Thermal-based technologies for the recovery of high-purity water and marketable salt as part of a ZLD system

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Introduction

The accumulation of salts in rivers and lakes from the secondary salinization (anthropogenic origin) through brine disposal creates an urgent ecological issue [1]. Hard coal mining in the Upper Silesian Coal Basin is the major contributor to the salinization of Poland's two largest rivers (Oder and Vistula rivers), which, together with their tributaries, cover as much as 70% of the national water demand. A study by Greenpeace conducted in 2022/2023, identified brine disposal from the mining industry as a major issue in Poland and proposed the implementation of modern desalination technologies by mining companies to mitigate this significant impact on water basins [2].

The Zero Liquid Discharge (ZLD) systems is a proposed solution and have been assessed for their implementation and efficiency in several studies and different streams. A ZLD system can be separated in three main sections, (a) the pre-treatment, (b) the concentration and (c) the thermal treatment. At the pre-treatment stage usually the suspended solids and the turbidity are reduced in order to protect the following systems. At the concentration step, membrane technologies, such as Reverse Osmosis (RO) and Electrodialysis (ED), are usually utilized in order to recover water. At the thermal treatment the systems of evaporation and crystallization are engaged in order to achieve the goal of the Zero Liquid Discharge, with the recovery of salts and distillate water.

The EU project LIFE BRINE-MINING, by identifying the ecological issue of Poland, has proposed a ZLD system that aims to treat the saline wastewater that derives from the Ziemowit coal mine with the recovery of salts (NaCl, $Mg(OH)_2$, $CaSO_4$, $CaCO_3$) and high purity water. The final step of this system is a Multi Effect Distillation (MED) evaporator and a Crystallizer. During the operation in Poland, the two systems operated achieving the recovery of dry Sodium Chloride (NaCl) salt, and high-quality distillate water.

Materials and methods

The two systems have been installed and operated in Poland through the implementation of the project. The MED evaporator has been designed to concentrate NaCl from 17.9% to 23.4%, following the principles of multi-effect distillation process. Featuring 5 evaporation effects in a forward feed configuration, the inflow of the system is transferred from one effect to the next, progressively increasing its solid content. In the first effect, brine is sprayed on the heat exchanger of the effects, which consists of horizontal tubes in rectangular arrangement. Service steam flows inside the first effect tubes and condenses as it transfers latent heat to the brine. The water content of the brine is evaporated on the external surface of the heat exchanger tubes. Then, in the form of superheated steam, it flows from the first effect to the inside of the heat exchanger tubes of the second effect, where it condenses to water, transferring latent heat to the brine of the second effect. Water is then subcooled further, recovering most of the heat content before it is collected in the water product vessel. The same process applies to all effects progressively. Steam from the last effect is condensed in a special condensing plate heat exchanger, using cooling water (brine) from the nearby pond.

The Crystallizer is designed to treat the concentrated stream of the MED evaporator. The system consists of a vertical rectangular tank and operates under vacuum. The bundle of the system is filled with saline influent up to 3.5 m. In the center of the crystallizer there is a coil connected with a vacuum pump. Under the influence of vacuum, water begins to evaporate from the surface of the saline effluent. The vapors enter the coil tube, passing through it, and the steam condenses and releases energy, through the walls of the coil, transferring it to the saline influent. Through a compressor, heat is transferred from the bottom of the unit to the top, maintaining constant evaporation. The salt from the evaporation smoothly falls and collected at the bottom of the unit. When enough quantity of salt accumulates at the bottom of the unit, is removed through a special outlet into a hydrocyclon. The hydrocyclon separates the crystallized solid salts from the saturated solution, which is returned to the crystallizer unit. The crystallized salt is collected to special bags for drainage obtaining a salt with final moisture of around 20%. In case further drying of crystals is needed a drying system can be utilized.

Results and discussion

During the operation in Poland, the mean inflow of the MED evaporator was around 179,000 mg/L (17.9%). The produced distilled water had a TDS concentration of approximately 80 mg/L (0.008%). The overall scope of the system was concentrating the inflow 1.3 times (Concentration Factor of 1.3 or 25% system recovery) and this goal was achieved resulting in a concentrated stream of around 234,000 mg/L (23.4%). The previous steps of the ZLD system ensured that the influent stream to the MED evaporator primarily consisted of sodium and chloride ions, which together accounted for 98.6% of the total TDS content. The remaining ions accounted only 1.36% of the overall TDS. The highly selective removal of ions during the pre-treatment and the concentration stages acted as a foundation for the recovery of high purity salt at the end of the process. The system's overall 25% recovery rate, resulted in the production of distillate water with density and purity that meet high standards, making it suitable for various applications requiring very pure water (e.g. industrial sector). The MED system had a mean specific energy consumption of 9 kWh/m^3.

Regarding the operation of the Crystallizer unit, the overall evaluation showed very promising results. At the end of the process, a high purity salt was recovered (up to 98%) of NaCl with low specific energy consumption, 4.6 kWh/m^3. The crystallizer can result to the recovery of 72 kg/h of NaCl salt and up to 0.26 m^3/day pure water. The recovered water from the crystallizer unit, achieved very low ion concentration.

	Conductivity (μS/cm)	**TDS**	**K^+**	**Na^+**	**Ca^{+2}**	**Mg^{+2}**	**Cl-**	**SO_4**
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Sample	177	81.1	0.11	23	4.1	3.1	49	1.8
Sample	136	90.5	0.09	26	2.4	4.9	55	2.2
Sample	190	78.5	0.21	24	3.2	2.1	47	2.1
Sample	255	84.5	0.08	21	4.1	5.3	52	2.1
Sample	230	78.3	0.10	19	5.3	3.9	47	3.2
Sample	210	85.1	0.10	22	4	4.3	53	1.7
Sample	145	78.5	0.06	21	3.6	3.8	48	2.1
Sample	108	81.4	0.08	23	4.1	3.5	49	1.8
Sample	132	80.3	0.11	22	2.9	4.1	50	1.2
Sample	95	84.9	0.10	23	4.2	4.2	52	1.6
Sample	120	80.9	0.04	24	2.5	3.1	49	2.3
Sample	109	70.4	0.15	22	1.9	2.2	42	2.2

Conclusion

The thermal technologies are the precondition to achieve the ZLD goal. However, the high energy consumption hinders their broad adoption in the market. The thermal systems presented in this work, have been designed to address this issue with innovative energy recovery sub-units and low temperature evaporation. The high achieved concentration factor, the recovery of high-purity water and the low overall energy consumption, showcase that those two systems are a great fit of a ZLD system.

References

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