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Treatment of raw brines from desalination plants

Description

The invention relates to a method for treating raw brines from desalination plants having a total salt content of more than 60 g/l and to a device for carrying out a method of this type.

It is known to use seawater to produce drinking water. For this process, the seawater is separated into fresh water and a raw brine in a seawater desalination plant. A known method for desalinating seawater is, for example, reverse osmosis (RO), as is known from WO 2010/123926 A2, for example. Different materials can be used as the membrane. This document proposes a membrane made of zeolite A, for example. The salt content of seawater is lowered from approximately 35,000 ppm to a total salt content of less than 500 ppm using a method of this type. Reverse osmosis (RO) is a membrane method that uses pressure. The osmotic pressure of seawater is 25 kg/cm^2. If seawater is subjected by the membrane in a reverse osmosis system to a pressure that is higher than its osmotic pressure, the seawater is separated into fresh water (permeate) and salt water (concentrate). The higher the total salt content, the higher the osmotic pressure. High-pressure pumps use a lot of energy and represent a substantial cost factor when producing fresh water. In conventional seawater reverse osmosis methods (SWRO), approximately 42 % fresh water is obtained from the water supplied, with 58 % concentrate remaining. The concentrate (raw brine) has a total salt content of approximately 60,000 ppm (almost 1.7 times the salt content of seawater). More thorough desalination is difficult to achieve not only on account of the pressure issues, but also due to the problems of clogging the membrane with gypsum and other seawater hardness minerals. These restrictions cannot be avoided, particularly when pre-treating untreated seawater with acid and adding chemicals in order to prevent deposits.

Another method for producing drinking water from seawater is thermal distillation. The most common distillation methods include multi-stage flash distillation (MSF), multiple-effect distillation (MED) and steam compression (DK). In MSF, the supplied water is heated and the pressure reduced such that the water is abruptly turned into steam. This process is one step of several successive steps, each of which has a lower pressure. In MED, the supplied water flows through a plurality of evaporators connected in series. The steam from one series is then used to evaporate the water in the next series. The DK method comprises evaporating the water supplied, compressing the steam, and subsequently using the heated, compressed steam as a heat source for evaporating additional water supplied. Some distillation plants are a hybrid consisting of more than one desalination technology. The waste product of these processes is a solution having a high salt concentration (raw brine). In conventional, thermal distillation processes, less than 47 % fresh water is obtained from the water supplied, with more than 53 % concentrate remaining. The concentrate has a total salt content of approximately 65,000 ppm (almost 1.8 times the salt content of seawater). These restrictions are connected with the production of deposits on heating surfaces of evaporators from seawater hardness minerals, in particular gypsum. Due to the anomalous effect of reducing the solubility of gypsum in hot solutions, this restriction is often referred to as a “gypsum barrier”.

In order to limit the production of gypsum deposits on the heating surfaces at least to some extent, it is already known from US 5,814,224 A that the seawater is liberated of calcium ions by means of ion exchange before being evaporated. A zeolite is used here as the ion exchanger and is treated using a magnesium chloride solution and a sodium chloride solution at ambient temperatures. The method according to the above-mentioned US patent application is used to obtain drinking water from seawater. A calcium-rich raw brine having a total salt content of more than 60 g/l remains as the waste product. This raw brine is often fed directly back to the sea and leads to an increase in the salt content thereof, having considerable environmental problems. The raw brine cannot be reprocessed further using the method set out in the above-mentioned US patent application, since the zeolite would already be exhausted and used up after passing through just a few times and would have to be replaced with new zeolite. The costs of constantly replacing the zeolite and also the staff required for replacing the zeolite would be very high, and therefore this is not carried out in practice or has only been seriously considered.

None of the industrial desalination methods mentioned is an environmentally friendly technology and they cause major contamination in marine fauna and flora. Each year, together all the desalination plants in the world convey approximately 9 cubic kilometres (9,000,000,000 m^3/year) of untreated concentrate directly to the coastal regions of the oceans, which leads to an ecological imbalance. This also has economic disadvantages.

The raw brine conveyed to the sea thus contains large amounts of valuable components such as magnesium, sodium, potassium and rare metals, which are not used.

In order to curtail these problems, additional methods have been developed which restrict the proportion of raw brine obtained. US 6508936 B1 describes a combined method for desalinating seawater in order to obtain a very high yield of fresh water. The method combines nanofiltration as a first desalination step and thermal distillation, such as multi-stage flash evaporation (MSF) or multiple-effect distillation (MED), such that the two processes interact. However, a disadvantage of this method is that the nanofiltration step is comparatively expensive for use for lowering the seawater hardness, and therefore more fresh water can then be obtained in the step of thermal distillation. In this method, too, a raw brine is also obtained.

A method for desalinating seawater without obtaining a raw brine that cannot be reprocessed any further is described in WO 2007132477 A1. In this method, the seawater is first subjected to nanofiltration in a pre-treatment step, divalent ions preferably being removed. In this case, the removal amounts to approximately 85 % per run and no more than 30 % of the monovalent ions reach the retentate either. This retentate having a high proportion of divalent ions is used to obtain magnesium and other divalent ions. For the permeate, which contains substantially no divalent ions, three-stage, high-pressure reverse osmosis desalination (HPSWRO) can be used to produce fresh water. The highly pure brine (HPSWRO concentrate flow having a total salt content of more than 85,000 ppm) can be used to obtain sodium hydroxide, chlorine and hydrogen by means of electrolysis. However, this method has some disadvantages. Nanofiltration and multi-stage HPSWRO require an additional expenditure of energy and are also expensive. In addition, in practice it is incredibly difficult to thoroughly and separately remove magnesium and calcium from the nanofiltration concentrate.

In light of the above-described prior art, the object of the invention is to provide a method that can be used to treat raw brine from desalination plants having a total salt content of more than 60 g/l using a small amount of energy and in a cost-effective manner.

The object is achieved by the claimed device according to claim 10 and by the claimed method for treating raw brines from desalination plants having a total salt content of more than 60 g/l according to claim 1.

Raw brine from seawater desalination plants, as well as seawater itself, contains considerably more magnesium ions than calcium ions. The zeolite A used in method step 1a) can accept both magnesium and calcium and releases these ions again when there is a distinct excess of sodium. The concentration, from step e), of sodium ions of the concentrated brine used in step f) is insufficient, however, to desorb both the magnesium ions loosely stored in the zeolite and the loosely stored calcium ions. In method step 1a), the zeolite A is therefore converted to a thermally modified zeolite (TMZ), in which all functional regions of the zeolite structure that can accept magnesium ions are blocked by the reservoir of magnesium ions having a large hydration shell. It is crucial for the blockage for the temperature of the solution containing magnesium ions to be between 75 °C and 100 °C and for the interior of the column to then be cooled to a value below 45 °C in step b).

In step c), the calcium form of the TMZ that is present following steps a) and b) is converted into the sodium form of the TMZ. In step d), calcium is then separated out of the raw brine to be reprocessed in the column, and conversely sodium ions are released into the eluate. However, the eluate is then separated into a more highly concentrated brine having a calcium ion concentration of less than 1000 mg/l, and water. In this case, the concentration of the more highly concentrated brine relative to the eluate originally obtained in step d) increases by the factor n. The total ion concentration of the eluate is preferably between 130 g/l and 300 g/l in this case.

Following completion of step d) of the method according to claim 1, the TMZ is mainly in the calcium form, i.e. the TMZ is barely occupied by any sodium ions and is instead in particular in calcium form. In step f), the TMZ is then converted into sodium form. Step d) can then be carried out again depending on the TMZ filling in the column. The concentrated eluate exiting the column in method step f) is then separated into solids and water.

According to method step h) of claim 1, method steps d) to g) are repeated until the capacity of the TMZ is exhausted. This is identified by the eluate in step d), immediately after conversion of the TMZ into sodium form by step f), already having a calcium ion concentration in the first bed volume conveyed through the first column, i.e. the volume that the TMZ filling takes up in the column, that, under otherwise identical conditions, is 20 % higher than the calcium ion concentration in the first bed volume conveyed through the first column in step d) immediately after performing steps a) to c). In step d), the sodium form of the TMZ is therefore converted into the calcium form and in the process calcium ions are accepted in the TMZ and the sodium ions are released into the eluate. In step f), the calcium form of the TMZ is reverted back to the sodium form by sodium ions from the concentrated brine from step e) being accepted in the TMZ and at the same time calcium ions being released into the eluate. This repetitive, cyclic working process can be repeated after separate measurements approximately 200 times before the capacity of the TMZ is exhausted. As the number of the aforementioned cyclic working processes increases, the ability of the TMZ to accept calcium in step d) progressively reduces. As soon as the calcium ion concentration in step d) that is measured in the first bed volume conveyed through the first column, i.e. in the eluate which is obtained in step d) directly after the TMZ is converted back into sodium form by step f), is 20 % higher than the calcium ion concentration in the first bed volume conveyed through the first column in step d) immediately after performing steps a) to c), i.e. directly after fresh production of the TMZ by means of method steps a) to c).

In step e) of the method according to claim 1, the concentration of the eluate is increased, with fresh water being obtained without calcium ions affecting the increase in concentration due to the production of undesirable deposits.

By means of the method according to the invention, it is possible for the concentration of the raw brine to be reprocessed to have already been significantly increased in method step e), with fresh water being obtained, and for the concentrated eluate produced in method step f) to already be very highly concentrated before it is further reprocessed and separated into solids and water in method step g). Reprocessing the concentrated eluate in method step g) is therefore far less expensive and requires less energy than in the case of direct separation of the raw brine into solids and water. The concentrated eluate preferably has a total ion concentration of between 130 g/l and 300 g/l in this case.

In step a) and in step d), the flow direction of the raw brine is, in relation to the vertical column, from top to bottom through the bed filling of zeolite A or TMZ. In contrast, in step c) and in step f), the flow direction is, in relation to the vertical column, from bottom to top through the bed of TMZ. This prevents undesirable mixing of calcium-rich and calcium-poor solutions. In step a) and in step d), the boundary between the calcium form of the TMZ and the sodium form of the TMZ migrates from top to bottom, while in method steps c) and f) the boundary migrates from bottom to top.

In a particularly preferred embodiment of the invention, the exhausted TMZ is reprocessed once again by repeating steps a) to c) according to claim 1. Exhaustion of the TMZ is indicated by the change in the calcium ion concentration of the eluate obtained in method step d), which change has already previously been made. Tests have shown that exhausted TMZ can be regenerated approximately 10 times. Taking into account the regeneration of the exhausted TMZ, method step d) can therefore be repeated approximately 2000 times with the same sorbent filling (200 times until the TMZ is exhausted, exhausted TMZ regenerated 10 times). Method step d) and method step f) usually each last for approximately four hours. Therefore, the overall service life of a single sorbent filling is approximately two years.

Only after the exhausted TMZ cannot be regenerated any more is the sorbent material replaced with fresh zeolite A and the method according to claim 1 is reapplied. The TMZ material in the column classes as no longer being regenerable and is replaced when the eluate in step d), immediately after performing the method according to claim 2, already has a calcium ion concentration in the first bed volume conveyed through the first column that, under otherwise identical conditions, is 20 % higher than the calcium ion concentration in the first bed volume conveyed through the first column in method step d) immediately after the zeolite A is converted into TMZ for the first time by performing method steps a) to c). By regenerating the exhausted TMZ, considerable costs for refilling the column with zeolite A can be saved.

In a particularly preferred embodiment of the invention, the method according to the invention is operated continuously by using an additional column having a bed filling that is the same as that of the first column. For this purpose, method steps a) to h) according to claim 1 are also performed in the additional column. However, the steps occur in the two columns in a manner temporally offset relative to one another such that steps d) and f) according to claim 1 are always performed simultaneously and alternatingly in the two columns. For example, for each non-straight run, step f) is carried out in the first column and step d) is carried out in the additional column at the same time, and for each straight run, step d) is carried out in the first column and step f) is carried out in the additional column at the same time. As a result, continuous operation of the method is possible. As a result of the continuous operation, in turn waiting times are eliminated and the overall amount of raw brine reprocessed per time can be doubled without all the components of a device for carrying out the method according to the invention also having to be doubled.

The temperature of the raw brine in method step d) of claim 1 is advantageously always higher than the temperature of the more highly concentrated brine in method step f) as it is conveyed through the TMZ in the same column. At higher temperatures, the ability of the TMZ to accept calcium ions instead of sodium ions improves. In contrast, at lower temperatures the capacity to accept ions changes in favour of the sodium ions. Since in step d) calcium ions are intended to be accepted, whereas, in step f), sodium ions are intended to be accepted, the acceptance of calcium in step d) and the release of calcium in step f) can be improved by the above-mentioned advantageous temperature selection.

In a particularly preferred embodiment of the invention, the concentration of the eluate in step e) is increased by the factor n and the flow speed in step d) is greater by the factor n than the flow speed in step f). As a result, method steps d) and f) always take the same amount of time, taking into account the increase in concentration and the resultant changes in volume. This makes it easier to continuously operate the method. This effect is particularly strong when the method is operated continuously by using two columns, as has already been described.

The magnesium ion-containing solution in step a) of claim 1 is advantageously conveyed through the bed of zeolite A or through the TMZ having an exhausted capacity until the chemical composition of the eluate is identical to the chemical composition of the magnesium ion-containing solution. This ensures that all positions of the zeolite A that are available to magnesium ions are occupied by magnesium ions and the zeolite A has therefore been completely converted into TMZ.

In a particularly preferred embodiment of the invention, the solution containing magnesium ions in step a) is formed of raw brine from seawater desalination plants having a total salt content of more than 60 g/l. The calcium-poor eluate exiting the column in step a) is then immediately subjected to step e) for additional treatment as a concentrated, partially decalcified brine, as long as the calcium ion concentration is less than $\frac{1000}{n}$ mg/l. In contrast, the calcium-rich eluate subsequently exiting the column having a calcium ion concentration of more than $\frac{1000}{n}$ mg/l is returned to the quantity of the raw brine from the desalination plant to be reprocessed. As a result, the eluate in step a) is then separated into a first part and a second part, the first part already being low in calcium ions and can therefore be further reprocessed, while the second part of the eluate is calcium-rich and, like the raw brine, still has to be reprocessed. As a result, the already calcium-poor eluate does not have to be subjected to method step d) unnecessarily, thus saving costs and time.

The sodium-containing solution in step c) is advantageously formed by the partially decalcified and concentrated brine of step e). This prevents the production of a separate sodium-containing solution. The decalcified and concentrated brine from step e) contains a sodium ion concentration of more than 50 g/l in this case. In the case of reprocessing raw brine from seawater desalination plants, the decalcified, concentrated brine from step e) usually contains approximately 63 g/l of sodium ions.

The separation of the eluate into water and concentrated brine in step e) is advantageously carried out by thermal distillation or membrane distillation, the total salt content of the concentrated brine being increased from 130 g/l to 300 g/l. Since the eluate from step d) is low in calcium, the concentration of the eluate can be considerably increased without the production of gypsum and limescale deposits hampering an additional increase in concentration in the form of the “gypsum barrier”.

The object of the invention is also achieved by a device for carrying out the method according to any of claims 1 to 9 having the features of claim 10. The device comprises a seawater desalination plant for separating seawater into drinking water that has a total ion content of less than 3 g/l, preferably less than 500 mg/l, and into a raw brine that has a total salt content of more than 60 g/l. The device further comprises a raw brine treatment plant downstream of the seawater desalination plant. The raw brine treatment plant in turn comprises a sorption unit for partially removing calcium ions from the raw brine according to step d) of claim 1, which sorption unit comprises at least a first and an additional column that are arranged vertically and filled with thermally modified zeolite (TMZ). The TMZ can be prepared in this case by means of a solution having a magnesium ion content of more than 1 g/l and a temperature of between 75 °C and 100 °C being conveyed through the vertical columns containing a filling of zeolite A. The zeolite A is in this case converted into TMZ. In order to stabilise the TMZ, the column filling is then advantageously cooled to a temperature below 45 °C. Method step d) can in general also be carried out in a sorption unit having just one vertical column. However, this then makes continuous operation more difficult.

According to i) of device claim 10, the raw brine treatment plant further comprises a desalination unit for separating the partially decalcified brine from the sorption unit into water that has a total ion content of less than 500 mg/l and into a concentrated brine according to step e) of claim 1. The desalination unit is preferably formed by a thermal distillation unit or a membrane distillation unit in this case.

The raw brine treatment plant also comprises a solids unit for separating the highly concentrated, calcium-rich brine into solids and into water that preferably has a total ion content of less than 500 mg/l according to step g) of claim 1. The solids unit is particularly preferably formed by a fractional crystallisation unit or a fractional vacuum crystallisation unit in this case. By means of the solids unit, the highly concentrated eluate from step f) of claim 1 can be completely separated into water and commercially usable salts.

The raw brine treatment plant also comprises at least three heat exchangers, a first and a second heat exchanger being connected in series and upstream of the inlet of the sorption unit from above either the first column or the additional column for optionally heating the raw brine. The first heat exchanger is formed by a recuperator, which can be heated together with the partially decalcified, concentrated brine from the desalination unit. The temperature of the second heat exchanger can be controlled by means of heated or cold water. However, the third heat exchanger is arranged downstream of the recuperator and upstream of the inlet of the sorption unit either at the bottom of the first column or at the bottom of the additional column. Said third heat exchanger is also formed to cool the still warm, partially decalcified, concentrated brine from the desalination unit exiting the recuperator before it enters the sorption unit. In an advantageous embodiment of the invention, the third heat exchanger is cooled by seawater or by raw brine. The first and the third heat exchangers are used to control the temperature conditions when fluids flow through the sorption unit. The recuperator is used to recuperate energy that is used for heating the liquids used in the method. This can reduce the operating costs.

In a preferred embodiment of the invention, a raw brine pretreatment group is arranged between the seawater desalination plant and the raw brine treatment plant. In this case, the raw brine pretreatment group comprises at least one column containing a granular material that removes solids and iron ions. The granular material is particularly preferably formed by a natural zeolite. Removing the solids and iron ions from the raw brine before it enters the sorption unit improves the longevity of the sorption unit.

Additional details and advantages of the invention can be found in the embodiment described below and shown schematically, in which:

Fig. 1 is a flow diagram of a method according to the invention on a device according to the invention,

Fig. 2 is a flow diagram and circuit diagram of the sorption unit and the heat exchanger from Fig. 1, and

Fig. 3 is a schematic flow diagram of the production, exhaustion and regeneration of TMZ.

In the following, elements of the method or the device that have the same function are provided with the same reference numeral, provided this is appropriate. The features of the embodiment explained below can of course also form the subject matter of the invention either individually or in other combinations.

Fig. 1 is a flow diagram of a device 2 according to the invention, on which the method according to the invention is also illustrated. Seawater having a total salt content of, for example, 35 g/l, shown by arrow 4, enters a seawater desalination plant 6. The seawater desalination plant can be formed of a thermal distillation plant (MSF, MED, steam compression) or a reverse osmosis plant (SWRO), for example. The seawater is separated in the seawater desalination plant 6 into drinking water, shown by arrow 8, having a total salt content of less than 3000 mg/l, in particular less than 500 mg/l, and into raw brine having, for example, a salt content of 65 g/l, shown by arrow 10. The drinking water enters a reservoir 12.

The raw brine enters a first portion of a raw brine treatment plant 14 comprising a sorption unit 16, a desalination unit 18 and a solids unit 20. Details of the raw brine treatment plant 14 are extensively described in Fig. 2. Fig. 1 merely gives a rough overview.

According to Fig. 1, the raw brine first enters the sorption unit 16. In the sorption unit 16, the calcium ions contained in the raw brine are retained and replaced with sodium ions. The brine that is at least partially decalcified in this way, shown by arrow 22, is conveyed to the desalination group 18. Here, the partially decalcified brine is separated into drinking water and a more highly concentrated brine having a total salt content of between 130 g/l and 300 g/l. The drinking water is conveyed from the desalination unit 18 to the reservoir 12, shown by arrow 24. The more highly concentrated brine is in turn conveyed from the desalination unit 18 to the sorption unit 16, shown by arrow 24. By means of the more highly concentrated brine, which contains few calcium ions and many sodium ions, the TMZ contained in the sorption unit 16 is converted from the calcium form into the sodium form and the calcium-rich, concentrated brine obtained thereby having a total ion content of from 130 g/l to 300 g/l is supplied to the solids unit 20, shown by arrow 26. The solids unit 20 is preferably formed by a fractional crystallisation unit or fractional vacuum crystallisation unit. Said unit separates the calcium-rich, concentrated brine into drinking water, which then enters the reservoir 12 from said solids unit, shown by arrow 28, and into crystallized-out solids that are obtained, such as calcium sulfate, sodium chloride and various potassium and magnesium salts, shown by arrows 30, 32 and 34.

Fig. 2 shows details of the raw brine treatment plant 14. At the beginning, zeolite A is converted into TMZ. For this purpose, raw brine having a salt content of for example 65 g/l, shown by arrow 10, is heated in a recuperator 36 and then in a first heat exchanger 38, to a temperature of between 75 °C and 100 °C, and is then conveyed through the valve 40 to the first vertical column 42, with a flow direction from top to bottom. The first vertical column 42 is filled with a column bed of zeolite A. On account of the raw brine containing a high number of magnesium ions that is conveyed through the zeolite A bed at a temperature of from 75 °C to 100 °C, the zeolite A is converted into thermally modified zeolite (TMZ) 44. At the same time, the boundary 46 between the calcium form of the TMZ and the sodium form of the TMZ moves in a flow direction from top to bottom. The first, calcium-poor part of the eluate from the column 42 is supplied to the desalination unit 18 via the valve 48. Here, the eluate is separated into fresh water and into a more highly concentrated, calcium-poor brine having a total salt content of between 130 g/l and 300 g/l. The eluate that then exits the first column 42 and is rich in calcium is conveyed back to the reservoir of the raw brine to be reprocessed, shown by the line 51 and the storage vessel 53.

The more highly concentrated brine is then conveyed via the line 52 in order to be cooled, firstly by the part 54 of the recuperator 36 that dissipates heat, and subsequently by the part 56 of the heat exchanger 58 that dissipates heat, and is thus cooled to a temperature below

45 °C. From here, the more highly concentrated brine is conveyed via the line 60 and through the valve 62 into the first column 42 from below. In the process, the calcium form of the TMZ is converted into the sodium form so that the boundary 46 between the forms is displaced upwards from below in the flow direction. The eluate, exiting the first column 42, of the calcium-rich, more highly concentrated brine is conveyed to the solids unit 20 via the line 64 and through the valve 66, where it is separated into solids and drinking water. The same method is used for the additional vertical column 68, which is filled in the same manner as the first column 42. After converting the zeolite A into the TMZ in the first column 42, the zeolite A is also converted into TMZ in the same way in the additional column 68 by closing the valves 40 and 48 associated with the first column 42 and opening the valves 80 and 82 associated with the additional column 68.

Continuous operation of the raw brine treatment plant 14 is then begun in accordance with recurring steps d) to h) of claim 1. Raw brine is supplied to the raw brine treatment plant 14 via the line 10 and is conveyed through the cooling part 70 of the recuperator 36 and the second heat exchanger 38 and is heated in the process to a temperature of between 30 °C and 45 °C. The raw brine is then conveyed to the first column 42 through the valve 40, the boundary 46 between the calcium form and the sodium form of the TMZ 44 shifting in the flow direction from top to bottom. The eluate of a partially decalcified brine, which eluate exits at the bottom end of the first vertical column 42, is supplied to the desalination unit 18 via the valve 48 and the line 50, where it is separated into fresh water and a more highly concentrated brine. The more highly concentrated brine is conveyed to the recuperator 36 via the line 52 and is conveyed from here to the third heat exchanger 58, where it is cooled to a temperature below 45 °C. Cooling is in particular necessary when the more highly concentrated brine has been previously heated in the desalination unit, for example in a distillation method.

After exiting the third heat exchanger 58 via the line 72 and the valve 74, the more highly concentrated, sodium-rich and calcium-poor brine is conveyed through the bed filling of TMZ of the additional column 68, in the flow direction from bottom to top. In the process, the calcium form of the TMZ is converted into the sodium form in the additional column 68 and the boundary 76 between the calcium form and the sodium form of the TMZ is shifted in the flow direction from bottom to top. The calcium-rich eluate, exiting the additional column, of the concentrated brine is supplied to the solids unit 20 via the line 64 and the valve 78 in order to be separated into solids and drinking water.

The first column 42 and the additional column 68 are then continuously operated at the same time. While, as shown in Fig. 2, raw brine initially flows through the first column 42 in step d), at the same time more highly concentrated brine is simultaneously conveyed out of the desalination unit via the open valves 74 and 78, in order to convert the calcium form of the TMZ back into the sodium form. As soon as calcium ions break through the TMZ bed 44 of the first column, the valves 40 and 48 as well as 74 and 78 are closed and the valves 80 and 82 as well as 62 and 66 are opened. The raw brine to be reprocessed then flows through the additional column 68 and is decalcified in the process, while the more highly concentrated brine from the desalination unit 18 enters the first column 42 via the valve 62 in the flow direction from bottom to top, where the sodium form of the TMZ is converted into the calcium form thereof. In this way, the columns 42, 68 are permanently operated both alternatingly and simultaneously.

Fig. 3 shows the conversion of the zeolite A 84 into TMZ 86 and the stabilisation 88 thereof. Magnesium ions, when dissolved in water, only have a small hydrate casing at a temperature of between 75 °C and 100 °C, and therefore magnesium ions can easily penetrate positions of the zeolite A that are available to magnesium ions, so that TMZ 86 is produced. The TMZ and the liquid remaining in the TMZ is then cooled to a temperature of less than 45 °C. As a result, the hydrate casing of the magnesium ions becomes considerably larger, and therefore the magnesium ion can no longer leave the TMZ. A stabilised form 88 of the TMZ is produced. The hydrate casing of the magnesium ions is shown in Fig. 3 by differently sized circles around the magnesium ion. As raw brine and more highly concentrated, decalcified brine are permanently conducted through the TMZ, the capacity thereof is exhausted by magnesium ions leaving the TMZ through the larger hydrate casing, despite being fixed. A cavity of the exhausted TMZ, which was previously occupied by a magnesium ion having a hydrate casing and has just become free, is shown by reference numeral 90. The exhausted TMZ 90 is then regenerated once again, shown by arrows 92 and 94.

Translator's note

Location in source text	**Term**	**Explanation/comment**
Page 7, lines 12-18	Sobald die … durch die Verfahrensschritte a) bis c).	This sentence appears to be incomplete; however, this has been translated as seen.