Eutectic Freeze Crystallization

Towards achieving zero liquid discharge in water treatment

Water treatment processes such as nanofiltration (NF), reverse osmosis (RO) and ion exchange (IEX) produce aqueous waste streams with a high salt content. The disposal of such brines is a growing concern in many parts of the world.

Traditional disposal methods include discharge to sea or other surface water bodies, discharge to sewer, deep well injection, distribution over land or storage in evaporation ponds. However, these disposal means are often hindered because of unavailability, costs of transportation, environmental impact, regulatory requirements and/or public perception. The need is to find efficient, cost-effective and sustainable management options for saline waste streams which do not simply shift a water quality problem from one area or one user to another. A promising way of managing the saline aqueous waste streams is to consider them a resource of salt(s) and water (Kim, 2011). There are two benefits associated with this approach. First, the recovery of salt and subsequent use (sale or integrated use) may offset the high operating costs that are typically associated with Zero Liquid Discharge (ZLD) processes (Kim, 2011). Second, reclamation of pure water from the waste stream reduces the volume of liquid waste to be disposed, eventually leading to cost savings.

Eutectic Freeze Crystallization (EFC)

Eutectic Freeze Crystallization (EFC) is a promising low temperature desalination technique that can retrieve salt and water in pure form from the saline waste streams (Figure 1), at a relatively low energy demand compared to conventional evaporation based separation processes (Van der Ham, 1999). The basis of EFC is the existence of eutectic point (EP) for every salt solution. The EP is a characteristic point in the phase diagram of a salt-water mixture where an equilibrium exists between ice, salt and solution with a specific concentration. This specific concentration is called eutectic concentration (EC) and the temperature at which the equilibrium is achieved is called the eutectic temperature (ET). EFC is less energy intensive compared to evaporative crystallization because the energy required to separate water as ice is significantly lower than that required for separating...
it as a vapour (i.e. by evaporation), indicated by the fact that the heat of fusion of ice (6.01 kJ/mol) is less than the heat of evaporation of water (40.65 kJ/mol) (Nathoo et al., 2009). Moreover, with EFC pure salts can be recovered from the solution, based on the difference between the respective EPs of the single salts.

The principle of EFC can be described by using a phase diagram of a binary salt-water system (Figure 2). When a solution in the unsaturated area with a concentration lower than eutectic concentration (A) is cooled down below its freezing point, ice crystals start to form (B). Further cooling decreases the temperature and increases the concentration of salt in the solution with the formation of ice crystals along the ice line (B to C). At point C (eutectic point), the concentration of salt reaches saturation and further cooling will result in the simultaneous formation of ice and salt crystals. Similarly, starting with a solution having higher concentration than eutectic concentration will first result in the formation of salt and reach the eutectic point (C) by following the salt solubility line (Genceli, 2008). The products (ice and salt) can be separated by gravitation based techniques (e.g. settling) because of their density difference. Salt crystals are heavier, therefore they sink to the bottom of the container and ice crystals rise to the surface. In a multi-component mixture, e.g. a ternary system consisting of Na₂SO₄, MgSO₄ and water, the dissolved salts will crystallize at different eutectic points along individual eutectic lines.

**Pilot study**

The following pilot study at DWP Botlek of Evides Industriewater looks at the feasibility of using EFC on spent CIEX regenerate.

Cation exchange (CIEX), with a strong acid cation resin, is a widely used hardness removal technique in water treatment. In this process multivalent cations, such as calcium (Ca²⁺) and magnesium (Mg²⁺), are removed from water by exchange with sodium ions (Na⁺) that are available on the surface and in the pores of CIEX resin beads. The CIEX resin needs to be regenerated periodically to recharge the CIEX resin. Regeneration is usually performed with approximately 10 wt% solution of NaCl, also known as the regenerant solution. In softening the spent regenerant usually contains a mixture of NaCl, CaCl₂, and MgCl₂ at a total concentration ranging from 2 to 4 wt%. The feasibility of applying the EFC process for treating CIEX regenerate (to reduce the volume of waste stream and recover NaCl) is under investigation at DWP Botlek where a skid mounted, semi-industrial pilot plant has been installed with the ability to treat 10-40 L/h of feed brine (Figure 3).
The pilot can be split into two different blogs of equipment that function simultaneously, namely the crystallizer unit and the separation unit. In the crystallizer, an ice slurry and a salt slurry are being produced and pumped to the separation unit. In the separation unit, the ice and salt crystals are separated from the accompanying mother liquor. The dry salt and dry ice are extracted out of the system, while the mother liquor is recycled back to the crystallizer.

In the heat exchangers of the crystallizer the heat transfer fluid is pumped at various measured and regulated flows to extract the heat from the solution in the crystallizer. Once the ice and salt are being formed, a scale layer will start forming on the heat exchangers. This will be scraped off with the advanced scraping system. Rotational speed of the scrapers can be varied, based on the process needs and the turbulence inside the crystallizer.

The separation unit consists of two vacuum belt filters, one for the ice slurry and one for the salt slurry. As the slurry is fed on a moving filter belt, vacuum is applied under the product cake, to suck the adhering mother liquor. The mother liquor is collected in vacuum separators/filrate receivers and then pumped with hose pumps to the buffer vessel. Both vacuum belt filters can be used for separating the ice and salt slurry and the decision to use one or another is based on the needs of the process.

DWP Botlek produces approximately 1,400 m³/h of demi water using fresh water from the Brielse Meer as its source. The raw water has a typical turbidity of 2 to 10 NTU, a typical conductivity of 500 to 850 µS/cm and approximate total hardness of 80 mg/L Calcium. At the DWP Botlek, the water is pre-treated with coagulation/flocculation, dissolved air flotation (DAF) and rapid filtration (anthracite/sand). This pre-treated water is then pumped to the softening section of the plant, where calcium (Ca) removal takes place by cation exchange (CIEX). After softening at DWP Botlek, the softened water is treated by reverse osmosis (RO) to remove 95% of the salinity. In order to achieve an acceptable removal of bicarbonate (HCO₃), caustic soda (NaOH) is dosed upstream of the RO. The remaining salinity in the reverse osmosis permeate is removed by mixed bed IEIX (strong acidic CIEX resins and strong basic AIEIX resins).

“the feasibility of continuously treating the spent regenerant from the softening CIEX process with EFC in order to reduce the volume of the brine and to recover NaCl”

The aim of the ongoing research project at DWP Botlek is to study the feasibility of continuously treating the spent regenerant from the softening CIEX process with EFC in order to reduce the volume of the brine and to recover NaCl.

The softening step at DWP Botlek consists of eight CIEX vessels, filled with strong acidic CIEX resins, which is regenerated using sodium chloride (NaCl) as regenerant. The regenerant is a ca. 10 w% NaCl solution, made by dissolving industrial grade NaCl in softened water from the plant itself. After regeneration the salinity of the spent regenerant drops to approximately 2-4 w%. The main components in the spent regenerant are Na, Ca, Mg and Cl and low(er) levels of sulphate, copper, nickel, iron and organic components. The concentration of these components in spent regenerate vary in time during a regeneration cycle.

Figure 4 shows the profile of Na, Ca and Mg concentration in time of the spent regenerant during regeneration.

The CIEX resin is regenerated with an overdose NaCl (approx. 70%) required to reverse the adsorption process. This overdose is rinsed out of the vessels and is available for recovery and reuse. Business case calculations show that with eight softeners and about 270 regenerations per softener each year there is a potential to recover 950 tonnes of NaCl per year at DWP Botlek. Moreover, the maximum amount of NaCl (440 kg per regeneration) can be recovered if the spent regenerant is collected from 27 to 64 minute and then used for salt recovery.

EFC is (economically) most feasible when the concentration of the salt to be recovered is close to the eutectic concentration. In the spent regenerant of DWP Botlek the concentration of salt ranges from 2-4 wt%. On the other hand, the eutectic concentration for pure NaCl solution is 23.3%. It means that the spent regenerant needs to be pre-concentrated before feeding to EFC. Figure 5 shows a conceptual model where Freeze Crystallization (FC) is proposed as pre-concentration step to the EFC process.

At this moment instead of concentrating the spent regenerant by techniques like Forward Osmosis (FO) or Freeze Crystallization (FC), a cocktail of NaCl, CaCl₂ and MgCl₂ is added in order to “mimic” the spent regenerant to feed the EFC installation. The presence of significant amounts of Ca²⁺ and Mg²⁺ ions reduces the Na⁻ concentration needed to achieve the eutectic composition. The tested feed stream of the EFC installation, therefore, has a ratio similar to a spent regenerate stream concentrated by FC. The tested feed stream contains 12.1 wt% NaCl, 10.9 wt% CaCl₂ and 2.8 wt% MgCl₂. Salt and ice will start crystallizing around -26.0°C. The more NaCl will be
removed from the solution, the influence of the other ions will be greater, therefore the eutectic temperature will drop. This temperature drop will result in the recovery of NaCl salt. The recovery of the NaCl is given by the operating temperature of the crystallizer, processing this stream. For a larger temperature interval, the NaCl recovery will be higher, following the solubility line of NaCl in this multicomponent matrix. From previous experiments, at -35°C, concentration of NaCl is 4.1 wt%, giving a NaCl recovery of 66%.

The tests were run in such a way as to obtain the maximum achievable recovery of NaCl. For example, during one of the test runs (100 hours), the eutectic temperature started around -25.8°C and dropped to -26.7°C in 13 hours. Figure 6 shows the logged temperature profile in the crystallizer. The high jump in temperature is caused by human error resulting in a temporary shutdown (approximately three hours) of the machine.

From the crystallizer and settler system, two slurries, containing mother liquor and crystals, are being extracted. From the top of the settler ice slurry is removed and from the bottom of the crystallizer salt slurry is extracted from the system. The solid liquid mixture has to be separated into a solid and a liquid. By filtration this can easily be done. However, some mother liquor is bonded to the solid crystals, causing contaminations in the products. Washing of ice and salt crystals can reduce the impurity in the products. For washing ice crystals, demi water or fresh regenerate can be used and for washing the crystal of NaCl, saturated solution of NaCl can be used. Experiments at the DWP Botlek have shown that the ice from the belt filters contained 6% NaCl impurity without any washing. However, the NaCl concentration could be reduced to around 1% by single step washing with demi water (300 mL per Kg ice). Impurity can further be reduced by integrating multiple step washing of ice.
The NaCl salt coming out of the crystallizer to the belt filter is fairly clean, having only a slight concentration of CaCl₂ and MgCl₂ (total under 3 wt%). As the NaCl is produced in an aqueous environment, a hydrated form of salt will be present, most probably NaCl*2H₂O. On the belt filter, the crystal water can be partly removed, which will wash away the CaCl₂ and MgCl₂ adhering mother liquor. Tests still need to be run to validate this. Another possibility would be to use a small amount of saturated NaCl solution at positive temperatures to wash away the adhering liquor, although the impurity level is not significant and shall not prevent the use of salt in applications where high purities are not required.

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Future outlook and opportunities

Conventional salt recovery or waste stream treatment processes in several cases consume too much power and generate too much chemical waste. The environmental awareness of the governments and society pushes the technology developers and the users for more sustainable technologies with reduced waste generation and energy consumption. Eutectic Freeze Crystallization offers potentially an economically, environmentally and socially attractive alternative for conventional separation techniques. A wide variety of process and waste streams can be treated with EFC, recovering both pure salt and ice crystals simultaneously from the feed stream using less energy and generating less waste. Moreover, huge amounts of valuable industrial aqueous streams that are currently too energy intensive to be treated, could be commercially decomposed into valuable materials when using EFC technology. The separation burden will be changed into a blessing by producing raw materials from waste streams by spending less energy. This is in line with the green concept: ‘from cradle to cradle’.

References


Authors

Danny Harmsen has worked at KWR for more than 20 years. Since 2003, Danny has worked as a researcher in the water systems and technology group, with specialisation in drinking water treatment. Danny is involved in projects related to membrane filtration (RO and FO) and advanced oxidation. Danny has been involved in the development of the ARO concept (reversing pollution of membranes by means of air-water flushing) and the OMBR concept (a system to purify wastewater with forward osmosis membranes). He has been involved in research into the development of a new type of UV lamp and a model that can help to predict the destruction of organic micropollutants with a UV/H₂O₂ reactor.

Arslan Ahmad is an internationally oriented water professional and a leading Research Scientist at KWR Watercycle Research Institute, with particular focus on the removal and recovery of (trace) metals from drinking water and aqueous waste streams. Arslan Ahmad is an elected member of the Executive Management Committee of the IWA Specialist Group on Metals and Related Substances.

Dragos Petrutiu finished his MSc in Water Technology from the Wetsus Academy, in the Netherlands. Dragos joined the EFC Separations B.V. in Rotterdam, a company that develops and commercializes the Eutectic Freeze Crystallization technology, due to his interest in thermodynamics and crystallization. Dragos is currently involved in the up-scaling of the EFC process from lab scale to operational pilot units, able to be deployed on industrial sites.

Vincent Toussaint studied chemical engineering at the University of Delft and graduated in the field of thermodynamics. Currently he works as a chemical engineer for Evides Industrial Water. Providing advice for several production facilities on the production of demineralized water, with expertise on ultrafiltration, sand filtration, reverse osmosis and ion exchange. Besides that he takes part in the design of new facilities and research projects.