(54) Title of the invention: Magnesium chloride production method from seawater

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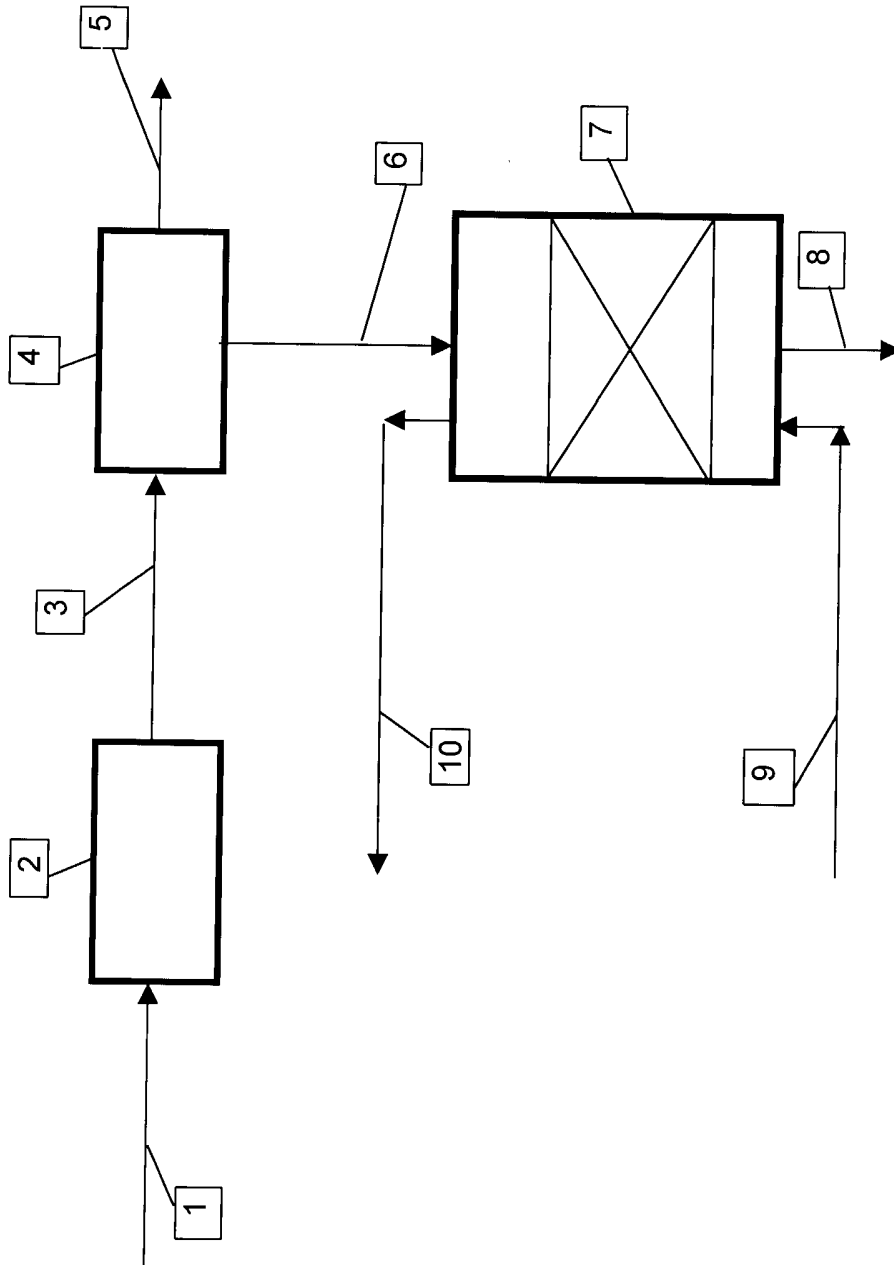**WA14 4NE, United Kingdom**

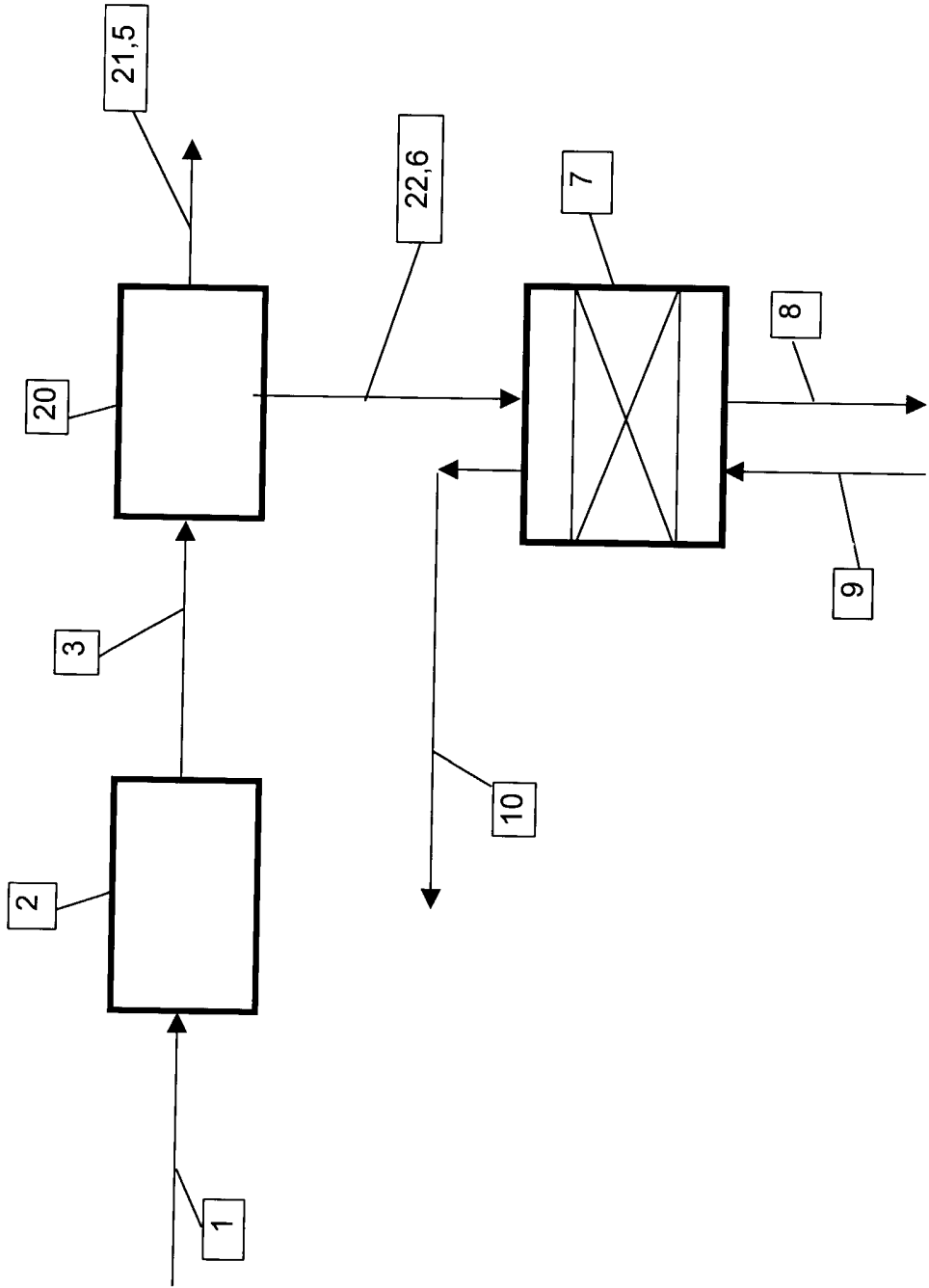2 39678

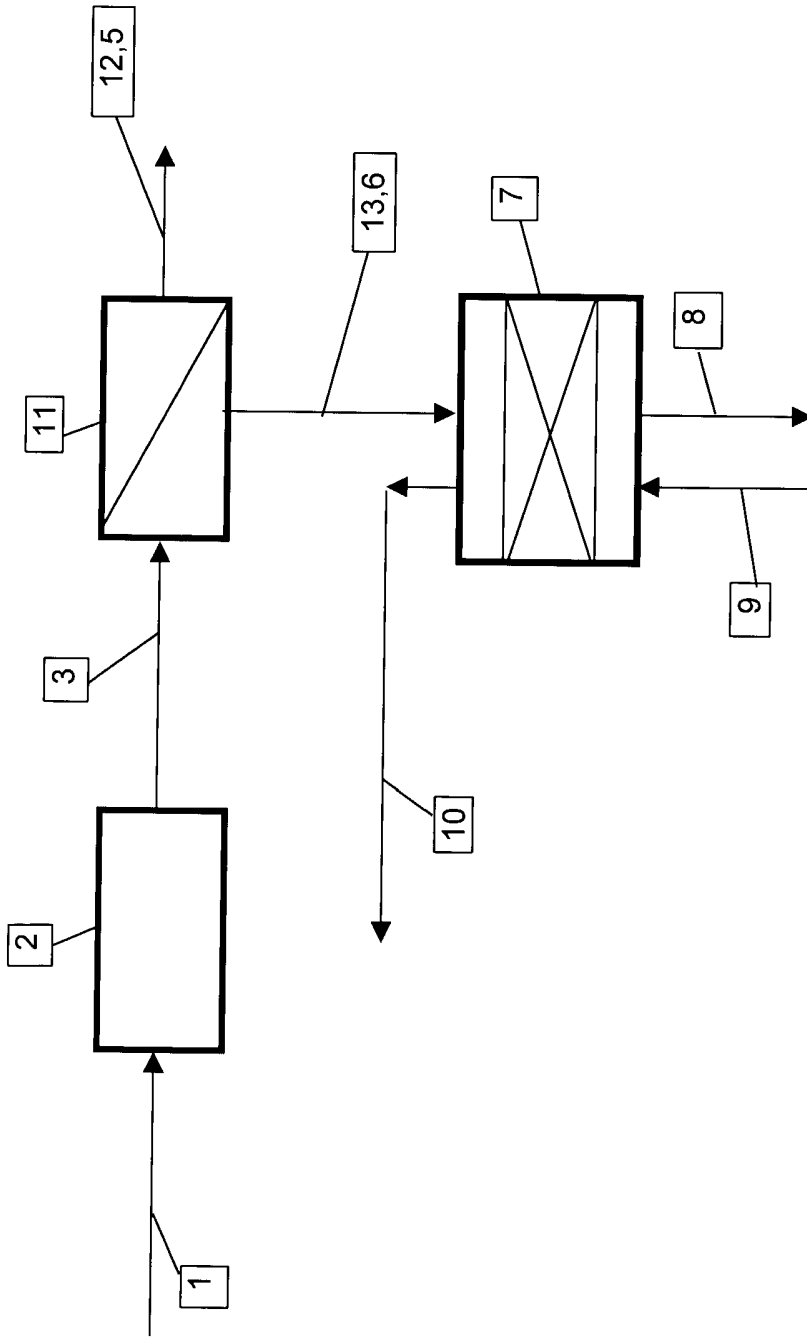**Figure 1**

Figure 2

Figure 3

Figure 4

Figure 5

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Figure 6

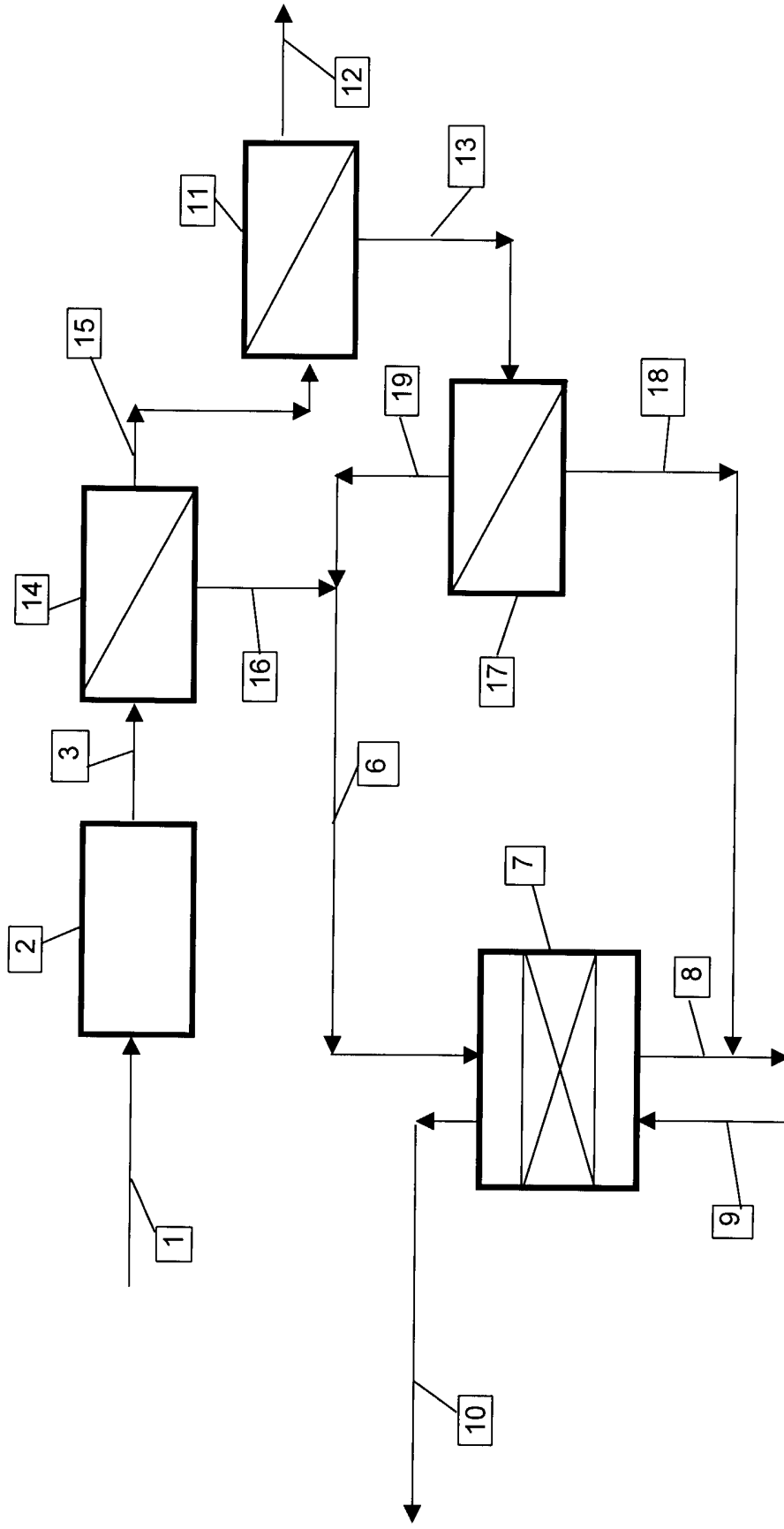1

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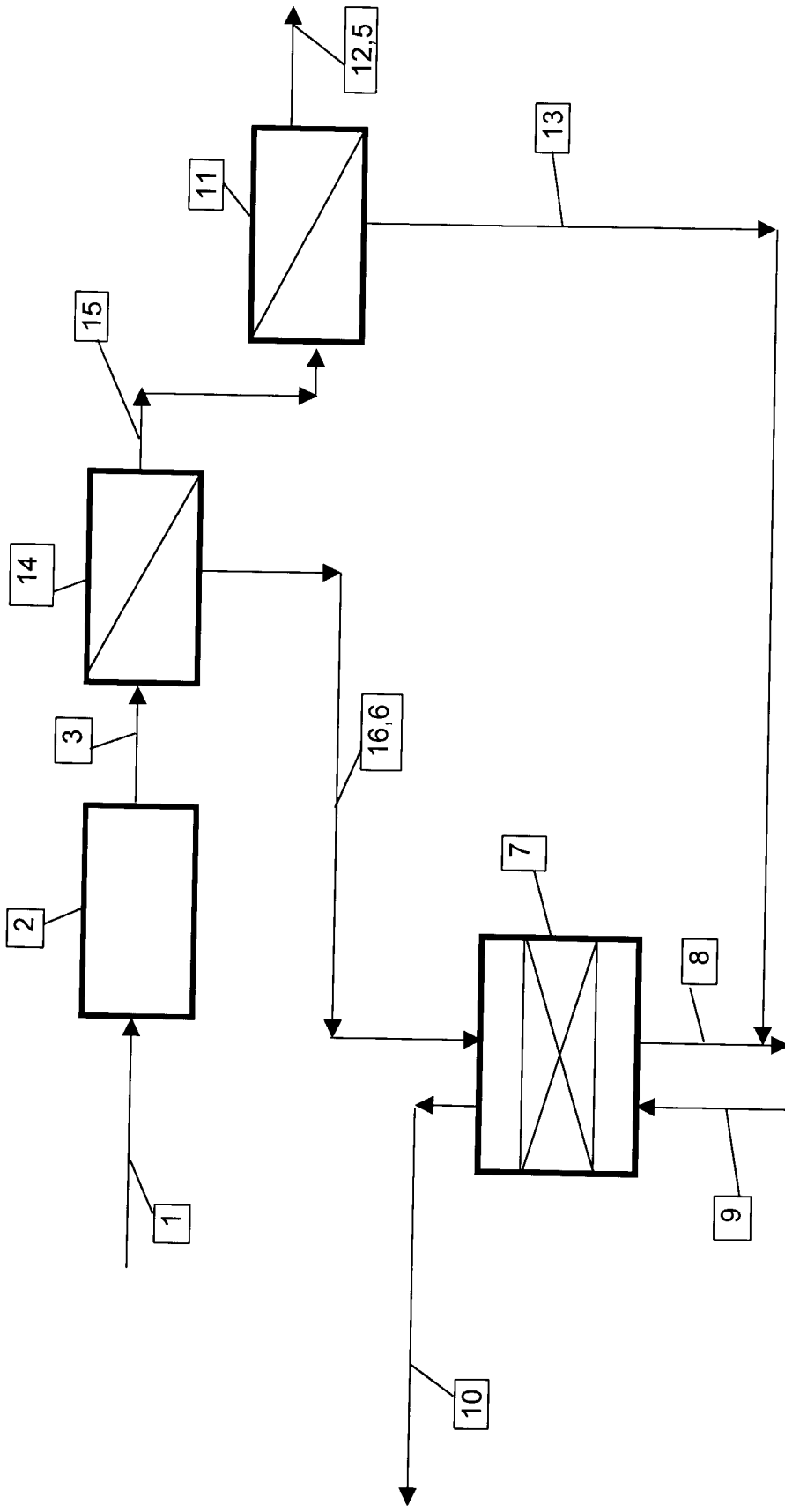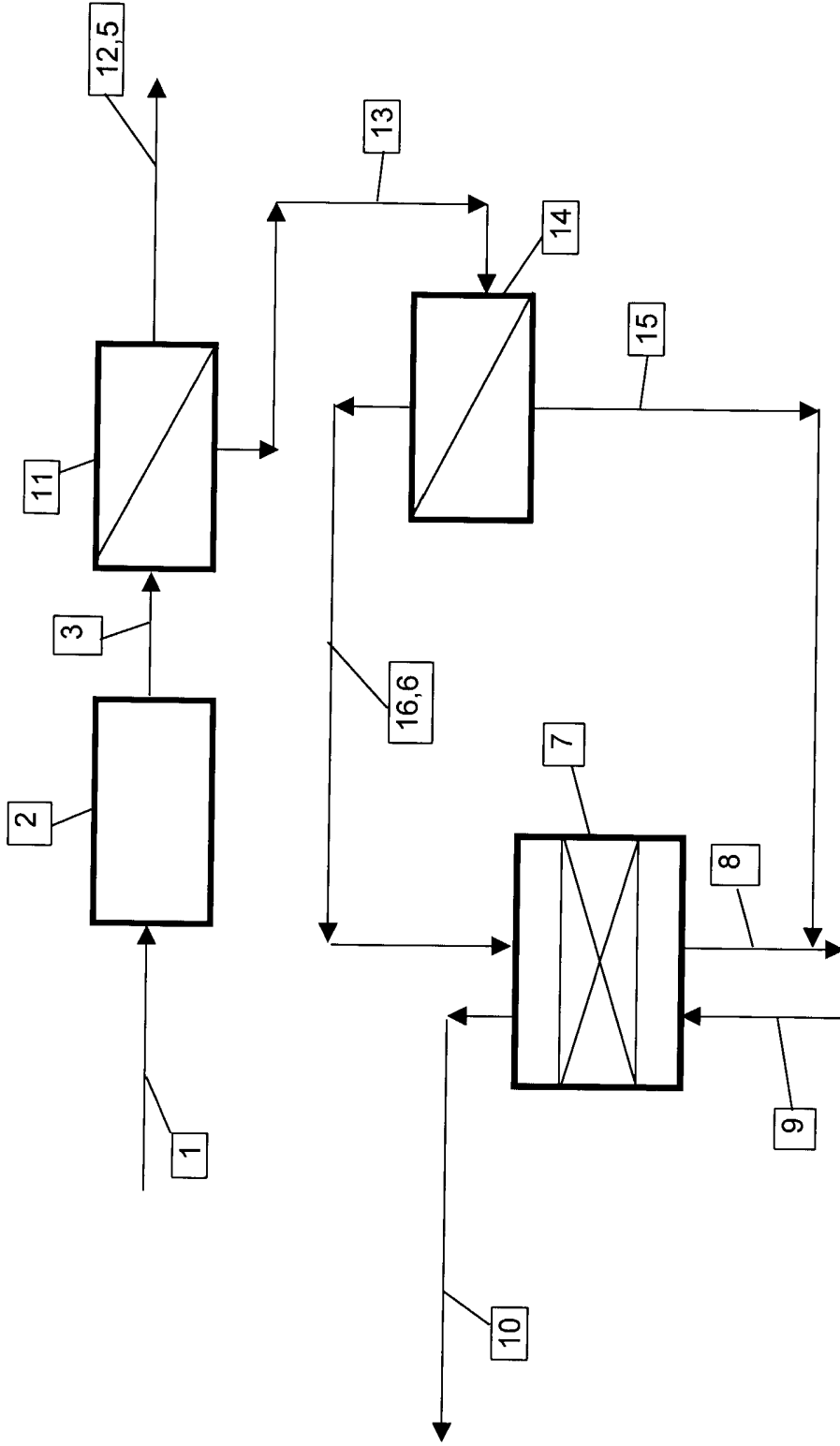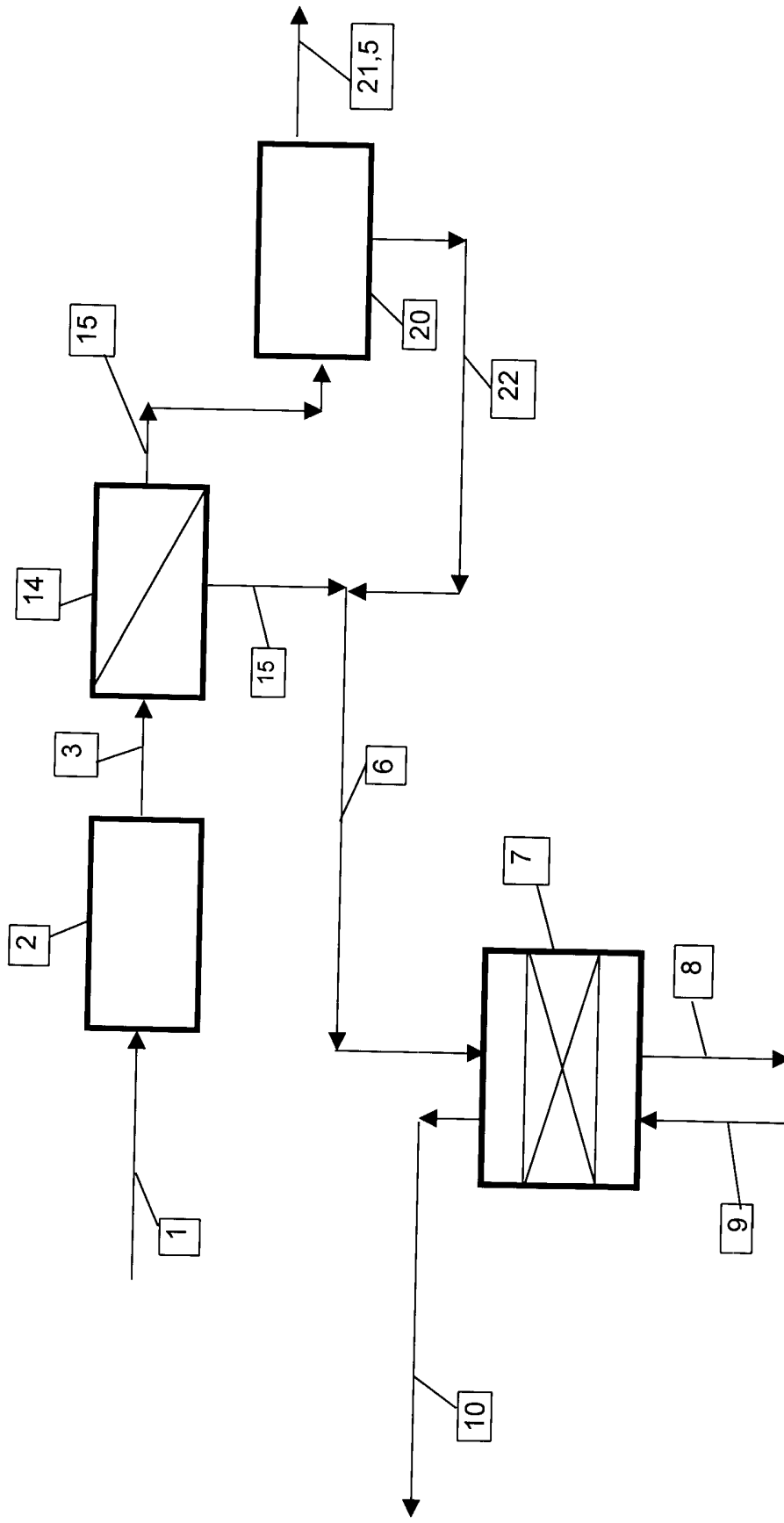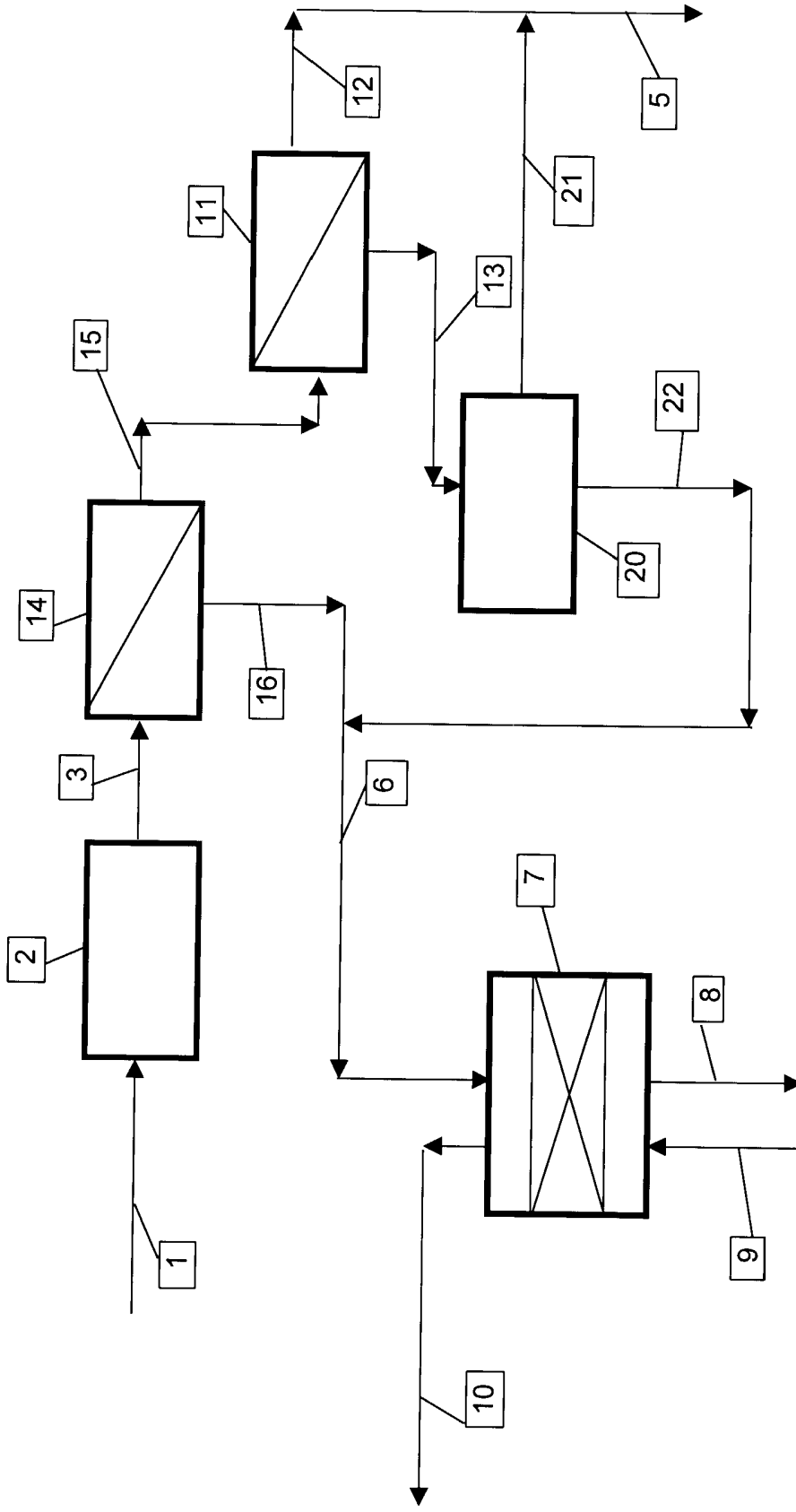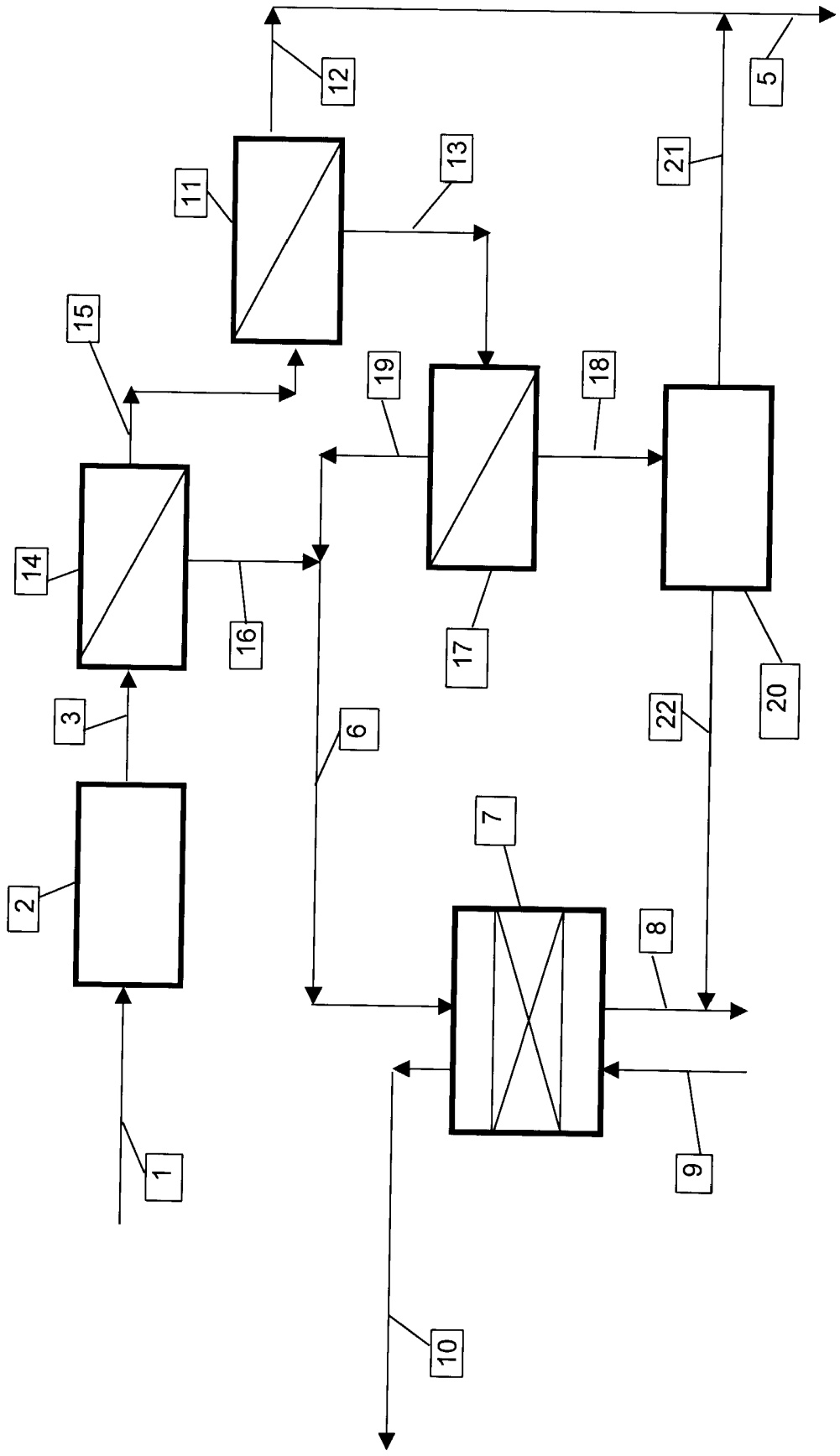
Figure 6

Figure 8

Figure 9

MAGNESIUM CHLORIDE PRODUCTION METHOD FROM SEAWATER.

Background of the Invention

Technical Field:

The invention concerns a method of producing concentrated magnesium chloride (MgCl$_2$) from seawater by the use of desalination processes combined with selective cation ion exchange process. Magnesium chloride is used as a raw material in the production of magnesium metal, and can be used as a raw material for the production of Magnesia (MgO).

Description of Related Art :

Magnesium chloride is most often recovered by the addition of large amounts of crushed rock ore e.g. dolomite, or magnesite to seawater to produce a magnesium hydroxide. The magnesium hydroxide is then purified and reacted with hydrochloric acid to produce magnesium chloride. These rock ore methods require that large quantities of rock be transported from mines to the coastal site of magnesium chloride production.

Magnesium chloride can also be produced by evaporation of seawater in solar ponds. This requires vast areas of land for evaporation. The method has several other disadvantages including contamination of the magnesium chloride by co-precipitation of other salts e.g. sodium chloride, potassium chloride, carbonates and sulphates.

When magnesium chloride solutions containing sulphates and carbonates are thermally concentrated then these sulphates and carbonates can precipitate out causing blockages to process flows and loss in heat transfer efficiency and product contamination. Often the sulphates have to be partly removed before thermal concentration by the addition of calcium chloride to the solution, which causes the precipitation of calcium carbonate and calcium sulphate. This adds to the cost of magnesium chloride production.

Seawater contains substantial amounts of boron. Boron can cause substantial losses in the efficiency of electrolysis of magnesium chloride into metal . Boron contamination must be reduced to very low levels in the magnesium chloride before electrolysis. Typically this requires the of solvent extraction methods on seawater derived magnesium chloride.

Desalination plants use seawater to provide a product of desalinated water and stream of concentrated brine. Seawater contains approx 1.3-1.7 g/l magnesium. The concentrated brine from desalination processes can contain from 2.2 - 11 g/l of magnesium. The concentrated brine from desalination is typically treated as a waste product and dumped back into the sea, which is a waste of a magnesium resource.

GB736276 discloses a method of using an ion exchange process for concentrating magnesium ions from seawater, however it makes no suggestion of using desalination magnesium enriched brine as a feed for the cation ion exchange process. The direct use of ion exchange as disclosed by GB73276 would require the following items not disclosed

- Seawater intake
- Inlet screening
- Inlet seawater pumping
- Fine filtration
- An outfall for the magnesium depleted brine.

These items substantially increase the cost of magnesium chloride production from seawater. One of the sizing parameters for a cation ion exchange process is the volumetric loading rate through the cation ion exchange process unit. Seawater has a low concentration of magnesium, which results in a very large the cation ion exchange process units.

WO0029327 discloses a method of production of magnesium from seawater using nanofiltration. In this method seawater is fed to a nanofiltration membrane, the retentate from the nanofiltration proceeds to a second stage of membrane nanofiltration. Crystallization of calcium sulphates is allowed to occur in the flow passing through the second stage nanofilter. This process is alleged to produce a concentrated magnesium chloride solution from seawater. The following points can be observed:

- The disclosure makes no mention of using desalination to reduce pre-treatment costs, or as way of providing the first stage nanofiltration membranes.

- Most commercial membrane manufacturers stipulate that the fed flow to their membranes must have a Silt Density Index (SDI) of less than 5. Crystallisation of calcium sulphate in the feed flow to the second stage of nanofiltration is likely to lead to the SDI exceeding 5.

- The disclosure does not use a cation ion exchange process for concentrating magnesium chloride.

Object of the invention

The object of the invention is to produce magnesium chloride from seawater by the using desalination processes to produce magnesium enriched brine, which is then concentrated by a cation ion exchange process. As a direct result of this magnesium chloride production method a number of advantages are realised including:

1. The costs for intake, outfall, and pre-treatment facilities required for a cation ion exchange process of magnesium chloride concentration can be greatly reduced, if not eliminated, because these facilities are already provided by the desalination processes.

2. The size of the cation ion exchange process units can be reduced because of the increased magnesium chloride concentration in the desalination enriched magnesium brine compared to seawater.

3. When using hydrochloric acid as the regenerant for the cation ion exchange process, a concentrated magnesium chloride solution very low in sodium chloride can be achieved.

4. Removal of sulphates and carbonates that can causing scaling when thermal evaporation processes are used to concentrate magnesium chloride solutions. Scaling can cause blockage of heat exchanger tubes and severe losses in thermal efficiency.

5. The source of magnesium is waste brine from desalination processes. No magnesium rock ore is required to be transported to the location of magnesium chloride production.

6. The cation ion exchange system enables very low boron levels to be achieved in the concentrated magnesium chloride. This removal is achieved without the use of solvent extraction methods.

These advantages and other objects of the invention are achieved by the method for producing magnesium chloride as described below. This invention is further described and characterised by the enclosed patent claims.

Essential features

The invention concerns a method for producing concentrated magnesium chloride from sea water that is characterised by the following steps.
(a) seawater is sent to a desalination process that produces a water stream and an enriched magnesium brine stream,
(b) enriched magnesium brine from the desalination process is used as a feed to a cation ion exchange resin process where magnesium ions are adsorbed, in preference to sodium ions, onto the cation ion exchange process resin,
(c) a regenerant is used to remove the magnesium ions from the resin into the regenerant solution, the spent regenerant leaving the cation ion exchange process contains a solution of concentrated magnesium chloride.

Important but non essential features

Preferably the cation ion exchange resin selected will not significantly adsorb sulphate ions as these ions can cause scaling of heat transfer surfaces during thermal concentration of magnesium chloride solutions.

Preferably the cation ion exchange resin selected will not significantly adsorb boron ions. Boron can adversely effect the efficiency of electrolysis of magnesium chloride into magnesium metal.

Preferably the regenerant will be an aqueous solution of hydrochloric acid but aqueous sodium chloride may also be used.

Preferably the cation ion exchange resin will have a higher affinity for magnesium over calcium. However a strong acid cation resin with a higher affinity for calcium over magnesium could also be used as it is more widely manufactured and cheaper to replace.

Preferably the nanofiltration membrane when used will have a high rejection of bicarbonate ions. However the feed water to the nanofiltration process can be pre-treated by acid addition and stripping of carbon dioxide to prevent precipitation of carbonates either on the membranes or on heat exchanger surfaces.

Preferably the concentrated magnesium brine from the cation ion exchange process may be sold direct as a product but it may be further concentrated using thermal evaporation processes, or it may be concentrated using high magnesium rejection nanofiltration, or it may be concentrated using solar evaporation.

Where further thermal concentration of the concentrated magnesium brine from the cation ion exchange process is used, then preferably the evaporated water and hydrochloric acid will be recovered for use as regenerant in the cation ion exchange process.

Preferably the pre-treatment required to protect the cation ion exchange process from fouling or excessive resin changes will already be provided by the requirements to protect the desalination plant system, but additional pre-treatment may be required for suspended solids removal or oxidant removal (e.g. chlorine).

Where the desalination processes uses nanofiltration to provide a feed to reverse osmosis, the nanofiltration membrane will have a high rejection of sulphates, this can prevent sulphate scaling on the reverse osmosis membrane.

Where the desalination processes uses nanofiltration to provide a feed to thermal desalination process, the nanofiltration membrane will have a high rejection of sulphates, this can enable the thermal desalination processes to operate at higher magnesium chloride concentrations without the formation of sulphate scales.

The magnesium depleted brine could be sent to a nanofiltration membrane with a high rejection for sulphates and lower rejection for hydrochloric acid. The nanofiltration permeate, which is low sulphate scaling ions, could be sent to a thermal concentration process such as Multiple Stage Flash, or Multiple Effect. The water vapours from the concentration process could be condensed and the hydrochloric acid liberated could be re-dissolved in water. This hydrochloric acid could be reused, as part of the regenerant for the cation ion exchange process.

Preferably the cation ion exchange process vessel would be counter current. The flow direction of the service flow (i.e. the magnesium enriched brine from the desalination processes) would be in the opposite direction of the regenerating flow. This will help maximise the magnesium concentration in the brine stream.

Detailed Description

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	-	Seawater following pre-treatment
Item 4	-	General desalination processes
Item 5	-	Water product for the desalination processes
Item 6	-	Magnesium enriched brine from the desalination processes
Item 7	-	Cation ion exchange process
Item 8	-	Magnesium depleted brine with sulphates and bicarbonates to outfall
Item 9	-	Regenerant feed to the cation ion exchange process
Item 10	-	Concentrated magnesium chloride solution
Item 11	-	Reverse osmosis membrane desalination system
Item 12	-	Reverse osmosis membrane permeate
Item 13	-	Reverse osmosis retentate

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 desalination process (4) and cation ion exchange process (7). The pre-treated seawater (3) is sent to a desalination process. The desalination process produces an enriched magnesium brine (6) and product water (5). The enriched magnesium brines (6) from the desalination process are used as to feed to a cation ion exchange process. A cation ion exchange process can be used to adsorb divalent cations including magnesium ions by replacing hydrogen or sodium ions (H^+/Na^+) . The magnesium depleted flow, which contains sulphates and bicarbonates, leaves the cation ion exchange process and is sent to the outfall for disposal (8).
At the end of a cation ion exchange process adsorption run, the resin is saturated with divalent ions it can be regenerated with a solution of aqueous hydrochloric acid $(HCl_{(aq)})$ or aqueous sodium chloride $(NaCl_{(aq)})$ (9). The magnesium ions are desorbed from the cation ion exchange resin by the regenerant and are replaced by hydrogen or sodium ions (H^+/Na^+). This desorbed magnesium ions end up in the spent regenerant (10). This spent regenerant will contain a concentrated solution of magnesium chloride.

The detailed description will examine:
- Methods for pre-treatment
- Configurations of the desalination process that can be used to produce the enriched magnesium brine
- The details of the cation ion exchange process including resin and regenerant type
- Methods for further concentration
- Example

Pre-treatment

Thermal, membrane, and hybrid (membrane & thermal) desalination processes all require seawater intake, inlet pump station, and fine screening (1mm –6 mm aperture). Thermal processes do not normally require a suspended solids filtration stage. If the magnesium enriched brine from the thermal desalination process contains large quantities of suspended solids, then it will require filtration before being sent to the cation ion exchange process to prevent blockage of the cation ion exchange process, or excessive resin replacement

If membrane processes such as nanofiltration or reverse osmosis are to be used then the pre-treatment system is required to achieve a Silt Density Index (SDI) limit imposed by the membrane manufacturer to prevent 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 membrane processes 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 a membrane. Microfiltration or ultrafiltration will greatly reduce the numbers of organisms available to colonise the membrane.

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 the cation ion exchange process.

Membrane desalination processes can become fouled with calcium carbonate scale. This can be prevent by one of the following methods:

a) Ensure that 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 bicarbonate into carbon dioxide in water and strip out the carbon dioxide.

Desalination Configurations

Desalination processes produce an enriched magnesium brine which can be fed to the cation ion exchange process. There are typically three main classes of desalination process for seawater that can be used to produce the feed to the cation ion exchange process, thermal, reverse osmosis, and hybrid. Each of these classes has numerous configurations.

<u>Thermal desalination Processes:</u>

A flow sheet for using thermal desalination as the desalination step is illustrated in figure 2

The pre-treated flow (3) can be sent to a thermal desalination process (20).

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 water product (21) with low salt content. The salt solution, that remains after evaporation, becomes more concentrated. For a seawater desalination plant using thermal processes the feed water to the thermal desalination process will contain magnesium chloride. The brine produced from the thermal process will have a magnesium chloride concentration higher that the feed concentration (22). This magnesium enriched brine can be used as a feed (6) to the cation ion exchange process (7) process.

These thermal technologies are well understood and widely applied in the desalination industry.
Full descriptions of these thermal processes and their sizing parameters for these processes 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 theses thermal methods who could also be contacted for further detailed technical information
MSF   - Doosan Engineering Korea, Weir Westgath Glasgow,
MED   - Sidem Paris, Weir Westgarth Glasgow
MVC MED   - Sidem Paris, Weir Westgarth Glasgow
TVC MED   - Sidem Paris, Weir Westgarth Glasgow

<u>Membrane Desalination Processes:</u>

The pre-treated flow (3) can be sent to a membrane desalination processes.

Examples of membrane desaliantion processes include :

a)   Reverse osmosis.

A flow sheet for using reverse osmosis as the desalination step is illustrated in figure 3.

Seawater, following pre-treatment (3), is pumped to a reverse osmosis membrane. The product water is passed through the membrane, which has a high rejection for salts, and is called reverse osmosis permeate (12). The salt solution that does not pass through the membrane becomes more concentrated and is called the reverse osmosis retentate (13). Where the salt water feed is seawater, magnesium concentration in the brine will be higher than in the feed. This enriched magnesium feed can be sent to the cation ion exchange process. Each of the major reverse osmosis membrane manufactures provides computer simulation software that enables the selection and sizing of the numbers of membranes required for a given seawater feed quality and permeate quality required. The membrane manufacturers also provide detailed design guidelines for their membranes. At the time of writing examples of leading membrane manufactures who could be contacted for further detailed information on reverse osmosis membranes are
▪   Dow FilmTec
▪   Hydranautics
▪   Koch Membranes
▪   Osmonics

b) Nanofiltration permeate - reverse osmosis

A flow sheet for using nanofiltration- reverse osmosis as the desalination step is illustrated in figure 4

The seawater following pre-treatment (3) is pumped to a nanofiltration membrane (NF) (14). 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. Nanofiltration for this application has a high rejection of magnesium and a much lower rejection for sodium chloride. The solution that passes through the NF membrane is called NF permeate (15). The brine solution that does not pass through the membrane becomes more concentrated. This brine solution is called the nanofiltration retentate (NF retentate) (16). The magnesium concentration in the NF retentate will be higher than in the feed. The NF retentate could be used as the enriched magnesium feed (6) to the cation ion exchange process.

The NF permeate is pumped to the reverse osmosis membrane (RO). The reverse osmosis permeate is the product water (5). The reverse osmosis concentrate (13) is discharged to the outfall for disposal
The use of nanofiltration as a pre-treatment to reverse osmosis is practised because it 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.
Most of the leading manufacturers of reverse osmosis membranes also manufacture nanofiltration membranes. These manufacturers can be contacted for further details on the membranes.

c) Reverse osmosis – nanofiltration

A flow sheet for using reverse osmosis - nanofiltration as the desalination step is illustrated in figure 5

The seawater following pre-treatment (3) is pumped to a reverse osmosis membrane (11). The product water with reduced salt content is passed through the membrane and called RO permeate (12). The brine solution that does not pass through the membrane becomes concentrated. This brine solution is called the R.O retentate (13). The RO retentate is fed to a nanofiltration membrane (14), which has a high rejection for magnesium ions and a lower rejection for sodium ions. The NF permeate (15) can be discharged to the outfall for disposal.

The magnesium concentration in the NF retentate (16) will be higher than in the RO retentate. The RO retentate magnesium concentration will be higher than in the feed to the RO membrane. The NF retentate would be used as the concentrated magnesium feed (6) to the cation ion exchange process.

d) Nanofiltration - reverse osmosis – nanofiltration

A flow sheet for using nanofiltration - reverse osmosis - nanofiltration as the desalination step is illustrated in figure 6.
This process is similar to b) except that the reverse osmosis retentate is sent to a second stage of nanofiltration (17). The retentate (19) from the second stage of nanofiltration contains an enriched magnesium brine which is sent to the cation ion exchange process. The permeate (18) from the second stage of nanofiltration can be sent to the outfall for disposal.

Hybrid desalination Processes

The pre-treated flow (3) can be sent to a membrane desalination process.

These processes would use a combination of membrane and thermal methods to produce desalinated water. Scaling of heat transfer surfaces can occur with thermal desalination processes. Nanofiltration with a high rejection of scaling ions, particularly bicarbonates and sulphates, can remove these scaling ions from the seawater feed to a thermal concentration process.

If the nanofiltration membrane allows substantial magnesium ions to pass as permeate then the thermal desalination process can be operated as a concentrator for magnesium chloride without the fear of sulphate or carbonate scaling occurring. Any of the thermal desalination processes previously mentioned could be utilised.

A blend of nanofiltered and non -nanofiltered seawater could be used as a feed to the thermal desalination unit, the blend being such that there is insufficient scaling ions present to result in scaling occurring at the operating final brine concentrations.

It should be noted that the operation of the thermal desalination plant as a brine concentrator results in a significant boiling point elevation of the brine, which may lower potential water production and make the production of water more inefficient with regard to steam usage. However it is assumed that the value of the enriched magnesium brine is adequate to compensate for any loss in thermal efficiency of the water production.

Example methods of hybrid desalination envisaged are:

.a) Nanofiltration – thermal desalination

A flow sheet for using nanofiltration – thermal desalination as the desalination step is illustrated in figure 7

The pre-treated seawater (3) is pumped to a nanofiltration membrane where sulphates and bicarbonates are removed. The magnesium enriched retentate (16) from the nanofiltration can be sent to the cation ion exchange process as its feed. The permeate (15) can be sent to a thermal desalination plant as a feed. The thermal desalination system (20) will enrich the magnesium brine by evaporating the enriched magnesium brine (22), which can also be sent to the cation ion exchange process for magnesium removal. The evaporated vapour would be condensed to form product water (21).

b) Nanofiltration – reverse osmosis – thermal desalination

A flow sheet for using reverse osmosis - nanofiltration – thermal desalination as the desalination step is illustrated in figure 8

The pre-treated seawater (3) is pumped to a nanofiltration membrane where sulphates and bicarbonates are removed. The magnesium enriched retentate (15) from the nanofiltration process can be sent to the cation ion exchanger as feed, and the permeate (15) can be pumped to a reverse osmosis membrane as feed. The reverse osmosis membrane (11) produces permeate (12) that is product water and a retentate (13), which contains some magnesium ions. This is sent to a thermal desalination plant as a feed. The thermal desalination plant produces an enriched magnesium brine by evaporation (22). The enriched magnesium brine can also be sent to the cation ion exchanger for magnesium removal. The evaporated vapour could be condensed to form product water (21).

c) Nanofiltration – reverse osmosis – nanofiltration -thermal desalination

A flow sheet for using nanofiltration reverse osmosis - nanofiltration – thermal desalination as the desalination step is illustrated in figure 9

The pre-treated seawater is pumped to a nanofiltration membrane where sulphates and bicarbonates removed. The magnesium enriched retentate (16) from the nanofiltration process can be sent to a cation ion exchange process (7) as feed, and the permeate (15) can be sent to a reverse osmosis plant as feed. The reverse osmosis plant produces a permeate (12) that is product water and a retentate (13) which is sent to a second stage of nanofiltration (17). The retentate (19) from the second stage of nanofiltration is sent to the cation ion exchange unit (7) as a feed. The permeate (18) is sent to a thermal desalination plant (20) as a makeup flow. The thermal desalination plant will concentrate the brine by evaporation. The magnesium enriched brine (22) can be sent to the cation ion exchange process for magnesium removal. The evaporated vapour can be condensed to form product water (21).

Ion Exchange Unit.

The magnesium enriched brine from the desalination process(es) is used as a feed to an ion exchange process (6). Magnesium is adsorbed on to the cation ion exchange resin and the magnesium depleted brine leaves the cation ion exchange process. The magnesium depleted brine can be discharged to the desalination plant outfall. Sulphate ions and bicarbonate ions also leave the cation ion exchange process in the magnesium depleted stream.

At the end of an adsorption run the cation ion exchange unit is regenerated. Resin regeneration requires isolating the service flow from the unit and passing regenerant solution through the resin bed in a direction counter current or co-current to the service flow. The regenerant solution replaces the magnesium on the resin with another cation. The spent regenerant now contains the magnesium that was removed by the cation ion exchange resin. An aqueous solution of hydrochloric acid (5-30 % w/w) can be used as the regenerant. A sodium chloride solution (10-25 % w/w) could also be used but hydrochloric acid(aq) is preferred as it will not result in large amounts of sodium ions in the spent regenerant.

The design of cation ion exchange processes to remove magnesium and calcium from water is well understood in the water industry. A significant differences when using the cation ion exchange process for magnesium concentration, is the desire to achieve a high magnesium concentration in the spent regenerant rather than trying to minimise the magnesium content of the magnesium depleted service stream.

The resin bed depths would be between 1.2 m and 5m , and a typical vessel diameter would be 3.5 m. (larger vessel diameters and deeper beds could also be used with the agreement of the resin manufacturer). Typical regeneration velocities (cross section area resin bed / regenerant flow rate) that can be used to regenerated the bed are between 1-20 m/hr. Typical service velocities (cross section area resin bed / enriched magnesium flow rate) allowed for ion exchange magnesium concentration are between 5-60 m/hr

The number of cation ion exchange vessels could be arranged such that when a vessel is being regenerated the magnesium enriched feed flow is diverted to another ion exchange vessel. Alternatively, to reduce capital costs, when a vessel is being regenerated the magnesium enriched brine flow from the desalination process could be diverted to the outfall.

Two types of ion exchange resins can be used a) Strong Acid Cation Ion exchange or b) Chelating Cation Ion exchange.

Strong Acid Cation Ion Exchange Resin :
The strong acid cation resin will remove both calcium and magnesium. These types of resin tend to have a higher selectivity for calcium than for magnesium. The run times between regeneration of the resin would be optimised, for the particular feed to the cation ion exchange resin, in order to maximise the content of magnesium ions in the spent regenerant relative to the other cation ions including calcium. An example of such a strong acid cation resin is Dowex Marathon C (Dow Chemical company).

Chelating Resins :
Special resins are commercially available called chelating resins. A chelating resin with a higher affinity for magnesium over calcium can be selected. Using such a resin the operation should result in concentrated magnesium chloride brine with lower calcium content than obtained when using a strong acid cation ion exchange resin. An example of such magnesium selecting chelating resin is Dowex APA-1 (Dow Chemical Company)

Ion Exchange Unit Volumetric Sizing
The volumetric loading of the cation ion exchange process is greatly reduced by using desalination processes to produce magnesium enriched brine feed to the cation ion exchange process from the seawater. The lower volumetric loading reduces the number of ion exchange vessels required for desalinating magnesium enriched brine compared to the number that would be required for raw seawater. If the market price of magnesium chloride is sufficiently high then it may be economically feasible to utilise nanofiltration retentate of seawater without subsequent desalination as means of enriching the magnesium feed to the cation ion exchange process.

The magnesium chloride concentration in the spent regenerant will typically exceed 8 % by weight. This compares to 0.7 % in seawater.

Further magnesium concentrating

The spent regenerant from the cation ion exchange process can be further concentrated by a number of methods including thermal concentration, solar evaporation, and nanofiltration. Thermal concentration can be achieved without sulphate or carbonate scaling occurring, because the sulphate and carbonate ions were removed by the cation ion exchange process in the magnesium depleted brine.

If hydrochloric acid is used as the regenerant, the first salt to crystallise by further concentration will be hydrated magnesium chloride. Since there is no simultaneous precipitation of other salts occurring this can lead to a magnesium chloride (hydrated) of high purity.

Some of the water and hydrochloric acid can be boiled off as a vapour mix by thermal concentration processes such as: Multiple Effect Distillation , Multiple Stage Flash Distillation, Mechanical Vapour Compressor, or Thermal Crystallisation. The vapour can be condensed and hydrochloric acid re-dissolved to form additional regenerant for the cation ion exchange process.

Solar ponds can also be used to bring the brine up to saturation and crystallise magnesium chloride.

A nanofiltration membrane could be used to further concentrate the magnesium chloride in the spent regenerant. The membrane would have a higher rejection for magnesium than for calcium or sodium. The feed to the membrane may need to be partly neutralised using either calcium hydroxide, magnesium hydroxide or sodium hydroxide. The degree of neutralisation would depend on the pH limit set by the membrane manufacturer. Nanofiltration would be the preferred method for further concentration, if the regenerant used for the cation ion exchange process is a sodium chloride solution.

The magnesium chloride produced by desalination combined with cation ion exchange can be used as feed stock for the production of magnesium metal or magnesia (MgO).

Example

The invention will be further illustrated by a non-limiting example with reference to figure 4

Persian gulf seawater with the following composition (ppm) is assumed for the seawater feed (1):
Sodium 13440 ppm, potassium 483 ppm, calcium 508 ppm, magnesium 508 ppm, chloride 24090 ppm, sulphate 3384, bicarbonate 176, boron 3 ppm. The flow of sea water (1) to pre-treatment is 9.3 m³/s.

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

- Seawater is extracted from the sea and screened to a size of 3mm.

- A coagulant such as ferric chloride may be added to improve solids capture. The sea water is then pumped to a multimedia pressure filtration process.

- 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.

- The seawater is then passed to a cartridge filter system, which will remove solids to a 5 micron size limit.

The pre-treated seawater water (3) is then pumped to a nanofiltration membrane process (14) with a flow of 9.3 m3/s. 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 4 %, sulphate 98 %, bicarbonate 86 % boron 60 % The ratio of permeate flow to feed flow is set at approximately 60 %, and a permeate flux of approx 12 (1/m²h).

The composition of the nanofiltration permeate (15) is approximately as follows: Sodium 12768 ppm, potassium 415 ppm, calcium 391 ppm, magnesium 388 ppm, chloride 23126 ppm, sulphate 68 ppm, bicarbonate 25 ppm, boron 1.2 ppm. The flow is 5.6 m³/s

The composition of the nanofiltration membrane process retentate (16) is approximately as follows: Sodium 14448 ppm, potassium 584 ppm, calcium 683 ppm, magnesium 3463 ppm, chloride 25535 ppm, sulphate 8358 ppm, bicarbonate 403 ppm, boron 5.7 ppm. The flow is 3.7 m³/s.

The Nanofiltration permeate is the pumped to a reverse osmosis membrane (example Hydranautics SWC4) at a pressure of 69 bar. This membrane has an approximate salt rejection of 99 %. The ratio of permeate flow to feed flow is set at approximately 50 %, and a permeate flux of approx 15 (1/m²h).

The composition of the reverse osmosis membrane permeate (12) is approximately as follows: Sodium 128 ppm, potassium 4 ppm, calcium 4 ppm, magnesium 4 ppm, chloride 231 ppm, sulphate 1 ppm, boron 0.3 ppm. The flow is 2.8 m³/s. This permeate (12) is the product water from the desalination process (5).

The composition of the reverse osmosis membrane process retentate (13) is approximately as follows: sodium 25408 ppm, potassium 827 ppm, calcium 778 ppm, magnesium 773 ppm, chloride 46022 ppm, sulphate 135 ppm, bicarbonate 49 ppm, boron 6.4 ppm. The flow is 2.8 m³/s. This flow is discharged as to the outfall.

The nanofiltration retentate (15) is the magnesium enriched brine (6) that is sent to a cation ion exchange process (7). The ion exchange system will operate in counter current mode. With the enriched magnesium brine (6) running from top to bottom and the regenerant running from bottom to top.

The resin used is this example is Dowex APA-1 (from Dow chemical company). The resin has a higher selectivity for magnesium over calcium, and a much higher selectivity for magnesium over calcium. The resin will not select sulphates, bicarbonates or boron.

The magnesium depleted stream (8) is discharged to the outfall.

The enriched magnesium brine (6) is passed through the resin bed until the magnesium depleted stream (8) shows an increase in pH. This indicates that the ion exchange sites are full and that the bed needs to be regenerated.

The regenerant (9) to be used is 15 % hydrochloric acid by weight, with a stoichiometric excess of 130 %. During regeneration the magnesium enriched brine is diverted to the outfall. The regenerant will replace the magnesium ions on the resin with hydrogen ions. The spent regenerant will contain concentrated magnesium chloride (10). This concentrated magnesium chloride will contain in excess of 9 % magnesium chloride. With 20 % capture of magnesium in the concentrated magnesium brine, there would be sufficient magnesium chloride to feed a 80,000 tonnes per year magnesium metal production plant.

Claims :

1. Method for production of a solution, which includes concentrated magnesium chloride, from seawater that is characterised by the following steps:

(d) seawater is sent to a desalination process that produces a water stream and an enriched magnesium brine stream,

(e) enriched magnesium brine from the desalination process is used as a feed to a cation ion exchange resin process where magnesium ions are adsorbed, in preference to sodium ions, onto the cation ion exchange process resin,

(f) a regenerant is used to remove the magnesium ions from the resin into the regenerant solution, the spent regenerant leaving the cation ion exchange process contains a solution of concentrated magnesium chloride.

2. Method according to claim 1, where the desalination process that produces the concentrated brine is a thermal desalination process including Multiple Stage Flash Distillation (MSF), Multiple Effect Distillation (MED), Thermo-Vapour Compression Multiple Effect Distillation (TVC-MED), Mechanical Vapour Compression Multiple effect Distillation, where the thermal desalination process is characterised by the production of desalinated water by the condensation of evaporated saltwater, and magnesium enriched brine is produced in the remaining liquid saltwater that has not been evaporated.

3. Method according to claim 1, where the desalination process is characterised in that: a) the seawater is pumped to a reverse osmosis membrane process, b) the reverse osmosis membrane process produces desalinated water as permeate, c) magnesium enriched brine is produced as retentate from the reverse osmosis membrane process

4. Method according to claim 1, where the desalination process is characterised by the following steps:
   a) the seawater is pumped to a nanofiltration membrane process with higher rejection of magnesium relative to sodium,
   b) the permeate from the nanofiltration membrane process is pumped to a reverse osmosis membrane,
   c) the reverse osmosis membrane process produces desalinated water as permeate,
   d) the enriched magnesium brine is produced as retentate from the nanofiltration membrane process.

5. Method according to claim 4, where the retentate from the reverse osmosis membrane process is sent to a second nanofiltration membrane process with a higher rejection for magnesium relative to sodium, the second nanofiltration membrane process produces magnesium enriched retentate.

6. Method according to claim 4, which is characterised in that some or all of the retentate from the reverse osmosis membrane process becomes the feed for a thermal desalination process.

7. Method according to claim 5, which is characterised in that some or all of the retentate from the second stage nanofiltration membrane process becomes the feed for a thermal desalination process.

8. Method according to claim 6 or 7, in that some or all of magnesium enriched brine produced by the thermal desalination process is sent as an additional feed to the cation ion exchange for magnesium concentration.

9. Method according to claim 2, characterized in that the feed to the thermal desalination process is achieved by the following steps:
   a) salt water is pumped to a nanofiltration membrane process,
   b) the magnesium enriched nanofiltration retentate is sent to a cation ion exchange process for magnesium concentration,
   c) some or all of the nanofiltration permeate from the nanofiltration membrane process becomes the feed for the thermal desalination plant.

10. Method according to claim 1, characterised in that the regenerant used is and aqueous solution of hydrochloric acid.

11. Method according to claim 1, characterised in that the regenerant used is a sodium chloride aqueous solution.

12. Method according to claim 1, characterised in that the feed to the desalination process is pre-treated using any one or a combination of the following process in order to prevent fouling of the desalination process or the cation ion exchange process:
    a) fine screening,
    b) sand filtration,
    c) multimedia filtration,
    d) activated carbon filtration,
    e) membrane microfiltration,
    f) membrane ultrafiltration.

13. Method according to claim 1, characterised in that the feed to the desalination process is pre-treated by acid addition and stripping of CO_2 to prevent precipitation of carbonates.

14. Method according to claim 1, characterised in that the concentrated magnesium chloride from the cation ion exchange process is further concentrated by thermal evaporation.

15. Method according to claim 14, characterised in that the evaporated water vapour, from thermal evaporation, is condensed and the released gaseous hydrochloric acid is re-dissolved in water, the aqueous hydrochloric acid is reused.

16. Method according to claim 1, characterised in that the concentrated magnesium chloride solution from the cation ion exchange process is further concentrated by solar evaporation.

17. Method according to claim 14, characterised in that the magnesium chloride, produced from thermal evaporation, is further concentrated by solar evaporation.

18. Method according to claim 1, characterised in that sulphate ions are not adsorbed by the cation resin and are discharged with the depleted magnesium service brine from the cation ion resin process.

19. Method according to claim 1, characterised in that bicarbonate ions are not adsorbed by the cation resin and are discharged with the depleted magnesium service brine from the cation ion resin process.

20. Method according to claim 1, characterised in that boron ions are not adsorbed by the cation resin and are therefore discharged with the depleted magnesium service brine from the cation ion resin process.

21. Method according to claim 1, characterised in that the concentrated magnesium chloride, from the cation exchange process, is later used in the production of magnesium metal or magnesia (MgO).

22. Method according to claim 1, in that the magnesium depleted brine from the ion exchange process is processed to recover hydrochloric acid by the following steps:

    a) the magnesium depleted brine is pumped to a nanofiltration process with a high rejection of sulphates relative to hydrochloric acid,

    b) the permeate form the nanofiltration membrane process is sent a thermal concentration process,

    c) the hydrochloric acid liberated in the thermal concentration process is re-dissolved in water.