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Water distillation method (options)

PERTINENT ART: technological processes

Invention relates to the technological processes of distillation or partial desalination of brackish and fresh water, mainly for artesian waters of increased (high) hardness with the iron content more than 0,1 mg/l and general mineralization more than 400 mg/l, and can be used for providing potable water as well as for providing treated water for usage in various technological processes.

Previous technical level

There is a known method of reverse osmosis extraction of crystals from mineralized water which includes passing water under pressure through semi-impermeable membranes of the roll membrane element with resulting permeate and concentrate directed to crystallizer where the crystals are extracted , and the clarified solution is mixed with the initial mineralized water, at the same time the concentrate is cooled at first in the heat exchanger with removing warm to the clarified solution and then in the crystallizer directing the latent warm of crystallization to the source of cold, after that the resulting suspension is sent to the separator where the crystals are extracted as dry product and the clarified solution is passed through the heat exchanger before mixing with initial mineralized water.

(see patent RF for invention № 2142329, МПК B01D61/02; C02F01/44, published on 10.12.1999 г.).

The main drawback of the above mentioned method is that it can be used only for desalination of highly mineralized water and assumes the usage of the additional equipment as well as the additional power sources.

There is also a method of deep desalination of fresh and brackish water, which includes the step-by-step processes: clarifying, treatment of the clarified water on the ion-exchanging filters and desalination in the reverse osmosis plants with concentrate withdrawal from each stage of purification. (see. The article “Experience of implementation of reverse osmosis plant”. УОО-166 at Nizhnekamsk HES-1. – Hodyrev B.N. etc // Power Stations , 2002 №6, с.54-62).

According to the known method the process of reverse osmosis desalination is performed at the constant value of applied pressure ~1070 kPa in the plants with equitype membrane elements at the significant value of concentrate discharge 15-30% of feed water consumption which the low values of permeate consumption ratio to concentrate n=2,3÷5,7 comply with. Such method of desalination allows to provide the mode of operation of reverse osmosis plant without mineral deposits in the membrane elements at the relatively shallow concentration of the treated water. At the same time this method as well as the previous ones does not allow to increase the production capacity of permeate and therefore the permeate consumption ratio to the concentrate, and also doesn’t allow to use the produced permeate as a generating solution of Na-cationic filters. In the result of the pointed analogue peculiarities, water consumption for own needs in the desalination plant as a whole is still high 23,5-51,4% of the desalinated water consumption. Besides, shallow desalination of water can be considered as the drawbacks of the known method (the value of the index of electroconductivity of permeate is from 7-8 to 40-50 mkCm\cm) owing to the absence of the additional stage of permeate H-OH-ionization and also in the result of membrane contamination with the organic deposits during the work in the water with increased content of organic substances, especially of technogenic origin. It is stipulated by absence of the step of effective water purification from dissolved organic substances at the stage of preliminary treatment.

The technical essence of the proposed invention is very close to the known method of deep desalination of fresh and brackish water, including the successive step-by-step processes : clarification, treatment of the clarified water on the ion changing filters and desalination in reverse osmosis stage with withdrawal of the concentrate from each stage of purification, at the same time the process of reverse osmosis desalination is carried out at least in two stages, at the higher pressure of the purifying water at the next desalination stage with the membranes meeting the required pressure while pressure of the purified water is set within the limits at the first stage not more than mPa 1,6 and not more than 4,0 mPa – at the last stage when the permeate consumption ratio to concentrate of the reverse osmosis stage is as whole within n=7-99. The concentrate withdrawal from the reverse osmosis stage is performed at each stage of regeneration of ion-exchanging filters, and permeate after reverse osmosis stage of purification is submitted to H-OH- ionization (see Patent RF for invention № 2283288, МПК C02F09/08; B01D61/12; C02F01/42; C02F01/44, published 10.09.2006 г.).

The drawback of the known method is impossibility to recover the working ion-exchange capacity of cationite by the concentrate of the reverse osmosis plant. In compliance with conditions of attaining equilibrium of chemical reaction of Na ion exchange by Ca and Mg, Na ions must be “ two times as much” than Ca and Mg . Only in this case the working exchange capacity of ion exchanger will be recovered to appropriate values. The cationite, being regenerated only by the concentrate of the reverse osmosis stage will recover only the half of the working exchange volume. At the next regeneration - the half of half and so on till the full exhaustion of Na ions.

The amount of acid drainage, produced at regeneration of the permeate H–OH ionization plant, is not sufficient for regeneration of the H-cationization or acidation plant with initial water before the reverse osmosis system. As permeate contains minimal amount of mineral admixtures, regeneration of permeate H–OH ionization plant will be performed much rarely than regeneration of the H-cationization plant.

It is not reasonable from technical and economical point of view to limit salt content of the concentrate of the reverse osmosis stage not more than 10 g/l because at adding common salt in this concentrate in amount necessary for regeneration performance of Na-cationization plant, the concentrate salt content will be 22-25 g/l. The manufacturers of the modern cationite resins are recommended to support the salt content of regenerative solution near 100-120 g/l (8-10%). Besides, at the salt content of the initial water about 1400mg/l, multiplicity of the concentrate concentrating will be n=7, it means that the amount of the concentrate withdrawn from the reverse osmosis stage will be 14% of the obtained permeate consumption. This circumstance significantly increases the volume of generated sewage water and limits the reasonableness of usage of the known method of desalination by the upper bound of the initial water salt content at the level 1000mg/l.

Disclosure of invention

The target of this invention is the increase of salts discharge efficiency, the decrease of produced sewages amount and significant economy of chemical reagents.

Technical result achieved by solving of this task is the significant increase of permeate specific yield from the reverse osmosis system of desalination, the decrease of the concentrate consumption in the desalination stages, and consequently the decrease of water consumption for own needs to 2,5-6%.

The stated technical result is achieved by the method of water desalination (according to the 1st option) which consists in the preliminary clarification of water, then water is sent to Na-cationic filters, while hardness of softened water is set within range 0,02-0,1mg-eq/l, then the solution of hydrochloric acid is dosed to the softened water , and the amount of acid is chosen equivalently to the amount of sodium bicarbonate, then in the calciner natural carbon dioxide is extracted from water, then water step-by-step is directed to the stages of the reverse osmosis system of desalination, while the process of the reverse osmosis desalination is being conducted at least in two stages *through the line of working concentrate*, at the first stage of the reverse osmosis system of desalination the initial flow ratio to the working concentrate is set within the range 70-75%, then the working concentrate is directed to the second stage of the reverse osmosis system of desalination. After the second stage the concentrate is used as initial water for the third stage of the reverse osmosis system of desalination , while the working pressure of the reverse osmosis desalination process is increased from the first step to the last one, from 10 to 50 bar, the working concentrate after the last step of reverse osmosis system of desalination is sent to the salt- solvent- tank where common salt is added and salt content is sufficient for regeneration of Na-filter of the working concentrate capacity after the last stage of the reverse osmosis system of desalination is set within the range 30-50 g/l (ppt) from the tank -salt- solvent the salt solution is pumped sequentially through anionite, then through cationite from the bottom to the top, with the spent regeneration solution draining after filter to disposal.

It is reasonable that the maximum salt content of the working concentrate coming from membranes of the reverse osmosis system of desalination is not less than 50g/l (ppt). Salt content of the working concentrate is set equal to initial water salt content multiplied by 3,5 in degree value of which is equal to amount of the stages of the reverse osmosis system of desalination.

The amount of sodium added into the tank-salt- solvent for mixing with the working concentrate is determined as sodium amount , g/l (ppt), in working concentrate entering the salt- solvent -tank, multiplied by 1,05-1,1.

The stages amount of the reverse osmosis system of desalination is determined from the formula $N=\log_n(25/s)+1$, where N- number of stages of the reverse osmosis system of desalination (it is approximated to more or less direction to the integral number) ; n- multiplicity of the concentrate salt content at the one stage of reverse osmosis , n=3,5; s – initial water salt content, mg/l; 25 –the concentrate salt content from next to last stage of the reverse osmosis, mg/l; 1 – a stage of the reverse osmosis desalination of initially salted water (concentration of salts at this stage is assumed to be in 2 - 2,5 times).

For removing ion bicarbonate from initial water the Cl-anionization technology can be used with observing some conditions, stipulated below instead of hydrochloric acid dosing.

The stated technical result is achieved also with the method of water desalination (according to the second option) which consists in the preliminary clarification of water, sending it to Na-cationite filters while hardness of softened water is set within the range 0,02-0,1 mg-eq/l, then the Cl-anionization plant is used for replacement of ion bicarbonate by chloride ion, if residual content of ion bicarbonate is not more than 0,2 mg-eq/l, then water is consequently directed to the stages of the reverse osmosis system of desalination, while the process of reverse osmosis system of desalination is conducted at least in two stages, at the first stage of the reverse osmosis system of desalination the ratio of the initial flow to the working concentrate is set within the range 70-75%, then the working concentrate is directed to the second step of the reverse osmosis system of desalination , after the second stage the working concentrate is used as the initial water for the third stage of the reverse osmosis system of desalination , at the working pressure of the reverse osmosis desalination process is increased from the first step to the last one, from 10 to 50 bar, the working concentrate after the last stage of the reverse osmosis system of desalination is directed to the tank-salt -solvent, where the common salt is added and salt content is sufficient for regeneration of Na-filter of the working concentrate after the last stage of the reverse osmosis system of desalination is set within 30-50 g/l, from the tank -salt- solvent the regeneration salt solution is sent to Cl-anionization plant with the help of pump where it is pumped through the column with spent anionite from the bottom to the top and than this regeneration solution is consequently pumped through the spent cationite of the Na-cationization plant from the bottom to the top with draining of the spent regeneration solution after the filter to disposal.

It is reasonable that maximum salt content of the working concentrate coming out from the membranes of the reverse osmosis system of desalination, is not less than 50g/l.

The salt content of the working concentrate is set equal to initial salt content multiplied by 3,5 in degree value of which is equal to the stages amount of the reverse osmosis system of desalination.

Sodium amount added to the tank-salt-solvent for mixing with the working concentrate is determined as sodium amount, g/l in the working concentrate, entering the tank-salt-solvent multiplied by 1,05 -1,1.

The stages amount of the reverse osmosis system of desalination is determined from the formula $N=\log_n(25/s)+1$, where N-number of the stages of reverse osmosis (rounded up and down to the integral number); n –multiplicity of the salt content increase of the concentrate at one stage of reverse osmosis, n=3,5; s – salt content of initial water, мг/л; 25 – salt concentrate from next to the last step of reverse osmosis, mg/l; 1 – stage of the reverse osmosis desalination of initially salted water (the salt concentrate at this stage is assumed to be in 2-2,5 times).

The specific yield increase of permeate occurs due to the usage of some stages of osmosis desalination. As a rule one stage of the reverse osmosis system of water desalination is used, so for achieving the required productivity for purified water it is necessary to use initial water more by 30%, surplus of which after the reverse osmosis system will be discharged to sewerage. When the stepped osmosis is used, the productivity for purified water is achieved with the usage of only 2,5 – 5 % of water consumption surplus from productivity for own needs. Percentage of permeate output from initial water at the stages of the reverse osmosis system of desalination is as follows: the first step is 70%, the second step is 21%, the third step is 4,4%.

For example : at usual technology of the reverse osmosis desalination in the first and only stage 100 $м^3$ of purified water is obtained from 145 $м^3$ of initial water. At the stepped osmosis from 105 $м^3$ of initial water 100 $м^3$ of purified water is obtained, while the first stage of osmosis produces 73 $м^3$, the second stage of osmosis produces 22,5 $м^3$, the third stage of osmosis produces 4,5 $м^3$ of permeate, totally 100 $м^3$ of permeate. It is achieved due to more full usage of the concentrate at the reverse osmosis stages.

The distillation process or partial desalination of water is carried out with the help of technology of the reverse osmosis desalination of water working in combination with ion exchanging technology of water treatment.

The ion exchanging technology is used for correction of ion content of water which then is desalinated with the help of reverse osmosis.

This process supposes the high coefficient of waste water usage, generated after the reverse osmosis desalination with the high Na salts amount for preparation of regeneration solution for Na-cationization of the preliminary water softening system. Thereby the total amount of discharged water is being considerably decreased as well the reagent consumption for the work of the softening system is being considerably decreased .

For the method of water desalination it is proposed to perform the concentrate concentration of the reverse osmosis stage to the salt content value determined basing on two conditions:

1) the amount of Na salts in volume necessary for regeneration of the working concentrate after the last stage of the reverse osmosis is about 40-45% of amount required for regeneration of softening filters . It is necessary to add into the tank-salt- solvent, into the working concentrate about 55-60% of common salt. After it the salt content of the working

concentrate also must be increased by 55-60% for obtaining from it the regenerative solution of necessary volume with salt content 65-110g/l . Thus salt content sufficient for regeneration of the working concentrate volume after the last stage of osmosis must be about 30-50 g/l;

2) from the condition (possibilities) of the membrane work. Maximum salt content of the working concentrate outcoming from membrane (Na_c) must not be more than 50 g/l.

According to these conditions, ion sodium concentration in the concentrate after the last stage of reverse osmosis will be Na_c=Na_{soft}*K (g/l), where Na_{soft} is Na concentration in the treated water after the softening system (g/l); K is multiplicity of salt content increasing in the concentrate in the reverse osmosis system of desalination. The concentration (amount) of sodium, which is necessary to be added into the tank-salt-solvent is determined according to the formula Na_{add}=$Na_к$*(1,05-1,1) (g/l of concentrate).

Short description of drawings

The essence of invention is explained with the following pictures :

fig. 1 – Technological flowsheet of the water treatment system and water flow consumption according to the first option ;

fig. 2 - Technological flowsheet of the water treatment system and water flow consumption according to the second option ;

Positions in the drawings denote the following :

1 – Na-cationite filters plant (two filters);

2 – Hydrochloric acid dosing plant ;

3 – Calciner ;

4 – The first stage of the reverse osmosis system of desalination;

5 - The second stage of the reverse osmosis system of desalination;

6 - The third stage of the reverse osmosis system of desalination;

7 – The fourth stage of the reverse osmosis system of desalination;

8 – Tank-salt-solvent ;

9 – Cl-anation plant .

Detailed description of the invention

The method of desalination provides two options of realization .

The proposed method of water desalination according to the first option is performed in the following way:

The method of water desalination contains the following technological stages. Water after preliminary clarifying comes to Na-cationite filter plant 1 (fig1). It is reasonable to set not less than 2 filters which work in non-stop mode (according to the system TWIN). Hardness of softened water must be 0,02-0,1 mg-eq/l. Hardness value of softened water will be determined by the degree of the concentrate salt content increase owing to the reverse osmosis plant. The degree of the salt content increase can have multiplicity to 100. Therefore at the degree of the salt content increase equal to 100, the hardness of the working concentrate after the last reverse osmosis system will be about 10 mg-eq/l.

Then the hydrochloric acid solution is dosed into the soften water from the hydrochloric acid dosing plant 2. The amount of the acid equally corresponds to bicarbonate amount.

In the result the amount of chloride ion is equivalently increased in water, while bicarbonate converts to water and carbon dioxide. Water pH drops .

Then in the calciner 3 the free carbon dioxide is extracted from water.

If bicarbonate ion is not removed from water, at frequent concentrating, the concentrate after the second stage of the reverse osmosis system of desalination will contain mainly backing soda (sodium bicarbonate), thus the concentrate pH will increase to 8,3-8,4 and the hardness salt deposit on the membranes of the second and the next steps of the reverse osmosis plant is possible.

Then water comes to the first stage 4 of the reverse osmosis system of desalination. The ratio of the initial flow to the working concentrate (recovery) must be about 70-75%. It is connected with providing the optimal parameters of the membrane work (pressure and water consumption) for obtaining the maximum productivity of permeate. Then the working concentrate after the first stage 4 of desalination comes to the input of the second stage 5 of the desalination system. The ratio of the flow values at the second stage 5 is supported at the same level as the first stage 4. After the second stage 5 the working concentrate is used as the initial water for the third stage 6 of the desalination system. At each step of the reverse osmosis system of desalination, the salt content will be increased in 3,5-4 times.

Thus the concentrate salt content will be equal to the initial salt content of water multiplied by 3,5-4 in degree, value of which is equal to the amount of the stages of the reverse osmosis system of desalination. If the salt content of initial water is 1000mg/l (ppm), the salt content of the working concentrate after three stages will be $1000*4^3 = 64000$ mg/l. The increase multiplicity of salt content will be 64. For simplification of calculation let’s assume that the whole salt remains in the concentrate (salt content of filtrate is 0).

For initial water with salt content of 500mg/l (ppm), we receive $500*4^3= 32000$mg/l. Therefore for water salt content of 500mg/l it is possible to use the fourth stage of osmosis desalination with "recovery"50%.

For initial water with salt content 5000 mg/l we receive $5000*4^3= 80000$ mg/l (ppm).

Water with initial salt content 5g/l (ppt) allows to carry out the water desalination process "recovery" 93,8%. That is the concentrate consumption from the permeate consumption will be 6,2% (for one-stage osmosis-30%).

For example, if the desalination plant productivity of permeate is 10 m^3 /h, the discharge of the concentrate with salt content 80 g/l will be 0,62 m^3 / h.

The working concentrate after the fourth stage 7 of the reverse osmosis comes to the tank-salt-solvent 8, wherein the common salt is added. The working concentrate consumption is 15 liters per 1 m^3 of initial water (dividing 1000 liters by magnification degree of increase of salt content 64, we receive 15 liters). "Recovery" is 98,5%. The amount of returning sodium ion with the concentrate theoretically is 50% of the amount required for regeneration of Na-cationite filters 1. The working capacity of cationite must be 50% of static exchanging capacity.

The working exchanging capacity of modern resins for optimal conducting of this softening process will be 1,0-1,2 g-eq/l of resin, that is 50% of static exchanging capacity of resin.

From the tank-salt-solvent 8 the solution is pumped though cationite from the bottom to the top. Preliminary cationite loosening with mixing of its layers is not advisable.

Thus the waste water discharge from the desalination plant will consist of only waste water of softening plant and the system of preliminary water clarification. The proposed scheme is sufficiently variable. It is possible to add hydrochloric acid with calcination at the first stage, and softening at the second stage . For water containing iron it will allow to stabilize iron of bivalent condition and remove it on the softening filter.

The invention (according to the first option) is illustrated by the following example.

Example. The usage of water treatment system according to proposed (combined) method of water desalination for fresh water of the artesian well.

The content of initial water is presented in the Table 1. Required productivity of purified water is 100 m^3/hour.

Table 1

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	7,0

Total alkalinity	mg-eq/l	4,2
Chlorides	mg/l	65
Sulphate	mg/l	84
Sodium + Potassium	mg/l	18
Salt content	mg/l	549
Silicon (H_4SiO_4)	mg/l	Not more than 3,0
Dissolved iron	mg/l	- not permitted at pH more than 6,8
Oxidability	mg/ O_2/l	0,2-0,5

The technological flowsheet of the water treatment system according to the first option, is presented in the fig.1. The initial water of this composition after the clarification system comes to the Na-cationite filters plant 1 of water softening. The plant consists of two filtering columns which work step-by-step. One column passes (softens) water, the second column is in the regeneration or in the waiting mode. The columns are filled with ion exchange resins for 70% of their volume.

Ion exchange resin (cationite) is initially the Na form. Calcium and magnesium ions contained in the initial water are exchanged in the column by sodium ions in the cationite volume. The residual hardness of the softened water must be from 0,02 to 0,1 mg-eq/l. The water consumption after the demineralization plant must be 101,4m^3 /hour. After the demineralization plant the hydrochloric acid solution is dosing into water with the help of dozing station. The dozing station consists of the feeder pump with water lifting and pressure pipelines with the reverse valve, and the polymer tank. Hydrochloric acid enters into interaction with bicarbonate ion, contained in water, transfers the latter into gaseous carbon dioxide and generates chloride ion and water. Residual content of bicarbonate ion in the treated water must be not more than 0,2mg-eq/l. Thus ionic composition of water is presented by strong electrolytes salts. The softened water composition with treatment by HCl is presented in Table 2.

Table 2

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,05
Total alkalinity	mg-eq/l	0,2
Chlorides	mg/l	213
Sulphate	mg/l	84

Sodium +Potassium	mg/l	178
Salt content	mg/l	472
Carbon dioxide	mg/l	241
pH	Unit pH	4,0

Then water is directed to the decarbonization stage. At this stage the carbon dioxide distillation from water is performed. The calciners are the column apparatus: atmospheric one with nozzle and injective nozzleless one. For decarbonization it is also possible to use membrane apparatus with hydrophobic membranes. After decarbonization stage water comes through thin purification cartridge filter on the first step of the reverse osmosis system of desalination. Water pressure is increased with the help of multistage centrifugal pump of high pressure, and water with 10 bar pressure comes to the membrane case which contains the membrane elements.

The membrane elements are selected basing upon the salt content of initial water. Owing to overpressure the water penetrates through the membrane elements surface. Filtration is arranged in such a way that not all water penetrates trough the membrane. At the first step only 70-73% of specified productivity of purified water is filtered through the membrane. Thus two flows are formed: permeate and concentrate. The permeate is the purified water coming directly to the customer or to the corrective treatment, the concentrate is a salt saturated flow coming to the second and the next step of the reverse the osmosis desalination. Parameters of the reverse osmosis desalination process are set with the regulation of the concentrate consumption and the level of water pressure at the entrance of the membrane block. The composition of concentrate after the first step of the reverse osmosis desalination is presented in the Table 3.

Table 3

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,175
Total alkalinity	mg-eq/l	0,64
Chlorides	mg/l	671
Sulphate	mg/l	293
Sodium +Potassium	mg/l	592
Salt content	mg/l	1608
Carbon dioxide	mg/l	3,7
pH	unit. pH	7,2

The composition of permeate after the first stage of the reverse osmosis desalination is presented in Table 4 .

Table 4		
Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,01
Total alkalinity	mg-eq/l	0,01
Chlorides	mg/l	10,9
Sulphate	mg/l	3,2
Sodium +Potassium	mg/l	8,86
Salt content	mg/l	23,8
Carbon dioxide	mg/l	3,1
pH	unit. pH	5,9

It is necessary to set the concentrate consumption after the first stage of softening at the level 30,42m ^{3} /hour therefore the permeate consumption from the first stage will be in amount 101,4-30,42=70,98 m^{3}/hour. Before the second stage the concentrate pressure of the first step is increasedto 15-18 bar with the help of the high pressure pump of the second stage. At the second stage of the reverse osmosis desalination the permeate and concentrate are also generated. The permeate purified from salts is directed to the customer, and the concentrate is directed to the third stage of the reverse osmosis desalination. The concentrate composition and permeate after the second stage of the reverse osmosis desalination are presented in Tables 5 and 6 respectively .

Table 5		
Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,52
Total alkalinity	mg-eq/l	2,08
Chlorides	mg/l	2245
Sulphate	mg/l	970
Sodium +Potassium	mg/l	1956
Salt content	mg/l	5310
Carbon dioxide	mg/l	4,2
pH	unit. pH	7,6
Index Langelier	-	-1,16

Table 6		
Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,005
Total alkalinity	mg-eq/l	0,005
Chlorides	mg/l	10,1
Sulphate	mg/l	3,0
Sodium +Potassium	mg/l	9,0
Salt content	mg/l	22,4
Carbon dioxide	mg/l	3,8
pH	unit pH	5,8

At the second stage only 20-22,5% of the required productivity of purified water is filtered through membrane. It is necessary to set the concentrate consumption after the second stage at the level 9,12 m^3 /hour, thereafter the permeate yield from the second stage will be 30,42-9,12=21,3 m^3 /hour. The concentrate after the second stage is sent to the third stage of the reverse osmosis system of desalination. Before the third stage the concentrate pressure of the second step is increased to 30-35 bar with the help of the high pressure pump of the third stage. At this pressure the process of reverse osmosis separation of water of this ion composition occurs. At the third stage only 4,0-6,5% of the required productivity of the purified water is filtered through membrane.

The compositions of the concentrate and permeate after the third stage of the reverse osmosis desalination are presented in Tables 7 and 8, respectively.

Table 7		
Parameter	Measuring unit	Value
Total hardness	mg-eq/l	1,73
Total alkalinity	mg-eq/l	6,65
Chlorides	mg/l	7414
Sulphate	mg/l	3212
Sodium +Potassium	mg/l	6465
Salt content	mg/l	17539
Carbon dioxide	mg/l	5,6
pH	unit. pH	7,7
Index Langelier	-	- 0,02

Table 8		
Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,005
Total alkalinity	mg-eq/l	0,005
Chlorides	mg/l	31,6
Sulphate	mg/l	4,5
Sodium +Potassium	mg/l	26
Salt content	mg/l	69
Carbon dioxide	mg/l	4,8
pH	unit pH	5,9

After the third stage the permeate is sent to the customer and the concentrate is sent to the fourth stage of the reverse osmosis system of desalination. The concentrate consumption after the third stage must be set at the level 2,74 m^3 /hour, therefore the permeate yield will be 9,12-2,74=6,4 m^3 /hour. Before the fourth stage the concentrate pressure of the third stage is increased to 50-55 bar with the help of the high pressure pump of the fourth stage. The fourth stage increases the concentrate salt content to the working value 35 g/l. The concentrate consumption after the fourth stage must be set at the level 1,37 m^3 /hour, therefore the permeate yield will be 2,74-1,37=1,37 m^3 /hour. The permeate after the fourth stage is sent to the customer. The concentrate and permeate compositions after the fourth stage of the reverse osmosis desalination are presented in Tables 9 and 10, respectively.

Table 9		
Parameter	Measuring unit	Value
Total hardness	mg- eq/l	3,46
Total alkalinity	mg-eq/l	12,9
Chlorides	mg/l	14814
Sulphate	mg/l	6423
Sodium +Potassium	mg/l	12921
Salt content	mg/l	35022
Carbon dioxide	mg/l	12,1
pH	unit. pH	7,7
Index Langelier	-	0,44

Saturation percentage for $CaSO_4$	%	19,84

Table 10

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,005
Total alkalinity	mg-eq/l	0,005
Chlorides	mg/l	26,7
Sulphate	mg/l	2
Sodium +Potassium	mg/l	19
Salt content	mg/l	49
Carbon dioxide	mg/l	9,5
pH	unit. pH	5,5

The permeate consumption is summarized of all four stages of desalination and is equal to 70,98+21,29+6,4+1,37=100 m^3 /hour. The concentrate consumption from the plant of the reverse osmosis desalination will be 1,37 m^3 /hour. The water flow consumption according to the example of the first option of the method is presented in the fig. 1.

Then the concentrate after the fourth stage with salt content 35 g/l comes to the tank -salt-solvent. Also common salt is added into the tank -salt-solvent or 26% of common salt solution. The solution salt content in the tank-salt-solvent is brought to 73,5 g/l (73,5 g/l=35 g/l+ 35 g/l* 1,1) when reagent NaCl is added. If 26% of common salt solution is added, the salt content of the generated solution in the tank-salt-solvent will be less than about 68 g/l. Then this solution is pumped with the help of the pump through the cationite column of the water softening plant which is discharged into regeneration. The regeneration is carried out with the common salt solution. For saving the common salt it is advisable to pump the solution from the tank-salt-solvent through cationite rom the bottom to the top. The salt solution is being pumped through the cationite not less than 1 hour.

Linear velocity of the solution passing through cationite must be in the range 3-5 m/h. Then the cationite washing from the regeneration products is performed with initial water. Specific consumption of washing water is 11 m^3 of water per 1 m^3 of cationite.

As seen from Tables 5, 7, 9 the saturation index Langelier at all stages of the reverse osmosis desalination has the negative value apart from the last stage. At the last (fourth) stage the index has value 0,44. Actually it means the absence of the process of temporary hardness salt deposit at all stages of the reverse osmosis water desalination. Percentage of $CaSO_4$ salt saturation is 19,84 at the last stage of desalination what tells about the absence of this salt deposit process in the membranes.

The proposed method of water desalination according to the second option is performed in the following way:

The method of water desalination contains the following technological stages. Water after the preliminary clarification comes to the Na-cationite filters plant 1 (fug.2). It is reasonable to install not less than two filters which work in nonstop mode (according to the system TWIN). The softened water hardness must be 0,02-0,1 ng-eq/l. The value of softened water hardness will be determined by the increase degree of the concentrate salt content of the reverse osmosis plant. The degree of increase of salt content can be to 100-fold. Consequently, when the degree of salt content increase is 100, the hardness of the working concentrate after the last reverse osmosis system will be about 10 mg-eq/l .

When ratio of the total initial water hardness (Ж) to ion bicarbonate (HCO_3) (mg-eq/l) is $\frac{Ж}{HCO_3} \geq 1{,}5$ and ratio of ion hydrocarbonate to the sum of anions of strong acids is $\frac{HCO_3}{\sum A_{so4}} \geq 1$, it is possible instead of water acidation to use the plant of Cl-anation of water 9 situated after Na-cationite water filters 1 before the first step 4 of the reverse osmosis desalination system. When ion bicarbonate is not sufficiently removed in the water Cl-anation plant 9, it is possible to use the hydrochloric acid dosing system 2 after the water Cl-anation plant 9 for removal of the ion bicarbonate deposit.

If ion bicarbonate is not removed from water, the multifold increase of the concentrate salt content after the second stage 5 of the reverse osmosis desalination system will contain mainly baking soda (Sodium bicarbonate) thereby the concentrate pH will increase to 8,3-8,4 and the hardness salt deposit on the membranes of the second and the next steps of the reverse osmosis plant is possible.

Then water comes to the first stage 4 of the reverse osmosis desalination system. The ratio if initial flow to the working concentrate (recovery) must be about 70-75% . It is connected with providing for optimal parameters of membranes work (pressure and water consumption) for receiving of maximum productivity for permeate. Then the work concentrate after the first stage 4 of desalination comes to the entrance of the second stage 5 of the desalination system. The ratio of the flows value to the second step 5 is supported at the level as for the first step 4 of the reverse osmosis desalination system. After the second stage 5 the working concentrate is used as initial water for the third stage 6. At each stage of the reverse osmosis system of desalination the concentrate salt content will be increased by 3,5-4 times.

The working concentrate after the last stage of the reverse osmosis system of desalination is directed to the tank-salt-solvent 8, where the common salt is added while the salt content sufficient for regeneration of Na-cationite filter 1 of the working concentrate volume after the last stage of the reverse osmosis system of desalination is set in the range 30-50 g/l. From the tank – salt-solvent 8 the regenerative salt solution is sent to the water Cl-anation plant with the help of the pump, where it is pumped through the column of spent anionite from the bottom to the top. Then this regenerative solution sequentially is pumped through the spent cationite of the Na-cationization plant 1 from the bottom to the top, with removal of spent regenerative solution after filter to disposal.

The invention (according to the second option) is illustrated in the following way .

Example. The usage of the water treatment system according to the proposed (composite) method of desalination for brackish waterof the artesian well. The composition of the initial water is presented in Table 11. Required productivity of purified water is 100m^3 /hour.

Table 11

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	24,0
Total alkalinity	мг-экв/л	11,2
Chlorides	mg/l	382
Sulphate	mg/l	288
Sodium +Potassium	mg/l	92
Salt content	mg/l	1865
Silicon (H_4SiO_4)	mg/l	Not more than 3,0
Iron	mg/l	- not permitted
Oxidability	mg O_2/l	0,2-0,5

The technological flowsheet of the water treatment system according to the second option is presented in the fig 2. The initial water of this composition after the water clarification system comes to the softening water Na-cationite plant. The plant consists of two filtering columns which work sequentially. One column passes (softens) water , the second column is in the regeneration or in the waiting mode. Columns are filled with ion exchange resin by 70% of their volume. Ion exchange resin (cationite) is initially in Na form. Calcium and Magnesium ions contained in the initial water are exchanged by sodium ions in the column with volume of cationite. Residual hardness of softened water must be from 0,02 to 0,1 mg-eq/l. The water consumption after the water softening plant must be104,2m^3/hour. After the water softening plant water is directed to Cl-anation. Softened water passing through Cl-anation plant substitutes sulphate and bicarbonate anions by chloride anions contained in anion exchange resin. Constructively this plant repeats the Na-cationing plant, only anion exchanging strongly basic resin is used as an ion exchange material . The residual content of ion bicarbonate in the treated water after Cl- anation plant must be not more than 0,2 mg-eq/l. The usage of Cl- anation process instead of hydrochloric acid dosing is possible under the following conditions: at ratio of total hardness of initial water (Ж) to bicarbonate ion (HCO_3) (mg-eq/l) $\frac{Ж}{HCO_3} \geq 1{,}5$ and ratio of hydrocarbonate ion to the sum of anions content of strong acids $\frac{HCO_3}{\sum A_{so4}} \geq 1{,}0$, instead of water acidation the water Cl- anation plant is used which is set after water Na-cationization before the first stage of the reverse osmosis system of desalination.

Thus ion content of water is presented by the strong electrolyte salts . Water composition after Cl- anation is presented in Table 12

Table 12

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,05
Total alkalinity	mg-eq/l	0,2
Chlorides	mg/l	722
Sulphate	mg/l	288
Natrium +Potassium	mg/l	642
Salt content	mg/l	1715
Carbone dioxide	mg/l	1,2
pH	Unit. pH	7,0

Then water comes through the fine purification cartridge filter to the first stage of the reverse osmosis desalination system. Water pressure is increased with the help of the centrifugal multistage pump of high pressure, and water with pressure 19 bar comes to the membrane case. In the case there are membrane elements. The membrane elements are matched basing upon the salt content of initial water. Due to excess pressure the water is penetrating through the surface of membrane elements. Filtration is arranged in such a way that not all water penetrates through the membrane. At the first stage only 70-73% of the required productivity for purified water is filtrated through the membrane. Thus two flows are formed: permeate and concentrate. The permeate is a purified water coming directly to the customer or to the corrective treatment, the concentrate is a flow saturated with salts coming to the second and next stages of the reverse osmosis desalination. The parameters of the reverse osmosis desalination process is set with the regulation of the concentrate consumption and the level of water pressure at the entrance of the membrane block. The concentrate and permeate contents after the first stage of the reverse osmosis desalination is presented in Tables 13 and 14.

Table 13

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,167
Total alkalinity	mg-eq/l	0,65
Chlorides	mg/l	2549
Sulphate	mg/l	953
Sodium +Potassium	mg/l	2121
Salt content	mg/l	5667
Carbone dioxide	mg/l	1,11
pH	Unit. pH	7,5

Table 14

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,005
Total alkalinity	mg-eq/l	0,005
Chlorides	mg/l	11,5
Sulphate	mg/l	3
Sodium +Potassium	mg/l	9
Salt content	mg/l	23,77
Carbone dioxide	mg/l	0,9
pH	Unit. pH	5,8

The concentrate consumption after the first stage of softening is necessary to be set at the level 31,26 m^3/hour, therefore the permeate consumption from the first stage will be received in amount of 104,2–31,26=72,94 $м^3$/hour. Before the second stage the concentrate pressure of the first stage is increased to 30-35 bar with the help of the high pressure pump of the second stage. At the second stage of the reverse osmosis desalination the permeate and concentrate are also formed. The permeate purified from salts is directed to the customer and the concentrate is directed to the third stage of the reverse osmosis desalination. The compositions of the concentrate and permeate after the second stage of the reverse osmosis desalination are presented in Tables 15 and 16 respectively.

Table 15

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,52
Total alkalinity	mg-eq/l	2,09
Chlorides	mg/l	8418
Sulphate	mg/l	3155
Sodium +Potassium	mg/l	7008
Salt content	mg/l	18718
Carbone dioxide	mg/l	2,1
pH	Unit. pH	7,7
Index Langelier	-	-1,127

Table 16

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,005
Total alkalinity	mg-eq/l	0,005
Chlorides	mg/l	36
Sulphate	mg/l	10
Natrium +Potassium	mg/l	28
Salt content	mg/l	74,8
Carbone dioxide	mg/l	1,65
pH	Unit. pH	5,9

At the second stage of the reverse osmosis desalination only 20-22,5% of the required productivity for purified water is filtered through the membrane. The concentrate consumption after the second stage is necessary to be set at the level 9,37 м^3/hour; therefore the permeate yield from the second stage will be 31,26-9,37=21,89 m^3/hour. The concentrate after the second stage is directed to the third stage of the reverse osmosis desalination system. Before the third stage the concentrate pressure of the second stage is increased to 50 bar with the help of the high pressure pump of the third stage. At this pressure the reverse osmosis process of this ion content the water separation occurs. At the third stage only 4,0-6,5% of the required productivity for purified water is filtered through membrane. The concentrate and permeate contents after the third stage of the reverse osmosis desalination are presented in Tables 17 and 18, respectively.

Таблица 17

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	1,21
Total alkalinity	mg-eq/l	4,75
Chlorides	mg/l	18669
Sulphate	mg/l	7009
Sodium +Potassium	mg/l	15548
Salt content	mg/l	41534
Carbone dioxide	mg/l	4,0
pH	Unit. pH	7,6
Index Langelier	-	-0,05
Saturation percentage for $CaSO_4$	%	10,42

Table 18

Parameter	Measuring unit	Value
Total hardness	mg-eq/l	0,005
Total alkalinity	mg/l	33,5
Chlorides	mg/l	2,2
Sulphate	mg/l	23
Sodium-Potassium	mg/l	59,7
Salt content	mg/l	3,35

pH	Unit. pH	5,6

After the third stage the permeate comes to the customer, the concentrate comes to the tank-salt-solvent. It is necessary to set the concentrate consumption after the third stage at the level 4,2 m^3/hour, therefore, the permeate yield from the third stage is 9,37-4,2=5,17 m^3/hour. The third stage increases the concentrate salt content to the working values 42 g/l. The permeate consumption is summarized for all four steps of desalination and it is equal to 72,94+21,89+5,17=100 m^3/hour. The concentrate consumption from the reverse osmosis desalination will be 4,2 m^3/hour. The water flow consumption of the example for the second option of the method is presented in the fig. 2.

Then the concentrate after the third stage with salt content 42 g/l comes to the tank-salt-solvent . Also common salt or 26% of common salt solution is added into the tank-salt-solvent. The solution salt content in the tank-salt-solvent is brought to 86,1 g/l (86,1 g/l=41g/l+41g/l*1,1), at NaCl dilution. If the common salt solution is added, the salt content of the resulting solution in the tank-salt-solvent will be less. Then this solution with the help of the pump is pumped consequently through the column of anionite of the Cl-anation plant, then through the column with cationite of the water Na-cationization plant, which are withdrawn to regeneration. The withdrawal of Na-cationization plant and Cl-anation plant to regeneration is performed simultaneously. The regeneration is performed with the common salt solution. For saving of the common salt it is recommended to pump the solution from the tank-salt-solvent through the cationite from bottom to the top. The salt solution is pumped through anionite then cationite for not less than 1 hour. Linear velocity of the solution passing through the ion exchange resins must be in the range from 3 to 5 m/h. Then washing of anionite and cationite from the regeneration products of initial water is carried out. The specific consumption of washing water is 11 m^3 of water per 1 m^3 of resin.

As we can see from the Tables 15 and 17 the saturation index Langelier at all stages of the reverse osmosis desalination has a negative value. Actually it implies absence of the salt deposit process of temporary hardness at all stages of the reverse osmosis of water desalination.

Saturation percentage of salts $CaSO_4$ is 10,42 at the last stage of desalination what tells about absence of these salt deposits process in membranes.

The usage of the mixed technology of water desalination according to the proposed method is comparable by costs with the traditional schemes of the reverse osmosis of water desalination. At that moment the waste water consumption for this scheme is about 2,5-6% of productivity. The waste water discharge after osmosis plant is absent. The waste water consumption in the traditional schemes of the reverse osmosis of water desalination is about 35-40% of productivity.

This invention is not limited by the above described examples presented only as illustrations of the specific options of its performance.

The proposed simple technology of water desalination allows to provide the increase of the salts extraction efficiency, the decrease of the produced waste water amount and sufficient economy of chemical reagents.

Patent claim

1. The water desalination method (according to the first option) including the preliminary clarification of water feeding to Na-cationite filters while the hardness of softened water is set within the range 0,02-0,1 mg-eq/l. Then a solution of hydrochloric acid in an equivalent amount to sodium bicarbonate is dosed into the softened water. Then in the calciner free carbonic acid is recovered from the water and sent to the reverse osmosis desalination stages, the reverse osmosis desalination process is performed at least in two stages *through the working concentrate line*, at the first stage of the reverse osmosis desalination system the ratio of the initial flow to the working concentrate is set within 70-75%, then the working concentrate is directed to the second stage of the reverse osmosis desalination system, after the second stage the working concentrate is used as the initial water for the third stage of reverse osmosis desalination system, while the operating pressure of the reverse osmosis desalination is increased from the first stage to the last one from 10 to 50 bar , the working concentrate after the last stage is sent to the tank -salt- solvent where the common salt is added. Salt content sufficient for regeneration of Na– filter of the volume of the working concentrate after the last stage is set in the range of 30-50g/l. Regenerative brine is pumped step-by-step through the anionite and then through cationite from the bottom to the top with the spent regeneration solution draining after the filter for disposal.

2. Method according to i.1, ***differing*** in that maximum salt content of the working concentrate coming from the membrane of the reverse osmosis desalination system must not be more than 50g/l.

3. Method according to i.1, ***differing*** *in that salt content of working concentrate* is set equal to the initial water salt content multiplied by 3,5, in degree value of which is equal to the stage amount of the reverse osmosis desalination system .

4. Method according to i.1, ***differing*** that sodium amount added into the tank-salt-solvent to mixing with the working concentrate is determined as the sodium amount , g/l/ in the working concentrate coming to the tank-salt-solvent multiplied by 1,05-1,1.

5. Method according to i.1, ***differing*** that the stages amount of the reverse osmosis desalination system N is calculated from

$$N=\log_n(25/s)+1,$$

Where n – multiplicity of the salt content increase of the concentrate at one stage of the reverse osmosis n=3,5;

s –the salt content of initial water, mg/l;

25 – the concentrate salt content from the next to the last stage of reverse osmosis, mg/l;

1 –the stage of initially salted water reverse osmosis desalination.

6. The desalination method includes preliminary clarification of water feeding to Na-cationite filters while the hardness of softened water is set within the range 0,02-0,1 mg-equ/l. Then the Cl-anation plant is used for substitution of ion bicarbonate by ion chloride when residual content of ion bicarbonate not more than 0,2 mg-equ/l, then water step-by-step is directed to the stages of the reverse osmosis desalination system. The reverse osmosis desalination process is performed at least in two stages *through the working concentrate line* At the first stage of the reverse osmosis desalination system the ratio of initial flow to the working concentrate is set within 70-75%, then the working concentrate is directed to the second stage of the reverse osmosis desalination system, then after the second stage the working concentrate is used as initial water for the third stage of the reverse osmosis desalination system, while the operational pressure of the reverse osmosis desalination process is increased from the first stage to the last one, from 10 to 50 bar, the working concentrate after the last stage of the reverse osmosis desalination system is directed to the tank -salt-solvent, where the common salt is added and the salt content is sufficient for regeneration of Na– filter of the working concentrate volume after the last stage of the reverse osmosis desalination system is set within 30-50 g/l, from the tank-salt-solvent the regenerative hydrochloric acid solution with the help of the pump is sent to the Cl–anation plant where it is pumped through the column of the spent anionite from the bottom to the top and then this regenerative solution is consequently pumped through the spent cationite of the Na-cationization plant from the bottom to the top with draining of the spent regeneration solution after the filter to disposal.

7. Method according to i.1, ***differing*** that the maximum salt content of the working concentrate coming from membranes of the reverse osmosis desalination system must not be more than 50 g/l .

8. Method according to i.6, ***differing*** that the working concentrate salt content is set equal to the initial salt content of water multiplied by 3,5 in degree value of which is equal to the amount of stages of the reverse osmosis desalination system.

9. Method according to i.1, ***differing*** that sodium amount added into the tank-salt-solvent for mixing with the working concentrate is determined as sodium amount, g/l in the working concentrate coming to the tank-salt-solvent multiplied by 1,05 -1,1.

10. Method according to i.1, ***differing*** that amount of stages of the reverse osmosis desalination system N is determined from

$$N=\log_n(25/s)+1,$$

where n – multiplicity of the concentrate salt content increase at the one stage of the reverse osmosis , n=3,5;

s – salt content of initial water mg/l;

25 –the concentrate salt content from the next to the last stage of reverse osmosis ,mgr/l;

1 –a stage of reverse osmosis desalination of initially salted water.

Water desalination method

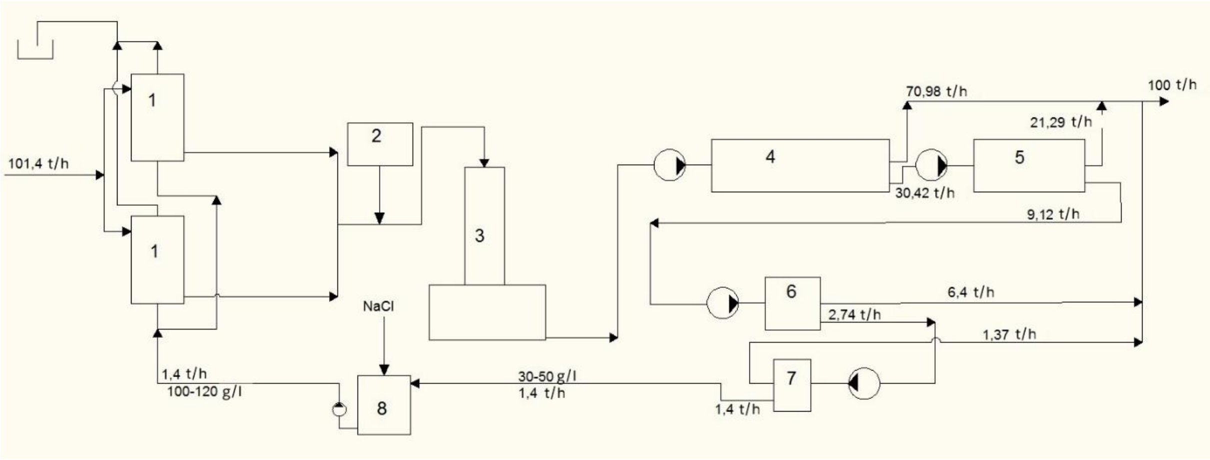

Fig.1

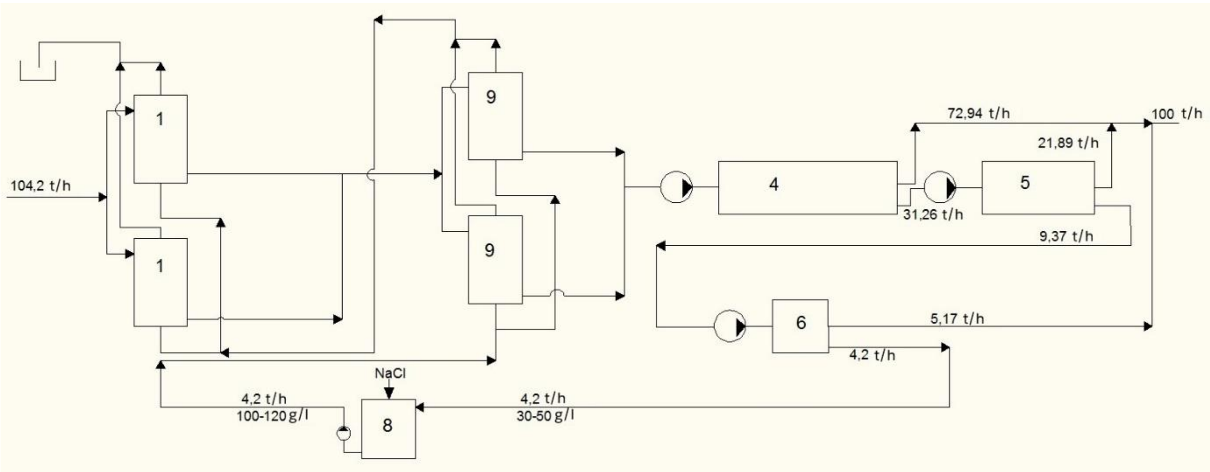

Fig.2

Water desalination method (Options)

Abstract:

The invention relates to the technological processes of distillation or partial desalination of brackish and fresh water, mainly for artesian water with increased (high) hardness and can be used to produce drinking water as well as to produce treated water for usage in different technological processes.

The method of the first option consists in the preliminary clarification of water feeding to Na-cationite filters while the hardness of softened water is set within the range 0,02-0,1 mg-eq/l. Then a solution of hydrochloric acid in an equivalent amount to sodium bicarbonate is dosed into the softened water. Then in the calciner free carbonic acid is recovered from the water and sent to the reverse osmosis desalination stages, the reverse osmosis desalination process is performed at least in two stages *through the concentrate line*, at the first stage of the reverse osmosis system of desalination the ratio of the initial flow to the working concentrate is set within 70-75%, then the working concentrate is directed to the second stage of the reverse osmosis system of desalination, after the second stage the working concentrate is used as the initial water fo cvfgyui9gfxr the third stage of the reverse osmosis system of desalination, while the operating pressure of the reverse osmosis desalination is increased from the first stage to the last one from 10 to 50 bar , the working concentrate after the last stage is sent to the tank -salt- solvent where the common salt is added. Salt content sufficient for regeneration of Na– filter of the volume of the working concentrate after the last stage of the reverse osmosis desalination is set in the range of 30-50g/l (ppt), regenerative brine is pumped from the tank -salt- solvent through the cationite from the bottom to the top with the spent regenerative solution draining after the filter for disposal.

The method according to the second option consists in the preliminary clarification of water feeding to Na-cationite filters while the hardness of softened water is set within the range 0,02-0,1 mg-eq/l. Then the Cl-anation plant for substitution of bicarbonate ion by chloride ion at the residual content of bicarbonate ion not more than 0,2 mg-eq/l is used, then water step-by-step is directed to the steps of the reverse osmosis desalination while the reverse osmosis desalination is performed at least in two stages *through the concentrate line*, at the first stage of the reverse osmosis desalination the ratio of the initial flow to the working concentrate is set within 70-75%, then the working concentrate is directed to the second stage of the reverse osmosis system of desalination, after the second stage the working concentrate is used as the initial water for the third stage of the reverse osmosis system of desalination, while the operating pressure of the reverse osmosis desalination is increased from the first stage to the last one from 10 to 50 bar, the working concentrate after the last stage is sent to the tank -salt- solvent where the common salt is added. Salt content sufficient for regeneration of Na– filter of the volume of the working concentrate after the last stage of the reverse osmosis desalination is set in the range of 30-50g/l (ppt), regenerative brine from the tank -salt- solvent is sent the Cl-anation plant with the help of the pump where is pumped through the column with the spent cationite of Na-cationization from the

bottom to the top with draining of regenerative solution after the filter for disposal. Technical effect is as follows:

Increase of the specific permeate output from the reverse osmosis desalination system, decrease the concentrate consumption over the desalination steps and therefore decrease of water consumption for the plant's own needs to 2,5-6%.

10 cl, 2 dwg, 18 Tables., 2 e.

Reviewer: Tikhonov I.A.