PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology 2022, **56**(1), p. 1–9

Chemistry

THE INFLUENCE OF ACIDIC TREATMENT OF MINERAL CONDITIONERS ON THEIR STRUCTURE-FORMING PROPERTIES

S. S. HAYRAPETYAN [*], M. S. CHOBANYAN [**], V. A. HOVHANNISYAN [***],
L. S. BANYAN [****], H. G. KHACHATRYAN [*****]

Chair of Inorganic and Analytical Chemistry, YSU, Armenia

The structure-forming properties of mineral conditioners caused by acidic treatment have been studied by means of turbidimetry as well as particles size distribution methods. Three types of mineral conditioner having CaO, SO_4^{2-} and PO_4^{3-} groups on the surface have been investigated. The first two types were treated with nitric acid, and the third with phosphoric acid. The treatment of mineral conditioners with phosphoric acid causes a decrease in the effluent turbidity, whereas when treating CaO group containing mineral conditioner with nitric acid a sharp increase in this parameter is observed. When treating sulfo group mineral conditioner this increase is not significant.

https://doi.org/10.46991/PYSU:B/2022.56.1.001

Keywords: mineral conditioner, acid treatment, particle size distribution, structure-forming.

Introduction. In the process of conventional wastewater treatment, one of the final steps involves the separation of solids from the water and drying or "dewatering" of the solids (or sludge).

Wastewater treatment processes produce large quantities of sludge commonly containing over 90% water. The most important part of sludge treatment prior to disposal is the reduction of the sludge volume by water separation in order to reduce the costs of transportation and handling.

Sludge is a colloidal system, in which small sludge particles form a stable suspension in water and are very difficult to separate it from the water phase [1].

In order to improve sludge dewaterability, it is important to reduce the sludge specific resistance by increasing the cake porosity and reducing the cake compressibility. For this reason, solid materials that are generally inert, with relatively high porosity and rigid structure can be beneficial during mechanical dewatering when mixed with a sludge with low dewaterability. These materials are physical conditioners and are sometimes called skeleton builders or filter aids, according to their role in building up the structural strength of sludge solids and in assisting filtration [2].

---

[*] E-mail: haysers@ysu.am

[**] E-mail: chobanyanmikayel@gmail.com

[***] E-mail: vahe.hovhannisyan@gmail.com

[****] E-mail: lilitbanyan@gmail.com

[*****] E-mail: gold@ysu.am

The surfaces of sludge solids particles and physical conditioners as well as chemical conditioners are often charged. Hence, interactions between the polyelectrolyte, the physical conditioner and the sludge colloids may occur, leading to the formation of a homogeneous mixture of the solids with strong and porous structure [1].

The presence of colloidal and supra colloidal range (>1 *nm*) particles in sludge often result in the deterioration of dewatering during mechanical dewatering. Without any pre-conditioning, mechanical dewatering of the sludge with colloidal solids (e.g. sewage sludge) is very difficult, or even impossible [2].

Although physical conditioners have been proved to be able to aid the sludge dewatering process, the application of conditioners is sometimes limited and affected by factors such as the dewatering method utilized, the properties of the conditioner, the properties of the sludge, etc. The type and condition of solid-liquid separation methods for sludge dewatering may affect the performance of the physical conditioner as a filter aid. When physical conditioners are used in conjunction with chemical conditioners, sludge dewaterability can achieve its optimum. Without chemical conditioners, which are used to manage sludge colloids, physical conditioners alone usually cannot function as filter aids to the same extent or at all. There are two widely accepted flocculation mechanisms: particle-particle bridging and surface charge neutralization [3–5]. When two particles come together, the loops and tails of one particle attach themselves to bare patches on the approaching particle to form bridges [6].

In the mechanism of surface charge neutralization, flocculation occurs, because the electrostatic force of repulsion between the charged particles is reduced. Hence, the polyelectrolytes with high charge density (CD) are more effective in the formation of flocs by surface charge neutralization. The zeta potential of the system can be used to measure the change in the surface charge during polyelectrolyte flocculation [7, 8].

The stability of flocs is also depending on the properties of polyelectrolyte. Homeyer et al. [9] found that molecular weight (MW) is an important factor for floc stability. High MW polyelectrolytes form large and loosely packed flocs, which are stable to shear and can have significantly better filtration performance. Contrary, low MW polyelectrolytes form shear sensitive flocs, which can be eroded by the hydrodynamic shear during the filtration processes and blind the filter medium reducing the filtration performance.

Gray and Ritchie [10] also studied the effect of polyelectrolyte’ MW and CD on floc strength and found that high MW polyelectrolytes produced stronger flocs than lower MW polyelectrolytes. For polyelectrolytes with very low charge density, weaker flocs are formed due to poor adsorption of polyelectrolyte on the floc, whereas for polyelectrolytes with high CD, electrostatic patch flocculation rather than bridging flocculation occurs and, therefore, weaker flocs are formed. Dewaterability of polyelectrolyte flocculated sludge can be further improved by conditioning the flocculated sludge with physical conditioners, often known as skeleton builders. These physical conditioners can form a permeable and more rigid lattice structure, which may remain porous during mechanical dewatering [10].

Experimental Part. The acidic treatment (AT) of mineral conditioner was carried out using nitric and phosphoric acids.

DB-11Ca and DB-11S3 samples have been treated with 10% nitric acid solution during 20 *h* at room temperature. Further, the samples were rinsed by distilled water till neutral reaction. DB-11P sample has been treated with 40% phosphoric acid solution. After obtaining a pasty mass at room temperature, it was thermally treated at 200°C.

Turbidity and Size Determination. The turbidity (Formazin Turbidity Unit, FTU) was measured after exposition with acids or the base in a Hanna turbidimeter model HI 93703. In addition, an aliquot of 1 *mL* was taken and diluted 10 times for the determination of the size distributions in the diluted suspension. For that purpose, a Malvern Zeta SizerNano Series instrument has been utilized. A 12 *mm* polystyrene cell was used to expose the samples to the light beam for further dynamic light scattering. Characterization of the particle sizes was intended due to the turbid suspension obtained by the addition of the polymer. Hence, these two techniques of light scattering were used for the description of the behavior of the polymer and its contribution to the turbidity in a broad range of pH (e.g. 1.6 to 12.4 for HCl and NaOH) at room temperature.

Results and Discussion. The influence of functional groups on the surface of mineral conditioners during the effluent treatment causing flocculation may be characterized issuing from effluent particles size distribution (PSD) after its treatment by mineral conditioners. Moreover, additional information may be obtained from turbidity values of obtained systems.

Table 1

The values of standard deviation, mean diameter and FTU of mineral conditioner DB-11Ca

Sample	Standard Deviation, *nm*	Intensity	Mean Diameter, *nm*	FTU
DB-11Ca				
5 *min*	79.89	35	540.5	995
15 *min*	95.17 968.2	16.5 7.3	492.0 3730	931
30 *min*	108.5	28	609.4	807
60 *min*	121.2	28.2	642.5	969
180 *min*	77.3	36	560.2	685
DB-11CaAT				
5 *min*	348.4	16	1041	812
15 *min*	410	15	1149	882
30 *min*	475.1 734.6	12.3 3.0	1138 4866	1193
60 *min*	608.1	12.4	1406	1122
180 *min*	526.2 49.27	13 2	1402 221.9	1300

In the case of DB-11Ca, a decrease in particles mean diameter (*D*) at the start of treatment (5–15 *min*) is observed (from 540.5 *nm* to 492 *nm*). The standard deviation shows a slight growth (from 79.89 *nm* to 95.17 *nm*). On this background an increase in FTU has to be observed, because particles mean diameter decreases, and the values of standard deviation increase. It is important to mark here that a bi-modal structure appears and the second peak is at *D*=3730 *nm* with a standard deviation of 968.2 *nm*. The intensity of this peak is 44% of the intensity of the first peak, i.e. a significant part of the particles have turned into large-size aggregates. One can assume that the decrease in FTU in this case may be connected with particles enlargement. Further treatment leads to an increase in the average size of particles together with some little increase in the value of the standard deviation, and the FTU decreases at this background (see Tab. 1 and Fig. 1).

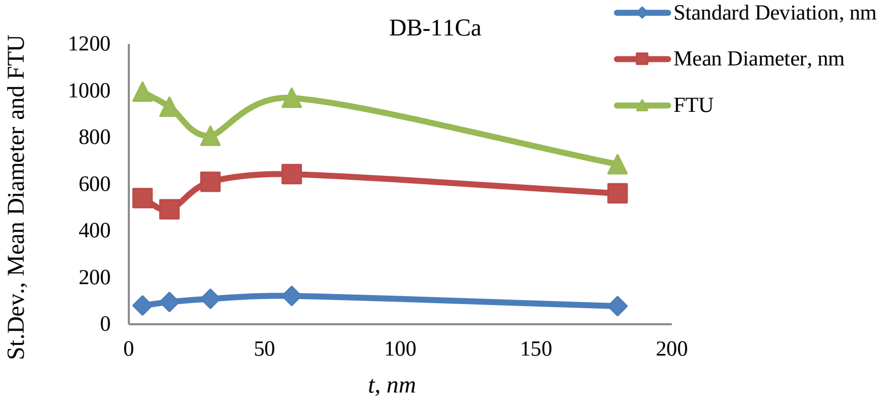

Fig. 1. The standard deviation, mean diameter and FTU changes, caused by acid treatment duration of mineral conditioner DB-11Ca.

A further slight increase of in mean diameter with a practically unaltered standard deviation and without secondary structure formation (and besides the intensity of PSD peak increases up to 28) causes an increase in FTU. Apparently, it is a result of de-agglomeration of big particles and an increase in the number of particles (after 60 *min*). During the further exposition from 60 *min* to 180 *min* PSD bimodality is not observed. On the background of slight decrease in mean diameter (from 642.5 *nm* to 560.2 *nm*) and comparatively slight decrease in standard deviation values, a decrease in FTU is observed (from 121.2 *nm* to 77.3 *nm*). It is possible that the changes in standard deviation values have stronger influence than the changes in average sizes of particles.

When comparing the curves presented at Figs. 1 and 2, it can be seen that the standard deviation curve for DB-11Ca conditioner does not exceed 150 *nm*, while in the case of DB-11CaAT conditioner (after acid treatment) these values grew up 3–4 times and equal to 400–600 *nm*. It is important here that the changes in mean diameter in the first case are within 600±100 *nm*, whereas for the sample after acid treatment a slight increase observed and it equal 1250±150 *nm*. Thus, the acidic treatment of DB-11Ca type mineral conditioner causes a sharp widening of PSD. However, the mean diameter of particles formed is almost unaltered. As expected with such a large scatter of the standard deviation values we can observe an increase in FTU values that is clearly visible, that namely the changes in standard deviation of the particles size are the main reason of FTU increase.

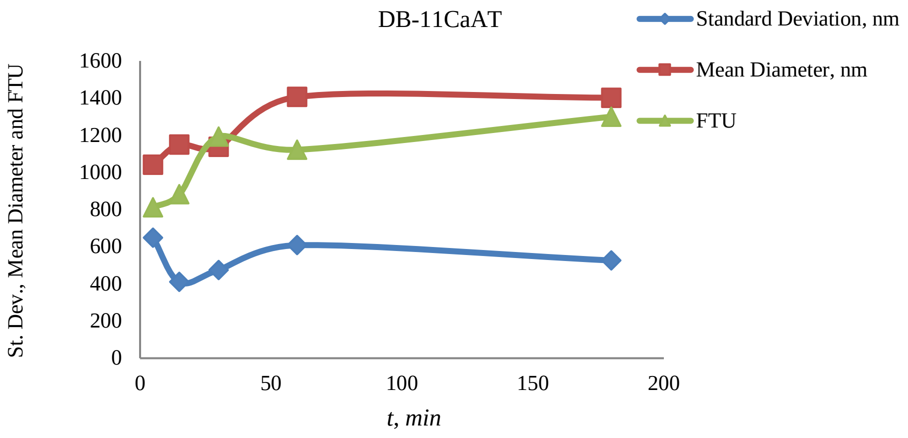

Fig. 2. The standard deviation, mean diameter and FTU changes, caused by acid treatment duration of mineral conditioner DB-11CaAT.

The curves of changes in the standard deviation, mean diameter and FTU depending on the treatment duration of mineral conditioner DB-11S3 are presented in Fig. 3, and the changes in the same values for DB-11S3AT conditioner are shown in Fig. 4 and Tab. 2.

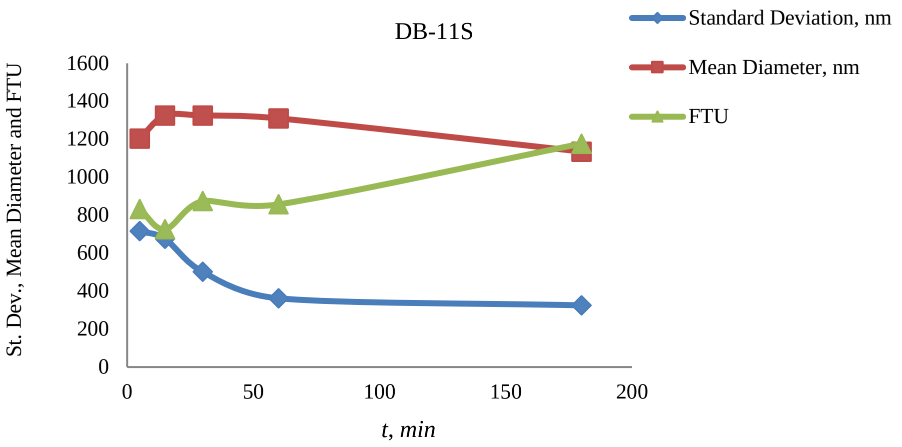

Fig. 3. The standard deviation, mean diameter and FTU changes, caused by acid treatment duration of mineral conditioner DB-11S.

For DB-11S conditioner on the background of decreasing *D* and standard deviation (at that the standard deviation decrease is much more intensive than that for *D*) FTU peak is observed after 30 *min*. The reason is that this sample shows a bi-modal PSD, and smaller particles appear in the 194.4 *nm* field with 15.5% intensity of that for the main peak.

During the further treatment bimodality disappears, *D* is practically unaltered (1325–1310 *nm*), and the standard deviation decreases largely (501.3–362.2 *nm*).

Some slight decrease in FTU values is observed. Then, the decrease in *D* (1310–1155 *nm*) and standard deviation values (362.2–325.0 *nm*) take place, and besides, *D* decreases more sharply than the standard deviation, and, as a result, an increase in FTU is observed.

Table 2

The values of standard deviation, mean diameter and FTU of mineral conditioner DB-11S

Sample	Peak	Standard Deviation, *nm*	Intensity	Mean Diameter, *nm*	FTU
DB-11S					
5 *min*	1	716	9.2	1204	832
15 *min*	1	675.3	9.0	1324	726
30 *min*	1 2	501.3 40.88	13 2	1325 194.4	874
60 *min*	1	362.2	15.5	1310	857
180 *min*	1	325	18	1135	1177
DB-11SAT					
5 *min*	1	634.1 580	9.2	1168 4964	1006
15 *min*	1	237.8 316.6	11	796.9 5389	794
30 *min*	1 2	510 39.53	19 2	1301 154.9	1170
60 *min*	1	367.7 24.62	13 1	1251 162.5	988
180 *min*	1	234	16 3	982	1275

Wherein, after treatment for 30 *min* in both cases similar paintings are observed, i.e. on the background of a decrease in the standard deviation and mean diameter values, a decrease in FTU takes place. Besides, in both cases the changes in the standard deviation are practically the same and the increase in FTU values can be explained by decreasing in mean diameter of particles. And it is quite logical, because the number of particles increases and, naturally, FTU values have to increase as well. Thus, the acidic treatment of DB-11S mineral conditioner does not practically affect its structure-forming properties.

Table 3

The values of standard deviation, mean diameter and FTU of mineral conditioner DB-12P

Sample	Peak	Standard Deviation, *nm*	Intensity	Mean Diameter, *nm*	FTU
DB-12P					
5 *min*	1	134.6	30	804.1	712
15 *min*	1	94.34	16.5	500.7	909
30 *min*	1	216.6	21.5	864.8	584
60 *min*	1	267.8	18.2	950	471
180 *min*	1	221.8	21.7	922.6	672

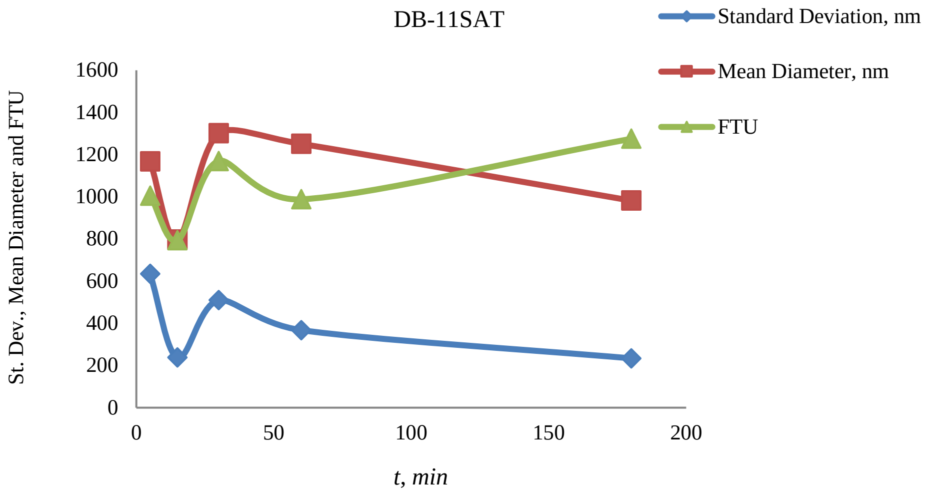

Fig. 4. The standard deviation, mean diameter and FTU changes, caused by acid treatment duration of mineral conditioner DB-11SAT.

When using a mineral conditioner treated with phosphoric acid, there is an increase in particles mean diameter and a sharp decrease in the standard deviation value compared to the mineral conditioner DB-12P. As a result, the lowest values for FTU are observed among all the studied mineral conditioners (see Fig. 5 and Tab. 3).

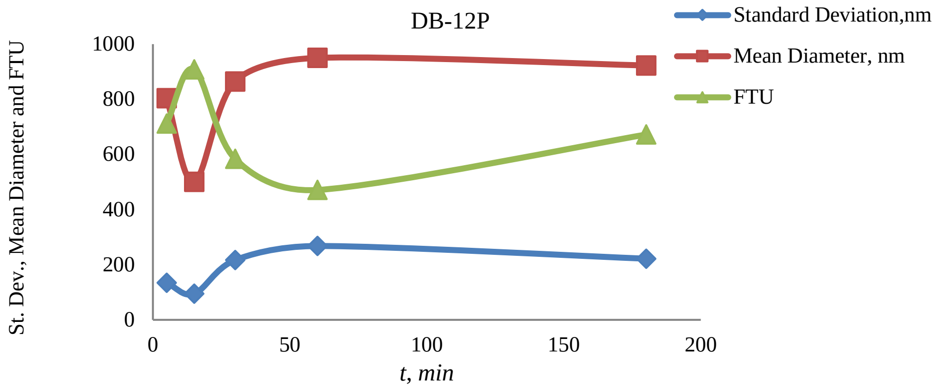

Fig. 5. The changes in standard deviation, mean diameter and FTU caused by acid treatment duration of mineral conditioner DB-12P.

The increase in FTU values on the background of an increase in particles mean diameter and standard deviation values may be explained by the fact that the curvature of the standard deviation curve is significantly more than that for *D* curve. Besides, the change in FTU values is more sensitive in relation to the changes in standard deviation compared to that for mean diameter values.

Conclusion.

1. Functional groups on the surface of mineral conditioners play an important role in the structuring of effluent dispersed particles, about which witnesses the influence of acidic treatment of mineral conditioners obtained on the base of bentonite and diatomite.

In this case the nature of the acid used for treatment is of great importance.

2. The treatment of mineral conditioners with phosphoric acid causes a decrease in the effluent turbidity, whereas when treating CaO group containing mineral conditioner with nitric acid a sharp increase in this parameter is observed. When treating sulfo group mineral conditioner this increase is not significant.

Received 27.01.2022
Reviewed 14.02.2022
Accepted 28.02.2022

REFERENCES

1. Patent US 515679.
2. Ying Qi, Thapa Kh.B., Hoadley A.F.A. Application of Filtration Aids for Improving Sludge Dewatering Properties. *Chemical Engineering Journal* **171** (2011), 373–384. https://doi.org/10.1016/j.cej.2011.04.060
3. Zhao Y.Q., Bache D.H. Conditioning of Alum Sludge with Polymer and Gypsum. *Colloids Surf. A* **194** (2001), 213–220. https://doi.org/10.1016/s0927-7757(01)00788-9
4. Thapa Kh.B., Qi Y., Hoadley A.F.A. Interaction of Polyelectrolyte with Digested Sewage Sludge and Lignite in Sludge Dewatering. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **334** (2009), 66–73. https://doi.org/10.1016/j.colsurfa.2008.10.007
5. Gregory J. Polymer Adsorption and Flocculation in Sheared Suspensions. *Colloids and Surfaces* **31** (1988), 231–253. https://doi.org/10.1016/0166-6622(88)80196-3
6. Bohm N., Kulicke W.M. Optimization of the Use of Polyelectrolytes for Dewatering Industrial Sludge of Various Origins. *Colloidal and Polymer Science* **275** (1997), 73–81. https://doi.org/10.1007/s003960050054
7. Caskey J.A., Primus R.J. The Effect of Anionic Polyacrylamide Molecular Conformation and Configuration on Flocculation Effectiveness. *Environmental Progress* **5** (1986), 98–103. https://doi.org/10.1002/ep.670050210
8. Bleier A., Goddard E.D. Flocculation of Aqueous Silica Suspensions Using Cationic Polyelectrolytes. *Colloids and Surfaces* **1** (1980), 407–423. https://doi.org/10.1016/0166-6622(80)80026-6
9. Homeyer A.V., Krentz D.O., Kulicke W.M., Lerche D. Optimization of the Polyelectrolyte Dosage for Dewatering Sewage Sludge Suspensions by Means of a New Centrifugation Analyser with an Optoelectronic Sensor. *Colloid and Polymer Science* **277** (1999), 637–645. https://doi.org/10.1007/S003960050435
10. Gray S.R., Ritchie C.B. Effect of Organic Polyelectrolyte Characteristics on Floc Strength. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **273** (2006), 184–188. https://doi.org/10.1016/j.colsurfa.2005.08.020

Ս. Ս. ՀԱՅՐԱՊԵՏՅԱՆ, Մ. Ս. ՉՈԲԱՆՅԱՆ, Վ. Ա. ՀՈՎՀԱՆՆԻՍՅԱՆ,
Լ. Ս. ԲԱՆՅԱՆ, Հ. Գ. ԽԱՉԱՏՐՅԱՆ

ՀԱՆՔԱՅԻՆ ԿՈՆԴԻՑԻՈՆԵՐՆԵՐԻ ԹԹՎԱՅԻՆ ՄՇԱԿՄԱՆ ԱԶԴԵՑՈՒԹՅՈՒՆԸ ԴՐԱՆՑ ԿԱՌՈՒՑՎԱԾՔԱՅՆԱՑՄԱՆ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԻ ՎՐԱ

Պղտորաչափության և մասնիկների չափի բաշխման եղանակներով ուսումնասիրվել են հանքային կոնդիցիոներների կառուցվածքայնացման հատկությունները: Դրանց թթվային մշակումից հետո հետազոտվել են մակերևութային CaO, SO_4^{2-} և PO_4^{3-} ֆունկցիոնալ խմբերով երեք տեսակի հանքային կոնդիցիոներներ: Առաջին երկուսը մշակվել են ազոտական թթվով, իսկ երրորդը՝ ֆոսֆորական թթվով:

Հանքային կոնդիցիոներների մշակումը ֆոսֆորական թթվով հանգեցնում է թափոնաջրերի պղտորության նվազման, մինչդեռ CaO խմբով հանքային կոնդիցիոներն ազոտական թթվով մշակելիս նկատվում է պղտորության արժեքի կտրուկ աճ: Սուլֆո-խմբերով հանքային կոնդիցիոներ մշակելիս այդ աճն էական չէ:

С. С. АЙРАПЕТЯН, М. С. ЧОБАНЯН, В. А. ОГАНИСЯН,
Л. С. БАНЯН, А. Г. ХАЧАТРЯН

ВЛИЯНИЕ КИСЛОТНОЙ ОБРАБОТКИ МИНЕРАЛЬНЫХ КОНДИЦИОНЕРОВ НА ИХ СТРУКТУРИРУЮЩИЕ СВОЙСТВА

Методами турбидиметрии и распределения частиц по размерам изучены структурирующие свойства минеральных кондиционеров после их кислотной обработки. Исследованы три типа минеральных кондиционеров с функциональными группами CaO, SO_4^{2-} и PO_4^{3-} на поверхности. Первые два типа были обработаны азотной кислотой, а третий – фосфорной кислотой.

Использование фосфорной кислоты приводит к уменьшению мутности эффлюента, в то время как при обработке азотной кислотой минерального кондиционера с CaO-группой наблюдается резкое увеличение значений мутности. При обработке минерального кондиционера с сульфогруппами это увеличение незначительно.