

**FLOTATION KINETICS OF MAGNESIUM HYDROXIDE SEDIMENTED
FROM SEA WATER****KINETIKA FLOTACIJE MAGNEZIJUM HIDROKSIDA TALOŽENOG IZ
MORSKE VODE**

M. Maksimović, Lj. Vukić, Đ. Vojinović, J. Mandić

*University of Banjaluka, Faculty of Technology, RS, BiH***Abstracts**

Synthetic sea water has been taken as a referential sample, in which $Mg(OH)_2$ had been sedimented, in order to reduce biological effects and confirm reproducibility of results of the familiar composition sample. The synthetic sea water was prepared according to the scientifically developed procedure. Flotation experiments were performed in the apparatus for flotation under pressure and recoveries of floated $Mg(OH)_2$ were determined depending on the time of flotation. The results obtained on the referential sample of the synthetic water were also tested on the sample of natural sea water and presented comparatively during work. Flotation kinetics is in most cases described by an equation of the first or second degree. However, it was established that flotation kinetics of $Mg(OH)_2$ as chemical sediment with both types of prepared magnesium hydroxide suspension, sedimented in both the synthetic and natural sea water corresponded to the velocity of reaction $n = 1.5$ degree, which fully corresponds to Horst Morris's theoretical postulates in the theory of flotation kinetics.

Key words: *magnesium hydroxide, sea water, flotation, kinetics*

Izvod

Za referentni uzorak u kojem je taložen $Mg(OH)_2$ upotrebljena je sintetska morska voda, kako bi se umanjili biološki efekti i potvrdila reproducibilnost rezultata uzorka poznatog sastava. Sintetska morska voda pripremana je prema naučno razrađenoj proceduri. Flotacijski eksperimenti izvedeni su u aparaturi za flotaciju pod pritiskom i određena su iskorišćenja flotiranog $Mg(OH)_2$ u zavisnosti od vremena flotacije. Dobijeni rezultati na referentnom uzorku sintetske morske vode testirani su i na uzorku prirodne morske vode i u radu komparativno prezentovani. Kinetika flotacije se u najvećem broju slučajeva opisuje jednačinom prvog ili drugog reda. Međutim, ustanovljeno je da kinetika flotacije $Mg(OH)_2$ kao hemijskog taloga kod oba tipa pripremljene suspenzije magnezijum hidroksida, taloženog i u sintetskoj i u prirodnoj morskoj vodi, odgovara brzini reakcije $n = 1,5$ reda, što se u teoriji kinetike flotacije u potpunosti slaže sa teorijskim postavkama Horst-Morris-a.

Ključne riječi: *magnezijum hidroksid, morska voda, flotacija, kinetika*

1. INTRODUCTION

The earliest records on obtaining magnesium oxide from sea water speak about short period of production existence in 1885 on the Mediterranean coast of France near the place Sète by application of lime as sedimenting substance. Obtaining magnesium hydroxide important for pharmaceutical application was started by the company “Marine Chemical Co.” in 1935 from South San Francisco applying shells of oyster as a lime source [1]. Production of magnesium from sea water represents approximately 1/3 of the world production of magnesium and its derivatives, i.e. 6 Mt in 1972 [2]. At present, there are a few plants in Europe, North America and Japan for production of magnesium oxide out of sea water. Apart from this, plants based on production of magnesium chlorides or sulphates from salty waters or stem lye obtained upon separation of kitchen salt by the sun energy [3] also operate. Majority of these plants operates on the principle of conventional flotation procedure. Lately, there are efforts to advance the procedure by conducting the flotation under pressure by the water carbonated with air, so-called DAF procedure (Dissolved Air Flotation), which significantly increases recovery of floated magnesium hydroxide [4] as well as separation of other water dissolvable resources by application of specific flotation reagents [5]. The DAF procedure found its application in both the processes of separation of minerals from water and in preparation of raw and treatment of waste water [6,7]. This paper presents results of research conducted over flotation kinetics of magnesium hydroxide floated by unconventional procedure of flotation in the apparatus under pressure. In order to realise an elementary act of flotation, i.e. adsorption of mineral particle on an air bubble, it is necessary that the particles collide with the air bubble in the flotation suspension, that is, the mineral particle and the bubble must find themselves in a certain position in space. In the process of flotation there are forces of attraction and tendencies of creating complex P, but also there are resistances to creating complex R, so that the velocity of flotation as well as velocity of any process is expressed as follows:

$$v_{float} = \frac{m_{float}}{\tau_{float}} = K \frac{\Delta P}{R} \quad (1)$$

that is, in the first approximation the velocity of flotation can be defined by the quantity of floated solid phase in a time unit. Provided that the quantity of floated solid phase is marked as recovery, it can be said that in the first approximation the flotation velocity is as follows:

$$v_{float} = \frac{m_{float}}{\tau_{float}} = \frac{\varepsilon}{\tau} \quad (2)$$

Flotation recovery depending on time is shown in Figure 1.

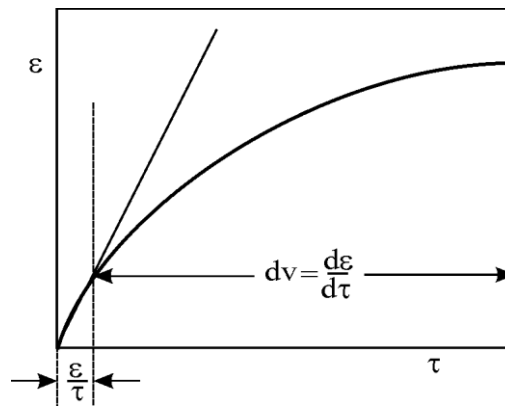


Figure 1. Flotation recovery depending on time

The figure shows that the expression (2) is valid only at the beginning of the flotation and subsequently it is not valid because the velocity expressed like this is not a direction. The longer the flotation, the number of particles of useful component in the suspension is smaller, and the number of collisions between bubbles and mineral particles is reduced. Therefore, with time, in the equal time intervals, smaller and smaller recovery increments are obtained, $\Delta\varepsilon$ is being reduced.

Therefore, the more appropriate expression for flotation velocity is as follows:

$$dv_{\text{flot}} = \frac{d\varepsilon}{d\tau} \quad (3)$$

However, analogous to the reaction velocity, it is more correct to take the ratio between the floated particles and the unfloated ones (Beloglazov):

$$\frac{dx}{(x_0 - x)^n} = k_1 N \varphi d\tau = K d\tau, \quad (4)$$

where: x ; $(x_0 - x)$, number of the floated particles and the unfloated ones, respectively,
 N , number of gas bubbles during flotation time,
 φ , solidity of particles connection - bubble,
 k_1 , characteristic constant,
 K , flotation velocity constant.

The exponent (n) can have different values, but the flotation kinetics is in most cases described by equations of the first and second degree.

Beloglazov takes it that $n=1$, therefore the flotation velocity constant is expressed as follows:

$$K = \frac{\ln \frac{1}{1-\varepsilon}}{\tau} \quad (5)$$

that is, the flotation recovery is:

$$\varepsilon = 1 - e^{-K\tau} \tag{6}$$

Other floaters partially even disagree with Beloglazov, but say that n does not equal 1, and that it is according to: Mitrofanov: $n=2$; Horst Morris: $n=1,5$; Berger: $n=1-6$. It can be claimed that the exponent value $n=1-2$ is the most appropriate, because the flotation is not pure “monomolecular” reaction of first degree. It can be assumed that even two particles can collide with the bubble at the same time, and not only one as assumed by Beloglazov, but it happens more rarely that 2 or even 6 particles collide as assumed by Berger. Therefore, we are somewhere in the middle between the reaction of I and II degree. If the exponent $n=2$ is accepted as with Mitrofanov, then the flotation velocity constant is as follows:

$$K = \frac{\varepsilon}{\tau(1-\varepsilon)}, \tag{7}$$

that is:
$$\varepsilon = \frac{K\tau}{K\tau + 1} \tag{8}$$

The flotation time is calculated from the above expressions in case that recoveries and average value of the flotation velocity constant are familiar. If constant value is obtained for the velocity constant in the flotation than the $\varepsilon=f(\tau)$ in the diagram is: faulty recoveries, and directions of the flotation velocity constants can be drawn in the same diagram (Figure 2).

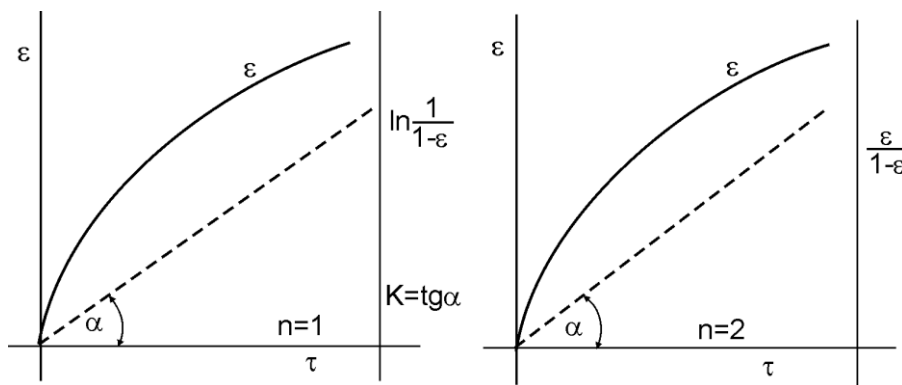


Figure 2. Flotation recovery depending on the flotation time and directions of flotation velocity constants ($n=1, n=2$)

When the average value of the flotation velocity constant has been experimentally determined K_{sr} , the flotation time can be determined in accordance with the following expressions:

$$\tau_{flot} = \frac{\ln \frac{1}{1-\varepsilon}}{K_{sr}}, n=1 \tag{9}$$

$$\text{that is, } \tau_{\text{flot}} = \frac{\varepsilon}{K_{\text{sr}}}, n=2 \quad (10)$$

2. EXPERIMENTAL PART

Referential samples of synthetic sea water in which $\text{Mg}(\text{OH})_2$ has been sedimented were prepared using Lyman and Fleming method [8], and the samples of original sea water were taken from the Mediterranean Sea, coastal area near the town Šibenik. Rare suspension of magnesium hydroxide for flotation was prepared stoichiometrically by sedimenting of $\text{Mg}(\text{OH})_2$ in 1dm^3 of the referential sample of synthetic and natural sea water. Sedimenting of $\text{Mg}(\text{OH})_2$ was conducted with 5% solution of sodium hydroxide in the duration of 1 min. including subtle mixing in magnetic mixer. Subsequently, the flotation reagents were added into the suspension as follows: collector sodium – dodecil hydrogensulphate Na-DHS, type A flocculant, produced in factory “Župa“ from Kruševac as well as bubble-originator n-octyle alcohol in optimal quantities as follows: $0.1\text{g}/\text{dm}^3$ of Na-DHS; $0.001\text{g}/\text{dm}^3$ of flocculant A_4 and 0.017g of n-octyle alcohol. Upon optimal time of suspension agitation and flotation reagents the suspension flotation was performed in the flotation apparatus with mechanical agitation and aeration and also the flotation in apparatus for flotation under pressure was performed. Only after 5 minutes of the flotation duration, the quantity of unfloated $\text{Mg}(\text{OH})_2$, that is, the magnesium retained in the apparatus flotation cell, was being determined complexometrically.

Based on the analyses of the retained magnesium in the flotation cell, recovery of flotation was being determined based on the balance of magnesium mass (1dm^3 of sea water contains 1.350g of Mg).

Due to significantly increased quantities of the flotation foam, which occurs during flotation of $\text{Mg}(\text{OH})_2$ in the apparatus for conventional procedure, research over flotation of $\text{Mg}(\text{OH})_2$ in the apparatus for flotation under pressure was approached. Figure 3. shows laboratory apparatus for flotation under pressure.

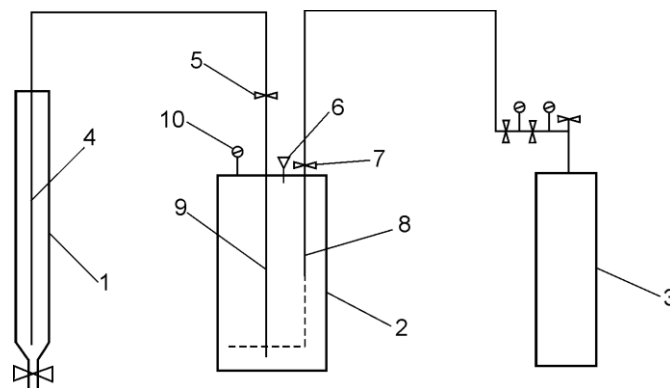


Figure 3. Laboratory apparatus for flotation under pressure

Flotation cell (1) is made of laboratory glass with a tap at the bottom for letting out the flotation suspension upon the experiment completion. The container under pressure (2) is made of a fire extinguisher, 8 dm³ in capacity, which is filled with distilled water through a funnel (6). Upon the filling, the tap on the funnel is closed. In the container (2), which is connected to the bottle for compressed air, the air which carbonates the distilled water is let in. During this, the valve (5), which serves for letting out the carbonated water in the flotation cell, is closed. When the pressure on manometer (10) reaches 5 bars the air intake is stopped. With this step the apparatus is prepared for the experiment. The experiment is performed in such way that 50 cm³ of previously prepared flotation suspension of magnesium hydroxide is poured in the flotation cell. Then, through a probe (4), with careful opening of the valve (5), carbonated water under pressure is let in the flotation suspension from the container (2). The quantity of carbonated water let in is related to dilution of the flotation suspension at which the research is performed. In the flotation suspension, immediately after letting in the carbonated water, due to reduction of pressure from 5 bars to the atmosphere pressure, separation of air bubbles starts, which implement floating of Mg(OH)₂ particles. Upon completion of the flotation process through the tap on the flotation cell (1) separating of the suspension from the flotation concentrate is performed. The flotation suspension is let out into the measurement flask of 250 cm³, which is filled with distilled water up to the line, and then complexometrically the quantity of unfloated Mg(OH)₂ is determined.

3. RESULTS AND DISCUSSION

Previously performed experiments with the conventional flotation procedure of Mg(OH)₂, sedimented from synthetic and natural sea water, reached the following recoveries of floated Mg(OH)₂:

- For synthetic sea water: $\varepsilon=89,1\%$
- For natural sea water: $\varepsilon=87,8\%$

The results of the flotation time influence on recovery of Mg(OH)₂ research, performed in apparatus under pressure, are shown in Figure 4.

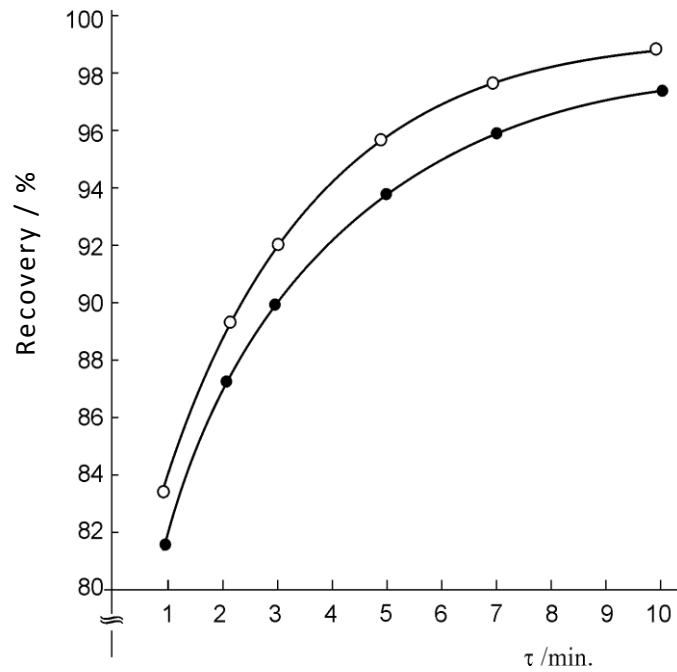


Figure 4. Influence of the flotation time on recovery of $Mg(OH)_2$, o – synthetic sea water; • - natural sea water

Based on the obtained values of recoveries in the flotation time, an estimation of the flotation velocity constants is performed for reactions of I and II degree and 1.5 degree, i.e.: K_1 , K_2 i $K_{1.5}$ and the values obtained are shown diagrammatically $K=f(\tau)$ in Figure 5 for synthetic and in Figure 6 for natural sea water.

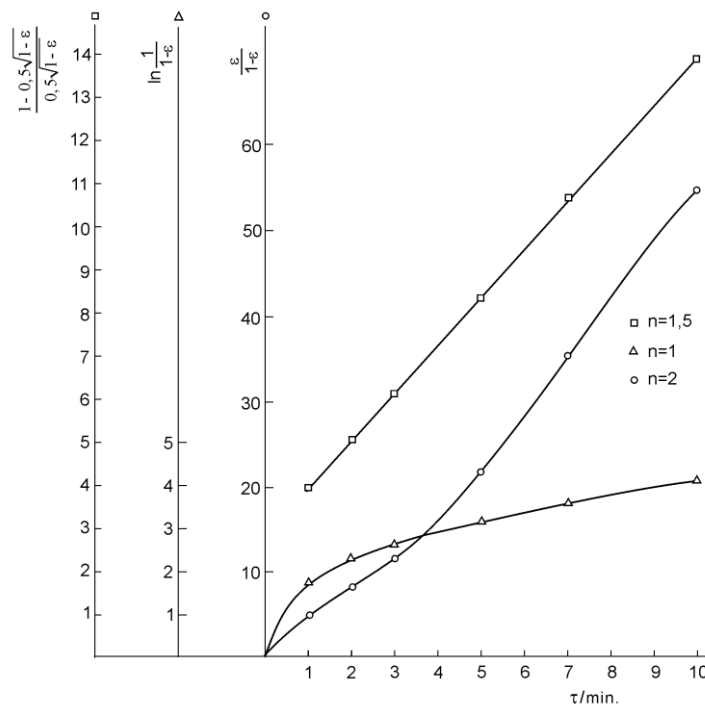


Figure 5. Flotation kinetics of $Mg(OH)_2$ sedimented in synthetic sea water and □ - direction of the flotation constant velocity, $n=1.5$

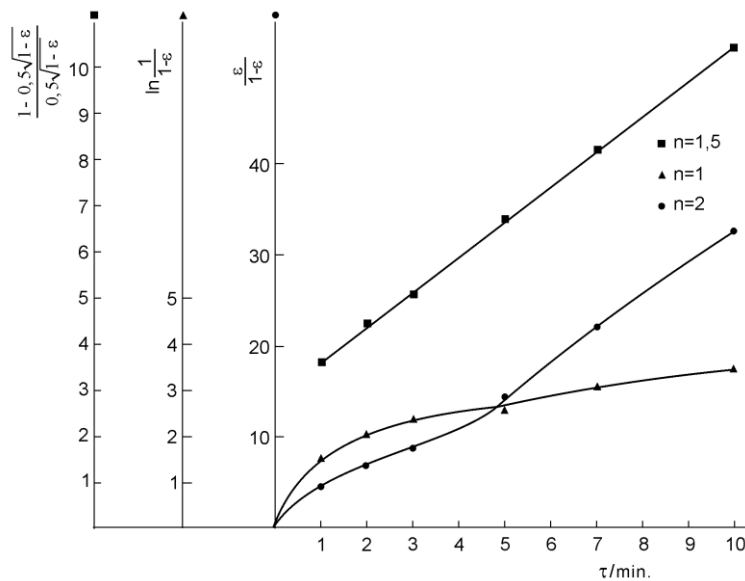


Figure 6. Flotation kinetics of $Mg(OH)_2$ sedimented in natural sea water and \blacksquare - direction of the flotation constant velocity, $n=1.5$

The diagram shows that in both cases, the estimation of the flotation velocity constant according to the expression in which the value 1.5 is taken for the exponent n , a direction is obtained, which implies that kinetics of 1.5 degree reaction is dealt with.

4. CONCLUSION

This paper proves that the flotation under pressure in comparison with the conventional flotation procedure reaches significantly higher recoveries of floated $Mg(OH)_2$ and the time required for flotation suspension treatment is up to 10% shorter, it reduces the time of flotation as well as reduced formation of foam as a consequence of smaller collectors quantity application and other flotation reagents and calmer regime of flotation in comparison with the conventional procedure. It has been established that the kinetics flotation of $Mg(OH)_2$ corresponds to the reaction of 1.5 degree.

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