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(54) Title: PROCESS TO MAKE HIGH-PURITY WET SALT, WET SALT SO OBTAINABLE, AND THE USE THEREOF IN AN ELECTROLYSIS PROCESS

(57) Abstract: The invention relates to an evaporative crystallization process to make salt compositions that includes a step wherein a mother liquor is formed that contains an effective amount of a crystal growth inhibitor that is selected from oligopeptides, polypeptides, and polymers bearing two or more carboxylic acid groups or carboxyalkyl groups and optionally further phosphate, phosphonate, phosphino, sulfate, and/or sulfonate groups, such as carboxymethyl cellulose with phosphate groups, to form salt crystals with a (111) face. The salt can be washed with a reduced amount of washing water while still containing lower amounts of K, Br, SO₄, and/or Ca. A wet salt can be obtained by partially drying the salt crystal that are formed.

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PROCESS TO MAKE HIGH-PURITY WET SALT, WET SALT SO OBTAINABLE, AND THE USE THEREOF IN AN ELECTROLYSIS PROCESS

The present invention relates to a process to make salt (sodium chloride) of high purity, as well as to the use of resulting high-purity, preferably wet, salt to make brine, a solution of said salt in water, for electrolysis operations, preferably the electrolysis process involving membrane cells.

Salt and wet-salt is long known. The conventional process to make said salt is an evaporative crystallisation of brine, followed by washing and drying steps. Said brine is typically produced by dissolving a natural source of NaCl in water. The brine will also contain K, Br, SO₄, and/or Ca, which moieties are typically present in the source of NaCl. A disadvantage of the conventional process is that the salt obtained has imperfections in the crystal lattice and contains occlusions, being small pockets of mother liquor of the evaporative crystallisation process (present in cavities in the salt crystals). Due to these imperfections and occlusions, the wet salt, and a subsequent brine produced therefrom, is contaminated with compounds present in the mother liquor. In particular, the amount of K, Br, SO₄, and/or Ca that is carried over is quite high. Hitherto, additional washing steps and drying steps, such as centrifuge steps, were employed, which are energy consuming, to reduce the levels of the contaminants.

Especially if a brine produced from the wet salt is to be used in the modern membrane electrolysis cells said contaminants are known to lead to less economic electrolysis operations.

For these reasons, there is a need for improved wet salt, having a lower level of contaminants, which can be produced more cost-effectively and which can be used to make a brine for electrolysis processes.

5 Surprisingly, we have now found that wet salt compositions can be produced with a reduced level of K, Br, SO₄, and/or Ca and using less energy in the washing operations. The process to make such high-purity wet salt compositions is characterized in that during the evaporative crystallization process, the mother liquor contains an effective amount of a crystal growth
10 inhibitor that is selected from oligopeptides, polypeptides, and polymers bearing two or more carboxylic acid groups or carboxyalkyl groups and optionally further phosphate, phosphonate, phosphino, sulfate, and/or sulfonate groups, such as carboxymethyl cellulose with phosphate groups, to form salt crystals with a (111) face. Said salt can be washed with a reduced amount of washing
15 water while still containing lower amounts of K, Br, SO₄, and/or Ca. A wet salt can be obtained by partially drying the salt crystals that are formed.

Preferably, the crystal growth inhibitor is a water-soluble polymer. More preferably, it is a water-soluble polymer bearing two or more carboxylic acid
20 groups and optionally further phosphate, phosphonate, phosphino, sulfate, and/or sulfonate groups, such as polyacrylates. If the final salt is to be used in electrolysis operations the use of peptides is less desired, since the nitrogen of the peptide can result in the formation of the highly undesired NCl₃ in said electrolysis process. Peptides that hydrolyze in the crystallization process to the
25 extend that they become ineffective crystal growth inhibitors are also less preferred. However, for table salt, peptides may be acceptable. If residual crystal growth inhibitor in the final salt is undesired, then the use of hydrolyzing

peptides can be preferred since the final salt, optionally after a washing step, can be free of the crystal growth inhibitor.

It is noted that it is known that adding certain chemicals to the evaporative
5 process can influence the crystal form of the salt and can influence the
formation of occlusions in the salt. Lead chloride, cadmium chloride,
manganese sulfate and carrageen in, for instance, have been reported to
reduce the amount of cavities, and consequently the amount of occlusions and
occluded mother liquor, when added to the evaporative crystallizing mass.
10 However, such chemicals are undesired. Not only can they adversely affect the
electrolysis operations, they may also spill over in table-salt that is produced
using the same installation, which is typically undesired.

The term wet salt is used to denominate "predominantly sodium chloride"
15 containing a substantial amount of water. More particularly, it is a water-
containing salt of which more than 50% by weight consists of NaCl. Preferably,
such salt contains more than 90% by weight of NaCl. More preferably, the salt
contains more than 92% of NaCl, while a salt being essentially NaCl and water
is most preferred. The wet salt will contain more than 0.5, preferably more than
20 1.0, more preferably more than 1.5% by weight of water. Preferably it contains
less than 10% by weight, more preferably less than 6% by weight and most
preferably less than 4% by weight of water. Typically the salt will contain 2-3%
of water. All of the weight percentages given are based on the weight of the
total composition.

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An effective amount of the crystal growth inhibitor is present if in the following
test any crystals with a (111) face show up. More particularly, to determine
whether enough crystal growth inhibitor is present, one adds a certain amount

of the crystal growth inhibitor to a glass beaker of 1000ml, equipped with a magnetic stirrer bar, and containing 450 ml of demineralized water and 150 g of high-purity NaCl (pharmaceutical grade). The beaker is covered with a glass plate, but the covering is such that the gas phase inside the beaker is in direct unrestricted contact with the air. The beaker is then heated till reflux conditions (about 110°C). The heat input is selected such that within a period of 15 to 60 minutes about 2 to 10g of salt is crystallized. The crystals are separated from the mother liquor, e.g. by centrifuging, and dried. For this test the level of drying is not crucial, as long as the crystals are not (re)dissolved or altered, e.g. by mechanical forces. If analysis by means of a (light) microscope shows crystals with (111) faces, a sufficient amount is used.

Preferably the amount of crystal growth inhibitor that is present in the feed of the evaporative crystallization process is less than 300 mg/kg for economic reasons. Typically more than 10 mg, preferably more than 12.5 mg, and most preferably more than 14 mg crystal growth inhibitor is used per kg of feed of the evaporative crystallization process.

It is noted that JP-A-01-145319 and JP-A-01 145 320 describe the use of sodium hexametaphosphate and polyacrylate, respectively, in an evaporative crystallisation process to make dried polyhedral salt with an improved flowability that can be used to improve the marketing of product to which the dried salt is fixed. Said dried salt is known to contain less than 0.5% of water. There is no disclosure that one of these chemicals can be used to make wet salt with less occlusions in a more economic way. Furthermore, the sodium hexametaphosphate was proven not to be suitable in the presently claimed evaporative crystallisation process for making wet salt due to hydrolysis of said hexametaphosphate.

It is furthermore noted that products like Belsperse® 164, which is a phosphino carboxylic polymer ex FMC Corporation, have been promoted for use as an anti-scaling additive in evaporative crystallizers. The product is typically used in an amount of 1-2 ppm, although a level up to 10ppm has been mentioned. However, such a concentration is not an effective amount in accordance with the present invention.

10 Experimental

In some test using a brine feed from our plant in Hengelo, a variety of crystal growth inhibitors, amongst which Belsperse® 164, were evaluated. Adding 25 mg/kg of Belsperse® 164 to the feed resulted in the formation of NaCl crystals with (111) faces, while at the same time K, Br, SO₄, and Ca levels in the resulting crystals was lowered by more than 20%, compared to the levels in salt produced from the same feed under the same conditions, without that the Belsperse® 164 was added. Said lowering of the K, Br, SO₄, and Ca levels is attributed to less occluded mother liquor and a lower amount of lattice imperfections. Also it was found that washing of the product was more efficient, so that the amount of wash water could be reduced. Furthermore, the centrifuge time to separate the wet salt from the wash water could be reduced, resulting in energy savings during washing and centrifuging of more than 1%.

25 The wet salt so obtained was preeminently suited for use in electrolysis processes since it required hardly any purification. This is of particular importance for electrolysis operations wherein membrane cells are used. Furthermore it was observed that the wet salt could be submitted to an extra drying step to make the

known high-purity dried salt. Such high-purity dried salt can, for example, be used as a pharmaceutical grade salt.

- 5 In further tests, Belsperse® 164 was added to a conventional continuous 4 effects vacuum salt production plant in an amount of 15 g per cubic meter of brine.

Compared to a production run that was equal except for the Belsperse® 164
10 addition, the quality of the resulting wet salt (samples were taken at regular intervals from the production line) was improved as follows:

- Br content from 25 to 38 % lower
SO₄ content from 30 to 60 % lower
K content from 29 to 37 % lower
15 Ca content from 27 to 50 lower.

Claims

1. Evaporative crystallization process to make salt compositions that includes a step wherein a mother liquor is formed that contains an effective amount
5 of a crystal growth inhibitor that is selected from oligopeptides, polypeptides, and polymers bearing two or more carboxylic acid groups or carboxyalkyl groups and optionally further phosphate, phosphonate, phosphino, sulfate, and/or sulfonate groups, such as carboxymethyl cellulose with phosphate groups, to form salt crystals with a (111) face.
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2. Process according to claim 1 further including a washing step of the crystallized salt.
3. Process according to claim 1 or 2 further including a drying step of the salt
15 wherein said salt is only partially dried, such that a wet salt is produced.
4. Electrolysis of a brine produced with salt resulting from the process of any one of claims 1-3.
- 20 5. Electrolysis in accordance with claim 4 wherein a membrane electrolysis cell is used.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/06502

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