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EFFECT OF 818A AND 827N FLOCCULANTS ON SEAWATER MAGNESIA PROCESS

VPLIV 818A IN 827N FLOKULANTA NA PROCES PRIDOBIVANJA MAGNEZIJE IZ MORSKE VODE

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Possibilities for the application of the anionic 818A flocculant (polyacrylamide) produced by the Dutch firm Hercules have been studied in order to increase the settling rate of magnesium hydroxide from seawater and to define the optimum conditions during the precipitation process. The efficiency of the 818A flocculant has been compared to the nonionic 827N flocculant. Examinations were carried out with different degrees of completeness of precipitation and with different quantities of the 818A flocculant. The dependence obtained was described by the appropriate analytical expression. The study has shown that the settling rate is higher during nonstoichiometric precipitation, i.e. precipitation when the quantity added is lower than the stoichiometrically required quantity of the precipitation agent. This has been explained by the $Mg(OH)_2$ particle model. In order to interpret the experimental data obtained by batch-settling tests a calculation of a continuous thickener was made applying the Kynch theory. It was observed that at 100% precipitation the quantity of the precipitate obtained was 23.05 kgh^{-1}, while that obtained at 80% precipitation was 52.69 kgh^{-1}, which indicates a considerable increase in the thickener productive capacity. Thus, it could be seen that the settling rate of the magnesium hydroxide slurry was very important in computing the thickening area required.

Key words: magnesium hydroxide from seawater, settling rate, nonstoichiometric precipitation, effect of flocculant

Preiskovana je bila uporaba anionskega 818A flokulanta (poliakriamida) nizozemskega proizvajalca Herkules z namenom povečanja hitrosti usedanja magnezijevega hidroksida iz morske vode in definiranja optimalnih pogojev usedanja. Učinkovitost flokulanta 818A smo primerjali z učinkovitostjo 827N flokulanta. Preiskave so bile narejene pri različnih stopnjah usedanja in različnih količinah dodanega 818A flokulanta. Dobljene odvisnosti so opisane z odgovarjajočimi analitičnimi izrazi. Rezultati preiskav kažejo na znatno povečanje hitrosti usedanja delcev pri nestehiometričnem usedanju, to je, usedanju pri uporabi manjše količine usedalnega sredstva od stehiometrično potrebne količine. Navedeno se pojasnjuje z modelom delca $Mg(OH)_2$. Na osnovi ugotovljenih usedalnih karakteristik suspenziji mahnezijevega hidroksida v mezuri pri pogojih diskontinuiranega usedanja, je bil narejen preračun za kontinuirano usedanje z uporabo Kynchove teorije. Pri 100% usedanju se pridobi 23,05, pri 80% usedanju pa 52,69 kgh^{-1} magnezijevega hidroksida, kar predstavlja znatno povečanje proizvodnosti usedalnika. Iz ugotovljenega je razvidno, da je hitrost usedanja suspenzije magnezijevega hidroksida zelo važna količina v proračunu potrebne površine usedalnika.

Ključne besede: magnezijev hidroksid, morska voda, hitrost usedanja, nestehiometrično usedanje, vpliv flokulanta

1 INTRODUCTION

The seawater magnesia process[1-6] is chemically very simple in principle, requiring only the addition of an alkaline base such as dolomite lime to precipitate the magnesium salts present in seawater as magnesium hydroxide. This reaction is the crucial part of the process.

The central problem is how to increase the magnesium hydroxide settling rate[7-10] since the magnesium hydroxide suspensions are characterized by low settling rates; also the precipitate is very difficult to filtrate. The settling rate is the "bottleneck" of this technology and it is one of the most important unit operations controlling the cost of production. The settling rate can be significantly increased if small quantities of organic long chain polymers[8-10] are used. In this study we have investigated the possibility of improving the settling rate by using the anionic (818A) and nonionic (827N) polyacrylamide flocculants for obtaining magnesium hydroxide from seawater with dolomite lime as the precipitation agent.

2 EXPERIMENTAL

The content of magnesium oxide and calcium oxide in the seawater used for the precipitation of magnesium hydroxide was MgO = 2.2339 g dm^{-3} and CaO = 0.5810 g dm^{-3}. The composition of dolomite lime used was as follows: MgO = 40.90 mass.%, CaO = 57.89 mass.%, SiO_2 = 0.102 mass.%, Fe_2O_3 = 0.319 mass.% and Al_2O_3 = 0.866 mass.%.

The seawater was pretreated for precipitation of magnesium hydroxide to remove the bicarbonate and carbonate ions by adding a defined quantity of H_2SO_4 with on-line control through pH measurement (pH = 3.8-4.0), and degassing the acidified water to remove the released CO_2. Degassing is accomplished in a desorption tower by blowing air.

Precipitation of magnesium hydroxide took place after pre-treatment of seawater.

The experimental procedure was similar to that employed in previous investigations[8,11].

Experiments were carried out in graduated glass cylinders of the same diameter. 1mm of the height of magnesium hydroxide precipitate is equivalent to a volume of 2.9268 cm^3 of the suspension. This method is suitable for tests with solid-liquid systems containing at least 0.1 mass.% of solid materials.

The powdery 818A and 827N flocculants used in these examinations were synthetic high molecular weight polymers (M(818A) = 3-4x10^6 , M(827N)=2x10^6) which are soluble in water. When in solution they ionize according to their ionic nature. The nonionic type (827N) can be dispersed in water and has a weak anionic character in dispersion. They are both with 100 mass percentage of active matter (the actual activity of the specific component from which it was prepared). The active groups over the molecular chain should probably be acryl and/or amide groups, because Hercofloc 818A and 827N are high molecular polymers of the poly-acrylamide type. The functionality (the number of active groups in relation to the chain length) of these flocculants was very low for the nonionic 827N flocculant and low for the anionic 818A flocculant. The prepared solution contained 0.05 mass percentage of active matter, and was prepared by dissolving 0.1 g of the flocculants in 190 cm^3 of distilled water, with gentle mixing. 1 cm^3 of the solution contained $5 \cdot 10^{-4}$ g of the flocculant 818A and/or 827N.

All the results presented are an average of 5. The results obtained were within the experimental error of approx. ± 0.5 mm. All measurements showed good reproducibility. Measurements were carried out at a temperature of 18.5 ± 1°C.

3 RESULTS AND DISCUSSION

Figures 1-4 show settling curves for different degrees of completeness of precipitation of magnesium hydroxide from seawater with the addition of 1.5, 1.7, 1.9, and 2.5 cm^3 of the 818A flocculant per 500 cm^3 of seawater respectively.

Figure 5 shows settling curves for different degrees of completeness of precipitation with the addition of 5.0 cm^3 of the 827N flocculant per 500 cm^3 seawater.

The results obtained indicate a difference in the settling rate during complete (stoichiometric) and incomplete (nonstoichiometric) precipitation, i.e. when the quantity of the precipitation agent is lower than that required stoichiometrically.

Different degrees of completion of precipitation indicate the difference of initial mass concentrations in such studies.

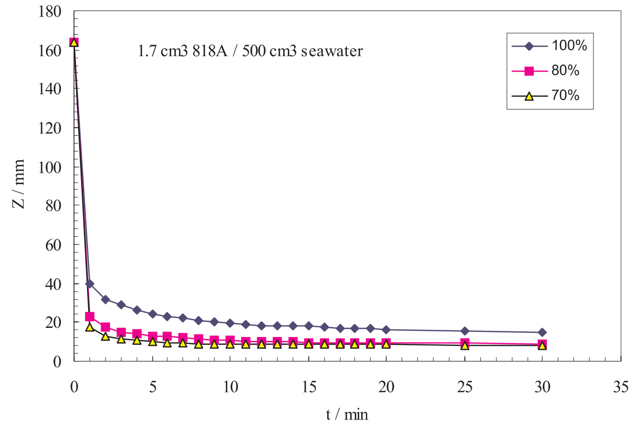

Figure 2: The dependence of precipitate level (Z) upon the setting time (t), for different degrees of precipitation completeness, with addition of 1.7 cm^3 of the 818A flocculant per 500 cm^3 of seawater

Slika 2: Odvisnost višine usedline (Z) v odvisnosti od časa usedanja (t) pri različnih stopnjah popolnosti usedanja magnezijevega hidroksida iz morske vode pri dodatku 1,7 cm^3 flukolanta 818A/500cm^3 morske vode

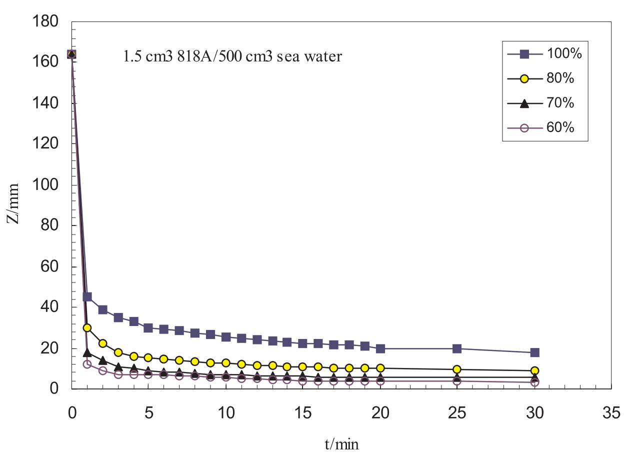

Figure 1: The dependence of the precipitate level (Z) upon the setting time (t), for different degrees of precipitation completeness, with addition of 1.5 cm^3 of the 818A flocculant per 500 cm^3 of seawater

Slika 1: Odvisnost višine usedline (Z) v odvisnosti od časa usedanja (t) pri različnih stopnjah popolnosti usedanja magnezijevega hidroksida iz morske vode pri dodatku 1,5 cm^3 flokulanta 818A/500 cm^3 morske vode

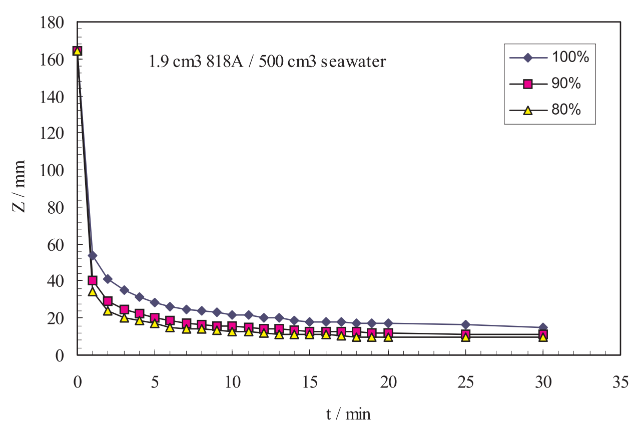

Figure 3: The dependence of the precipitate level (Z) upon the setting time (t), for different degrees of precipitation completeness, with addition of 1.9 cm^3 of the818A flocculant per 500 cm^3 of seawater

Slika 3: Odvisnost višine usedline (Z) v odvisnosti od časa usedanja (t) pri različnih stopnjah popolnosti usedanja magnezijevega hidroksida iz morske vode pri dodatku 1,9 cm^3 flukolanta 818A/500cm^3 morske vode

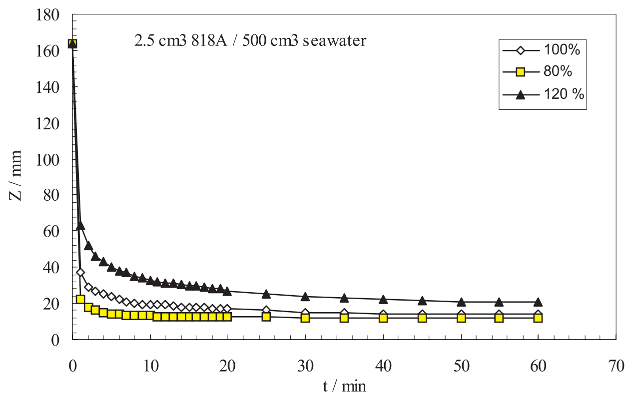

Figure 4: The dependence of the precipitate level (Z) upon the setting time (t), for different degrees of precipitation completeness, with addition of 2.5 cm^3 of the 818A flocculant per 500 cm^3 of seawater

Slika 4: Odvisnost višine usedline (Z) v odvisnosti od časa usedanja (t) pri različnih stopnjah popolnosti usedanja magnezijevega hidroksida iz morske vode pri dodatku 2,5 cm^3 flukolanta 818A/500cm^3 morske vode

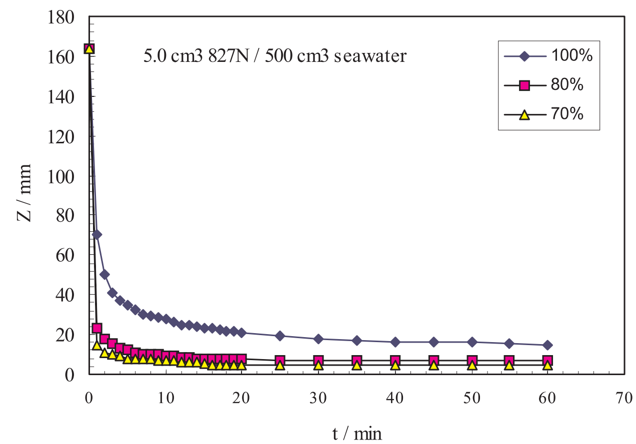

Figure 5: The dependence of the precipitate level (Z) upon the setting time (t), for different degrees of precipitation completeness, with addition of 5.0 cm^3 of the 827N flocculant per 500 cm^3 of seawater

Slika 5: Odvisnost višine usedline (Z) v odvisnosti od časa usedanja (t) pri različnih stopnjah popolnosti usedanja magnezijevega hidroksida iz morske vode pri dodatku 5,0 cm^3 flukolanta 827N/500cm^3 morske vode

Figures 1 to 5 show that the settling rate is higher the lower the initial mass concentration of magnesium hydroxide.

If the mass concentration of the solid phase in suspension increases, density and viscosity of the suspension increase, and thus the settling rate decreases.

In concentrated suspensions porous aggregates are formed that significantly reduce the settling rate. Thus, the suspension properties are largely affected by mass concentration, and, by association, by the quantity of the reagent (precipitation agent) added. In other words, settling taking place with excess Mg^{2+} ions is more efficient than that with surplus OH^- ions, both as regards the settling rate and the filtration rate.

Taking into account that the mass concentration of magnesium hydroxide, i.e. the mass of solids per unit volume of slurry varies for different degrees of completeness of the precipitation, concentrations were equaled mathematically in order to eliminate their effect on the settling rate. The material balance for the solid phase in the slurry, used in the comparison of stoichiometric and nonstoichiometric precipitation, has the form:

$$\frac{Z_o}{Z_1} = \frac{\gamma_o}{\gamma_1} \qquad (1)$$

where Z is the height of the interface, and γ the mass concentration of the solid phase. Subscript "o" denotes 100% (stoichiometric) precipitation, and the subscript "1" incomplete (nonstoichiometric) precipitation.

It then follows that Z_1 is the height which the slurry would occupy if all the solids phase present were at the mass concentration γ_o.

Starting from this value of Z_1 i.e. the value for which concentrations are equal for different degrees of completeness of precipitation, the change in the precipitate level, $\Delta Z = Z_1 - Z_2$, was determined for the time interval of 20 minutes. **Table 1** shows the values obtained for Z_1 and Z_2 where Z_1 is the precipitate level determined according to expression (1) and Z_2 is the precipitate level 20 minutes after Z_1. The relations obtained ΔZ = f (% stoich.) **(Figure 6)** indicate the degree of completeness of precipitation for which the quantity of the flocculant added is the optimum one. For the maximum value of change in the precipitate level ΔZ, that degree of completeness of precipitation is determined for which the settling rate is maximal for the flocculant addition examined.

Table 1: Dependence of Z_1 and Z_2 on the degrees of completeness of precipitation for different additions of flocculant 818A and 827N

Tabela 1: Odvisnost Z_1 in Z_2 od stopnje popolnosti usedanja pri različnih količinah dodatka flokulantov 818A in 827N

Flocculant	cm^3 of the flocculant per 500 cm^3 of sea water	Degree of completeness of precipitation %	Z_1/mm	Z_2/mm
818A	1.5	60	12.00	4.00
		70	14.00	5.50
		80	16.00	9.50
		100	20.00	17.00
	1.7	70	13.00	8.50
		80	15.00	9.50
		100	18.50	15.00
	1.9	80	15.00	10.00
		90	17.00	11.00
		100	19.00	15.00
	2.5	80	18.00	12.50
		100	22.50	16.00
		120	27.00	22.00
827N	5.0	70	15.00	5.00
		80	17.50	7.00
		100	22.00	16.50

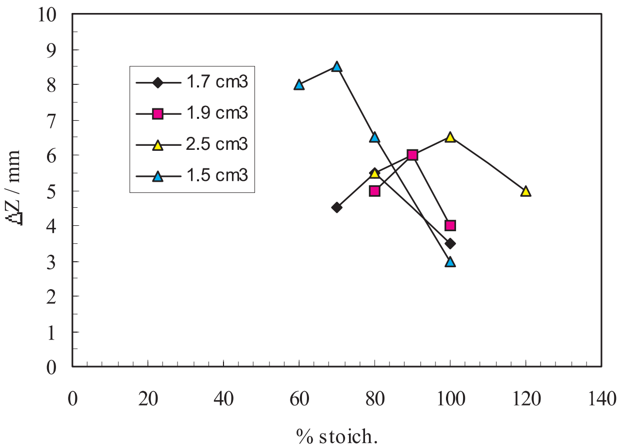

Figure 6: The dependence of the change in the precipitate level (ΔZ) upon the degree of precipitation completeness of magnesium hydroxide from sea water, with different additions of the 818A flocculant per 500 cm^3 of seawater

Slika 6: Odvisnost spremembe višine usedline (ΔZ) od stopnje popolnosti usedanja magnezijevega hidroksida iz morske vode pri različnih količinah dodanega flukolanta 818A/500cm^3 morske vode

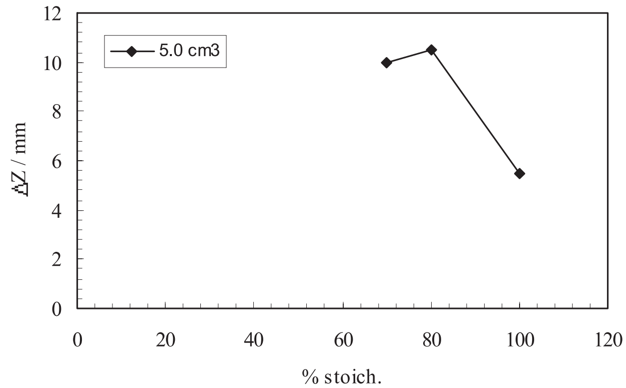

Figure 7: The dependence of the change in the precipitate level (ΔZ) upon the degree of completeness of precipitation of magnesium hydroxide from sea water, with addition of 5.0 cm^3 of the 827N flocculant per 500 cm^3 of seawater

Slika 7: Odvisnost spremembe višine usedline (ΔZ) od stopnje popolnosti usedanja magnezijevega hidroksida iz morske vode pri dodatku 5,0 cm^3 flukolanta 827N/500cm^3 morske vode

In this way, the optimum degree of completion of precipitation for the 818A flocculant addition examined is determined from the settling rate measurement results and vice versa.

The experimental results obtained in examination of the settling rate of magnesium hydroxide from seawater indicate that there is a certain relation between the addition of the 818A flocculant and the degree of completion of precipitation under optimum settling conditions. Therefore, a mathematical analysis of the experimental results was performed in order to obtain a function that would best describe this dependence.

The relations obtained have been described by the polynomials of the second and third degree:

$Y = 2 \cdot 10^{-3}x^2 - 0.276x + 12.56$ $\quad r = 2.20\%$

$Y = 1.333 \cdot 10^{-4}x^3 - 0.032x^2 + 2.587x - 67$ $\quad r = 0.20\%$

where: Y = the volume of the 818A flocculant in cm^3 per dm^3 of seawater, x = the degree of completeness of precipitation, and r = the mean relative error.

The mean relative error, r, being much lower in the function with the form of the third degree polynomial, this function may be concluded to approximate the dependence shown.

To explain this behavior of synthetic polymeric compounds, one could say that the affinity of the 8181A polyelectrolyte to the surface of the solid phase suspended in the suspension is one of its more important properties. These long straight polymeric chains adsorb on to particles suspended forming strong bonds between the polymers and solid particles. After one end of the molecule adsorbs on to the particle, the rest of the molecule is still free in the suspension to adsorb on to other particles, and this leads to fast agglomeration and flocculation of the particles suspended. Owing to this phenomenon (known as "bridging"[12]) large agglomerates of suspended particles and polyelectrolyte chains are formed, that, due to their large diameters and mass, greatly accelerate the settling process.

Bearing in mind the significant advantages of the substoichiometric (80%) precipitation that has been established in previous studies[8,9,13], applicability i.e. efficiency of the nonionic 827N flocculant was examined for this precipitation mode.

The results obtained for the magnesium hydroxide settling rate for 80% precipitation **(Figure 5)** with the addition of the 827N flocculant indicate that much higher quantities of this flocculant are needed to obtain the optimum process conditions. The results obtained for the functional dependence ΔZ = f (% stoich.), **(Fig. 7)**, have shown that the optimum quantity of nonionic 827N flocculant is 5.0 cm^3 per 500 cm^3 seawater, i.e. 10.0 cm^3 per dm^3 of seawater.

The comparison with the previously examined 818A flocculant indicates that, although 1cm^3 of the solution of both examined flocculants contains $5 \cdot 10^{-4}$ g 818A (827N) of flocculant, the quantity of anionic flocculant needed is much lower (approx. 3 times) i.e. that it is more effective in improving the settling rate. The results obtained can lead to the conclusion that the 818A flocculant, being negatively charged, has a greater number of active groups in the molecule chain, while the effect of the nonionic 827N flocculant is most probably based on the polarity of its molecule. This leads to different ionization degrees in the solution.

To interpret the experimental results obtained by analysis of the settling properties of the magnesium hydroxide suspension in a graduated glass cylinder in conditions of discontinuous precipitation (batch-settling tests), a calculation of the continuous thickener[14,15] has been made, applying the Kynch theory.

It was interesting to see how the results obtained were important for the design of the thickener as its construction is the time-controlling factor in plants of this type.

Table 2 shows the characteristic thickener sizes for different degrees of completion of precipitation (80%, 90%, and 100% precipitation) for the optimum addition of the 818A flocculant.

The first part of **table (I)** shows the thickener dimension (diameter and area) values obtained for the constant volume flow of the suspension entering the thickener (Q_{in} = 3.6 $m^3 h^{-1}$). The density (mass of solid per unit volume of slurry) of the underflow after 30 minutes (ρ_{out}) was found to be greater for the lower degree of completion of precipitation, while the thickener area, A, and its diameter, d, are much smaller.

The second part of the **table (II)** shows the values for the range of the volume flow of the suspension fed per unit time to the thickener (Q_{in}) and the thickener dimensions (A and d), based on the constant density of the underflow (ρ_{out} = 45.0297 kg m^{-3}) and the mass flow of the solid phase fed per unit time to the thickener (Q_m = 23.0458 kg h^{-1}). It has been observed that Q_{in} increases, while the thickener dimensions (A and d) significantly decrease with the decrease in the degree of completion of precipitation.

The third part of **table (III)**, shows the values for the range of the volume flow of the entering suspension (Q_{in}) and the quantity of precipitate obtained in the unit of time (Q_m), based on the constant density of the underflow (ρ_{out} = 45.0297 kg m^{-3}) and thickener dimensions (A = 1.77 m^2 and d = 1.5 m). The quantity of magnesium hydroxide obtained (Q_m), the volume flow at the entrance (Q_{in}), and the volume flow at the overflow (Q_p) were found to be much higher for lower degrees of completion of precipitation. The quantity of precipitate obtained in the unit of time was 23.046 kg h^{-1} for 100% precipitation and 52.693 kg h^{-1} for 80% precipitation, which represents an increase in the thickener productive capacity by approximately 128%.

The improvements observed in the settling rate of the magnesium hydroxide obtained by nonstoichiometric (80%) precipitation are due to lower viscosity and density of the magnesium hydroxide suspension, which results in faster settling of the precipitate formed. Also, taking into account the electrokinetic potential ζ, that decreases in the presence of excess Mg^{2+} ions, as well as different adsorption of individual ions on to the surface of the magnesium hydroxide particle (Mg^{2+} ions are bound to the surface with stronger adsorption forces than Ca^{2+} ions), the much improved precipitate settling rate in nonstoichiometric precipitation can be explained by the $Mg(OH)_2$ particle model.

4 CONCLUSIONS

- Application of the powdery 818A flocculant (polyacrylamide) to improve the settling rate of magnesium hydroxide in seawater is much more efficient than that of the nonionic flocculant 827N
- Based on the functional dependence ΔZ = f (% stoich.), the optimum quantity of the nonionic 827N

Table 2: Characteristic values of the thickener for different degrees of incomplete precipitation (80%, 90% and 100% respectively) and with optimal addition of the 818A flocculant

Tabela 2: Karakteristične velikosti usedalnika pri različnih stopnjah usedanja magnezijevega hidroksida iz morske vode pri optimalnem dodatku flokulanta 818A

Part	% stoich.	flocculant 818A dm^3m^{-3}	ρ_{in} kgm^{-3}	ρ_{out} kgm^{-3}	Q_{in} m^3h^{-1}	Q_m kgh^{-1}	Q_{out} m^3h^{-1}	Q_p m^3h^{-1}	q kgm^2h^{-1}	A m^2	d m
I	80	3.4	5.1212	46.2612	3.60	18.4363	0.40	3.20	27.61	**0.67**	**0.9**
	90	3.8	5.7610	46.2077	3.60	20.7396	0.45	3.15	11.41	**1.82**	**1.5**
	100	5.0	6.4016	45.0297	3.60	23.0458	0.51	3.09	13.01	**1.77**	**1.5**
II	80	3.4	5.1212	**45.0297**	4.48	**23.0458**	0.51	3.99	29.77	**0.77**	**0.99**
	90	3.8	5.7610	**45.0297**	3.99	**23.0458**	0.51	3.49	12.02	**1.92**	**1.56**
	100	5.0	6.4016	**45.0297**	3.60	**23.0458**	0.51	3.09	13.01	**1.77**	**1.5**
III	80	3.4	5.1212	**45.0297**	10.29	52.6929	1.17	9.12	29.77	**1.77**	**1.5**
	90	3.8	5.7610	**45.0297**	3.69	21.2754	0.47	3.22	12.02	**1.77**	**1.5**
	100	5.0	6.4016	**45.0297**	3.60	23.0458	0.51	3.09	13.01	**1.77**	**1.5**

Symbols:
ρ_{in} - is the density (mass concentration) of feed, kg m^{-3}
ρ_{out} - is the density (mass of solids per unit volume of slurry) of underflow, kg m^{-3}
Q_{in} - is the volume flow of the incoming suspension, m^3 h^{-1}
Q_m - is the mass of solids fed per unit time to thickener, kg h^{-1}
Q_{out} - is the volume flow of overflow, m^3 h^{-1}
Q_p - is the volume flow of overflow, m^3 h^{-1}
q - is the capacity of the thickener, kg m^2 h^{-1}
A - is the surface of the thickener, m^2
d - is the diameter of the thickener, m

flocculant was found to be 10.0 cm^3 per dm^3 seawater for 80% precipitation
- Based on the functional dependence $\Delta Z = f$ (% stoich.), the optimum quantity of the anionic 818A flocculant was found to be 3.4 cm^3 per dm^3 seawater for 80% precipitation
- The results obtained indicate that the 818A flocculant, being negatively charged, has a greater number of active groups along the molecular chain, while the action of the nonionic 827N flocculant is probably based on the polarity of its molecule. This results in different degrees of ionization in the solution
- Mathematical analysis has yielded the most appropriate function for the dependence of the quantity of the 818A flocculant added (Y) on the degree of completeness of precipitation (x) under optimum settling conditions. The dependence obtained is described by the third degree polynomial: $Y = 1.333 \cdot 10^{-4}x^3 - 0.032x^2 + 2.587x - 67$
- When results obtained for 80% and 100% precipitation are compared, the calculation for the continuous thickener indicates that the thickener productive capacity is much higher (by approx. 128%) if the anionic flocculant 818A is used in 80% precipitation (nonstoichiometric) of magnesium hydroxide from seawater.

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