A State of the Art Paper on Improving Salt Extraction from Lake Katwe Raw Materials In Uganda

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Abstract

The characteristics of Katwe salt lake are briefly discussed. The lake is the largest of the eight saline lakes in the Katwe-Kikorongo volcanic field and is a major source of salt production in Uganda. Today, salt production at the lake is carried out using traditional and artisanal mining methods. Attempts to mechanize the production of domestic and commercial grade salt at the lake were unsuccessful due to the use of a wrong technology. In this paper, the most common available technologies for salt extraction from brine are described. These are divided into four broad categories, namely thermal, membrane, chemical and hybrid processes. A review of the state of the art, previous research and developments in these technologies is presented. A detailed analysis of the processes used was done based on studies reported in the literature. From the analysis, it was observed that thermal salt production processes, especially distillation and solar evaporation have the highest share in installed capacities worldwide. Membrane technologies such as Electro-dialysis, Reverse Osmosis and chemical technologies have not found wide application in the commercial salt industry. Electro-dialysis and Reverse Osmosis have been used mainly as pre-concentration processes for subsequent thermal processes. Prospects for application of hybrid systems for salt production through integration of thermal desalting processes should be investigated for better performance efficiencies and recoveries at the salt lake.

Keywords: Lake Katwe, salt, salt recovery and purification, separation processes.

1. Introduction

Salt, also known as sodium chloride, the most common evaporate salt is an ionic chemical compound which has a chemical formula NaCl. It is an inexpensive bulk mineral also known as halite which can be found in concave rocks of coastal areas or in lagoons where sea water gets trapped and deposits salt as it evaporates in the sun. Originally, salt was produced for human consumption purposes and later on its significant applications were discovered. This has made salt one of the most important commodities for centuries, comparable to the importance of oil in the present times (Korovessis and Lekkas, 2009). The use of salt as a food preservative together with its economic significance began to decline after the industrial revolution hence finding its extensive use in the chemical industry and other applications. There are more than 14,000 reported usages of halite, and it, along with other salts, has played a very important role in human affairs (Kilic and Kilic, 2005).
Today, the annual world production of salt has increased to an estimated 270 million tonnes (US Geological Survey, 2011). Statistics also indicate that the chemical industry accounts for about 60 percent of the total production followed by 30 percent for human consumption and lastly 10 percent for other applications such as road de-icing, water treatment, production of cooling brines, and in agriculture. The chemical industry uses the salt as a raw material for production of chlorine, caustic soda and soda ash for petroleum refining, petro-chemistry, organic synthesis and glass production (Sedivy, 2009).

Almost two thirds of the world countries have salt producing facilities, ranging from traditional solar evaporation in salt pans to advanced, multi-stage evaporation in salt refineries (Abu-Khader, 2006). Over 100 countries produce a significant amount of salt with many others on a small scale. The Chinese salt industry is the largest world producer of salt (US Geological Survey, 2011). In the year 2011, its production accounted for about 22.2 percent of the world’s total production followed by the United States at 16.7 percent. Other major producers are India, Australia, Mexico, Germany and Canada.

There are three methods used to produce dry salt based on the method of recovery (Abu-Khader, 2006).

(a) **Underground mining**: Also known as rock salt mining, this process involves conventional mining of the underground deposits through drilling and blasting whereby solid rock salt is removed. Mining is carried out at depths between 100 m to more than 1500 m below the surface.

(b) **Solar evaporation method**: This method involves extraction of salt from oceans and saline water bodies by evaporation of water in solar ponds leaving salt crystals which are then harvested using mechanical means. Solar energy of the wind and sun is used in the evaporation process. The method is used in regions where the evaporation rate exceeds the precipitation rate. Over a third of the total global annual salt production is produced using this method.

(c) **Solution mining**: Evaporated or refined salt is produced through solution mining of the underground halite deposit and removing the water from the saline brine which is pumped to the surface. The water is evaporated from the brine using mechanical means such as steam-powered multiple effect or electric powered vapour compression evaporators. In the process, thick slurry of brine and salt crystals is formed.

Among the above methods, solar evaporation is the most widely used salt production technique at Lake Katwe in Uganda. The process is carried out following ancient traditional and artisanal methods leading to low qualities and limited production. An attempt to mechanize the production of domestic and commercial grade salt from the lake was conceived in 1975 with a chemical plant being installed to enable purification of the brines. The plant was commissioned, worked for a few years and later collapsed mainly due to a poor design that subsequently led to corrosion of the poorly designed heat exchanger tubes (Mathers, 1994). Several attempts to revamp salt production through re-establishment of the plant or a process that would recover the salt together with its purification failed and thus the plant has remained inactive implying that the country’s salt resources have not been fully exploited to effectively contribute towards the country’s economic growth.
The objective of this study is to gain an understanding of the available salt mining and extraction technologies, determine the previous and current state of research in the salt recovery techniques, highlighting benefits and limitations of the processes with a view to devise suitable practical and sustainable methodologies that could be implemented in order to realize the commercial potential of Lake Katwe salt raw materials.

2. **Lake Katwe general characteristics**

2.1 **Location and Access**

Lake Katwe is the largest of the eight saline crater lakes within the Katwe-Kikorongo volcanic field in Western Uganda and situated on the floor of the western rift valley and south-east of the Rwenzori mountains (Figure 1). Preliminary investigative fieldwork studies indicate that the lake contains the best salt reserves evident in its brines and evaporate deposits. There are 22.5 million tonnes of crystalline salts in Lake Katwe which can sustain a plant for over 30 years at 40,000 tonnes/a NaCl production (UDC, 1997).

![Figure 1: Location of Katwe salt deposit and surrounding areas (Hinton, 2011)](image)

Apart from Lake Katwe, it is reported that limited quantities of salt for human and animal consumption have been extracted from the hot spring waters at Lake Kibiro located in the Albertine region and at Lake Kasenyi on the shores of Lake George. At Kibiro, salt is produced from the waters of the spring and the saline muds around the lake. Reserves for industrial salts such as Trona also occur at Katwe, Kasenyi and Kibiro respectively. They however exist on a larger scale at Lake Katwe and Kasenyi (Mathers, 1994).

2.2 **Geological setting**

The salt lake lies on the floor of an explosion crater formed in tuffs with about 230 meters of rock separating Lake Edward from the crater at the closest point. The explosion crater ejected pyroclastics, tuffs with abundant granite and gneissic rocks from the basement which dominate the area (Figure 2). The volcanic rocks are mainly composed of pyroclastics and
ultramafic xenoliths which are deposited on the extensive Pleistocene lacustrine and fluvial Kaiso beds and in some places directly on Precambrian rocks. The salinity of Lake Katwe and the other closed saline lakes is derived mainly by evaporative concentration of mineral spring waters (Arad and Morton, 1969). The saline spring waters filled the crater during Pleistocene vulcanism. Suggestions have indicated that salt has also been leached out of the surrounding tuffs by water percolating from Lake Edward into Katwe crater which lies about 30 m below the fresh lake level (Barnes, 1961).

![Image: The geology of the Katwe-Kikorongo volcanic field and surroundings (Bahati and Natukunda, 2008)](image)

2.3 Climate

Although there is not much detailed meteorological data available, the region experiences two dry seasons between January to March and July to September every year. It is within these periods that salt is traditionally mined and extracted from the lake.

2.4 Chemistry of the deposit

A number of studies have been done on the Lake Katwe salt deposit mainly in the chemistry of the mineral springs, feasibility of commercial production through estimation of the salt reserves and chemical characterization of the salt resources.

Arad and Morton, 1969 investigated the mineral springs and saline lakes of the Western rift valley. Analysis of the brine samples from various depths in the evaporite deposit at Lake Katwe reported various concentrations in the solutes. Interstitial brines from over 6 meters deep were poorer in K⁺, Cl⁻ and Br⁻ than those near the surface at about 2 meters from the top of the deposit. There was also a high proportion of sodium carbonate and bicarbonate in the evaporate deposit. In addition, the mineral waters within the region possess relatively high
sulphate contents as compared to those of the Eastern Rift. They also possess lower fluoride contents hence suitable for usage in production of food grade salt.

In another investigation, Morton, 1969 carried out a sample chemical analysis of salt grades produced at the lake. It was observed that Lake Katwe salt varies in composition due to presence of a number of impurities. It was observed from the analyses that the chief minerals present in the Lake Katwe salts were Halite (NaCl), Hanksite (9Na₂SO₄·2Na₂CO₃·KCl), Burkeite (Na₂CO₃·2Na₂SO₄) and Trona (Na₂CO₃·NaHCO₃·2H₂O). Indeed, composition varies considerably even within the same grades of the salts produced. The best quality (No.1) salt grade contains over 90 % NaCl but the remainder contains as much as 50 % of Na₂CO₃, Na₂SO₄, KCl and mud. No purification was carried out as the complex chemistry of the deposit prevents this from being done by simple methods (Dixon and Morton, 1970).

Morton, 1973 reported systematic sampling of the Lake Katwe brine done in 1967 at different depths of the lake both in the dry and wet season respectively. It was noted that, the salt lake brine had its ion composition mainly dominated by Na⁺ and Cl⁻ with lesser amounts of SO₄²⁻, K⁺, and CO₃²⁻ ions. Furthermore, it was noted that the compositional extremes resulted from the effects of dilution during the wet and evaporation during the dry season. There was no determination of the mean ion concentration of the salt lake brine in a yearly cycle and thus no detailed study was done to determine the mineralogical and chemical composition of the raw material.

Nielsen and Dahi, 1995 carried out a study on the fluoride contamination and mineralogical composition of a rock salt sample from Lake Katwe. Through chemical and mineralogical analysis, it was concluded that the salt lake contains no fluoride holding minerals. This was attributed to a very low fluoride concentration of about 0.02 mg/g. In addition, the salt lake raw material also consists of Trona mixed with Burkeite and Halite. The evaporite from Lake Katwe contains much more halite than that from other saline lakes in East Africa such as Lake Natron and Lake Magadi. This is attributed to the high chloride concentration of Lake Katwe brine which have an equivalent Cl/TAL ratio of 2-3 as compared to 0.23-1.0 for Lake Magadi and Lake Natron brines.

3. Salt extraction technologies

To date, several technologies can be used to extract valuable domestic and commercial salts and minerals from saline water. Based on the type of separation process, the technologies are classified into four categories:

(a) Thermal processes: These are phase change processes involving use of thermal energy to evaporate feed water to generate steam which is then condensed, a process known as distillation. Alternatively, saline water is frozen followed by the separation of pure ice and salts. Distillation can use any heating source such as fossil fuels, nuclear energy with solar energy being a low-tech option. Application of this technique includes solar distillation (SD), multi-effect distillation (MED) or multiple effect evaporation (MEE), multi-stage flash distillation (MSF), mechanical vapour compression (MVC), eutectic freezing crystallization (EFC) and open pan boilers.
(b) **Membrane processes**: They involve separation of dissolved salts from the feed water by mechanical or chemical/electrical means using a selective membrane barrier between the feed water and product. This principle is applied in Reverse Osmosis (RO) and Electro-dialysis/Electro-dialysis Reversal (ED/EDR). These processes do not lead to a phase change.

(c) **Chemical change processes**: These involve application of chemical techniques to extract salts from feed water. The principle is applied in the ion exchange, reactive precipitation and calcination processes.

(d) **Hybrid processes**: They involve combination of the above processes in a single unit or in sequential unit or in sequential steps. Examples include: membrane distillation (MD), membrane crystallization (MCR), RO with MSF or MED (Gude *et al.*, 2010).

In the salt crystallization plants, saturated brine or rock salt and solar salt can be used as a raw material for the process. A summary of the possible processes for the production of crystallized salt based on rock salt deposits is shown in Figure 3. Processes that are used in the production of vacuum salt from sea water or lake brines as a raw material are also shown in Figure 4. The present technologies together with emerging technologies for salt production are discussed next.

![Figure 3: Processes for production of crystallized salt based on rock salt deposits](Westphal *et al.*, 2010)
Figure 4: Processes for salt production from brine (Westphal et al., 2010)

4. Thermal processes

4.1 Distillation

Several forms of distillation are used for salt recovery and are classified into conventional and commercial salt production techniques. Processing methods other than solar evaporation are used commercially in the production of salts, usually in the making of refined (table salt) and purification of crude salt. These involve MSF, MEE, MVC and open pan boilers. Such techniques are used to make refined salt in many countries where the climate is temperate or cold (Aral et al., 2004). The operating principle behind these processes is that the vapour pressure of the feed water within the unit is lowered for boiling to occur at lower temperatures without further heat addition.

Conventional distillation

Solar distillation of saline water is a conventional salt production process practised widely all over the world. It is a simple operation carried out in specially designed shallow salt pans or ponds. It is within the shallow ponds that the sun evaporates most of the water. Within the ponds, brine from the sea or lake evaporates due to the effects of the sun and wind followed by the crystallization process. Here, the salt crystals begin to grow to a point when the salt layer is thick enough for harvesting. After harvesting, the salts are washed to meet the required standards and stockpiled to drain and dewater. Notable areas where the method is predominantly used for salt production on a large scale include Great Salt Lake in the United States, Dead Sea in Jordan, and Salar de Atacama in Chile (Aral et al., 2004).

Open pan evaporation is another conventional salt production technique involving addition of heat in open pans. The large and shallow open pans or boilers are made in dimensions of 6 m x 12 m x 1 m. Evaporated salt forms on the brine surface supported by surface tension. This
is an outdated technology that was replaced by wood burning furnaces which have also been observed to be unsustainable in terms of the energy use (Bauschlicher, 1983).

**Commercial distillation**

The Multi-Stage Flash process is based on the principle where saline feed water is heated and evaporated by pressure reduction as opposed to temperature increment. It involves regenerative heating where saline water flashing in each flash stage gives up some of its heat to the saline water going through the flashing process. Heated water from an initial stage passes to another stage at a lower pressure hence forming vapour which is led off and condensed to pure water using cold brine which feeds the first heating stage. Concentrated brine is then passed to a second chamber at a lower pressure hence more water evaporates with vapour being condensed. The principle of operation of the process is shown in Figure 5. The process is repeated through other stages up to atmospheric pressure. It can contain from 4 to about 40 stages. The process is considered to be the most reliable and most widely used. Recrystallization is a similar technique as MSF involving saturation of under saturated recirculating brine with solid solar or rock salt at about 100°C and fed downstream to several flash crystallizers (Westphal et al., 2010).

![Flash & Heat Recovery](image)

Figure 5: Schematic diagram of a basic multi-stage flash (MSF) system (Evans and Miller, 2002)

Multiple Effect Evaporation is similar to Multi Stage Flash in principle except that energy from an external source is used to heat up the saline water in only the initial stage. The resulting vapour or steam is used in the subsequent stages to evaporate the water and the brine is used to cool and condense the vapour in each successive stages hence having a temperature fall across each stage (Figure 6).
In the Mechanical Vapour Compression process, the heat for evaporation of the saline water comes from the evaporator. The process operates on the principle of compressing vapour to increase its temperature and pressure. The saline water feed is heated by steam, and part of it is vapourised. A mechanical compressor and a steam jet are used to condense water vapour which produces sufficient heat to evaporate the incoming saline feed water (Figure 7).

Multiple distillation methods have been used to extract salts from a salt lake as reported by Kilic and Kilic, 2005. In their study, sodium chloride (NaCl) was produced from the lake
brine through evaporation up to a specific gravity of 1.240. This was followed by cooling to -10°C thus forming Thenardite and Bloedite. Further evaporation produced Carnalite, Halite, Langbeinite and Sylvite. At the last stage, Bischofite and Kieserite were obtained. The same technique demonstrated by Nie et al., 2009 recovered salts from a salt lake using multiple isothermal evaporation technique at 25°C. In another similar laboratory investigation, Wang et al., 2011 performed multiple-evaporation after freezing of salt lake brine to recover salts. In their study, brine was first frozen at 263.15±0.2 K for a period of two days to a specific gravity of 1.1115 g/cm³ where Natron (NaCO₃·10H₂O) and Hydrohalite (NaCl·2H₂O) precipitated. Isothermal evaporation at 288.15±0.2 K was then performed on the mother liquor to recover more salts with increasing specific gravities.

In previous studies, salts have been recovered from desalination plants effluent using this technique. Mohammadesmaeili et al., 2010, recovered mixed salts through isothermal evaporation of RO concentrate. Specifically, sodium sulphate, sodium chloride and potassium salts were produced through continuous evaporation of the desalination concentrate. The feedstock concentrate had been previously treated with a lime-soda process before evaporation. In addition, isothermal and isobaric evaporation of reject brine of a desalination plant has also been carried out to recover various salts for industry and agriculture. Various salts such as NaCl, KCl, CaSO₄, MgSO₄·7H₂O were recovered from the process (Hajbi, et al. 2009, 2011).

Further research studies have also demonstrated the feasibility of extracting commercial salts from saline effluent using the SAL-PROC technology. SAL-PROC is an integrated process for the selective recovery of dissolved elements from saline waters in the form of valuable salt minerals, slurries and liquid compounds. It involves controlled chemical reactions in combination with evaporation and/or cooling stages, thus causing precipitation and crystallization followed by conventional mineral and chemical processing. The process is particularly suitable for brine with high levels of dissolved sulphate, potassium and magnesium salts and can be operated at a commercial scale (Ahmed et al. 2001, 2003). Ahmed et al., 2003 did not implement the feasibility study experimentally.

Sedivy 2000, describes the THERMOSAL salt processing technology developed at Sales Monzon in Spain as an option for the enhancement of natural evaporation of brine in open ponds through the use of residual waste heat. When combined with SALEX salt purification process, the process is the economic alternative to vacuum crystallization for production of top quality industrial and food grade salt. The process is applicable whenever the raw salt is available as brine.

Domestic and commercial salts have been produced from geothermal brines in Iceland using the vacuum evaporation technique with the geothermal wells being the source of salt-brine and process steam. Specifically, multiple effect evaporation is used to concentrate the brine before crystallization (Kristjánsson, 1992).

A refrigerator heat pump desalination scheme has been used for recovery of fresh water and salt from sea water as proposed by Reali, 1984. In the investigation, sea water was continuously refilled in a salt-water chamber via atmospheric pressure. Evaporation of the sea water into a vacuum chamber was done hence allowing the water vapour to condense on top of the fresh water chamber while the salt precipitated at the bottom of the evaporation chamber.
The evaporation and cooling technique has also been used as an initial or final stage in the recovery of salts from lake brine and sea waters and for disposal of the effluent from desalination plants (Vergara-Edwards and Parada-Frederick, 1983, Al-Harahsheh and Al-Itawi, 2005, Ravizky and Nadav, 2007). An advanced solar dryer has been demonstrated to optimize the recovery of salts from brine effluent of a desalination plant (Pereira et al. 2007).

A number of processes for salt recovery based on the evaporation and cooling technique have been developed. Winkler, 1985 developed a process for the treatment of brine elutriate drawn off after evaporation of the brine at an elevated temperature in order to separate some of the sodium chloride. In the investigation, crude brine containing sodium sulphate and potassium chloride is cooled in a chamber whereby NaCl, KCl and Na₂SO₄ salt mixture is separated off by crystallization. The remaining parent solution can be returned for renewed evaporation to recover NaCl without disturbing the equalized balance of the secondary salts in the brine to be processed. The NaCl present in the mixture is recovered by deposition with refrigerated water and separation of Na₂SO₄.

Ninawe and Breton, 1989 invented a process for the production of salt in which sodium chloride is crystallized in form of spheres by evaporation of sodium chloride brine and the spheres obtained are then broken up. The salt produced by the process is particularly suitable for the food industry. Extension of the research by Ninawe, et al., 2004 developed a process for the production of sodium chloride crystals from sodium chloride brine contaminated by potassium chloride and sulphate ions. In their research, a calcium compound is added to brine to crystallize Glauberite (Na₂CaSO₄)₂, which is isolated. The resulting solution is then subjected to evaporation in order to crystallize sodium chloride which is then collected, and the mother liquor from the crystallization is subjected to cooling hence crystallization of Glaserite (K₃Na(SO₄)₂).

Vohra, et al., 2004 developed a process for recovery of common salt, potassium chloride, concentrated magnesium chloride with enriched bromide, and high purity magnesia from brine in an integrated manner. Chirico, 1979 also presented a continuous process for the recovery of chemicals in saline water which involves converting the sulphates in the saline water feed to sodium sulphate, separating and recovering in the oxide forms, essentially all of the magnesium and calcium from the saline water feed, preparation of sodium chloride fortified solution by mixing the feed with recycled sodium chloride, crystallizing and re-crystallizing and then separating sodium chloride crystals in two evaporative crystallization processes.

### 4.2 Eutectic Freezing Crystallization

The eutectic freezing crystallization separates aqueous solutions of inorganic solutions into pure water and pure salt (Van der Ham et al., 1999). The process is characterized by operation near the eutectic point of the solution where both ice and salt crystallize simultaneously (Vaessen et al., 2003). Figure 8 shows a typical EFC process scheme.
Figure 8: Schematic representation of EFC for production of pure water and salt from waste or process streams (Van der Ham., 1998)

Compared with the conventional evaporation and cooling techniques, this process is capable of reducing energy costs by up to 70%. However, the high investment costs together with the scale limitations make the process unfavourable but can be overcome with time (Van der Ham et al., 1998). Experimental investigations of the eutectic temperatures of various proportions of ions commonly found in natural waters show that the process operates well at temperatures not lower than -25°C (Bardurn and Manudhane, 1979).

The process has been used to demonstrate separation of ice and KCl crystals from brine based on the direct cooling technique (Stepakoff et al., 1974). In another investigation, Van der Ham et al., 2004 demonstrated separation of ice from CuSO$_4$·5H$_2$O crystals in a cooled disk column crystallizer based on indirect cooling. The process has also been applied at an industrial scale to study the recovery of purified MgSO$_4$·H$_2$O from a magnesium sulphate industrial stream emitted from a flue gas desulphurization process (Himawan et al., 2006). Experimental techniques have also been used to validate theoretical models developed for predicting alternative pathways for seawater freezing and crystallization (Marion et al., 1999). However, according to Westphal et al., 2010, the freezing process for the production of salt from saline water has not got practical importance.

5. Membrane processes

These processes use a selective synthetic polymeric membrane or resin to recover dissolved salts when subjected to a pressure gradient or an electrical potential across the membrane surface. This technique is currently used in RO and ED/EDR. Other pressure driven membrane processes similar to the RO principle are Ultrafiltration (UF) and Nanofiltration (NF). ED/EDR is an electro-membrane process.

5.1 Pressure driven membrane processes

Osmosis is the transfer of water through a semi-permeable membrane from a lowly concentrated to a highly concentrated solution until an equilibrium osmotic pressure is achieved. In the RO process, pressure greater than the osmotic pressure is applied to the
highly concentrated side of the membrane hence leading to the diffusion of water through the membrane to the fresh water side leaving dissolved salts behind with an increase in salt concentration. Higher salt concentration in the feed water would require higher pressure. An illustration of both processes is shown in Figure 9.

![Diagram of Osmosis and Reverse Osmosis](image)

**Figure 9: Reverse osmosis vs. osmosis (Krukowski 2001 cited in Younos and Tolou, 2005)**

NF and UF, in concept and operation are similar to RO. NF is used to partially soften water and is successful at removing low total dissolved solids as well as dissolved organic carbon. It uses a coarse form of RO membranes hence has feed pressures lower than those used in RO systems. UF is a technique for separation of dissolved molecules on the basis of size implying that larger molecules than the membrane pore size are retained at the surface of the membrane. The only difference between UF, NF and RO is the size of the molecules that each process retains. Pre-treatment is very important for RO processes since the membrane is prone to fouling due to dissolved solutes and impurities. UF is used for the pre-treatment of Seawater Reverse Osmosis (SWRO) plants (Van Hoof, et al. 1999). Commercial RO membranes are manufactured from modern plastic materials in the form of sheets or hollow fibres.

Pressure driven membrane processes are widely being used for separation and recovery of salts from water. However, such processes do not recover salts from water to the low levels achieved in distillation processes (Clayton, 2006). An assessment of the capacities of NF and RO high-pressure membrane systems to separate a high-concentration water solution was done by Karelin et al., 1996. In their study, RO membranes were capable of retaining NaCl at a very high concentration in an aqueous solution even when the concentration is near the saturation level. In addition, NF membranes were capable of separating multi-component solutions into binary ones, from which salts can be recovered by vaporization. In other previous works, the membrane separation technique has been used for salt recovery from waste brine at a sugar decolourisation plant on a pilot-scale (Wadley, et al. 1995), dye-salt separation using weak acid polyelectrolyte membranes (Xu and Spencer, 1997), brackish water desalting (Almulla, et al. 2002, Lee, et al. 2004), separation of salts from concentrated organic/inorganic salt mixtures (Freger, et al. 2000), salt recovery from industrial effluents resulting directly from a dyeing industry (Allègre, et al. 2004).
5.2 Electro-chemical separation processes

ED/EDR is an electro-membrane process which consists of a stack of ion-exchange membranes (Figure 10) which are arranged between an anode and a cathode. These membranes are selective to positive and negative ions. Under the influence of an applied electric potential difference, the ions are forced to migrate towards the electrodes. The cations pass through a cation membrane while the anions pass through the anion membrane thus converting the feed saline water into two streams of concentrated brine and fresh water. Fouling of the ion exchange membranes by dissolved impurities is overcome by EDR which involves reversing the direction of the electric current. The process is applicable for pre-concentration of brine in arid regions unsuitable for solar ponds and having no rock salt deposits (Bauschlicher et al., 1983).

![Figure 10: An Electrodialysis stack (Brunner, 1990 cited in Younos and Tolou, 2005)](image)

The production of table salt from sea water by use of ED to concentrate NaCl up to 200 g/l prior to evaporation is a technique developed and used exclusively in Japan. More than 350,000 tons of table salt are produced annually using this technique thus requiring more than 500,000 m$^2$ of installed ion-exchange membranes (Noble and Stern, 1995). The process has also been used for salt production in the Middle East (Kobuchi et al., 1983). ED-MSF-crystallization was also demonstrated for a dual purpose desalination-salt production system (Turek, 2002). ED-EDR double step electrodialytic pre-treatment and pre-concentration of coal-mine brine was examined for purposes of salt production (Turek et al., 2005). Furthermore, the technique was also demonstrated for table salt production using waste brine accompanied with a mining process (Kawahara, 1994), brine discharged from a RO seawater desalination plant (Tanaka et al., 2003).

ED has been observed to be more economically advantageous compared to the evaporation process according to Tanaka, 1999. In this analysis, it was observed that to produce a ton of NaCl, ED would consume 151.3 kWh as compared to 1000 kWh for evaporation. However, Turek and Dydo, 2003 noted that electricity as an energy carrier is about 7-10 times more expensive than in the form of steam.
6. Chemical processes

6.1. Ion exchange

This process involves a chemical reaction involving exchange of ions between a liquid phase and a solid phase. The solid phase, also known as an organic resin, is contained in a column where the liquid phase is passed hence leading to the exchange of ions. For salt recovery purposes, the feed saline water is passed over the organic resin beds where dissolved Na\(^+\), Cl\(^-\) and other ions are exchanged for ions of similar charge. The beds are normally arranged in series as shown in Figure 11. Ion exchange materials are classified as either cationic or anionic, implying that the cation resins interchange H\(^+\) ions for positively charged ions while the anion resins exchange OH\(^-\) ions for negatively charged Cl\(^-\) ions hence producing water and salt. It should be noted that the number of charges on the ions removed from solution must be equivalent to number of charges on the ions exchanged from the material.

Figure 11: Schematic diagram of the ion exchange process (Al-Kharabsheh, 2003)

This technique is environmentally friendly, has cheap maintenance and long life of the resins. Nonetheless, it has limitations in that the volume of desalted water produced in the process is inversely proportional to the ionic concentration in the water. In addition, the higher salinity of the water requires larger ion exchange equipment which at times is not economical due to the high cost of the organic resins. This therefore implies that the process is suitable for low salinity water (Guyer, 2010). The process is also prone to fouling of the resin due to organic matter or Fe\(^{3+}\) ions. The technique also has environmental implications in that the waste water for disposal after regeneration contains all the minerals removed from the water and the salt. Previous studies, investigations and assessments have demonstrated the feasibility of this process for recovery of salt from saline water (Ginde and Chu, 1972, Kobuchi et al., 1983, Tanaka, 2003, Ghaly and Verma, 2008).

6.2. Chemical extraction techniques

Saline water is an inexhaustible source of common salt together with other valuable salts such as sodium sulphate, magnesium chloride, magnesium sulphate, calcium sulphate etc. Chemical process techniques have been developed and applied to purify crude salts from
saline waters and their preparation as feedstock for production of value added products from the salts (Aral et al., 2004). Attractive chemical processes involve calcination which is a thermal decomposition process and reactive precipitation. Chemical processes are conventionally applied in extraction of salts having similar chemical properties which would make it difficult for high purity extraction (Lee and Bauman, 1980). The technique is not applicable in extraction of sodium, potassium and magnesium chlorides since they somewhat possess similar chemical properties. Sodium and potassium chlorides would be extracted out of solution by the evaporation and cooling technique (Kilic and Kilic, 2005).

Recovery of magnesium hydroxide, Mg(OH)₂ from samples of waste brine or bitterns at a salt processing plant in Ghana by precipitation has been demonstrated by Larney, 1997. In this study, the waste brine samples were precipitated with NaOH followed by washing to yield products which contained some NaCl and Potassium impurities. Calcination of Mg(OH)₂ yielded MgO which also contained some impurities. Rigorous washing of Mg(OH)₂ was suggested for quality improvement. Reactive precipitation has also been applied to recover CaCO₃ from nanofiltration retentate by adding NaHCO₃/Na₂CO₃ aqueous solutions to the retentate. In this investigation, the sodium (bi) carbonate solutions had been produced by reactive absorption of CO₂ into sodium hydroxide solutions (Drioli et al., 2004). The same technique has also been used in the precipitation of magnesium sulphate from lake brine (Estefan and Nassif, 1976), precipitation of basic magnesium carbonate from high sulphate content brines followed by calcinations at 1100°C to produce high quality magnesia (Estefan and Nassif, 1980).

The recovery of potassium chloride from Dead Sea brines by precipitation and solvent extraction has been demonstrated by Epstein et al., 1975. In their study, Potassium was recovered from brines by precipitation as potassium perchlorate, followed by conversion to potassium chloride by liquid anion exchange with a tertiary amine in the form of its hydrochloride. The Dow chemical process has also been observed as a classical economic process of MgCl₂ extraction from desalination brines. It is accomplished by addition of lime to sea water bitterns to precipitate Mg(OH)₂ followed by addition of HCl to precipitate MgCl₂ (Al Mutaz and Wagialia, 1990). Chemical precipitation techniques have been coupled with evaporation-crystallization processes for more efficiency and purity of recovered salts (Atashi et al., 2010).

7. Hybrid technologies

Conventional salt recovery technologies are both energy and cost intensive if they were to operate stand-alone (Gude, 2010). In this regard, several conventional techniques have been combined in order to hybridize the salt recovery process to increase system performance efficiency and reduction of final disposable brine hence maintaining zero-discharge. Examples would involve integration of UF-NF-MSF-crystallization or UF-NF-RO-MSF-crystallization systems (Turek, 2002), MC⁻⁻NF-RO (Drioli et al., 2006). Such processes have been applied to desalt solutions of extremely high concentration which other conventional techniques such as RO are incapable of handling.

MD and crystallization have been used to obtain pure crystalline products and pure water from solutions of NaCl and MgSO₄ of concentrations near to saturation (Mariah, 2006). Drioli et al., 2004, demonstrated an integrated system for recovery of CaCO₃, NaCl and
MgSO$_4$·7H$_2$O as solid products from a NF retentate stream. Specifically, chemical precipitation techniques were used to precipitate Ca$^{2+}$ ions followed by a final membrane crystallization unit to recover both NaCl and Epsom salts. Pre-filtration, neutralization, NF and RO have been used for recovery and re-use of salts present in dye house effluent (Allègre, 2004). Innovative techniques have developed to desulfate brine according to Bader, 2007. The techniques are an alternative to NF as a stand-alone process for desulfating brine due to scale and hydraulic boundaries at the membrane surface. The proposed techniques integrate NF with liquid-phase precipitation (LPP) and MD with LPP.

Hybrid techniques involving RO, chemical separation and crystallization have been applied for salt production from coal mine brines in Poland (Ericsson and Hallmans, 1996). Further research investigations by (Turek et al., 2005, 2008) have demonstrated that ED/EDR-evaporation-crystallization and NF-evaporation-crystallization as opposed to a stand-alone evaporation-crystallization method can be applied to the recovery of salt from coal mine brines. In both investigations, it was observed that there were considerable improvements in the plant outcome. There was a reduction in the unit energy consumption and reduced amount of salt in post-crystallization lye.

8. Discussion and synthesis of the findings

This section provides a discussion and synthesis of the literature review findings of this paper. The discussion includes a comparison of the different salt extraction processes and technologies. The discussion primarily addresses the following fundamental questions:

(a) How do the processes and technologies compare with each other in terms of their performance characteristics?
(b) What are the potential challenges and benefits of the technologies?

8.1 Comparison of the processes and techniques

The review elucidated the different available salt production technologies. In the evaluation of the different processes, it is important to select a technique that is suitable for a particular operation. The important factors that should be considered for such a selection in particular are the following (Wade, 1993, Gude et al., 2010, Westphal et al., 2010):

(a) Availability of raw materials (brine, raw salt),
(b) Impurities of the raw material,
(c) Availability, reliability and energy costs (power, steam, primary energy),
(d) Water situation (quantity and quality),
(e) Commercial readiness,
(f) Environment (waste products disposal, use of chemicals),
(g) Economic feasibility (financing, capital costs, operating costs).

Based on the above criteria, a comparative summary of the relative pros and cons of the identified technologies together with their characteristics as applied to salt production from brine is provided in Table 1. A few notable salt production plants based on the extraction technique are highlighted in Table 2.
<table>
<thead>
<tr>
<th>Process</th>
<th>Size of application</th>
<th>Brine initial concentration (ppm)</th>
<th>Energy consumption (kWh/t of salt)</th>
<th>Output quality, % (Purity NaCl)</th>
<th>Main key features (Benefits and limitations)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Processes</td>
<td></td>
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</tr>
<tr>
<td>MSF</td>
<td>Medium-large</td>
<td>10,000-50,000</td>
<td>45 (Output 20 tons /hour)</td>
<td>99.97</td>
<td>• High initial capital investments</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Requires highly qualified personnel and intense process control.</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Undersaturated brine causes serious problems</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Prone to corrosion and erosion</td>
</tr>
<tr>
<td>MEE</td>
<td>Small-medium</td>
<td>10,000-50,000</td>
<td>25 (Output 150 tons /hour)</td>
<td>99.97</td>
<td>• Has moderate to good efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Easy to operate since it’s a once through.</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Preferred for simple process operation and dual purposes</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Expensive to start</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Prone to corrosion and erosion</td>
</tr>
<tr>
<td>MVC</td>
<td>Small</td>
<td>10,000-50,000</td>
<td>155 (Output 30 tons /hour)</td>
<td>99.97</td>
<td>• Has high energy efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Requires electricity, high maintenance and pressure for operation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Great potential for corrosion and erosion.</td>
</tr>
<tr>
<td>Solar Evaporation</td>
<td>Small-medium</td>
<td>30,000</td>
<td>155 (Output 36 kg/m²/year)</td>
<td>98.54 (un washed) 99.75 (washed)</td>
<td>• Uses free energy, requires no maintenance and is environmentally friendly. Simple and cheap technique.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Can achieve up to 72% salt retrieval</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Difficult to get high quality salt</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Has significant waste of salt</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>• Requires a lot of space and time.</td>
</tr>
<tr>
<td>Processes</td>
<td>Type</td>
<td>Inputs</td>
<td>Outputs</td>
<td>Efficiency</td>
<td></td>
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<tr>
<td>--------------------</td>
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</tr>
<tr>
<td>Open pan evaporation</td>
<td>Small to medium</td>
<td>30,000</td>
<td>2,708 (Output of 5 tons/hour)</td>
<td>99.98</td>
<td></td>
</tr>
<tr>
<td>EFC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>RO</td>
<td>Small</td>
<td>1,000-10,000</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ED/EDR</td>
<td>Small-large</td>
<td>1,000-5,000</td>
<td>151.3</td>
<td>97.47</td>
<td></td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Small</td>
<td>1,000-5,000</td>
<td>-</td>
<td>97.47</td>
<td></td>
</tr>
<tr>
<td>Precipitation</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Hybrid Processes</td>
<td>(1) Pretreatment-RO-Separation-Crystallization (2) NF-Evaporation etc</td>
<td>Small-large 10,000-30,000 (Output 12.5 tons/hour) 450</td>
<td>&gt;99.6</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

- **Membrane Processes**
  - **EFC**
    - Process capable of reducing energy costs by up to 70% compared to distillation.
    - High investment costs and scale limitations.
    - Process has not got commercial application.
  - **RO**
    - Used as a pre-concentration stage for evaporation crystallization. Mainly for desalination.
    - More pre-treatment of brine needed than thermal process.
    - Uneconomical for salt production.
  - **ED/EDR**
    - Concentrates brine from 3.5 to 15-20% NaCl before thermal evaporation.
    - Energy use proportional to salt recovered.
    - Long membrane lifetime and high efficiency.
    - High capital and operational costs.
- **Chemical Processes**
  - **Ion exchange**
    - Environmental limitations with disposal of chemical resins.
    - Impractical for high saline water hence uneconomical for salt production.
  - **Precipitation**
    - No commercial importance in table salt manufacturing industry.
- **Hybrid Processes**
  - Low energy consumption and high performance efficiencies.
  - Able to overcome problems of scale formation caused by CaSO₄, CaCO₃ and Mg(OH)₂.
Table 2: Some notable commercial salt production plants

<table>
<thead>
<tr>
<th>Plant Location</th>
<th>Total capacity tonnes/year</th>
<th>Process and remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poland (Debiensko)</td>
<td>109,500</td>
<td>Hybrid: First stage-Pretreatment and RO Second stage: Post- treatment of permeate Third stage:  Evaporative crystallization</td>
<td>Ericsson and Hallmans, 1996</td>
</tr>
<tr>
<td>Japan, Korea, Taiwan</td>
<td>1,722,990</td>
<td>ED with exchange membranes and MEE</td>
<td>Kobuchi et al., 1983, Kawate et al., 1983, Noble and Stern, 1995, Tanaka et al., 2003</td>
</tr>
<tr>
<td>Dead Sea, Jordan</td>
<td>25,000</td>
<td>Solar evaporative crystallization</td>
<td>Abu-Khader, 2006, Bashitialshaer et al., 2011</td>
</tr>
<tr>
<td>Mexico (Guerrero Negro)</td>
<td>17.5 x 10^6</td>
<td>Solar evaporative crystallization</td>
<td>Baja Quest, 2011, Westphal et al., 2010</td>
</tr>
<tr>
<td>Spain</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Sals Monzon</td>
<td>120,000</td>
<td>Brine purification-crystallization ponds-SALEX. Crystallization based on THERMOSOL technique. Evaporation due to solar radiation and wind</td>
<td>Sedivy, 2000, Nolan, 2011</td>
</tr>
<tr>
<td>2. Torrevieja</td>
<td>700,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Netherlands</td>
<td>1.2 x 10^6</td>
<td>MEE</td>
<td>Westphal et al., 2010</td>
</tr>
<tr>
<td>Italy (Magherita Di Sovoia)</td>
<td>550,000</td>
<td>Solar evaporative crystallization</td>
<td>Zeno, 2009</td>
</tr>
<tr>
<td>United States (Louisiana)</td>
<td>820,000</td>
<td>Brine pre-treatment-Crystallization driven by MVR</td>
<td>Westphal et al., 2010, Shintech, Inc, 2011</td>
</tr>
<tr>
<td>France</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. (Varangeville)</td>
<td>600,000</td>
<td>Hybrid: MVC-MSF Solar evaporation</td>
<td>Westphal et al., 2010</td>
</tr>
<tr>
<td>2. Aigues-Mortes</td>
<td>400,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Algeria, Bangladesh, Germany, Greece, Iran, and Turkey</td>
<td>260,000</td>
<td>Recrystallization also similar to MSF</td>
<td>Westphal et al., 2010</td>
</tr>
</tbody>
</table>
Considering Tables 1 and 2 above, it can be observed that thermal processes are in a mature phase of technical development and have gained commercial readiness in the salt industry. However, there is scope for further improvement in the materials selection in order to address issues regarding to corrosion and erosion which would lead to breakdowns and huge maintenance costs. MED has the least energy consumption among the thermal processes. The technology is less complex than MSF and MVC in terms of auxiliary equipment and pumps hence well suited for remote applications. Thermal methods are more effective than membrane methods in terms of production of highly concentrated brines (Turek and Dydo, 2003).

The procedures of ED and RO have not found commercial application in the salt industry though. They remain restricted to special cases, since they involve high energy costs most especially in driving the process pumps. In places where they have been applied for salt production purposes, they have only been used for production of concentrated brine (Westphal et al., 2010). This brine is fed to crystallization plants to avoid expensive evaporation of water thus maintaining high energy efficiencies. According to Wade, 1993, these processes have considerable scope for future technology in regard to the membrane technology, pre-treatment and detail engineering. Membrane technologies are not tolerant of the initial feed water concentrations than distillation technologies. In this regard, membrane performance and life can be adversely affected by contamination of the feed water thus having a big effect on reliability and availability. More research efforts are being done in integrating the different salt production technologies (Ericsson and Hallmans, 1996, Ahmed et al., 2001, Turek and Dydo, 2003, Turek et al., 2008).

9. Conclusions and outlook

Various salt production technologies from brine have been reviewed and analysed in literature with respect to energy consumption, raw material treatment needs, cost, availability, reliability and commercial readiness. It was observed from the literature that distillation involving evaporation either by solar or thermal processes, and the cooling techniques are the most widely used technologies for both traditional and commercial salt production worldwide today. Membrane, chemical and hybrid salt production technologies are also emerging. Several research efforts in these areas have been conducted most especially at demonstration scale thus their full scale commercialisation for salt production has not been fully realized. The use of solar evaporation technologies and distillation techniques mainly multiple-effect evaporation would be appropriate in terms of sustainability. Thermal processes have the largest share in the installed capacity of commercial salt production implying that these technologies have gained technical maturity over the years. With increasing demand for usage of renewable energy technologies for sustainability, there is need to investigate the feasibility of integrating solar thermal technologies with proven distillation processes such as MEE for commercial salt production, most especially in areas with favourable climatic conditions such as Lake Katwe. This would ensure better recovery and process efficiencies, low costs and simple brine pre-treatment procedures, hence sustainable salt production.
References


Espetein J.A, Altaras, D, Feist, E.M, and Rosenzweig, J. 1975. The recovery of Potassium Chloride from Dead Sea Brines by precipitation and solvent extraction. Hydrometallurgy, 1: 39-50


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