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The integration of desalination plants and mineral production

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ABSTRACT

A noticeable increase in the number of seawater reverse osmosis (SWRO) desalination plants has been observed during the last decade. This is due to the low energy consumed by reverse osmosis technology and the high freshwater recovery when compared to other desalination technologies. The desalination of seawater is the main source of freshwater in Kuwait. However, SWRO desalination plants generate huge volumes of concentrated brine, which is considered a potential source of mineral content. Some of these minerals are expensive and scarce on earth. The recovery of these minerals from brine can help in increasing the freshwater recovery, reducing the overall cost of desalinated water, offering a new source of raw materials, and decreasing the environmental impact from discharging brine to the sea. This study gives an overview of the different technologies used for the treatment of SWRO brine and explores the benefit to recover and reuse valuable potential minerals in brine. The study is motivated by the strong need to establish a local industry in Kuwait based on the extraction of potential valuable minerals from SWRO brine. Such industries can be combined with desalination plants to form a complex cogeneration of plants that accommodate desalination and power plants.

Keywords: Reverse osmosis; Brine; Mineral production

1. Introduction

Sustainability and availability of fresh potable water has become a worldwide concern for many countries. The Middle East and North Africa (MENA) countries are considered as the highest water scarcity than any other region. Population growth, increasing demand of water, global climate change, and shrinking of water led to rapid depletion of available resources. The integration between electricity and desalination of seawater to produce freshwater is a common principle in MENA countries. Unfortunately, seawater desalination is energy intensive and depends on the burning of fossil fuels, which has negative impacts on the environment due to the emission of greenhouse gases that contribute to global climate change (noticeable interest and an urgent need are emerged since the last decade to increase water production and reduce water costs, as well as reduce pressure on the environment). Over the last decade, an urgent need and noticeable interest has generated to increase water production, reduce water costs, and reduce pressure on environment.

The Global Water Intelligence [1] reported that the total global desalination capacity is 66.4 million m^3/d and is expected to be 100 million m^3/d by the year

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2015. The report showed the most common technologies used worldwide (Table 1). These technologies are reverse osmosis (RO) and multistage flash (MSF) technology, which present almost 60 and 26%, respectively, of the total global desalination capacity.

1.1. Desalination in Gulf Cooperation Council

The largest number of desalination plants worldwide is located in the Gulf Cooperation Council (GCC) region where most of the desalination plants are integrated with power plants for energy production. GCC consists of six country members that include the Kingdom of Saudi Arabia (KSA), the United Arabs Emirates (UAE), Oman, Kuwait, Bahrain, and Qatar. The GCC region is located in arid ecosystem areas therefore suffers from water scarcity and limited renewable water resources. Mezher et al. [2] expected that by the year 2030, the water resources would decrease to less than 50% when the population growth reaches 56 million people. Thus, the desalination plants in the GCC region can be used to fulfill the increase in freshwater demand caused by the increase in population.

Dawoud and Mulla [3] studied the environmental impacts of seawater desalination in the GCC region. They mentioned that in year 2012, the total number of desalination plants in GCC was more than 199 plants and they expected to build more than 38 desalination plants in the nearest future. In addition, they found that the total capacity of seawater desalination plants in the GCC region is about 5,000 million m^3/year, which represents ≃45% of the total worldwide production and is expected to increase to 9,000 million m^3/year by the year 2030.

The common desalination technologies used in the GCC region are MSF, Multiple Effect Distillation, and RO. The RO technology is now the most common membrane technology applied in seawater desalination to produce freshwater in the GCC region. In addition, when compared to other desalination technologies, RO technology has the advantage to produce the highest water production with the lowest footprint and low cost. Freshwater produced by RO technology varies between 40 and 50% of the feed seawater, which is limited by trans-membrane pressure [4]. This means that 50–60% of the seawater feed stream is rejected as waste named brine, or concentrate, with high total dissolved solids (≃70,000 ppm) [5]. Therefore, the huge volume of concentrated brine generated from RO desalination plant should be treated and managed carefully to enhance the environmental sustainability and the overall desalination process.

Table 1
The total global desalination capacity by technology

Technology	Capacity (%)
Reverse osmosis (RO)	59.85
Multi stage flash (MSF)	25.99
Multiple effect distillation (MED)	8.2
Electrodialysis (ED)	3.53
Hybrid	0.71
Others	1.02

The key environmental issues related to seawater desalination technologies are the high salinity brine discharges to the marine environment and the energy demand. These key issues are considered as major environmental problems that can impact and cause a potential serious threat to the marine ecosystem surrounding the desalination plants. Roberts et al. [6] reported from laboratory experimental and toxicological investigations that the discharge of rejected brine to the sea impacts aquatic organisms and especially fragile ecosystems such as corals. In addition, as a result of the direct discharge of the brine to sea, certain contaminated heavy metals, such as copper, iron, zinc, nickel, chromium, can cause water eutrophication, accumulation of those heavy metals, and variation in seawater pH and temperature [7]. The environmental impact of desalination plants depends on the location of desalination plant, the concentration of the inlet and outlet streams, and the technology used in the desalination plant. Another important issue to be considered is the brine disposal cost, which depends on its characteristics, volume, and method and level of treatment before being discharged to the environment. For coastal desalination plants, the cost to dispose brine to the sea ranges from 5 to 33% of the total desalination cost, while the cost of brine disposal is higher for inland desalination plant [7,8]. Concentrated brine is a growing problem of serious consequences posing major challenge to the future of desalination process. However, the concentrated brine contains valuable elements such as sodium (Na), magnesium (Mg), potassium (K), calcium (Ca), chlorine (Cl), sulfate (SO_4), iodine (I), bromine (Br), boron (B), strontium (Sr), and lithium (Li). Extraction of elements is a powerful approach offers a multifaceted solution to this growing problem. By extraction elements from such waste stream and getting converted into much needed, usable, good quality minerals that are ready to replace and save part of the current over consumed non-renewable minerals used in several industries.

The world mine production and major end uses of minerals are shown in Table 2 [9–11]. The data shown in Table 2 present the massive amount of minerals

Table 2
World mine production, resources, and end uses for valuable minerals

	World mine production (million tons)			
Mineral/year	2012	2013	World resources	Major end uses
Sodium chloride (salt) (metric tons)	259,000	264,000	World resources of salt are unlimited, and the salt content in the oceans is virtually inexhaustible. Nearly all world countries have salt deposits or solar evaporation operations of various sizes	Sodium chloride is used in the manufacture of chemical feedstock, chlorine, caustic soda, for highway deicing, for food processing, and for agricultural and primary water treatment
Magnesium compounds (metric tons)	802	910	Natural resources from which magnesium may be recovered vary from large to unlimited and are globally widespread. Magnesium produced from brines is estimated to be billions of tons	Magnesium is used in the manufacture of refractory's, agricultural fertilizers, construction materials, and chemicals
Sodium carbonate (soda ash) (metric tons)	13,900	14,200	Soda ash is obtained from trona, which is a gray mineral of a hydrated carbonate and bicarbonate of sodium. Soda ash is rich in brine. The world's largest deposit of trona is in the Green River Basin of Wyoming, USA, which is being depleted at the rate of about 15 million tons/year. Overall, global demand for soda ash is expected to increase annually by 1.5–2% in the following years	Sodium carbonate is used in the manufacture of glass, chemicals, soap, detergents, flue gas desulfurization, pulp and paper, and in water treatment
Potassium oxide (potash)	32,700	34,600	An estimated total world potash resource is about 250 billion tons. The world's largest resource of Potash is in Belarus and Canada. World consumption of potash, for all applications, is expected to increase by about 3% per year over the following years	Potash is used in the manufacture of fertilizers and chemical industries
Bromine	505,000	560,000	Bromine is found principally in seawater. The world's largest resource of Bromine is in Jordan, the Dead Sea, which is estimated to contain one billion tons of bromine. Seawater contains about 65 ppm of bromine, or an estimated 100 trillion tons. Bromine is recovered from seawater as a by-product during evaporation to produce salt	Bromine is used in the manufacture of dyes, perfumes, pesticides, insect repellents, pharmaceuticals; in drilling fluids water treatment, mercury control, flame retardants, photographic chemicals, and paper
Boron (metric tons)	4,420	4,900	Deposits of borates are associated with volcanic activity and arid climates. The largest economically viable deposits are located in the Mojave Desert, USA, the Alpide belt in southern Asia, and the Andean belt of South America	Boron is used in the manufacture of glass, ceramic, detergents, fertilizer, abrasives, insecticides, and in the production of semiconductors
Lithium (metric tons)	435,000	435,000	Lithium resources are 5.5 million tons in the United States and approximately 34 million tons in other countries such as Bolivia, Chile Argentina, China, Australia, Canada, Russia, Serbia, and Brazil	Lithium is used in the manufacture of ceramic, glass, batteries, lubricating greases, continuous casting mold flux powders, in air treatment, polymer production, and primary aluminum production

(*Continued*)

Table 2 (*Continued*)

	World mine production (million tons)			
Mineral/year	2012	2013	World resources	Major end uses
Calcium carbonate (limestone) (metric tons)	348,000	350,000	World resources of limestone and dolomite are very large	Calcium carbonate is used in the manufacture of fertilizers, and in fluxing and sulfur removal
Calcium sulfate (gypsum)	152,000	160,000	Gypsum reserves are large in such as Canada and Mexico. A total of 83 countries produced gypsum in the year 2013	Calcium sulfate is used in the manufacture of wall board and plaster products, cement, and fertilizers
Iodine	328,000	328,500	Seawater contains 0.06 parts per million iodine, or approximately 90 billion tons	Iodine is used in the manufacture of many intermediate iodine compounds, surfactants, pharmaceuticals, and disinfectants
Strontium	228,000	245,000	World resources of strontium are thought to exceed 1 billion tons	Strontium is used in the manufacture of glass, pharmaceuticals, alloys, pigments, and toothpaste

produced by mining, which can lead, in the long term, to the depletion of non-renewable minerals. In addition, mineral production requires large amounts of energy and water, which may affect water shortage and fossil fuel in the future and constrain mining production. Therefore, it is of utmost importance to look toward an alternative mineral resource to decrease the depletion of natural mineral resources, avoid the impact produced by mines and extraction technologies, and meet the increasing demand of minerals in industries. Figs. 1–9 show the trend in variation price and sources for different minerals between year 2009 and 2013 [10]. Most of the prices of minerals decreased in 2010 and then increased in the following years. Iodine, strontium, and magnesium are the most expensive elements. In the year 2013, a metric ton of magnesium was US$3,170, where as a kilogram of iodine and strontium was US$42 and US$67, respectively. Table 2 and Figs. 1–9 illustrate the huge amount of minerals produced from non-renewable sources, which in the long term affect mining processes and cause depletion of natural mineral resources. For example, sodium chloride is very rich in seawater reverse osmosis (SWRO) brine and is considered to be a valuable source for many chemical industries and can be easily converted to saleable

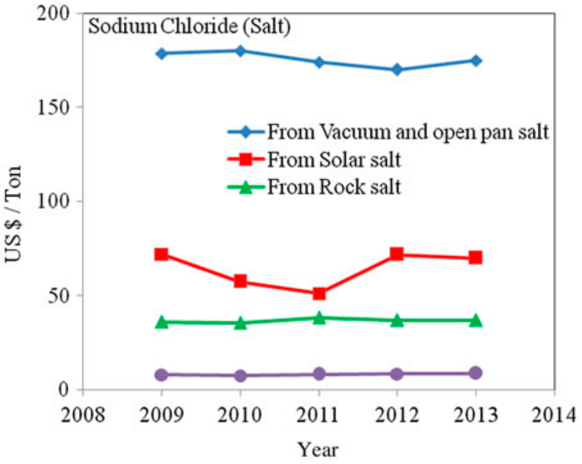

Fig. 1. Trend price variation for sodium chloride.

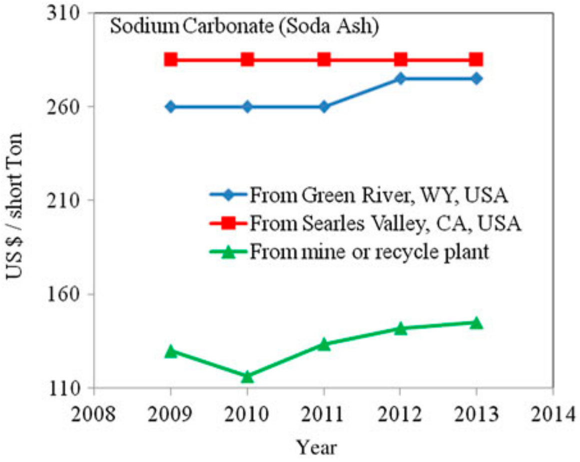

Fig. 2. Trend price variation for sodium carbonate.

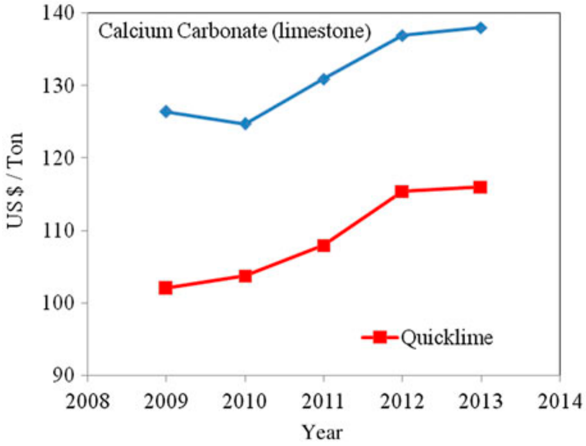

Fig. 3. Trend price variation for calcium carbonate.

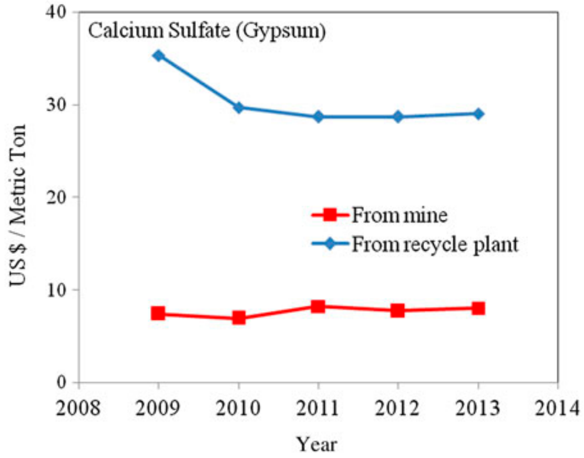

Fig. 4. Trend price variation for calcium sulfate.

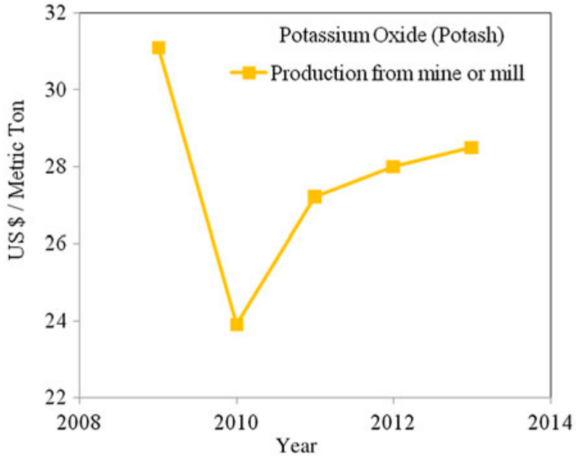

Fig. 5. Trend price variation for potassium oxide.

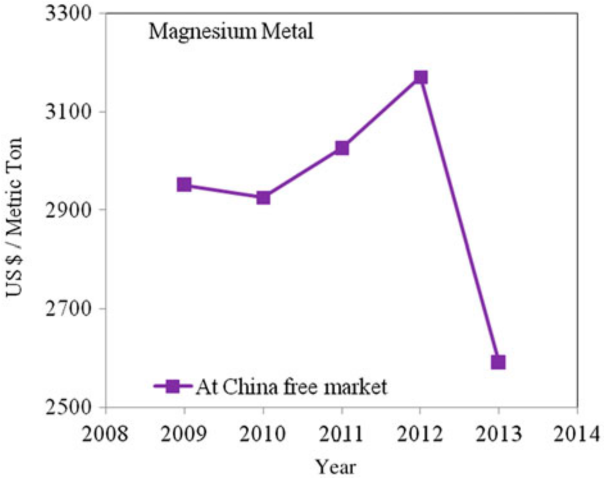

Fig. 6. Trend price variation for magnesium metal.

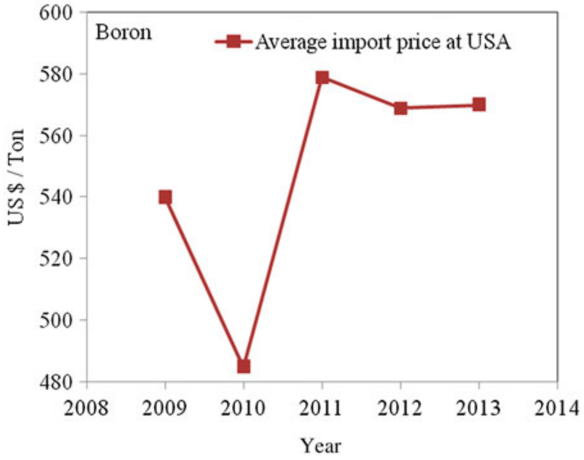

Fig. 7. Trend price variation for boron.

products. In 2012, 28 companies in the United State of America (USA) were operating 67 salts producing plants and selling it at a total value of more than US $1.6 billion. Likewise, Gypsum (Calcium sulfate) is rich in SWRO brine and used mainly in construction. In 2013, the production of crude gypsum in USA was estimated to be 16.3 million tons with a value of about US$130 million. The other minerals are much higher in values, according to the US Geological Survey (2014).

Hence, the recovery of minerals from concentrated brine would provide two main benefits:

(1) Economically, by converting minerals to commercial saleable products. In addition, increasing total water recovery and reducing the cost of desalinated water [12,13].

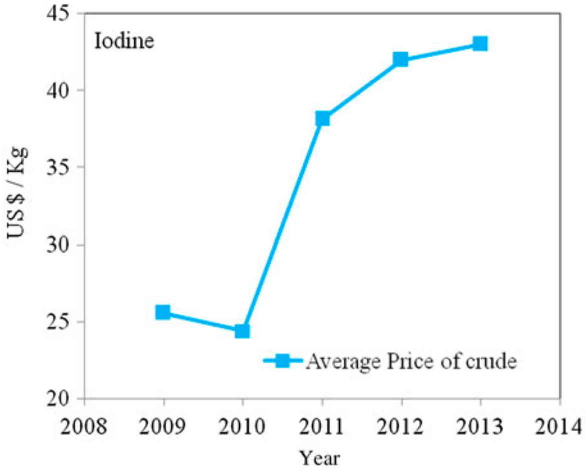

Fig. 8. Trend price variation for iodine.

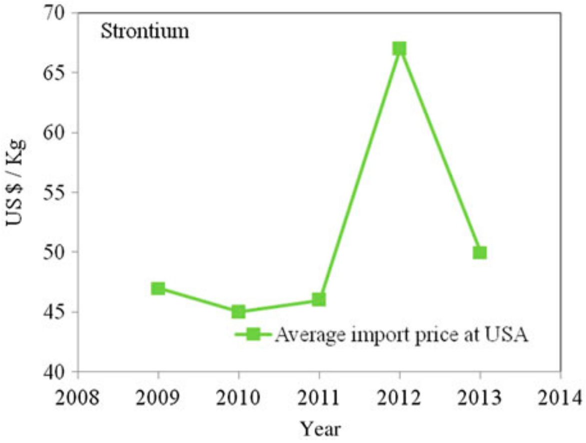

Fig. 9. Trend price variation for strontium.

(2) Environmentally, by discharging less concentrated brine to the Arabian Gulf, therefore decreasing the impact on the marine ecosystem and approach liquid zero discharge [14,15]. In addition, reducing the depletion in natural mining resources and the water and energy used.

1.2. RO desalination plants in Kuwait

Kuwait relies a 100% on desalination of seawater for domestic and industrial supplies [16]. In the year 2014, the total freshwater produced from the SWRO plant in Kuwait was 30 MIGD and is expected to be 160 MIGD by the year 2017 [17]. In the year 2014, the brine produced from the SWRO plant was 45MIGD and is expected to increase to 240 MIGD in the year 2017. As obvious as it appears, the expected huge production of concentrated brine from SWRO desalination plants is a growing problem with serious consequences and poses a major challenge to the future of desalination processes.

Therefore, this study reviews the different technologies used to recover valuables minerals from rejected brine from desalination plants. These minerals can be fed to several large chemical industries which in turn/and can be combined with the existing SWRO desalination plants to form more complex cogeneration plants to accommodate seawater desalination, power generation, and chemical industries for chlor-alkali, recovery of magnesia, bromine, potash, fertilizer, iodine, and in other industries.

1.3. Technologies for recovery of minerals from SWRO brine

Previous studies showed that the main technologies used to treat concentrated brine depended on several parameters such as climate, location of the desalination plant, salt concentration of feed seawater, and economic conditions. These technologies include solar evaporation ponds, wind-aided intensified evaporation (WAIV), electrodialysis (ED), ion exchange, eutectic freezing crystallization, membrane separation, evaporation, salt solidification and sequestration process (SAL-PRO), and crystallization and chemical processes. This study will review the most common and successful technologies used in desalination plants to treat brine and recovery valuables of minerals.

A solar evaporation pond is the common technology used to reduce the volume of concentrated brine produced from a desalination plant. Brine is disposed into evaporation ponds to allow the evaporation of water and the precipitation of salt. The salinity of brine affects the rate of evaporation, as when salinity increases, the rate of evaporation decreases. In addition, evaporation rates are dependent on wind speed, weather temperature, and vapor pressure. To obtain the highest evaporation rate of brine, Mickley et al. [18] suggested that the optimum pond depths should range from 25 to 45 cm. They also found that the drying and cracking of the liners of the evaporation pond are due to low depth (>25 cm). Ahmed et al. [19] studied the use of evaporation ponds for brine disposal. They determined the brine evaporation rate, and the evaporation enhancement methods in their study. In addition, they proposed the following formula to design evaporation ponds.

$$A_{\text{open}} = \frac{V_{\text{reject}} f_1}{E}$$

where A_{open} is the open surface area of evaporation ponds (m^2), V_{reject} is the volume of reject water (m^3/d), f_1 is a safety factor, and E is the evaporation rate (m/d). Evaporation pond technology is the least costly methods for brine disposal in countries with high evaporation rates and low land costs. They are easy to construct, require low maintenance and operation compared to other technologies. However, the disadvantage of evaporation ponds technology is the need for large tracts of surface area when evaporation rate is low or the volume of rejected concentrated brine is high. The productivity is also low, about 4 L/m^2d, and poorly constructed evaporation ponds can contaminate the underlying potable water aquifers.

Wind-aided intensified evaporation (WAIV) technology was developed to reduce the desalination footprint, total operating cost, and to accelerate the evaporation rate of brine. The evaporation process is a function of temperature, wind direction, wind speed, and relative humidity. WAIV technology uses natural energy sources such as solar and winds. The technology consists of a support structure, which includes a number of sheets suspended vertically from a support frame where the brine is distributed across those sheets. When wind passes across the surface of the sheets, the brine flows down in the vertical sheets, the concentrate falls, due to the evaporation of water, and the concentrated brine is collected at the base of the system. Both evaporation ponds and WAIV technologies are unfeasible for large amounts of disposal brine.

Literature reviews and studies show that the zero liquid discharge from desalination plants can involve two or more integration technologies. However, integrated technologies are complex and require high costs compared with other options. Nevertheless, salt and mineral production could contribute to reduce overall cost.

The combination of evaporation and cooling processes to recover salts is applied in desalination. Estefan and Nassif [20], Estefan et al. [21], Estefan [22], Lozano [23], Hammi et al. [24], and Hajbi et al. [25] studied the recovery of minerals from concentrated saline lake water and brine using evaporation and cooling. They allowed brine to evaporate until reaching a specific gravity of 1.240 to recover sodium chloride (NaCl) and then by cooling to (−10˚C), thenardite (Na_2SO_4) and bloedite ($Na_2SO_4MgSO_4{\cdot}4H_2O$) are recovered. Followed by evaporation, carnalite ($KMgCl_3{\cdot}6H_2O$) and langbeinite ($2MgSO_4{\cdot}K_2SO_4$) are recovered, and as a final product, bischofite ($MgCl_2{\cdot}6H_2O$) and kieserite ($MgSO_4{\cdot}H_2O$) are obtained.

Electrodialysis (ED) technology is developed at industrial scale to produce NaOH and HCl, which are highly required in industries. Electrodialysis technology can be combined with renewable energy such as solar and wind energy. However, electrodialysis is not suitable for highly concentrated brine due to scaling on the membranes. Turek [26,27] studied the dual-purpose for desalination and salt production using electrodialysis technology. He proposed a system of integration electrodialysis with MSF desalination forward by crystallization (ED-MSF-crystallization) where 90% water recovery is obtained. In addition, calcium, magnesium, and sulfate are recovered with a concentration of 3.35, 12.16, and 26.18 g/l, respectively. In addition, it is found that freshwater is produced at a cost of US\$0.44/m^3 by the integration of ED-MSF-crystallization system with an estimated salt production of 23.7 kg/m^3. Moreover, the hybrid system UF-NF-MSF-crystallization system is able to produce freshwater at a cost of US \$0.71/m^3, while for the UF-NF-RO-MSF-crystallization system, the produced water cost is US\$0.43/m^3.

Davis and Rayman [28] developed the technology zero discharge desalination to treat SWRO brines (Patent PCT/US03/24250). The technology aimed to increase the production of freshwater as well as recovery of valuable salts such as sodium chloride (NaCl), magnesium hydroxide $Mg(OH)_2$, and bromine (Br_2). This technology is based on the integration of ED technology and crystallization process. Researchers concluded that NaCl and $Mg(OH)_2$ in SWRO brine can be recovered by 75 and 99%, respectively, by pretreatment with Na_2CO_3. The mathematical model showed that about 0.38 tons of bromine ions could be recovered from 3.79 million m^3 of brine SWRO.

Tanaka et al. [29] examined experimentally the production of sodium chloride from brine rejected from a SWRO desalination plant using ion exchange membrane electro-dialectic. Researchers concluded that the energy consumption in a salt manufacturing process using the brine discharged from the SWRO desalination plant was less by 20% of the energy consumption in the process using seawater. During evaporation, electrodialysis can reduce the concentration of calcium or sulfate ions to eliminate the crystallization of gypsum. However, fouling by colloidal material, organics, and bio-growth should be treated to maintain the life time of the electrodialysis.

Lehmann et al. [30] presented an improvement to the extraction of magnesium from SWRO brine by proposing a new approach for cost-effective recovery of three magnesium solutions: $MgCl_2$, $MgSO_4$, and $Mg(HCO_3)_2$. The new approach is based on adsorption of $Mg(OH)_2$(s) to the surface of magnetite (Fe_3O_4) microparticles, followed by magnetic solids separation of the mixture from the bulk seawater brine. The results show a recovery of the three magnesium solution of more than 97%. In addition, researchers conducted a rough cost analysis showing that the production of $MgSO_4$ and $Mg(HCO_3)_2$ is attractive cost wise, while $MgCl_2$ can be produced at a cost that is similar to commercial products.

Jeppesen et al. [31] examined the potential economic impact of the recovery of three by-products (sodium chloride, phosphorus, and rubidium) from SWRO brine. They concluded that the recovery of sodium chloride can significantly reduce the cost of water production for integration of ultrafiltration–nano-filtration–reverse osmosis (UF-NF-RO) with MSF. Additionally, rubidium can be recovered using liquid–liquid extraction technology. Benzyl-phenol is used for the extraction, and the recovery of rubidium is more than 80%. Finally, removal of phosphorus from SWRO brine is slightly economic; however, it is environmentally important to decrease the eutrophication environmental problem that results from increasing phosphorus levels in seawater.

Le Dirach et al. [32] specified the potential valuable minerals that can be economically recovered from SWRO brine. The selection of elements is on the basis of economic, physical–chemical, and technical criteria. The elements are sodium, magnesium, potassium, rhodium, phosphorus, indium, cesium, and germanium. They recovered phosphorus through purification by alum (iron and aluminum sulfides), and cesium through liquid–liquid extraction technology using hydrochloric acid and calixarenes. Indium was recovered by liquid–liquid extraction using organic acids, and then, rubidium is recovered using cation exchange resin. Germanium and magnesium are recovered using hydrochloric acid at 90°C. Finally, sodium and potassium are recovered using electrolytic process.

Jibril and Ibrahim [33] conducted a series of chemical reactions in a laboratory to produce sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), and ammonium chloride (NH_4Cl) from concentrated sodium chloride (NaCl) solutions. Batch gas (ammonia) is bubbled to sodium chloride solution at 22°C to a ratio of 1:2 of NH_3/NaCl and followed by CO_2 gas. A highest NaCl conversion of 82.2% is obtained at these conditions.

Drioli et al. [34] developed an integrated membrane system to recover calcium carbonate, sodium chloride, and magnesium sulfate from nano-filtration brine. The system consisted of membrane, crystallizer, and chemical precipitator. The researchers found that this integration system improved freshwater recovery from 64 to 95% as well as for a feed flow rate of 1 m^3/h, the recovered sodium chloride, calcium carbonate, and hydrated magnesium sulfate are 35.5, 2.95, and 8.4 kg/h, respectively. However, it was found that the integration of MSF-ED and chemical process is relatively expensive in producing salts when compared to nano-filtration, membrane crystallization, evaporation, and ion exchange technologies.

Perez-Gonzalez et al. [35] presented an overview on the potential treatment technologies used to achieve the highest freshwater recovery and to extract valuable compounds contained in the brines. Recently, Perez-Gonzalez et al. [36] proposed a system to evaluate the viability to remove divalent ions (Ca^{2+}, Mg^{2+}, and SO_4^{2-}) from SWRO desalination brines to obtain a highly concentrated and purified NaCl solution. The proposed system consists of combined cationic- and anionic-exchange stages to remove divalent ions contained in SWRO brines.

1.4. Salt solidification and sequestration process (SAL-PROC)

It is an integrated process for the sequential recovery of a number of valuable by-products from rejected brine of desalination plants by evaporation, cooling, de-sulfation, crystallization, washing, and finally dewatering. SAL-PROC has already been evaluated for various desalination plants to recover valuable by-products from rejected brine streams as well as achieving ZLD. SAL-PROC is suitable for high saline brine that contains high concentrations of magnesium, potassium, and sulfate. The by-products produced from SAL-PROC are sodium chloride, calcium chloride, gypsum, calcium carbonate, magnesium hydroxide, and sodium sulfate. A desktop pre-feasibility study using SAL-PROC technology is conducted using real data resulting from four desalination plants in Oman [37]. The technical feasibility showed that the by-products produced are in high quality and in demand by various industries. Researchers estimated that by processing 405,000 m^3/y of SWRO brine, commercial by-products worth US$895,000 per year can be obtained. Arakel et al. [38] linked the operation of RO and SAL-PROC in a process known as ROSP, which enabled the recovery of useful salt minerals and chemical compounds such as $CaCO_3$, Na_2SO_4, and NaCl.

2. Conclusions

This study presents technical, commercial, and ecological overview of salt and mineral production from SWRO brine and focuses on the benefits and importance to integrate salt and mineral production with SWRO desalination plant. The cost prices of common salt and minerals found in brine are presented along with their potential end use in industries. Moreover, the common technologies used to extract valuable salt and minerals from brine produced from SWRO desalination plants are reviewed and evaluated according to their operational drawbacks and economic considerations. In addition, the pros and cons of each technology are discussed. Common recovery technologies include—evaporation ponds, wind-aided intensified evaporation electrodialysis, evaporation and cooling, liquid–liquid extraction, and other integration technologies such as membrane crystallization and conventional thermal technology, SAL-PROC, and ROSP technologies. Integrated technologies show good results for extraction of minerals and for achieving ZLD such as evaporation, cooling, precipitation, and crystallization. Mineral recovery from SWRO brine can provide a new source of potential, valuable, and scarce minerals on earth, which will help diversify national economy and provide new jobs, investment opportunities, and will help in increasing the Gross Domestic Product.

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