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Desalination of hypersaline brines with joule-heating and chemical pre-treatment: Conceptual design and economics

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ABSTRACT

Conventional seawater desalination technologies and fossil energy operations produce large volumes of hypersaline brines requiring proper management. Zero liquid discharge desalination processes can offer an economic and environmentally responsible method to manage these complex streams. The objective of this study was to assess preliminary economics for a novel Joule-heated desalination process design. Aspen Plus® was employed to model two scenarios, one with a chemical precipitation pretreatment using sodium sulfate, sodium hydroxide and calcium carbonate (scenario A) and the other using CO_2 instead of calcium carbonate as precipitating agent in the pretreatment stage (scenario B). The conditions for the water desalination step were 22.1 MPa and 430 °C. Internal Joule-heating provides the energy in the supercritical water separation step. The preliminary economic model projects a cost of \$4.29 per m^3 feed (\$0.68/bbl feed) for scenario A and \$7.10 per m^3 feed (\$1.13/bbl feed) for scenario B.

1. Introduction

The water desalination industry experienced exponential growth through 2010 in response to increased global fresh water demand [1]. Over the past six years, there has been a sharp decline in worldwide contracted desalination capacity, resulting from the lingering effects of the 2008 economic downturn. However, this contracted capacity is expected to increase as the global population increases at a projected rate of 80 million people per year. The UN Water Coordination Mechanism predicts freshwater demand will increase to > 60 billion m^3 per year. With only 3.5% of global water resources being freshwater, research is currently focused on making desalination processes less energy intensive with greater cost-competitiveness and sustainability.

In general, natural or produced saline water sources can present different levels of salinity. Brackish water refers to a water that has a higher salinity than freshwater but lower salinity than seawater. The standard ocean seawater salinity is 3.5 wt% (35 g of salt per liter). Hypersaline water sources have salt concentrations that surpasses that of seawater ($>$ 3.5 wt%).

Today, there is an increasing demand for desalination of man-made sources of hypersaline waters. For example, in seawater desalination, conventional water recovery plants produce vast amounts of hypersaline water globally [1]. Giwa et al. recently reviewed technologies for managing reject brine and highlighted the need for minimization and reuse of these streams by recovering value-added chemicals such as salts and metals [2]. Another example is hydraulic fracturing. In the U.S. alone, it is estimated that from 2008 to 2014, 930 million m^3 of water were employed in hydraulic fracturing operations [3] resulting in nearly an equivalent volume of flowback and produced impaired waters requiring management. Other energy-related operations, such as geological CO_2 sequestration, may also produce large amounts of extracted hypersaline water streams over an extended period of time [4–6].

Some hypersaline wastewater streams can be disposed back into the ocean, recycled or injected into local underground wells. However, when these options are not viable, a less favorable option is the disposal of the saline wastewater in publicly owned treatment works (POTWs). However, POTWs are not designed for wastewater desalination or removal of certain trace heavy metals, resulting in their discharge to the local watershed [7]. In the U.S., the EPA under the Clean Water Act (CWA), establishes regulation for the disposal of wastewaters in POTWs to prevent discharge of pollutants, with many states banning this practice altogether. Therefore, as a result of the combination of more restricted regulations and disposal costs (e.g., wastewater transportation and industrial wastewater treatment fees) and the demands of the water markets, the exploration of in situ desalination treatment alternatives has become more attractive.

In terms of final product form, desalination processes can be broadly divided into two main categories: water recovery (WR) processes, and

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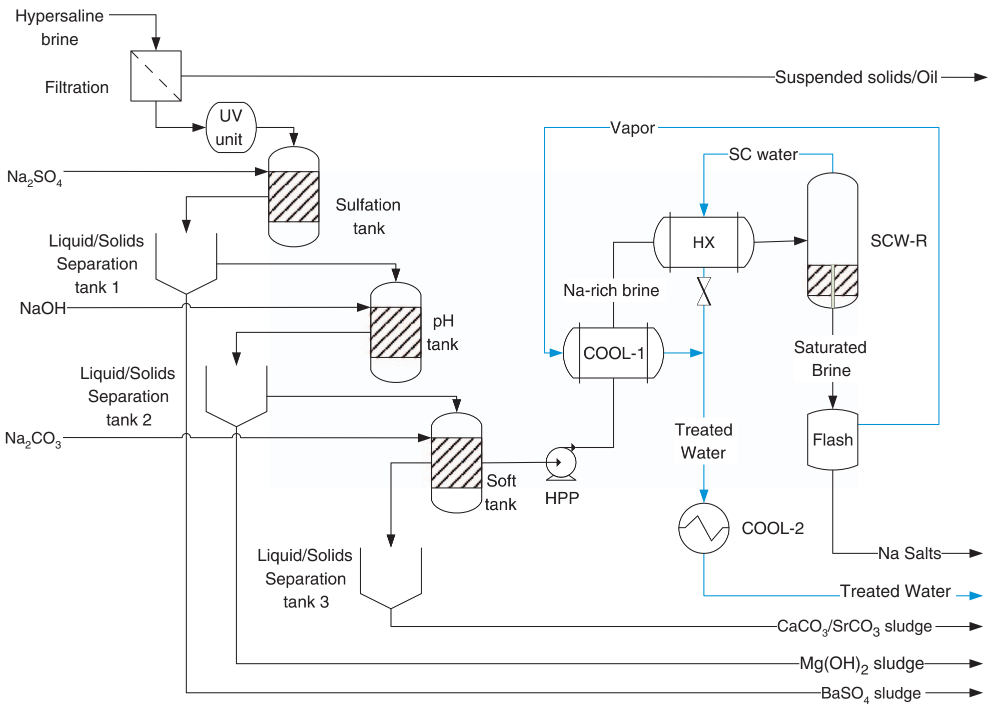

Fig. 1. Process flow diagram of the multi-stage SCW desalination of hypersaline water with chemical precipitation pretreatment and zero liquid discharge.

zero liquid discharge (ZLD) processes. WR processes are the least expensive and most common approach to desalination. Some examples of this type of desalination processes are mechanical vapor compression (MVC) [8,9] and reverse osmosis (RO) [10,11]. These methods produce a treated water stream and a concentrated – typically hypersaline – brine product. In contrast, ZLD processes produce a treated water stream and a solid mineral product.

While water recovery processes have been extensively studied, there are very few studies dealing with ZLD processes [17,18]. Morillo et al. recently reviewed a number of WR and ZLD technologies and concluded ZLD processes incur very high desalination costs [19]. Little is known about the cost of supercritical water (SCW) desalination which is an emerging technology based on the changing polarity of water under supercritical conditions. Inorganic salts are separated from less polar water as a result of reduced solubility [20]. Therefore, the main water/salt separation occurs at supercritical conditions leaving no concentrated liquid stream behind. The challenge of the SCW-ZLD process is the corrosive environment - due to high chloride concentrations – and energy requirements.

To the best of our knowledge, there is no peer-reviewed literature available on conceptual economics of the SCW-ZLD desalination processes. In this study, we present an initial estimate for the economic feasibility of a SCW-ZLD desalination process that employs internal Joule heating. This methodology allows the desalination process to utilize fossil and/or renewable electrical power, when low-cost power is available at off-peak time periods. Two pretreatment cases were considered, one using chemical (sodium sulfate, sodium hydroxide and sodium carbonate) precipitation pretreatment and the other utilizing CO_2 as softening agent in the brine pretreatment stage instead of sodium carbonate. This study also provides for the first time a model in Aspen Plus® for the SCW-ZLD desalination including salts.

2. Conceptual process design and economic assessment

2.1. Conceptual process design

A hypersaline brine feedstock may contain significant amounts of suspended and/or dissolved inorganic and organic contaminants. In order to treat these impaired water streams, a multi-stage desalination concept with ZLD was developed in this study. The desalination pathway can be divided into three main processing areas: 1) primary water treatment, 2) chemical softening, and 3) supercritical water salt separation. A brine flow rate of 113.6 m^3 per hour (500 GPM) at 25 °C and 0.1 MPa (1 bar) was selected as the input basis for the design.

In primary treatment, suspended solids are usually separated by sock-filtration or sedimentation. Also at this stage, insoluble organic substances, such as free and emulsified oils are typically separated from water by employing membranes [21], hydro-cyclones or centrifuges. The treatment for microbial contamination was also considered part of this first area. Commercial UV light treatment has been shown to effectively deactivate bacterial DNA. Therefore, the filtered brine is treated with UV light before chemical treatment, where 99.9% of the bacterial contamination is assumed to be removed.

After the separation of suspended contaminants from the brine in the primary treatment stage, softening can be used to reduce the amount of total dissolved solids (TDS). The ions usually present in hypersaline water streams are monovalent cation Na^+, alkali earth metal cations Ca^{2+}, Ba^{2+}, Mg^{2+} and Sr^{2+}, and anions, Cl^- and SO_4^{2-}. Other ions typically present in minor proportions include, K^+, Li^+, Fe^{+2}, Ra^{+2}, Fe^{+3}, Co^{+2}, Co^{+3}, Mn^{+2}, Br^-, NO_3^-, and HCO_3^- but were considered out of the scope of the current model. In this study, an averaged composition of a hydraulic fracturing produced water obtained from the literature was chosen to represent the water chemistry of the hypersaline water system. The ion concentrations were averaged from field-derived produced water samples generated from the Marcellus shale [22]. Bicarbonate (HCO_3^-) was found in a single sample at very low concentration (48 mg/L) so it was not included in the model. Hence, only chloride and sulfate were considered. To preserve electro-neutrality, Cl^- was adjusted to 90,869 mg/L, which is $<$ 5% different from the reported average Cl^- value for these samples, 86,457 mg/L [22].

Alkaline earth metals, such as Ca^{2+}, Ba^{2+}, Mg^{2+} and Sr^{2+} can readily form sulfate and carbonate scales even at low temperatures. Therefore, the objective of the softening steps is to reduce the concentration of potential scale-forming salts before thermal desalination treatment. Two scenarios were considered for the softening step: A)