# PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology

2020, **54**(1), p. 26–32

Chemistry

# STRUCTURING OF EFFLUENT PARTICLES BY MEANS OF TREATMENT OF BENTONITE BASE MINERAL CONDITIONERS

### S. S. HAYRAPETYAN \*, L. S. BANYAN \*\*, G. P. PIRUMYAN \*\*\*

#### Center for Ecological Safety, YSU, Armenia

The turbidimetric and Z-potentiometric methods were used for the assessment of some properties of diatomite – bentonite based conditioners for dewatering of effluents from the digestate of a biogas plant. These physical conditioners were prepared based on natural porous highly dispersible systems such as bentonite and diatomaceous earth. Three types of modified systems in the forms of CaO were used, which differ from each other in the ratio of the content of bentonite and diatomite. The role of the silica-containing component is to ensure the structuring of these systems. Diatomite was used for this purpose.

*Keywords*: particle size, particle size distribution, turbidity.

**Introduction.** In a conventional waste water treatment process one of the final steps involves the separation of solids from the water and drying or "dewatering" 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 be separated from the water phase [1].

In order to improve sludge dewaterability, it is important to reduce the sludge specific resistance by increasing cake porosity and reducing cake compressibility. For this reason, solid materials that are generally inert, with a relatively high porosity and a rigid structure can be beneficial during mechanical dewatering when mixed with 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 the sludge solids and in assisting in filtration [2].

Physical conditioners as filtration aids can be loosely divided into two groups: the minerals and the carbon-based materials. A wide range of carbon-based materials has been used as physical conditioners, including char [3], coal fines [3, 4] and bio-waste such as wood chips and wheat dregs [5] and bagasse [6]. Minerals including fly ash [2, 6, 7], cement kiln dust [6] and gypsum [8, 9] have also been used. A physical

<sup>\*</sup> E-mail: haysers@ysu.am

<sup>\*\*\*</sup> E-mail: gpirumyan@ysu.am

<sup>\*\*</sup> E-mail: lilitbanyan@gmail.com

conditioner can be used alone to enhance sludge dewatering [10]. But more often the addition of a physical conditioner follows coagulation or flocculation with a chemical conditioner. Minerals include industrial materials and waste, such as fly ash, which is probably the most used and studied skeleton builder [6, 7, 11, 12], cement kiln dust [6], lime [2] and gypsum [9, 12]. Carbon-based materials studied include char [3, 13], coal fines [3, 4] and, most recently, a low-rank coal lignite [14], as well as carbonaceous waste wood chips and wheat dregs [5, 10], bagasse [6].

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

The presence of colloidal and supracolloidal (>1  $\mu m$ ) range particles in sludge often results in the deterioration of dewatering during mechanical dewatering. Without any preconditioning, mechanical dewatering of the sludge by colloidal solids (e.g. sewage sludge) is very difficult or even impossible. Flocculation and coagulation help to increase the sludge particle size by agglomerating the small fines of the sludge colloids, which cause blinding, to form large flocs, which can be more easily separated from the water [2].

Although physical conditioners have been proved to be able to aid the sludge dewatering process, the application of the 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 the solid–liquid separation methods for sludge dewatering may affect the performance of a 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 [15–17].

**Materials and Methods.** Bentonite of the Sarigyukh deposit (Tavush Region, Armenia) and diatomite of the Dzhradzor deposit (Armavir Region, Armenia) were used. 3 types of mineral conditioners were obtained – DB-13Ca, DB-12Ca and DB-11Ca. The figures show the weight ratio of diatomite to bentonite.

**Turbidity and Size Determination.** The turbidity (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 to determine the size distributions in the diluted suspension. For that purpose, a Mavelrn Zeta Sizer Nano Series instrument was utilized. A 12 *mm* polystyrene cell was used to expose the samples to a light beam for further dynamic light scattering. A characterization of the particle sizes was intended due to the turbid suspension. Hence, these two techniques of light scattering were used for the description of the behavior of the suspensions and their contribution to the turbidity at room temperature.

**Results and Discussion.** The effect of functional groups (in particular, CaO) on the surface of mineral conditioners on the structuring processes during dewatering of the effluent can be characterized on the basis of the particle size distribution (DPS) of the effluent after its treatment with mineral conditioners. In addition, the turbidity of the resulting systems also provides additional information.

Fig. 1 shows the pictures of the DPS of the effluent after its treatment with mineral conditioners with a functional group – CaO, for 5, 15, 30, 60, and 180 *min*. From Fig. 1 it follows that during treatment with mineral conditioners, the suspended particles in the effluent undergo various structuring. Larger particles are formed, then with further processing, the destruction of these clusters is observed, as evidenced by the bi- and trimodal parts of the DPS, i.e. the formed structures are very labile and eventually decompose or form new structures.



There is a clear trend. When passing from a sample of mineral conditioner DB-13Ca to DB-12Ca and DB-11Ca, the DPS (with a decrease in the amount of bentonite in the mineral conditioner) become narrower and move towards smaller aggregate sizes of the obtained samples generally. Of course, some sharp broadening of the DPS is observed (for example, for DB-12Ca during 60 *min* of treatment, and for DB-11Ca during 15 *min* of treatment). In the first case, the peak width at the base is in the range of 800–4000 *nm*, and in the second – 1800–6500 *nm*. In both cases, during further processing, a sharp narrowing of the DPS is observed.

It should be noted that the decomposition formed relatively large formations during prolonged treatment with mineral conditioner DB-13Ca is minimal. In this case, more stable structures are formed and there is a tendency to enlarge secondary large formations. Only in a sample treated for 180 *min* does the formation of small particles occur. The intensity of this DPS peak is only 10% of the intensity of the main DPS peak (see Fig. 1). This can be explained by the fact that this sample of mineral conditioner has the highest content of bentonite and functional groups in comparison with DB-12Ca and DB-11Ca.

With a decrease in the amount of bentonite in the composition of mineral conditioners (DB-12Ca), the DPS maxima are moved to the left towards small particles. In the case of DB-12Ca, more compact DPS were observed. In the case of DB-11Ca, a similar pattern of DB-12Ca was observed (see Fig. 1).

28

Structuring under the influence of mineral conditioners can be characterized by a change in the in the average particle size (D) and the standard deviation of the particle size from the average size (St. Dev.) (see Table and Fig. 2).

Exposition time, <i>min</i>	St. Dev., nm	Intensity	D, nm	FTU
DB-13Ca				
5	357	15	1034	1045
15	422.6	13.5	1136	1031
30	370.4	16.5	1167	718
60	379.9	14.0	1037	674
180	475	14.5	1367	916
DB-12Ca				
5	150.5	34	984.1	1127
15	97.42	30	577.9	1078
30	358.8	17.5	1168	930
60	574.1	11.5	1781	850
	81.49	7.5	574.1	
180	167.8	26	867.1	976
DB-11Ca				
5	79.89	35	540.5	995
15	95.17	16.5	492.0	931
	968.2	7.3	3730	
30	108.5	28	609.4	807
60	121.2	28.2	642.5	969
180	77.3	36	560.2	685

Some parameters of the structuring of effluents particles by means of treatment of mineral conditioners

The effect of mineral conditioners on the structuring of effluent particles seems to depend on the dispersibility of these materials in the aquatic environment (in the effluent). It is assumed that there is a period of dispersion (deagglomeration) of the mineral conditioner, during which the complete destruction of the agglomerates of particles of these systems occurs. During this period unpredictable structuring occurs, which affects St. Dev. and *D*. After some time it will be possible to judge the influence of one or another air conditioner on the structuring processes.

In the case of DB-11Ca, in the initial treatment period (5–15 *min*), D decreases from 540.5 to 492 *nm*; St. Dev. has a slight increase from 79.89 to 95.17 *nm*. Against this background, an increase in FTU was to be observed as D decreases and St. Dev. increases. It is important to note here that a bimodal structure appears and the second peak is in the region D = 3730 *nm* with St. Dev. of 968.2 *nm*. The intensity of the second peak is 44% of the intensity of the first peak, i.e. a significant part of the particles turned into large aggregates. It is assumed that the decrease in FTU in this case is associated with particle enlargement.

Further processing leads to an increase in the average particle size with a slight increase in standard deviation, and FTU decreases against this background. A further insignificant increase in D with the practical constancy of the standard deviation and without secondary structuring increases in FTU. Apparently, this is the result of deagglomeration of large particles and an increase in the number of particles (after 60 *min*). Further exposure from 60 *min* to 180 *min*, the RFR bimodality is not

observed, and against the background of a slight decrease in the D (from 642.5 to 560.2 *nm*) and a relatively insignificant decrease in the St. Dev. (from 121.2 to 77.3 *nm*), a decrease in FTU is observed. Here, apparently, a change in the standard deviation has a larger effect than a change in the average particle size.



In the case of DB-12Ca, after 15 *min* of treatment, a minimum is observed for the D and St. Dev.. Turbidity in this case tends to decrease, which continues after passing the minimum D and St. Dev. until reaching its maximum values (after 60 *min* of processing). The initial decrease in FTU is due to the period of dispersion of the particles of the mineral conditioner. The further behavior of the turbidity curve is explained by the fact that with an increase in the D and a moderate increase in the St. Dev. compared to D, the FTU decreases, and by the same logic, when the opposite picture takes place, the FTU increases.

By the same analogy, the minimum FTU is also observed for the DB-13Ca sample. The observed maximum D and an insignificant minimum at the St. Dev. have a minimum FTU. With a further increase in processing time, a comparable increase in D and St. Dev. is observed, but FTU increases. Apparently, with a comparable increase in these values, the FTU is more affected by the change in the St. Dev. than D. **Conclusion.** 

1. It was shown that when processing effluent with mineral conditioners based on bentonite, the content of bentonite and functional groups on their surface are important in the structuring of effluent particles.

2. It is shown that an increase in the average particle size and a decrease in the mean deviation leads to a decrease in FTU.

Received 25.10.2019 Reviewed 24.03.2020 Accepted 10.04.2020

#### REFERENCES

- 1. Williams J.R. Dewatering System for Sludge Removal. US 5156749, CO2F 11/12 (1992).
- Qi Y., Thapa K.B., F.A. Hoadley A. Application of Filtration Aids for Improving Sludge Dewatering Properties. *Chemical Engineering Journal*, **171** (2011), 373–384.
- Zall J., Galil N., Rehbun M. Skeleton Builders for Conditioning Oily Sludge. Water Pollut. Control Fed., 59 (1987), 699–706.
- Albertson O.E., Kopper M. Fine-coal-aided Centrifugal Dewatering of Waste Activated Sludge. Water Pollut. Control Fed., 55 (1983), 145–156.
- Sander B., Lauer H., Neuwirth M. Process for Producing Combustible Sewage Sludge Filter Cakes in Filter Presses. US 4840736, CO2F 11/14: CO2F 1/52 (1989).
- Lin Y.F., Jing S.R., Lee D.Y. Recycling of Wood Chips and Wheat Dregs for Sludge Processing. Bioresour. Technol., 76 (2001), 161–163.
- Benitez J., Rodriguez A., Suarez A. Optimization Technique for Sewage Sludge Conditioning with Polymer and Skeleton Builders. *Water Res.*, 28 (1994), 2067–2073.
- Chen C., Zhang P., Zeng G., Deng J., Zhou Y., Lu H. Sewage Sludge Conditioning with Coal Fly Ash Modified by Sulfuric Acid. *Chem. Eng. J.*, **158** (2010), 616–622.
- Zhao Y.Q. Enhancement of Alum Sludge Dewatering Capacity by Using Gypsum as Skeleton Builder. *Colloids Surf.*, A 211 (2002), 205–212.
- 10. ZhaoY.Q. Involvement of Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) in Water Treatment Sludge Dewatering: A Potential Benefit in Disposal and Reuse. *Sep. Sci. Technol.*, **41** (2006), 2785–2794.
- Soerensen B., Soerensen P.B. Structure Compression in Cake Filtration. J. Environ. Eng., 123 (1997), 345–353.
- 12. Tenney M.W., Cole G.T. Use of Fly Ash in Conditioning Biological Sludges for Vacuum Filtration. J. Water Pollut. Control Fed., 40 (1968), R281–R302.
- Jing S.R., Lin Y.F., Lin Y.M., Hsu C.S., Huang C.S., Lee D.Y. Evaluation of Effective Conditioners for Enhancing Sludge Dewatering and Subsequent Detachment from Filter Cloth. *J. Environ. Sci. Health*, A 34 (1999), 1517–1531.
- Novak J.T., Goodman G.L., Pariroo A., Huang J.C. The Blinding of Sludges during Filtration. J. Water Pollut. Control Fed., 60 (1988), 206–214.
- Zhao Y.Q., Bache D.H. Conditioning of Alum Sludge with Polymer and Gypsum. *Colloids Surf.*, A 194 (2001), 213–220.
- Thapa K.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.
- Gregory J. Polymer Adsorption and Flocculation in Sheared Suspensions. *Colloids and Surfaces*, 31 (1988), 231–253.

#### Ս. Ս. ՀԱՅՐԱՊԵՏՅԱՆ, Լ. Ս. ԲԱՆՅԱՆ, Գ. Պ. ՓԻՐՈՒՄՅԱՆ

# ԷՖԼՅՈՒԵՆՏԻ ՄԱՍՆԻԿՆԵՐԻ ԿԱՌՈՒՑՎԱԾՔԱՅՆԱՑՈՒՄԸ ԲԵՆՏՈՆԻՏԻ ՎՐԱ ՀԻՄՆՎԱԾ ՀԱՆՔԱՅԻՆ ԿՈՆԴԻՑԻՈՆԵՐՆԵՐԻ ՄԻՋՈՑՈՎ

#### Ամփոփում

Կենսագազի արտադրության էֆլյուենտի ջրազրկման հատկությունները բենտոնիտային հիմքով կոնդիցիոներների ազդեցությունը գնահատելու համար կիրառվել են տուրբիդիմետրական և Z-պոտենցիալաչափական մեթոդները։ Այս ֆիզիկական կոնդիցիոներները պատրաստվել են այնպիսի բնական ծակոտկեն դիսպերս համակարգերի հիման վրա, ինչպիսիք են բենտոնիտը և դիատոմիտը։ Օգտագործվել են CaO-ով ձևափոխված համակարգերի երեք տիպեր, որոնք միմյանցից տարբերվում են բենտոնիտի և դիատոմիտի պարունակությամբ։ Սիլիկահողային բաղադրիչի դերն այս համակարգերի կառուցվածքայնացման ապահովումն է։ Այդ նպատակի համար կիրառվել է դիատոմիտ։

## С. С. АЙРАПЕТЯН, Л. С. БАНЯН, Г. П. ПИРУМЯН

# СТРУКТУРИРОВАНИЕ ЧАСТИЦ ЭФФЛЮЕНТА С ПОМОЩЬЮ ОБРАБОТКИ МИНЕРАЛЬНЫМ КОНДИЦИОНЕРОМ НА БЕНТОНИТОВОЙ ОСНОВЕ

## Резюме

Для оценки некоторых свойств кондиционеров на основе бентонита при обезвоживании эффлюента из биогазовой установки были использованы турбидиметрический и Z-потенциометрический методы. Эти физические кондиционеры были приготовлены на основе природных пористых дисперсных систем, таких как бентонит и диатомовая земля. Были использовали три типа модифицированных CaO-систем, которые отличаются друг от друга соотношением содержания бентонита и диатомита. Роль кремнеземсодержащего компонента заключается в обеспечении структурирования этих систем. Для этой цели был использован диатомит.