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Figure 1

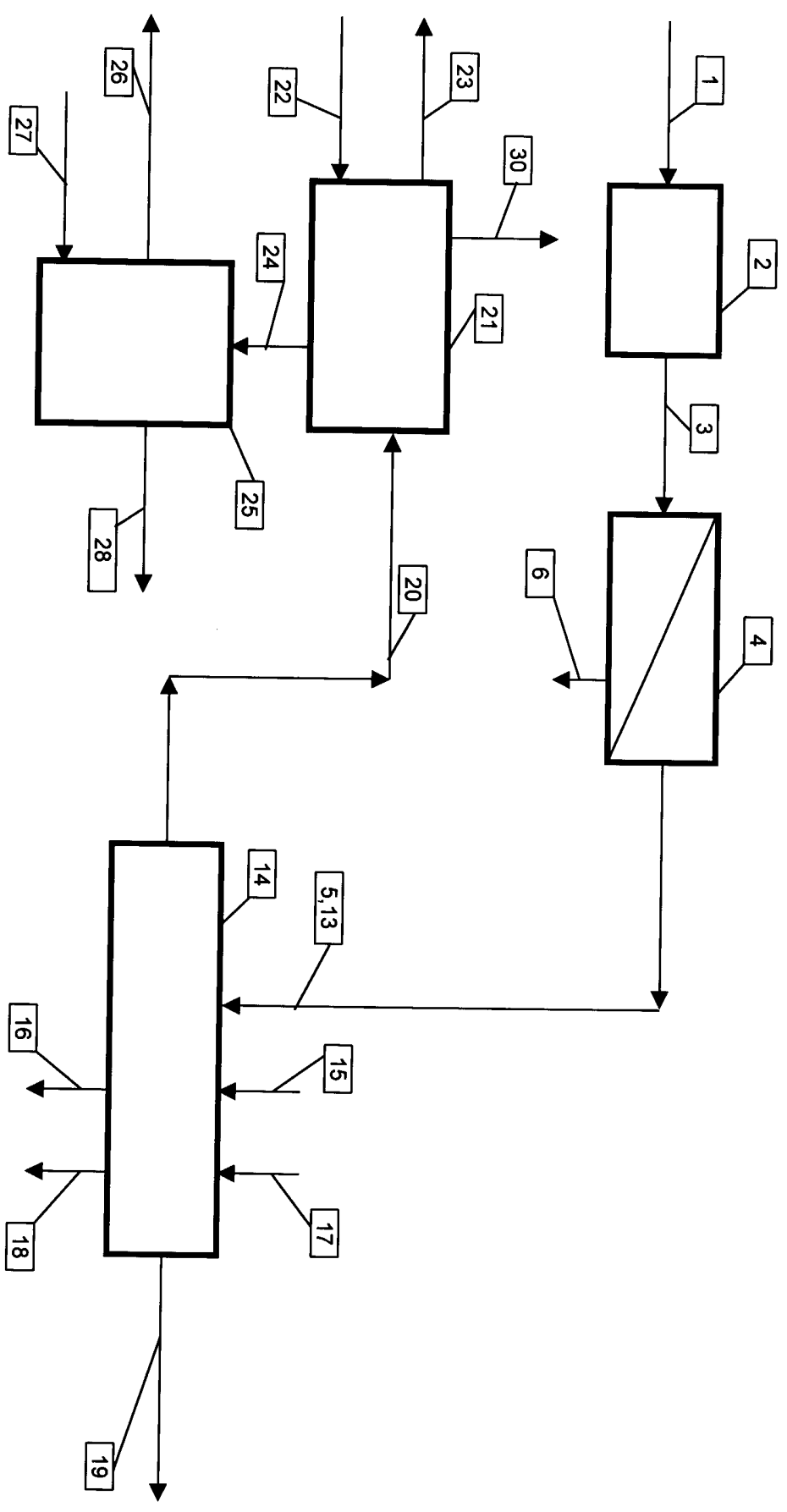


Figure 2

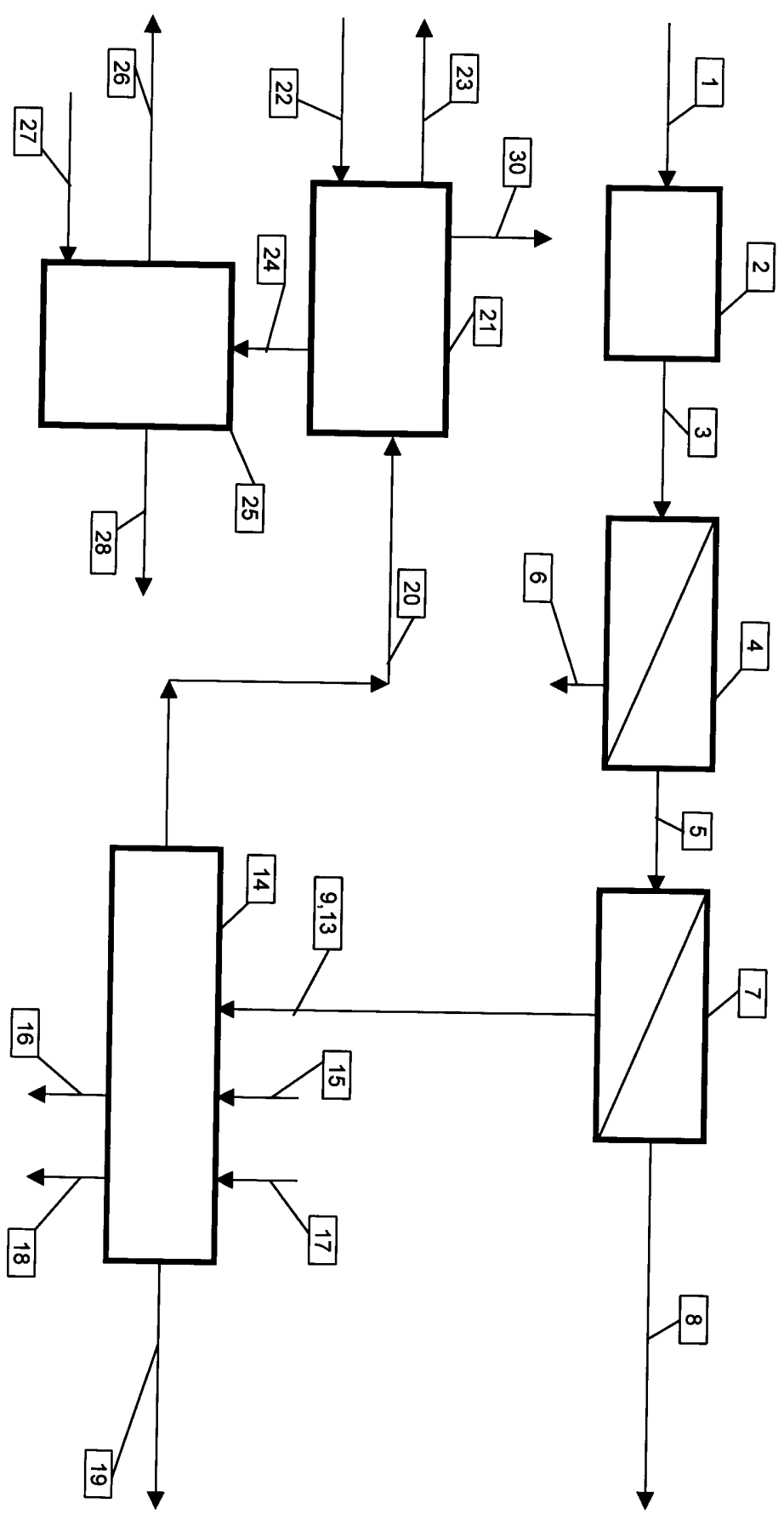


Figure 3

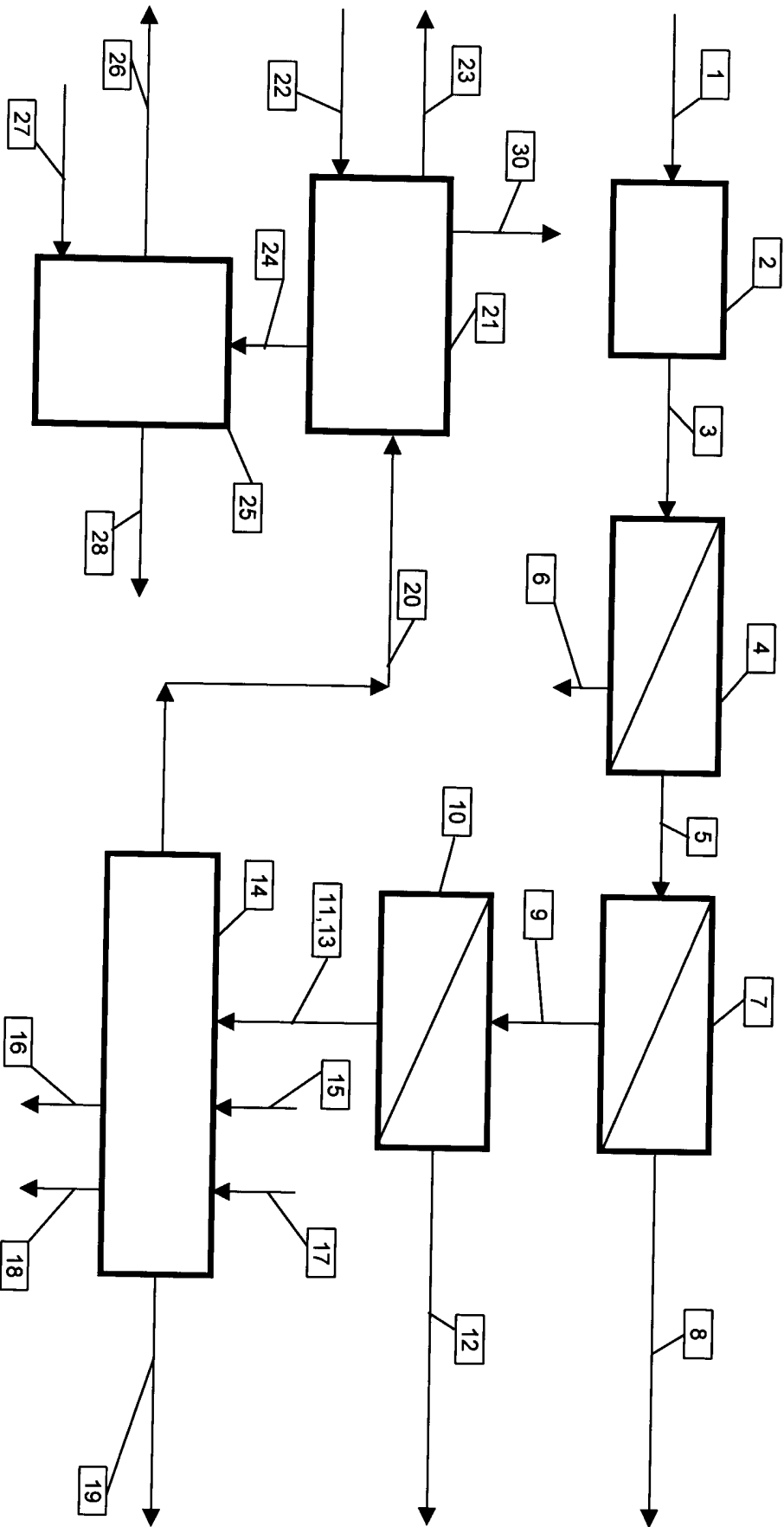


Figure 4

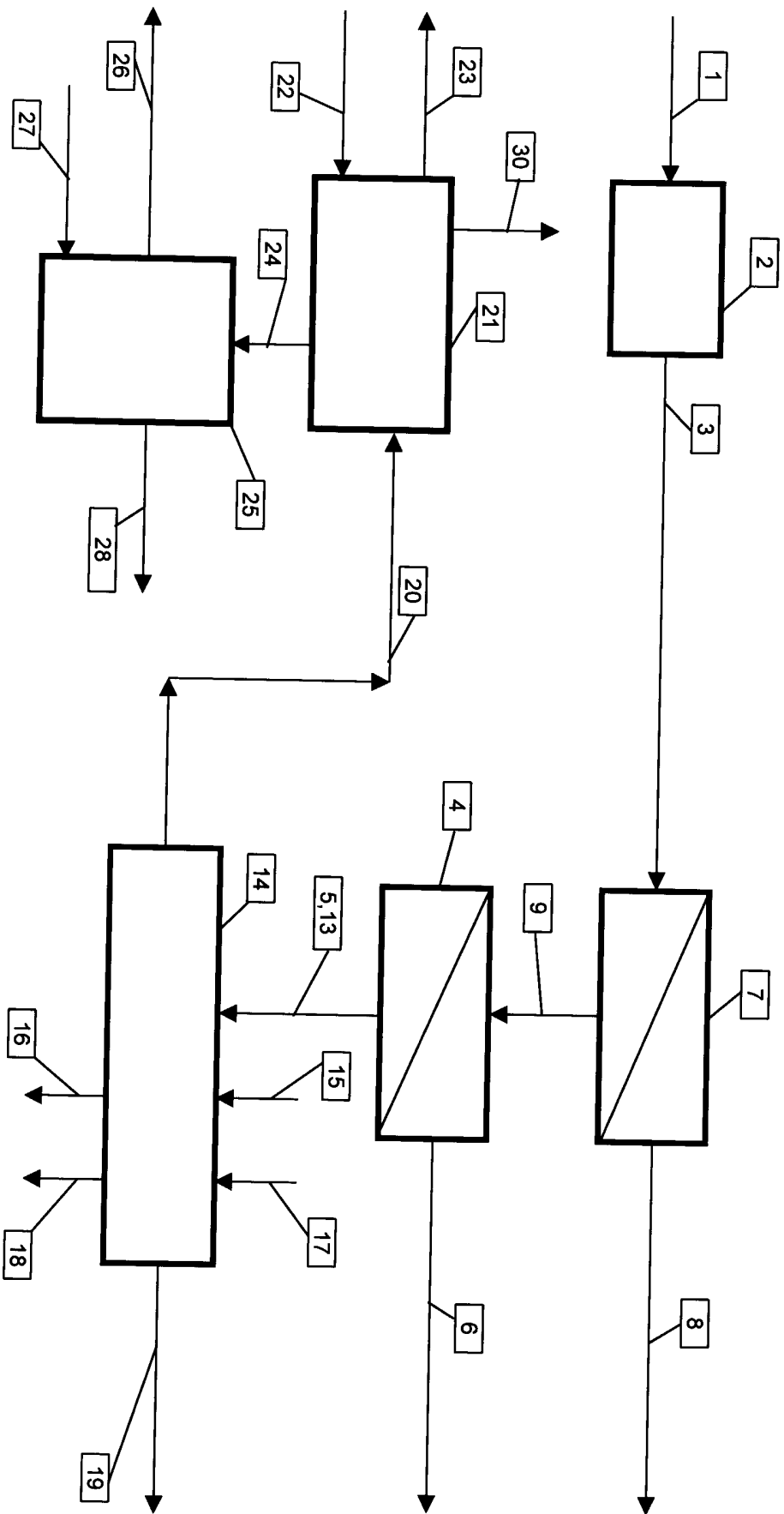
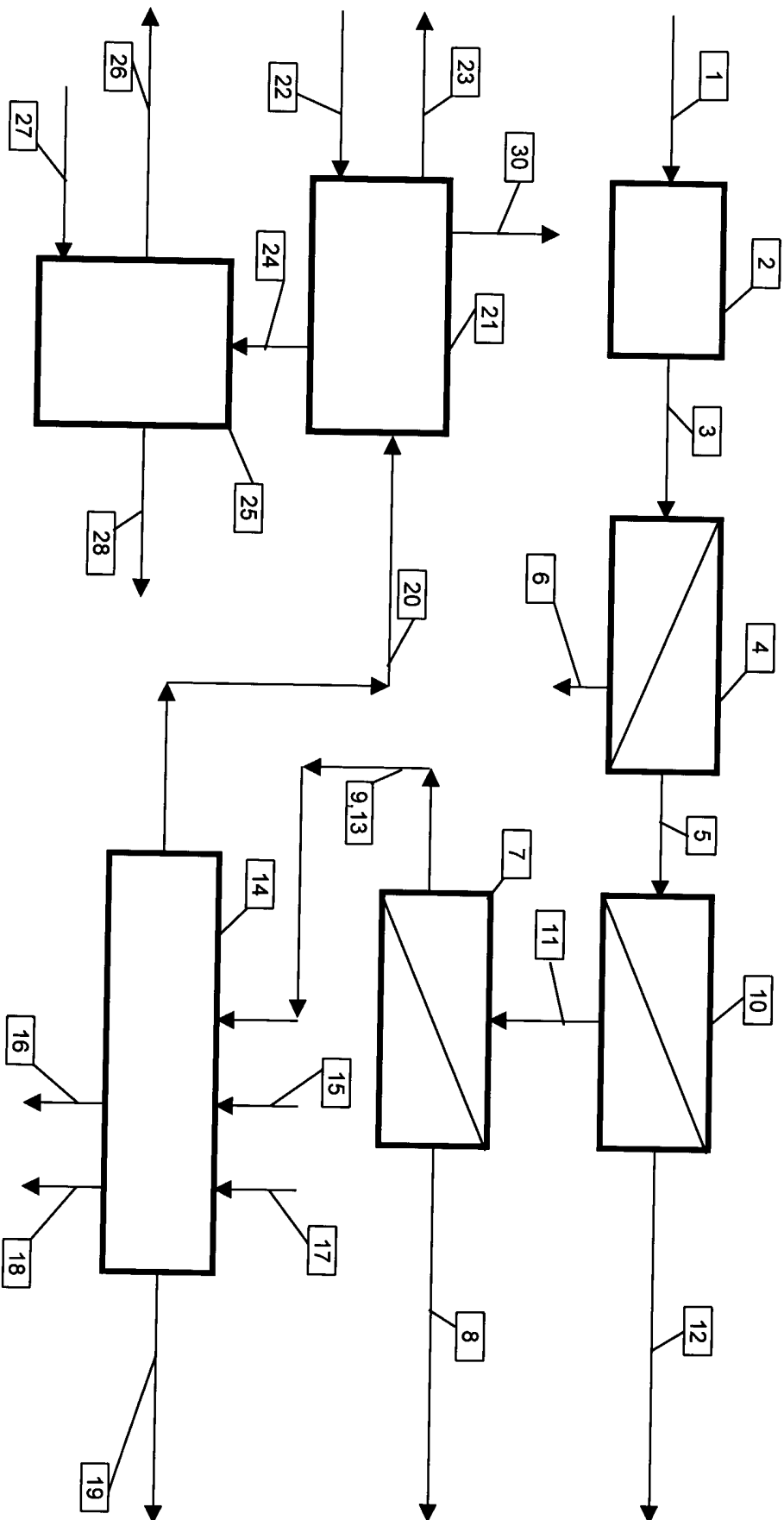


Figure 5



Title

METHOD FOR THE PRODUCTION OF SODIUM CHLORIDE FROM SEAWATER

Background of the InventionTechnical Field:

The invention concerns a method of producing high purity sodium chloride (NaCl) from seawater by the use of an ion selective nanofiltration process combined with thermal desalination. The sodium chloride can be used in many applications, for example, as a raw material in the chlor-alkali industry, as an ion exchange regenerant, and in the food industry.

Description of related Art:

Sodium chloride from seawater is most often recovered by the use of solar ponds. These ponds use solar evaporation to gradually concentrate the brine solution. As the brine solution is concentrated, various salts precipitate, starting with the least soluble. Initially calcium carbonate precipitates followed by calcium sulphate, followed by sodium chloride. When the brine solution has become saturated with sodium chloride, the solution is transferred to a crystallisation pond where sodium chloride starts to precipitate. The precipitated salt is harvested and washed. This method of salt production from seawater has several disadvantages including:

- a) Calcium carbonate and calcium sulphate also precipitate while sodium chloride is precipitating in the crystallisation pond. This reduces the purity of the salt.
- b) The machinery to extract the salt from the crystalliser can cause contamination of the salt product e.g. from sand on the wheels.
- c) Seawater salt can contain substantial quantities of very fine insoluble suspended solids that can contaminate the final.
- d) The seawater salt can contain substantial quantities of other contaminants for example: magnesium, boron, and iron.

The chlor-alkali industry uses large quantities of sodium chloride. The use of solar sea salt for electrolysis, to produce sodium hydroxide and chlorine, typically requires at least primary brine treatment with the following steps to reduce magnesium and calcium concentrations:

- a) Re-saturation with deionised water,
- b) Addition of sodium hydroxide and precipitation of magnesium hydroxide,
- c) Addition of sodium carbonate and precipitation of calcium carbonate.

If the salt electrolysis process uses a membrane method of electrolysis, then the solar salt is required to receive additional secondary brine treatment which typically consists of:

- a) Fine media filtration for solids removal,
- b) Ion exchange to further remove divalent ions such as calcium, magnesium and iron to parts per billion levels.

Desalination plants use seawater to produce a product of desalinated water and a waste stream of concentrated brine. Persian gulf seawater typically contains 35g/l of sodium chloride, and the concentrated brine from desalination processes contains up to 70g/l of sodium chloride. The concentrated brine from desalination processes is typically treated as a waste product and dumped back into the sea, which is a waste of a potential sodium chloride resource.

Desalination brines contain substantial quantities of calcium and sulphate ions. If further thermal concentration of these brines by evaporation is attempted then calcium sulphate can precipitate out on heat transfer surfaces causing blockages to process flows and loss in heat transfer efficiency. This normally limits thermal concentration of seawater by desalination to less than 70 g/l sodium chloride.

If typical desalination brine is crystallised by thermal or solar pond evaporation, then calcium sulphate can precipitate out while sodium chloride precipitates thereby contaminating the sodium chloride product with calcium sulphate. It is desirable to prevent the co precipitation of calcium sulphate.

Application WO9916714 and WO01142256 disclose the use of a pre-treatment step called nanofiltration before thermal desalination to remove sulphate ions. The aim in these applications was to enable the top brine temperature of the thermal desalination process to be elevated in order to increase the distillate production of the

thermal equipment per unit of heating steam utilised. The brine from these applications is still treated as a waste and discharged to the outfall. These applications were concerned with desalination for water production only. There is no mention of the potential use of nanofiltration with desalination as a means of enabling the operation of thermal desalination processes as brine concentrators to recover the sodium chloride in the brine or how this could be executed.

Application WO09916714 also discloses the use of nanofiltration as pretreatment for a reverse osmosis desalination processes. The nanofiltration pretreatment enables the reverse osmosis process to operate at high flux rates (i.e permeate flow per unit membrane area).

Object of the Invention

The object of the invention is to produce high purity sodium chloride from seawater by the pre-treatment of the make-up to a thermal desalination process with nanofiltration and operating the thermal desalination process as a brine concentrator. The brine from the thermal desalination process is then saturated and crystallised by evaporation. The crystallised sodium chloride is dewatered to produce a sodium chloride product. As a direct result of this sodium chloride production method a number of advantages are realised including:

- a) The thermal desalination process can be operated as a sodium chloride brine concentrator without the formation of calcium sulphate scales on heat transfer surfaces. This prevents blockages of heat transfer tubes and loss of heat transfer efficiency.
- b) The sodium chloride in the brine from the desalination process can be recovered as a product instead of being discharged as a waste to an outfall.
- c) The use of nanofiltration will result in a salt that is free of suspended solids when it is redissolved in water. This will eliminate the need for media filtration during secondary brine treatment for chlor alkali electrolysis.
- d) When the sodium chloride becomes saturated it will precipitate alone without co-precipitation of calcium sulphate or other salts. This will give a very pure sodium chloride product (after a distilled water wash). This will greatly reduce if not eliminate the need for further cation (e.g. calcium) removal before chlor alkali electrolysis of sodium chloride.
- e) There will be no sodium hydroxide or sodium carbonate required to precipitate magnesium hydroxide and calcium carbonate to purify the salt.

Essential features

The invention is a method for the production of high purity sodium chloride from seawater that is characterised by the following steps:

- a) Seawater is sent to a nanofiltration process with a higher rejection of sulphate relative to sodium ions or chloride ions.
- b) The permeate from the nanofiltration process is sent to a thermal desalination process as the make-up.
- c) The thermal desalination process increases sodium chloride concentration in the discharge brine relative to the make-up and produces product water.
- d) The thermal desalination brine is further evaporated to reach the saturation point of sodium chloride.
- e) The sodium chloride is precipitated out in a crystalliser by further evaporation until the saturation limit of another salt is reached.
- f) The sodium chloride crystals are removed from the sodium chloride slurry by a dewatering process.

It is essential that the nanofiltration process removes sufficient sulphate and/or calcium ions such that the calcium sulphate does not precipitate in the thermal desalination and brine crystallisation processes.

Important but non essential features

It is preferable that pre-treatment of the seawater be provided before nanofiltration to prevent excessive fouling of the nanofiltration membrane. If inadequate pre-treatment is provided before the nanofiltration process then excessive cleaning of membranes and frequent replacement could result.

Preferably, the seawater is pumped to a nanofiltration membrane process and the nanofiltration permeate is pumped to the reverse osmosis process. The reverse osmosis produces permeate that is water product. The retentate from the reverse osmosis process is the feed for the thermal desalination concentration process. The pre-treatment required to protect the nanofiltration process for salt production from fouling or excessive membrane replacement will already be provided by the requirements to protect a reverse osmosis desalination plant system.

It is preferable that the nanofiltration process has high rejection of all multivalent metal ions e.g. calcium, magnesium, barium, strontium, and zinc alternatively lower quality of final salt purity may be accepted.

It is preferable that acid is added to the feed before nanofiltration. This will enable high ratios of permeate flow to feed water to be achieved without calcium carbonate or magnesium hydroxide scaling. Alternatively, specialist anti-scalant chemicals can be dosed to the nanofiltration feed, or a lower ratio of permeate to feed flow may be used.

It is preferable that the nanofiltration process has such a high rejection of calcium, bicarbonate, and magnesium that neither magnesium hydroxide nor calcium carbonate precipitates in the thermal desalination or crystallisation process. Alternatively, acid can be added up stream of the make-up to the thermal desalination process with removal of the generated carbon dioxide.

Preferably, multistage flash distillation is used as the thermal desalination process. Alternatively, one of the following could be used a) multiple effect distillation b) thermo vapour compression multiple effect distillation c) mechanical vapour compression - multiple effect distillation.

Preferably, the retentate from the nanofiltration will be used as a feed source for other mineral recovery processes such as a feed for a magnesium chloride concentration process. Alternatively, the retentate could be discharged to an outfall.

Preferably, the bittern liquor extracted from the dewatering of crystallised sodium chloride will be used as a feed source for other mineral recovery processes such as a feed for a magnesium chloride concentration process. Alternatively, the bittern liquors could be discharged to an outfall.

Preferably, the sodium chloride brine from the nanofiltration permeate is concentrated using a reverse osmosis process followed by a thermal evaporation processes. Alternatively, it may be concentrated using solar evaporation ponds.

Preferably, the concentrated sodium chloride solution would be crystallised using thermal evaporation processes. Alternatively, it may be crystallised using solar crystallisation ponds.

Preferably, the thermal desalination processes and saturation/crystallisation processes are separate units so that each process may be optimised separately. Alternatively, the thermal desalination step could be combined with the saturation or crystallisation.

To obtain the highest purity salt, it is preferable that the water, used for final washing the of sodium chloride from crystallisation, be product water from desalination. It is the end use of the salt that will dictate the purity requirement of the wash water and indeed if the salt needs to be washed at all.

Drawings

The invention will be further described with reference to the drawings. The items on the drawings have all been labelled with numbers. These numbers are used in the detailed description. The key to these items is as follows

- Item 1 - Seawater feed
 - Item 2 - Seawater pre-treatment system
 - Item 3 - Pre-treated seawater
 - Item 4 - First stage nanofiltration process
 - Item 5 - Permeate from first stage nanofiltration process
 - Item 6 - Retentate from first stage nanofiltration process
 - Item 7 - Reverse osmosis process
 - Item 8 - Permeate from reverse osmosis process
 - Item 9 - Retentate from reverse osmosis process
 - Item 10 - Second stage nanofiltration process
 - Item 11 - Permeate from second stage nanofiltration process
 - Item 12 - Retentate from second stage nanofiltration process
 - Item 13 - Make-up for a thermal desalination process
 - Item 14 - Thermal desalination process
 - Item 15 - Heating source steam for thermal desalination process
 - Item 16 - Condensed heating steam
 - Item 17 - Cooling water
 - Item 18 - Spent cooling water
 - Item 19 - Distilled water product from thermal desalination process
 - Item 20 - Concentrated brine from thermal desalination process.
 - Item 21 - Sodium chloride saturation and crystallisation process
 - Item 22 - Heat source for saturation and crystallisation process
 - Item 23 - Evaporated steam from the saturation and crystallisation process
 - Item 24 - Crystallised sodium chloride in saturated brine, called magma.
 - Item 25 - Dewatering process
 - Item 26 - Bitterns (dewatered liquors)
 - Item 27 - Salt washing solution
 - Item 28 - Sodium chloride product
 - Item 30 - Distilled water product from saturation and crystallisation process
-
- Figure 1 - Process flow sheet Nanofiltration – Thermal Desalination
 - Figure 2 - Process flow sheet Nanofiltration – Reverse Osmosis -Thermal desalination
 - Figure 3 - Process flow sheet First Stage Nanofiltration – Reverse Osmosis – Second Stage Nanofiltration -Thermal Desalination
 - Figure 4 - Process flow sheet Reverse Osmosis- Nanofiltration -Thermal Desalination

Detailed Description

A flow sheet for the general process is shown in figure 1

Seawater (1) is sent to a pre-treatment system (2). The pre-treatment system is designed to prevent fouling of the nanofiltration process (4). The pre-treated seawater (3) is pumped to a nanofiltration process (4) to remove sulphate ions. The sulphate ions leave in the nanofiltration retentate (6). The nanofiltration permeate (5) is sent as the make-up (13) to a thermal desalination process (14).

The thermal desalination process evaporates water from the nanofiltration permeate (5) to increase the brine sodium chloride concentration and produce product water. The removal of the sulphate ions enables high salt concentration factors to be achieved in the thermal desalination brine (20) without scaling. A steam heat source may be used to provide the heat for the evaporation (15). The condensed heat source steam (16) may be either returned to the boiler or used to provide additional product water. Cooling water (17) may be used to help condense steam generated in the thermal desalination process. The spent cooling water may be discharged to an outfall (18).

The brine (20) from the thermal desalination process is sent to a sodium chloride saturator/crystalliser (21). By evaporation, the brine concentration is first brought up to the solubility limit for sodium chloride. Further evaporation proceeds to precipitate the sodium chloride as solid crystals. Further evaporation and crystallisation

is allowed to proceed until the solubility limit of another compound is reached (e.g. potassium chloride) at which point the evaporation is terminated. A heat supply (22) is required for the evaporation and crystallisation. The evaporation generates a steam vapour (23), which may be condensed to produce water product. The crystalliser produces a magma (24) (crystallised sodium chloride in saturated solution) which is sent to a dewatering process (25). The crystalliser also produces distilled product water (30).

In the dewatering process (25) some of the free liquor bittern surrounding the precipitated sodium chloride is removed. The bittern (26) is either discharged to the outfall or sent to other processes for mineral recovery (e.g. magnesium and potassium). A sodium chloride product with some remaining liquor is produced (28). This sodium chloride may be further processed by washing, or by drying, or by re-saturation combined with ion exchange to produce an enhanced purified sodium chloride product.

The detailed description will further examine:

- Methods for pre-treatment
- Configurations of the nanofiltration process that can be used as a feed for the thermal desalination process.
- Thermal desalination brine concentrator processes
- Saturation and crystallisation
- Dehydration

Pre-treatment (2)

A seawater source is required. The seawater extraction may include a seawater intake or beach ground wells, inlet pump station, and fine screening (1mm –6 mm aperture). Typical seawater sources include, but are not limited to, Persian gulf, Gulf of Oman, Mediterranean sea, Dead sea, Red sea, Caspian sea, or the Pacific ocean. The seawater may have been previously used as cooling water for a power station.

Since membrane processes such as nanofiltration are to be used, the pre-treatment system is required to achieve a Silt Density Index (SDI) limit imposed by the membrane manufacturer to restrict particulate fouling. This limit is typically set at value of 3,4, or 5. To achieve these SDI limits one or several of the following processes may be utilised: multimedia filtration, microfiltration, or ultrafiltration.

Pre-treatment for a nanofiltration membrane process also needs to address biological fouling of the membrane. This can be reduced by encouraging biological growth on the filtration media to deplete the available substrates for biological growth at the membrane. Microfiltration or ultrafiltration will greatly reduce the numbers of organisms available to colonise the membrane. Disinfection of the membrane feed can also be practised using chlorination combined with dechlorination, using chloramine, or by using ultraviolet radiation etc.

The measures mentioned to achieve acceptable SDI limits for the membrane and for preventing biological fouling of the membranes will also reduce the risk of solids blockage and biological fouling of any potential process using the nanofiltration retentate.

The nanofiltration process can become fouled with calcium carbonate scale. This can be prevented by one of the following methods:

- a) Ensure that nanofiltration retentate brine concentration is sufficiently low to prevent calcium carbonate precipitation.
- b) The addition of specialist antiscalant chemicals to disrupt crystal formation and growth.
- c) The addition of an acid to the seawater to convert the carbonate into bicarbonate. Dissolved carbon dioxide may be then stripped from the seawater

The thermal desalination plant can become fouled with calcium carbonate scale and magnesium hydroxide scale. This can be prevented by one of the following methods:

- a) The addition of an acid to the seawater converts the bicarbonate into carbon dioxide and reduces the hydroxide ion concentration. The carbon dioxide can be stripped out.
- b) Selection of a nanofiltration membrane with high rejection of calcium, magnesium and bicarbonate.
- c) The addition of specialist antiscalant chemical to the thermal desalination process to disrupt crystal formation and growth. This is standard practice for thermal desalination plants. However the final salt quality may require that this step is removed due to potential contamination of the final salt.

Nanofiltration membrane process configuration

A flow sheet to illustrate a nanofiltration configuration for salt production is given in figure 1.

The pre-treated seawater (3) is pumped to a nanofiltration (NF) membrane process (4). The nanofiltration membrane has a high degree of selectivity for some ions. That is some ions pass more easily through the membrane than other ions. The nanofiltration process selected for this application must have a high rejection of sulphate relative to sodium and chloride. The solution that passes through the NF membrane is called NF permeate (5). The brine solution that does not pass through the membrane is called the nanofiltration retentate (6). It is preferable but not essential that this membrane also has a high rejection of multivalent metal cations (e.g. magnesium and calcium), silica, and bicarbonate. The permeate (5) is sent to the thermal desalination plant as make-up (13). The retentate (6) may be discharged to an outfall or may be sent to a minerals recovery process to extract material such as magnesium.

The nanofiltration membrane manufacturers provide detailed design guidelines for their membranes. At the time of writing examples of leading membrane manufacturers, who may be contacted for further detailed information on nanofiltration membranes for seawater are:

- Dow FilmTec
- Hydranautics
- Koch Membranes
- Osmonics

Other configurations using nanofiltration can be used to provide the make-up to the thermal desalination process. These include:

a) Nanofiltration – Reverse Osmosis

A flow sheet to illustrate this nanofiltration configuration is given in figure 2.

The pre-treated seawater (3) is pumped to a nanofiltration process (4). The nanofiltration permeate (5) is pumped to the reverse osmosis system (7). The reverse osmosis system produces permeate as product water (8). The reverse osmosis retentate (9) is used as the feed (13) to the thermal desalination process.

The use of nanofiltration as a pre-treatment to reverse osmosis reduces the possibility of fouling of the RO membrane and it lowers the osmotic pressure of the feed to the RO membrane. This enables high permeate throughputs to be attained from the reverse osmosis membrane. The reverse osmosis membrane should have a high rejection of sodium chloride.

Most of the leading manufacturers of nanofiltration membranes also manufacture reverse osmosis membranes. These manufacturers can be contacted for further details on the membranes.

The nanofiltration retentate (6) could be either discharged to an outfall or could be sent to a process for mineral recovery of components such as magnesium, sulphate or calcium.

b) Nanofiltration – Reverse Osmosis - Nanofiltration

A flow sheet to illustrate this nanofiltration configuration is given in figure 3

The pre-treated seawater (3) is pumped to a first stage nanofiltration process (4). The nanofiltration permeate (5) is pumped to the reverse osmosis system (7). The reverse osmosis system produces permeate as product water (8). The reverse osmosis retentate (9) is sent to a second stage nanofiltration process (10). The second stage nanofiltration (10) should have a high rejection for divalent cations, particularly calcium and magnesium, relative to sodium or chloride. The permeate (11) from the second stage nanofiltration process is sent as the make-up for the thermal desalination process (13)

The first stage nanofiltration retentate (6) could be either discharged to an outfall or could be sent to a process for mineral recovery of components such as magnesium, sulphate or calcium.

The second stage nanofiltration retentate (12) could be either discharged to an outfall, or recycled as a part feed to the first stage nanofiltration, or could be sent to a process for mineral recovery of components such as magnesium, sulphate or calcium.

This configuration has the advantage that it further reduces the contamination of divalent ions in the final salt product.

c) Reverse Osmosis - Nanofiltration

A flow sheet to illustrate this nanofiltration configuration is given in figure 4.

The pre-treated seawater (3) is pumped to a reverse osmosis process (7). The reverse osmosis system produces permeate as product water (8). The reverse osmosis should have high rejection for sodium, chlorides, potassium, calcium, magnesium, sulphate ions.

The reverse osmosis retentate (9) is sent to a nanofiltration process (4). The nanofiltration process will have a high rejection of sulphate. The permeate (5) from the nanofiltration process is sent as the make-up to the thermal desalination process (13).

The nanofiltration retentate (6) could be either discharged to an outfall or could be sent for mineral recovery of components such as magnesium, sulphate or calcium or could be returned to the feed of the reverse osmosis system.

d) Nanofiltration-Nanofiltration – Reverse Osmosis

This arrangement could be used if magnesium recovery from nanofiltration retentate is to be executed. A flow sheet to illustrate this configuration is given in figure 5.

The pre-treated seawater (3) is pumped to a first stage nanofiltration process (4). The first stage nanofiltration will have a high rejection of sulphate and magnesium and a lower rejection of calcium and sodium. The first stage nanofiltration permeate (5) is sent to a second stage nanofiltration process (10). The first stage nanofiltration retentate is sent to magnesium recovery.

The second stage nanofiltration process (10) will have a high rejection of sulphate, calcium and magnesium with a lower rejection of sodium and chloride. The second nanofiltration permeate (11) is sent to a reverse osmosis process (7). The second stage nanofiltration retentate (12) may be discharged to outfall.

The reverse osmosis process (7) produces permeate as product water (8). The reverse osmosis retentate (9) is sent to a second stage nanofiltration process (10). The second stage nanofiltration (10) should have a high rejection for divalent cations, particularly calcium and magnesium, relative to sodium or chloride. The permeate (11) from the second stage nanofiltration process is sent as the make-up for the thermal desalination process (13)

The first stage nanofiltration retentate (6) could be either discharged to an outfall or could be sent to a process for mineral recovery of components such as magnesium, sulphate or calcium.

This configuration has the advantage that it further reduces the contamination of scaling ions in the final sodium chloride salt product, and it provides the magnesium recovery stream with a higher ratio of magnesium to calcium. Higher magnesium to calcium ratio can enable a higher capture of magnesium by ion exchange processes which could be employed by a magnesium recovery process.

Thermal desalination brine concentrator processes (14) :

The make-up flow (13) from the nanofiltration configuration can be sent to a thermal desalination process (14).

Thermal processes include the following:

Multiple Stage Flash Distillation (MSF).

Multiple Effect Distillation (MED).

Mechanical Vapour Compression Multiple Effect Distillation (MVC MED)

Thermo Vapour Compression Multiple Effect Distillation. (TVC MED).

These processes all evaporate salt water and condense the vapour to form a thermal desalination water product (19) with low salt content. The brine solution, that remains after evaporation, becomes more concentrated. The brine produced (20) from the thermal process will have a sodium chloride concentration higher than the feed concentration.

The maximum total dissolved concentration of the multiple stage flash (MSF) desalinated seawater brine is less than 70 g/l, with a top brine temperature of 120 deg C, due to concerns with regard to calcium sulphate scaling. The temperature limit is reduced to 70 deg C for the thermal desalination processes using multiple effect distillation (MED). Using nanofiltration removes the scaling potential and therefore the total dissolved solids concentration can be increased. The greater the removal of calcium sulphate by the nanofiltration then the higher will be the permissible brine total dissolved solids concentration.

The thermal desalination plant produces two products, concentrated sodium chloride brine (20) and distilled water (19). Increased concentration of total dissolved solids in the brine causes boiling point elevation of the brine. Higher boiling point elevation results in decreased energy efficiency in the production of distilled water. Higher brine concentrations in the thermal desalination plant results in lower capital costs to increase the salt concentration to saturation point downstream of desalination. The selection of the thermal desalination final brine concentration will be an economic balance between the costs of water and salt production and the revenues of water and salt concentration.

The MSF and MED thermal desalination processes use cooling water (17) for the following reasons

- a) to provide a heat sink to enable vapours produced to be condensed.
- b) to maintain acceptable distillate and brine temperatures.

This cooling water may be seawater. MVC-MED and TVC-MED may not require cooling water as a heat sink, as the vapour from the last stage can be recompressed to form some of the heating steam for the first effect.

The spent cooling water (18), where used, will either be discharged to outfall or could be used as a feed to the pre-treatment system enabling higher permeate fluxes to be achieved in the nanofiltration and reverse osmosis processes. Higher feed temperature allows membrane processes to operate at higher fluxes.

The heat source (15) for the MVC-MED and TVC-MED can come partly or fully (MVC-MED only) from mechanical or steam recompression of vapour from the final effect. For all other thermal processes (MSF, MED) the heat source is most likely to be low pressure steam (0-5 bar). This steam can be obtained from a power generation steam turbine, or from power station heat recovery steam generator, or a separate boiler, or the exhaust steam from the crystallisation of salts.

The condensate (16), obtained from condensing the heating steam, can be used as distilled water product or returned to a boiler to generate further steam.

It would be preferable that dosing with antiscalants and antifoam are minimised, as these chemicals can contaminate the final salt product. The use of nanofiltration will prevent calcium sulphate scaling. Calcium carbonate and magnesium hydroxide scaling potential may be greatly reduced by selecting a nanofiltration membrane with a high rejection of calcium, magnesium and bicarbonate. Acid (preferably hydrochloric) may be dosed to the thermal desalination make-up to further reduce scaling potential from magnesium and carbonate. The carbon dioxide generated by addition of the acid may be removed by the degassing of the make-up. The acid dosing would be preferably located upstream of the nanofiltration process.

Care is needed in the selection of materials for the desalination system as the concentration of sodium chloride brine will be elevated. Preferably, titanium or stainless steels with a pitting resistance equivalent number of greater than 40 should be used for the heat transfer tubes.

These thermal technologies are well understood and widely applied in the desalination industry.

Full descriptions of these thermal processes and their sizing parameters can be found in the following reference "Encyclopaedia of Desalination and Water Resources" published by Eolss Publishers Ltd. The following are examples of manufacturers who are specialists in these thermal methods, who could also be contacted for further detailed technical information

MSF	- Doosan Engineering Korea, Weir Westgath Glasgow, Fisia Italy, Hitachi-Zosen Japan.
MED	- Sidem Paris, Weir Westgarth Glasgow, Aquachem
MVC MED	- Sidem Paris, Weir Westgarth Glasgow, Aquachem
TVC MED	- Sidem Paris, Weir Westgarth Glasgow, Aquachem

Saturation & crystallisation processes (21).

The brine (20) from the thermal desalination process (14) is sent to a saturation and crystallisation process (21). There are standard industrial designs in the salt industry to achieve saturation and crystallisation using technology such as multiple effect calandria (also called vacuum pans) and forced circulation evaporators.

In these processes the water in the thermal desalinated brine is evaporated to bring the brine up to saturation point with respect to sodium chloride. Further evaporation results in the precipitation of sodium chloride crystals into the saturated brine. The evaporation may be carried out in several effects where the steam from each effects may be used to heat the brine in the next effect. Each effect operates at a low pressure than the previous effect. The evaporation may also be carried out in single effects where the steam produced is mechanically recompressed to form the heating medium for the brine heater.

The heat source (22) for the first effect can be provided by several means including

- a) Low pressure steam can be obtained from a power generation steam turbine,
- b) Low pressure steam from a boiler,
- c) Mechanical compression of some or all of the vapour from the final effect,
- d) Steam compression of some of the vapour from the final effect using a thermo compressor,
- e) Application of flame heat to the brine.

The vapour (23) from each effect can be condensed and used as an additional source of distilled water. If a steam boiler has been used to raise the steam then some of the condensate may be returned to the boiler.

The sodium chloride should precipitate on its own without simultaneous precipitation of calcium sulphate due to the removal of sulphate and calcium ions by nanofiltration. The evaporation in the crystalliser is stopped when saturation point of another salt (e.g. potassium chloride) is reached.

The magma (crystallised sodium chloride in saturated solution) (24) produced in the crystalliser is sent to the dewatering process (25).

Dewatering process (25)

The dewatering process (25) removes most of the free liquor from the sodium chloride magma. To reduce the size of the final dewatering equipment, the magna may be first thickened. Thickening of the sodium chloride magma can be accomplished by numerous established techniques such as:

- a) Gravity settlement
- b) Hydro cyclone
- c) Gravity belt thickener
- d) Thickener centrifuge

The thickened salt magma is then preferably dewatered using a pusher centrifuge to a dry solids content exceeding 95 % by weight. Alternatively other dewatering devices may be used such as a membrane plate press, rotary vacuum filter or a belt filter press.

The liquors (26) produced by the thickener and pusher centrifuge can be discharged to the outfall, or sent to other processes for minerals recovery of such compounds as magnesium chloride and potassium chloride.

The pusher centrifuge may utilise a wash water to further to reduce the impurities in the final salt. This wash water could be comprised of a saturated solution of sodium chloride in distilled water from the thermal desalination process. The wash water (27) could also be comprised of some of the nanofiltration permeate (same as the feed water to the thermal desalination plant), or final product water.

Some of the wash water could be recovered by passing some of the dewatering liquors through an ion exchange process to remove divalent ions.

A sodium chloride product (28) with a 99.9 % purity by weight will be achievable.

Further processing

Further purification may be required to achieve the end salt specification. Remaining impurities in the salt can be further reduced by:

1. Washing the dewatered salt again with a saturated solution of sodium chloride in distillate from the thermal desalination plant. The distillate quality could be further improved by passing the distillate through an ion exchange system to remove some contaminants such as divalent cations (e.g. calcium or magnesium.).
2. The salt may require further purification to remove divalent ions for use in membrane electrolysis. Salt may be re-dissolved in desalination distillate and passed through an ion exchange resin to remove the contamination level of divalent ions to parts per billion by weight. However it is preferable that this step be taken at the location of the electrolysis plant in order to avoid problems due to salt contamination in transport.

Example

The invention will be further illustrated by a non-limiting example with reference to figure 2

Persian gulf seawater with the following composition is assumed for the seawater feed (1): Sodium 13440 mg/kg, potassium 483 mg/kg, calcium 508 mg/kg, magnesium 1618 mg/kg, chloride 24173 mg/kg, sulphate 3384, bicarbonate 176 mg/kg, boron 3 mg/kg. The flow of seawater (1) to pre-treatment is 1100 kg/s.

The pre-treatment (2) steps for the seawater are:

- Seawater is extracted from the sea and screened to a size of 3mm.
- The sea water is then pumped to a multimedia pressure filtration process. A coagulant ,such as ferric chloride may be added to improve solids capture and removal of colloidal material.
- Hydrochloric acid is added to remove the bicarbonate.
- Two-stage multimedia pressure filtration is used to remove suspended solids and to achieve a silt density index of less than 5. Typical service velocities in each stage of the filter can be 10 m/hr with backwash velocities of 40 m/hr. The pressure filters are periodically back washed with filtered effluent. The spent backwash is discharged to the final effluent outfall (approx 100 kg/s)
- The seawater is then passed to a cartridge filter system, which will remove solids to a 5 micron size limit.

The pre-treated seawater has the following composition (3):

Sodium 13440 mg/kg, potassium 483 mg/kg, calcium 508 mg/kg, magnesium 1618 mg/kg, chloride 24275 mg/kg, sulphate 3384, boron 3 mg/kg. The flow 1000 kg/s.

The pre-treated seawater water (3) is then pumped to a nanofiltration process (4) . The nanofiltration membrane, e.g. Dow Filmtec nanofiltration membrane type SR90-400, is operated at a typical pressure of 20 bar. This membrane has the following approximate rejection characteristics: Sodium 5 %, potassium 14 % , calcium 23 % , magnesium 76 %, chloride 10 %, sulphate 98 %, boron 60 %. The ratio of permeate flow (5) to feed flow is set at approximately 60 %, with a permeate flux of approx. 12-15 (1/m²h).

The composition of the nanofiltration permeate (5) is approximately as follows: sodium 12768 mg/kg, potassium 415 mg/kg, calcium 391 mg/kg, magnesium 388 mg/kg, chloride 21838 mg/kg, sulphate 68 mg/kg, boron 1.2 mg/kg. The flow is 600 kg/s

The composition of the nanofiltration membrane process retentate (6) is approximately as follows: Sodium 14448 mg/kg, potassium 584 mg/kg, calcium 683 mg/kg, magnesium 3463 mg/kg, chloride 27931 mg/kg, sulphate 8358 mg/kg, boron 5.7 mg/kg. The flow is 400 kg/s. This flow is discharged to the outfall.

The nanofiltration permeate (5) is then pumped to a reverse osmosis process (7) (example Hydranautics SWC4) at a pressure of 69 bar. This membrane has an approximate salt rejection of 99.4 %. The ratio of permeate flow to feed flow is set at approximately 45 %, with a permeate flux of approx. 28 (1/m²h).

The composition of the reverse osmosis membrane permeate (8) is approximately as follows: Sodium 77 mg/kg, potassium 2 mg/kg, calcium 2 mg/kg, magnesium 2 mg/kg, chloride 131 mg/kg, sulphate 0.41 mg/kg, boron 0.45 mg/kg. The flow is 270 kg/s. This permeate (8) is product water .

The composition of the reverse osmosis membrane process retentate (9) is approximately as follows: sodium 23152 mg/kg, potassium 123 mg/kg, calcium 709 mg/kg, magnesium 704 mg/kg, chloride 39599 mg/kg, sulphate 123 mg/kg, boron 1 mg/kg. The flow is 330 kg/s. The reverse osmosis retentate is sent to the thermal desalination process (14) as make-up (13).

Multiple stage flash (MSF) is used in this example for the thermal desalination process (14). This is a brine recirculation type MSF. The make-up (13) is discharged to the suction side of the MSF recirculation pump. A recirculation flow of 2564 kg/s is used. Thirteen stages of heat recovery are used with three heat reject stages. The top brine temperature selected is 121 Deg C. The brine concentration after the brine heater is 234 g/l tds ,

the brine concentration leaving the MSF (20) is 259 g/l tds. The MSF produces 247 kg/s of distillate product water (19). The 136 kg/s of 3 bar heating steam (15) is used this steam is obtained from the discharge of a back pressure steam turbine of a power generation plant. The condensed heating steam (16) is returned to the power plant. 3792 kg/s of seawater is used as a coolant (16) in the heat reject section. The spent coolant seawater is discharge to an outfall (17). The material selection for the heat transfer tubes is UNS C71640 for the brine heater and first four stages of the heat recovery section, UNS C70600 for the remaining heat recovery section stages and UNS R50400 for the heat reject section. The heat exchange areas are: 1336 m² for the brine heater , 2164m² for each heat recovery stage and 4220 m² for each heat reject stage. The tube diameters are 32 mm and the tube wall thickness is 1 mm for the brine heater and heat recovery stage and 0.7 mm for the heat reject stage.

The brine from the thermal desalination process is sent to a forced circulation evaporator for saturation and crystallisation. In this example a single effect mechanical vapour recompression evaporator will be used. The salt slurry is pumped from the bottom cone of the effect chamber through tubes in a vertical heat exchanger, where heat is added, and back into the effect chamber where the brine boils forming salt crystals. These salt crystals continue the circulation-heating- evaporation cycle, until they grow to a sufficient size to settle in the leg of the evaporator.

Some of the evaporated vapour from the vessel is recompressed to a higher pressure and temperature using a mechanical compressor. The evaporating flash pressure is 2 bar. The compressor is required to increase the pressure by 1.89 bar. The temperature difference across the brine heater (steam to brine) is 5 deg C. With a brine recirculation rate of 5520 kg/s the evaporation rate will be approx. 58 kg/s with electrical requirement of approx. 55 kW

/tonne water produced. The evaporated water is product water the quantity of distilled water produced is 58 kg/s. The bitters (25 kg/s) are discharge to the outfall.

The sodium chloride magma (magma) from the crystalliser is then thickened to 25-50 % dry solids (for example using a belt thickener Ashbrook Aquabelt). The thickened salt slurry is dewatered to approx. 97 % dry solids using a centrifuge (for example Baker Hughes Bird Universal Pusher Centrifuge). The sodium chloride salt is washed in the centrifuge using a saturated solution of sodium chloride in distilled product water. The dewatering liquors from the belt thickener and from the pusher centrifuge are recycled to the forced circulation evaporator.

The dewatered salt product as 97 % dry solids. Approx 1300 tonnes/day of sodium chloride salt would be produced with a water production of approx. 49,500 tonnes/d.

Claims:

1. Method for production of high purity sodium chloride from seawater that is characterised by the following steps:
 - a) seawater is sent to a nanofiltration process with a higher rejection of sulphate ions relative to sodium ions or chloride ions,
 - b) the permeate from the nanofiltration process is sent to a thermal desalination process as the make-up,
 - c) the thermal desalination process increases the sodium chloride concentration in the discharge brine relative to the make-up and produces product water,
 - d) the thermal desalination brine is further evaporated to reach the saturation point of sodium chloride,
 - e) the sodium chloride is precipitated out in a crystalliser by further evaporation until the saturation limit of another salt is reached,
 - f) sodium chloride crystals are removed from the sodium chloride slurry by a dewatering process.

2. Method according to claim 1, where the thermal desalination process is characterised by one of the following processes, Multiple Stage Flash Distillation (MSF), Multiple Effect Distillation (MED), Thermo-Vapour Compression Multiple Effect Distillation (TVC-MED), Mechanical Vapour Compression Multiple Effect Distillation.

3. Method according to claim 1, which is characterised by the use solar evaporation to concentrate the sodium chloride solution instead of a thermal desalination process 1(c)

4. Method according to claim 1, which is characterised in that step 1 (d) uses solar evaporation to saturate the sodium chloride brine produced by 1 (c).

5. Method according to claim 1, which is characterised in that step 1 (e) uses solar evaporation to crystallise the sodium chloride brine produced by 1 (d).

6. Method according to claim 1, which is characterised by the additional step after 1 (a) of the use of a cation ion exchange process before the thermal desalination process to reduce the concentration of divalent ions in the feed to the thermal desalination process.

7. Method according to claim 1, which is characterised by the additional step after 1 (c) of the use of a cation ion exchange process on the discharge brine from the thermal desalination process in order reduce the concentration of divalent ions in the brine solution.

8. Method according to claim 1, which is characterised by the additional steps, after 1(e), of the re-saturation of the brine with distilled water followed by the use of a cation ion exchange process to further reduce the concentration of divalent ions in the brine solution.

9. Method according to claim 1, which is characterised by the following steps as a replacement of 1(b)
 - I. the permeate from the nanofiltration membrane is pumped to a reverse osmosis process,
 - II. the reverse osmosis process has a high sodium & chloride rejection,
 - III. the reject from the reverse osmosis process is used as the make-up for the thermal desalination process,

10. Method according to claim 9, which is characterised by the following steps
 - a) the retentate from the reverse osmosis membrane is sent to a second nanofiltration membrane instead of to a thermal desalination process, the second nanofiltration process has a higher rejection of divalent cations than for sodium or chloride ions,

- c) the permeate from the second stage of nanofiltration is used as the make-up for the thermal desalination process,
11. Method according to claim 1, which is characterised by the replacement of 1 (a) by the following steps
- The seawater is pumped to a reverse osmosis process, the reverse osmosis process has a high sodium chloride rejection,
 - the retentate from the reverse osmosis membrane is sent to a nanofiltration process
 - the nanofiltration membrane has a higher rejection of divalent cations than for sodium or chloride ions
 - the permeate from the nanofiltration is used as the make-up for the thermal desalination process,
12. Method according to claim 1, which is characterised in that the feed to the nanofiltration process is pre-treated using any one or a combination of the following processes in order to prevent fouling of the desalination processes or the nanofiltration process:
- fine screening,
 - sand filtration,
 - multimedia filtration,
 - disinfection
 - activated carbon filtration,
 - membrane microfiltration,
 - membrane ultrafiltration.
13. Method according to claim 1, which is characterised in that the feed to the nanofiltration process is pre-treated by acid addition and stripping of carbon dioxide gas to prevent precipitation of calcium carbonate or magnesium hydroxide.
14. Method according to claim 1, which is characterised in that the nanofiltration results in a final salt product that contains a negligible amount of insoluble suspended solids.
15. Method according to claim 1, which is characterised in that the nanofiltration results in a final salt product of at least 99.9 % purity .
- 16 Method according to claim 1, which is characterised in that thermal desalination can be operated as a brine concentrator without the formation of sulphate scales on the heat transfer surface areas.