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(54) Title: PROCESSES INVOLVING THE USE OF ANTISOLVENT CRYSTALLIZATION

(57) Abstract: The present invention pertains to a process involving the use of an antisolvent comprising the steps of - feeding water to a salt source to form an aqueous solution comprising said salt if the salt source is not yet in the form of an aqueous salt solution, - feeding said aqueous solution to a crystallizer/settler, - contacting said aqueous solution with one or more antisolvents which force the salt to at least partly crystallize, with one or more crystal growth inhibitors being present in the antisolvents and/or in the aqueous solution, and/or one or more scaling inhibitors being present in the antisolvents and/or in the aqueous solution, - subjecting an overflow of the crystallizer/settler comprising one or more antisolvents and an aqueous salt solution to a separation step wherein one or more antisolvents are separated from the aqueous salt solution by one or more techniques selected from the group consisting of adsorption, ion-exchange, a temperature change induced phase split, a pH change induced phase split, a complexation induced phase split, a pressure induced phase split, evaporation, and extraction, optionally in combination with a nanofiltration step, - removing the crystallized salt from the crystallizer/settler in an aqueous slurry, - optionally, recycling the one or more antisolvents to the crystallizer/settler, and - optionally, recycling mother liquor from the slurry to the first dissolution step and/or to the crystallizer/settler. Preferably, the process is a closed loop process and the salt is sodium chloride. Preferably, the process further comprises a reverse osmosis step before the overflow of the crystallizer/settler is subjected to the separation step.

WO 2006/045795 A2

PROCESSES INVOLVING THE USE OF ANTISOLVENT CRYSTALLIZATION

The present invention relates to a process to make inorganic salt compositions comprising the crystallization of said salt from a crude aqueous salt solution using an antisolvent, and to a process for the preparation of drinking and/or process water from a crude aqueous salt solution.

Many inorganic salts are made industrially from aqueous salt solutions produced by dissolving a natural source of the salt in water. The salt is usually obtained by crystallizing it from the aqueous solution by evaporation of the water, which is generally accomplished using multiple-effect or vapour recompression evaporators. Multiple-effect systems typically contain three or more forced-circulation evaporating vessels connected in series. The steam produced in each evaporator is fed to the next one in the multiple-effect system to increase energy efficiency. Vapour recompression forced-circulation evaporators consist of a crystallizer, a compressor, and a vapour scrubber. The aqueous salt solution enters the crystallizer vessel, where salt is crystallized. Vapour is withdrawn, scrubbed, and compressed for reuse in the heater. Both recompression evaporators and multiple-effect evaporators are energy-intensive because of the water evaporation step involved. Furthermore, aqueous salt solutions produced by dissolving a natural source of said salt in water normally contain a quantity of contaminations. Therefore, additional purification steps of the salt solution prior to crystallization, additional washing of the inorganic salt produced, and/or energy-consuming drying steps have to be employed to reduce the levels of contaminants.

These problems also arise in conventional processes for the preparation of sodium chloride compositions. The conventional process to make sodium chloride and wet sodium chloride involves producing a brine by dissolving a natural source of NaCl in water and subsequent evaporative crystallization of said brine. The brine will contain quantities of dissolved K, Br, SO_4, Mg, Sr, and/or Ca, since these contaminations are typically present in natural NaCl sources. A disadvantage of such a process is that the salt obtained has imperfections in the crystal lattice and contains occlusions, *i.e.* small pockets of mother liquor of the evaporative crystallization process, which are present in cavities in the salt crystals. Due to these imperfections and occlusions, and due to adhering brine, the (wet) salt, as well as the brine produced therefrom, is contaminated with compounds present in the mother liquor. In particular, the quantities of K, Br, SO_4, Mg, Sr, and/or Ca that are carried over are quite high. Therefore, additional washing steps are required to reduce the quantities of contaminants. In addition to occlusions of mother liquor in the imperfect salt crystals, there is a second mechanism resulting in contaminations ending up in the salt. Potassium and bromide ions both have physical properties and dimensions that are close to those of sodium and chloride ions, respectively. This means that these ions are built into the salt crystal lattice. Depending on the nature and the number of imperfections in the crystal lattice, that is, imperfections on an ion scale, the process of building a potassium or bromide ion into the crystal lattice is enhanced or inhibited. Therefore, the partitioning coefficient of bromide, *i.e.* the content of bromide in the salt produced [mg/kg] over the concentration of bromide in the mother liquor [mg/l], depends on the crystallization conditions. The same applies for the partitioning coefficient of potassium. It is also noted that the partitioning coefficients for potassium and bromide increase with temperature, which makes the conventional processes performed at elevated temperature less attractive. Furthermore, during evaporative crystallization in conventional evaporators (multiple-effect or vapour recompression installations), usually operated at elevated temperature, the carbon dioxide, bicarbonate, calcium, sulfate, and carbonate present in the raw sodium chloride aqueous solution will cause scaling of $CaSO_4$, $CaSO_4 \cdot 2H_2O$, and $CaCO_3$, especially at the surface of the heat exchangers. As a result of the scaling, the production capacity of the sodium chloride plant decreases with time, as does the energy efficiency of the process. The most common procedure for dealing with the problems mentioned above is to purify the raw aqueous solution before it is fed to the evaporation plant. However, these extra process steps result in extra purification costs, additional handling, or a poor salt quality.

It is known that antisolvent crystallization can be an energy-saving alternative for the production of inorganic salts normally produced by evaporative crystallization. In antisolvent crystallization the salt is obtained by the addition of an antisolvent to an aqueous salt solution, which induces crystallization of the salt, followed by a filtration step. The antisolvent is usually recovered to allow the creation of a continuous, industrially useful process.

A special antisolvent crystallization process for inorganic salts is described by D.A. Weingaertner *et al.* in *Ind. Eng. Res.*, 1991, Vol. 30, pages 490-501. Said antisolvent crystallization process is an extractive crystallization process wherein particular salts, such as sodium chloride and sodium carbonate, are recovered from their purified concentrated aqueous solutions by the addition of an organic solvent. Solid salt is formed because water is transferred from the aqueous phase to the organic phase, resulting in direct shrinkage of the aqueous phase, and/or because of solvent entering the aqueous phase, resulting in a diminished solubility of salt in that phase. Either way, precipitation and crystal growth of a solid salt phase take place, after which the salt is removed. The solvent is recovered by shifting the temperature to a level at which two liquid phases are formed, one solvent-rich and the other water-rich. Separation thereof subsequently yields a relatively dry solvent phase and an aqueous phase.

Said document is not concerned with the production of inorganic salt compositions of high-purity, *i.e.* with a reduced level of contaminants.

Three main factors that determine the quality of a salt product are the size distribution of the formed particles, the purity of the product, and the shape of the particles. However, a general drawback of antisolvent crystallization methods is that due to the high supersaturations involved, contaminations tend to precipitate together with the salt. Moreover, the occurrence of agglomerates or morphological instabilities is often observed. Since the voids inside the agglomerates will be filled with mother liquor, these growth forms increase the extent of mother liquor entrapment. Therefore, contaminations which do not pose a problem when using evaporative crystallization, such as antisolvent molecules, can become a problem as well. Hence, additional washing steps or recrystallizations are usually needed to obtain salt with the desired purity. Because of the high supersaturations typical of antisolvent crystallization, the dominant mechanism for crystal formation is primary nucleation. As a result, most antisolvent crystallizations result in very small crystals and crystal aggregates. An important disadvantage of these crystal slurries is that they can hardly be separated from the mother liquor using centrifuges that are typical for the conventional multi-effect evaporation process. Consequently, washing of the salt slurry and separation of the salt slurry from the mother liquor in such a way that the moisture content of the slurry is below 10 wt%, which is typically needed, becomes a very costly step.

It is an object of the present invention to provide an improved salt crystallization process which is less energy-consuming and less water-consuming than the conventional processes, while still resulting in the desired product quality.
Surprisingly, we have now found that an improved antisolvent crystallization process makes it possible to produce inorganic salt compositions with a reduced level of contaminants using less energy and less water than conventional evaporation or antisolvent crystallization processes.
In more detail: the process to make the high-purity salt compositions according to the present invention comprises the steps of

- feeding water to a salt source to form an aqueous solution comprising said salt if the salt source is not yet in the form of an aqueous salt solution,
- feeding said aqueous solution to a crystallizer/settler,
- contacting said aqueous solution with one or more antisolvents which force the salt to crystallize, with one or more crystal growth inhibitors being present in the antisolvents and/or in the aqueous solution, and/or one or more scaling inhibitors being present in the antisolvents and/or in the aqueous solution,

- subjecting an overflow of the crystallizer/settler comprising one or more antisolvents and an aqueous salt solution to a separation step wherein the one or more antisolvents are separated from the aqueous salt solution by one or more techniques selected from the group consisting of adsorption, ion-exchange, a temperature change induced phase split, a pH change induced phase split, a complexation induced phase split, a pressure induced phase split, evaporation, and extraction, optionally in combination with a nanofiltration step as disclosed in co-pending international application EP2004/004383,
- removing the crystallized salt from the crystallizer/settler in an aqueous slurry,
- optionally, recycling the one or more antisolvents to the crystallizer/settler, and
- optionally, recycling mother liquor obtained from the slurry to the first dissolution step and/or to the crystallizer/settler.

It is noted that the term “contacting” as used throughout this specification is meant to comprise any conventional technique for adding the antisolvent(s) to the aqueous solution comprising the inorganic salt. In the case of liquid or gaseous antisolvent(s), the antisolvent(s) is/are preferably contacted with the aqueous solution such that the antisolvent(s) and said aqueous solution are able to at least partially dissolve in one another, partially meaning that in a 1:1 mixture of an antisolvent and water, at least 0.5 wt%, preferably at least 2 wt% of the antisolvent will dissolve in the aqueous solution, and/or that at least 0.5 wt%, preferably at least 2 wt% of water will dissolve in the antisolvent.

In general, additional purification steps or recrystallization steps are not necessary when using at least one crystal growth inhibitor in the process according to the present invention. This is because the crystal growth inhibitor(s) prevent(s) primary nucleation of the salt crystals, which finally results in relatively coarse salt crystals (*i.e.* crystals with a diameter of about 300 microns) with reduced impurity levels and having a uniform crystal size distribution. Thus, these crystals can be easily separated from the aqueous slurry, *e.g.* by use of a centrifuge. The narrow crystal size distribution makes it possible to also apply conventional centrifuges at relatively small average crystal sizes.

The process according to the present invention is applicable for the crystallization of inorganic salts. Preferably, said process is used for the crystallization of inorganic salts usually produced by evaporative crystallization. Furthermore, it is noted that the process can also be used to selectively remove contaminations from a solution, for example the removal of calcium sulfate from brine by application of an antisolvent specific for calcium sulfate. Also, the production of sodium sulfate from a sulfate-rich brine is possible by application of this technology. Preferably, the process is used for the crystallization of alkali or alkaline earth salts of halides, phosphates, carbonates, sulfates, (per)chlorates, ammonium salts, or nitrates. Preferably, the process is not used for the crystallization of Ca or Sr salts. However, if the process is used for the crystallization of $CaCO_3$, $SrCO_3$, $CaSO_4$ or $SrSO_4$, it is noted that the antisolvent or the aqueous solution preferably does not comprise one or more scaling inhibitors for these salts. Preferably, the process is used for the crystallization of $MgSO_4$, Na_2CO_3 or Na_2SO_4, and most preferably, the process is used for the crystallization of sodium chloride. Preferably, the sodium chloride used as raw material is rock salt and/or a subterraneous salt deposit. More preferably, it is a subterraneous salt deposit exploited by means of dissolution mining. The process may also be used for the crystallization and purification of solar salt (sodium chloride or saturated brine obtained by evaporating water from brine using solar heat), including solar sea salt, which is typically obtained from sea water. In that case, the sea water, optionally after a concentration step, can be fed directly to the crystallizer/settler. It is noted that hereinafter embodiments are discussed in which the salt source is a solid salt source.

It is noted that the term “sodium chloride” as used throughout this document is meant to denominate all types of sodium chloride of which more than 25 wt% is NaCl. Preferably, such sodium chloride contains more than 50 wt% of NaCl. More preferably, the sodium chloride contains more than 75 wt% of NaCl, while a sodium chloride containing more than 90 wt% of NaCl is most preferred.

The present invention will now be explained in more detail with reference to a preferred embodiment as depicted in Figure 1.

Fig. 1 is a schematic depiction of a preferred flow chart for the above-disclosed novel process. Water (1) is fed to a salt source (A), where it dissolves at least part of the salt. When the solution leaves the source (2), it is preferably saturated with salt and generally will comprise contaminants, such as dissolved K, Br, SO_4, Mg, Sr, and/or Ca ions. The (saturated) aqueous solution is fed to a conventional crystallizer/settler (B), which preferably comprises an inlet pipe. One or more antisolvents (3) are also fed to the crystallizer/settler (B), with one or more crystal growth inhibitors being present in the antisolvent(s) and/or one or more scaling inhibitors being present in the antisolvent(s). The one or more crystal growth inhibitors and/or one or more scaling inhibitors may also be present in the (saturated) aqueous solution. The crystalline salt composition formed is removed from the crystallizer/settler (B) as an aqueous slurry (6) and preferably fed to a centrifuge. Since said salt slurry (6) removed from the crystallizer/settler (B) by one or more outlets may still contain relatively large quantities of antisolvent, preferably, before said salt slurry is fed to a centrifuge, it is fed to a washing leg. For example, if the salt slurry is to be used for electrolysis purposes, it may be desirable to wash the adhered mother liquor, *i.e.* the residual solution which remains after the crystallized salt(s) has/have been removed, and/or the antisolvent from the salt crystals. This can be realized by feeding said salt slurry to a conventional washing leg operated with a raw aqueous salt solution or a purified aqueous salt solution as washing medium. It is noted that a purified aqueous salt solution can be produced by washing the salt crystals with water on a centrifuge. In this way, the production of such a purified brine is combined with an additional washing step of the salt crystals on the centrifuge.

The overflow (4) of the crystallizer/settler which comprises the combined antisolvent and aqueous salt solution is subjected to a separation step in a separation unit (C), where the one or more antisolvents are separated from the aqueous salt solution by one or more techniques selected from the group consisting of adsorption, ion-exchange, a temperature change induced phase split, a pH change induced phase split, a complexation induced phase split, pressure reduction, evaporation, and extraction. This separation unit (C) can be any conventionally used unit capable of handling solids and/or liquids and allowing their separation. Preferably, the separation unit is a unit selected from the group consisting of settlers such as stirred vessels, conventional separation columns, centrifuges, and heat-exchangers. After being separated from each other, the aqueous solution (5), which is undersaturated with salt, and the antisolvent (7) are removed from the separation unit. Preferably, the recovered antisolvent (7) is reused by being recycled to the crystallizer/settler.

In a particularly preferred embodiment the process is a continuous, closed loop process wherein the aqueous salt solution, being undersaturated for salt after being separated from the one or more antisolvents, is recycled to the salt source. There it is used to dissolve more salt, thus producing a, preferably saturated, aqueous solution which can be fed to the crystallizer/settler. In an even more preferred embodiment, the crystalline salt composition is removed from the crystallizer/settler (B) and fed to a centrifuge as a slurry, after which the liquid effluent of the centrifuge (also denoted as mother liquor) is recycled back to the crystallizer/settler and/or to the salt source. Such a process, hereinafter called a closed loop antisolvent crystallization process, has the major advantage that there is no discharge of aqueous salt solution flows.

An antisolvent suitable for use in the process according to the present invention is a liquid compound or mixture of liquid compounds in which the salt to be crystallized is less soluble than in water at 20°C and which differs in chemical composition from the employed crystal growth inhibitor(s) and scaling inhibitor(s). Moreover, an antisolvent can be employed which is a gaseous or solid component. More particularly, the term “antisolvent” as used throughout this application is meant to include each component, liquid compound, or mixture of components and/or liquid compounds which leads to the crystallization of 5 g or more of salt after the addition of 500 g of the antisolvent to 1,000 ml of saturated aqueous salt solution at a temperature between –10 and 110°C. The exact temperature at which said crystallization is performed depends on the salt, the liquid compound(s), and/or component(s) used, and on the desired processing temperature. Preferably, one or more antisolvents which are fluid at 20°C are used in the process according to the present invention. More preferably, a liquid compound which is an organic solvent, an ionic solvent, or an organic or inorganic complex is used as the antisolvent. Most preferably, an organic solvent is used as the antisolvent. The testing temperature is the temperature at which the crystallization according to the invention is conducted.

In a preferred embodiment, the antisolvent(s) is/are used in a total amount of at least 10 g per litre of aqueous salt solution. More preferably, at least 50 g and most preferably, at least 200 g of antisolvent(s) is used per litre of aqueous salt solution. Preferably, the total amount of antisolvent(s) used in the present process is no more than 10,000 g, more preferably no more than 5,000 g, even more preferably no more than 2,500 g, and most preferably no more than 1,000 g per litre of aqueous salt solution.

In order to be able to obtain salt with the desired product quality in the process according to the present invention, at least an effective quantity of one or more crystal growth inhibitors and/or one or more scaling inhibitors should be present either in the antisolvent(s) or in the aqueous solution before said aqueous solution is contacted with the antisolvent(s). Whether or not an additive is suitable for use as a crystal growth inhibitor according to the invention can be determined using the following tests. It is noted that it is sufficient if the additive is considered to be a crystal growth inhibitor according to one of these tests.

1) In a stirred glass beaker, 200 mg/l of bromide (added as NaBr) is dissolved in 1 l of distilled water. Subsequently, the salt to be crystallized is added in such an amount as to produce a saturated salt solution. This solution is heated to boiling point under atmospheric conditions, and water is evaporated until a volume of 800 ml is reached. The precipitated salt is filtered off, washed with 500 ml of saturated acidified aqueous salt solution

(0.1 M HCl), centrifuged, and dried. Subsequently, the quantity of occluded water is measured by heating the sample up to 700°C while nitrogen is passed over it, followed by performing a conventional coulometric titration. The quantity of bromide is determined (in mg Br per kg of dried salt) by conventional spectrophotometry measurements. From the bromide content in the salt crystals and in the final mother liquor the partition coefficient is calculated. Said partition coefficient is the Br content in the salt crystals divided by the Br content in the mother liquor. This is the blank experiment.

The above-described procedure is repeated using additionally 200 mg/l of an additive, and the obtained values for occluded water in the crystals and the partition coefficient are compared to the ones obtained in the blank experiment. An additive is considered to be a crystal growth inhibitor if at least one of the following observations is made: the quantity of occluded water decreases by more than 5%, the partition coefficient decreases by more than 5%, or analysis by means of a (light) microscope shows crystals with (111) faces.

2) In a stirred glass beaker, 200 mg/l of bromide (added as NaBr) is dissolved in 1 l of distilled water. Subsequently, the salt to be crystallized is added in such an amount as to produce a saturated salt solution. This solution is heated to reflux. The boiling solution is then saturated again by the addition of extra salt. The saturated solution is left in a hood at room temperature for 48 h. The precipitated salt is filtered off, washed with 500 ml of saturated acidified aqueous salt solution (0.1 M HCl), centrifuged, and dried. Again the quantity of occluded water and the quantity of bromide are determined as described above for test 1. This is the blank experiment.

The above-described procedure is repeated using additionally 200 mg/l of an additive. The obtained values for occluded water in the crystals and the partition coefficient are compared to the ones obtained in the blank experiment. An additive is considered to be a crystal growth inhibitor if at least one of the following observations is made: the quantity of occluded water decreases by more than 5%, the partition coefficient decreases by more than 5%, or analysis by means of a (light) microscope shows crystals with (111) faces.

3) In a stirred glass beaker, 200 mg/l of bromide (added as NaBr) is dissolved in 1 l of distilled water. Subsequently, the salt to be crystallized is added in such an amount as to produce a saturated salt solution. This solution is left in a hood at room temperature for 1 week. The precipitated salt is filtered off, washed with 500 ml of saturated acidified aqueous salt solution (0.1 HCl), centrifuged, and dried. Again the quantity of occluded water and the quantity of bromide are determined as described above for test 1. This is the blank experiment.
The above-described procedure is repeated using additionally 200 mg/l of an additive. The obtained values for occluded water in the crystals and the partition coefficient are compared to the ones obtained in the blank experiment. An additive is considered to be a crystal growth inhibitor if at least one of the following observations is made: the quantity of occluded water decreases by more than 5%, the partition coefficient decreases by more than 5%, or analysis by means of a (light) microscope shows crystals with (111) faces.

Whether or not an additive is suitable for use as a scaling inhibitor according to the present invention can be determined using the following four tests. It is noted that it is sufficient if the additive is considered to be a scaling inhibitor according to one of these tests.

1) Additive test as described in S. Patel, M.A. Finon, *Desalination* 124 (1999) 63-74, where the inhibition is more than 5%.

2) Additive tests for the inhibition of crystallization and scaling of $SrCO_3$ and/or $CaCO_3$:

a) In a stirred glass beaker, the salt to be crystallized is added to 1 l of distilled water in such an amount that the final concentration of the salt is 10 wt% below the solubility of the salt at room temperature (*e.g.* for NaCl: 90 wt% * 318 g/l = 286 g/l is dissolved). Subsequently, 2.0 meq/l of Ca (added as $CaCl_2$), 0.1 meq/l Sr (added as $SrCl_2$), 10 meq/l of CO_3 (added as Na_2CO_3), 6 meq/l of OH (added as NaOH), and 120 mg/l of Br (added as NaBr) are dissolved in the salt solution. After the addition of the impurities more of the salt to be crystallized is added in such an amount as to produce a saturated salt solution. This solution is stirred and heated to 90°C under atmospheric conditions and 100 mg/l of Socal® P2 seeds ex Solvay Chemicals (*i.e.* $CaCO_3$ crystals) is added to the salt solution. Water is evaporated until a volume of 500 ml is obtained. The reaction mixture is filtered over a 0.2 micron filter and the quantity of dissolved Ca, Sr, and CO_3 in the mother liquor is determined by means of conventional ICP (Inductively Coupled Plasma) spectrometry (for the quantity of Ca and Sr ions) and titrimetry (for the quantity of CO_3). This is the blank experiment. The procedure is repeated using additionally 10 ppm of additive. The quantities of Ca, Sr, and CO_3 in the mother liquor are now compared to the quantities of Ca, Sr, and CO_3 in the mother liquor as observed for the blank experiment. An additive is considered to have scale inhibiting properties if at least one of the dissolved quantities of Ca, Sr, and CO_3 increases by more than 5%.

If the salt to be crystallized is an inorganic salt which is not a sulfate salt, tests 2b-e, 3, and 4 can also be used:

b) In a stirred glass beaker, 360 meq/l of SO_4 (added as Na_2SO_4), 2.0 meq/l of Ca (added as $CaCl_2$), 0.1 meq/l of Sr (added as $SrCl_2$), 10 meq/l of CO_3 (added as Na_2CO_3), 6 meq/l of OH (added as NaOH), and 120 mg/l of Br (added as NaBr) are dissolved in 1 l of distilled water. Subsequently, the salt to be crystallized is added in such an amount as to produce a saturated salt solution. This solution is heated to boiling point under atmospheric conditions and water is evaporated until a volume of 500 ml is obtained. The reaction mixture is filtered over a 0.2 micron filter and the quantity of dissolved Ca, Sr, and CO_3 in the mother liquor is determined by means of conventional ICP (Inductively Coupled Plasma) spectrometry (for the quantity of Ca and Sr ions) and titrimetry (for the quantity of CO_3). This is the blank experiment. The procedure is repeated using additionally 10 ppm of an additive. The quantities of Ca, Sr, and CO_3 in the mother liquor are now compared to the quantities of Ca, Sr, and CO_3 in the mother liquor as observed for the blank experiment. An additive is considered to have scale inhibiting properties if at least one of the dissolved quantities of Ca, Sr, and CO_3 increases by more than 5%.

c) In a stirred glass beaker, 360 meq/l of SO_4 (added as Na_2SO_4), 2.0 meq/l of Ca (added as Na_2SO_4), 0.1 meq/l Sr, 10 meq/l of CO_3, 6 meq/l of OH (added as NaOH), and 120 mg/l of Br (NaBr) are dissolved in 1 l of distilled water. Subsequently, the salt to be crystallized is added in such an amount as to produce a saturated salt solution. To this solution are added 5 g of Socal® P2 ex Solvay Chemicals (*i.e.* $CaCO_3$ crystals). The mixture is heated to boiling point under atmospheric conditions and water is evaporated until a volume of 500 ml is obtained. The reaction mixture is filtered over a 0.2 micron filter and the quantities of dissolved Ca, Sr, and CO_3 in the mother liquor are determined. This is the blank experiment. The procedure is repeated using 10 ppm of an additive. The quantities of Ca, Sr, and CO_3 in the mother liquor are now compared to the quantities of Ca, Sr, and CO_3 in the mother liquor as observed for the blank experiment. An additive is considered to have scale inhibiting properties if at least one of the dissolved quantities of Ca, Sr, and CO_3 increases by more than 5%.

d) Test for the inhibition of crystallization and scaling of Ca and/or Sr carbonate:

The same test as test 2b, but at reflux conditions and a temperature of 90°C and with 100 mg/l Socal® P2 seeds ex Solvay Chemicals.

e) The same test as test 2d, but without the addition of Socal® P2 seeds in the blank experiment.

3) Additive test for the inhibition of crystallization and scaling of $CaSO_4$ (anhydrite). Two stirred glass beakers containing 0.5 kg of water are prepared. Subsequently, 200 meq/l of Ca (added as $CaCl_2$) is dissolved in one beaker and 200 meq/l of SO_4 (added as Na_2SO_4) is dissolved in the second beaker. After the addition of the Ca and the SO_4, the salt to be crystallized is added to both beakers in such an amount as to produce a saturated solution. Subsequently, the solutions are mixed together. This solution is heated to a temperature of 100°C for 1 h with stirring in the presence of 5 g/l of anhydrite crystals. Subsequently, a sample is taken which is filtered. Then the quantity of dissolved Ca is determined by ICP and the quantity of dissolved SO_4 is determined by ion chromatography or titrimetry. This is the blank experiment. The above-described procedure is repeated using additionally 10 ppm of an additive. An additive is considered to be a scaling inhibitor if the quantity of Ca and/or SO_4 dissolved in the mother liquor increases by more than 5%. Preferably, the pH is controlled and 10 meq/l OH is added.

4) Additive test for the inhibition of crystallization and scaling of $CaSO_4 \cdot 2H_2O$ (gypsum). Two stirred glass beakers containing 0.5 kg of water are prepared. Subsequently, 100 meq/l of Ca (added as $CaCl_2$) is dissolved in one beaker and 600 meq/l of SO_4 (added as Na_2SO_4) is dissolved in the second beaker. After the addition of the Ca and the SO_4, the salt to be crystallized is added to both beakers in such an amount as to produce a saturated solution. Subsequently, the solutions are mixed together. This solution is stirred at a temperature of 20°C for 1 h in the presence of 5 g/l of gypsum crystals. Subsequently, a sample is taken which is filtered. Then the quantity of dissolved Ca and SO_4 is determined. This is the blank experiment. The above-described procedure is repeated using additionally 10 ppm of an additive. An additive is considered to be a scaling inhibitor if

the quantity of Ca and/or SO_4 dissolved in the mother liquor increases by more than 5%. Preferably, the pH is controlled and 10 meq/l OH is added.

If one or more crystal growth inhibitors are used in the process according to the present invention, they have to be present in an effective quantity. An effective quantity of crystal growth inhibitor is present if at least one of the following observations is made: the quantity of occluded water decreases by more than 5%, the partition coefficient decreases by more than 5%, or analysis by means of a (light) microscope shows crystals with (111) faces, compared to salt produced from the same salt solution under the same conditions, but without the addition of a crystal growth inhibitor.

If one or more scaling inhibitors are employed in the process according to the present invention, they have to be present in an effective quantity. An effective quantity of scaling inhibitor is present if at least one of the dissolved quantities of Ca, Sr, and CO_3 in the mother liquor increases by more than 5%, compared to mother liquor produced from the same salt solution under the same conditions, but without the addition of a scaling inhibitor. It is noted that the term “high-purity salt” as used throughout the specification is meant to denote salt which is crystallized according to the process of the present invention using an effective quantity of crystal growth inhibitor and/or scaling inhibitor.

If crystal growth inhibitors are employed in the process according to the present invention, typically, the total quantity of said crystal growth inhibitors present in the mother liquor (*i.e.* the combination of antisolvent(s) and aqueous solution minus the precipitated salt) is less than 5,000 mg per kg of mother liquor. Preferably, less than 1,500 mg/kg and more preferably less than 300 mg/kg is used. However, a total concentration of crystal growth inhibitors higher than 5,000 mg per kg mother liquor is also possible as long as it is lower than the total concentration of antisolvent. Typically, more than 10 mg, preferably more than 12.5 mg, and most preferably more than 14 mg of crystal growth inhibitors is used per kg of mother liquor.

If scaling inhibitors are employed in the process according to the present invention, typically, the total quantity of said scaling inhibitors present in the mother liquor–antisolvent system is less than 5,000 mg per kg of mother liquor as well. Preferably, less than 1,500 mg/kg and more preferably less than 300 mg/kg is used. However, a total concentration of scaling inhibitors higher than 5,000 mg per kg mother liquor is also possible as long as it is lower than the total concentration of antisolvent. Typically, more than 1 mg, preferably more than 3 mg, and most preferably more than 5 mg of scaling inhibitors is used per kg of mother liquor.

Preferably, only one antisolvent is employed. The antisolvent may be, but is not necessarily, (partially) miscible with pure water. It is also possible to use an antisolvent or a mixture of antisolvents which will result in the formation of an emulsion after it/they is/are added to the aqueous salt solution. Preferably, the antisolvent(s) used in the process according to the present invention is/are environmentally friendly, and more preferably it/they is/are also food grade. Moreover, the preferred antisolvents are solvents which are inexpensive and readily available. The choice of the one or more antisolvents depends on the solubility characteristics of the salt being crystallized. Preferred antisolvents are selected from the group consisting of alcohols such as methanol, ethanol, propanol, butanediol; ketones such as acetone, butanone; amines, such as diisopropylamine, ethylamine, ethylene diamine, butylamine, diethylene triamine, polyethylene imine; quaternary ammonium salts, preferably with chloride as counterion, such as polydimethyldiallyl ammonium chloride (known as Polyquat®, ex Katpol-Chemie); phosphonium salts, preferably with chloride as counterion; sulfonium salts, preferably with chloride as counterion; acetonitrile; formic acid; acetic acid; polyethylene glycol; polyoxyethers; polypropylene glycol; 1-methyl pyrrolidone; polyvinyl pyrrolidone; the sodium salt of ethylenediamine tetraacetic acid (EDTA), and the sodium salt of diethylenetriamine pentaacetate (DTPA).

In a preferred embodiment, ionic liquids are employed as the antisolvent(s). Examples of ionic liquids suitable for use as an antisolvent in the process according to the present invention include but are not limited to choline chloride based ionic liquids such as choline chloride/urea, choline chloride/phenol, or choline chloride/saccharide. Most preferably, the antisolvent is selected from the group consisting of ethanol, acetone, acetic acid, choline chloride, polyethylene glycol, and Polyquat®.

Crystal growth inhibitors suitable for use in the present process of antisolvent crystallization of a salt include all conventional crystal growth inhibitors for said salt. Preferably, the crystal growth inhibitor for a sodium chloride crystallization process is selected from the group consisting of (poly)phosphates, polycarboxylic acids, phophinocarboxylic acids, oligopeptides, polypeptides, polymaleic acids, polyacrylates, polymers comprising sulfate and/or sulfonate groups, (functionalized) saccharides, cyclodextrines, ferrocyanide salts, humic acids, and ureas. Most preferably, the crystal growth inhibitor is selected from the group consisting of phosphinocarboxylic acids, humic acids, and saccharose.

In the preferred closed loop antisolvent crystallization process, preferably, a crystal growth inhibitor is used which during the separation step to separate the antisolvent(s) from the aqueous salt solution will remain in the antisolvent stream subsequently recycled to the crystallizer/settler.

It was found that by adding the crystal growth inhibitor according to the invention to the antisolvent during the production process of salt, the crystal size distribution could be influenced. It appeared that increasing quantities of crystal growth inhibitor in the antisolvent resulted in the production of crystals with a narrower size distribution. It was also found that the d50 crystal diameter, *i.e.* the diameter at which 50 wt% of the crystals have a larger crystal diameter and 50 wt% of the crystals have a smaller crystal diameter, could be shifted by more than 10% compared to the size of crystals grown in the absence of a crystal growth inhibitor just by adapting the quantities of crystal growth inhibitor in the antisolvent. The crystal size distribution can be determined by means of conventional techniques such as sieve analysis or using a light microscope. Furthermore, it was found that the use of a crystal growth inhibitor in the process according to the present invention not only resulted in a salt with improved purity, but depending on the choice of the crystal growth inhibitor and the process conditions, the shape of the crystals could be altered as well from cubic to spherically or octahedrally shaped crystals. Spherical crystals can be obtained by using smaller amounts of the crystal growth inhibitor than those which yield octahedrally shaped crystals.

Scaling inhibitors suitable for use in the process of antisolvent crystallization of a salt include any conventional scaling inhibitor. Preferably, the scaling inhibitor for a brine crystallization process is selected from the group consisting of polycarboxylic acids, oligopeptides, polypeptides, (poly)phosphates, polyacrylates, phosphinocarboxylic acids, polymaleic acids, polymers comprising sulfate and/or sulfonate groups, (functionalized) saccharides, cyclodextrines, sodium citrate, sodium gluconate, citric acid, humic acids, surfactants from a natural source such as disproportionated rosin acid soap, lactic acid, phospholipids, a suspension of yeast cells, a suspension of algae, amylase, protease, polyepoxysuccinic acid, polyacrylamide, fatty acids, orange juice, and apple juice. Most preferably, the scaling inhibitor is selected from the group consisting of (poly)phosphates, polyacrylates, polymaleic aicds, phosphinocarboxylic acids, and sucrose. In the preferred, closed loop antisolvent crystallization process according to the present invention, preferably a scaling inhibitor is used which during the separation step to separate the antisolvent(s) from the aqueous salt solution will remain in the antisolvent stream subsequently recycled to the crystallizer/settler.

For the water in the present process, any water supply normally used in conventional salt crystallization processes can be employed. In the preferred, closed loop antisolvent crystallization process according to the present invention, only small quantities of water are needed. First, water is needed to start the crystallization process by dissolving part of the salt source. During the process, an aqueous salt slurry is removed from the crystallizer/settler. A quantity of water which preferably equals the quantity of water lost via the aqueous salt slurry is then added to the salt source in order to allow continuation of the process. The quantity of water needed in order to preserve a continuous crystallization process can be lowered even further if the recycle of the centrifuge, to which the crystallized salt in an aqueous slurry is preferably fed, is at least partially fed into the crystallizer/settler and/or to the salt source.

In a specially preferred embodiment of the present invention, the salt source is a subterraneous sodium chloride deposit in a well exploited by means of dissolution mining. In a closed loop process, the undersaturated aqueous salt solution which is removed from the separation unit and recycled to the sodium chloride deposit will contain certain levels of contaminants, such as K, Br, SO_4, Mg, Sr, and/or Ca contaminations. When it is recycled to the sodium chloride source, it will not only become saturated with sodium chloride, but contaminations present in the deposit will also dissolve. As a consequence, the concentrations of said contaminations in the saturated aqueous salt solution leaving the sodium chloride deposit will increase during the process until said solution is also saturated with these contaminations. As a result, a stationary phase will be reached in which there is no driving force anymore for new contaminations present in the sodium chloride deposit to dissolve in the aqueous solution. In this embodiment, addition of water is only needed to fill the cavity which is formed upon dissolution of the natural salt source.

In another embodiment, preferably a specific volume of the mother liquor is purged in order to avoid unacceptable accumulation of contaminants in the aqueous salt solution because of the recycle.

It is known that the purity of aqueous salt solutions in evaporation processes can be increased by reducing the quantity of the contaminations, such as anhydrite, gypsum, and polyhalite (and/or their strontium analogues) that dissolve in said aqueous solutions. This is typically done by adding certain agents to the water used in the process, or by mixing such agents with the salt source before adding the water. Such agents are conventionally called “retarding agents.” Although such agents are not required for the production of high-purity salt via the process of the present invention, if desired, these types of additives may be added to the water supply.

The one or more antisolvents and the aqueous salt solution making up the overflow of the crystallizer/settler can be separated from each other by one or more techniques selected from the group consisting of adsorption, ion-exchange, a temperature change induced phase split, a pH change induced phase split, a complexation induced phase split, a pressure induced phase split, evaporation, and extraction, optionally in combination with a nanofiltration step as disclosed in co-pending international application EP2004/004383. Each of these techniques, which are commonly known in the art, is discussed in detail below. Which of these techniques or combination of techniques is preferably used to separate the one or more antisolvents and the aqueous solution from each other depends on the nature of the antisolvent and can be easily determined by the skilled person using the directions mentioned in this specification together with his common general knowledge.

A. Adsorption

This technique involves the adsorption of antisolvent(s) onto the surface of one or more solid adsorbents suitable for adsorbing the specific antisolvent(s) used in the process. Preferably, one or more adsorbents are employed selected from the group consisting of natural or treated clays, zeolites, activated carbon, carbon molecular sieves, adsorbing resins, and adsorbing polymers. Contacting the solid absorbent(s) with the overflow of the crystallizer/settler that contains the antisolvent(s) is preferably done by flowing the overflow through a fixed bed of adsorbent(s), by moving adsorbent(s) preferably in a countercurrent manner through the overflow or by a simulated moving action in a conventional simulated moving bed system (SMB).

Desorption of the adsorbed antisolvent for its reuse can be achieved by contacting the solids with water or an aqueous salt solution at increased temperature; by washing with water or an aqueous salt solution at an adequate pH value; by applying centrifugal force during a wash with water or an aqueous salt solution; with the aid of ultrasound; by washing with a supercritical fluid such as CO_2, after which said supercritical fluid and antisolvent can be separated from each other; or by washing with an organic solvent or an ionic liquid, followed by separation of the antisolvent(s) from the organic solvent or ionic liquid by, for example, evaporation or distillation. In this way, the adsorption step has functioned either as a concentration step or as a separation step for the antisolvent.

B. Ion-exchange

This technique is suitable for separating an antisolvent which is composed of cations and anions from the aqueous salt solution. Furthermore, this technique is preferably used when the efficiency of the antisolvent is such that at least 70 wt%, and more preferably at least 85 wt% of the salt present in the aqueous solution is forced to crystallize in the crystallizer/settler before being contacted with the antisolvent. For this purpose, the overflow of the crystallizer/settler is contacted with a combination of a weakly basic ion exchanger and a weakly acidic ion exchanger. The acidic resin will adsorb the cation of the salt, whereas the basic resin, being protonated, will adsorb the anion. These two types of ion exchangers can be applied as two separate materials, but can also be present in one and the same material, commonly known as an amphoteric ion exchanger.

As in the case of adsorption, contacting the ion exchangers and the overflow comprising the antisolvent(s) is preferably done by flowing the overflow through a fixed bed comprising one or more ion exchangers or by moving one or more ion exchangers, preferably in a countercurrent manner, through the overflow. In the first case, the process runs in a semi-continuous manner, whereas in the second it is usually operated as a continuous process.

The recovery of the adsorbed antisolvent(s) on the ion exchangers can be achieved by washing the ion exchangers with water or with a diluted aqueous salt solution, preferably by increasing or decreasing the temperature such that the antisolvent(s) is/are released from the ion-exchanger. Thus a two-step system is created which allows easy separation of the antisolvent(s) from the aqueous solution. In this way, the ion-exchange step has functioned as a concentration step for the antisolvent.

C. Separation via a temperature change induced phase split

This separation technique is preferably used if one or more antisolvents are employed which form a one-phase system with an aqueous salt solution at the crystallizing temperature, but which are immiscible or only slightly miscible with said aqueous salt solution at a temperature higher or lower than this temperature. The antisolvent(s) can be recovered by increasing or decreasing the temperature of the overflow to a value where the mutual solubilities of the antisolvent and the aqueous salt solution are low, thus creating a two-phase system with an antisolvent-rich phase and a water-rich phase. These two liquid phases can be easily separated from each other by conventional methods, such as by decanting the antisolvent-rich phase.

This technique can also be employed if the one or more antisolvents precipitate from the overflow upon increasing or decreasing the temperature thereof to form a solid antisolvent-phase and a liquid water-rich phase instead of two liquid phases. In that case, the antisolvent can be recovered from the aqueous salt solution in solid form, for example by conventional filtration methods. It is noted that this technique is a less preferred embodiment according to the present invention.

D. Separation via a pH change induced phase split

This separation technique is preferably used if one or more antisolvents are employed which form a one-phase system with an aqueous salt solution at the pH value during crystallization, but which are immiscible or only slightly miscible with an aqueous salt solution at a pH value higher or lower than this pH value.

The antisolvent(s) can be recovered by adding either acid or base to the overflow such that a pH value is reached where the mutual solubilities of the antisolvent and the aqueous salt solution are low, thus creating a two-phase system with a liquid antisolvent-rich phase and a liquid water-rich phase. Preferably, HCl or NaOH is used for this purpose. These two phases can be easily separated from each other by conventional methods, such as by decanting the antisolvent-rich phase.

This technique can also be employed if the one or more antisolvents precipitate from the overflow upon the addition of either acid or base thereto to form a solid antisolvent-phase and a liquid water-rich phase instead of two liquid phases. In that case, the antisolvent can be recovered from the aqueous salt solution in solid form, for example by conventional filtration methods or by decantation.

Preferably, the thus recovered antisolvent is treated with acid or base such that it recovers its original form and subsequently it is recycled.

E. Separation via a complexation induced phase split

This separation technique is preferably used if one or more antisolvents forming a one-phase system with an aqueous salt solution are employed which are capable of forming a complex with one or more complexing agents to subsequently form either a two-phase liquid-liquid system or a two-phase solid-liquid system with the aqueous salt solution. Preferably, the formation of such a complex is reversible. In this separation technique, one or more complexing agents are added to the overflow, upon which two phases are formed consisting of an antisolvent-rich phase where the antisolvent(s) is/are complexed, and a water-rich phase. The antisolvent-rich phase can be either a liquid phase or a solid phase. If it forms a liquid phase, the two phases can be easily separated from each other by conventional methods, such as by decanting the antisolvent-rich phase. If it forms a solid phase, the two phases can be separated from each other by, for example, a conventional filtration method.

Preferably, the antisolvent-rich phase is subsequently treated to decomplex the antisolvent and obtain it in its pure form in order to allow reuse of the antisolvent(s). Preferably, the antisolvent(s) is/are decomplexed by a temperature change induced decomplexation, or a pH change induced decomplexation, preferably by using HCl, CO_2 or NaOH. An example of preferred complexing agents are cyclodextrins, since they form inclusion complexes with the antisolvent(s).

F. Separation via a pressure induced phase split

This separation technique is preferably used if one or more antisolvents are used which are gaseous at atmospheric pressure. These antisolvents are preferably contacted with the aqueous solution at a pressure of at least 1.5 bar, more preferably at least 10 bar, and most preferably at least 15 bar. Preferably, no pressures higher than 120 bar, more preferably 100 bar, and most preferably 90 bar are employed. Under these conditions, part of the antisolvent will be dissolved in the aqueous salt solution and the salt will be forced to crystallize. What pressure range will give the best results depends on the properties of the antisolvent and can be easily determined by those skilled in the art by routine experimentation.

Said antisolvent(s) can be recovered by reducing the pressure, upon which the antisolvent concentration in the aqueous salt solution will decrease. Preferably, the recovery of antisolvent is performed at a pressure which is far below the pressure employed during the crystallization, in order to achieve maximum recovery. Preferably, the pressure is not reduced below atmospheric pressure.

Preferred gaseous antisolvents which can be separated from the aqueous phase include but are not limited to carbon dioxide, dimethylether, ammonia, dimethylamine, and trimethylamine.

G. Evaporation

If one or more antisolvents having a boiling point lower than water are used, they can be recovered from the overflow of the crystallizer/settler by evaporation thereof from the aqueous solution. Preferably, this technique is used when antisolvent(s) is/are used of which the boiling point is below 85°C at atmospheric pressure. Although less preferred, it is also possible to evaporate the water. Any evaporative technique conventionally used can be employed, such as evaporation by heating and/or pressure reduction, distillation or pervaporation. Preferably, the evaporated antisolvent(s) is/are condensed, whereupon they are preferably recycled in the process. Preferred antisolvents which can be separated from the aqueous phase include but are not limited to acetone, methyl acetate, ethanol, and propanal.

H. Extraction of antisolvent into extraction liquid

A further method to separate the one or more antisolvents in the overflow of the crystallizer/settler from the aqueous salt solution involves contacting a suitable extraction solvent in which the antisolvent(s) will dissolve with the overflow of the crystallizer/settler, during which process a two-phase liquid-liquid system with the aqueous salt solution is generated. This can be easily done by conventional methods, such as by using an extraction column or in a conventional mixer-settler configuration. Preferably, contacting the overflow with the extraction solvent is performed in an extraction column. The extraction solvent and the one or more antisolvents can subsequently be separated from each other using one of the previously discussed separation techniques such as distillation, adsorption, ion-exchange, a temperature change induced phase split, a pH change induced phase split, complexation using one or more complexing agents, or evaporation. Preferably, the recovered extraction solvent and/or antisolvent(s) is/are recycled in the process.

In this embodiment, an extraction solvent is used which forms a two-phase system with the aqueous salt solution. Preferably, an extraction solvent selected from the group consisting of toluene, diethyl ether, hexane, cyclohexane, and an ionic liquid is used.

The crystallizer/settler suitable for use in the process according to the present invention may be any conventional crystallizer/settler. Preferably, it is a crystallizer/settler with a vertical feed hose system and no impeller or other moving parts, which comprises a continuous phase in the crystallizer containing the one or more antisolvents so that the salt will crystallize continuously. More preferably, the crystallizer/settler is a reactor for precipitating and/or crystallizing a substance comprising at least a bottom wall, a vertical wall preferably having a cylindrical cross-section, at least a first inlet, preferably at least first and second inlets for feeding first and second reactants to the reactor, and an outlet. Such a crystallizer/settler is for example described in US 4,747,917. However, most preferably, a crystallizer/settler is used wherein the one or more inlets comprise respective discharge openings arranged to direct the reactants to a surface and cause them to collide with the same, which is for example disclosed in NL 7215309.

The crystallized salt is removed from the crystallizer/settler as an aqueous slurry. Preferably, it is fed to a centrifuge, where a wet salt is produced. The term "wet salt" is used to denominate salt containing a substantial quantity of water. More particularly, it is water-containing salt of which more than 50 wt% consists of the pure salt. Preferably, such salt contains more than 90 wt% of the pure salt. More preferably, the salt contains more than 92 wt% of the pure salt, while a salt of essentially the pure salt and water is most preferred. The wet salt will contain more than 0.5, preferably more than 1.0, more preferably more than 1.5 wt% of water. Preferably, it contains less than 10 wt%, more preferably less than 6 wt%, and most preferably less than 4 wt% of water. All of the weight percentages given are based on the weight of the total composition. If desired, the wet salt may be dried in a conventional manner to obtain dried salt comprising less than 0.5 wt% of water.

In another embodiment according to the present invention, the process further comprises a reverse osmosis step before the overflow of the crystallizer/settler comprising antisolvent(s), water, and salt is fed to a separation unit. This embodiment is particularly preferred if the overflow has an osmotic pressure of less than 60 bar, more preferably less than 40 bar, and most preferably less than 20 bar. In said reverse osmosis step, water is removed from the mixture of the aqueous solution comprising the salt and the antisolvent(s), thus resulting in a more concentrated aqueous solution. As a consequence, more of the salt will be forced to crystallize out.

The process of osmosis is well-known and may be defined in general terms as the diffusion which proceeds through a semipermeable membrane separating two solutions comprising a solute in unequal concentrations. By means of diffusion of one of the solvents into the other solution, the concentration of the solute in each solution will be equalized. For example, in the osmosis operation pure water will diffuse from a first aqueous solution having a lower solute concentration through the semipermeable membrane into a second aqueous solution having a higher solute concentration. When the second aqueous solution is subjected to an elevated hydraulic pressure relative to the hydraulic pressure existing in the first solution, diffusion of the water through the membrane is restrained. The pressure at which diffusion into the second solution is substantially halted is called the osmotic pressure. If the hydraulic pressure applied to the second solution is further increased relative to that of the first solution so that the osmotic pressure of the second solution is exceeded, reverse osmosis occurs, *i.e.* water from the second aqueous solution is transported through the membrane into the first aqueous solution. For example, the osmotic pressure of saturated brine relative to water is approximately 300 bar. This means that for reverse osmosis, hydraulic pressures higher than 300 bar are required to crystallize salt. Such high pressures require special equipment. Moreover, high energy costs are involved. However, when an antisolvent is added to the brine, the solubility of the salt will decrease. As a consequence, the osmotic pressure may also decrease, resulting in a more economic process.

In said particularly preferred embodiment of the process according to the present invention, a solution which essentially consists of water is used as a first solution, whereas for the second solution use is made of the overflow of the crystallizer/settler comprising antisolvent(s), water, and salt. The pressure applied to the second solution preferably is such that water will be transported into the first solution. The pressure at which said reverse osmosis takes place is generally dependent upon the composition of the second solution. Normally, pressures between 1-250 bar, preferably 5-150 bar are required. More preferably, pressures between 8-100 bar are applied, even more preferably pressures between 10-80 bar, and most preferably pressures between 10-50 bar are applied. The first solution preferably is water of high quality which can be used as drinking water and/or process water or, if so desired, may be safely discharged into streams, rivers, lakes, and the like, without additional treatments. It is noted that the antisolvent-membrane technology according to the invention is suitable for the production of drinking water or process water from aqueous solutions comprising salt, using one or more antisolvents. Especially in regions where water is very scarce, reverse osmosis up to very high concentrations of the second solution is desired.

The economic feasibility of this process according to the present invention depends on the pressure required to filter the brine through the reverse osmosis unit. It is noted that the pressure required for the reverse osmosis step can be reduced when the first solution, which comprises water, is combined with an aqueous waste stream comprising alkali and/or alkaline earth salts, such as raw brine or an ion-comprising waste stream of a different process.

Preferably, after the reverse osmosis step, 5-40 wt%, more preferably 10-25 wt% of the second solution is recycled into the crystallizer/settler, whereas 95-60 wt%, more preferably 90-75 wt% is subjected to one or more separation steps according to the present invention. Feeding part of said second solution to the crystallizer/settler has the advantage that the supersaturation level in the overflow of the crystallizer/settler will decrease, so that the quantity of salt which crystallizes during the reverse osmosis step will be lowered. It is noted that if the antisolvent and/or the aqueous solution comprises one or more crystal growth inhibitors, nucleation will be inhibited, which will also help to reduce the quantity of salt which crystallizes during the reverse osmosis step.

The semipermeable membrane to be used in the reverse osmosis step according to the invention can be any conventional semipermeable membrane which has a definite permeability to water, while at the same time it is practically impermeable to the contaminants present in the aqueous solution and the antisolvents used. Preferably, the semipermeable membrane has a permeability of less than 25% to antisolvent and contaminants, more preferably less than 15%, even more preferably less than 5%, and most preferably less than 0.1%. In the reverse osmosis step preferably at least 10 wt% of water, based on the total weight of the aqueous solution comprising the salt, is removed. More preferably, at least 50 wt% of water, even more preferably at least 75 wt%, and most preferably at least 99 wt% of water, based on the total weight of the aqueous solution comprising the salt, is removed.

Furthermore, in a special, optimized embodiment of the present invention, preferably one or more hydrophilic antisolvents are used which form a two-phase system with pure water. By “hydrophilic antisolvent” is meant an antisolvent as defined above which will take up at least 5 wt% of water, more preferably at least 10 wt% of water, and most preferably at least 20 wt% of water, based on the total weight of the antisolvent. The hydrophilic antisolvent preferably does not take up more than 60 wt% of water, more preferably 50 wt% of water, and most preferably 40 wt% of water, based on the total weight of the antisolvent. Such a hydrophilic antisolvent will extract water from the aqueous solution comprising the salt, thus forcing said salt to crystallize. In a preferred embodiment, a hydrophilic antisolvent is applied which has a density of less than 1,200 kg/m^3, even more preferably of less than 1,150 kg/m^3, and most preferably of less than 1,125 kg/m^3. In that case, a two-phase system will be formed inside the crystallizer/settler (B), with the overflow of the crystallizer/-settler (B) being mostly antisolvent comprising water. As is known in the literature, only a small quantity of the salt will dissolve in said antisolvent/water phase. In said preferred process the overflow of the crystallizer/settler is fed to the separation unit (C) wherein the antisolvent(s) are separated from the aqueous solution. Preferably, the recovered antisolvent(s) is/are recycled to the crystallizer/settler (B), whereas the recovered aqueous solution can be drained off. Preferred hydrophilic antisolvents include but are not limited to choline chloride/phenol ionic liquid and polypropylene glycol.

It is furthermore possible to feed said overflow to the reverse osmosis unit as described above. Due to the fact that the osmotic pressure of the antisolvent/water mixture in the overflow relative to water is now lowered, such a reverse osmosis step will be more economic.
In said reverse osmosis step, preferably at least 10 wt% of the total quantity of water dissolved in the antisolvent stream fed to the reverse osmosis unit is removed. More preferably, at least 50 wt% of the total quantity of water, even more preferably at least 75 wt% of the total quantity of water dissolved in the antisolvent stream fed to the reverse osmosis unit is removed. Preferably, to prevent crystallization of the salt present in said antisolvent stream, at most 90 wt% of the total quantity of dissolved water is removed in the reverse osmosis step.

It is noted that any additive suitable for improving the flux of the membrane in the reverse osmosis membrane by preventing the membrane from fouling may be added to the antisolvent(s) and/or the aqueous salt solution. Preferably, surfactants are added to the antisolvent in order to increase the flux of the membrane.

In a specially preferred embodiment of this reverse osmosis comprising process according to the present invention, the salt is sodium chloride. (Wet) sodium chloride according to the present invention is preferably used to prepare brine for electrolysis processes and most preferably for the modern membrane electrolysis processes. The sodium chloride produced in the above-described manner can also be used for consumption purposes. It is for instance suitable as table salt.

The present invention is elucidated by means of the following non-limiting Examples. In said examples, a raw brine sample from the brine field in Hengelo, The Netherlands, was used as the sodium chloride source.

Examples

Example 1

The adsorbents Ambersorb® 563 (ex Rohm and Haas), Amberlite® XAD-4 (ex Rohm and Haas), Norit ROX® (ex Norit) or sodium montmorillonite (ex Southern Clay Products) were applied for the separation of the antisolvents choline chloride (ex Acros), polydimethyldiallyl ammonium chloride (known as Polyquat®, ex Katpol-Chemie), polyoxyalkylene amine (known as Jeffamine XTJ-500, ex Huntsman), and polyglycol A1100 (ex Clariant) from water.

Up to 5.2 g of one of the listed adsorbents was introduced into 25 ml of water containing 10 g/l of an antisolvent and 20 ppm of polymaleic acid (added as a 50 wt% aqueous solution, *i.e.* Drewsperse® 747A, ex Ashland). After the equilibrium was reached, a sample of the liquid phase was taken and the concentration of antisolvent in it was measured by analyzing the Total Organic Carbon (TOC) content in the sample using a TOC-$V_{CPH+TNM-1}$ analyzer (Shimadzu Corporation, Kyoto, Japan). With that value known, the adsorbed amount of antisolvent was determined.

Depending on the adsorbent, a maximum of 78% of choline chloride (using sodium montmorillonite), 69% of Polyquat (using norit), 86% of Jeffamine (using sodium montmorillonite), and 83% of polyglycol (using sodium montmorillonite) initially present in the solution was removed from the water. The measured capacities in mg/g of the adsorbents towards the antisolvents are summarized in Table I:

	Polyquat	Choline Chloride	Polyglycol	Jeffamine
Ambersorb	24 mg/g	45 mg/g	180 mg/g	100 mg/g
Amberlite	23 mg/g	5 mg/g	142 mg/g	132 mg/g
Norit	59 mg/g	25 mg/g	157 mg/g	142 mg/g
Sodium montmorillonite	49 mg/g	109 mg/g	211 mg/g	200 mg/g

Example 2

Sodium hexanoate, which is miscible with brine under the crystallizing conditions, was recovered by means of a pH change induced phase split. For this purpose, carbonic acid, *i.e.* carbon dioxide under pressure, was used to convert the sodium hexanoate into hexanoic acid. To this end, 300 ml of an aqueous solution containing 130 g/l of sodium hexanoate, 30 g/l of sodium chloride, and 20 ppm of polymaleic acid (added as a 50wt% aqueous solution, *i.e.* Drewsperse® 747A, ex Ashland) were introduced into a pressure vessel in which they were contacted with CO_2 at pressures between 5 and 35 bar. Subsequently, a two-phase system was formed comprising a hexanoic acid-rich top layer and a water-rich bottom layer. These two liquid phases were separated from each other by decanting the antisolvent-rich phase. By contacting the hexanoic acid-rich layer with a saturated solution of sodium hydrogen carbonate, the conversion of hexanoic acid back into the original sodium hexanoate was achieved.

From about 10% at equilibrium at 5 bar CO_2 pressure up to about 70% at equilibrium at 35 bar CO_2 pressure of the initial quantity of 130 g/l of sodium hexanoate was recovered from the aqueous solution in this manner. The thus recovered hexanoate can be recycled.

Example 3

In a stirred glass beaker an aqueous solution was made containing Polyglycol A500 (ex Clariant), further denoted as PEG, as antisolvent in demineralized water. Two different solutions were prepared with 2 and 10 wt% of the polyglycol, respectively. To 1 l of each of the prepared solutions were added 360 meq/l of SO_4 by addition of Na_2SO_4, 2.0 meq/l of Ca by addition of $CaCl_2$, 0.1 meq Sr by addition of $SrCl_2$, 10 meq/l of CO_3 by addition of Na_2CO_3, 6 meq/l of OH^- by addition of NaOH, and 120 mg/l of Br^- by addition of NaBr. Subsequently, NaCl was added in such an amount that saturated NaCl solutions were obtained. The resulting solutions were stirred and heated to the boiling point of the mixture under atmospheric conditions. 100 mg/l of Socal P2 seeds ex Solvay Chemicals (*i.e.* $CaCO_3$ crystals) was added to each salt solution. Stirring was continued and water was evaporated until each solution had a volume of 500 ml. It is noted that the antisolvent was not evaporated and, thus, its concentration was increased by about a factor 2. The solutions were filtered over a 0.2 micron filter. The quantity of dissolved Ca and Sr in the obtained mother liquors was determined by ICP and the quantity of carbonate was determined by titrimetry. These were the blank experiments.

The above-described procedure was repeated for each of the three solutions while adding 5 ppm of polymaleic acid (PMA, added as a 50wt% aqueous solution, *i.e.* Drewsperse® 747A, ex Ashland). The obtained values for Ca, Sr, and carbonate in the mother liquors were compared to the quantities of Ca, Sr, and CO_3 in the mother liquors as observed for the corresponding blank experiments.

It is noted that in the presence of the PEG two phases exist at temperatures above 70°C. Only the bottom phase, *i.e.* the aqueous phase, was sampled for analysis and used for comparison.

The results are summarized in Table II:

Components present in mother liquor			**[Ca] x [CO_3] (mg^2/kg^2)**	**[Sr] x [CO_3] (mg^2/kg^2)**
NaCl	2 wt% PEG	-	482	578
NaCl	2 wt% PEG	5 ppm PMA	1806	1659
NaCl	10 wt% PEG	-	370	635
NaCl	10 wt% PEG	5 ppm PMA	1304	2041

It was shown that the value for the $CaCO_3$ and $SrCO_3$ ion products in the mother liquor increases significantly if PMA, having scale inhibiting properties, is added to the antisolvent. Since an increased amount of these products thus will not end up in the crystallized sodium chloride crystals anymore, as a result the obtained sodium chloride crystals have the desired high purity. Furthermore, a more efficient process is obtained.

Example 4

In a stirred glass beaker an aqueous solution was made containing Polyglycol A500 (ex Clariant), also denoted as PEG, in water. Two solutions were prepared with 2 and 20 wt% of PEG, respectively. In 1 l of both of the prepared solutions 200 mg/l of Br was dissolved by addition of NaBr. Subsequently, NaCl was added in such an amount that saturated NaCl solutions were obtained. The solutions were stirred and heated to the boiling point of the mixture under atmospheric conditions. Stirring was continued and water was evaporated until both samples had a volume of 800 ml. It is noted that the antisolvent was not evaporated and, thus, its concentration increased. The precipitated sodium chloride was filtered off, washed with 500 ml of PEG, and dried. The quantity of occluded water was measured by heating the samples up to 700°C and subsequently performing conventional gravimetric measurements. Furthermore, bromide and chloride quantities were determined by ion chromatography and titration, respectively. The Br and Cl quantities in the mother liquors were also measured. These were the blank experiments.

The above-described procedure was repeated adding 200 ppm of polymaleic acid (PMA, added as a 50 wt% aqueous solution, *i.e.* Drewsperse® 747A, ex Ashland) to both samples. The Br/Cl ratios were calculated for both the solid sodium chloride samples and the mother liquors. The bromide partition coefficient was subsequently calculated for both samples by dividing the Br/Cl ratio for the solid sodium chloride by the Br/Cl ratio of the mother liquor. The calculated partition coefficients in the presence of PMA were compared to the partition coefficient as found for the blank experiments.

It is noted that in the presence of the PEG two phases exist at temperatures above 70°C. Only the bottom phase was sampled for analysis and used for comparison.

The results are summarized in Table III:

	Mother liquor: Br content (mg/kg)	**Mother liquor: Cl content (mg/g)**	**Solid NaCl: Br content (mg/kg)**	**Solid NaCl: Cl content (mg/g)**	**Br/Cl ratio (solid NaCl) divided by Br/Cl ratio in mother liquor (*1000)**	**Solid NaCl : occluded water content (wt%)**
2 wt% PEG	124	166	25	604	55	0.339
2 wt% PEG + PMA	172	161	22	604	34	0.237
20 wt% PEG	115	154	26	602	58	0.468
20 wt% PEG + PMA	132	154	27	605	52	0.262

It was shown that the partition coefficient and the quantity of occluded water in the sodium chloride crystals significantly decrease if PMA, also having crystal growth inhibiting properties, is added to the antisolvent. Thus, sodium chloride crystals having the desired high purity were obtained.

Claims

1. A process involving the use of an antisolvent comprising the steps of
   - feeding water to a salt source to form an aqueous solution comprising said salt if the salt source is not yet in the form of an aqueous salt solution,
   - feeding said aqueous solution to a crystallizer/settler,
   - contacting said aqueous solution with one or more antisolvents which force the salt to at least partly crystallize, with one or more crystal growth inhibitors being present in the antisolvents and/or in the aqueous solution, and/or one or more scaling inhibitors being present in the antisolvents and/or in the aqueous solution,
   - subjecting an overflow of the crystallizer/settler comprising one or more antisolvents and an aqueous salt solution to a separation step wherein one or more antisolvents are separated from the aqueous salt solution by one or more techniques selected from the group consisting of adsorption, ion-exchange, a temperature change induced phase split, a pH change induced phase split, a complexation induced phase split, a pressure induced phase split, evaporation, and extraction, optionally in combination with a nanofiltration step,
   - removing the crystallized salt from the crystallizer/settler in an aqueous slurry,
   - optionally, recycling the one or more antisolvents to the crystallizer/-settler, and
   - optionally, recycling mother liquor from the slurry to the first dissolution step and/or to the crystallizer/settler.

2. A process according to claim 1 wherein at least part of the overflow of the crystallizer/settler is subjected to a reverse osmosis step before it is subjected to the separation step.

3. A process according to claim 2 wherein in the reverse osmosis step 10-99 wt% of water, based on the total weight of the aqueous solution comprising the salt, is removed.

4. A process according to claim 3 wherein the removed water is used as drinking or process water.

5. A process according to any one of the preceding claims which is a continuous closed loop process, wherein the aqueous salt solution after being separated from the one or more antisolvents is recycled to the salt source.

6. A process according to any one of the preceding claims wherein the crystallized salt in an aqueous slurry is fed to a centrifuge, optionally after being fed to a washing leg.

7. A process according to claim 6 wherein the recycle of the centrifuge is fed to the crystallizer/settler and/or to the salt source.

8. A process according to any one of the preceding claims wherein the salt source is selected from the group consisting of a sodium chloride, a sodium carbonate, and a sodium sulfate source.

9. A process according to claim 8 wherein the salt source is a subterraneous sodium chloride deposit.

10. A process according to any one of the preceding claims wherein the antisolvent is selected from the group consisting of alcohols such as methanol, ethanol, propanol, butanediol; ketones such as acetone, butanone; amines, such as diisopropylamine, ethylamine, ethylene diamine, butylamine, diethylene triamine, polyethylene imine; quaternary ammonium salts, preferably with chloride as counterion, such as

polydimethyldiallyl ammonium chloride (known as Polyquat®, ex Katpol-Chemie); phosphonium salts, preferably with chloride as counterion; sulfonium salts, preferably with chloride as counterion; acetonitrile; formic acid; acetic acid; polyethylene glycol; polyoxyethers; polypropylene glycol; 1-methyl pyrrolidone; polyvinyl pyrrolidone; the sodium salt of ethylenediamine tetraacetic acid (EDTA) and the sodium salt of diethylenetriamine pentaacetate (DTPA), choline chloride, and choline chloride based ionic liquids.

11. A process according to any one of the preceding claims wherein the crystal growth inhibitor is selected from the group consisting of (poly)phosphates, polycarboxylic acids, phophinocarboxylic acids, oligopeptides, polypeptides, polymaleic acids, polyacrylates, polymers comprising sulfate and/or sulfonate groups, (functionalized) saccharides, cyclodextrines, ferrocyanide salts, humic acids, and ureas. Most preferably, the crystal growth inhibitor is selected from the group consisting of phophinocarboxylic acids, humic acids, and saccharose.

12. A process according to any one of the preceding claims wherein the scaling inhibitor is selected from the group consisting of polycarboxylic acids, oligopeptides, polypeptides, (poly)phosphates, polyacrylates, phosphinocarboxylic acids, polymaleic acids, polymers comprising sulfate and/or sulfonate groups, (functionalized) saccharides, cyclodextrines, sodium citrate, sodium gluconate, citric acid, humic acids, surfactants from a natural source such as disproportionated rosin acid soap, lactic acid, phospholipids, a suspension of yeast cells, a suspension of algae, amylase, protease, polyepoxysuccinic acid, polyacrylamide, fatty acids, orange juice, and apple juice.

13. A process according to claim 11 wherein the total quantity of crystal growth inhibitors is between 10 and 5,000 mg/kg of mother liquor, preferably between 14 and 300 mg/kg of mother liquor.

14. A process according to claim 12 wherein the total quantity of scaling inhibitors is between 1 and 5,000 mg/kg of mother liquor, preferably between 5 and 300 mg/kg of mother liquor.

15. A process according to any one of the preceding claims wherein a total amount of antisolvent of between 10 and 10,000 g per litre of aqueous salt solution, preferably between 200 and 1,000 g per litre of aqueous salt solution, is employed.

16. A process according to any one of the preceding claims wherein a hydrophilic antisolvent is used which will take up at least 5 wt% of water, based on the total weight of the antisolvent.

Figure 1 of 1