

## Purification of Drainage Water from Dumps of Solid Household Wastes Using Calcium Oxide for Premembranous Treatment

V. V. GONCHARUK, Z. N. SHKAVRO, V. P. BADEHA, D. D. KUCHERUK, A. M. SOVA and V. M. KOCHKODAN

*Institute of Colloid Chemistry and Water Chemistry, National Academy of Sciences of Ukraine, Pr. Vernadskogo 42, Kiev 252680 (Ukraine)*

*E-mail: honch@kiev.ua*

(Received April 27, 2005)

### Abstract

Potentiality to use the process of treatment of drainage water from the dumps of solid household waste by calcium oxide as a method of premembranous preparation has been studied. The flow diagram has been developed for purification of drainage water with processing of the resulting slimes into marketable products. The suggested technology assumes the re-use of the obtained products in this technological process and their salvaging within other branches of the national economy. Technological dependences of the variation in the baromembrane processes parameters after a prior reagent purification of drainage water from dumps have been obtained. Tests of a semiindustrial setup have been performed under field conditions.

### INTRODUCTION

Creating ranges to store solid household waste from big cities assumes alienation of significant ground areas and leads to deterioration of the environmental situation in the nearby settlements [1]. The basic environmental problem is associated with infiltrates spread from dumps into superficial and underground waters and therewith in the wells for drinking purpose. In consequence of the biochemical processes, which occur in the dump layers, an infiltrate is formed, which is collected through a drainage system into a holding lagoon. Physicochemical composition of the infiltrate varies depending on the “age” of dumps and on geological conditions; nevertheless, typical of the infiltrate is a high content of mineral (up to 15 000 mg/dm<sup>3</sup>) and organic (COD index of 4000–15 000 mg O/dm<sup>3</sup>) matters. In addition, polluting components are characterized by the high dispersion degree, by predominance of soluble

matter in their composition and by a wide qualitative spectrum of mineral and organic compounds, which complicates purification of drainage water from dumps (DWD).

Currently there is no any unified, efficient enough and economical method for DWD purification and this motivates a necessity of working out a process that would combine various purification procedures.

Efficiency studies using the coagulation, adsorption and biological ways for DWD purification, as a rule, have an exploratory character [2]. To take an illustration, encouraging results of biological destruction of organic matters through anaerobic and aerobic ways have been achieved. However, the suggested methods involve essential limitations such as a necessity of applying additional reagents (in particular, phosphoric salts), a necessity of performing the demineralization and the removal of a variety of residual components of the purified drainage water (surface-active substances,

heavy metals, ammonium nitrogen and so forth) [2–6].

In the case of using adsorbents (for example, absorbent carbons, active silt) for DWD purification, their consumption must be much more even in comparison with coagulating reagents, the requirement of which is an order of magnitude higher than that is needed for coagulation water treatment from the natural superficial sources [5, 7, 8].

As opposed to the methods listed above, reverse osmosis has already gained application in practice as the way for purification of drainage water from dumps of solid household wastes [9, 10].

With allowance made for the modern-day requirements on creating the non-waste processes and taking into account the analysis of foreign and many-year's experience of the Institute of Colloid Chemistry and Water Chemistry (ICWC), NAS of Ukraine, into treatment of mineralized mine, sea and drainage waters, their comprehensive processing with the use of reverse osmosis to separate the components is envisioned to be the most rational and economical solution. This way has provided the basis for the being developed non-waste technology of comprehensive processing of DWD of solid household waste. Application of this method allows obtaining water, which complies with the specifications for a discharge into the water bodies or into the municipal combined sewerage system and obtaining a series of products that are important for the national economy.

As was shown by the operational experience of the stations for purification of DWD of solid household waste, which are presently functioning, the use of reverse osmosis makes the greatest effect when the high-mineralized waters are purified. The low energy intensity of this method is one of its important advantages. However, despite a high purification degree by reverse osmosis, the problem of DWD desalting remains a complex scientific and technical problem. Thus, the operating experience in application of reverse osmosis (in particular, in the units of Pall-Rohem corporation) has proved its efficiency, but has revealed also some limitations, for example, a low operational life of reverse-osmotic modules and a large

reagent consumption for washing out the membranes with a short time of inter-regeneration cycles. In addition, the questions of recycling the concentrates being formed in the process are still wait to be solved [9].

Theoretically, it is possible to provide an increase of the membranes operational life through preliminary purification of DWD, in particular, by the reagent method; however, there are only few works in the scientific literature that deal with this issue.

Modern requirements on the protection of water sources, soils and atmosphere assume the maximum waste disposal; therefore, when working out the flow chart of DWD purification, the potentials for complete recycling of the products, which are obtained during the treatment, should be taken into consideration. Consequently, picking the reagents should be performed not only with allowance for their efficiency and economic prerequisites, but also with a prospect for simplification of the process of remaking the slimes to yield the products useful in the national economy.

The selection of such reagent as lime for premembranous purification of DWD is based on economic and ecological (the freedom from the secondary pollution) preconditions and it has been made with the allowance for a possibility to control physicochemical characteristics of changes in DWD admixtures both in the solid and in the liquid and gaseous states. Interaction of calcium ions with organic and mineral components allows an isolation of organomineral materials to form a deposit. Simultaneously, alkaline medium creation provides conditions for transferring the nitrogen-bearing compounds into the gas phase (the content of ammonium nitrogen in DWD is in a range from 350 to 1800 mg/dm<sup>3</sup>).

The purposes of this work are to study the efficiency of preliminary purification of DWD by the reagent method, in particular through liming; to explore the effect of such treatment on technological parameters of baromembrane processes; to develop the flow diagram for DWD purification with allowance for the directions of utilization of waste products that are formed during the purification.

## EXPERIMENTAL

Experiments were made under laboratory conditions with a reverse-osmotic cell (volume of 300 ml, the area of a membrane of 21.4 cm<sup>2</sup>) that was equipped with a magnetic stirrer and under real conditions of dumps with a pilot plant (the productivity of 0.5 m<sup>3</sup>/h) designed in ICCWC, NAS of Ukraine. Nano-filtration process was performed in a flow-through regime with the use of the OPMN-P membrane at the working pressure of 1 MPa and with that of reverse osmosis, at the pressure 1.5 MPa, under monitoring of the permeate withdrawal degree. DWD of Kiev solid household waste (range No. 5, the village of B. Dmytrovychi, Kiev Region) was used as the research object.

Quality assurance for DWD purification was performed according to the concentration of mineral and organic matters by determination solid and calcinated residue, COD, optical density, colour, content of ammonium salt ions, etc. [11].

## RESULTS AND DISCUSSION

As it was shown by the research, a reasonably high consumption of reagents is needed for purification of a much-polluted DWD (Table 1). As judged from the COD indices, it can be seen that the residual concentrations of organic matter in DWD upon its treatment with various reagents are virtually identical.

It should be noted that when the coagulants are applied for DWD clarification, the limitations include not only their high consumption rate and an increase in the operational expenses related with the procedure, but also aggravation

TABLE 1

Efficiency of organic matter removal from DWD with various reagents

Reagent	Concentration, g/dm <sup>3</sup>	COD*, mg O/dm <sup>3</sup>	pH
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.50–0.80	4986/1879	4–5
FeSO <sub>4</sub>	0.55–0.75	5020/2030	8–9
MgSO <sub>4</sub>	0.55–0.80	5020/2193	10–11
CaO	30.0–40.0	5216/1568	12.7

\*First values – before purification, second ones – after.

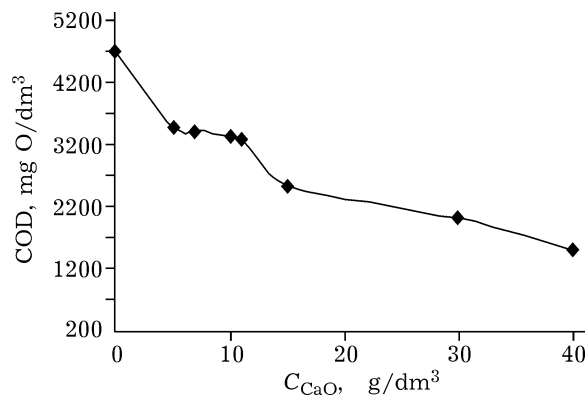


Fig. 1. COD dependence of the clarified drainage water on the concentration of calcium oxide.

of the problem of utilization of slimes that are formed in large quantities. Moreover, these slimes are amorphous and they are typified by a lower water loss as compared to calcium deposits, which requires additional expenses for dehydration. As judged by the COD values (see Table 1), an extent of DWD purification from organic matters when using calcium oxide is somewhat higher in comparison with coagulants. The content of mineral substances in the clarified infiltrate also decreases with the use of CaO, since carbonates, calcium sulphates, magnesium and calcium phosphates and some hydroxides of metals, in particular Mg(OH)<sub>2</sub>, precipitate.

The efficiency of organic matter removal with liming of DWD is virtually in direct dependence on the concentration of calcium oxide (Fig. 1).

As the concentration of organic and mineral substances in the solution is increased (in

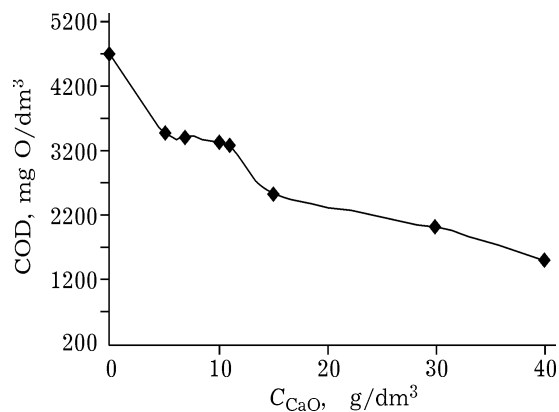


Fig. 2. Dependence of optical density (*D*) of the clarified drainage water from dump (1), concentrate after nano-filtration of drainage water (2) and their mixture with a mass ratio 1 : 1 (3) on the concentration of calcium oxide.

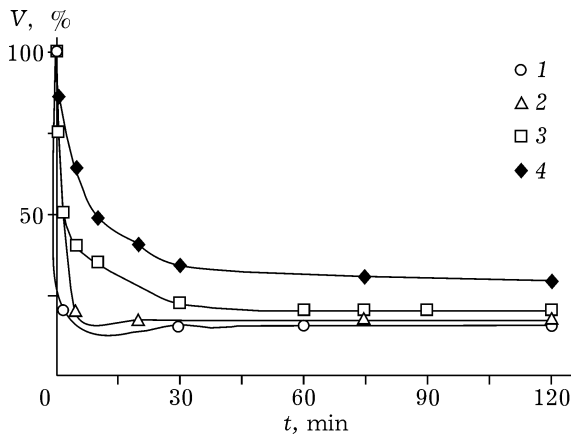


Fig. 3. Rate  $V$  of slimes sedimentation, obtained upon liming of drainage water from dump (1, 2), of concentrate after nanofiltration (4) and their mixture with the mass ratio 1 : 1 (3).  $C_{CaO}$ ,  $g/dm^3$ : 25 (1), 30 (2), 40 (3, 4).

particular, in a concentrate being formed during DWD purification by the nanofiltration procedure), the doses of calcium oxide, which are needed for the treatment, increase (Fig. 2). Optical density data demonstrate that upon mixing the concentrate from nanofiltration with the initial DWD, the purification degree of the mixture is increased supposedly at the expense of dispersion interaction of nanoparticles with the larger heterogeneous particles (see Fig. 2). Sedimentation process is somewhat slowed down at  $CaO$  concentrations over  $30 g/dm^3$  and meanwhile, the volume of the formed deposit (Fig. 3) is augmented. It can be seen that the more clear dependence of sedimentation characteristics on the concentration of calcium oxide is typical for the beginning of the process (the time interval of 15–30 min). In the further process, free settling gives way to the constrained one and to the subsequent compacting of the deposit.

Decrease in the rate of sedimentation and compacting of the deposits, which have been obtained during the clarification of the concentrate after nanofiltration with higher  $CaO$  concentrations, is attributable to the fact that organic impurities in the concentrate as compared to DWD exist in a soluble form or in the form of nanodispersed particles of a certain size. Therefore, the formed agglomerates show a considerably smaller hydraulic coarseness. In addition, the content of mineral and organic admixtures in the concentrate is so high that it

represents a supersaturated structured solution in its essence, where the processes of aggregation and dehydration are somewhat slowed.

We have found experimentally that with the use of the nanofiltration method, it would suffice to conduct the preliminary process of DWD clarification with lime at pH 10.0–10.5 and this allows a considerable reduction in the consumption of calcium oxide (from 20–30 to 8–15  $g/dm^3$ ).

The point is that this quantity of pH is still not enough to form aggregates with the hydraulic coarseness that ensures effective sedimentation; nevertheless, because of the sizes of associates being formed, they can be held back by means of nanofiltration. Thus, the nanofiltration process can serve as an intermediate stage between the reagent purification and reverse-osmotic demineralization of DWD. Applying the nano-filtration, one can simultaneously reduce the consumption of a reagent at the first stage of purification and can conduct the subsequent reverse-osmotic demineralization process at a lower working pressure. Extraction of colloids, macromolecules and multiple-charged ions from the solution at the stage of preliminary purification will allow a considerable reduction in the osmotic pressure of the solution during reverse osmosis.

The developed flow diagram for purification of infiltrate (Fig. 4) involves delivering of DWD, of the concentrate, which has been produced at its purification through the nanofiltration and of “lime milk” in the central feed tube of a vertical settling tank, the tube serving as a mixer.

Lime is dosed automatically based on the water pH monitoring. “Lime milk” is prepared in a separate container 10 by hydraulic stirring with the help of the pump. Upon mixing the components in a settling tank 1, a significant part of organic and mineral admixtures precipitates. The clarified solution is fed into a deaeration tower 2 where it is bubbled by air. Under the alkaline condition, ammonium ions form  $NH_4OH$  molecules, which are decomposed to form  $NH_3$  and  $H_2O$ . Ammonia is readily blown off by air and is caught at the outlet from the settling tank by sulphuric acid inside the tank 9. Sulphuric acid, absorbing ammonia, converts it to  $(NH_4)_2SO_4$  salt (nitrogenous fertilizer). The

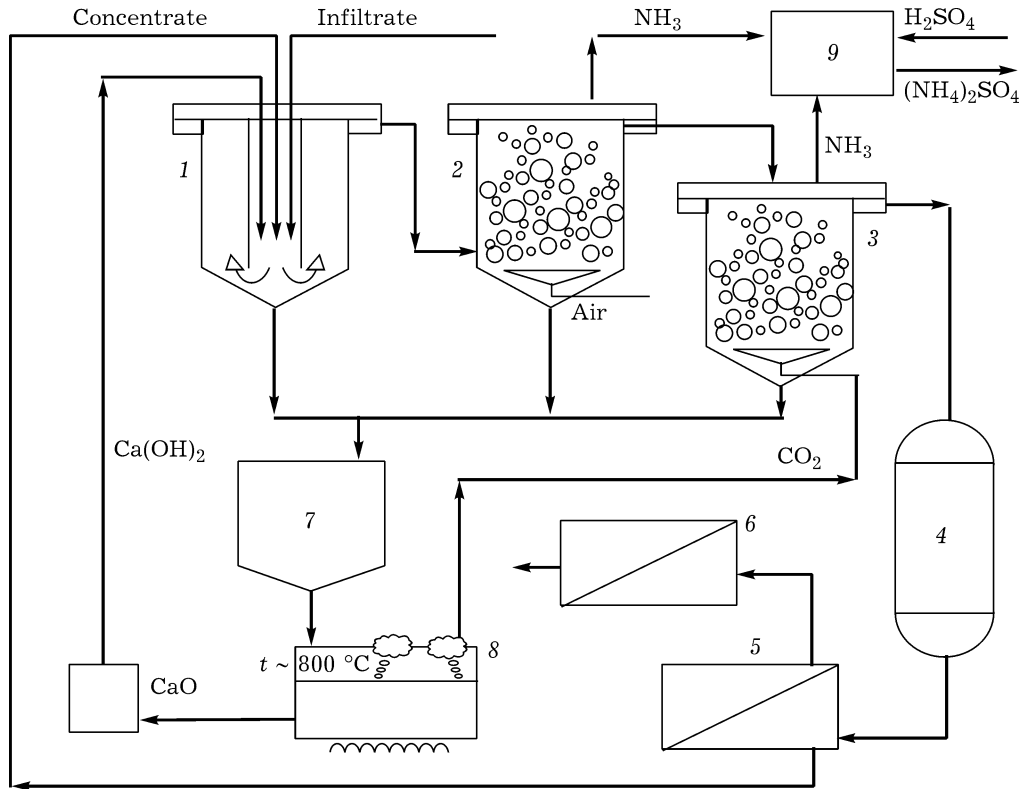


Fig. 4. Process flow diagram for the purification of drainage water from dump: 1 – vertical settling tank with the built in mixer, 2 – deaeration tower, 3 – carbonizer, 4 – pressure sand filter, 5 – module for nanofiltration, 6 – module for reverse osmosis, 7 – container for collecting the slimes, 8 – unit for roasting of the deposit, 9 – container to produce the nitrogenous fertilizers, 10 – container for preparation of lime milk.

presence of carbonic acid in the blasted air promotes precipitation of lime carbonate in the tapered bottom of the deaeration tower. Then the solution enters the carbonizer 3, where carbonic acid is fed to attain the complete removal of calcium ions. In consequence of this, the solid phase of lime carbonate forms and precipitates and coincidentally with this, pH drops (from 12.0 to 8.0). All slimes are diverted

from the settling tanks into the deposit collector 7, while the infiltrate is first delivered to the pressure sand filters 4 for additional clarification and then to the nanofiltration module 5 equipped with semipermeable membranes OPMN-P. After the nanofiltration, permeate is fed to the reverse-osmotic module 6 for demineralization and concentrate, to the “head” of sewage disposal plants, *i.e.* to the reagent

TABLE 2

Efficiency of purification of drainage water from dump (DWD) at various stages

Water sample	$Q$ , %	$V$ , $\mu\text{m/s}$	$P$ , Pa	pH	COD, $\text{mg O/dm}^3$	$C_{\text{NH}_4^+}$ , $\text{mg/dm}^3$	Solid residue content, $\text{mg/dm}^3$
Initial DWD	–	–	–	8.0	4956	1810–963	11000
Decontaminated CaO	–	–	–	12.0	1620	856–440	4940
Permeate from nanofilter	78	5.1	1.5	7.65–8.2	368	620–236	3320
Concentrate from nanofilter	22	5.1	1.5	8.2	5920		
Permeate from the reverse osmosis				8.0–8.7		80–100	60–264

TABLE 3

Basic characteristics for baromembrane desalting method of DWD, previously purified with the "lime milk"

Components	Content, mg/dm <sup>3</sup> , preceded by		
	liming	nanofiltration	reverse osmosis
K <sup>+</sup>	2199	1700	26
Na <sup>+</sup>	1880	195	34
Ca <sup>2+</sup>	–	16	2
Fe <sup>3+</sup>	0.86	0.028	0.01
NH <sub>4</sub> <sup>+</sup>	610	323	80
Chlorides	2840	1850	57
Solid residue	5540		97
pH	7.35	7.07	9.56

purification stage. The concentrate from the process of reverse osmosis is subject to evaporation.

Experimental approbation of the suggested flow diagram is performed in a pilot unit on the range No. 5.

Data concerning the efficiency of DWD purification, which have been acquired when carrying out the pilot trials on the range, are presented in Table 2.

It should be pointed out that when crude (initial) DWD is filtered, the productivity of the reverse-osmotic module drops by approximately 40 % after 2 h of work.

It has been found in the experimental investigations performed on the range No. 5 that the addition of the reagent stage and the stage of nanofiltration before the reverse osmosis allows its productivity to be considerably raised and the duration of interregeneration cycles to be simultaneously increased. This result is achieved due to a decreased effect of polydisperse impurities, some portion of which is removed first at the reagent purification stage and then at the stage of nanofiltration purification. This ensures a decrease in osmotic pressure of DWD that enters the reverse-osmotic module. Results of progressive purification of DWD by calcium oxide, by nanofiltration and reverse osmosis are presented in Table 3.

It is evident that pretreatment of DWD with lime and following purification using nanofiltration with the subsequent desalting by reverse osmosis provides the high quality purification.

The nanofiltration membranes applied hold back high-molecular organic substances and multiple-charged ions thus providing a further decrease in osmotic pressure during the subsequent reverse-osmotic process. Studying an influence of the preliminary purification of DWD by lime on the functioning of the nanofiltration module has demonstrated that the process can be performed in the low working pressure regime (1.5 MPa) with the permeate withdrawal degree being as great as 80 %.

As it was found (Fig. 5), irrespective of the permeate withdrawal degree, the osmotic pressure is lowered with an increase in the concentration of calcium oxide that is used for DWD treatment. Reducing the working pressure of

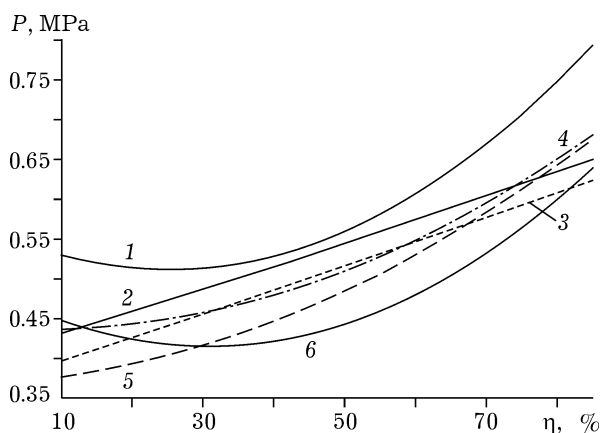


Fig. 5. Dependence of osmotic pressure ( $P$ ) on the permeate withdrawal degree ( $\eta$ ) during the nanofiltration of DWD that was cleansed with CaO using different concentrations, g/dm<sup>3</sup>: 0 (1), 5 (2), 7 (3), 9 (4), 11 (5), 15 (6). Plots are represented by polynomial trend lines of the 2nd power.

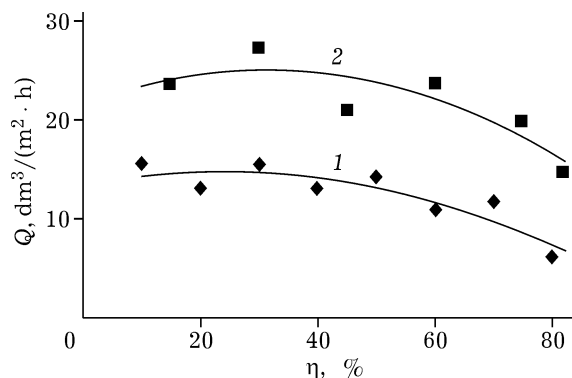


Fig. 6. Dependence of the productivity ( $Q$ ) of the OPMN-P nanofiltration membranes on the permeate withdrawal degree ( $\eta$ ) during the purification of the initial DWD (1) and of the DWD that was previously cleansed with the use of calcium oxide (2).  $C_{\text{CaO}} = 15 \text{ g/dm}^3$  (dry mass). Bringing pH to the value of 8.5 was performed using  $\text{CO}_2$  purging.

the nanofiltration module makes possible a decrease in operational expenses of this purification technology and a simultaneous rise in the productivity of the nanofiltration process.

The results of the investigations have demonstrated that applying the liming method for pre-purification of DWD makes it possible to increase the productivity of OPMN-P membrane by a factor of 2 with the permeate withdrawal degree being 50–80 % (Fig. 6), whereas the duration of the cycle between membrane washings shows a 3-fold rise.

When making the work, we have considered also the questions of disposal of waste formed during DWD purification, including the deposits being formed upon the reagent treatment of the nanofiltration concentrate. Taking into consideration the circumstance that the concentrate formed during the nanofiltration is ecologically dangerous and is subject to

liquidation, we performed the investigations into the combined purification of the concentrate and DWD at the reagent stage. With the aim to improve sedimentation characteristics and to decrease required reagent doze for purification of the concentrate, the process of its joint purification with the initial DWD in different proportions has been studied. Data, which are represented in Fig. 3 (curve 3), correspond to mixing of DWD and the nanofiltration concentrate up to 50 vol. %. With a decreased fraction of the nanofiltration concentrate in the mixture, the purification degree rises and sedimentation characteristics approach the indices characteristic of initial DWD. In technological process, the volume of the formed concentrate, as a rule, does not exceed 20 vol. % from the clarified DWD volume, which allows delivering it to the stage of reagent purification.

In an effort to reach the maximum recovery of waste products that are formed during purification of DWD, the process of high-temperature mode regeneration of CaO using the slimes from the reagent purification stage and the efficiency of the repeated use of slimes was examined. The deposit was calcined at a temperature of 800 °C, then the produced CaO was employed at the stage of reagent purification. Results on the efficiency of DWD clarification with technical lime and with lime produced from the waste of reagent treatment are presented in Table 4.

It can be seen that the efficiency of DWD purification with calcium oxide, which has been obtained from waste, is a little higher relative to technical CaO (GOST 8677–76). This is due to the fact that  $\text{Mg}^{2+}$  ions (even at small concentrations of DWD), as they precipitate under the alkaline condition in the form of magnesium hydroxide, transform to magnesia during roasting and upon multiple re-use of the calcinated slimes, magnesia will accumulate and enhance the adsorption process during the reagent purification. The by-product arising in thermal method of producing a marketable CaO from slimes is carbonic gas, which can be useful for the carbonization process in the settling tank 3 (see Fig. 4).

TABLE 4

Efficiency of DWD clarification (based on the variation of optical density  $D$ ) with the use of technical CaO (GOST 8677–76) and with CaO produced by roasting from slimes of technological process of purification

CaO	Content, mg/dm <sup>3</sup>	$D$	pH
Technical (GOST 8677–76)	10.0	0.635	12.50
	15.0	0.618	12.55
	20.0	0.600	12.57
Produced from wastes	10.0	0.614	12.50
	15.0	0.592	12.55
	20.0	0.571	12.50

## CONCLUSIONS

Thus, a ponderable argument in favour of adoption the liming procedure at the stage of the premembranous purification of DWD is solving the problem of slimes disposal, which are formed during the process of reagent purification. Heat treatment of slimes (800 °C) ensures elimination of toxic organic matters and facilitates formation of highly effective calcium oxide and carbonic gas to be re-used in the process of reagent purification. Recycling of the nanofiltration concentrate to the “head” of sewage disposal plants (to the reagent stage) permits solving a serious environmental problem of its neutralization [12]. Ammonia is reclaimed in the form of nitrogenous fertilizers.

Preliminary purification of DWD with lime ensures a high quality of the subsequent membranous stage of purification and at the same time, significantly reduces operating costs for regeneration of membranes. The incorporation of the nanofiltration module with preliminary reagent purification of DWD improves the work of the reverse-osmotic module and 3 times enhances operational life of membranes.

In addition, the use of CaO provides the conditions for conducting the reverse-osmotic process at the working pressure to 2 MPa, which, in its turn, reduces operational expenses.

As can be seen from the presented results, the developed flow diagram of DWD purification in general shows a comprehensive character and it is suited to the growing ecological requirements for the technologies being brought into practice.

## REFERENCES

- 1 I. Madzyuk, *Ekotehnologiya i Resursoberezhniye*, 3 (2003) 41.
- 2 K. Forster, D. Ways, *Ekologicheskaya biotekhnologiya*, Khimiya, Leningrad, 1990.
- 3 A. Zaboulis, M. Loukidon, K. Christodolou, *Chemosphere*, 44, 5 (2001) 1103.
- 4 R. Saint-Fort, *Env. Sci. Health, A.*, 37, 2 (2002) 237.
- 5 J. Michelin, *J. Chem. Techn. Biotech.*, 76, 8 (2001) 793.
- 6 F. Gegen, *Water Sci.*, 27, 2 (2001) 177.
- 7 K. Seiler, P. Comer, M. Wagner, *Abwasser*, 48, 12 (2001) 1769.
- 8 Pat. 66206 Ukraine, 2004.
- 9 Prospects of Pall-Rohem, Gamburg, Germany, 2002.
- 10 A. Povarov, V. Pavlova, L. Erekhina, M. Shinenkova, in: 2 Mezhdunar. kongr. po upravleniyu otkhodami, Moscow, 2001, p. 159.
- 11 Yu. Lurie, *Unifitsirovannye metody analiza vod*, Khimiya, Moscow, 1972.
- 12 Pat. 66584A Ukraine, 2004.