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Modernization of conventional spiral wound module—principles to design RO without pretreatment and concentrate effluents

A.G. Pervov

Department of Water Supply, Moscow State University of Civil Engineering, Moscow, Russian Federation, Tel. +7 495 766 7644; emails: info@waterlab.ru, waterlab@yandex.ru

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ABSTRACT

The present work is aimed at development of a new approach to reduce RO concentrate flow and to increase recovery. The described techniques enable us to remove calcium carbonate from RO concentrate by means of "seed" crystallization. These proposed techniques use "open channel" spiral wound membrane modules that can directly treat water with high scaling and fouling potentials without pretreatment. The experimental procedure is described and experimental plots are presented that describe precipitation kinetics. The test membrane unit was operated in circulation mode and recovery values reach 95% or higher. RO concentrate constantly passed through the precipitation reactor where seed crystals were contained. Seed crystal formation was initiated by injecting caustic solution to RO concentrate. The driving force for crystal growth was constantly created by RO process due to increase in calcium and carbonate ion concentration values. Fouling control is achieved by providing sufficient cross-flow velocities, flushings and cleanings. Coagulated suspended matter after membrane flushes is collected, sedimented and finally dewatered. The concentrated solution that contains rejected salts and impurities constitutes not more than 1% of initial feed water volume and can be withdrawn together with wet sludge as sludge moisture. The described technical procedure enables us to completely utilize concentrate and produce quality product water, softened water and sludge.

Keywords: Reverse osmosis concentrate; Concentrate utilization; Calcium carbonate precipitation; Seed crystallization

1. Introduction

Two main economic factors that influence successful RO industrial application are: operational costs to ensure pretreatment and the handling of concentrate disposal [1,2]. Both of these problems and their solutions are closely connected: the necessity of adequate pretreatment is attributed to the fouling and scaling hazard as suspended particles, organics and sparingly soluble salts can form sediments on membrane surfaces and decrease membrane product flow and rejection values. To increase recoveries, a number of techniques are being developed such as withdrawal of calcium sulphate from concentrate by precipitation on the seeds in reactor [3], lime softening to withdraw carbonate [4] and to apply air stripping to increase pH values [5]. Zero Liquid Discharge tools are being implemented by increasing recoveries and reduction of concentrate volume followed by evaporation. Control of scale formation in membrane channels can also be implemented by means of "seed" precipitation

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described in [6]. In these experiments tubular membrane modules were used. The "open" membrane channel of tubular modules provided safe operation of the pilot unit without the fear of seed particle "trapping" by a spacer mesh and fouling, which exists when spiral wound membranes are used. Also recovery can be increased using a "contact stabilization" process [7], where RO concentrate passes through a "contact" mass filter bed and calcium carbonate is precipitated on the "contact mass".

This article offers a new approach to solving pretreatment and concentrate disposal problems, based on the understanding of fouling mechanisms in membrane channels and the introduction of new "open channel" membrane modules with decreased fouling potential as a tool to simplify pretreatment and increase recoveries.

High values of concentrate flow are mainly attributed to the "fear" of exceeding the solubility limits of main sparingly soluble constituents such as calcium sulphate and calcium carbonate in RO concentrate, as it is recognized as subversive to membrane performance. As it was shown in a number of previous publications, fouling and scaling in commercial RO modules are attributed to the module design and channel geometries [8,9].

The main disadvantages of spiral wound modules are attributed to the presence of separation spacer mesh in the feed channel as it traps fouling particles and increases cross-flow channel resistance. The places (spots) where the mesh connects to the membrane surface provide "dead areas" without cross-flow that result in high concentration increase at the membrane surface, initiating the formation of crystals. Organic and colloidal matter coagulates and sediments within "dead areas", promoting expansion of the foulant layer around the "dead area". The accumulation of foulant around mesh bundles increases flow resistance —an increase that follows the filtration theory mechanism.

Fig. 1(a) shows results of author's observations during his research devoted to understanding scaling and fouling mechanisms. The boundary layer where the concentration polarization effect occurs can be considered a "chemical reactor", where flocculation of the suspended, colloidal and organic matter, as well as calcium carbonate crystal nucleation processes take place (Fig. 1). This idea to use membrane concentration process as a driving force to remove turbidity, colour and hardness seems very attractive, as no reagent is required. Foulants that sediment on the membrane surface are easily removed using hydraulic flushes.

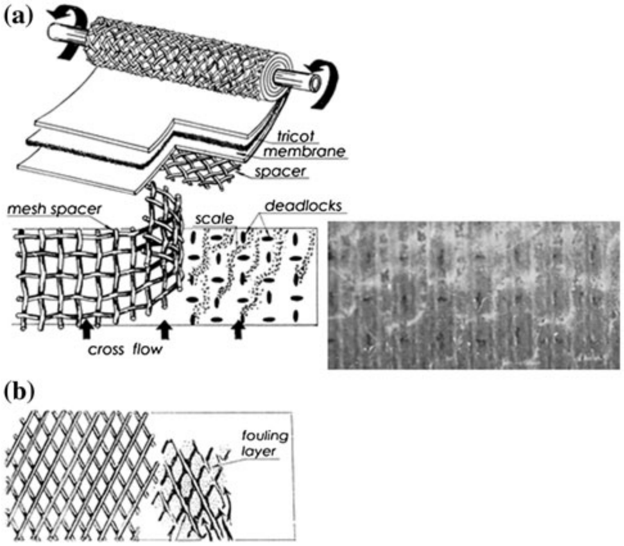

Fig. 1. Fouling and scaling: influence of space. Formation of crystals in dead areas: (a) formation of scale crystals; (b) particle trapping and fouling layer formation.

Fig. 1. Formation of "dead" areas on membrane surface in spiral wound membrane modules (a) and their elimination in an "open channel" configuration. Application of spiral wound membranes substantially reduces operating costs due to lower required cross-flow values as compared with the use of tubular configuration. This technique uses "open channel" spiral wound membranes where tubulation mesh and its influence on flow resistance is eliminated and hydraulic conditions are similar to those of the tubular configuration. The open channel configuration is described in [8]. Technical considerations to improve membrane channel geometry and avoid formation of "dead areas" are shown in Fig. 2. Modernization of the channel is developed by the author and patented.

Application of the developed "open channel" membrane modules in RO facilities that treat surface water and well water can exclude pretreatment. This, in turn, can significantly reduce start-up and operational costs of building pretreatment [8]. Elimination of the spacer mesh from the feed channel in spiral wound modules eliminates "dead" regions that provide scaling and fouling conditions. This novel concept of spiral wound module with an "open channel" configuration offers a new way to prevent scaling and fouling, and develop a new way to treat water with high fouling potential. The risk of sparingly soluble salts precipitation (calcium carbonate, etc.) is minimized by the strong stability of calcium carbonate solutions. Introduction of the "open channel" configuration also helps to exclude measures that control

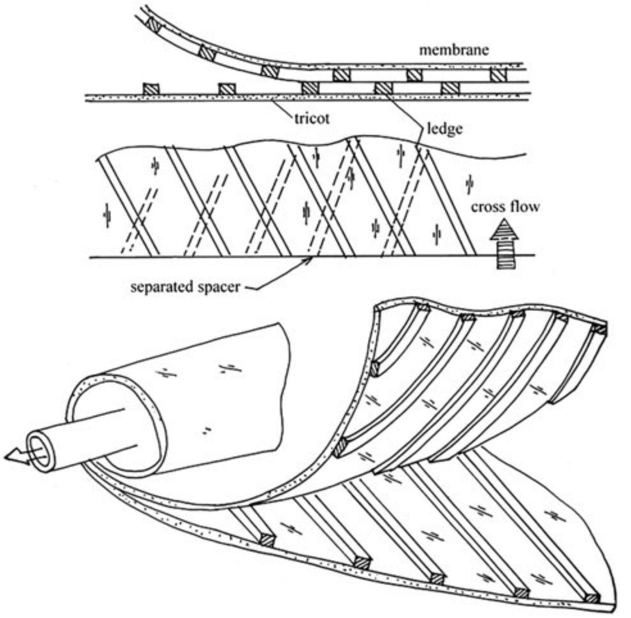

Fig. 2. Open channel configuration in spiral wound module.

Fig. 3. Nanofiltration unit for surface water treatment: 1—pressure feed water tank; 2—prefilter 50—100 micron; 3—feed water pump; 4—flush water tank; 5—nanofiltration modules; 6—solenoid valves; 7—clean water outlet; 8—concentrate and flush water discharge.

scaling—such as antiscalant dosing, softening, acid addition and timely cleanings. As it was already mentioned [8], fouling control is achieved by providing sufficient cross-flow velocities, flushes and cleanings.

As it was discussed above, elimination of the spacer mesh from the feed channels of spiral wound modules eliminates “dead” regions that provide scaling and fouling conditions while also reducing the risk of particle trapping and associated dramatic increase of cross-flow resistance. To control colloidal fouling, automatic flushes are applied by opening of solenoid valves located on the concentrate line at the outlet of the module. Hydraulic flushes destroy fouling layers and withdraw foulants from membrane surface due to cross-flow velocity increase and water hammer initiation through rapid pressure drop. Flush modes (time intervals between flushes and flush durations) are very important in maintaining fouling control and flow velocities on the desired level.

Fig. 3 shows membrane unit for surface water treatment featuring “open channel” modules and built-in flushing system. Feed water is pressurized by a centrifugal pump and is forwarded to membrane module and small pressurized accumulation tank. When the solenoid flush valve is open, flow pressure drops and cross-flow velocity increases. To ensure high cross-flow velocity value, pressurized feed water tank is used.

Typical industrial scale NF and RO units to treat surface water and to produce 10–50 m^3 of drinking water per day are shown in Fig. 4. The units include membrane modules, pumps, built-in flush systems, product water tanks and re-pressurization pump systems tailored with ultraviolet sterilizers. The units are designed to fit into standard 20 feet containers.

Application of the open channel modules provides safe operation without scaling problems when well water is treated. As it was already discussed earlier [8,10], calcium carbonate solutions are stable and it is possible to operate membrane units with high recoveries beyond calcium carbonate solubility limits in concentrate. As an example of RO unit with decreased concentrate discharge, a membrane system with product water capacity of 15 m^3/h to remove hardness, fluoride and strontium from the well water is shown on Figs. 5, 6 and 7. A low concentrate flow value is reached through the use of membrane modules on the second stage to further decrease concentrate flow. Fig. 5(a) shows a membrane unit (one line) that produces 5 m^3/h of product water. Fig. 5(b) shows the process flow diagram. Feed water is pumped into nanofiltration modules (in the first stage) where it is separated into product flow and first stage concentrate flow. First stage product flow is forwarded to the product water tank and first stage concentrate enters the second stage nanofiltration modules where it is further concentrated and separated into second stage

Fig. 4. Nanofiltration units for surface water treatment: (a) production of 10–15 m^3/d of quality drinking water; (b) production of 50 m^3/d.

product water and second stage concentrate. The second stage product is added to the feed water and concentrate is discharged into the sewer. Fig. 6 shows flow diagram of described process to produce 20 m^3/h unit where mass balance is presented. Concentrate flow is 1 m^3/h. The 20 cubic per hour unit consists of four 5 cubic metre lines shown in Fig. 5 connected in parallel. Fig. 7 shows a membrane treatment station that includes a well water treatment pavilion, membrane unit located in container and the product water tank. The interior of container is shown in Fig. 7(a) and the general view of the station is shown in Fig. 7(b).

Membrane modules with an open channel can be successfully operated even when surface water has high fouling potential. Foulants are removed from membrane surface by flushings. To reduce concentrate amount, concentrate flow can be blended with product water. Fig. 9 shows the flow diagram of RO process to treat surface water to remove turbidity and colour. The membrane unit is operated in circulation mode and recovery could reach 90–95% value. Water after flushes is collected in a special sedimentation tank. After suspended matter contained in the flush water is sedimented, water is blended with the feed water. The sedimented sludge is further dewatered. Thus, the sedimented sludge contains all main impurities that should have been removed from the feed water, such as suspended and colloidal particles, fulvic and humic compounds that form water colour that adsorb at coagulated particle surfaces.

Concentrate is blended with product water. Thus, quality drinking water is produced. It is obvious that concentrate can contain some suspended matter and bacteria that decrease product quality. To remove dissolved organics, bacterial and colloidal matter concentrate can be treated by nanofiltration membrane.

Fig. 9 shows a flow diagram of the process described above where concentrate flow is treated by a nanofiltration membrane before it is blended with the product water. This treatment aims to reject excessive TOC, suspended solids, colour, hardness and bacteria from the concentrate. We use low-rejection nanofiltration membranes that poorly reject monovalent ions (by 40–50%) that provide NF product water TDS only 23–30% lower than the feed water TDS. The determined values of main water ingredients and ionic species in the feed water, product water and concentrate flows are presented in Table 1.

The values of oxidity, TOC, turbidity, colour and suspended solids concentration are determined experimentally during pilot testing [8]. Fig. 10 shows the calculated balance of flows and TDS values of concentrate and product water. Balance calculations accounted for the amount of salts that entered the test unit and was withdrawn from it with the product flow (both first stage product flow and second stage NF product flow) and with dewatered sludge as sludge turbidity. It was also accounted that NF product water does not withdraw all salts contained in RO first stage concentrate. To reach salt "equilibrium", the second stage NF unit is designed to provide higher product flow than first RO stage concentrate flow. The NF membrane second stage unit is operated periodically using first stage RO concentrate as feed water collected in flushing tank (8). Its operation is

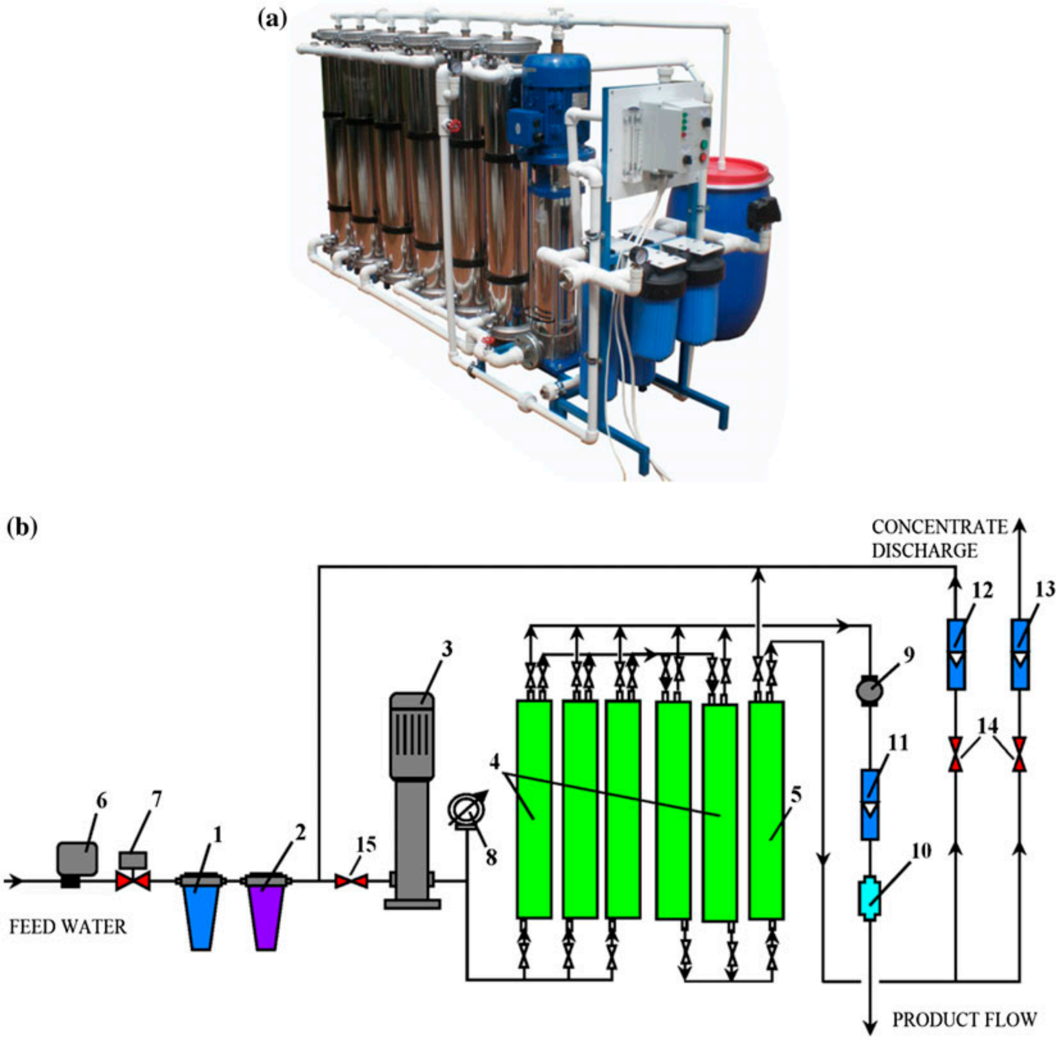

Fig. 5. Membrane system with a reduced concentrate disposal: (a) photograph of one block, 5 m^3/h; (b) flow diagram; 1—100 micron prefilter; 2—solid state antiscalant cartridge; 3—centrifugal pump; 4—membrane module; 5—second stage membrane module for concentrate flow reduction; 6—pressure relay; 7—solenoid valve; 8—manometer; 9—product water counter; 10—conductivity meter sensor; 11—concentrate flow meter; 12—bypass flow meter; 13—concentrate flow meter; 14—pressure gauges.

controlled by the float switch concentrate. The amount of salts containing RO first stage concentrate that enters flush tank (8) thus equals to the amount of salts in second stage NF product water and sludge.

The remaining part of the concentrate flow could be further concentrated and withdrawn with the wet sludge as sludge moisture. The amount of water in the wet sludge constitutes about 0.8–1% of the feed water amount.

Calcium carbonate scaling hazard is recognized as a main factor that disturbs multiplied concentration of the feed water in membrane modules. The use of “open channel” modules enables us to concentrate solutions that are supersaturated by calcium carbonate and calcium sulphate, and to develop a reagent-free technique to remove calcium carbonate water.

The present report aims to investigate the possibilities of decreasing concentrate discharge (to increase recovery) and reducing pretreatment expenses mainly connected with the use of chemicals and facilities to initiate flocculation and to predict calcium precipitation. To increase recovery values, a new process is developed that uses continuous crystallization of calcium carbonate at a constant supersaturation level provided by a constant raise of concentrate TDS while RO is operated in circulation mode.

The investigations of scaling mechanisms on membrane surfaces enable us to simulate it, implement it

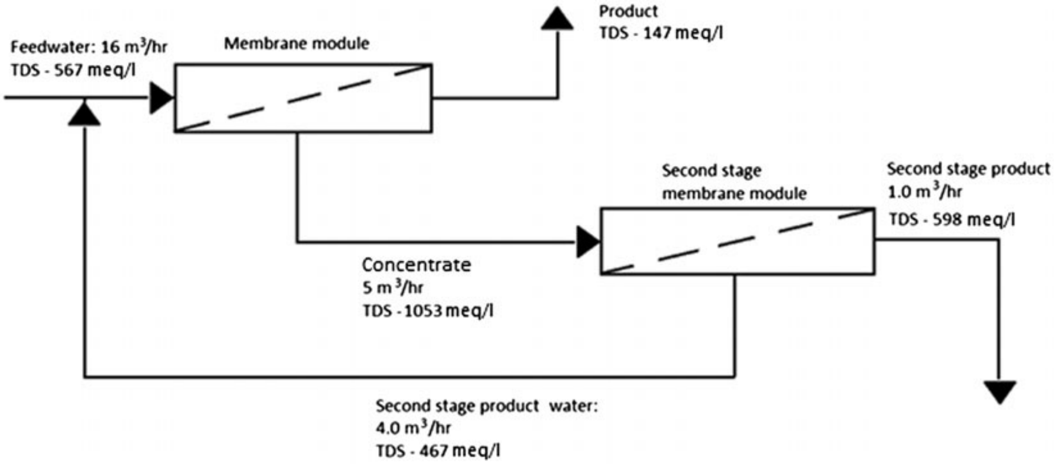

Fig. 6. Flow diagram of membrane unit producing 15 m^3/h, showing flow and TDS values.

"outside" the membrane module and withdraw calcium and bicarbonate ions from the concentrate stream.

The described process can be implemented only on the condition that sparingly soluble salts are not precipitated on membrane surface in the module during its operation. To provide high supersaturation values in circulation solution, the investigation uses newly developed RO spiral wound modules that have an "open channel" without the conventional spacer mesh. This spiral wound module eliminates "dead areas" that provide nucleation and scaling conditions while also reducing the risk of particle "trapping" and associated dramatic cross-flow resistance [7]. Membrane modules maintain high cross-flow velocities that provide a "shear-off" effect for suspended particles. Colloidal matter that adheres to membrane surfaces can be withdrawn from the module by flushing the membrane, therefore eliminating the need to remove colloidal matter from the feed water to control fouling.

In majority cases, when drinking water is produced by RO unit, only partial removal of hardness, fluoride, ammonia and strontium is required. Thus, the largest part of concentrate flow can be blended with the product flow. The described approach enables us to utilize the concentrate by separating the feed water into product water flow and sedimented sludge flow (Figs. 8 and 9).

The principles of RO concentrating of solutions containing sparingly soluble salts and recovery increase are described in [8,9] in respect to calcium sulphate. The supersaturated solution (concentrate) after RO unit enters sedimentation tank where excessive calcium sulfate is precipitated and sedimented. Concentrate after calcium sulphate separation is forwarded back to RO unit where it is further concentrated. Thus, concentrate [11] amount can be substantially diminished. Calcium carbonate system has a different nature and cannot be withdrawn the same way [12,13]. To initiate calcium carbonate precipitation, a constant "driving force" should be applied to maintain constant supersaturation level. This was implemented by caustic addition in [13] and by air-stripping [5] that increased pH in RO concentrate.

The present work aims to develop a new approach to concentrate utilization: seed mass is added to RO concentrate and excessive calcium carbonate is precipitated on the seed mass, then softened concentrate is blended with RO product water. Thus, softened water is produced that can be used either for drinking or technical purposes (such as boiler feed or cooling water). The described water softening method does not require chemicals (such as lime and soda), does not produce brines like sodium-cationite regeneration solution or RO concentrate to be discharged.

The main challenge to initiate calcium carbonate precipitation on the seed crystals is to create a "driving force" for crystal growth—to maintain high supersaturation levels. Calcium carbonate supersaturation depends on calcium and carbonate ion concentration values. Carbonate concentration depends on pH values. As shown previously in [12,13], the addition of seed crystals to calcium carbonate supersaturated solution does not initiate crystal growth as the reduction of carbonate ions decrease the pH value and thus decrease the supersaturation level.

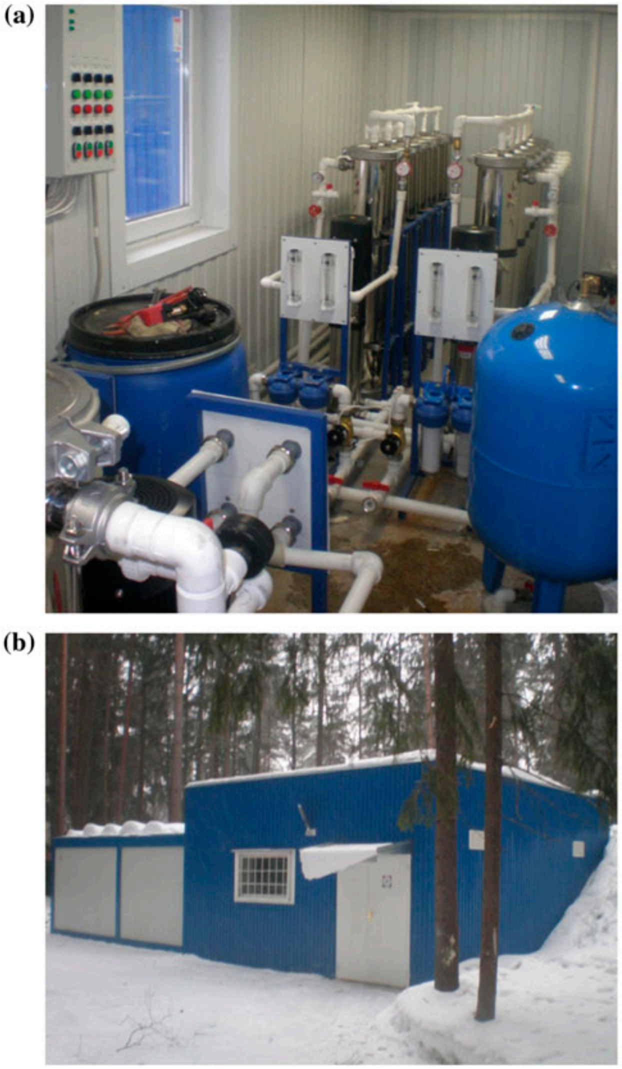

Fig. 7. Water treatment station mounted inside the container: (a) interior of the container; (b) outside view of container attached to water intake.

2. Experiments materials and methods

During RO system operation, calcium and bicarbonate concentration values in RO concentrate constantly increase, providing a driving force for calcium carbonate crystal growth. The present article shows the experimental results of precipitation kinetics study that are influenced by various factors (such as seed concentration, supersaturation, crystal age, etc.).

A flow diagram of the experimental procedure is presented, showing the circulation loop (Fig. 14). Spiral wound modules of 1812 standard (12´´ length and 1.8´´ in diameter) tailored with low pressure RO membranes (BLN-type) manufactured by CSM (Korea) were used in experimental studies for comparison with newly developed modules. New "open channel" spiral wound modules were manufactured using the same flat sheet membranes having the same dimensions and fitting the same size pressure vessel. Modules were manufactured in accordance with configuration shown in Fig. 2 using rolling machine "Model No. RS 4040A" supplied by "Hydrocomponents and Technologies", CA.

A test unit flow diagram is shown in Fig. 10. Feed water is pumped from feed water tank 1 into membrane module 3 using centrifugal pump 2. The working pressure value was 8 Bars. In RO module, feed water stream is separated into two streams: product and concentrate. Product is forwarded to product tank 4 while concentrate is returned back to feed water tank 1. Feed water was concentrated by six times throughout the test run. Feed water tank volume was 60 L. By the end of each test run concentrate volume equalled 10 L.

Natural water (surface and groundwater) was used as test solutions in experiments. To increase fouling and scaling potential of the test solution (to increase hardness, colour or turbidity), natural water was preconcentrated using RO modules.

To initiate calcium carbonate scaling, a test procedure should provide supersaturation conditions as a driving force for crystallization [8,9,12,13]. In described experiments high scaling potential (supersaturation) was constantly arranged due to operation of the test unit in concentration mode where product water was withdrawn.

The feed water is constantly concentrated as the product is constantly withdrawn. "Seed" crystals were produced by addition of caustic solution to RO concentrate. In our experiments, feed water (well water) was preconcentrated six times by volume and stoichiometric amount of 1 N caustic solution was added to concentrate collected in flush water tank 5 to form calcium carbonate. After nucleation occurred and crystal formation phase is finished, the crystals are sedimented during 3–4 h, collected and added to the feed water tank 1. Throughout the test run, feed water is constantly concentrated and samples are collected that correspond to concentration factor values 2, 3, 4 and 6. Calcium and bicarbonate ionic concentrations are determined in these samples. In the end of each test run, membrane "flushings" are applied that last 5–6 s. Concentrate (flush water) is collected in the tank 5. Crystals that are suspended in concentrate and removed from membrane surface are sedimented in tank 5 during 4–6 h and then used in the next experimental cycle.

Thus, calcium carbonate is constantly withdrawn from the circulating solution as supersaturation

Table 1
Chemical compositions of feed water, product water and concentrate

				First stage RO				Second stage RO			
		Feed surface water (River Desna)		Product flow recovery 75%		Concentrate flow (recovery 75%)		Product flow (recovery 93, 75%)		Concentrate flow (recovery 93, 75%)	
No.		mEq/L	ppm	mEq/L	ppm	mEq/L	ppm	mEq/L	ppm	mEq/L	ppm
1	Calcium	3.8	76	1.7	34	9.5	190	5.3	106	22	440
2	Sodium	+	27.6	0.9	10.8	6.5	78	3.6	43.2	15	180
3	Sodium	5.7	131.1	2.6	59.8	13.6	312.8	1.81	41.63	9.2	211.6
4	Chlorides	2.1	73.5	1.4	49	4.2	147	2.8	98	8,4	294
5	Sulphate	0.8	38.4	0.1	4.8	2.9	139.2	1.25	60	7,8	374.4
6	Bicarbonate	5.9	359.9	3.7	225.7	12.5	762.5	6.66	406.26	30	1830
7	pH	6.85		6.75		7.6		7.3		8	
8	Oxidity	6.48			3.0		108		90		141
9	Colour	4.2		17.5			368		164		911
10	Turbidity		12.1		0.1		145				
11	TDS	635.9		384.1		1629.5		775.09		3,330	
12	Flow %	100		75		25		18.75		16.25	

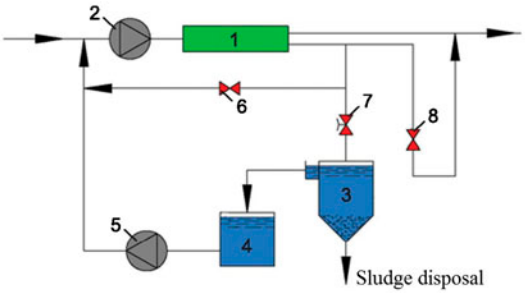

Fig. 8. Flow diagram of RO process to treat surface water for removal of turbidity and colour: 1—open channel module; 2—recirculation pump; 3—flush water tank; 4—water for reuse; 5—water reuse pump; 6—circulation valve; 7—solenoid valve; 8—pressure gauge.

constantly provides a driving force for crystal growth. Small crystals sediment on membrane surface during membrane operation and are easily flushed from the membrane surface by applying "flushings".

3. Discussion of results

Figs. 11 and 12 shows dependencies of calcium and bicarbonate ion concentrations in the circulating feed water solution on the concentration ratio, which is determined as a ratio of feed water volume to concentrate volume, during a test run. Fig. 11 shows calcium and bicarbonate concentrations versus concentration factor for two cases: without seed crystals addition and in the presence of seed crystals. The amount of the added calcium carbonate was 10 g (250 mEq). Fig. 12 shows the influence of the seed mass and cross-flow value on the seed crystal growth rate. Addition of the double amount of seed crystals (20 g) decrease concentrations of calcium during the test run as compared with experimental curve that corresponds to addition of 10 g. Decrease of cross-flow value also decreases concentrations of calcium in the samples collected throughout test run that indicates that calcium carbonate growth intensiveness increases. The curves 2 and 4 are shown in Fig. 15 correspond to cross-flow rates 100 and 25 L/h, respectively.

Fig. 13 shows results of experiments conducted to understand the influence of the mass of precipitated calcium carbonate mass on the scaling rate of the seed crystals. Dependencies of calcium concentrations versus concentration ratio throughout 10 test runs are presented in Fig. 13. Seed crystals after each test run were sedimented, collected and added to the feed water tank 1 for the next test run.

Figs. 14 and 15 present results of calcium carbonate growth rate determination. Amounts of precipitated calcium carbonate as a function of time are shown in Fig. 14. Amounts of precipitated calcium carbonate were determined by means of calcium mass balance as a difference between calcium contained in the feed water and concentrate. Calcium carbonate scaling rate values are plotted versus concentration factor (Fig. 15). Scaling rates are determined as tangents of the slope of the plots shown in Fig. 15.

Fig. 15 confirms that calcium precipitation rate does not decrease after 10 cycles of test runs while

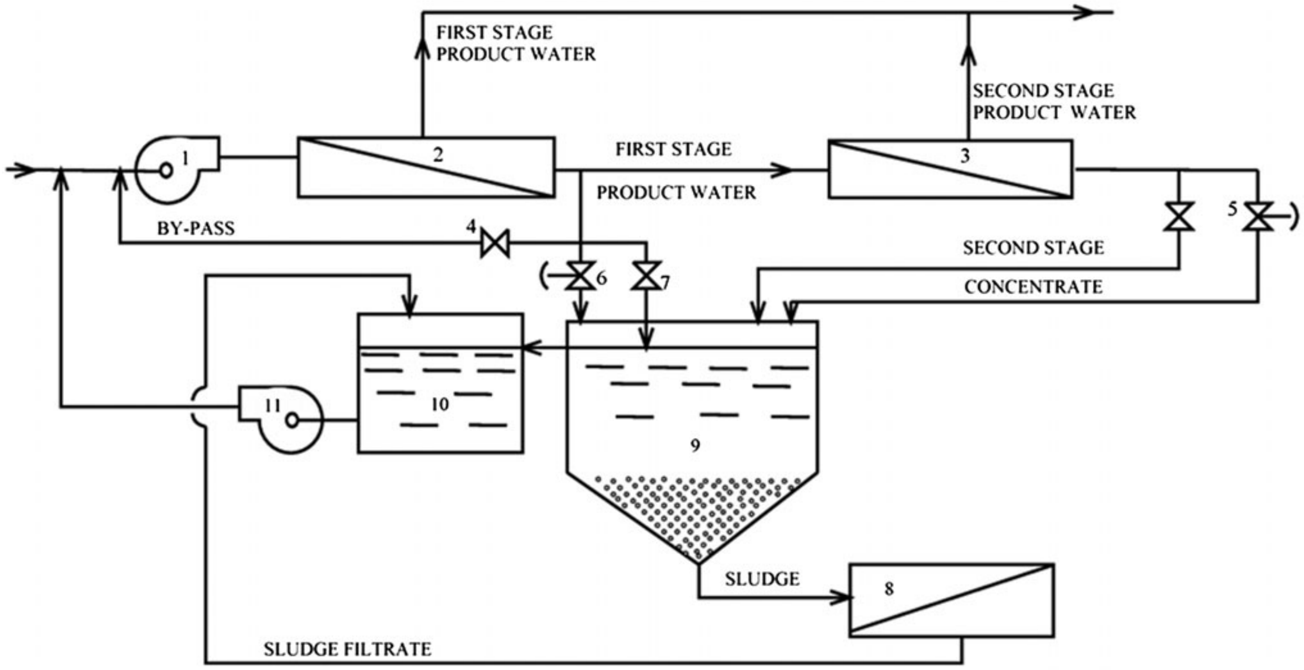

Fig. 9. Flow diagram of RO process with concentrate treated by nanofiltration: 1—pump; 2—RO membrane module; 3—nanofiltration second stage membrane; 4—bypass valve; 5,6—solenoid valves for flushing; 7—pressure gauges; 8—sludge dewatering system; 9—flush water sedimentation tank; 10—water reuse tank; 11—water reuse pump.

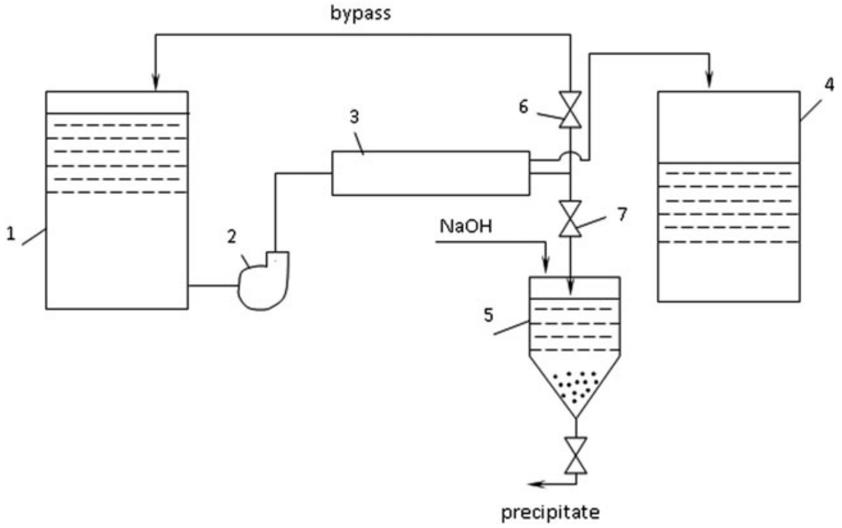

Fig. 10. A test unit flow diagram: 1—feed water tank; 2—feed water pressure pump; 3—RO membrane module; 4—product water collect tank; 5—flush water seed crystals sedimentation tank; 6—bypass valve; 7—flush solenoid valve.

seed crystals grow and their weight and size increase. Seed crystals should be replaced after their size increase to avoid their sedimentation on membrane surface. Observations of seed crystals sedimentation revealed that it took from 1 to 4 h to sediment calcium carbonate crystals collected after flush cycle. About 30% of all crystals collected after 10th test run sediment during one hour. Fig. 18 shows microphotographs of crystals at different growth stages.

After contact with the “seed” mass, concentrate can be blended with product water to produce softened water with a decreased TDS value (by the value

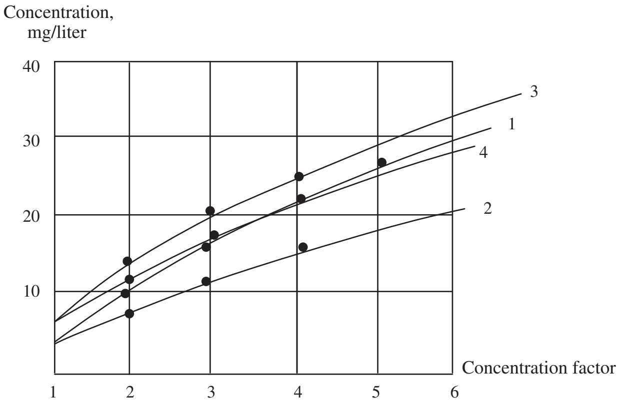

Fig. 11. Experimental results of calcium carbonate growth on seed crystals. Concentrations of calcium and bicarbonate ions in circulation solution versus concentration factor: 1—calcium ion (well water, without seed addition); 2—calcium ion (well water, after addition of 250 mEq of calcium carbonate); 3—bicarbonate ion (well water, without seed addition); 4—bicarbonate ion (well water, after addition of 250 mEq of calcium carbonate).

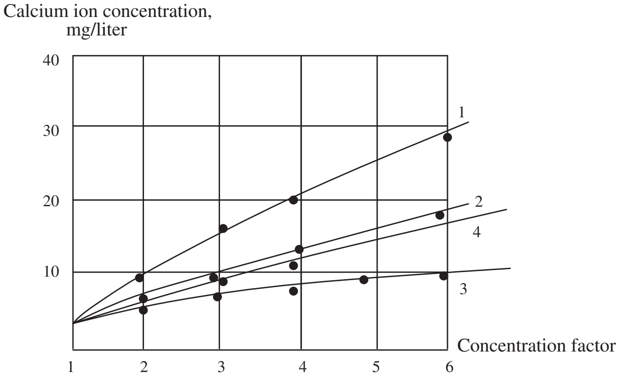

Fig. 12. Investigation of the influence of the mass of added seeds and cross-low rate on the rate of calcium carbonate growth on seed crystals. Calcium ion concentrations in circulating solution versus concentration factor: 1—well water, without seed addition; 2—well water, after addition of 250 mEq of calcium carbonate, cross-flow rate—100 L/h; 3—well water, after addition of 500 mEq of calcium carbonate, cross-flow rate—100 L/h; 4—well water, after addition of 250 mEq, cross flow—25 L/h.

of withdrawn calcium carbonate). Table 2 shows the concentration of ionic species in the feed water, concentrate, product water and blended solution.

Thus, the use of described techniques enables us to produce softened water without the use of reagents (as during lime and soda softening), high TDS brines (as during ion-exchange softening) or RO concentrate flows.

The main disadvantage of the process, shown in Fig. 10, is its "periodical" operational mode that limits practical application. For industrial application of results a "continuous" operational mode is developed. Fig. 16 shows a flow diagram of the unit operated in "continuous" circulation mode with constant concentrate and precipitate discharge.

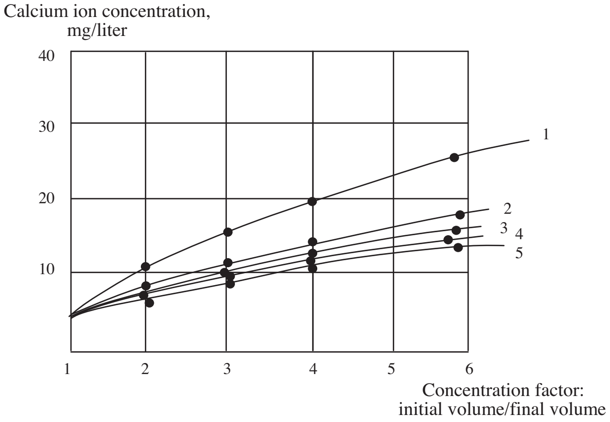

Fig. 13. The influence of the mass of precipitated calcium carbonate on crystal growth rate. Calcium ion concentrations versus concentration factor at different stages of crystal growth: 1—well water, without seed addition; 2—well water with addition of 250 mEq of calcium carbonate, first cycle; 3—well water with addition of seed crystals after two cycles; 4—well water with addition of seed crystals after five cycles; 5—well water with addition of seed crystals after 10 cycles.

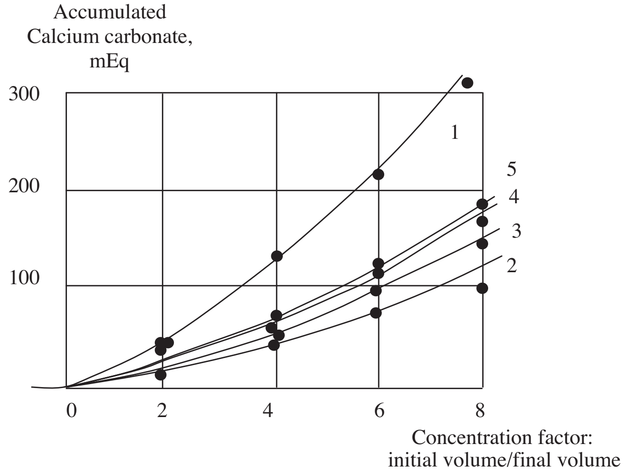

Fig. 14. Mass of calcium carbonate accumulated on the seed throughout test run versus concentration factor at different stages of crystal growth: 1—well water, without seed addition; 2—well water with addition of 250 mEq of calcium carbonate, first cycle; 3—well water with addition of seed crystals after 2 cycles; 4—well water with addition of seed crystals after 5 cycles; 5—well water with addition of seed crystals after 10 cycles.

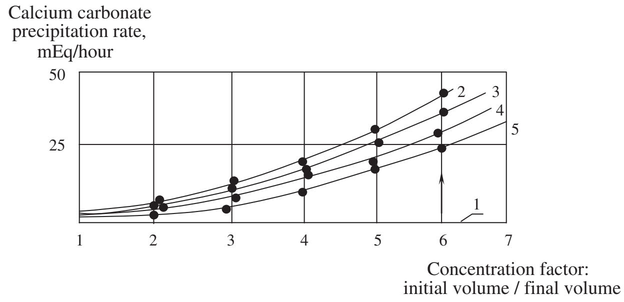

Fig. 15. Determined calcium precipitation rate values versus concentration factor: 1—well water, without seed addition; 2—well water with addition of 250 mEq of calcium carbonate, first cycle; 3—well water with addition of seed crystals after two cycles; 4—well water with addition of seed crystals after five cycles; 5—well water with addition of seed crystals after 10 cycles.

The unit is operated in circulation mode, main part of concentrate is circulated and the other part is discharged. Seed crystals are suspended in circulation solution. To avoid crystals sedimentation on membrane surface, high cross-flow velocities are maintained in membrane channels. Flushings are arranged after 2–3 h of operation. Flushing occurs after solenoid valve 3 is open and increased cross-flow provides a shear force to remove sedimented crystals from membrane surface. Flush water is collected in the tank 4. Large and heavy crystals are sedimented in tank 4, smaller crystals flow into tank 5 and are pumped to the inlet of the unit. As a part of suspended seed crystals is sedimented in the tank 4, it should be replaced by new crystals. Calcium carbonate seed crystals are obtained through addition of caustic solution in tank 5 where nucleation and precipitation occurs.

The consumption of sodium hydroxide and required amount of calcium carbonate seed mass should be determined. As the unit is operated in continuous mode, the amount of calcium precipitated on the circulating seed mass during one hour should correspond to scaling rate value determined experimentally for the certain feed water and recovery conditions. For a "model" membrane test unit with 1,000 L/h capacity, feed water calcium concentration and recovery value 0.83 we can calculate the amount of calcium carbonate precipitated on seed crystals and withdrawn from concentrate constitutes 2,400 mEq/h. Fig. 18 shows calcium carbonate growth rate values versus recovery. For well water and recovery value 0.83 scaling rate equals 21 mEq/h. The test run was conducted using spiral wound module with 0.5 m^2 surface (1812 standard). Product rate throughout test run was 7–8 L/h and pump pressure was 6 Bars. The "model" unit with 1,000 L/h product flow rate operated under the same conditions, requires 60 m^2 membrane surface, thus calcium carbonate growth rate in 1,000 L/h unit is 120 times higher, than in the test unit with 8 L/h capacity and constitutes 2,400 mEq/h. Therefore, the amount of added seed crystals in the "model" unit should be 120 times more than the amount of seed crystals used during test runs (Fig. 18).

In 1,000L/h test unit, the amount of seed crystals circulating in concentrate should be 30,000 mEq of calcium carbonate, or 1,200 g.

To develop the seeding process on industrial level, caustic solution consumption, caustic dosing mode and crystal sedimentation tank parameters should be determined.

As it was already discussed, calcium carbonate seed crystal growth rate does not change significantly throughout the whole period of their growth in the

Table 2
Experimental data sheet

Parameters	Feed water	Concentrate, recovery value 90%	Concentrate after contact with seed crystals recovery value 90%	Product water	Mixture (concentrate and product)
Calcium, mg/L	4.6	38.6	10.4	0.32	1.3
Hardness, mEq/L	6.7	57.8	33.4	0.71	4.1
Alkalinity, mEq/L	6.1	47.6	28.1	1.4	4.1
Chlorides, mg/L	37.9	331	326	16.4	49.1
pH	6.8	8.0	7.9	6.1	6.7

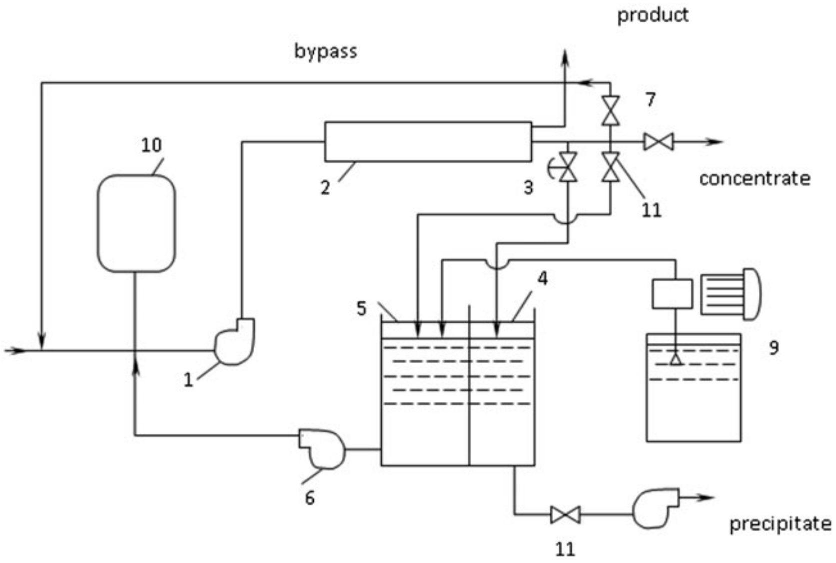

Fig. 16. A flow diagram of natural water treatment with reverse osmosis membranes without concentrate discharge: 1—high pressure pump: 2—membrane module; 3—solenoid valve for flushing; 4—flush water sedimentation tank; 5—concentrate collection tank; 6—concentrate return pump; 7—concentrate bypass valve; 8—pressure regulation valve; 9—caustic dosing unit; 10—feed water pressure tank; 11—precipitate discharge valve.

circulation loop. Fig. 17 shows that amount of calcium carbonate precipitated on seed crystals by the end of the first test run constitute 136–140 mEq. Assuming that the mass of seed crystals added to circulating feed water was 250 mEq, the total mass of seed crystals after the 10th test run equals 1,610 mEq. To reach this amount, the unit should be operated in continuous flow mode (Fig. 16) about 80 h. As it was already mentioned above, about 30% of all flushed crystals are sedimented in tank 4 (Fig. 16). The last 70% of seed crystals enter tank 5 and are pumped to the inlet of the unit. During experimental test runs, the added seed mass was 250 mEq. To replace 30% of the seed mass, about 82 mEq of precipitated calcium

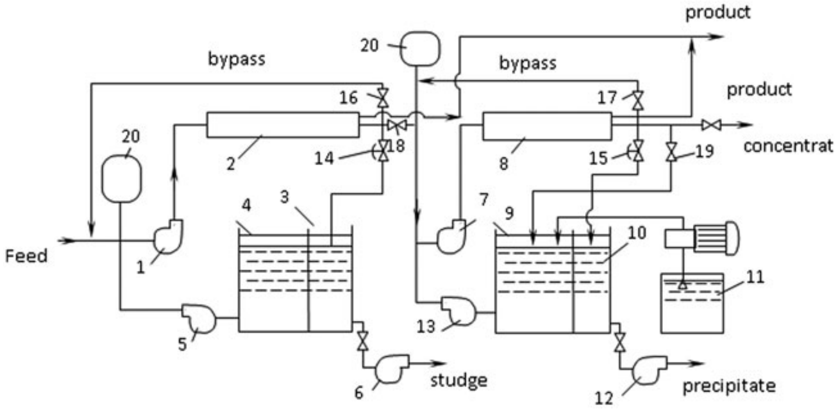

Fig. 17. Double stage membrane unit to treat surface water and utilize concentrate and withdraw suspended matter sludge and precipitated calcium carbonate separately: 1—feed water pump: 2—first stage RO module; 3—flush water collecting tank; 4—sedimented flush water tank; 5—sedimented flush water return pump; 6—sludge discharge pump; 7—second stage pressure pump; 8—second stage membrane module; 9—concentrate and flush water tank to be returned to the second stage; 10—second stage flush water collect tank; 11—caustic dosing unit; 12—precipitated calcium carbonate discharge pump; 13—seed crystals flow pump; 14,15—solenoid valves for flushing; 16,17—bypass valves; 18,19—pressure regulation valves; 20,21—feed water pressure tanks.

carbonate is required. The amount of concentrate required for precipitation of this amount is 4.4 L (for the test unit) and 528 L for the 1,000 L/h unit. The amount of sodium hydroxide added to concentrate is stoichiometric amount of required calcium carbonate. The caustic amount required to produce 30% of added seed crystals (250 mEq) equals 83 mEq. During 10 cycles of test runs, 2000 mEq of calcium was removed that required 83 mEq of caustic, which is only 4% of required stoichiometric amount.

To utilize concentrate, a second stage nanofiltration unit can be used (Fig. 16). Product water after nanofiltration unit is mixed with first stage RO product and concentrate is withdrawn together with precipitated calcium carbonate.

When surface water (or well water containing iron hydroxide) is treated, the continuous mode unit flow diagram (Fig. 16) can include two stages (Fig. 17) to flush out, sediment and withdraw colloidal sedimented sludge and precipitated calcium carbonate separately.

Through the use of the described "seed mass precipitation" techniques, softened water is obtained. The described approach does not require chemicals for calcium carbonate precipitation (as in case of lime and soda softening) or ion-exchange bed regeneration (as in case of ion-exchange softening).

To reach the required removal of dissolved impurities such as fluoride, ammonia, strontium and arsenic part of the softened water is blended with the concentrate. The amount of blended flow is calculated using equilibrium equations.

The developed techniques provide a chemical-free method without wastewater discharge (identified as "liquid discharge"). According to this technique, a part of the product water is blended with the "softened" concentrate after its contact with the "seed" mass. Thus, feed water is divided into two streams: deionized product water (used for steam production) and softened water with a TDS value that does not exceed the feed water TDS (used for heating or cooling). Low hardness values (0.005 mEq/L) or low TDS values could be achieved by implementation of double stage RO.

Suspended and colloidal foulant contained in the feed water can be flushed out of the membrane module, sedimented and dewatered. Growing seed mass can be withdrawn separately from the system and sedimented. To withdraw sedimented suspended matter and precipitated calcium carbonate separately, double stage RO process can be used (Fig. 17). Each membrane stage is operated separately in circulation mode. Different cross-flow velocities are maintained in different stages. First RO stage is used to collect and withdraw suspended matter. Low values of cross-flow velocities are selected to facilitate sedimentation and coagulation of suspended particles on membrane surface. As it was already discussed [3], high cross-flow velocities provide a shear force for particles, suspended in the flow. Fig. 8 shows results of experimental determination of fouling rate values as a function of cross-flow rates and recovery for surface water treatment containing 38 ppm of suspended solids [14]. Experimental test unit contained standard size 1812 module with "open channel". For the certain suspended solids concentration value in the feed water and RO unit operational mode (cross-flow and recovery) fouling rate can be determined (Fig. 18). To ensure all suspended matter is sedimented on membrane surface in the first stage modules (Fig. 17), the amount of foulant accumulated on membranes during one hour should be equal to amount of foulant that enters membrane unit during one hour. To ensure strong fouling low values of cross-flow velocities are maintained in the first stage RO modules (Fig. 17). As an example, we can evaluate parameters of the first stage of RO unit (Fig. 17) with product flow 1,000 L/h. Feed water turbidity is 38 ppm (Fig. 18). If recovery value of the double stage unit, shown in Figure is 0.87 and product flow rate is 1,000 L/h, concentrate flow will be 142 L/h and feed water flow, respectively, will equal to 1,142 L/h. Concentration of suspended solids in feed water is 38 ppm, and 43,396 mg/h enters RO unit. In the test module with 0.5 m^2 membrane surface fouling rate is 120 times less than in 1,000 L/h unit. This value equals to 361 mg/h. Figure shows that this

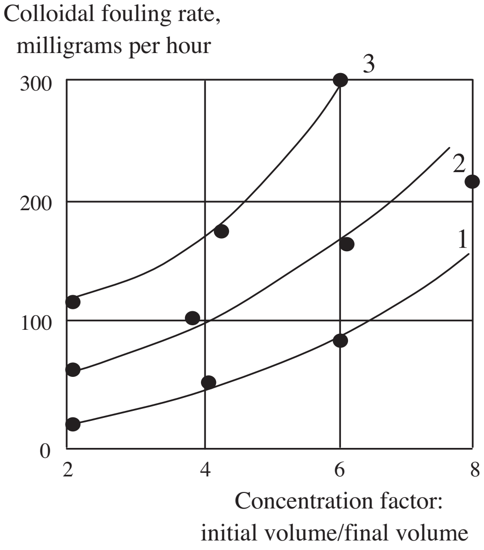

Fig. 18. The influence of cross-flow velocities on particulate fouling rates. Fouling rate values versus concentration ratio for surface water with turbidity value 40 ppm. Cross-flow rates: (1) 25 L/h; (2) 100 L/h; (3) 250 L/h.

value of fouling rate corresponds to recovery value 0.67 and cross-flow 25 L/h. Concentrate flow after the first stage is 380.6 L/h and product low is 761.4 L/h. Thus, product flow of the second stage is 238.6 L/h. Experimental testing can help to determine the required amount of seed crystals, calcium concentration in concentrate, required caustic consumption, etc.

The described approach to utilize RO concentrate by calcium carbonate precipitation and withdrawing is distinguished by the use of RO process as a driving force to provide supersaturation and crystallization. Caustic solution is used not to maintain supersaturation values, as during conventional reagent softening, but to produce seed crystals (initiate homogenous crystallization). The required caustic amount is by 30–50 times lower than stoichiometric value required for conventional calcium carbonate precipitation.

4. Conclusions

Results of conducted studies could be used to introduce new water treatment techniques to directly treat natural water with high fouling and scaling potential using proposed "open channel" spiral wound modules tailored by nanofiltration and reverse osmosis membranes. Elimination of the "dead areas" responsible for scale formation provides a new solution to increase recovery and utilize concentrate.

A new technique is described that enables us to increase recoveries and utilize RO concentrate that consists of calcium carbonate precipitation on the "seed" crystal mass, withdrawal of excessive calcium carbonate and further blending of softened concentrate with RO product water. As a result, softened water is obtained with lower TDS and hardness than of the initial feed water.

The developed techniques do not require chemicals and do not discharge concentrated brines.

The increase of the seed mass increases precipitation rate. The obtained results indicate that even small amounts of seed crystals added to the feed water provide an efficient softening of the feed water. Calcium carbonate mass withdrawn from the feed water by 25–30 times exceeds the mass of seed crystals. After contact with seed mass, concentrate can be blended with product water to produce softened water with a decreased TDS value (by the value of withdrawn calcium carbonate).

References

[1] C. Ventresque, V. Gisclon, G. Bablon, G. Shagneau (France), An outstanding feat of modern technology: The Mery-sur-Oise nanofiltration treatment Plant (340,000 cu. meter per day), Proceedings of the Conference on Membranes in Drinking and Industrial Water Production, Paris, France, 3–6 October 2000, pp. 1–16.

[2] D.E. Potts, R.E. Ahlert, S. Wang, A critical review of fouling of reverse osmosis membranes, Desalination 36 (1981) 235–264.

[3] Y. Cohen, Interstage chemical demineralization for high recovery RO demineralization, The 3-rd Sede Boqer Conference on Water Technologies 2012 "Advanced Technologies in Water Management", 15–17 October 2012. Book of Abstracts, 55 p.

[4] J. Jack Gilron, Flow reversal as a tool in use of crystallizer/secondary RO treatment for high recovery desalination, The 3-rd Sede Boqer Conference on Water Technologies 2012 "Advanced Technologies in Water Management", 15–17 October 2012. Book of Abstracts, 56 p.

[5] R. Segev, D. Hasson, R. Semiat, Improved high recovery brackish water desalination process based on fluidized bed air stripping, Desalination 281 (2011) 75–79.

[6] R.C. Harries, A field trial of seeded reverse osmosis for the desalination of a scaling type mine water, Desalination 56 (1985) 227–236.

[7] S. Veespareni, R. Bond, Getting this last drop: New technology for treatment of concentrate, Tianjin IDA World Congress 2013 on Desalination and Water Reuse, 20–25 October, China, 2013, TIAN 13-357.

[8] A.G. Pervov, Scale formation prognosis and cleaning procedure schedules in reverse osmosis systems operation, Desalination 83 (1991) 77–118.

[9] A.G. Pervov, A.P. Andrianov, Application of membranes to treat wastewater for its recycling and reuse: new considerations to reduce fouling and increase recovery up to 99 percent, Desalination and water treatment 35 (2011) 2–9.

[10] A. Pervov, Utilization of concentrate in reverse osmosis in water desalination systems, Tianjin IDA World Congress 2013 on Desalination and Water Reuse, 20–25 October, China, 2013, TIAN13-216.

[11] C. Niewersch, B. Zayat-Vogel, T. Melin, M. Wessling, Nanofiltration for sulphate elimination in groundwater affected by open coal mining, The conference book of the 6th IWA Specialist, Conference on Membrane Technology for Water and Wastewater Treatment, 4–7 October, Aachen, Germany, 2011, p. 151–257.

[12] M. Okazaki, S. Kimura, Scale formation on reverse osmosis membranes, Desalination 21 (1977) 145–151.

[13] L. Reitz, Development of a broad-spectrum antiscalant for reverse osmosis system, 12-th Annual Conference Water Supply Improvement Association, Orlando, Fla, 13–18 May 1984, Technical Proceedings, vol.1, Sess. 1–6, Topsfield, Mass. s.a., F 1-26.

[14] A. Pervov, A simplified RO process design based on understanding of fouling mechanisms, Desalination 126 (1999) 227–247.