

Salt Production

A reference book for the Industry

Promotion of Benchmarking Tools for Energy Conservation
in Energy Intensive Industries in China

Energy Efficiency Component

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Disclaimer

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Beijing, 2009

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SUMMARY AND ACKNOWLEDGMENTS

This reference book for the industry is a compilation of best available technologies and research in the salt industry. Information has largely been derived from the websites of various salt industry associations.

As part of the BMT-Tool set (BMT = Benchmarking – Monitoring – Targeting) this reference book provides sector specific information regarding the salt industry in general, frequently used technologies, energy consumption of key processes and other relevant aspects connected with the energy and environment performance of salt production. Energy benchmarks are discussed as typical ranges of energy consumption (MJ or kg standard coal) per production unit (ton of salt). The report is divided into a number of Chapters as follows:

- The first chapter provides an introduction on salt as an important good for industry and daily life including an historical perspective.
- The second chapter summarizes the worldwide figures of salt production, showing China taking the lead position during the recent years overtaking the US.
- The third chapter describes the most relevant processes and technologies in detail; diversifying between salt rock mining, vacuum pan refining and solar salt production, each technology covering a third of total production of salt worldwide.
- The fourth chapter describes the relevant energy consumption patterns for each main process route with emphasis on vacuum pan refining.
- The fifth chapter deals with a specific challenge of the industry to tackle harmful impurities of salt.
- The sixth chapter reviews existing environmental regulations for the salt industry in the western countries.

1. INTRODUCTION

Salt, or sodium chloride, is a chemical compound with the chemical formula NaCl; for every gramme of salt, almost 40 per cent is sodium (Na), the sixth most abundant element on Earth, and a little over 60 per cent is chlorine (Cl). Salt is a white, crystalline compound, has low toxicity and is completely non-flammable. Salt is added to food as a flavour enhancer (table salt) and is a daily diet requirement of humans. It is commonly applied to roads and pavements as a de-icer, used as a feedstock for chlorine and sodium hydroxide (caustic soda) manufacture both of which are used to make 'consumer-related end-use products' such as polyvinyl chloride (PVC), a plastic made from chlorine, and paper pulping chemicals manufactured from sodium hydroxide (USGS, 2007).

There are three types of salt classified according to method of recovery; rock salt, from the surface or underground mining of halite deposits; solar salt, from the solar evaporation of seawater (also known as sea salt), landlocked bodies of saline water, or primary or by-product brines (such as from the desalinations of mine water) as well as vacuum pan salt, from the mechanical evaporation of a purified brine feedstock; and brine, from the solution mining of underground halite. These are described in more detail in section 3.

1.1 Properties

Salt is a chemical compound with the following properties:

- crystals or white crystalline powder;
- transparent and colourless in crystalline form;
- crystallises in the isometric system, usually in the form of cubes;
- soluble in water (35.6g/100g at 0°C and 39.2g/100g at 100°C);
- slightly soluble in alcohol, but insoluble in concentrated hydrochloric acid;
- melts at 801°C and begins to vaporize at temperatures just slightly above its boiling point of 1,413°C;
- hardness of 2.5 on the MOH scale of hardness;
- specific gravity of 2.165;
- non combustible;
- low toxicity;
- hygroscopic thereby absorbing moisture from damp atmospheres above 75% relative humidity below which it will dry out.

In its natural form, salt often includes traces of magnesium chloride, magnesium sulphate, magnesium bromide, and others. These impurities can tint the otherwise transparent crystals, yellow, red, blue or purple.

1.2 Uses

Salt can be used as a feedstock to produce other compounds of industrial and commercial interest. Chlorine compounds of commercial importance include hydrochloric acid, and sodium hypochlorite. Important sodium compounds include sodium carbonate (soda), sodium sulphate, baking soda, sodium phosphate, and sodium hydroxide. Some of these are described in more detail below.

When an electric current is passed through a strong solution of salt in water, electrolysis occurs and three products are formed:

- chlorine (Cl_2)
- sodium hydroxide (NaOH)
- hydrogen (H_2)

Hydrogen and chlorine gases can be explosive when mixed and therefore need to be stored separately. All three products are useful individually and they can also be combined together to make further products. Sodium hydroxide and chlorine combine to form sodium hypochlorite solution (NaOCl), which is widely used in the home as domestic bleach; a stronger solution of sodium hypochlorite is used as a dairy and industrial disinfectant.

Under different reaction conditions, sodium hydroxide and chlorine will react to form sodium chlorate (NaClO_3); this is produced as white crystals that can be highly explosive or inflammable if mixed with organic matter; solutions of sodium chlorate are widely used as herbicide.

Hydrochloric acid (HCl) is manufactured by dissolving hydrogen chloride, formed by burning chlorine gas in hydrogen, in water. This process produces very pure hydrochloric acid, which can be used safely in the food and pharmaceutical industries.

Salt is widely used as a preservative for meats and is employed in some refrigeration processes, in dyeing, and in the manufacture of soap and glass. Because they are transparent to infrared radiation, salt crystals are used for making the prisms and lenses of instruments used in the study of infrared radiation.

Chlorine is used in the manufacture of PVC, which is contained in a vast number of products including blood bags and the tiny catheters used to help keep premature babies alive.

In some areas, groundwater passes through chalk or limestone before arriving in reservoirs, rivers and abstraction wells. The calcium and magnesium carbonates picked up by the water are not normally harmful, but cause lime-scale to build up inside kettles, boilers and water heaters, making them inefficient and more costly to run.

Both industrial and domestic water can be softened economically, using an ion-exchange process. In its original state, the ion exchange polymer or resin carries sodium ions on its surface; this has a strong affinity for larger, more highly charged calcium and magnesium ions. When hard water passes over the resin, the sodium ions are displaced; as sodium salts are more soluble than calcium and magnesium. Although chemical and other methods can bring some control over hardness, only ion-exchange can remove the calcium and magnesium ions which cause it.

When the sodium ions are exhausted, the hardness will reoccur but by passing a concentrated salt solution (brine) over the resin, the calcium and magnesium are displaced by sodium and the resin reactivated; this process is called regeneration. Regeneration is usually automatic, either when a certain volume of water has been used or at a set frequency, when the water softener is out-of-use. In industry, several resin vessels are used and one is periodically taken 'off-line', to avoid interruption to production. In domestic situations, regeneration usually takes place early morning, or a twin tank system is used. Modern domestic machines are designed to be highly salt-efficient. These require special grades of salt to optimise performance. The salt is very pure and larger than normal table salt, to produce brine quickly. Some machines use salt tablets, produced from compressed salt. Softened water is so effective in dishwasher operation that a softener is often built into the machine. The salt used should be of a dishwasher grade, rather than table salt grade.

A major use of unrefined salt or rock salt (halite) is as a highway deicer. Weak brine solutions have a freezing point that is lower than water at about -4°C . In countries, where ground surface temperatures seldom fall lower than this temperature, salt can be used to prevent the build-up of ice on roads. Large quantities of salt are stockpiled by local authorities in such countries for rapid application as required depending on predicted weather conditions. However, these weak brines are corrosive and so their use is balanced against need.

1.3 History

Sir Humphrey Davy (1778-1829) first separated salt into its constituent parts of sodium and chlorine in 1807. At the time, no one could think of anything useful to do with them, but subsequently their properties became the bedrock for many manufacturing industries.

The discovery that salt could be used as a way to preserve food was fundamental to the progress of the human race. It also meant that salt became a highly prized, tradable commodity and this fact had a profound effect on the economies of many countries. Due to its value salt was often the cause of many bitter wars. In 2200 BC, the Chinese emperor Hsia Yu levied one of the first known taxes by taxing salt.

Greek slave traders often bartered salt for slaves, and Roman legionnaires were paid in salt; a *salarium*, the Latin origin of the word "salary" and the Roman Empire carefully controlled its price, increasing it periodically to raise money for wars. The "gabelle" salt tax was enacted in France in 1286 by Charles of Anjou. In Britain the monarchy supported itself with a high salt tax resulting in a 200 mile 'Salt March' protest against the salt tax in colonial India, led by Mahatma Gandhi in March 1930.

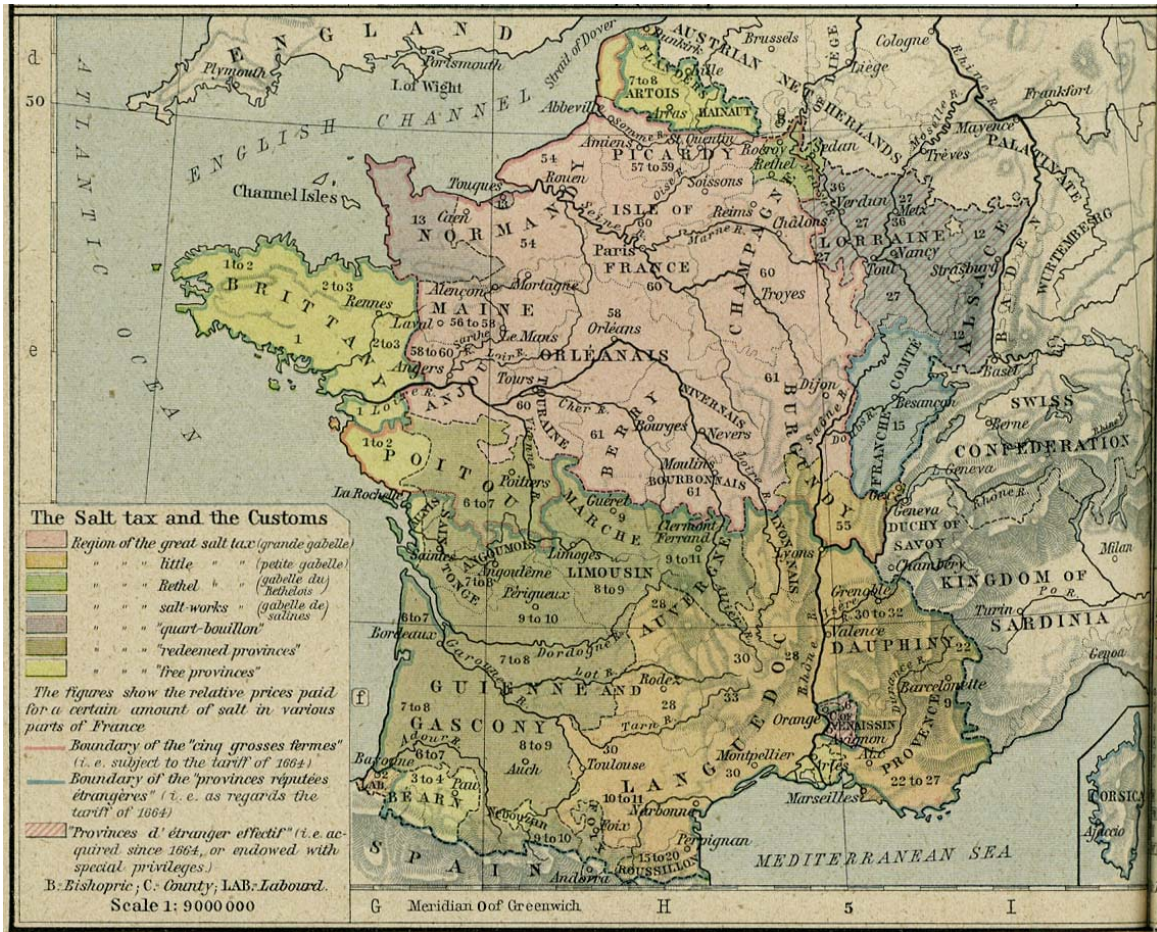
1.4 Historical Uses

Approximately 4,700 years ago in China a document called the Peng-Tzao-Kan-Mu was published and part of the writing described 40 kinds of salt, including a discussion of two methods of extracting and processing salt that are similar to those used today. In ancient Egypt salt was used as in mummification and as early as 2000 BC salt was being used to preserve meat and fish.

In European medieval society, with relatively poor transportation systems, villages had to be practically self-sufficient in food to feed the community during winter (non productive) months. Methods were therefore developed for the preservation of many types of food using salt; beef and pork were salted and dried as joints, hams, and sausages and butter were salted, (with the excess being scrapped off before it was eaten), and vegetables were stored under brine.

In the 14th century in Germany, salt glazing of pottery was invented, a technique still used today, whereby salt is added to the chamber of a hot kiln. The resulting finish is a glossy, translucent effect that enhances the natural colour of the pot.

During the 19th century salt started to be used in manufacturing including the treatment of leather and for dyeing textiles. Chemists began to find other uses for the components of salt, which coincided with an increase in the deep mining and excavation of salt.



2. WORLD PRODUCTION, RESERVES AND RESOURCES

China and the US are the two largest producers of salt, together producing approximately 40% of the 250,000,000 tons of salt produced each year worldwide (Salt Institute, 2009). Salt producers use three basic technologies to create salt; these are described in further detail in Section 4.

2.1 Salt Production Worldwide

The annual world production of salt currently exceeds 200 million tons; more than one third of which is produced by solar evaporation of sea water or inland brines. Another third is obtained by mining of rock salt deposits, both from underground and from surface quarrying. The balance is obtained as brines, mainly by solution mining. Brines can be used directly (for example in diaphragm electrolysis) or thermally evaporated to produce vacuum salt.

<i>Production Method</i>	<i>'000 tons per year</i>
<i>Solar salt</i>	<i>80,000</i>
<i>Rock salt</i>	<i>60,000</i>
<i>Vacumn Salt (from brines)</i>	<i>70,000</i>

Table 2.1: World production by salt type (2000).

The purity of washed solar salt produced in India and China is estimated to be 99 - 99.5% (NaCl, dry bases); solar salt produced in Australia and Mexico is 99.7 – 99.8% pure; and vacuum salt is usually 99.8 - 99.95% pure.

Producing Country	Production ('000 tons)	
	2000	2008^e
China	31,300	60,000
United States	45,600	46,000
Germany	17,700	19,000
India	14,500	15,800
Australia	8,800	12,000
Canada	12,200	12,000
Mexico	8,900	8,400
Brazil	-	7,000
France	7,000	6,000
United Kingdom	5,800	5,800
Ukraine	-	5,500
Chile	-	5,000
Netherlands	5,000	5,000
Spain	-	4,600
Poland	-	4,400

Turkey	-	2,700
Romania	-	2,500
Egypt	-	2,400
Italy	-	2,200
Russia	-	2,200
Iran	-	2,000
Austria		1,300
Other Countries	57,300	29,500
World Total	212,000	260,000
^e Estimated		
*Modified from USGS ,Mineral Commodity Summaries, January 2009.		

Table 2.2: Production of salt during 2007 and 2008.

2.2 Salt Consumption Worldwide

The chemical industry is the largest consumer of salt using approximately 60% of the total production mostly producing chlorine, caustic soda and soda ash required for industrial purposes including petroleum refining, petrochemistry, organic synthesis, and glass production.

The second largest group of salt users is the food industries, which use approximately 30% of the total salt produced as: table salt, cooking salt and salt for food production.

Approximately 10% of salt is needed for road de-icing, water treatment, production of cooling brines and other smaller applications.

Generally, the purer the salt, the more valuable it is; the issue of impurities is addressed in Section 4.

2.3 World Resources

USGS reports that world continental resources of salt are 'practically unlimited' and the salt content in the oceans is 'virtually inexhaustible'. USGS also considers that economic and sub-economic deposits of salt are substantial in principal salt producing countries but most countries have salt deposits or solar evaporation operations of various magnitudes.

2.4 Substitutes

There are currently no economic substitutes or alternatives for salt; calcium chloride, calcium magnesium acetate, hydrochloric acid and potassium chloride can be substituted in de-icing, some chemical processes and in food flavouring but all at a greater cost. With the abundance of salt and the lack of a cheaper substitute, it is unlikely that an alternative will need to be found.

3. SALT PRODUCTION PROCESSES

There are three main methods of producing salt for various uses.

- Direct mining of rock salt (halite)
- Solar evaporation of seawater
- Thermal evaporation of brines

3.1 Rock Salt Mining

Halite occurs in extensive beds of sedimentary evaporite minerals that result from the drying up of enclosed lakes, lagoons, and seas. Salt beds may be up to hundreds of meters thick. Salt domes are vertical diapirs or pipe-like masses of salt that have been essentially "squeezed up" from underlying salt beds by mobilization due to the weight of overlying rock. In addition to sodium chloride both sedimentary halite deposits and salt domes also contain other minerals including: anhydrite, gypsum, potash and native sulfur. Underground deposits are worked by conventional shaft (or adit) mining, whereby solid rock is removed

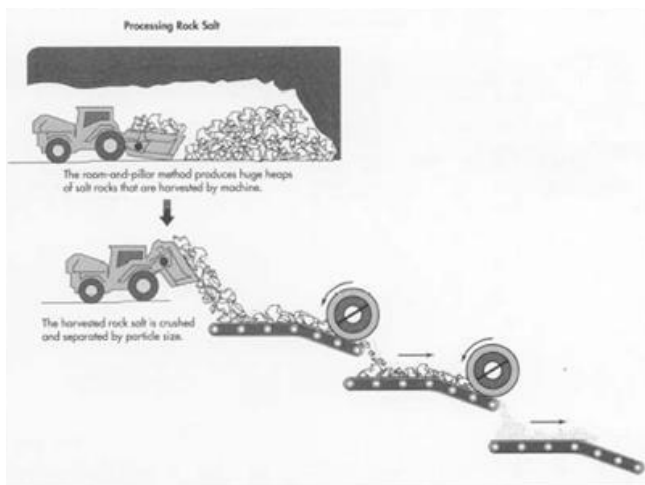


Halite

Rock salt (mineralogically halite) is commonly mined at depths of between 100m to more than 1500m below surface using two techniques: cut and blast mining and continuous mining. Both of these are a form of room and pillar mining whereby approximately 35-55% of the deposit is left as support pillars for the roof of the excavation; the optimum size of which is calculated through rock mechanics for maximum salt extraction, while maintaining safety and stability. Notably, underground salt mine are considered to be amongst the safest of mines due to their natural stability and the fact that salt is inflammable. Both mine types are accessed via vertical shafts or inclined adits. The mining processes have been described in more detail below.

3.1.1 *Cut and Blast Mining*

A 100 to 200mm wide slot is cut at the base of the rock face using a machine called an undercutter, with a jib carrying a series of tungsten-carbide picks. The face is then drilled with a series of carefully sited holes, using an electro-hydraulic rotary drill. The holes are charged with explosives and the face is blasted, yielding between 750 and 1500 tonnes of broken rock salt. The rock is crushed into a manageable size, using a feeder-breaker. It is then carried on a conveyor belt to the main crusher at the ground surface, which breaks it down into smaller pieces, passing through a sieve or screen to ensure that it has reached the correct size for use in road de-icing. See Figure 3.1



Underground Salt Mining Operations

3.1.2 *Continuous Mining*

A boring machine, with a rotating head carrying tungsten-carbide tips, is used to grind the salt directly at the mine face. The resulting arisings are of a smaller size than those produced by drill and blast and are taken directly to a crushing and screening plant, without the need to be crushed by a feeder-breaker first.

Above ground processing for both methods usually involves screening of the mined salt into various marketable sizes before storing in stockpiles or storage bins according to size or product. Before storage, salt is commonly treated with an anti-caking agent to stop the pieces coagulating. This ensures that it can be held in local storage depots, ready for use on the roads. Anti-caking agents usually comprise ferric-ferro cyanide (FFC) also known as yellow prussiate of soda (YPS).

3.2 *Vacuum Pan Refining*

Evaporated salt (sometimes called “refined salt”) is produced by solution mining the underground deposit and removing the water from the saline brine pumped to the surface.

Solution mining is the process whereby wells are drilled into the salt deposit at a spacing of between approximately 50m and 250m depending on the deposit type, depth and well size. These wells are connected via lateral drilling and water is pumped down one well dissolving the salt and the resultant brine is forced to the surface through another well from where it is piped into large tanks for storage.

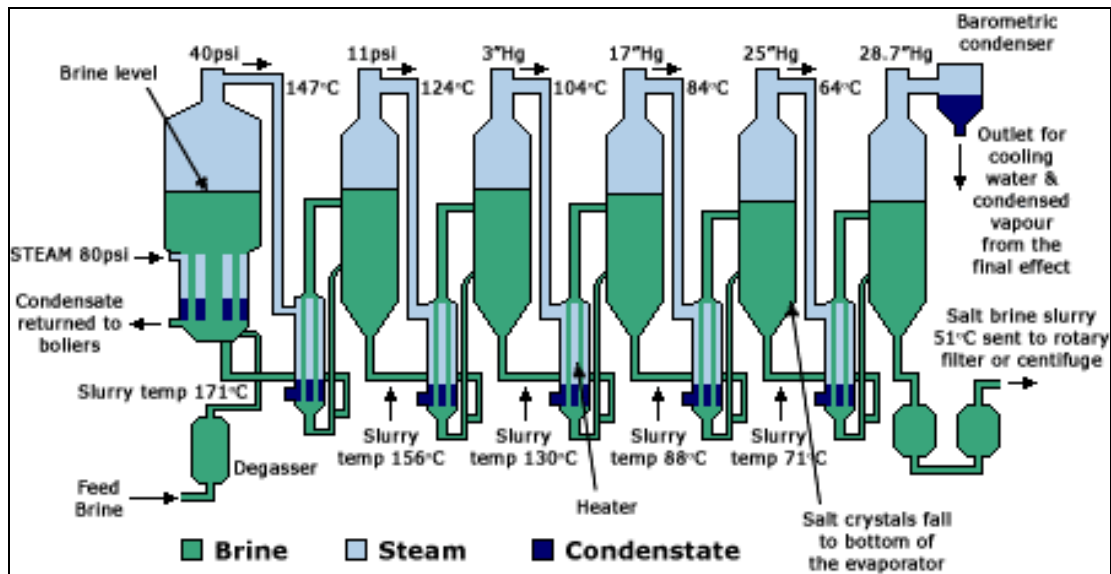


Figure 3.2: A typical vacuum pan salt plant.

A typical vacuum plant as illustrated in Figure 3.2 consists of a series of closed cylindrical vessels, or 'effects', containing steam chambers, which in turn contain a number of tubes. Water is evaporated from brine using steam-powered multiple-effect or electric-powered vapor recompression evaporators. Multiple-effect systems typically contain three or four forced-circulation evaporating vessels connected together in a series.

Brine is circulated through the tubes with steam condensing on the outer surface. The first effect receives low-pressure steam into its steam chamber. The brine boils at a temperature dictated by the inlet steam pressure and water evaporates as a result. This produces further steam and causes salt crystals to grow. As the brine boils and the water is “driven off”, a thick salt slurry of brine and salt crystals is formed. This is fed to the second effect and circulated through a second heater unit, which utilises the exhaust steam from the first effect. Pressures (and boiling temperatures) are successively reduced at each successive stage (boiling point reduces with reduced pressure). Vacuum pans can operate with boiling points as low as 40°C, while final stages operate under vacuum and enable the brine to boil at much lower temperatures, which is more fuel-

efficient. The slurry from the final effect is fed into a centrifuge to extract more free moisture. The resulting undried vacuum salt is then stored in bulk, for supply to the chemical industry.

For food and allied industries, dried salt is required. Salt from the centrifuges is fed into fluid bed drier-coolers - rather like hair-driers - for further drying. The salt is then sieved and graded before being transferred into large storage hoppers ready for distribution.



The evaporators operate under a vacuum to reduce the energy requirements. Steam from boilers is recycled/fed from one evaporator to the next to increase energy efficiency in the multiple-effect system. Vapor recompression forced-circulation evaporators consist of a crystallizer, a compressor, and a vapor scrubber. Feed brine enters the crystallizer vessel, where salt is precipitated. Vapor is withdrawn, scrubbed, and compressed for reuse in the heater. The crystallized salt is removed in slurry, dewatered using a centrifuge, dried in a rotary kiln or fluidized bed dryer, treated with any additives (e.g. potassium iodide or iodate making iodized salt) and packaged. In all vacuum pan refining the weak brine remaining after the salt is crystallized is usually recycled to the solution-mined cavern.

A lesser common method of producing evaporated salt is the less energy-efficient method where the brine is crystallized in open pans known as 'grainers'. The brine is

chemically purified and pumped into a long open pan heated by steam running through pipes immersed in the brine. The brine is heated to a temperature slightly below the boiling point and flakes of salt form on its surface as it evaporates. Usually a temperature of about 90°C is used. Lower temperatures produce larger flakes and higher temperatures produce smaller flakes. The flakes grow until they sink to the bottom of the pan, where they are collected and dried. Grainer salt consists of small flakes rather than cubes and is preferred for certain uses in food processing. Sometimes the Alberger process is used, in which the brine is first partially evaporated in a vacuum evaporator then moved to a grainer. This process produces a mixture of flakes and cubes. The flakes of salt have an extremely low bulk density that is highly prized in the fast food industry due to a high flavor content for a given volume, which results from the 'cup-shaped' structure instead of in the cubic form of normal salt crystals. This has led to the 'low-sodium' or 'low salt' food revolution.

3.3 Solar Evaporation Method

Salt is extracted from oceans and saline lakes (e.g. Great Salt Lake, Dead Sea, Caspian Sea, Issak Kul in Kyrgyzstan, Lake Eyre in Australia and Chilwa in Malawi), through evaporation of water to leave salt crystals that can then be harvested mechanically. Any impurities that are present in the brine are drained off and discarded prior to harvesting. This is only possible in climates where the evaporation rate exceeds the precipitation rate, either annually or for extended period and the body of water is not recharged via other sources, such as inflow from rivers, in the meantime.

Commonly two types of pond are used. First is the concentrating pond, where the brine is concentrated, followed by the crystallizing pond, where the salt crystallizes, which is fed by a continuous flow of brine. Natural chemical impurities are returned to the salt water source.



4. ENERGY EFFICIENCY OF SALT PRODUCTION PROCESSES

4.1 Introduction

The energy efficiency of salt production, like most raw material production industries, is heavily dependent upon the end use requirement. Salt use as a highway de-icing agent does not require high grade sodium chloride (typically 90% to 98% NaCl). The size of particles and their ease of bulk transport are as important as operational performance. There is usually little processing of the halite (rock salt) raw material once this has been mined and crushed to an appropriate particle size. Quality control of rock salt is usually carried out in advance of the mining face. Impurities are minimised by mining the best *insitu* rock salt grades. Once mined there is little need for further processing other than size classification, indeed, it is usual to blend small quantities of anti-caking agents that assist with distribution.

Energy efficiency in the mined – de-icing salt market largely comes down to studies of mining methods including energy utilisation of excavation processes, load-haul-dump cycles, crushing, screening and storage, and of the subsequent distribution requirements. However, these are not topics that are central to this reference book. Therefore, while further reference will be made to the overall energy equivalents of rock salt production for comparison purposes, no detailed analysis of energy efficiency of mined rock salt will be included.

The production and collection of salt from natural solar evaporation of confined bodies of seawater has been going on for millions of years. In pre-historic times, salt as a daily biological need by both humans and animals have drawn both to areas where they are naturally available. In terms of energy efficiency, reliance on the sun and natural climate makes this source of salt to be highly energy efficient. However, this source can only provide a fraction of the present days production requirement, and like salt generated from underground mining has a limited quality control capability. Little further reference will therefore be made to this source of salt.

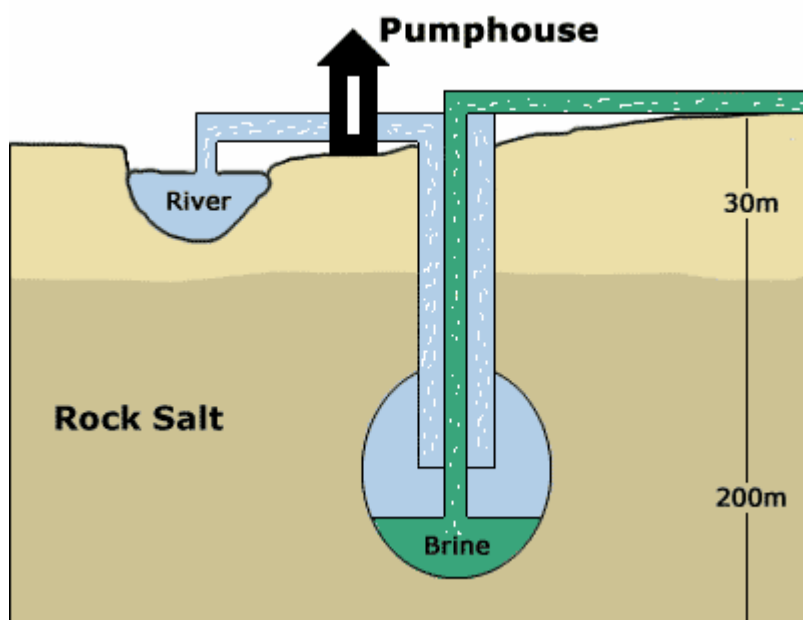
In addition to naturally occurring salt deposits that are being generated by climatic and environmental conditions, as much as 30% of the current world production of high grade salt (>99% NaCl) is still generated by solar power in regions where climatic conditions are favourable; albeit the salt production rate is enhanced and accelerated by technological innovation. Technology in this area however, remains low key, and usually comprises the establishment of a series of evaporation pans, with pumps to transfer brines of increasing saturation from pan to pan and the use of mechanical salt collection equipment. However, the primary source of energy use remains solar. Therefore this semi-mechanised production process, while very energy efficient is limited in volume

capacity and to suitable regional climate types. Further passing reference will be made for this process in tables for comparison purposes.

Notwithstanding the above, a large and growing proportion of food and chemical grade salt (>99.5% NaCl) is now produced by energy intensive methods in northern and eastern developed and developing countries. In these regions, the climatic conditions may not be suitable for salt production by solar methods. Vacuum pan and Open Grainer and Alberger processes take natural or artificially produced brines and through energy input, concentrate the salt by forced evaporation of water. These methods are capable of producing salt of high purity, and as stated at the beginning of this section, the required salt purity remains a governing factor especially for food and chemical industry end uses. These techniques are therefore considered in greater detail to establish baseline energy requirements and potential energy efficiencies.

4.2 Brine Production

In solution mining, water is forced under pressure into a bore-hole drilled into an underground salt bed or dome. The salt is dissolved, turning the water into brine and creating a cavern in the salt-bed. The saturated raw brine is then withdrawn and pumped to the purification plant where calcium, magnesium and other impurities are removed prior to the evaporation process.



Chemical treatment of the brine, followed by settling, reduces levels of dissolved calcium, magnesium and sulphate. Sulphuric acid treatment or chlorination may be

used to remove hydrogen sulphide, and hydrochloric acid will neutralize brine used in diaphragm cell production of chlorine and caustic soda.

Brine purification has become increasingly important to produce high purity salt for use in chlor-alkali production, particularly in Europe where dry salt is used extensively for this purpose.

Energy efficiency options in this field are mainly linked with pumping technologies of large volumes of water with large vertical displacements. A site specific balance needs to be developed to promote the most cost-effective temperature of injection water, combined with geological rock-salt temperature, to promote the most efficient salt dissolution process. By product water from the later evaporation stages can be recycled to use as input water together with remaining dissolved salt minerals.

4.3 Vacuum Pan Salt Production

Using the accelerated vacuum pan salt production process, water is evaporated from purified brine using multiple-effect or vapour recompression evaporators.

Multiple-effect systems typically contain three or four forced circulation evaporating vessels connected together in series. Steam from boilers supplies the heat for evaporators and is fed from one evaporator to the next to increase energy efficiency in the multiple effect system.

The technology is already well established worldwide.

Vapour recompression forced-circulation evaporators consist of a crystallizer, compressor and vapour scrubber. Feed brine enters the crystallizer vessel where salt is precipitated. Vapour is withdrawn, scrubbed and compressed for re-use in the heater.

Recompression evaporators are more energy efficient than multiple effect evaporators, but require higher cost electrical power for energy input. The development of single stage compressors has significantly reduced costs.

Ultimately, weak brine from either process is recycled to the solution mined cavern. Crystallized salt is produced as slurry which is dewatered first by centrifuging or vacuum drying and then in kiln or fluidized-bed dryers where moisture content of the final product is reduced to 0.05% or less. During this century, salt producers have made significant advances in lowering energy consumption and in reducing salting and scaling in evaporators.

Evaporated salt is manufactured by evaporating the water from brine, under vacuum. This entails the use of heat energy, with implications for CO₂ emissions. The vacuum process maximises energy efficiency which is closely monitored for both commercial and environmental reasons. In Europe, the steam used for the evaporation process is generated in accordance with Integrated Pollution Prevention and Control (IPPC) regulations and, wherever possible, is reused within the manufacturing process.

Whilst rock salt mining does require energy input, this is considerably lower than for evaporated salt. All manufacturers monitor and seek to maximise their energy efficiency. Users are encouraged to weigh the overall energy impact, including the lower distribution energy usage of indigenous supplies.

4.1 Salt Production from Brine

The highest standards of quality are set by vacuum salt. Usually, vacuum salt is produced from brine obtained by solution mining of underground deposits and chemically purified. Such brines are almost saturated, containing approx. 25% NaCl and, therefore, to crystallise 1 ton of salt, 3 tons of water need to be evaporated. In a six effect evaporation plant, 0.62 tons of live steam used six times is required (Kondorosy, 2006). Assuming 10 bar steam, the heat transferred through steam condensation into the system is 390kWh/t (48kgce/t or 1,405MJ/t) of salt. Assuming further that the steam boiler is generating steam with 75% efficiency, 450kWh (55kgce or 1,621MJ) of energy per ton of salt is required.

4.2 Salt Production from Brine by Mechanical Vapour Recompression

Where electrical power is cheap and there is a regular source, recompression of vapour from the evaporator in a radial compressor can be employed. The compressor elevates the vapour temperature to such a level that the vapour can condense in a heat exchanger against the circulating brine, bringing it to boil. This system uses about 160kWh of electricity per tonne of salt. Assuming 35% power generating efficiency, also approx. 450kWh (55kgce or 1,621MJ) of energy per tonne of salt is required in this system (Kondorosy, 2006). Thermal evaporating plants (vacuum plants) and their operation are costly and so is the vacuum salt. As it is crystallized from brine containing up to 4% of sulphate, vacuum salt always contains sodium sulphate (frequently in the range of 200-500ppm). Despite the low calcium and magnesium content in the 1-10ppm range, vacuum salt will seldom exceed 99.95% purity.

4.3 Salt Production by Solar Evaporation of Sea Water

Sea water, having density of 1020 to 1029kg/m, contains 30.09 kg NaCl/m and 998.64kg of water (Baseggio, 1976); 89.9% of this water needs to be evaporated before the first crystals of NaCl can crystallise. A further 6.16% of water is evaporated before the brine becomes so concentrated that the evaporation slows down considerably, further evaporation would diminish the salt quality and therefore the brine (bitterns) would need to be discarded, still containing 8.37kg NaCl per original 1 m³ of sea water. Thus 21.72kg of NaCl can be recovered from 1m³ of sea water by solar evaporation. Per each 1kg of NaCl crystallised, 43.74kg of water needs to be evaporated compared with 3kg of water in thermal evaporation processes starting from almost saturated brine; that said, solar energy is free.

Of the incoming solar energy, which originates from the sun (Mottershead, 2006), 26% of the incoming solar energy is reflected by atmosphere and by clouds back to space, 16% is absorbed by atmosphere, 3% is absorbed by clouds and 4% is reflected from the surface. Therefore, 51% of the incoming solar energy reaches the surface and is absorbed by land, oceans and solar salt works. 23% is converted into water vapour and is carried to atmosphere and to clouds in the form of latent heat of evaporation. The balance is returned to atmosphere by conduction and radiation and finally, all of the solar energy received from the sun is radiated back to space.

Relevant for the operation of solar salt works is the 51% of the incoming solar energy that reaches the surface (surface insolation), which equals 51% of 1366Wm⁻² +/- 3.4% or 674–719Wm⁻² when the sun stands at its peak. Averaged over 24 hours per day in sub-tropical zones where most of the solar salt works are located, it corresponds to 200–300W/m² daily radiation average; the absorbed solar energy is therefore 5–7kWh m⁻² d⁻¹. Latent heat of water evaporation is, at 30°C, is 0.675kWhkg⁻¹. Therefore, 5–7kWhm⁻²d⁻¹ of surface insolation, if absorbed completely, could evaporate 7–10mm of water per day. However, winds not only carry away the water vapour from the salt works area, they also cool the brine by heat conduction; this accounts for 7% of the absorbed heat. In addition 15% is radiated to the atmosphere and 6% to the space. The balance, 23% of the insolation is converted into latent heat of water evaporation from brine, the ultimate driving force behind solar salt production. Therefore, instead of 7–10mm of water per day, only 3–5mm d⁻¹ or 1.1–1.8 m y⁻¹ is actually evaporated in average solar salt works, resulting in production of 27–44 kg NaCl m⁻² y⁻¹. In terms of salt layer in crystallisers, which represent about 10% of productive salt works area, 270–440 kg NaCl m⁻² y⁻¹ having a density of about 2 t/m³, forms a layer about 13–22cm thick. Exceptions to this average are known to exist in areas with very high wind temperature, for example near deserts, when the hot air actually heats the brine by conduction, instead of cooling it. In those places, salt layer thickness of half a meter or so in a year can be formed.

4.4 Summary

Comparing the efficiency of solar energy conversion into final product, 23% out of 51% surface insolation is directly converted into salt, representing 45% conversion efficiency. This compares favourably with 8–15% conversion efficiency of photovoltaic cells, 30% conversion efficiency of solar collectors with stirling engine, a device that converts heat energy into mechanical power by alternately compressing and expanding a fixed quantity of air or other gas (the working fluid) at different temperatures, and even with 40–45% efficiency of super critical steam power plants burning fossil fuels that incur additional 4-12% losses in the existing power distribution grids.

5. SALT COMPOSITION AND IMPACT ON PROCESSES

The purer the salt the more valuable it is; impurities present decrease its value and reduce the potential end uses. Apart from insolubles, impurities in salt are largely from sea water. Solar sea salts, as a rule are just a few months old, are all similar. Rock salts are commonly millions of years old and vary greatly in quality and purity, from pure to dirty, from white to black. Lake salts usually contain components leached from the ground of the surrounding rocks in variable quantities. Calcium sulphate is the most common impurity; in rock salt, calcium sulphate is present as anhydrite, hemihydrate or Polyhalite and natural brines are largely saturated with calcium sulphate. Gypsum is found both in sea salt and in lake salt. Magnesium salts are also always present in the sea salt, usually at a ratio of approximately one and a half weight units of magnesium chloride to one weight unit of magnesium sulphate. In lake salts, magnesium sulphate is usually accompanied by sodium sulphate, for example in Sambhar Lake salts from Rajasthan in India or in Azraq salts from Jordan.

Component	Rock Salt	Sea Salt	Lake Salt	Brines
CaSO ₄	0.5 - 2%	0.5 - 1%	0.5 - 2%	Saturated
MgSO ₄	Traces	0.2 - 0.6%	Traces	Traces
MgCl ₂	0.3 - 1%	Traces	Traces	Traces
CaCl ₂	Traces	Traces	Traces	Traces
Na ₂ SO ₄	Traces	Traces	Traces	Traces
KCl	Traces	Traces	Traces	Traces
NaBr	Traces	Traces	Traces	Traces
Insolubles	1 - 10%	0.1 - 1%	1 - 10%	1 - 10%

Table 5.1: Impurities commonly found in different types of salt.

Magnesium chloride also occurs together with calcium chloride, for example in the Dead Sea brines where also potassium chloride and sodium bromide are found in exceptionally high concentrations. Insolubles are present in salts of all origins in greatly fluctuating quantities.

5.1 Impact of Impurities in Salt

In the chemical industry, salt is mostly dissolved together with the impurities in water or brine. Prior to feeding to the process, the brine is purified; failure to purify the brine may have serious, even lethal consequences. The problems and issues are addressed below.

5.1.1 **Hydrogen evolution**

In electrolytic cells, excessive magnesium causes hydrogen evolution on the anode. Since, hydrogen and chlorine form an explosive mixture there is potential for an explosion in the cells or in the chlorine liquefaction section, which could damage the equipment and release chlorine gas to the environment; chlorine gas is highly poisonous. Stringent safety measures are taken in the chlor-alkali industry to avoid this and, therefore the elimination of magnesium is of prime concern.

5.1.2 **Mercury butter**

It also is important to reduce levels of certain heavy metals that result in the formation of 'mercury butter' (or thick mercury). Impure brine in mercury cells will cause butter formation and butter will disturb mercury flow, causing short circuits that burn the electrodes. Alternatively, a large electrode gap must be maintained, though this would increase the power consumption. Butter removal will expose workers to mercury vapours that are damaging to health and disposal of mercury butter is costly and undesirable for the environment.

5.1.3 **Contaminated sludge**

Sludge from brine purification in chlor-alkali plants with mercury cells is contaminated with mercury. Sludge decontamination by distillation requires high temperatures, is costly and never complete. The disposal of mercury contaminated sludge is environmentally objectionable and very costly. Avoiding the formation of sludge is better than having to dispose of it. This requires salt of high purity.

5.1.4 **Membrane damage**

Calcium and magnesium will damage the ion exchange membranes irreversibly. Erratic impurity content in salt may cause hardness breakthrough to the membrane cells. Membranes cost a fortune. The purer the salt, the more remote is the danger of membrane damage.

5.1.5 **Encrustation**

In soda ash production, excessive sulphate reduces the value of the product. Accumulating calcium in the process causes encrustations. Periodical scale removal is costly and leads to loss of production. Salt may be a cheap commodity but impurities in salt and their removal often cost more than the salt itself.

6. ENVIRONMENTAL EMISSIONS AND REGULATIONS

Any extractive industry necessarily disturbs the natural environment, though removing salt from the sea makes no real change in the volume or salinity levels of the ocean; nor does a rock salt mine or solution mining operation significantly alter the landscape, though underground operations must be carefully managed for structural stability. Both solar salt works and solution mine/vacuum pan-refining plants produce a saline waste stream that also requires proper management as does stockpiling and shipping of salt.

When a rock salt mine blasts away the solid seam of salt, the explosion leaves pieces ranging from boulders of salt to fine salt dust. As the salt is crushed to the size specified by each customer, further unusable fine salt dust is created. These “fines” are routinely used to fill some of the vast expanse created when the usable salt is hoisted to the surface.

In the final production of salt, to prevent the crystallization of other minerals which would degrade the purity of the sodium chloride, the crystallising pond is drained of the concentrated solution containing salt and other minerals, termed “bitterns”. Sometimes, the salt producer further processes the bitterns to extract other saleable materials before discharging the natural remnants to the sea.

In producing evaporated salt, the process water is re-used until all salt is removed that is economically recoverable and the remainder is generally deep well-injected (there is legislation governing injection well permits that will vary with each country but will most likely be obtained from the governing environmental agency). The size and shape of solution-mined caverns is also likely to be regulated by environmental permits. For example, in the US when a cavity has reached its planned size, it is closed and sealed under the terms of another environmental permit or, as is increasingly the case, is used to store petroleum or natural gas reserve supplies; regulation in the EU is further addressed below.

Moving salt from its production site to salt users can also impose environmental stress; a 2008 study conducted for the Port of Toronto documented that waterborne salt deliveries offer significant reduction in the “carbon footprint” of salt deliveries over land-based delivery options.

As stated, sodium chloride is not classified as dangerous to the environment and the manufacture of salt does not require registration under EU Directives and the IPPC Regulations, though, in Europe, the industry is regulated through a number of EU Directives governing operating practices, food safety and environmental performance. Environmental compliance for each manufacturing site is regulated through a combination of individual Local Authority (LA) permits and Environment Agency (EA)

licences. The LA permits cover the control, monitoring and reporting regimes that each company must have in place, for controlled processes, to demonstrate compliance to standards relating to such matters as dust control, noise levels and air quality (where applicable). Where relevant, the EA licences cover water abstraction requirements, discharges to water and operation of boiler plants. As manufacturing and mining processes continue to evolve, industry develops technology and improves best practice; generally operators seek to meet and often exceed the standards of international best practice.

6.1 Regulations and Good Practice

As a mineral which is not chemically altered in processing, rock salt is covered by Annex III of the REACH (Registration, evaluation and authorisation of chemicals) EU Directive. This means that it is exempt from any obligation to register. However, the Salt Industry will continue to monitor the development of the regulations and take all necessary steps to ensure that information is supplied to regulatory authorities as and when it may be required.

The UK Environmental Agency and the Winter Maintenance industry have developed a variety of guidance documents. The EA guidance note PPG10 outlines the requirements for salt storage in depots. Wherever possible, salt supplies should always be stored under cover. Industry guidance emphasises the need for proper calibration of spreading vehicles, gives recommended spread rates and advocates the use of forecasting systems to ensure that the de-icing activity only, but always, occurs when weather conditions demand.

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