University of Belgrade
Technical Faculty in Bor

Chamber of Commerce
and Industry of Serbia

XV International Mineral Processing & Recycling Conference

IMPRC
INTERNATIONAL MINERAL PROCESSING & RECYCLING CONFERENCE

Proceedings

Editors:
Jovica Sokolović
Milan Trumić

17-19 May
2023

Belgrade
SERBIA

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XV International Mineral Processing & Recycling Conference

PUBLISHER:
University of Belgrade, Technical Faculty in Bor

FOR THE PUBLISHER:
Dean: Prof. Dr Dejan Tanikić

EDITORS:
Prof. Dr Jovica Sokolović
Prof. Dr Milan Trumić

PROCEEDINGS COVER DESIGN:
Vojislav Jotović

PRINTED BY:
Grafomed - Trade Bor d.o.o., Bor, Serbia
Printed: 200 copies

PUBLICATION YEAR:
2023

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CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

622.7(082)
502.131.1:628.477.6(082)
628.477.6(082)

INTERNATIONAL Mineral Processing and Recycling Conference (15 ; 2023 ; Belgrade)
Proceedings / XV International Mineral Processing and Recycling Conference, IMPRC, 17-19 May 2023, Belgrade, Serbia ; editors Jovica Sokolović, Milan Trumić. - Belgrade : University, Technical Faculty in Bor, 2023 (Bor : Grafomed Trade). - XII, 634 str. : ilustr. ; 25 cm

Na vrhu nasl. str.: Chamber of Commerce and Industry of Serbia. - Tiraž 200. - Bibliografija uz većinu radova.

ISBN 978-86-6305-133-1

а) Руде -- Припрема -- Зборници б) Отпадне материје -- Одрживи развој -- Зборници в) Отпадне материје -- Рециклажа -- Зборници

COBISS.SR-ID 114566153

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Conference is financially supported
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ROLE OF PARTICLE SHAPE IN THE FLOATABILITY OF TONER PARTICLE

M.S. Trumić[#], K.S. Balanović
University of Belgrade, Technical Faculty in Bor, Bor, Serbia

ABSTRACT – This paper aims to research the influence of the particle shape of the iron oxide-containing toner on flotation efficiency and to test first-order and second-order kinetics models to determine the model which better describes the flotation of the coarse plate-like particles.

Hallimond tube flotation were carried out on two toner samples (regular round plate-like and irregular plate-like particles), with no collector in use. Contact angle measurements were conducted by sessile drop method. The results show that both samples have the same high value of contact angle which indicates that the toner samples are hydrophobic. High toner flotation recovery is achieved with round plate-shaped toners after prolonged time and flotation kinetics of toner was described by classical first order flotation model. The toner with the irregular plate-shape has reduced flotation recovery even after a long time of flotation and flotation kinetics of toner was described by modified first order flotation model.

It should be emphasized that no significant differences were observed when measuring the contact angle of samples, and that the lower recovery obtained for sample with irregular plate-like particles can be attributed to the different shape of the particles.

Keywords: Flotation, Hydrophobicity, Contact Angle, Flotation Kinetics, Toner, Particle Shape.

INTRODUCTION

Particle shape plays an important role in flotation, and that role is difficult to define for few reasons. First, the method of obtaining particles of different shapes leads to a change in the roughness of the surface and thus to a change in hydrophobicity. Second, flotation depends on reagent concentration and type, particle surface hydrophobicity, particle size, and other factors such as the speed of agitating, solid content in the suspension, etc. [1-6].

The mechanism of particle shape affecting particle floatability is discussed by several authors [1,3,7]. Namely, they all pointed out that by grinding, the surface roughness changes and thus the hydrophobicity of the particles, and that changes in flotation efficiency cannot be attributed only to changes in particle shape, that often occur due to comminution. That is why these studies were carried out on synthetic toner samples, of different shape but with the same hydrophobicity.

Flotation kinetics for small spherical particles has been described by the second-order flotation model [5], and the aim here will be to define order of the flotation model which better describes flotation of coarse plate-like particles.

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EXPERIMENTAL

Materials and methods

A Laser Jet 1018 printer was used to prepare realistic synthetic sample (free toner particles). Toner particles produced from laser toner are usually plate, regular round or irregular shaped in deinking suspension [3]. According to the material safety data sheet (MSDS, 2022), the toner inside the cartridge is mainly composed of a styrene/acrylate copolymer (<55 wt %), iron oxide (<50 wt %) and amorphous silica (<3 wt %). Its solubility in water is negligible, and it is partially soluble in toluene and xylene. The material should soften between 100°C and 150°C, and decomposition temperature is > 200 °C. The density of the toner is 1.4 g/cm^3.

On the foil thickness 100 µm previously coated with (PVA) polyvinyl alcohol [8], circles with a diameter of 1 mm were printed, and after agitation in a mechanical stirrer, plate-shaped particles were obtained. After wet sieving, two samples were formed for microflotation experiments (Table 1 and Figure 1).

Table 1 Characteristics of toner particles

Sample 1			
size (diameter) of screens d (µm)	W (%)	average size (diameter) of particles, d_{sr} (µm)	Shape
-1000+600	100	800	regular round plate-like
-600+150	0		
Sample 2			
-1000+600	48	500	regular round plate-like, irregular plate-like
-600+150	52		

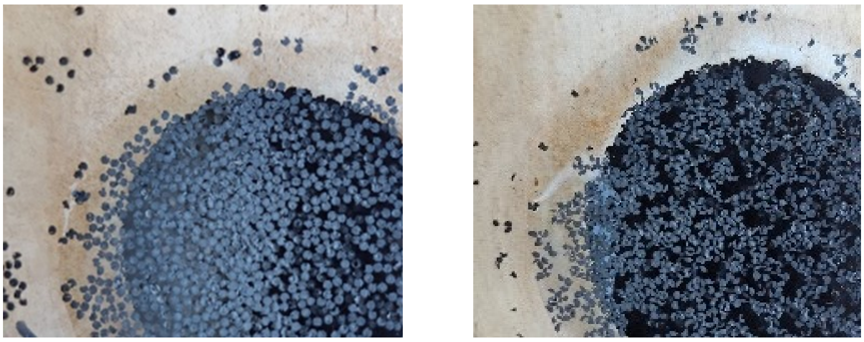

a) b)

Figure 1 Shape of samples: a) regular round plate-like, b) irregular plate-like

Based on contact angle measurements, the surface properties of the toner sample were characterized. Measurements were made with a sessile drop method [9] using an optical goniometer (Advex Instrument) with appropriate software SeeSystem. The liquid used was distilled water and a 0.1 µL droplet formed using a micropipette (VITRUM/VVR) that was captured after dropping onto the toner surface. After manually selecting the three points on the droplet's perimeter, the software automatically calculates the value of the contact angle.

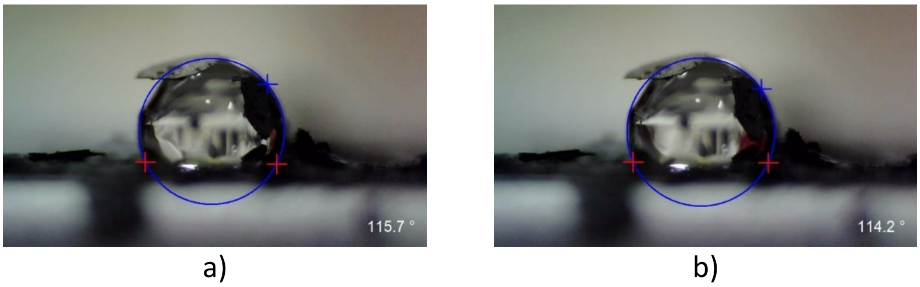


Figure 2 Images of a water drop onto surface of toner before microflotation a) after 30 s and b) after 60 s

Liquid (water) surface wetting and liquid (water) spreading are very important aspects of practical surface chemistry, which is the basis of the microflotation process. Microflotation experiments were performed in a modified Hallimond flotation cell (Figure 3) which is often called a monobubble Hallimond tube in the literature [10].

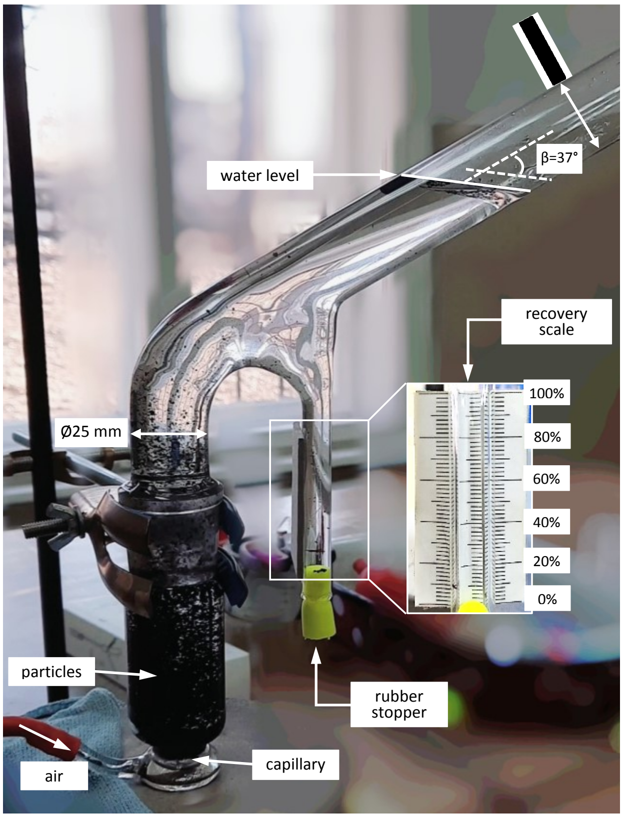


Figure 3 Monobubble Hallimond tube with recovery scale

The experimental apparatus consists of a glass tube placed on a magnetic stirrer, a capillary for creating air bubbles and a digital camera. A sample of toner particles, with a solids concentration of 2.5 g/L, was placed in a 120 ml glass tube and diluted with constant volume of distilled water to create the toner suspension. The suspension was mixed at 400 rpm for fixed period of time, and then a constant air flow of 40 L/h through the capillary of the Hallimond tube generated bubbles, and the process of particle flotation was recorded with a digital camera in a time interval of 60 min. Toner recovery was read directly from the recovery scale. After drying, the contact angle was determined on floatable and non-floatable particles.

The results are presented in the form of recovery of floatable particles (I), as a function of flotation time (t), in order to represent the flotation kinetics of the toner particles through a suitable flotation model. All microflotation experiments were performed in distilled water at a temperature of 20 °C without a collector.

RESULTS AND DISCUSSION

Figure 4 shows flotation recovery of floatable toner particles as a function of time. In general, increasing the flotation time resulted in an increase in the flotation recovery of floatable toner, and higher recovery was achieved at longer flotation times.

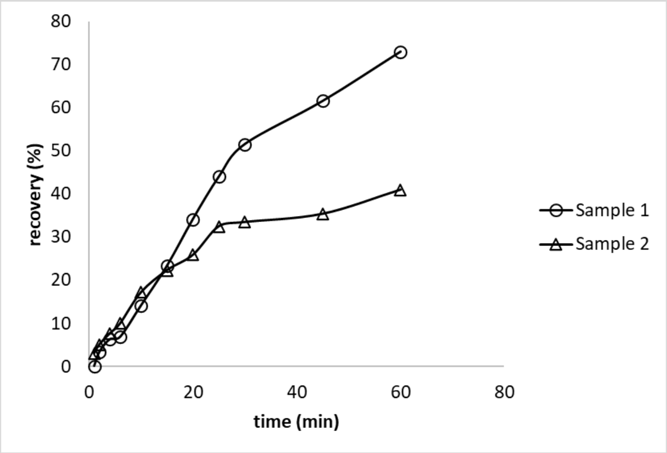


Figure 4 Microflotation kinetics of toner

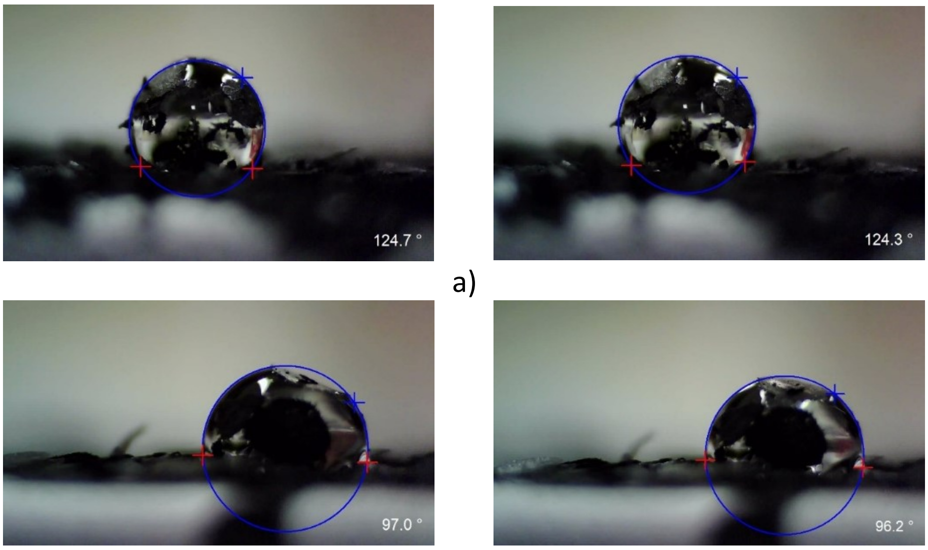
At the 15 minutes of microflotation, the recovery of both toner samples was 22%. After the 25 minutes of microflotation, toner recovery on sample 1 (d_{sr}=800 µm, regular round plate-like particles) initially increases with the time, and max achieved recovery value was 72% after 60 minutes. For the same time interval (after 25 minutes of microflotation), toner recovery on sample 2 (d_{sr}=500 µm, regular round plate-like particles and irregular plate-like particles), levels off at a maximum constant value (around 36%). Drzymala emphasized in his research [10] that the mentioned (for sample 2) generally occurs between 10 and 15 minutes of flotation, depending on the size of the particles (10 minutes for calcite d_{sr}=180 µm, 15 minutes for calcite d_{sr}=112.5 µm). From Figure 4, it can be seen that in these studies it takes a longer time

(25 minutes) to achieve a constant toner recovery value with a larger d_{sr}=500 µm, which indicates that in addition to the particle size, the shape of the particles also has a great influence (calcite has a cubic shape and toner has a regular round plate and an irregular plate shape).

Many authors in their research [1-3], have shown that the influence of the shape of particles on the floatability is of great importance. It was emphasized that irregular, elongated and plate-shaped particles have a higher recovery compared to round and spherical particles during the flotation of minerals that have a higher density [3]. Schmidt and Berg [11] based their research on small round plate-like toner particles, which have a significantly lower density than minerals, and concluded that these particles are less likely to adhere to an air bubble.

From Figure 4, it can be seen that the recovery of toner with round flat particles is significantly higher (by 32%), compared to toner with irregular plate shaped particles, which may indicate that mechanical carryover occurred. This assumption should be verified in subsequent studies by monitoring the dependence of the toner flotation kinetics and the pH value of the solution, and which would confirm the observations of the authors Drzymala and Lekki [12].

The toner particles exhibited a high floatability without the addition of a collector. This can be understood by considering the measured value of the contact angle (114.2°), which indicates that the toner samples are hydrophobic.



a)

b)

Figure 5 Images of water droplets onto surface of sample 1 after flotation
a) floatable particles after 30 s (left), after 60 s (right) and b) non-floatable particles after 30 s (left), after 60 s (right)

It should be emphasized that no significant differences were observed when measuring the contact angle of sample 1 and sample 2, and that the lower recovery obtained for sample 2 can be attributed to the different shape and size of the particles.

Given that the assessment of flotation kinetics requires the analysis of the flotation rate, first- and second-order flotation models were used in the paper for the assessment of toner flotation kinetics [5,13-15].

Pan et al. [13] in his research described the flotation kinetics of ink particles under laboratory conditions by the classical model of the first order kinetics using the expression (1), and conclusion was that the value of kinetic constant of flotation, k, can be determined from the expression (1) as long as the flotation time is short and the diameter of the ink particles is constant.

$$ln(1/(1-I)) = kt \tag{1}$$

where: I- flotation recovery of ink particles in froth product, t- flotation time, k- kinetic constant of flotation.

Trumic and Antonijevic [15] in their research on the flotation of cube-shaped toners made the observation that only for a short flotation time, up to 4 min, the particle flotation process follows first-order kinetics with a good correlation, which also Nikolaev [5] confirmed in the case of toner flotation of spherical shape for a total flotation time of 2 min.

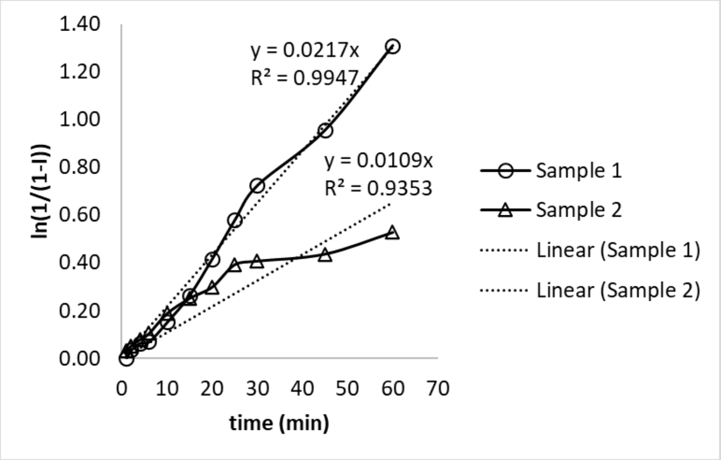


Figure 6 The classical first order fitting of flotation responses, fitting for the total flotation time 60 min

In Figure 6, it can be clearly seen that for sample 2 (d_{sr}=500 µm, regular round plate particles and irregular plate particles), the break between the two linear parts of each curve implies that two flotation mechanisms are operating: one is a short time mechanism and the other longer time mechanism. That is why Pan [13] implied that no single value of the constant k is sufficient to express the data even if the minimum value R^2 Volk [16], for a correlation is reached (R_{min}^2=0.447). For sample 1 (d_{sr}=800 µm, regular round plate-like particles), for the total tested time of 60 min, the model is valid, which indicates that the uniformity of the particles and the shape of the particles have a significant impact on the application of this model.

The second model (Figure 7) that was tested is the first-order model modified by Trumic and Magdalinovic, expression (2) [15].

$$I/(1-I) = kt \tag{2}$$

where I- flotation recovery of ink particles in froth product, t- flotation time, k- kinetic constant of flotation.

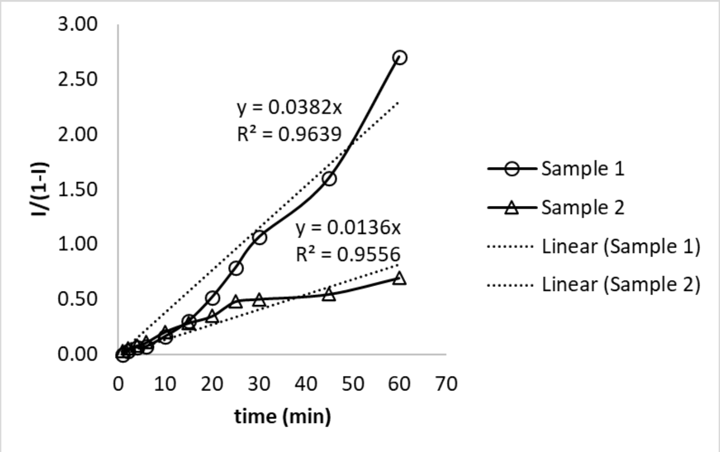


Figure 7 The modified first order by Trumic and Magdalinovic fitting of flotation responses, fitting for the total flotation time 60 min

The correlation coefficient R^2, for sample 2, has a higher value and the points on the curve better follow the dependence of the straight line, that is, only, the mechanism for a long time of flotation is present which can be represented by single value of the constant k.

Several authors [5,17] obtained the linearity of experimental toner flotation data via second-order flotation kinetics, using expression (3).

$$t/I = (t/I_\infty) + (1/I_\infty^2 k) \tag{3}$$

where I_∞- maximum flotation recovery, I- flotation recovery of ink particles in froth product, t- flotation time, k- kinetic constant of flotation.

For both samples (Figure 8), it can be said that there is a break between the two linear parts of each curve, implying that two flotation mechanisms are functioning: one is a short time mechanism of up to 6 min and the other is a longer time mechanism. The correlation coefficients, R^2, have a significantly higher value, but linearity was not achieved for the total flotation time of 60 min. Nikolaev [5] showed that the flotation kinetics of the toner, spherical in shape, for a short flotation time of 2 min, is described by second order flotation model.

There are several studies [5,14,15] in the literature showing first-order and second-order kinetics for the flotation of toners with the smallest particle sizes, spherical and cubic, in short flotation times. Therefore, in this work there are no experimental data that could be compared with the results obtained for coarse particles, regular and irregular in shape, in a long time of flotation.

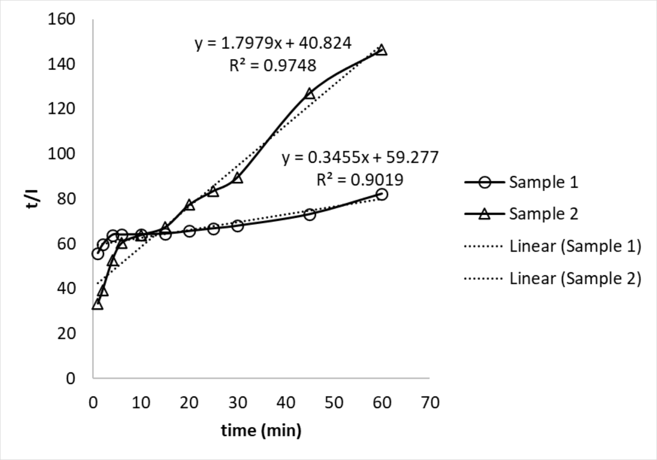


Figure 8 The second order fitting of flotation responses, fitting for the total flotation time 60 min

CONCLUSION

Coarse toner particles, consist of iron oxide, regular round and irregular plate-like shape have high degree of hydrophobicity. High toner flotation recovery is achieved in pure water with round plate-shaped toners after prolonged time. The toner, which contains 50% of the irregular plate-shaped toner, did not float effectively even after a long time of flotation, (toner flotation recovery reduced by approximately 50%), due to the influence of particles of irregular plate shape. Generally, flotation kinetics of the toner (coarse plate particles), is described by first order flotation model. The flotation rate constant k, was slightly lower in the flotation of toners containing regular and irregular plate-shaped particles.

A flotation test using a Hallimond tube of known hydrodynamic pattern can enable the distinction between mechanical transfer, non-contact and collector flotation. In order to confirm the assumption that under the given conditions mechanical carryover of round plate particles took place, further research is necessary.

ACKNOWLEDGEMENT

"The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-47/2023-01/200131".

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ISBN-978-86-6305-133-1