PRODUCTION OF SODIUM CHLORIDE [1]

1. History ................................................................. 1
2. Formation and Occurrence of Salt Deposits .. 1
3. Production .......................................................... 1
   3.1. Mining or Rock Salt from Underground and Surface Deposits ......................................................... 1
      3.1.1. Mining by drilling and blasting ............................... 2
      3.1.2. Continuous mining ........................................... 2
      3.1.3. Upgrading or Rock Salt ...................................... 2
      3.2. Brine Production ................................................ 3
         3.2.1. Natural Brine Extraction .................................. 3
         3.2.2. Solution Mining ............................................ 3
         3.2.2.1. Drilling and Construction of the Borehole ....... 3
         3.2.2.2. The Process of Solution Mining ...................... 3
         3.2.2.3. Other systems .......................................... 4
         3.2.2.4. Equipment ............................................... 4
         3.2.3. Combined Dry and Solution Mining ..................... 4
         3.3. Vacuum Salt .................................................. 4
            3.3.1. Brine Purification ..................................... 5
            3.3.2. Open-Pan Evaporation ................................ 6
            3.3.3. Multiple Effect Process ............................... 6
            3.3.4. Mechanical Vapor Recompression (MVR) Process ........ 6
            3.3.5. Recrystallization Process ............................. 7
            3.3.6. Evaluation of the different processes .......... 7
         3.4. Production of Solar Salt .................................... 7
            3.4.1. Production from Sea Water ............................ 7
               3.4.1.1. The Main Factors Governing Production of Sea Salt ...................................................... 7
               3.4.1.2. Production Stages in a Modern Salt Field ...... 8
            3.4.2. Crystallization from Mined Brine ..................... 8
            3.4.3. Extraction from Salt Lakes ............................. 9
         4. Environmental Aspects ....................................... 9
         5. References ..................................................... 9

1. History [2-8]

Sodium chloride was used almost exclusively as a food and preserving substance for millennia. Presumably, human salt consumption became necessary with the change from nomadic hunters to settled farmers. Before this, eating meat covered human salt demand.

Finds at Hallstatt in the Austrian Salzkammergut, at Schwäbisch Hall in Germany, and in many other places prove that salt was already extracted in prehistoric times. As early as 1000 B.C. salt was extracted in Hallstatt, perhaps the oldest salt mine in the world, and in Schwäbisch Hall from ca. 500 B.C. A series of finds in Wieliczka and Bochnia in Poland indicate that extensive salt production existed already before 1000 A.C., using brine springs emergent at the earth’s surface as raw material.

The salt mine in Wieliczka has been a world cultural heritage site since 1978. In Egyptian grave paintings salt production was already described in 1450 B.C. In ancient China the majority of the salt was obtained by evaporation of seawater. Inland brine sources were opened up by boring. Around 2700 B.C. the Peng-Tzao-Kan-Mu, probably the earliest known treatise on pharmacology, was published in China. A major portion of this writing was devoted to a discussion of more than 40 kinds of salts, including descriptions of two methods of extracting salt and putting it in usable form that are amazingly similar to processes used today.

2. Formation and Occurrence of Salt Deposits [9]

Sodium chloride deposits are found in different types, in solid state, as mineral halite, or in solution (examples include):

- Seawater: the oceans and seas
- Natural brines: Alpine brine in Bad Reichenhall, Germany; Presov, Slovakia; Cheshire, UK
- Salt lakes: Great Salt Lake in the United States; Lake Baskunchak, Russia
- Lake basins: Salar de Atacama, Chile; Searles Lake, California
- Bedded salt: Germany, France, Poland, Romania, Russia, Switzerland, USA
- Salt domes: U.S. Gulf Coast; Zechstein Basin in Germany

3. Production

3.1. Mining or Rock Salt from Underground and Surface Deposits

Rock salt has been mined in Europe for 3000 years. A salt deposit near ground level in the Eastern Alps was developed by tunnelling and worked by excavation around 1000 B.C.

Mine Shafts. Access from the surface to the salt deposit is usually by vertical shafts 5 m in diameter. There must be at least two shafts, so that in case of damage to one of them, the underground workforce has an emergency route to the surface.

To sink the shaft, the rock is broken up by drilling and explosives. The rock debris is loaded into skips by grabs, and taken to the surface. In most cases, the upper layers of the overlying rock are water-bearing,
and sometimes consist of unstable loose rock and moving sand capable of exerting pressure. Therefore, before sinking the shaft, these strata must be solidified and stabilized. This can be achieved by freezing via holes drilled around the area where the shaft is to be sunk. The freezing equipment must be kept in place for the duration of the sinking of the shaft.

Another method of preventing the movement of water in the overlying strata and immobilizing loose rocks is the injection of cement, synthetic resins, or other hardening materials via boreholes. This technique is also suitable for sealing the mine shaft against the ingress of water and for stabilizing the rock at the bottom of the shaft.

### 3.1.1. MINING BY DRILLING AND BLASTING

As with any mining operation, the method of extracting salt depends on the thickness and spatial formation of the deposit.

Drilling and tunnelling into the adjacent rock should be avoided as far as possible to prevent ingress of water or gas from these strata into the mine.

**Mining in Bedded Salt Deposits**

In most salt mines, a systematic extraction procedure is possible due to the uniformity of the deposit over large areas. In salt deposits with horizontal or gently inclined seams, the standard method is room and pillar mining. In this method, the extraction process produces large chambers with rectangular cross sections.

Fresh air is provided by an inlet ventilation road above the haulage tunnel. The used air is removed through return air galleries and by the main ventilating fan, which is usually underground, and blown through the exhaust shaft to the surface.

The mining of the salt during the construction of the tunnels and in the extraction chambers is by drilling and the use of explosives.

Various drilling and blasting processes are used. In the undercutting method, the working face is undercut to a distance of 4–5 m. The cut, 15–20 cm wide, is produced by a machine resembling a chain saw. An electro-hydraulic mobile drilling machine drills 35–38 mm diameter holes for the explosive. In another process, a wide hole up to 7 m in length and 0.45 m in diameter is drilled into the middle of the working face to provide an initial extension space for the salt at the moment of explosion, a function that is performed in the undercutting process by the undercut.

The extraction chambers are created by widening the access tunnels. If these are driven through the lower part of the deposit, this is performed by the use of explosives in long inclined boreholes directed upwards.

In the main extraction phase, the salt that has been broken up by explosives is left lying in the space created, and the final position of the roof of the chamber is created by blasting, working from the top of the heap of loose salt.

The most commonly used explosive is ANFO (ammonium nitrate/fuel oil mixture) in the form of loose prills.

**Mining in Diapirs**

Steep to vertical rock salt deposits are generally mined by the stepped face method, as used, for example, in North German mines at depths of 400–850 m, with working levels at vertical intervals of 100–250 m and intermediate sublevels at intervals of 15–20 m.

To load the mined material after blasting and to transport it to the first crusher, diesel-powered front loaders with bucket capacities of up to 18 t are used (LHD: Load, Haul, Dump System).

The most prominent open-pit salt operations are at the Salar Grande de Tarapacá deposit, located in the North Chilean coastal mountain chain approximately 80 km south of Iquique. Operations are carried out on the surface, and consist of a classic combination of drilling, blasting, loading, and transportation.

### 3.1.2. CONTINUOUS MINING

Continuous miners or boring machines have been used since the late 1950s for salt mine development and for production. These machines have movable, rotating heads with carbide-tipped cutting bits. Continuous miners bore into the salt and eliminate undercutting, drilling, and blasting. A typical single drum head miner weighs 130 t.

Excessive fines were a problem in the past, but newer machines have reduced fines production. Advantages of continuous mining are high productivity and no residues from blasting (wires, plastic) in the extracted rock salt. Furthermore, there is no explosion-related vibration at the surface.

### 3.1.3. UPGRADEING OF ROCK SALT

In mines where the salt has a purity of > 99% NaCl, in most cases, the salt can be marketed directly after grain-size classification.
Where the natural purity is low (e.g., 94% NaCl in South German mines), or the salt is intended for use in the chemical industry, upgrading is necessary. The mechanical dressing of the extracted salt pursues the objectives of removing secondary minerals and increasing salt content.

The choice of separating procedure is dependent on the grain size of the feed material and on the nature of the secondary material to be removed.

In practice the following procedures are used, sometimes in combination with each other:

- Selective Comminution and Sieving
- Separation in a Throw Parabola
- Manual Sorting
- Heavy-Medium Separation: the rock salt is suspended in a heavy medium, which consists of saturated brine with magnetite.
- Flotation: In many types of rock salt the impurities (anhydrite, insolubles) are dispersed throughout the crystalline salt. The final product quality attainable by flotation therefore depends not only on salt grinding, and thus on minerals separation, but also on removal of the impurities with the foam product, which is influenced by the used flotation reagents. Selective separation of anhydrite from fine-ground rock salt requires grinding to 250 mm and the use of sulfated fatty acids. Attention must be paid to the complicated handling of the flotated salt and its residual flotation reagents, and a suitable possibility for disposal of the tailings must be available. A few flotation plants are located next to potash mines for sulfate removal from byproduct rock salt for use in chlor-alkali electrolysis plants using mercury and membrane cells.
- Electrostatic Separation: Preheated salt with the grain size of 0.2–4 mm is fed to a rotating metal roll, above which a corona producing electrode is placed. The salt and anhydrite/ clay particles become charged, but only the conducting anhydrite/clay particles can lose their charge.
- Magnetic Separation
- Thermoadhesive Process: Basically, the thermoadhesive process consists of exposure of crude rock salt to radiant heating, which selectively heats the impurity particles.

Three methods can be distinguished for the production of brine:

### 3.2.1. NATURAL BRINE EXTRACTION

The brines are generated by natural solution mining of the salt mountain [10].

Brines often contain high concentrations of bromide. Certain brines contain relatively high concentrations of iodine.

### 3.2.2. SOLUTION MINING

Solution mining technology originated in China over 1000 years ago; today, this technology has been developed to high levels of perfection, capable of constructing caverns with optimal shapes, conforming to precise specifications, at depths down to 3000 m and with volumes of up to 800 000 m³ and more.

For this method certain preconditions must be fulfilled, especially with regard to the geology of the deposit (type, formation, and depth of the salt).

In addition, an adequate supply of water must be available.

#### 3.2.2.1. Drilling and Construction of the Borehole

The drilling and completion of the trial boring and the design and installation of the brine wells (also known as the cavern wells) closely resemble those of petroleum and natural gas wells. The method of operation and the geological conditions determine the size, type, and position of the casing that protects the walls of the borehole against the effects of permeable strata, and prevents solid material from the rock from falling into the borehole.

The casings are cemented up to ground level. The outer casing must be installed and cemented with special care, and each individual joint as well as the whole casing must be tested for tightness.

#### 3.2.2.2. The Process of Solution Mining

Two alternative methods allow precise control of the development of cavern shape:

1. Direct leaching through the inner tubing secures a more speedy development of the lower region of the cavern
2. Indirect leaching via the inner annulus producing highly concentrated brine ensures faster development of the upper region of the cavern

Fresh water is pumped into the borehole through the annular space between the two inner pipes. The...
water dissolves salt from the walls of the cavern. The solution sinks as its salt content increases, and the saturated brine formed then rises to the surface in the central pipe due to the applied pressure.

The outermost annulus is always reserved for the injection of the blanket, a protective medium incapable of dissolving the salt and lighter than water and brine that prevents leaching in the roof area of the cavern. This can be a hydrocarbon such as diesel fuel or even nitrogen or compressed air.

3.2.2.3. Other systems

Individual boreholes for extracting brine can generally only be operated economically in thick salt deposits or salt domes. However, thin salt deposits can also be exploited economically in some cases. Here, two or three boreholes are linked together by injecting water to dissolve the salt and to fracture it by hydraulic action [11, 12, 13]. Fresh water enters via the first borehole, and the brine is collected from the second or last borehole. Here also, dissolution of the roof is prevented by a blanketing medium.

The stability of the cavern spaces cannot be guaranteed, as there is a risk of uncontrolled dissolution processes.

3.2.2.4. Equipment

The equipment requirements normally consist of:

1. Equipment for supplying water, sometimes including a pipeline
2. A pumping station with a distribution system delivering water to the individual solution mining operations
3. A blanket station
4. A pipeline for transporting the brine to the consumers (salt factory, chlor-alkali electrolysis, soda ash plant)
5. A central system for supervising and controlling the entire processing equipment

The water is injected by high-pressure centrifugal pumps at a pressure determined by the difference in the densities of the two media

The addition of polyphosphates to the water, including hexametaphosphates, reduces the dissolution rate of calcium sulphate (anhydrite), the primary impurity in many salt formations, and leads to brine with reduced contents of sulphate and calcium ions. At lower concentration (i.e., up to 50 ppm in the brine) hexametaphosphates are found to be the most effective agent, and sodium hexametaphosphate (Graham’s salt) is the preferred retarding agent [14]. Another retarding agent that reduces the solubility of calcium sulphate is dodecylbenzenesulfonic acid, with typical feed rates to the leaching water of 10–15 ppm [15].

3.2.3. COMBINED DRY AND SOLUTION MINING

Water flushing (intermittent or continuous dissolution in chambers) is the extraction process usually used in the alpine salt deposits in Germany and Austria. Tunnels, shafts, and chambers are usually first produced by mining techniques.

A single worked stratum is divided into separate districts of a given size in which several extraction chambers are set up. A block of definite dimensions (length, breadth, and height) is allocated to each chamber based on a predetermined degree of extraction. The block encompasses a space of irregular configuration produced by the extraction process and the pillars left between the extracted spaces, which are also of irregular shape.

The production of the initial space is usually divided into the following stages: sinking a borehole for examination of the deposit in the region to be excavated, vertical development by sinking a wide borehole and further widening of the borehole by controlled dissolution, forming a funnel-shaped space at a depth extending from 100 to 125 m.

The initial space (chamber) is slowly filled with fresh water, which dissolves salt from the side walls and roof.

3.3. Vacuum Salt

The term “vacuum salt” is used for crystalline salt that is obtained from saturated brine in evaporative crystallizers. The feed for salt crystallization plants can be saturated brine (for brine production) or rock salt (for rock salt production) and solar salt (for solar salt production). Vacuum salt is normally produced in closed evaporators by dehydrating brine with heat alone or in combination with a vacuum.

The basic processes for vacuum salt production are brine purification, evaporation, and crystallization. Three salt crystallization processes are in use:

1. Multiple-effect evaporation
2. Mechanical Vapor recompression
3. Recrystallization

In an evaporative crystallizer, the salt normally crystallizes at 40–150ºC, whereby the solubility of sodium chloride increasing only slightly with temperature.

Brine is generally obtained by dissolving crude salt that contains many impurities. The production of high-purity salt requires chemical purification of the brine. The high purity is the major difference to rock salt. Purification is also necessary to avoid scale
formation in the heat exchangers and the evaporation equipment.

### 3.3.1. BRINE PURIFICATION

Brine purification is an important step in the production of sodium chloride for the chemical industry, pharmaceutical uses, and water treatment. Magnesium and calcium ions must be removed from the saturated brine to avoid scale formation and also impurities such as hygroscopic magnesium chloride in solid sodium chloride.

The most common and most problematic impurities in crude salt are the sulphates, chlorides, and, to some extent, the carbonates of calcium and magnesium, as well as the triple salt poly-halite. In addition, the water which is used for dissolving rock salt contributes to the content of impurities in the crude brine. The principal impurities of crude brine are therefore calcium, magnesium, and sulphate ions, but also strontium ions (usually dissolved in relatively low concentrations in crude brine, all of which take part in scale formation.

The following chemical methods are used to purify crude brine:

**Purification with Lime or Caustic Soda and Soda Ash.**

Traditional brine purification is performed in the Schweizerhalle process, named after a Swiss saline. It consists of two steps:

1. **Addition of calcium hydroxide** to precipitate magnesium ions as magnesium hydroxide and produce gypsum due to the increase in the concentration of calcium ions in a solution already saturated with calcium sulphate.

   Usually, solid calcium oxide is preferred over milk of lime, because it does not dilute the saturated sodium chloride solution further. Since lime is hydrated much more slowly in brine than in water, it is important to use highly reactive, fine-grained lime.

2. **The addition of soda ash** to precipitate the remaining calcium ions as calcium carbonate.

   The crystallization of calcium carbonate can also be achieved by purging the alkaline brine with carbon dioxide, easily available in the form of combustion gas, which contains about 10–14 vol% carbon dioxide.

   After these two reactions, magnesium and calcium ions are removed almost quantitatively.

### Continuous Brine Purification Process

The brine purification processes described above are carried out as batch operations, but in a few cases continuous processes are used.

Sedimentation is accelerated by adding flocculating agents, usually anionic polyacrylates. In the continuous process, the solid precipitates are removed in thickeners.

In this case, the conical vessel employed is filled with crude brine and mother liquor from the bottom and milk of lime from the top. The formation of gypsum causes caustification. Sodium hydrogencarbonate is added and, due to the equilibrium with hydroxide ions, carbonate ions are formed, which precipitate calcium carbonate.

**Gypsum Slurry Process.**

In the majority of cases purified brine is evaporated. The gypsum slurry process is used, particularly in the USA. In Europe it finds only occasional use [16]. In this process raw brine with suspended finely ground gypsum is evaporated. Calcium sulphate from brine evaporation precipitates as anhydrite, remains in suspension, and does not form incrustations on the metallic surfaces of the evaporators and heat exchangers. Chemical brine purification is not necessary. The gypsum is removed from the produced vacuum salt by backflow washing with raw brine in the leg of the evaporator and in a thickener–washer unit.

The procedure is relatively cheap but supplies vacuum-salt quality with increased contents of calcium, magnesium, and sulphate that is no longer sufficient for all uses.

**Mother Liquor Concentration.**

Soluble ions such as K⁺ and Br⁻ cannot be precipitated in brine purification process. In an electrolysis plant they end up in the products as KOH and Br₂.

Following NaCl crystallization by evaporation of the brine in multistage or MVR processes, the obtained mother liquor still contains among others SO₄²⁻, K⁺, and Br⁻. Further concentration of this mother liquor by evaporation results in the precipitation of both NaCl and Na₂SO₄, and a more strongly concentrated mother liquor with respect to both K⁺ and Br⁻ remains. This concentrated mother liquor is drained off. The Na₂SO₄ is dissolved in brine and then returned to the brine purification process, thereby lowering both the K⁺ and Br⁻ levels in the purified brine. As a consequence the contents of both K⁺ and
\[ \text{Br}^- \text{ of the NaCl of the first evaporator steps are reduced.} \]

**Nanofiltration.**

In chlor-alkali plants nanofiltration (NF) of brine has been known since 1996 [17]. Nanofiltration removes sulphate as a small-volume, high-concentration stream and can reduce direct purge volumes by as much as 95%, or can eliminate the handling of toxic and expensive barium compounds and disposal of sulphate-containing solid waste.

Sulphate removal is based on selective filtration of brine through a NF membrane under high pressure.

The NF membrane process has great potential for improvements in producing high-grade vacuum salt. The use of a NF separation unit to recover the sulphates with a reduced content of K\(^+\) and Br\(^-\) ions and to obtain a brine with more or less no sulphates not only enables high-grade salt production but also reduces the purge or the bleed-off by using additional evaporator steps [18].

Pre-treated seawater is also suitable for nanofiltration. Nanofiltered seawater is sent to a thermal desalination plant, which operates as a sodium chloride concentrator and a distilled-water producer.

**Quality of the Purified Brine.**

Purified brine still contains low concentrations of problematic ions [19]

A minimum concentration of magnesium ions in brine is reached with a hydroxide concentration of about 0.003 mol/L in the brine. The solubility of calcium and strontium ions is temperature-dependent. Soda ash is usually used with 0.003–0.004 mol/L in excess.

The low-concentration alkaline earth metals in the purified brine form primarily carbonate scales in the evaporators, with the following composition: 71.5% calcium carbonate, 22.2% strontium carbonate, 2.1% magnesium carbonate.

These carbonate incrustations must be removed with acids. To avoid this problem, ion exchangers can be used to remove the remaining alkaline earth metal ions. This strategy is mainly used for the production of ultrapure brine for membrane chlor-alkali electrolysis.

Another method is keeping these ions dissolved by using complexing additives, usually polyphosphates or phosphonates. Such antiscalants prevent the formation of insoluble carbonates. The alkaline earth metal ions then accumulate in the mother liquor [19].

### 3.3.2. OPEN-PAN EVAPORATION

Evaporated salt can also be produced with the addition of heat in open pans. The grainer or open-pan process uses open, rectangular pans with steam-heated immersion coils to evaporate the water in the brine.

The open-pan process cannot be operated successfully in regions with high humidities because the evaporation rate is too slow and more energy is required to evaporate the water from the brine.

### 3.3.3. MULTIPLE-EFFECT PROCESS

The multiple-effect evaporation process is a classical process for the production of vacuum salt. Several evaporators are connected in series. The boiling point of the brine is reduced in each evaporator stage by ca. 12–20\(^\circ\)C by decreasing the pressure above the brine from unit to unit with the aid of a vacuum pump. The first effect is heated by live steam, and the following stages are heated by the vapors of the upstream unit. The vapor of the last stage enters a cooling water system (loss stage). The brine feed is preheated with condensate from the evaporators.

In salt plants the number of effects used varies between two and six.

### 3.3.4. MECHANICAL VAPOR RECOMPRESSION (MVR) PROCESS [20,21]

An MVR plant works like an open heat pump (Carnot process) in which the vapors are recompressed up to the pressure level of the heating steam. Vapor-recompression forced-circulation evaporators consist of a crystallizer with one or several heating loops, a compressor, a vapor scrubber, and a preheating system.

Recompression evaporators are more energy-efficient than multiple-effect evaporators but require more expensive electrical power for energy input.

A thermocompression plant with a steam ejector instead of a mechanical thermocompressor involves less capital expense but higher energy costs. The heat pump in salt works is one of the oldest applications of heat recovery. In Austria, Bavaria, Slovakia, and Switzerland the entire salt production is based on MVR technology.
A large hybrid plant at Varangeville/France consists of a first, single unit operated by compression while a second unit operates in five-stage evaporation [22].

### 3.3.5. Recrystallization Process [23]

The recrystallization process was first introduced in the salt industry in 1951 by International Salt as the Richards process and by Salins du Midi as the Pompe à Sel process [24, 25].

The recrystallization process is similar to flash-evaporation desalination of seawater or a multiflash evaporation plant. In the preferred hot-dissolution process the undersaturated recirculation brine becomes saturated with solid salt at about 108ºC and is fed downstream to several flash crystallizers working at different pressures. Supersaturation is achieved in the vacuum crystallizers by simultaneous evaporation of water and adiabatic cooling of the brine feed, and consequently crystallization of salt starts. The purge from the last crystallizer is pumped to preheater columns, where the cold saturated brine is mixed with the hot vapors coming from the evaporators. Finally, the output from the columns is an undersaturated brine at nearly 100ºC which goes back to the saturators. Process heat losses are compensated by means of booster heaters built into the hot brine recirculation pipeline. The heat content of the vapor from the last evaporator is lost.

### 3.3.6. Evaluation of the Different Processes

The selection of the technology for a new vacuum salt plant must consider the following criteria in particular:

- Availability of raw materials (brine, raw salt)
- Impurities of the raw material
- Availability and energy costs (power, steam, primary energy)
- Water situation (quantity and quality)

The multiple-effect process is frequently employed in combination with an oil- or gas-fired co-generation plant.

The different evaporation systems are characterized by specific energy consumptions that are in the focus of the cost management of salt factories.

### 3.4. Production of Solar Salt

In his Historia Naturalis, PLINY THE ELDER already referred to the technique of producing salt by the natural evaporation of seawater. Even today, this method of exploiting the oceans, seas, salt lakes, and chotts is still widespread. It is practiced in nearly all regions of the world where climate and topography allow.

While some methods have changed very little, such as those of the “Paludiers” working the salt marshes along the Atlantic coast of Portugal and France, other modern methods are now applied, combining productivity with strict environmental protection. This applies to the vast majority of salt fields in the Mediterranean basin, on the west coast of Australia, and Guerrero Negro, the world’s largest salt field in Mexico at the southernmost tip of Baja California.

The term “solar salt” refers to crystalline salt which is obtained from seawater, salt lakes, and brine by evaporation and crystallization with solar energy. For salt which is extracted from seawater the term “sea salt” is also used.

### 3.4.1. Production from Sea Water

The water of the seas and oceans contains all the known elements, most of them present in small amounts [26].

#### 3.4.1.1. The Main Factors Governing Production of Sea Salt

The pond areas containing the brines or saline solutions must also be as level as possible, ideally below sea level, and stepped in elevation. This reduces the number of intermediate pumping stations required and helps to optimize the design of the ponds, dikes, channels, and culverts making up the salt field.

#### Concentration of Sea Brines

After being pumped from the sea, the seawater passes through the salt field from pond to pond. As it passes through the ponds, the NaCl concentration in the seawater rises. At this point, the brine begins to deposit its salt.

Apart from the physicochemical process described above, a biological process develops in the evaporating and crystallizing ponds that is equally important to the production of salt [27]. Surprisingly, despite rising salinity, life in the basins of the salt works does not stop.

Seawater organisms gradually disappear as they move from the initial pan to the hostile environment of the others. However, other organisms develop in their place and, as there is no competition, they proliferate. Such large populations of different organisms can survive in areas with different concentrations, that is, in different pans. Thus, in
parallel with the physicochemical process, a chain of microorganisms develops in the evaporating ponds system, constituting the biological process of the salt production process.

The nature of the biomass in salt ponds depends on the salinity [28]:

- Low salinity ponds: micro-algae, bacteria, protozoa, fish, mangroves, sea grasses, seaweeds
- Intermediate salinity ponds: Artemia salina, brine fly larvae
- High salinity ponds: Dunaliella salina, red halophilic bacteria

The small crustacean Artemia salina, also called brine shrimp, is the key organism in this biological chain. The biological system is in admirable harmony with the production process of the salt works in three ways:

- It produces the appropriate quantity of organic matter, which is a source of energy for the various organisms, and reduces the permeability of the bottom of the ponds, thus minimizing brine losses.
- It colours the brines in the crystallizers red and thus maximizes the evaporation rate by maximizing the rate of solar energy absorption and eliminating reflection of solar radiation from the colourless salt bed. The red colour of the brines is due to Halobacterium and to the monocellular seaweed Dunaliella salina.
- Finally, it creates and maintains appropriate conditions in the evaporation ponds and crystallizers for continuous and maximal production of high-quality salt, which is characterized by clear, compact, and mainly thick granules.

Crystallization of Sodium Chloride

When the brines approach the NaCl saturation point, they are fed through feed channels into the crystallizers, which represent the production units.

3.4.1.2. Production Stages in a Modern Salt Field

The production process features the following stages:

1. Seawater pumping: the salt field is supplied with seawater.
2. Concentration of seawater in the ponds: in this stage, the water flows through shallow ponds and is allowed to concentrate until approximately 90% of the initial water content has evaporated. The brines are moved pond to pond by gravity or by pumping as dictated by the local topography.
3. Deposition of NaCl in the crystallizers.
4. Salt harvesting: in batch-operated salt fields, salt harvesting begins at the end of the salt production period.
5. Transport, washing, and storage: the harvested salt is loaded onto trucks or tractor-drawn trailers for transport to a washing plant where most of the impurities are removed. Washing removes all solid impurities from the salt (substances insoluble in water) along with the accompanying bitterns (solutions of magnesium or potassium compounds). The salt is kept in suspension in saturated brine. The salt–brine mixture is then dewatered and centrifuged. The salt travels up an inclined gantry conveyor and is poured on top of one of the huge salt stockpiles that are a familiar feature of salt production sites.

Solar Salt Quality.

It has been widely recognized in the salt community that healthy biological systems in solar salt works lead to higher salt production and better salt quality.

In solar salt works, salt is harvested from crystallizing ponds as mixture of salt crystals and mother liquor (bitterns) containing soluble impurities in high concentrations. During outdoor storage, the content of soluble impurities is reduced, until it becomes constant after six months. This phenomenon is known as ‘natural purification’.

3.4.2. Crystallization from Mined Brine

One large solar salt production, which starts from mined brine, is located in Torrevieja in Spain. The saturated brine is pumped via a 52 km pipe from the Cabeza de Pinoso salt deposit to the 1400 ha solar lagoon at the coast of the Mediterranean Sea. Salt is obtained by evaporating the water of the brine by the combined action of solar radiation and wind.

Some 120 000 t/a of pure NaCl is being produced at Sales Monzon in Spain by utilizing the residual heat from production of 17 MW of electricity with gas turbines. By using the residual heat from cogeneration the brine from solution mining caverns is heated to ca. 80ºC before entering the crystallization ponds. The evaporation rate at that temperature is ten times higher than at 30ºC. As a result, the ponds required are much smaller than solar evaporation ponds and the salt layer is much thicker [29].
3.4.3. EXTRACTION FROM SALT LAKES

Evaporation of saline waters over geological time has resulted in terminal lakes of saline waters in many countries of the world. In these deposits, concentrations of the salts are much higher than in seawater and the recovery of a range of salts from salt lakes and their processing to other products is carried out in commercial operations.

The production of salt from salt lakes occurs in similar way to that of seawater by evaporation with solar energy.

4. Environmental Aspects

During rock salt production by blasting attention must be paid to the gaseous reaction products (CO, NOx), and to vibration from blasting. Subsidence effects at the surface as consequence of underground salt extraction are usually not observed, since this is considered in the static calculation of the extraction plan. Further, the empty chambers are filled with tailings from salt dressing or residues from other industries and waste incinerators.

Brine production by leaching salt caverns is associated with the risk of land subsidence. Caverns must be measured at regular intervals depending on the subsidence rate.

On the other hand, the ecological value of solar salt works stems from their shallow ponds whose floors produce highly suitable food for birds, shellfish, and other animals.

Energy Consumption. Obviously, less fossil energy is needed for the production of solar salt than for the extraction of rock salt and the production of evaporated salt. Most of the energy required to extract sodium chloride from seawater or brine is free. Seawater is evaporated by the power of the sun and wind. The lowest consumption of fossil energy is in traditional solar works, where the harvesting is performed by the human workforce [30].

For rock salt energy savings compared with evaporated salt can be up to 70% [31].

5. References

18. W.M. Samhaber, K. Krenn: “Potential of Membrane Technology for Improving the Brine Purification...
PRODUCTION OF SODIUM CHLORIDE

10


