioned quadratic dependence of the capture efficiency of particles by bubbles on the ratio of their dimensions, it can be easily shown that the capture efficiency of ballotini by fine bubbles will be roughly 70 times higher compared to the capture efficiency by coarse bubbles. By comparison, the capture efficiency of fine bubbles with ballotini attached to their surface, by coarse bubbles, will be around 50 times higher compared to the capture efficiency of free ballotini particles. If we take into account that, according to [17,18], fine bubbles loaded with ballotini are capable of forming very coarse aggregates comprising tens of fine bubbles, then the capture efficiency of these aggregates by coarse bubbles will be even higher. Therefore, the flotation efficiency can be significantly increased provided the process is split into two successive sub-processes, namely: 1—selective deposition of ballotini particles on fine bubbles and formation of large aggregates in the process of transferring the pulp through the TFR; 2—separation of aggregates produced in the TFR from the pulp with coarse bubbles generated in the flotation column.

5.1. Effect of Collector Dosage

Figures 4 and 5 present the dependencies of the concentrate grade and iron recovery on the dosage of fine bubbles for the following conditions: collector dosage 20 or 24 g/t, TFR diameter—Ø6 mm, and treatment time in TFR—7.5 s. These findings demonstrate that, for the collector dosage of 20 g/t, the concentrate grade (iron content) increases from 66.6% to 68.2% with the increase in the fine bubble dosage from 0 to 0.21 mL/g; however, in the range of fine bubble dosage from 0.21 to 0.33 g/L, the concentrate grade dramatically drops. For a collector dosage of 24 g/t, the concentrate grade increases from 66.8% to 69.4%
when a bubble dosage increases from 0 to 0.33 mL/g. However, in terms of recovery, at the collector dosage of 20 g/t with the increase in fine bubble dosage from 0 to 0.21 mL/g, the recovery decreases from 92.5% to 88.9%, and, at the point 0.33 mL/g, it plunges to 75.3%. When the collector dosage is 24 g/t, with the increase in the fine bubble dosage from 0 to 0.16 mL/g, the recovery essentially reduces from 90% to 79.6%, and, at the point 0.33 mL/g, it then goes up to 84.7%.

Figure 3. Cumulative volumetric distribution functions of ballotini and microbubbles.

Figure 4. Dependence of concentrate grade on fine bubble dosage at the CTAB dosage of 20 and 24 g/t. Treatment time—7.5 s; TFR diameter—6 mm. (Error bars represent the standard deviation obtained from 3 test repeats).
This intricate behavior shown in the obtained relationships is the result of the interaction of many factors. First, we should take into account that CTAB, being a cationic collector, is also a very efficient frother. Moreover, in combination with the non-ionic frother PPG-600, this leads to a synergistic effect of enhanced frothing that induces increased hydraulic entrainment of both magnetite particles and ballotini. In addition, in the presence of a cationic collector, the application of a depressant will not guarantee the suppression of the floatability of magnetite particles. Since magnetite particles are by far smaller than ballotini, and their concentration is significantly greater, while passing through the TFR, they would compete with ballotini for a place on the fine bubbles’ surface. This was proven by the observations that, at a CTAB dosage of 20 g/t, and microbubble dosages above 0.21 mL/g, both the iron recovery and the concentrate grade fall. Thus, this suggests that the increase in the microbubble dosage raises the entrainment of magnetite particles rather than that of ballotini. When the collector dosage goes up to 24 g/t, the iron recovery decreases further; however, at the same time the concentrate grade improves when fine bubble dosages are at the range above 2.1 mL/g. This suggests that, when pulp flows through the TFR, it leads to the formation of hetero-aggregates comprising magnetite particles, ballotini, and fine bubbles.

### 5.2. Effect of Iron Hydraulic Entrainment into Tailings

Although a depressant for magnetite flotation was used in all tests, a certain portion of magnetite was carried into the tailings by true flotation and partially by hydraulic entrainment. Since application of fine bubbles leads to enhanced water recovery in froth, this should also increase the entrainment of finely dispersed mineral into the froth product. Thus, iron recovery into tailings \( R_{\text{Tail}} \) can be presented as the sum

\[
R_{\text{Tail}} = R_{\text{Flot}} + R_{\text{Entr}}
\]
where $R_{Flot}$ and $R_{Entr}$ are true flotation and entrainment recovery components, respectively. Based on the data of the water recovery, it is feasible to estimate the contribution of hydraulic mechanism into the iron loss in tailings by the formula

$$R_{Entr} = k_{Entr} \frac{C_C V_t}{C_P V_0} \times 100\%$$  \hspace{1cm} (6)

where $V_t$ and $V_0$ are volumes of water recovered in froth, and water passed through the TFR, $k_{Entr}$ is the coefficient of hydraulic magnetite entrainment, and $C_P$ and $C_C$ are the iron concentration in pulp and the aqueous phase of column, respectively. In the first approximation, $C_C$ can be estimated by the formula

$$C_C = k_s C_P$$  \hspace{1cm} (7)

where $k_s$ is the dilution coefficient of pulp on its entry into a column. From the substitution of $C_C$ from (7) into (6) and further substituting $R_{Entr}$ from (6) into (5), we obtain

$$R_{Flot} = R_{Tail} - k_s k_{Entr} \frac{V_t}{V_0} \times 100\%$$  \hspace{1cm} (8)

According to [20], the coefficient of hydraulic entrainment $k_{Entr}$ depends on particle size. For particles smaller than 10 $\mu$m, this coefficient is around 0.9. In terms of the dilution factor $k_s$, in the first approximation it can be estimated by the formula

$$k_s \leq \frac{V_0}{V_0 + V_F}$$  \hspace{1cm} (9)

where $V_F$ is double volume of water inside a flotation column between the point of pulp feed and the point of the froth product spill over, which amounted to 0.77 L. The fact that, in all tests $V_0 = 0.94$ L, suggests that the dilution coefficient did not exceed 0.55. From the substitution of coefficients $k_{Entr} = 0.9$ and $k_s \leq 0.38$ into the Equation (8), we obtain

$$R_{Flot} \geq R_{Tail} - 0.34 \frac{V_t}{V_0} \times 100\%$$  \hspace{1cm} (10)

The share of flotation recovery of iron into tailings was established based on the data of the total iron recovery into tailings and the calculations by Formula (10). Figures 6 and 7 show the dependencies of these values on the microbubble dosage when CTAB dosages were 20 and 24 g/t, and the treatment time in the 6 mm diameter TFR was 7.5 s. The data presented in Figure 6 show that, at a CTAB dosage of 24 g/t, the hydraulic entrainment of iron into tailings is significantly higher compared to the value at dosage 20 g/t, which can be explained by the higher froth stability due to the coalescence with the increase in the total concentration of the frother (PPG-600 + CTAB). By comparison, the data presented in Figure 7 show that, for a CTAB dosage of 20 g/t, with the increase in the fine bubble dosage from 0.21 to 0.33 mL/g, the iron recovery into tailings by flotation grows significantly, which is in line with the conclusions discussed in the above section.
were 0.21 mL/g and 20 g/t, respectively. These dosages were used in the tests designed to define the optimal time of pulp treatment in TFRs having 4 and 6 mm diameters. The findings presented in Figures 4 and 5 show that high concentrate grade and acceptable level of iron recovery were achieved when fine bubbles and collector dosages were 0.21 mL/g and 20 g/t, respectively. These dosages were used in the tests designed to define the optimal time of pulp treatment in TFRs having 4 and 6 mm diameters. The obtained results are presented in Figures 8 and 9. According to the data in Figure 8, the best grade of the concentrate was achieved for a 7.5 s treatment time; furthermore, the treatment time in the 6 mm diameter TFR was 7.5 s. TFR inner diameter is 6 mm. Coefficient of the hydraulic entrainment of iron into tailings by flotation remains significant, which is in line with the conclusions discussed in the above section.

Dependence of the share of hydraulic entrainment of iron in tailings (froth product) on the fine bubble dosage at CTAB consumptions of 20 and 24 g/t. Treatment time in a TFR is 7.5 s. Coefficient of the hydraulic entrainment of iron $k_{Entr} = 0.9$, coefficient of pulp dilution in column $k_s = 0.38$.

**Figure 6.** Dependence of the share of hydraulic entrainment of iron in tailings (froth product) on the fine bubble dosage at CTAB consumptions of 20 and 24 g/t. Treatment time in a TFR is 7.5 s. TFR inner diameter is 6 mm. Coefficient of the hydraulic entrainment of iron $k_{Entr} = 0.9$, coefficient of pulp dilution in column $k_s = 0.38$.

Dependence of the share of flotation recovery of iron in tailings (froth product) on the fine bubble dosage at CTAB consumptions of 20 and 24 g/t. Treatment time in a tubular reactor 7.5 s. TFR inner diameter is 6 mm. Coefficient of the hydraulic entrainment of iron $k_{Entr} = 0.9$, coefficient of pulp dilution in column $k_s = 0.38$.

**Figure 7.** Dependence of the share of flotation recovery of iron in tailings (froth product) on the fine bubble dosage at CTAB consumptions of 20 and 24 g/t. Treatment time in a tubular reactor 7.5 s. TFR inner diameter is 6 mm. Coefficient of the hydraulic entrainment of iron $k_{Entr} = 0.9$, coefficient of pulp dilution in column $k_s = 0.38$.

### 5.3. Effect of Treatment Time in TFR

The findings presented in Figures 4 and 5 show that high concentrate grade and acceptable level of iron recovery were achieved when fine bubbles and collector dosages were 0.21 mL/g and 20 g/t, respectively. These dosages were used in the tests designed to define the optimal time of pulp treatment in TFRs having 4 and 6 mm diameters. The obtained results are presented in Figures 8 and 9. According to the data in Figure 8, the best grade of the concentrate was achieved for a 7.5 s treatment time; furthermore, the treatment...
in the 4 mm diameter TFR resulted in producing concentrate having a grade that was 0.5% higher than the grade of the concentrate treated in the 6 mm diameter TFR. Therefore, as follows from Figure 9, in this case, the iron recovery levels of 86.5% and 87.3% achieved in the 4 and 6 mm TFRs, respectively, were also acceptable.

Figure 8. Dependence of the concentrate grade on suspension treatment time in TFRs having 4 and 6 mm inner diameters. CTAB dosage 20 g/t, microbubble dosage 0.21 mL/g. (Error bars represent the standard deviation obtained from 3 test repeats).

Figure 9. Dependence of iron recovery on suspension treatment time in TFRs having 4 and 6 mm inner diameters. CTAB dosage 20 g/t, microbubble dosage 0.21 mL/g. (Error bars represent the standard deviation obtained from 3 test repeats).
Rather complex dependencies of iron recovery on the treatment time in the TFR can be explained by the ratio of iron entrainment in the froth product by hydraulic and flotation mechanisms. Figure 10 shows the dependencies of the hydraulic entrainment of iron in tailings on the treatment time in the TFR calculated by the Formulaes (6) and (7), based on the substitution coefficient of the hydraulic entrainment of iron $k_{\text{Entr}} = 0.9$ and coefficient of pulp dilution in the column $k_s = 0.38$. The above data clearly show that, in both TFRs, the hydraulic recovery of iron in tailings monotonically decreases. The short duration of treatment in the TFR may not be sufficient to ensure considerable coarsening of fine bubbles; hence, when they reach a total froth flow, this effect promotes the increase in froth density and, thus, a higher water flow rate in the froth concentrate and the hydraulic entrainment of magnetite. When treatment time in the TFR is extended, fine bubbles manage to enlarge in size and hence promote the decrease in the froth product density and water entrainment in it, in addition to entrainment of magnetite particles. Regarding the flotation recovery of iron in tailings, according to the data in Figure 11, with the increase in the pulp treatment time in the TFR, flotation entrainment increases because, in this case, the number of magnetite particles that attach to the surface of the fine bubbles increases, thus boosting the flotation mechanism of iron entrainment in tailings. In the 4 mm diameter TFR for a pulp treatment duration above 7.5 s, the flotation component of iron entrainment in tailings starts to decrease; this effect is most likely explained by the fact that, at high shear rates, fine bubbles coalesce quickly and may shed some magnetite particles that previously attached to their surface.

![Figure 10](image-url)  
**Figure 10.** Dependence of the share of the hydraulic entrainment of iron in tailings (froth product) on the treatment time in TFRs having 4 and 6 mm inner diameters. CTAB dosage—20 g/t, fine bubbles dosage—0.21 mL/g.
5.4. Effect of Shear Rate in TFR

As noted above, the turbulence level in the TFR is determined by the mean of the shear rate of the flow. The measurements performed in [18] showed that, at the pulp consumption of 21 L/h, the mean shear rates in 4 and 6 mm tubes were 1000 and 500 s\(^{-1}\), respectively. Since the rates of processes such as aggregation (coalescence) of fine bubbles and particles essentially depend on the shear rate, it will be of interest to explore the effects of the shear rate on the performance of magnetite separation from the ballotini particles. Figures 12 and 13 present the dependencies of the concentrate grade and iron recovery on a microbubble dosage for a 7.5 s treatment time of pulp in 4 and 6 mm diameter TFRs. The obtained results show that, in the 4 mm diameter TFR, the maximum concentrate grade of 68.7% is achieved for the fine bubble dosage of 0.21 mL/g, and this value is 0.5% higher compared to the value obtained in the 6 mm diameter TFR, and 1.9% better than the value registered without the application of fine bubbles. In addition, the iron recovery is practically the same and amounts to 89.5%.

Particular consideration should be given to the pattern of the concentrate grade curve related to the 4 mm diameter TFR in the range of low fine bubble dosages. The occurrence of a high maximum at the point 0.032 mL/g and a deep minimum at the point 0.064 mL/g indicate that, in the first case, primarily ballotini were attaching to fine bubbles. This is because ballotini are far bigger in size than magnetite particles and, as shown in Figure 14, the flotation entrainment of magnetite in tailings was rather low. Considering that the fine bubble dosage calculated with reference to the mass of ballotini amounted to 0.283 mL/g, then, according to the data on the individual flotation of ballotini [18], this effect can promote their maximum recovery from the mixture with magnetite. However, doubling the dosage of fine bubbles produced an additional surface, which could be taken by magnetite particles; as a result the flotation iron into tailings increased by more than 5.6-fold. Respective data are shown in Figure 14. Since the hydraulic entrainment of iron in tailings weakly depends on a fine bubble dosage, as shown in Figure 15, this behavior of the concentrate grade curve in the case of pulp treatment at high shear rates most likely can be attributed to the nature of interactions of magnetite particles with fine bubbles by means of electrostatic surface forces. This offers a plausible explanation of the effect that,

Figure 10. Dependence of the share of the hydraulic entrainment of iron in tailings (froth product) on the treatment time in TFRs having 4 and 6 mm inner diameters. CTAB dosage—20 g/t, fine bubbles dosage—0.21 mL/g.

Figure 11. Dependence of the share of the flotation recovery of iron in tailings (froth product) on the treatment time in TFRs having 4 and 6 mm inner diameters. CTAB dosage—20 g/t, fine bubbles dosage—0.21 mL/g.
with the increase in the fine bubble dosage, the flotation of iron in tailings is of an order of 1%, as shown in Figure 14.

**Figure 12.** Dependence of the concentrate grade on fine bubble dosage upon treatment in TFRs having 4 and 6 mm inner diameters. CTAB dosage—20 g/t, treatment time—7.5 s. (Error bars represent the standard deviation obtained from 3 test repeats).

**Figure 13.** Dependence of iron recovery on fine bubble dosage upon treatment in TFRs having 4 and 6 mm inner diameters. CTAB dosage—20 g/t, treatment time—7.5 s. (Error bars represent the standard deviation obtained from 3 test repeats).
When fine bubbles are formed in a solution of non-ionic surfactants (for example, in polypropylene glycol mixture PPG-600), their surface is charged negatively. When bubbles enter a solution with sufficiently high concentration of cationic surfactant, which was the case in these tests, molecules of non-ionic surfactant on their surface are partially replaced by molecules of cationic surfactant (in our case CTAB); this leads to a partial decrease in their negative charge, or even to the reversal of the sign of the charge to the positive one. Concurrently, CTAB molecules are desorbed from a particle surface, where they were initially adsorbed, also becoming more negatively charged. This process is significantly accelerated with the vigorous agitation of the mixture, as happened in the 4 mm diameter TFR, and with the increased number of fine bubbles fed into the mixture. As demonstrated by the DLVO theory [23,24] and the theory of fine particle flotation [25], the correlation and the sign of the charge of particles and bubbles significantly influence their capacity to form aggregates. Thus, it is quite plausible that the significant increase in the fine bubble concentration and the corresponding increase in their surface may lead to the appearance of an electrostatic barrier between bubbles and magnetite particles. As a result, at dosages of fine bubbles above 0.13 mL/g the flotation of magnetite into tailings was not higher than 1.1%.
Figure 14. Dependence of the share of the flotation recovery of iron in tailings (froth product) on the fine bubble dosage after treatment in TFRs having 4 and 6 mm inner diameters. CTAB dosage—20 g/t, fine bubble dosage—0.21 mL/g.

Figure 15. Dependence of share of the hydraulic recovery of iron in tailings (froth product) on the fine bubble dosage after treatment in TFRs having 4 and 6 mm inner diameters. CTAB dosage—20 g/t, fine bubble dosage—0.21 mL/g.

6. Conclusions

Hydrodynamic treatment of an artificial mixture of ultrafine magnetite and fine glass beads in a tubular flotation reactor (TFR), conducted upon the introduction of fine bubbles into the mixture, significantly affects the performance of reverse column flotation of magnetite. There is a complex dependence of iron recovery and concentrate grade on factors such as fine bubble dosage, time of the mixture treatment in the TFR, the dosage of the cationic collector, and the turbulence level in the TFR.

The major cause of iron loss in flotation tailings (froth product) is the magnetite entrainment effect, which is more pronounced with the increase in the collector and microbubble dosages, particularly in the range of values above 0.21 mL/g, and reduces with the increasing treatment time of the mixture in the TFR.

Iron losses in the flotation tailings conditioned by attachment of magnetite particles on bubbles (flotation entrainment) depend, in a complicated manner, on fine bubble dosage, cationic collector dosage, and on the turbulence level and the time treatment of the mixture in the TFR. The flotation recovery of iron rises with the increase in the time of treatment in the TFR in the range from 2.5 to 7.5 s. When the mixture is treated in the TFR for 7.5 s at the turbulence level corresponding to the shear rate of 500 s$^{-1}$, the dependence of iron flotation entrainment on fine bubble dosage has a small maximum of 3.3% at the point 0.032 mL/g, whereafter the flotation entrainment practically monotonically increases to 17.2% with the growth in the dosage of fine bubbles to 0.334 mL/g. For treating the mixture in the TFR for 7.5 s at the turbulence level corresponding to the shear rate of 1000 s$^{-1}$, the dependence of iron flotation entrainment on fine bubble dosage has an acute maximum height of 8.5% at the point 0.064 mL/g, and afterwards the flotation entrainment practically monotonically falls to 1.1% with the rise in the dosage of fine bubbles to 0.334 mL/g.

The experimentally obtained dependencies allowed the establishment of the optimal conditions for reverse column flotation of magnetite from the mixture with ballotini as follows: collector (CTAB) dosage—20 g/t; treatment time in the TFR—7.5 s; shear rate in
the TFR—1000 s$^{-1}$; and fine bubble dosage—0.032 or 0.21 mL/g. The iron recovery and the concentrate grade achieved at the bubble dosage 0.032 mL/g were 88.1% and 68.3% Fe, respectively, but at the bubble dosage of 0.21 mL/g, the iron recovery was 89.4% for the concentrate grade of 68.7% Fe.

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**References**


