Desalination 407 (2017) 93–102

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Investigation of the depletion of ions through freeze desalination

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ARTICLE INFO

Article history:
Received 5 August 2016
Received in revised form 7 December 2016
Accepted 15 December 2016
Available online xxxx

Keywords:
Freeze desalination
Suspensions crystallization
Crystallization
Water treatment

ABSTRACT

Producing potable water is an important but cost- and energy-intensive process. Small scale machines for insular solutions are not yet available. Whereas drinking water is regulated to a maximum concentration of 0.05 wt% sodium chloride, sea water normally ranges from 3 wt% NaCl to more than 4 wt% NaCl. Freeze crystallization therefore can provide an energy- and cost-effective way to utilize small equipment as a good compromise between energy consumption and low maintenance effort. Because of this, different methods were investigated with respect to their desalination effect, ice growth and implementability. One method was a cooled plate in which dependencies of throughput and ice purity were tested as a function of operation conditions. Another procedure was heterogeneous heat transfer via droplets of non-miscible organic fluids. The last method was classical suspension crystallization were a vessel is cooled down and stirred to produce ice from a solution. Because no pure ice could be produced directly, centrifuging and pressing were investigated for ice purification post-treatment. To prove the whole concept, natural samples from the Atlantic Ocean were desalinated. The final result is that independent from the used freezing process all ice could be desalinated combining the ice production with adjacent mechanical drainage.

1. Introduction

The future supply of potable water is especially vulnerable in areas around North Africa, Southeast Europe, the Middle East, Southwest Asia, the West Coast of North America and the Southwest Coast of South America [1]. In Europe and North America, the water crisis is mainly generated by agriculture. The transportation of fruits with a high water content from countries with water demand to countries without increases water scarcity [2]. Most other countries suffer from too little rain or the increasing effects of the climate change. This leads to different demand for drinking water depending on the population density in the area and the existing wealth. Comparatively, countries in Africa or islands on the coast of Panama have fewer opportunities to install desalination plants compared to countries in the Middle East or the Canary Islands [3,4]. This enhances the necessity to develop new desalination plants to satisfy every need independent of the number of households in a fixed area. Unfortunately, investment costs will always have an influence but can still be lowered for small plants powered by renewable energies [5].

Currently, desalination of seawater, as already mentioned one for the future eminently important technology, is mainly based upon processes such as reverse osmosis or evaporation. Both methods are optimized to a high grade so technology-based innovations are not expected beyond improving pre- or post-treatment [6]. A prospective technology could be desalination by freeze crystallization because it combines the low energy demand of reverse osmosis with a lack of necessary chemicals and the possibility of solar-driven drinking water production. A theoretical approach showed, for example, a perspective possibility to combine freeze crystallization and reverse osmosis for a better post-treatment of the brine and thus an environmentally friendly and a more cost effective process [7]. Although known for many years, it never came beyond basic research and therefore was only investigated by a few scientists. The result is that there is no real plant producing potable water by crystallization [8]. Compared to distillation processes, the enthalpy of evaporation is approximately 7 times larger than that of fusion, a lower working temperature is necessary, causing less fouling and corrosion, and no chemicals have to be used. Disadvantages are an inhibited heat transfer caused by phase change from liquid to solid due to ice layers on the heat exchanger plates, a subsequent phase separation and a necessary post-treatment causing high investment costs [9], [10]. As the necessity of desalination often correlates with high solar incidents, electricity produced by photovoltaic systems can

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http://dx.doi.org/10.1016/j.desal.2016.12.009

power this plant. This idea includes the concept of heat pumps to use the change from electrical into thermal energy and therefore the advantage of small temperature gradients through heat recovery and so a high coefficient of performance (COP) [11].

The freezing process is necessary because sodium chloride, the main pollutant in seawater, cannot be crystallized by lowering the temperature, and concentrations of other ions are too low (Fig. 1). Therefore, freezing the solvent is the only way to separate the water and ions. The process is based on the physical effect of ion expulsion from growing crystals when ice is formed by lowering the temperature of the solution until the freezing point is reached and further thermal energy is extracted. Additionally, in pure crystals concentrated brine is trapped within intercrystalline channels or pores. The volume of those channels increases with the concentration of ions in seawater until complete volumes can be seen. With more trapped liquid between ice crystals, the whole mass is like a slurry [12,13]. Changing operation conditions such as the temperature or turbulence of the solution or intensifying the heat contact causes different growth rates. Higher growth rates lead to more complex ramifications in the ice crystal and so to narrow channels with higher streaming resistance and less ion expulsion [13]. This happens when the solution surrounding the ice has a higher concentration and so a lower freezing point than the rest of the solution, inhibiting further crystal growth at this point of the ice front but forcing growth at another point, causing liquid inclusions. This is preventable through higher turbulence of the liquid to reduce the concentration gradient near the ice front [14].

Previously investigated methods include block ice-, round cell-, suspension- and plate-crystallization. The common result of these experiments is that there is no way to obtain potable water without post-treatment. Usually ice is washed by melted clean water, causing less product [12,15–19]. Qin et al. studied the ice behavior during a washing step in a counter-current wash column. The main impact factor on ice purity was the temperature of the wash water, which led to channeling or freezing. However, no statement about the economic efficiency could be made [20]. Another method Kiesskalt described in 1966 noted that pressing and centrifuging are better methods to treat ice but recommended only centrifuging [21]. To prevent ice is freezing on the cooled surface, Cao suggested a flake ice maker in which a scratcher is integrated. However, no experiments were described, nor what post-treatment would look like or how the ice would be moved or melted [22]. Another experiment done by Fujioka investigated the transfer of the freezing method from the food industry to the desalination of sea water. Unfortunately, it was not able to produce potable water [23]. In addition to salt water, other scientists investigated options to clean waste water from the oil, vinegar or mayonnaise industries, from pharmaceutically active compounds as well as from sucrose and chromium [24–27].

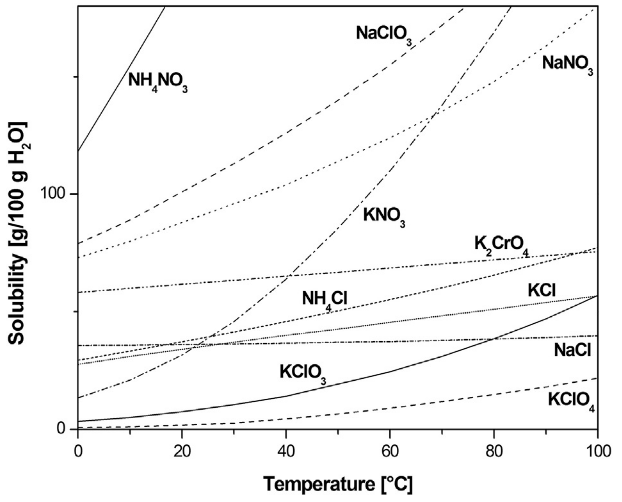

Fig. 1. Temperature dependence of solubility of different molecules in water [28].

In this paper, different processes are investigated to produce ideally clean ice with high performance in combination with pressing or centrifuging to obtain potable water. Finally, the best combination is tested with natural water from the Atlantic Ocean to demonstrate the functionality of the process.

2. Materials and methods

2.1. Reagents & sample analysis

Samples were prepared prior to the experiments with deionized water and sodium chloride purchased from Sigma Aldrich. To determine the salt concentration in the water or melted ice, a Greisinger GMH 5450 conductivity meter was used, and for the sample from the Atlantic Ocean, an ICP-MS and an IC were used.

2.2. Experimental setup

Three different setups were used to investigate whether they can be used to produce potable water, what the dependencies are and whether would it be possible for an upscale to compete with already installed desalination plants.

2.2.1. Static freezing

Normal plate heat exchanger or cold fingers can be used to produce ice and can easily be simulated in laboratories. A special heat exchanger can be achieved through cooling a double walled plate and letting water flow along it (Fig. 2). The setup is similar to that published by Williams [29] besides the fact that the surface is not flat but ripped like a heater. This should lead to ice growth away from the surrounding solution. The noncrystallized water can be collected and pumped up to flow along the plate again whilst the concentration of the brine is increasing. Distribution of the water is realized by a pipe with even localized holes right above the groove. The time necessary to grow ice should lead to a drain of liquid inclusions and so to better ice quality.

The angle of the plate can be varied between 7.6° and 54.5° compared to the ground to increase the turbulence of the water on the growing ice front (Fig. 3). The lowest possible angle of 7.6° and the highest possible angle of 54.5° were thereby limited by the construction. The size of the plate is approximately 2000 mm in length and 1000 mm in width. Unfortunately, the ice can only be moved by scratching it away or through heating the plate so ice is sliding downwards. To cool the whole plate, a heat pump with 5.5 kWel power was used. Cooling was achieved by pumping an ethylene glycol/water-solution through a meander-like double wall.

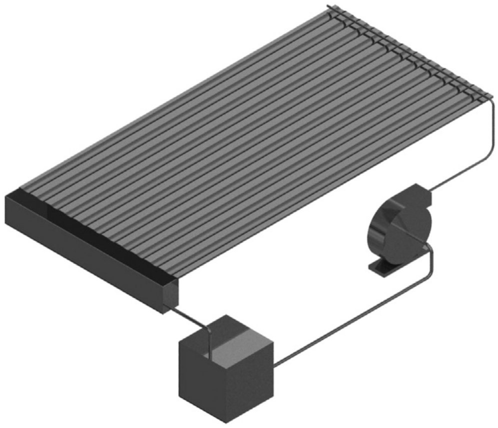

Fig. 2. Construction drawing of the static freezing setup with a double walled plate, a collecting vessel and a circulation pump.