Sodium Chloride

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. History [1–7]

In the Odyssey, Homer wrote: "travel . . . until you meet mortals who do not know the sea and who never eat food seasoned with salt". Elsewhere he refers to salt as "holy". Justus von Liebig appreciated the importance of sodium chloride for human life: "Among all precious stones salt is the most precious".

Sodium chloride was used almost exclusively as a food and preserving substance for millennia. Presumably, human salt consumption became

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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 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. CONFUCIUS reported borings with a depth of more than 500 m in ca. 600 B.C. Indian history recalls the prominent role of salt. There was even a caste of salt diggers. During British colonial days, salt motivated the Great Hedge of India and its role in the British salt starvation policy and GHANDI'S resistance to British colonial rule.

Salt also had military significance. For instance, it is recorded that thousands of Napoleon's troops died during his retreat from Moscow because their wounds would not heal as a result of a lack of salt. In 1777, the British Lord HOWE was jubilant when he succeeded in capturing General Washington's salt supply.

Throughout history the essentiality of salt has made it subject to governmental monopoly and special taxes. The Chinese, like many other governments over time, realizing that everyone needed to consume salt, created a government salt monopoly, and made salt taxes a major revenue source. French kings developed a salt monopoly by selling exclusive rights to produce it to a favored few who exploited that right to the point where the scarcity of salt, and the gabelle, the salt tax, was a major contributing cause of the French Revolution. Similarly, the Russians Czars' salt taxes were an important revenue source. In Germany a tax of 60 €/t was levied on all salt used in food. This tax was discontinued at the beginning of 1993, following the establishment of the Common Market in the European Union. In Europe two salt monopolies established by the Cantons in the 19th century exist in Switzerland today still.

Salt was of crucial importance economically. A far-flung trade in ancient Greece involving exchange of salt for slaves gave rise to the expression "not worth his salt". Special salt rations given to early Roman soldiers were known as "salarium argentum", the forerunner of the English word "salary". Possession of the precious materia salt meant wealth and power over centuries. Cities such as Salzburg in Austria and Lüneburg in Germany blossomed with salt production and the salt trade. The value of salt diminished with the industrial revolution in the 1800s. Since salt was needed as a raw material in the emergent chemical industry, salt deposits were opened up by dry mining and exploited with improved drilling technology, and saturated brine from boreholes was increasingly used in salt works.

In many museums, e.g., the German Museum in Munich, the Musée du Marsal in France, the Salt Museum of Northwich in the UK, the Zigong Salt Museum of Sichuan in China, the Salt Palace, Grand Saline, Texas in the USA, and in the Salt and Tobacco Museum in Tokyo, salt history is presented vividly. Today, visitors can take tours through salt mines such as those in Wieliczka/Poland, Berchtesgaden/Germany, Hallstatt/Austria, Bex/Switzerland, and the 19th century Khewra Salt mines in Pakistan.

2. Properties [8]

Sodium chloride, NaCl, M_r 58.443, is a colorless salt with good solubility in water. Chemically pure NaCl crystallizes from aqueous solutions in well-formed cubes, which under the influence of surface tension often grow together into funnel-shaped, hollow, square-based pyramids. In the presence of impurities, octahedra or dodecahedra are sometimes formed. Crystallization from hydrochloric acid solution gives long, fibrous, needle-shaped crystals.

During crystallization, small amounts of water can be trapped in holes in the crystals. When this vaporizes on heating, it causes the crystals to explode with audible decrepitation. In salt from natural deposits, inclusions of gases such as methane, carbon dioxide, and hydrogen sulfide can occur.

In the crystal, the Na and Cl ions alternate. The ions of each type form a face-centered cubic lattice, in which each ion is surrounded octahedrally by six ions of the other type at a distance of $a/2$ (lattice constant $a = 0.56273$ nm). The modulus of elasticity perpendicular to the surface of the cube is 41 074 MPa. Under high pressure, slow flow takes place. Sodium chloride is highly transparent to light of wavelength between 200 nm (ultraviolet) and 15 μm (infrared). Ionizing radiation causes lattice defects (color centers) which give the salt a blue color. On heating to ca. 250 °C, this color disappears.

Some important physical properties are listed below and also in Tables 1–3.

Melting point	801 °C
Boiling point	1465 °C
Density at 25 °C	2.1615 g/cm^3
Mohs hardness	2 – 2.5
Brinell hardness	14 HB
Dielectric constant	5.9
Refractive index n_D^{20}	1.5443
Electrical resistivity at 20 °C	4.6×10^{16} Ω cm
Electrical resistivity at 100 °C	1.38×10^{13} Ω cm
Thermal conductivity at 17 °C	0.072 W cm^{-1} K^{-1}
Linear coefficient of expansion	40.5 μm m^{-1} K^{-1}
Specific heat capacity at 25 °C	850 J kg^{-1} K^{-1}
Enthalpy of formation at 25 °C	−410.9 kJ/mol
Entropy at 25 °C	72.36 J mol^{-1} K^{-1}
Latent heat of fusion	0.52 kJ/g
Latent heat of evaporation	2.91 kJ/g
Viscosity of saturated aqueous solution	1.93 mPa · s
Density of molten NaCl at 801 °C	1.549 g/cm^3
Viscosity of molten NaCl at 850 °C	1.29 mPa · s
Surface tension of molten NaCl at 850 °C	110 mN/m
Electrical conductivity of molten NaCl at 850 °C	3.7 S/cm

Thermodynamic properties of aqueous solutions are given in [9].

Table 1. Solubility of NaCl in water

Temperature, °C	g NaCl/100 g H_2O	NaCl, wt %	Density of solution, g/cm^3	NaCl content of solution, g/L
0	35.76	26.34	1.2093	318.5
20	35.92	26.43	1.1999	317.1
40	36.46	26.71	1.1914	318.2
60	37.16	27.09	1.1830	320.5
80	37.99	27.53	1.1745	323.3
100	39.12	28.12	1.1660	327.9
180	44.9	30.99		

Table 2. Density of aqueous solutions of NaCl

	Density, g/cm^3				
NaCl, wt %	0 °C	20 °C	40 °C	60 °C	80 °C
4	1.03038	1.02680	1.01977	1.0103	0.9988
8	1.06121	1.05589	1.04798	1.0381	1.0264
12	1.09244	1.08566	1.07699	1.0667	1.0549
16	1.12419	1.11621	1.10688	1.0962	1.0842
20	1.15663	1.14779	1.13774	1.1268	1.1146
24	1.18999	1.18040	1.16971	1.1584	1.1463

In the system NaCl–H_2O (Fig. 1), only one hydrate, NaCl · 2 H_2O, exists. It crystallizes as monoclinic, thin, beveled platelets that decompose into solid sodium chloride and saturated brine at 0.15 °C. Below this temperature it is the stable solid phase. However, it crystallizes so slowly that, on rapid cooling, the phase diagram follows the broken curve in Figure 1. The metastable eutectic point reached is ca. 1.3 K below the true cryohydric point at − 21.12 °C. Its property of depressing the freezing point of water enables sodium chloride to be used in freezing mixtures and as a deicing salt. The crystals of NaCl · 2 H_2O, although similar to ice in appearance, are birefringent and account for freezing of moist stockpiles of highway de-icing salt during storage in cold weather.

Table 3. Vapor pressure of aqueous solutions of NaCl (in kPa)

	NaCl content				
Temperature, °C	5 %	10 %	15 %	20 %	25 %
0	0.59	0.57	0.55	0.51	0.47
20	2.26	2.18	2.09	1.97	1.81
40	7.13	6.88	6.58	6.20	5.72
60	19.26	18.58	17.78	16.76	15.53
80	45.75	44.16	42.49	39.97	37.09
100	97.89	94.43	90.44	85.52	79.67

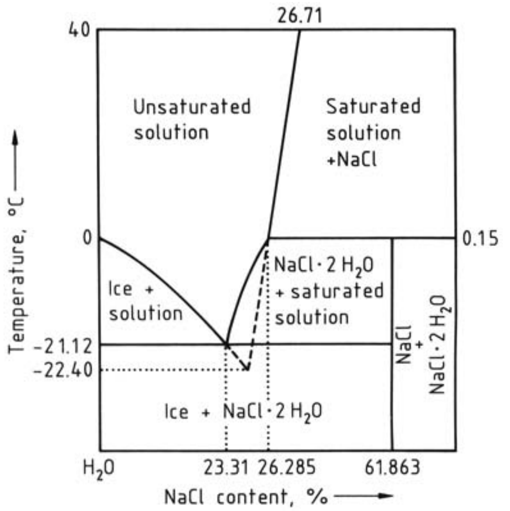

Figure 1. Phase diagram of H_2O–NaCl system (schematic, not to scale)

The aqueous solution has a pH of 7 in the absence of impurities. The saturated aqueous solution boils at 108.7 °C.

Sodium chloride has good solubility in aqueous ammonia. At low temperatures, fine colorless needles of composition $NaCl \cdot 5\ NH_3$ separate out. Addition compounds with urea, glucose, and sucrose also exist. Solubilities in pure methanol and in pure ethanol at 25 °C are 1.31 and 0.065 g NaCl/100 g solvent, respectively. Sodium chloride is also soluble in glycerine, and dissolves in high-pressure steam, the solubility being 0.1 % at 17 MPa, and 0.6 % at 19.5 MPa. Chemically pure sodium chloride is not hygroscopic, but if magnesium salts are present as an impurity it becomes so.

Sodium chloride solutions are corrosive to base metals, and therefore dilute solutions of NaCl are used in corrosion tests (e.g., ISO 9227, ASTM B 117-07a). Solutions of pure NaCl are more corrosive than those that also contain salts of Mg or Ca [10]. Iron and steel are attacked only fairly slowly by pure NaCl solutions, but much more quickly when the solutions contain oxygen. Corrosion by NaCl solutions is accelerated by the presence of local electrolytic cells [11]. Mixtures of organic acids with sodium chloride, (e.g., in perspiration) are highly corrosive [12].

The corrosivity of NaCl solutions is strongly influenced by the amount of oxygen present in the solution. Table 4 lists values for solutions at 25 °C and 133 kPa. The greatly decreased solubility of oxygen in strong brines explains why the interior surfaces of steel tanks holding saturated brine are comparatively free from corrosion below the liquid level.

Table 4. Solubility of oxygen in aqueous sodium chloride solutions (25°C, 133 kPa)

c(NaCl), mol/L	O_2 solubility, cm^3/L
0.0	5.78
0.125	5.52
0.25	5.30
0.5	4.92
1.0	4.20
2.0	3.05
3.0	2.24
4.0	1.62

Crystalline NaCl has a very low conductance, but the fused salt is an excellent conductor (Table 5). The conductivity increases almost as a linear function of temperature at moderate temperatures. Impurities may promote abnormally high conductivity. The conductivity is considerably higher than in aqueous solution: a conductivity of 5 S/m corresponds to a salinity of 35 g/kg at about 23 °C. The mean conductivity of the oceans (excluding the shallow seas) is 3.27 S/m. Measurement of electrical conductivity is usually applied in brines only in a concentration range near to or below that of seawater. The electrical conductivity of strong brines is so high that sensitivity is lost. Electrical salinity indicators are used for monitoring boiler water and condenser systems, and to warn of entry of salts into fresh water systems.

3. Formation and Occurrence of Salt Deposits [13]

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

Table 5. Electrical conductivity σ of liquid sodium chloride

T, °C	σ, S/m
800	3.58
850	3.75
900	3.90
1000	4.17
1100	4.39

- 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

When rocks are chemically weathered, salts are dissolved, carried into natural running waters, and collect in the oceans and inland lakes and seas. Where evaporation is predominant, the salts become concentrated until the solutions are supersaturated and crystallization occurs.

The proportion of sodium chloride in the salts of seawater is ca. 78%. Although the oceans contain the largest quantity of dissolved salts, the majority of salt is bound in the form of solid deposits. In Germany alone, the quantity is estimated to be ca. 100 000 km^3.

The chemical-sedimentary genesis of salt deposits has been accepted ever since Ochsenius (1877) proposed his bar theory. Inspired by the contemporary example of the Kara-Bugas bay (Caspian Sea), he suggested that bodies of seawater become almost completely isolated from the open sea by bars. Then, due to the evaporation that takes place in arid climatic regions, the seawater is concentrated. The sparingly soluble carbonates and sulfates are then the first to crystallize, followed by the more soluble chlorides.

In the case of the most important European salt deposit, the Zechstein Formation, communication with the North Sea has been proved by fossil finds, thus demonstrating the marine origin of the Zechstein salts, which extend over ca. 500 000 km^2 from England to Central Poland, and from Denmark to Thuringia/Hesse (Germany). The bar theory can satisfactorily account for even the 800–1000 m thickness of the Zechstein salt deposit, and is also valid, in modified form, for marine salt deposits. A depth of 100 m seawater produces a salt layer only 1.5 m thick on complete evaporation.

It is now believed that, for the European Zechstein salt deposit, the salt lakes were connected to the ocean by an extended saturation shelf lake where considerable amounts of $CaSO_4$ were deposited. The minor and major salt lakes were filled with salts during four largely identical deposition cycles, each having the sequence clay, calcium–magnesium carbonates and calcium sulfate, sodium and potassium chlorides, and ending with a recessive transition [sodium chloride, calcium sulfate (anhydrite), and clay] to the next cycle. The concentrations of the various soluble salts reached saturation successively as the seawater became gradually more concentrated, so forming the geographical sequence of salts. This explains why the composition does not correspond to that of normal seawater at any point in the salt profile, why all the types of salt are not deposited everywhere, why salts of differing solubilities are precipitated simultaneously at different saturation regions, and why the chlorides of potassium and magnesium are deposited only at the centers of the lakes.

The intermediate layers of clay sediments in each cycle are the result of influxes of fresh seawater. Eolian (airborne) transportation of clay minerals into the salt basin can also occur.

The depths of the brine in the deposition basins have been calculated from the bromine contents for each phase of deposition. The results obtained were: first cycle (Werra region) 330 m, second cycle in the Stassfurt region 860 m, and third cycle in the Leine region 95 m. In some cases the salt basin dried out during the third cycle. Sediments of younger formations covered and protected the Zechstein salts from dissolution.

In the North West German depression zone, a layer of overlying rock up to 5 km thick was formed. The pressure due to this denser rock, together with the interior heat of the Earth, caused metamorphosis of the salt, which became plastic and migrated. It then accumulated in zones of deformation and ascended, forming salt domes (diapirs) which sometimes extended as far as the earth's surface. These were slowly dissolved by groundwater, leading to the formation of very flat secondary intermediate layers next to the overlying rock.

The upward movement of the salt during the formation of salt domes deformed the salt layers into folds, with predominantly steeply inclined strata. Under the thinner overlying rocks at the edge regions, the flat deposits remained undisturbed.

Marine rock salt deposits occur in most geological formations (see also → Potassium Compounds). In the following list, the names of countries or areas printed in italics have salt deposits that are economically exploited. Connected regions are separated by commas, and disconnected regions in a country by a semicolon. Countries and regions are separated by periods.

Cambrian. Canada: NW territories. Australia. *Siberia. Iran. Pakistan.*

Ordovician. Canada and United States: Williston Basin with parts of Manitoba and Saskatchewan (Canada) and parts of Dakota, Montana, and Wyoming (United States).

Silurian. United States and Canada: Salina Basin with Maryland, *Michigan, New York, Ohio*, Pennsylvania, West Virginia (United States), and Ontario (Canada).

Devonian. United States and Canada: Williston Basin with North Dakota, Montana (United States), and Alberta, Manitoba, Saskatchewan (Canada). CIS: *Siberia; Byelorussia,* Baltic, *Dnieper-Donets Basin.* Australia.

Carboniferous. Canada and United States: Williston Basin with New Brunswick and Nova Scotia (Canada), Virginia (United States), Paradox Basin with Colorado and Utah (United States). Brazil: Amazon Basin.

Permian. American Permian Basin: Colorado, *Kansas*, Oklahoma, *New Mexico*, and Texas; American Supai Basin: Arizona, New Mexico; American Williston Basin. Mexico: Chihuahua. Peru: E Cordillera. CIS: *Kama Basin*; *Donets Basin*, Volga Basin, Caspian Basin; Baltic. Bulgaria. Greece.

European Zechstein. England, *the Netherlands, Denmark, Germany, Poland.*

New Red Sandstone. Germany, *the Netherlands, Portugal.*

Muschelkalk. *Germany, France, Switzerland.*

Keuper. Germany, *England, France, Spain,* Algeria, Libya.

Triassic Alpine. *Germany, Austria.*

Triassic, unstructured. Mexico: Tehuantepec. Bulgaria. Greece. Morocco. Tunisia.

Jurassic. United States: *Idaho*, Utah; Gulf Coast: *Texas, Louisiana, Mississippi.* Cuba. *Chile. Yemen.* Kuwait. Morocco. Tadzhikistan. Germany.

Cretaceous. United States: Florida. Bolivian Cordillera, Brazil: Sergipe-Alagoas Basin, *Argentina, Colombia*. Angola, Congo, Gabon, Morocco, Algeria. Tadzhikistan.

Eocene. United States: Green River Basin Wyoming. Belize. Spain. Yugoslavia.

Oligocene. France, Germany. *Spain. Anatolia*, Caucasus Mountains, Iran, Iraq.

Miocene. *Czechoslovakia, Polish, Russian,* and *Romanian Carpathian foreland, Yugoslavia, Anatolia,* Cyprus, Syria, Iraq, Iran, Golf of Suez, *Algeria, Sicily, Tuscany, Spain.* Sudan. *Dominican Republic.*

Pliocene. United States: Nevada, Utah. Jordan, Israel.

4. Production

4.1. Mining of 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 tunneling and worked by excavation around 1000 B.C.

Salt-bearing regions are revealed by the presence of surface springs of saline water, and these were the areas where the possibility of mining was always investigated by sinking shafts. The main precondition for success is the presence of dry overlying rock, and it was this circumstance that enabled the first German salt mine to be opened in 1825 near Schwäbisch Hall. In other parts of Europe, salt was mined long before this, e.g., in Poland before 1000 A.D., and in England since the 1600s.

The purity of the salt mined from rock salt deposits is between 90 and 99% NaCl, and sometimes higher. The other minerals present in the rock salt are mainly clay and anhydrite, often intimately intergrown.

Rock salt and potassium chloride have the same marine origin, often occurring together in a single deposit, and have essentially the same mechanical strength properties. Hence, the development and mining of rock salt deposits is similar to that of potash mineral deposits.

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.

As rock salt is a water-soluble mineral, it is especially important to ensure that the lining of the shaft is watertight when it is sunk through water-bearing strata. In older shafts, the sealing system consists of ring-shaped sections of cast iron or steel bolted together. Newer shafts have a watertight lining consisting of a welded sheet-steel cylinder, an inner hollow cylinder of reinforced concrete, and an outer asphalt-filled ring.

Material is hoisted up the shaft in 20 t skips at rates of up to 1000 t/h. These travel between wooden or steel guide rails, or in a few cases between tensioned guide cables.

If the salt deposit appears as an outcrop, or is at low depth (< 100 m), the salt can be extracted by drift mining (tunneling) or by means of an inclined shaft. In these cases, the salt can be transported to the surface with conveyor belts or trucks. One of the richest European salt deposits is in Petralia, Sicily, where an enormous lens of salt, trapped in the heart of a mountain that rises 1100 m above sea level, extends over 2 km^2 with a thickness of 250 m and a salt purity of 99.9%. Construction of industrial mining structures began in 1972. The entire production process takes place below ground, from extraction of the salt to its packaging, with subsequent transportation of the bulk and packed salt onto the surface by truck.

4.1.1. 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.

A characteristic feature of salt mining is that the haulage and ventilation tunnels servicing the excavation chambers are driven through rock salt, whereas in other types of mine they are often coated in the adjacent rock. In salt mining this is generally not necessary, as the deposits are usually thicker. Furthermore, drilling and tunneling 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 of ca. 50–400 m^2 and lengths of up to 500 m. The parallel extraction chambers are separated from each other by rock salt pillars left behind during mining. These pillars must be of such dimensions that they can carry the weight of the overlying rock. Generally, additional support is not required, and the ground above is protected against subsidence.

The pressure exerted by the overlying rock increases with depth, so that the salt pillars must be wider. For example, in a salt mine at a depth of

200 m, the pillars are 15 m wide and the chambers 15 m; at a depth of 500 m, the pillars are 30 m wide and the chambers 20 m; and at a depth of ca. 700 m, the pillars are 50 m wide, and chambers 22 m. The salt pillars result in a ca. 40–70 % loss of product, depending on their dimensions.

The salt extraction process starts with the construction of a central haulage tunnel. At right angles to this, tunnels leading to the working faces are driven. The tunnels are developed upward or downward to form chambers if the deposit is so thick that it extends above or below them. The salt pillars produced by this mining technique are usually not cut through.

If the deposits have a workable thickness of < 10 m, the pillar and chamber method with long pillars is often changed to one with short, square pillars (room and pillar system). Here, the transverse tunnels usually have the same height and width as the long ones.

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. If the tunnel runs through the upper part of the deposit, the salt is extracted from the floor, i.e., by drilling long holes downwards into the salt.

Figure 2 shows a vertical section through a South German mine where the rock salt deposit is 20 m thick and 200 m deep. The haulage and

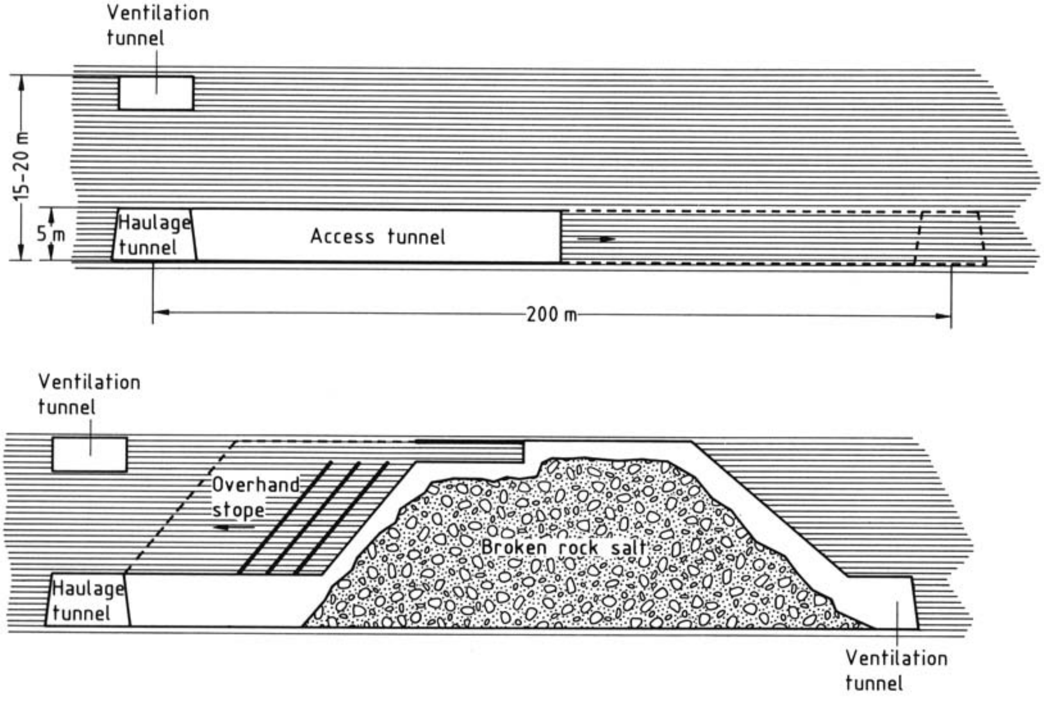

Figure 2. Vertical section through a South German salt mine

working roads are located in the lower part of the deposit, and the main ventilation road in the upper part. 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. After scaling, the roof can then be collected without the danger of roof falls.

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

Due to the strength of the salt rock, it is possible in most mines to keep the mined space open without supports. At great depths, where the pressure is high, or where breakup of the deposit leads to danger to the miners from roof falls of salt, rock bolts are used.

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. Between the sublevels, there are working faces which are drilled and blasted, beginning with the lowest, using long boreholes. In one mine, the openings produced are 20 m wide, 42 m high, and 100 m long, and, in another, 20 m wide, 100 m high, and 60 m long.

To maintain stability of the rock, salt masses must also be left behind using the grid wall system, the vertical pillars being 10–30 m thick, and the horizontal pillars between the sublevels, 8 m thick.

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). For economic reasons, there should be a straight road between loading and discharging points not longer than ca. 300 m. For longer distances, the interrupted system is more economic, with special loading equipment and dumper trucks of up to 50 t capacity.

After crushing the salt to < 300 mm using equipment near to the working face, it is transported by band conveyors to the hoisting shaft.

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. This sedimentary deposit is composed almost exclusively of sodium chloride with a degree of purity that surpasses 98% NaCl. The deposit is 45 km long and has an average width of 5 km with a saline thickness that can reach more than 100 m. Operations are carried out on the surface, and consist of a classic combination of drilling, blasting, loading, and transportation.

4.1.2. 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.

Once the rock has left the face it goes to the crushing and screening plant to be crushed and graded into different sizes, depending the use (0–5 or 0–10 mm).

4.1.3. Upgrading 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.

To remove secondary minerals, the salt must be milled to such an extent that the secondary minerals are available as single free grains beside the salt in the bulk material. This first preparation step is already partially carried out underground in the mine, so that the secondary minerals remain in the mine. 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. Rock salt is more brittle than secondary materials such as clays and anhydrite that are frequently present. The salt is therefore ground more finely in an impact mill than these secondary minerals, and the larger clay and anhydrite grains still present after comminution can be separated by sieving. Rejection of the oversize increases the salt content, for example, from 94 to 96.5%.

Separation in a Throw Parabola. Density differences of minerals with approximately the same grain sizes lead to different throwing ranges at the end of a conveyor belt ends. By using a splitter the materials can be separated.

Manual Sorting. In mines with drilling and blasting manual sorting of large pieces of secondary material sorted from crude rock salt is still widely used, employing a slow running conveyor belt or a sieve.

Optical Sorting. Automated optical sorters can be used to replace manual sorting and to increase salt quality for special uses like water softening. The procedure exploits differences in color, brightness, transparency, and reflectivity of the minerals. Each single particle is individually scanned with a digital camera. Brightness thresholds enable identification of reject material that is ejected with compressed air. Installed plants have throughput rates of up to 80 t/h with a maximum reject percentage of 15%, while the feed size is 15–80 mm. The economy of the procedure depends on the consumption of compressed air, the amount of which is related to the percentage of rejected material.

Heavy-Medium Separation. Differences in mineral densities are used for separation in heavy-media plants. The rock salt is suspended in a heavy medium, which consists of saturated brine with magnetite. The raw salt components are separated with the help of centrifugal forces in hydrocyclones. A German plant separates salt of 1–12 mm grain size from clay and anhydrite, with a throughput of 500 t/h. The magnetite is recycled with drum-type magnetic separators. The rock salt thus produced is low in sulfate and suited for use in chlor-alkali electrolysis [14].

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 μm and the use of sulfated fatty acids. Sulfate contents of 500 ppm in the final product are achievable. Disadvantages of salt flotation result from the very fine grains, which can be hard to debrine and require additional effort during later production of brine. 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. The charged nonconducting salt is attracted to the opposite charge, becomes electrostatically attached to it, and moves with the surface of the roll. The anhydrite/clay particles are discharged rapidly on the grounded roll surface and thrown free. The disadvantage of electrostatic separation is the high power consumption. Depending on the purity of the crude salt a quality improvement of nearly 1.5% NaCl is achievable.

Magnetic Separation. Magnetic separation relies on the different behavior of individual mineral particles under the influence of a magnetic field. While salt is nonmagnetic, clay is weakly magnetic due to traces of transition metals such as iron and can be removed with rare-earth magnetic roll separators, which reach field strengths of up to 22 T. If anhydrite is intergrown with clay, part of the anhydrite is also separated simultaneously with the clay. A short conveyor belt envelops a magnetic roll and a tensioning idler roll. A suitable feeder discharges salt onto the belt and, as the salt is conveyed over the magnetic roll, weakly magnetic clay particles adhere to the conveyer belt while in contact with the magnetic roll, whereas the nonmagnetic salt particles flow freely off the end of the conveyor.

In a 1 t/h pilot plant installed in the Heilbronn salt mine in 1992, 0.2–4 mm rock salt was purified with a four-stage rare-earth magnetic roll separator. The maximal achievable purity was salt with 0.1% anhydrite and 0.3% clay. The results depended on the feed quality and the degree of intergrowth between clay and anhydrite. Another German salt mine operates a multistage rare-earth magnetic roll separator plant for purification of Muschelkalk salt, which is intended for use in membrane chlor-alkali electrolysis.

Thermoadhesive Process. Basically, the thermoadhesive process consists of exposure of crude rock salt to radiant heating, which selectively heats the impurity particles. Subsequently, the heated particles are removed by adhesion to a heat-sensitive coating on a conveyor belt. This method was found to be effective in improving both the quality and appearance of rock salt by rejection of the dark impurity particles. The first commercial unit employing the thermoadhesive method of dry separation of minerals was installed in 1957 underground at the Detroit rock salt mine. The plant was fed with rock salt of grade 7–9.5 mm. The concentrate contained 98% of sodium chloride, with resin losses of 45 g/t [15].

4.1.4. Utilization of the Chambers

Salt mining is mainly carried out without backfilling, i.e., the chambers produced during mining need not be backfilled with other material to support the roof of the mine and increase the load-bearing capacity of the salt pillars.

Where processing of the rock salts produces residues that must be disposed of, these are usually dumped in the empty chambers. Hence salt mines do not produce heaps of tailings at ground level.

In some cases, empty chambers are utilized for disposing of waste materials, e.g., wastes from combustion processes and the chemical industry. Salt mines are well suited for long-term or “perpetual” disposal of solid wastes, and especially for residues that have high leachability. They offer a unique closed environment for storage: natural gas-impermeable salt layers, well isolated (depth from 150 to 1000 m), very dry, with stable atmosphere, allowing very long term conservation. Natural water barriers (impermeable layers such as clay and anhydrite) protect the salt layers against water hazards (infiltration or flooding). In addition, artificial barriers can be added to natural ones, if necessary, creating further reliable sealing measures (packing, brick walls, massive damming walls) against any outside communications. This combination ensures secure isolation of wastes which represent a hazard to humans and the environment in above-ground landfills due to their water solubility and concentration of toxic substances (e.g., dioxins and furans, mercury, and also residues from air pollution control).

Salt mines are considered to be ideal disposal sites for incinerator fly-ash and flue-gas cleaning residues. Usual criteria for acceptance are:

- Nonexplosive
- Nonradioactive
- Not spontaneous combustible
- No generation of toxic or explosive gases
- No reactions between the wastes or with the rock salt
- No spreading of diseases
- No penetrating odor
- Sufficient stability

For mine filling, main additional criterion for accepting residues is that the compressibility under the maximum overburden pressure may not be higher than 22%, in order to obtain the best resistance and avoid any collapse of the mine, which is the purpose of the filling. Such a condition may be achieved by a proper mixing of the waste with some mine salt residues (covering of big bags with salt tailings) or with incineration slag (bottom ashes), or other mining techniques.

Underground salt mines in operation have void space of many million cubic meters, and this resource is growing permanently, giving unlimited potential for a long-term safe storage of items such as art works, pictures, books, pieces of furniture, archives, licenses, and records under controlled temperature and humidity conditions.

4.2. Brine Production

Three methods can be distinguished for the production of brine:

- Extraction of natural brine
- Solution mining
- Combined dry and wet mining

The most widely used and most economic process today is solution mining (see Section 4.2.2). A combination of dry and wet mining for production of brine is employed in alpine salt deposits (see Section 4.2.3). In a few cases, subsurface solution mining is also carried out at depths of 100–140 m. The work-face dissolution process, in which dissolution is carried out in chamberlike tunnel sections, is no longer used.

The rock salt, which may be present in a pure state (e.g., geologically undisturbed crystalline salt deposits) or in a mixed mineral in finely divided form (e.g., in alpine salt deposits), is dissolved by the action of fresh water on the rock formation and converted to a concentrated salt solution (brine with an NaCl content of 312 g/L or 27 %).

In all mining processes, the brine is produced in underground excavations made by conventional mining or solution mining. The extraction processes result information of chambers. Between the chambers in which the brine is produced and extracted, pillars of considerable size are left behind to maintain stability of the rock [16, 17].

4.2.1. Natural Brine Extraction

Natural brines containing up to 20% salt, pumped from Pennsylvanian, Mississippian, Devonian, and Silurian beds, are a source of halite and a basis for the chemical industry in southern Ohio and West Virginia in the USA. Similarly, another commercial center is associated with brine resources in the Mississippian and Middle and Lower Devonian beds in Michigan. In general, brines from the older and deeper lying beds are of higher concentration. The brine pumped in the neighborhood of a flooded salt mine at Solivar near Presov in Slovakia contains 292 g/L of salt [18]. Natural Alpine brines are processed in the salt works at Bad Reichenhall in Germany. The concentrated brines are a result of underground brine discharge from the Quaternary layers of the Reichenhall Basin. The brines are generated by natural solution mining of the salt mountain [19].

Brines often contain high concentrations of bromide such as in the Smackover Formation of southern Arkansas and Mississippi in the USA, which is known for its bromine production (Harben). Certain brines contain relatively high concentrations of iodine, for example oilfield brines in the USA, Japan, Indonesia, and the former USSR. Iodine-bearing brines may be classified as of Japanese or Oklahoma type. The former occur in young rocks (i.e., Miocene, Pliocene, and Pleistocene) and are probably derived from seawater. Their maximum iodine content is 150 ppm. Brines of the Oklahoma type occur in older formations and have an iodine content of as much as 1500 ppm [20].

4.2.2. 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 m^3 and more.

Controlled solution mining is the modern, economical method of extracting rock salt from underground deposits, and contrasts with conventional mining (see Section 4.1). However, for this method certain preconditions must be fulfilled, especially with regard to the geology of the deposit (type, formation, and depth of the salt). Economic operation of the solution mining process requires that the deposit – whether a diapir (salt dome) or a flat stratum of salt – should fulfill the following geological conditions:

1. Adequate thickness and extent of the salt deposit
2. High purity of the rock salt without inclusions of potassium chloride
3. Largely undisturbed stratification at medium depth

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

4.2.2.1. 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 (see → Oil and Gas). 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. A standard pattern for the casing diameters in a cavern well (see Fig. 3) is as follows:

1. 0–15 m: 24.5 inch pipe
2. 0–300 m: 16 inch pipe
3. 0–20 m (max.) beyond the projected roof of the cavern in the deposit: 11.75 inch pipe

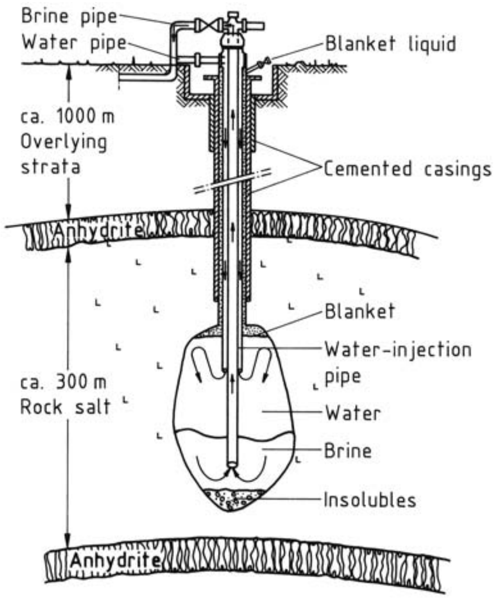

Figure 3. Method of brine production

The casings described in 2) and 3) above are cemented up to ground level.

Geophysical borehole measurements and tests on the cores obtained during sinking of the borehole not only give information about mineralogical composition, but also yield physical data about the overlying rock and the salt deposit. The most important characteristics of the overlying rock are its thickness and strength. Also, to enable the dimensions of the cavern and the proposed extraction process to be decided upon, the strength and thickness of the salt deposit and the solubilities of its component parts must be known.

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. After this, the well is completed by inserting two concentric pipes (of diameter between 8.625 and 5.5 inches); the final preparative work being the assembly of the well head and making all the pipe connections (Fig. 3).

4.2.2.2. 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

As shown in Figure 3, 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.

Insoluble materials collect at the bottom of the cavern.

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.

The cavern shape can be controlled according to the design specifications by alternate use of the above-mentioned leaching methods, combined with different setting depths of the leaching strings, different leaching rates, and varying blanket levels [21–24]. Thus, the dimensions of the realized cavern can reach diameters of up to 60–100 m and heights of several hundred meters. The resulting brine (8–10 m^3 of water dissolves ca. 1 m^3 of salt) is withdrawn via the inner annulus or the inner tubing depending on the method used.

The extraction process is controlled by continuously measuring the salt content of the brine, the blanket pressure, and the quantity of brine extracted. The cavern space produced is calculated from these data by computer, and the spatial extent of the cavern is continuously determined by echometric surveying. The actual cavern produced can then be continuously compared with the planned cavern.

4.2.2.3. Planning of the Extraction Process

The safety of caverns can be ensured if pillars of adequate width are left between neighboring caverns and if there is a thick enough mass of solid salt at the top of each cavern. The width of the pillar and the thickness of the roof depend on the planned cavern dimensions, the cavern shape, and, in particular, on the mechanical properties of the salt deposit. The latter have been investigated in detail [24–30].

Furthermore, correlations and formulas have been derived that enable the forces produced in the rock to be calculated from the size and shape of the cavern, the interior pressure produced by the solution mining process or subsequent use for storage purposes, the depth and thickness of the overlying rock, and the mechanical properties of the surrounding rock formations. The decrease in the volume of large caverns (convergence) caused by elastoplastic properties of the rock salt are determined from formulas and confirmed by data from practical experience [25–34].

Irrespective of the widths of the pillars calculated with these equations, the wells in a brine field should be arranged in a hexagonal pattern (Fig. 4), which gives optimum utilization of the available area.

The distance between the brine wells is the sum of pillar width, the maximum cavern diameter, and a safety factor to allow for deviation of the borehole from the vertical. If a borehole must be relocated due to the situation at ground level, the hexagonal arrangement below ground can be maintained by adjusting the drilling direction (Fig. 5).

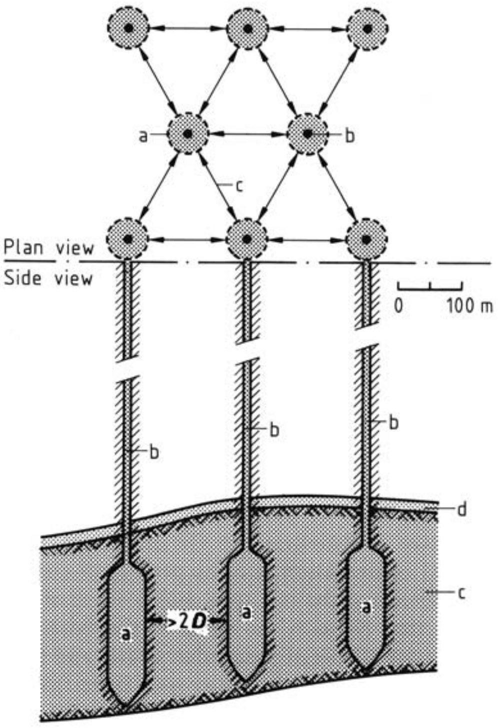

Figure 4. Hexagonal arrangement of caverns in a brine field with a level salt deposit a) Cavern (diameter $D = 60–100$ m); b) Borehole; c) Pillar of stable rock salt (thickness of pillar: 2 D); d) Upper layer of anhydrite

4.2.2.4. 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 [23, 35, 36]. 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 floor is dissolved first, then the roof. With thin seams of salt, the strength and impermeability of the overlying strata are very important.

Control of this method of solution mining is more difficult than with individual brine wells.

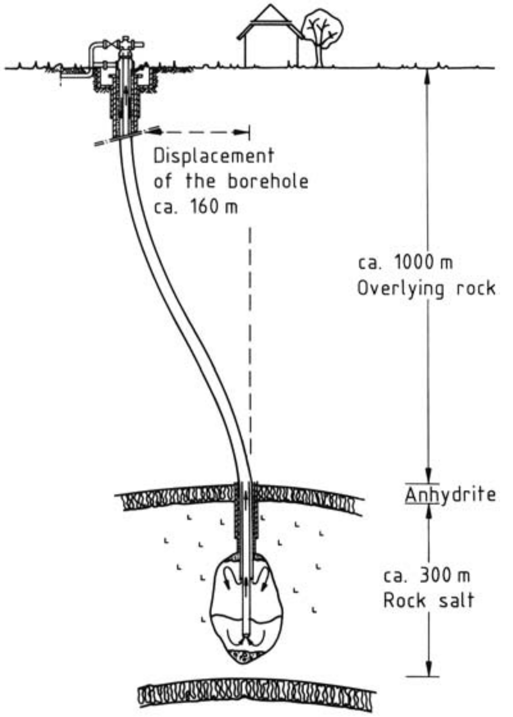

Figure 5. Directional drilling in the production of a cavern

The stability of the cavern spaces cannot be guaranteed, as there is a risk of uncontrolled dissolution processes. Thus, this method of solution mining is only used in countries with few salt deposits where there are sparsely populated areas above thin salt strata.

4.2.2.5. 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 (water and brine) and the friction losses in the pipes. The salt at the working face dissolves and passes through the central pipe as saturated brine to the well head and into the piping system. The low residual brine pressure at this point is sufficient to deliver it to the pumping station, where delivery pumps force the brine into the pipeline that takes it to the consumer industries.

The addition of polyphosphates to the water, including hexametaphosphates, reduces the dissolution rate of calcium sulfate (anhydrite), the primary impurity in many salt formations, and leads to brine with reduced contents of sulfate 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 [37]. Another retarding agent that reduces the solubility of calcium sulfate is dodecylbenzenesulfonic acid, with typical feed rates to the leaching water of 10–15 ppm [38].

4.2.2.6. Storage Caverns

The caverns remaining after extraction of the sodium chloride can be used for storage of mineral oil, mineral oil products, and gases such as natural gas and ethylene.

Emergency reserves of mineral oil or mineral oil products can be injected through a pipeline into the brine-filled caverns by a high-pressure pump. In place of the two concentric pipes used in solution mining, a brine removal pipe is suspended in the cavern with its open end just above the sump region. The mineral oil is forced into the annular space between the outer pipe and the brine removal pipe and displaces the brine, which rises through the brine removal pipe to the surface and is fed into the brine network, and then to the production plant. To discharge the oil, the process is reversed.

Caverns in rock salt are also suitable for gas storage. For example, natural gas is stored to compensate for seasonal and daily variations in demand. The conversion of a cavern to a gas-storage system is more complex than conversion to liquid storage. To protect the outer piping against pressure and temperature variations during operation, a protective pipe is fitted. The annular space between this pipe and the outer pipe is pressurized so that the welded pipes are under a constant load. For the first filling operation with gas, a brine extraction pipe is lowered to the bottom of the cavern. The gas in the annular space between the protective pipe and the vertical central pipe is compressed to a high pressure, and displaces the brine from the cavern until the latter is completely empty. The gas storage system operates by the principle of compression–decompression. The gas in the cavern required to maintain the minimum residual pressure required for stability of the cavern is called the cushion gas, but when it is filled up to its maximum operating pressure, it is known as the working gas.

To meet peak electrical demand, air is compressed using cheap electricity and stored in a salt cavern. Later air is expanded through a gas turbine coupled to an electric generator to produce high-value, peak electricity. Before expansion, the air is heated in a compression chamber using natural gas or diesel oil as fuel. The compressed-air energy-storage facility at Huntorf in Germany, which has been in operation since 1979, has the following characteristics [39]:

- Three salt caverns (300 000 m^3 total, 650 m depth)
- Pressure range 50–70 bar
- Input (compression) 60 MW (8 h)
- Output (discharge mode) 290 MW (2 h)

Salt caverns have been used for several decades to store various hydrocarbon products. More recently, the use of salt caverns for disposal of oil-field wastes has received increased attention. In the early 1990s, several Texas brine companies obtained permits to receive oil-field wastes, much of which was drilling waste [40].

Descriptions of cavern storage systems can be found in [41–44]. A worldwide information exchange service is provided by the Solution Mining Research Institute (SMRI) [45].

4.2.3. 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. An initial space is first created, which is a funnel-shaped (Germany), or circular chamber (Austria). A shaft or tunnel is first driven from the main tunnel or a transverse tunnel to the center of the intended block at the bottom of the worked strata. A shaft is then sunk by mining techniques, from which the initial chamber of a specific size is created at the lowest point by drilling and explosive methods (Austria). In Berchtesgaden, Germany, the initial space (Fig. 4) required for excavation is created by drilling and water-injection processes. An important feature of this process is that the initial space is funnel-shaped, and is generated by controlled dissolution, starting from a wide borehole, so that the insoluble components of the deposit can be raised by airlifting equipment and removed by a hydraulic pump as a solid–brine mixture [16]. The production of the initial space is usually divided into the following stages (Fig. 6): 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. During this phase, the space normally attains a volume of 3000–5000 m^3, depending on the quality of the deposit, with a height of 4–6 m and a diameter of 30–32 m. The creation of the initial space completes the preparation for the extraction process. The space is next extended further, conditions now having been established for continuous, high-yield, cost-effective brine production. The initial space (chamber) is slowly filled with fresh water, which dissolves salt from the side walls and roof. The insoluble components, such as clay, anhydrite, and polyhalite sink to the floor of the chamber. Fresh water is continuously added, raising the liquid level, so that water remains continuously in contact with the roof of the chamber until the water in the chamber is completely saturated. The dwell time depends on the salt content of the rock, the size of the chamber, the ease of dissolution of the salt, and

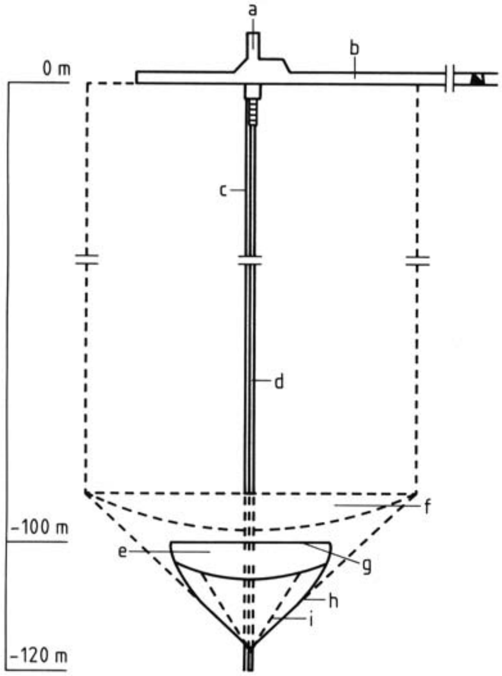

Figure 6. Production of the initial extraction chamber by drilling and water flushing, and brine production operating below the main tunnel (Salzbergwerk Berchtesgaden, Germany) a) Drilling chamber; b) Main tunnel; c) Borehole (76 mm); d) Wide borehole (670 mm); e) Initial extraction space; f) Developed extraction space; g) Chamber roof; h) Angle of boundary; i) Angle of repose of solid residues

the surface area of the chamber roof, and is usually between 10 and 30 d. After complete saturation has been attained (312 g/L), the brine is removed, either by pumping out of the excavated space (if working below the tunnel level), or by draining off to the level below. The space is then refilled with fresh water. This procedure (filling, saturation, emptying), is known as intermittent water flushing, and is repeated until the chamber roof area has reached ca. 3000–3200 m^2. The chamber is then ready for continuous brine production by the continuous water flushing process. The water flows at a rate appropriate for the parameters of the deposit, with simultaneous removal of concentrated brine by draining or pumping. Brine is now almost invariably produced below the main haulage level (Germany and Austria), i.e., working upwards from the bottom. Each day, 1–1.5 cm of rock salt is dissolved from the surface of the roof of the chamber. The chambers take on a funnel-shaped to cylindrical configuration (Fig. 6). Chamber heights in Austria are 20–30 m (normal working) or 50–80 m (deep working), depending on the diameter [46, 47]. In Berchtesgaden, Germany, the exploitable height of the chamber is 100 m. The initial space is created in the region between 100 m and 125 m below the level of the tunnel.

To calculate the efficiency of extraction of the deposit, the salt content of the rock and the size of the rock mass assigned to the particular operation point (cavern), including the horizontal safety pillars, must be taken into account. In Berchtesgaden, Germany, when the size of the horizontal and vertical pillars, the average salt content of alpine deposits (50%), and the usable height of the chamber (100 m) are taken into account, the total quantity of brine available per chamber is 1.1×10^6 m^3. This corresponds to an extraction efficiency of ca. 12% [16]. In Austrian salt extraction operations, the following total available quantities of brine have been quoted, depending on the type of extraction chamber [46, 47]: 200 000–400 000 m^3 for normal operations, and 700 000–1 000 000 m^3 for deep operations.

4.3. Vacuum Salt

The term "vacuum salt" is used for crystalline salt that is obtained from saturated brine in evaporative crystallizers. Synonyms for vacuum salt are "evaporated salt" and "vacuum pan salt". The feed for salt crystallization plants can be saturated brine (for brine production, see Section 4.2) or rock salt (for rock salt production, see Section 4.1) and solar salt (for solar salt production, see Section 4.4). Vacuum salt is normally produced in closed evaporators by dehydrating brine with heat alone or in combination with a vacuum, with recovery of most of the energy. In spite of the term "vacuum salt", neither "vacuum" nor "pressure" is a characteristic factor for salt crystallization.

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

1. Multiple-effect evaporation (see → Evaporation, Section 2.2.
2. Mechanical vapor recompression (MVR, see → Evaporation, Section 2.3.
3. Recrystallization

Table 6. Percentage compositions of rock salt from various sources

	Bad Ischl, Austria [48]	Drang, Mandi District, India [49]	Fairport, Ohio, USA [50]	Huitrin, Argentina [51]	Khanguet el Melah, Algeria [51]	Lyons, Kansas, USA [50]	Pugwash, Nova Scotia, Canada [52]	Stassfurt, Germany [53]
NaCl	97.00	69.50	97.26	99.27	97.80	95.94	94.5	92.4
KCl							0.02	0.05
K_2SO_4	0.59							
$MgCl_2$		0.08	0.04	0.04	0.004	0.10		0.03
$MgSO_4$	*		0.02		0.070			0.05
$CaCl_2$			0.02	0.09		0.01		
$CaSO_4$	1.60	0.54	2.2	0.44	0.680	2.06	3.0	7.4
Na_2SO_4	*		0.01					
$NaNO_3$					0.003			
Insolubles		28.70	0.3		0.830	1.68	2.2	0.07
Water	0.16	1.18**	0.15	0.14	0.612	0.18	0.2	

*The combined amount of sodium sulfate and magnesium sulfate is 0.65%.

**Includes water and other salts.

In an evaporative crystallizer, the salt normally crystallizes at 40–150 °C, whereby the solubility of sodium chloride increasing only slightly with temperature (see Table 1).

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 (see Table 6). Purification is also necessary to avoid scale formation in the heat exchangers and the evaporation equipment. Additionally, the use of pure salt in industrial processes causes less waste than the use of rock salt. On the other hand, the purification of brine itself causes wastes, because of the foreign ions in the crude salt.

A summary of possible processes for the production of crystallized salt based on rock salt deposits is shown in Figure 7.

4.3.1. Brine Purification

Brine purification is an important step in the production of sodium chloride for the chemical

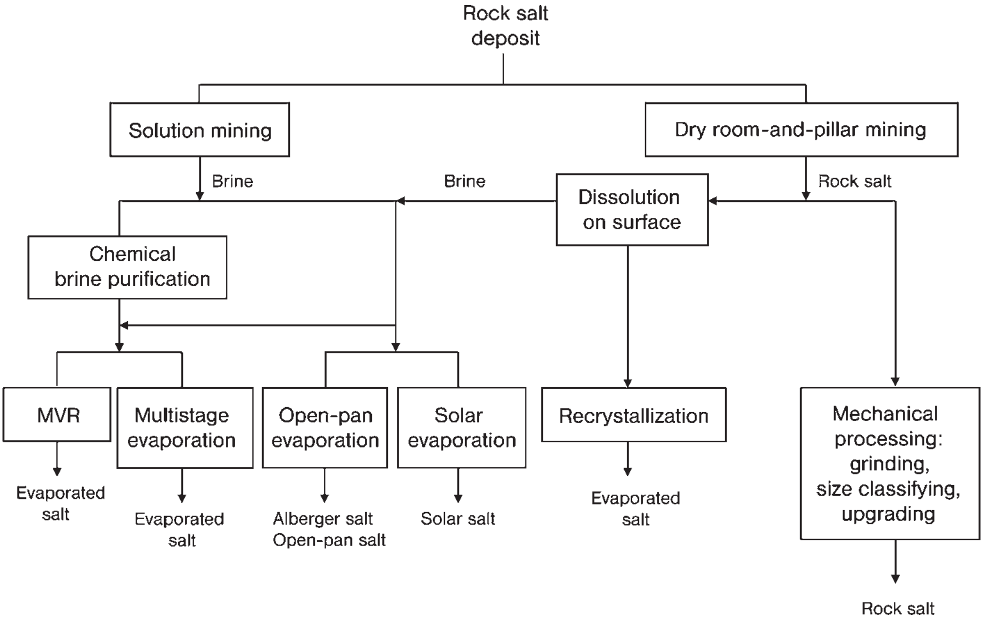

Figure 7. Processes for the production of crystallized salt based on rock salt deposits

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 sulfates, chlorides, and, to some extent, the carbonates of calcium and magnesium, as well as the triple salt polyhalite ($K_2SO_4 \cdot 2\ CaSO_4 \cdot MgSO_4 \cdot 2\ H_2O$). In addition the water which is used for dissolving rock salt contributes to the content of impurities in the crude brine. Most of the magnesium compounds are very soluble in crude brine. Furthermore, the crude brine is saturated with calcium sulfate in many cases. Sodium chloride brine significantly enhances the solubility of calcium sulfate [54]. This effect is called "salting-in".

The principal impurities of crude brine are therefore calcium, magnesium, and sulfate ions, but also strontium ions (usually dissolved in relatively low concentrations in crude brine; see Table 7), all of which take part in scale formation. Potassium ions are irrelevant for the formation of incrustations in the evaporation equipment due to their high solubility. They only play a role as impurities in the final high-purity product [55].

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 sulfate:

   $$Mg^{2+} + SO_4^{2-} + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4$$

   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. However, if a higher degree of utilization of the calcium oxide is desired, milk of lime with a content of about 20 % calcium oxide can be used as well [55]. Where cheap sodium hydroxide is available, it can be used instead of calcium hydroxide, thus avoiding additional input of calcium ions. In this step, an excess of base is always added to reach a pH of about 11.3.
2. The addition of soda ash to precipitate the remaining calcium ions as calcium carbonate:

   $$Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2\ Na^+$$

   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

Table 7. Compositions of crude and purified brine, and mother liquor (in g/L, unless otherwise noted)

	Mixed crude brine from three Austrian mines [56]	Crude brine, Bernburg, Germany, values calculated from [53]	Some analyses of purified brine [55]	Mother liquor, Ebensee, Austria [56]	Max. limits for ultrapurified brine for membrane chlor-alkali electrolysis [57]
Na^+	117.82	125.52		120.85	
K^+	2.487	0.57		46.26	
Mg^{2+}	1.500	0.05	0.0002		**
Ca^{2+}	0.809	1.53	0.005*		**
Sr^{2+}	0.025		0.004*		< 400 ppb
Ba^{2+}					< 500 ppb
Fe^{2+} and Fe^{3+}					1 ppm
Cl^-	183.24	191.08		189.97	
Br^-	0.065				
I^-					< 200 ppb
F^-					< 500 ppb
SO_4^{2-}	8.69	3.66		50.24	< 4–8 g/L
HCO_3^-	0.102				
CO_3^{2-}				1.02	

*Concentrations at 14 °C.

**The combined concentration of Mg^{2+} and Ca^{2+} must be < 20 ppb.

about 10–14 vol% carbon dioxide. Although a minimum concentration of dissolved calcium ions is obtained at a pH of about 9.5, purging is usually stopped at a pH of approximately 11.2, thus avoiding the formation of soluble calcium hydrogencarbonate, which can hardly be removed [55].

After these two reactions, magnesium and calcium ions are removed almost quantitatively (see Table 7). The insoluble compounds are decanted and filtered after each purification step. The resulting basic sludge is generally considered to be useless and is therefore suspended in water and pumped back into abandoned caverns of the salt mine or brine field, or washed into rivers, lakes, or the sea. There it covers the ground and thus may threaten the equilibrium of the aquatic ecosystem.

Sulfate is not removed completely from the crude brine in this purification process. Salt is obtained from the purified brine by evaporation, which is stopped prior to the onset of sodium sulfate crystallization. The residual solution is called "mother liquor" and contains sodium and potassium chloride, sulfate, and carbonate (due to the excess of soda ash in the second reaction; see Table 7). The saturation concentration of sulfate depends on the composition of the purified brine, but normally the value is about 48 g of sodium sulfate per kilogram of mother liquor. Brine with a higher potassium content allows a higher sulfate concentration in the mother liquor without crystallization of an alkali metal sulfate [55]. After removing the mother liquor, it can be fed to an flash evaporator, where a second fraction of pure sodium chloride can be produced with an extent about 50 kg of sodium chloride per cubic meter of mother liquor. Recycling of sodium sulfate (solid or liquid form) from the purge flow of the crystallization process back to the brine purification tanks (or adding of external sodium sulfate) reduces the solubility of $CaSO_4$, as the solubility product $[Ca^{2+}][SO_4^{-2}]$ is constant. Adding some excess lime generates NaOH, which can be converted to sodium carbonate by injection of CO_2. In this way savings of costly sodium carbonate are achieved. The residual solution can be used for the production of sodium sulfate, or, in combination with purified brine, for the production of soda ash, where sodium sulfate is also an appropriate sodium source. Since a high sulfate concentration in the brine for the Solvay process causes formation of gypsum scales during the recovery of ammonia with milk of lime (see → Sodium Carbonates, Section 1.4.1.2.), this strategy is not entirely without problems.

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. Continuous processes require an almost constant composition of the crude brine. On the other hand, they use smaller reactor vessels than batch processes. In both methods, the impurities are allowed to settle and are then removed. Sedimentation is accelerated by adding flocculating agents, usually anionic polyacrylates (→ Flocculants, Section 2.3.1. and → Flocculants, Chap. 4.). In the continuous process, the solid precipitates are removed in thickeners.

Continuous brine purification can be carried out in a single reactor vessel as well [55]. 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. The precipitates settle, and clarified brine is taken from the top. The resulting sludge contains about 60% solids and is removed from the bottom. The main disadvantage of this process is that the brine has to be kept at a temperature between 80 and 100 °C.

Gypsum Slurry Process. In the majority of cases purified brine is evaporated. For the evaporation of crude brine in multiple-effect or thermal and mechanical vapor recompression plants, the gypsum slurry process is used, particularly in the USA. In Europe it finds only occasional use [58]. In this process raw brine with suspended finely ground gypsum is evaporated. Calcium sulfate 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 sulfate 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 Br_2.

Following NaCl crystallization by evaporation of the brine in multistage or MVR processes, the obtained mother liquor still contains among others SO_4^{2-}, K^+, and Br^-. Further concentration of this mother liquor by evaporation results in the precipitation of both NaCl and Na_2SO_4, and a more strongly concentrated mother liquor with respect to both K^+ and Br^- remains. This concentrated mother liquor is drained off. The Na_2SO_4 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 Br^- of the NaCl of the first evaporator steps are reduced. From crude brine containing 50 mg/L Br^-, a low-bromide salt with 27 mg/kg Br^- can obtained which is highly suitable for the production of chlorine. One-fifth of the total salt production occurs in the mother liquor concentrator. This second salt stream contains 247 mg/kg $Br^-$and has to be used for other purposes like road de-icing [59, 60].

Nanofiltration. In chlor-alkali plants nanofiltration (NF) of brine has been known since 1996 [61]. Nanofiltration removes sulfate 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 sulfate-containing solid waste.

Sulfate removal is based on selective filtration of brine through a NF membrane under high pressure. The NF membrane has charged groups that selectively reject multivalent anions such as SO_4^{2-}, while allowing monovalent ionic species such as Cl^- from the feed solution to pass through.

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 sulfates with a reduced content of K^+ and Br^- ions and to obtain a brine with more or less no sulfates not only enables high-grade salt production but also reduces the purge or the bleed-off by using additional evaporator steps [62].

Pretreated 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. The concentrated sodium chloride solution is then crystallized. This process should provide a high purity sodium chloride suitable for many industries [63].

A supplementary NF step to the Schweizerhalle method as third purification step is proposed for obtaining highly pure brine. The concentrate from this step is recirculated into the first stage of brine purification. The production of low-bromide vacuum salt is expected [64].

Quality of the Purified Brine. Purified brine still contains low concentrations of problematic ions [55] (Table 7).

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 (for some limit values, see Table 7 and → Chlorine, Section 7.2.1.).

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 [55].

Byproducts. Chemical brine purification leads directly or indirectly via the concentrated mother liquor from the evaporation to several byproducts which can be sold after processing: sludge as fertilizer and sodium sulfate.

A typical value for the amount of sludge is 15 kg/m^3 of crude brine or 50–55 kg/t of evaporated salt. In Austria, for example, the composition of the water- and salt-free brine purification mud is 58.8% calcium sulfate, 23.4% calcium carbonate, 16.8% magnesium hydroxide, and 1.0% clay minerals, which are impurities of the limestone [65].

Recently, the use of this sludge as a lime fertilizer has been discussed. However, three aspects must be considered:

1. The brine purification mud must be washed thoroughly to remove most of the chloride. A fertilizer should contain $< 1\%$ chloride [66].
2. The sludge must have a sufficiently low water content (≤ 28 wt%) if conventional fertilizer-distributing machines are to be used [66].
3. Such fertilizer does not contain significant amounts of the three major macronutrients nitrogen, phosphorus, and potassium. Earlier studies on the growth of plants on similar wastes show that growth is limited primarily by the low content of phosphorus [67].

Sodium sulfate can be produced by crystallization from sulfate-rich mother liquors from multistage or vapor recompression processes.

The potassium-rich Alpine brines enable the salt factories to produce potassium sulfate from the evaporator mother liquor. A plant for potassium sulfate production from evaporator mother liquor was realized in Ebensee/Austria. The process includes the intermediate reaction of potassium chloride and sodium sulfate to give glaserite [68, 69].

4.3.2. 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 resulting grainer salt consists of flakes and is used for food and bath applications where a coarser flake salt product is desired. Salt crystals forming on the surface of the brine are supported by surface tension. As they become heavier, they fall to the bottom of the pan as incomplete cubes or hopper-shaped crystals. The product is collected by a mechanical rake and dried in the same way as vacuum pan salt. The grainer process, similar to the historic process of open-pan boiling, is suitable where waste steam is available or where waste lumber products provide an inexpensive source of heat. Since the grainer process is energy-inefficient, it was modified to make it less costly to operate. One such variation still in use is the Alberger process, which results in a combination of flakes and cubic crystals of salt. The pans are shallow, circular units with external heating units rather than heating coils. 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. Alberger salt is less dense than granulated-evaporated salt and, like grainer salt, is typically used where coarser salt is required, as in koshering [70].

4.3.3. Multiple-Effect Process

The multiple-effect evaporation process is a classical process for the production of vacuum salt (Fig. 8). Several evaporators are connected in series. The boiling point of the brine is reduced in each evaporator stage by ca. 12–20 °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. The consumption of live steam can be reduced by decreasing the number of effects. In salt plants the number of effects used varies between two and six. The expected live-steam consumption can roughly be estimated as $M = B/Z \cdot (1 + 0.05\ Z)$, where M is the live-steam consumption, B the total water evaporation, and Z the number of effects.

Today, four- or five-stage evaporator installations with production capacities of up to 150 t/h of vacuum salt are usual. The largest evaporator lines, which use the multiple-effect principle, can be found in The Netherlands. The salt factory at Harlingen has a design capacity of 1.2×10^6 t/a of vacuum salt [71].

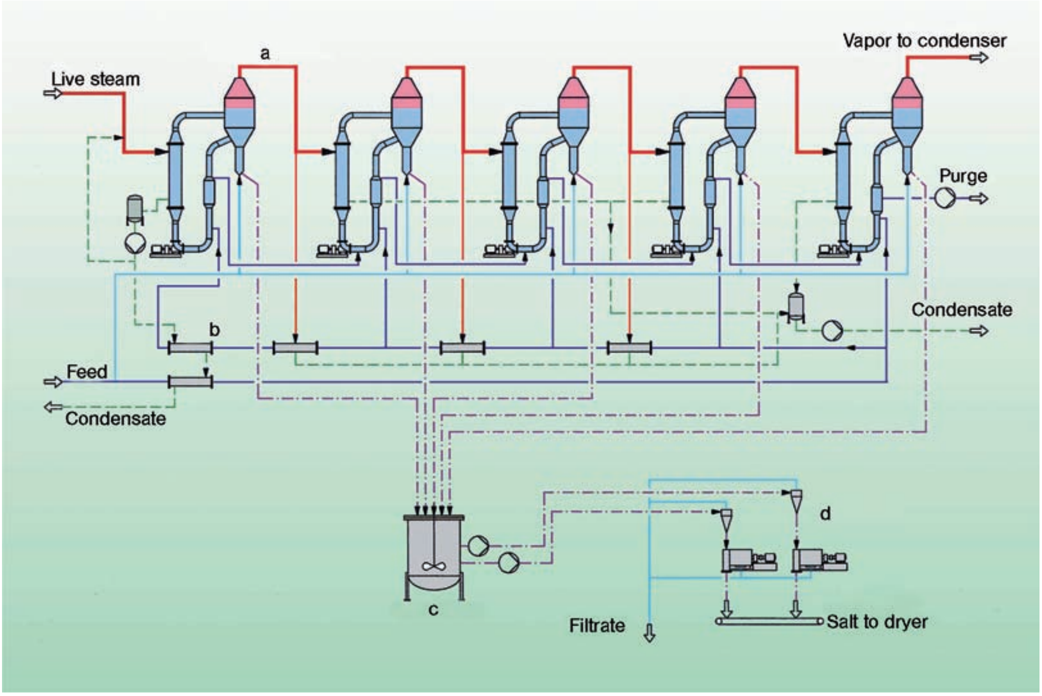

Figure 8. Multiple-effect evaporation (Source: Evatherm AG, Othmarsingen/CH) a) Crystallizers; b) Preheaters; c) Slurry tank; d) Centrifuges

To ensure optimal plant efficiency in terms of primary energy consumption, the steam should be generated at high pressure in order to utilize the energy for power generation by a counterpressure steam turbine or a gas- or steam-turbine cogeneration unit. The backpressure steam can be used to heat the evaporation plant. At a smaller evaporation capacity, where utilization of a cogeneration system is not possible or feasible, the overall efficiency can be improved by thermal vapor recompression with a steam ejector.

4.3.4. Mechanical Vapor Recompression (MVR) Process [72, 73]

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 (Fig. 9). Feed brine enters the crystallizer vessel where salt is precipitated. Vapor is withdrawn, scrubbed, and compressed for reuse in the heater. Crystallized salt is removed from the elutriation leg as a slurry.

Recompression evaporators are more energy-efficient than multiple-effect evaporators but require more expensive electrical power for energy input. The compressor can be a radial turbo type compressor or industrial blowers connected in series. The development of single-stage compressors has significantly reduced costs.

The recompression system is widely used where cheap electrical energy is available. 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. The world's largest two single-stage sodium chloride MVR crystallizers each with an annual salt capacity of 820 000 t are installed in Plaquemine,

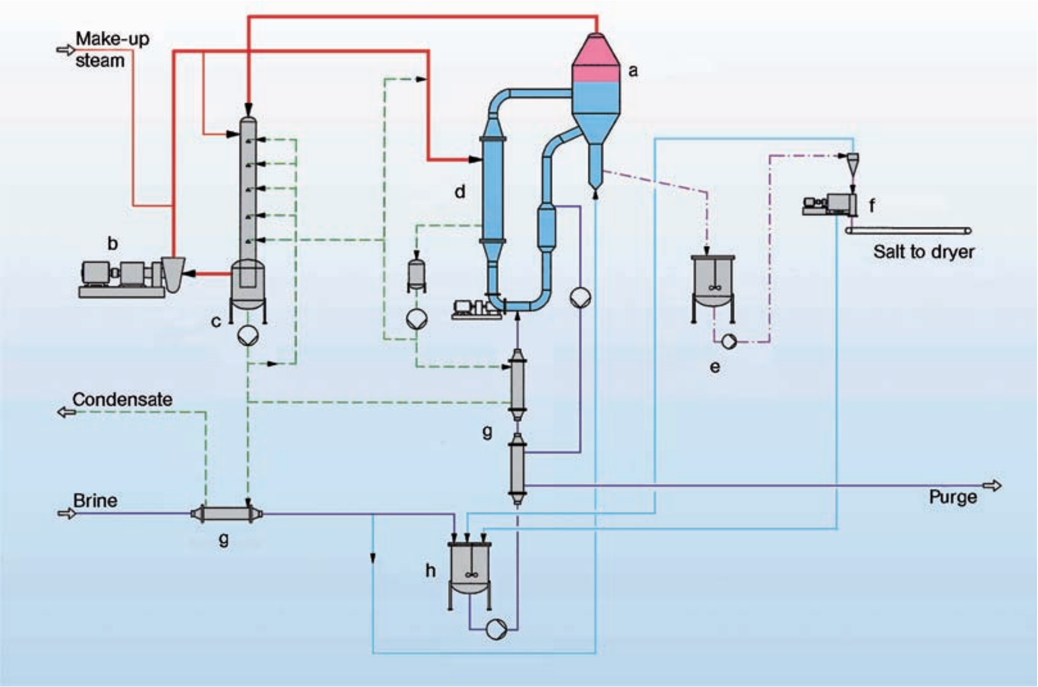

Figure 9. Mechanical vapor recompression (Source: Evatherm AG, Othmarsingen/CH) a) Crystallizer; b) Compressor; c) Scrubber; d) Heat exchanger; e) Slurry tank; f) Centrifuge; g) Preheaters; h) Balance tank

Louisiana at the Shintech chlor-alkali electrolysis plant [74].

Hybrid systems are also used with multistage and vapor-recompression evaporators [75, 76]. In combined methods high-pressure steam is passed through backpressure turbines, and the exhaust steam heats a multistage evaporation plant. The mechanical power is available for compressing the vapors. 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 [58]. This plant has a yield of 600 000 t/a, with the following brine boiling temperatures: MVR 116, 1st stage 124, 2nd stage 105, 3rd stage 86, 4th stage 69, 5th stage 49 °C.

4.3.5. Recrystallization Process [77]

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 [78, 79]. It starts with rock or solar salt as feed input and ends up with vacuum salt. In principle cold and hot dissolution of the solid salt is possible.

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 108°C 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 100 °C 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. Another thermal concept uses the vapors from the last evaporator by mechanical vapor

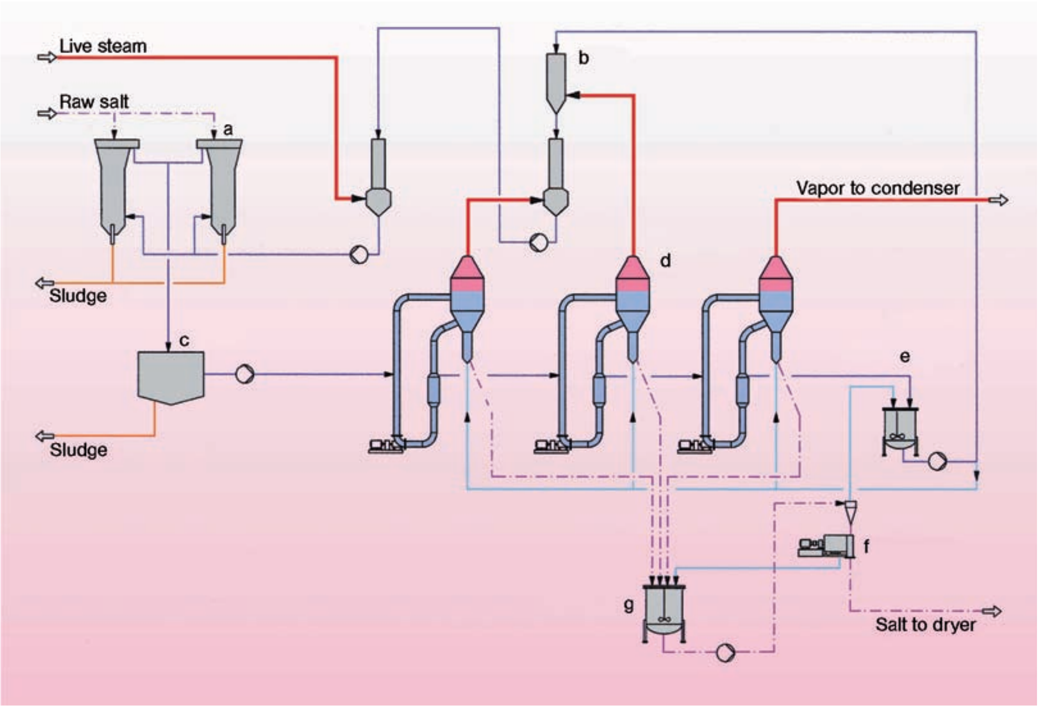

Figure 10. Recrystallization process (Source: Evatherm AG, Othmarsingen/CH) a) Dissolvers; b) Preheaters; c) Clarifier; d) Crystallizers; e) Cold brine tank; f) Centrifuge; g) Slurry tank

recompression up to the pressure of the heating system.

The hot-dissolution process has, among others, two big advantages. As $CaSO_4$ solubility is strongly inverse, only a small amount of $CaSO_4$ remains in solution and hence $CaSO_4$ remains undersaturated in the whole process. Depending on the raw salt quality and the metallic construction materials, no or only some alkaline chemicals (caustic soda, milk of lime) must be added for pH control. Insolubles such as sand, mud, and clay must be removed downstream of the saturators by means of decanters, sand filters, etc.

Figure 10 shows a schematic of a typical recrystallization plant.

The recrystallization process is well proven to convert low-quality rock and solar salts to ultrapure vacuum salt, even for use in manufacturing pharmaceuticals. This technology is used in Algeria, Bangladesh, Germany, Greece, Iran, and Turkey. The capacities reach up to max. 260 000 t/a, whereby the number of flash evaporators is between three and seven.

4.3.6. Other Process Steps

In all vacuum salt processes removal, washing, and drying of the salt crystals occur in the same manner. The crystal suspension is removed from the bottom of the conical evaporators. To completely remove the sulfate-containing mother liquor, which is purged continuously, the crystals can be washed with purified brine, which enters the evaporator at the bottom, or in a pusher centrifuge. Hydrocyclones (→ Hydrocyclones) or decanters are used to separate the salt crystals from the solution before centrifuging [80]. After centrifuging, the salt still contains ca. 2–4% moisture. Further drying can be carried out in fluidized-bed driers. At the end of the fluidized-bed dryer there is usually a cooling zone into which cold air is blown, or a separate cooler can be used. Also in use are rotary vacuum filter dryers, in which the crystal suspension is poured onto the surface of a rotating drum. The brine is sucked into the drum leaving a cake of salt on the drum surface, which is dried with hot air. In less than one revolution the slurry is transformed into dry salt. Hot drying reduces the moisture content of the final product to 0.05% or less. Rotary coolers or fluidized-bed coolers lower the temperature of the salt before screening, storage, further processing, and packaging. A salt temperature of max. 40 °C, or better max. 30 °C, is recommended. Directly fired rotary kiln dryers are no longer common; they are used only for special purposes such as removal of the internal crystal moisture before feeding to cells for molten salt electrolysis (see → Drying of Solid Materials, Chap. 2.).

Table 8. Typical dried vacuum salt qualities[a]

Process	Multiple-effect[b]	MVR[b]	Recrystallizer
NaCl (dry basis), %	99.97	99.97	99.98
Moisture (120°C, 2), %	0.05	0.05	0.05
Moisture (550°C, 1 hr), %	0.1–0.3	0.1–0.3	0.1–0.3
Calcium (ppm)	5–10	5–10	40
Magnesium, ppm	0.5	0.5	0.5
Potassium[c] (ppm)	100 (max. 1000)	100 (max. 1000)	20
Bromide[c], ppm	50 (max. 250)	50 (max. 250)	15
Sulfate, ppm	250	250	90
Insolubles, ppm	10	10	< 10

[a] Unwashed.

[b] With Schweizerhalle brine treatment.

[c] Depending on raw brine or raw salt quality.

4.3.7. 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. Both the steam produced and the electric power generated are used for the evaporation. The co-generation unit is driven according to the steam demand of the evaporation plant. The surplus electric energy is delivered to the public grid. Mechanical vapor recompression does not presuppose the operation of its own power station. Normally cheap electric energy, e.g., from hydropower stations, is purchased. The small steam demand for plant start-up, adjusting purposes, and salt drying is produced in a low-pressure steam boiler.

Advantages of the recrystallization procedure are the dispensation with classical chemical brine purification and the possibility to use raw salts with high calcium sulfate contents. The procedure has an almost neutral water balance and therefore it can also be used in water-poor regions for production of vacuum salt from rock salts and solar salts. The increased investment expenditure compared to the other processes is disadvantageous. All three procedures supply a salt quality with a sodium chloride content of at least 99.95%, whereby recrystallized salt is characterized by a low sulfate content of ca. 100 ppm and the salts from the multiple effect and mechanical vapor recompression processes are characterized by the low calcium content of less than 10 ppm. Typical analyses of salt produced by evaporation of crude and purified brines are given in Table 8.

The multiple-effect process and recrystallization require considerable amounts of cooling water (20 m^3/t of salt), which are taken from open or closed cooling-water circuits.

The different evaporation systems are characterized by specific energy consumptions that are in the focus of the cost management of salt factories (Table 9).

Three types of evaporators are used in general. The simplest type is a flash evaporator with forced circulation, but without heaters. This type is used for recrystallization and for the utilization of hot mother liquor from MVR plants. Most frequently evaporators with forced circulation and heaters in the brine circuit are used. Both evaporator types supply die-shaped crystals with a mean grain size of 450 µm. With increasing grain size the salt grains are rounded off. The Oslo evaporator delivers coarse grains of lens to spherical shape ca. 1–2 mm in size. In this crystallizer type circulation brine and fresh brine are evaporated after heating in the heater. Crystal growth occurs in supersaturated brine, which flows through the central tube into the crystallizer and from there from below up through the crystal bed (Fig. 11).

Table 9. Energy consumption of the different vacuum salt processes

Process	Energy	Specific energy consumption
Five-stage effect (150 t/h)	live steam, 4.5 bar (saturated)	750 kg/t
	electrical energy	25 kWh/t
MVR (30 t/h)	live steam, 3.5 bar (saturated)	1000 kg/h (for startup)
	electrical energy	155 kWh/t
Seven-stage recrystallizer (20 t/h)	live steam, 2 bar (saturated)	450 kg/t
	electrical energy	45 kWh/t

Evaporation in open pans produces the largest, hollow, pyramidal crystals with an edge length of up to 24 mm.

Saline solutions and moist, saline air lead to considerable corrosion damage in salt works if unsuitable materials are used. Corrosion is strongly dependent on temperature, pH, and the oxygen content of the brine. The evaporator bodies are mostly manufactured from Monel or Monel-plated steel. Also evaporators made of titanium, Inconel 625, Duplex steel, and rubber-lined steel are in use. The tube plates of the heaters consist of Monel or Inconel 625. The tubes in the heaters are manufactured from titanium grade 12 [81].

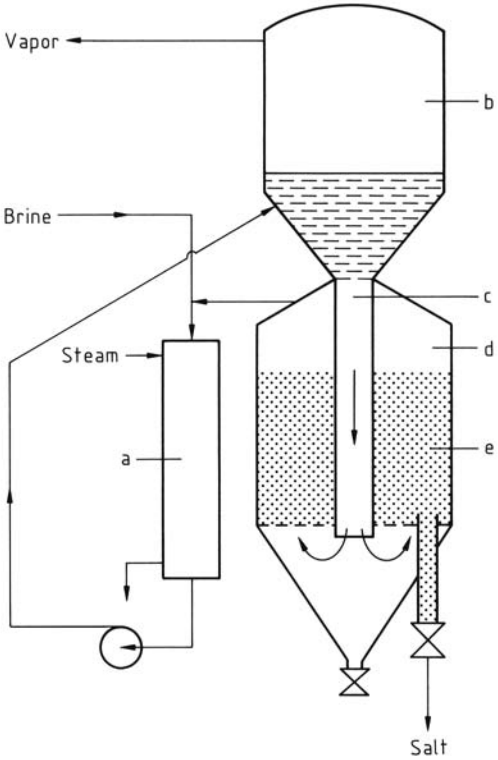

Figure 11. Oslo evaporator a) Heat exchanger; b) Vacuum evaporator; c) Down pipe; d) Crystallizer; e) Bed of crystals

4.3.8. Vacuum Salt based on Seawater as Raw Material

Processes that can be used in the production of vacuum salt from seawater are shown in Figure 12.

The conventional process includes the use of a solar saline pond to produce the crude salt, which is recrystallized in a vacuum plant using vacuum-cooling or vacuum-evaporation crystallization.

In regions of less favorable climatic conditions, it can be advantageous to use the solar pond for producing concentrated brine instead of crude salt. This brine is processed to vacuum salt in a subsequently arranged vacuum-evaporation crystallization plant. This ensures production even under unfavorable weather conditions.

In arid regions and regions unsuitable for solar ponds and without rock salt deposits, electrodialysis of seawater is an alternative preconcentration process. Because of its higher $CaSO_4$ concentration, concentrated seawater poses some difficulties. Vacuum salt is produced in a downstream vacuum-evaporation crystallization plant [82].

Electrodialysis with ion-exchange membranes is superseding the traditional methods (channeled and sloping salt-terrace methods) for seawater concentration in Japan, Korea, and Taiwan. Electrodialysis concentrates seawater from 3.5 to 15–20% of salinity before it enters multiple-effect plants for the salt production [83].

Besides electrodialysis, reverse osmosis can also act as a preconcentration process, although the degrees of concentration that can be obtained are lower than with electrodialysis. This process

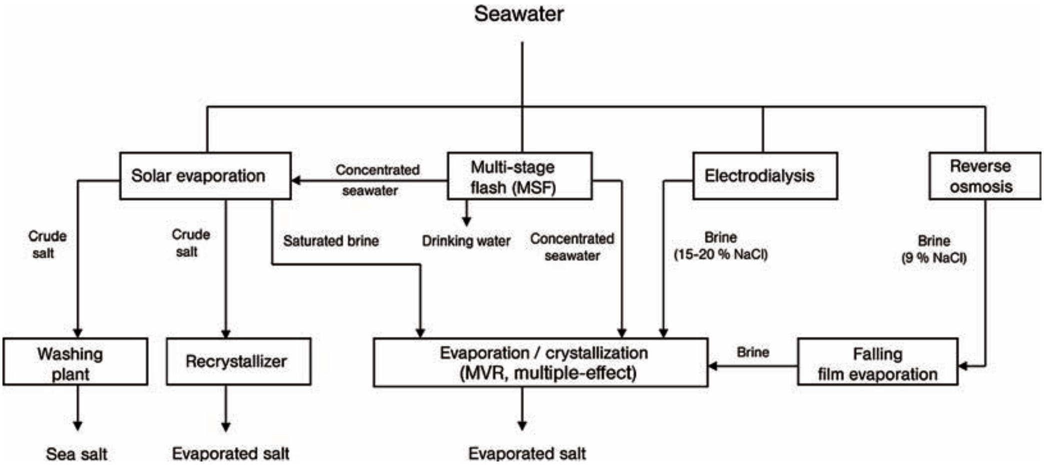

Figure 12. Processes for salt production from seawater

is also followed by vacuum-evaporation crystallization.

In Poland reverse osmosis is also used as a first stage for the concentration of salty coal-mine water to an NaCl concentration of 80–90 g/L. The saturated brine for the MVR crystallizer is then made in a falling-film evaporator [84].

The procedures of electrodialysis and reverse osmosis have not found wide application in the salt industry. They remain restricted to special cases, since they involve high energy costs. Crystallization plants for salt should be always fed, if possible, with concentrated brine or crude salt in order to avoid expensive evaporation of water, without simultaneous production of crystallized salt (“blind” evaporation).

4.4. Production of Solar Salt

Introduction. 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.

4.4.1. Production from Sea Water

The water of the seas and oceans contains all the known elements, most of them present in small amounts [85]. Sodium chloride is the most important compound in terms of concentration, averaging 28 g/L.

Sea water also contains significant amounts of magnesium, sulfur, and calcium, the other important sea-water-based process being the production of magnesium compounds.

The salinity (grams of salt per kilogram of seawater) of ocean and seawater varies with location and depth [86]. This dispersion, due either to dilution by precipitation or drainage pattern, or to local overconcentration caused by strong evaporation, is more evident in inland seas.

The average salinity is 3.5%, corresponding to a relative density of 1.026. It reaches 4.1% in the Red Sea and is only 3% in the Baltic Sea.

Table 10. Typical climatology of solar saltfields [86]

	South of France	Australia	Indonesia	Taiwan
Annual evaporation *, mm	1700	3600	1850	1660
Annual rainfall, mm	550	300	1300	1400

[*] Fresh water.

The salt mixture in seawater has the following typical composition (in wt%) [86]:

NaCl	77
$MgCl_2$	10
$MgSO_4$	6
$CaSO_4$	3.9
KCl	2

4.4.1.1. The Main Factors Governing Production of Sea Salt

To produce sea salt economically, the amount of water evaporating must exceed the amount of precipitation (rain or dew) for a long and continuous period of at least three months during the year.

Table 10 lists the main types of climate compatible with the production of sea salt. In Taiwan, a borderline case, sea salt production calls for a maximum of ingenuity. In Western Australia, by contrast, the climate is ideal, notwithstanding the risk of cyclones, and sea salt can be produced all year round.

In practice, evaporation at a given production site is measured over fresh water with an evaporometer. Since the total concentration of dissolved salts is known, the evaporation is determined approximately from an empirical curve, an example of which is shown in Figure 13 [87].

It follows that 1 cm of evaporation over fresh water corresponds to *a* cm for the body of water in question; *a* normally ranges from 0.95 for seawater to 0.55 for saturated brines depositing their salt.

In addition to a favorable climate, a particular topography is required, and the ground must be as impermeable as possible to minimize brine seepage.

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.

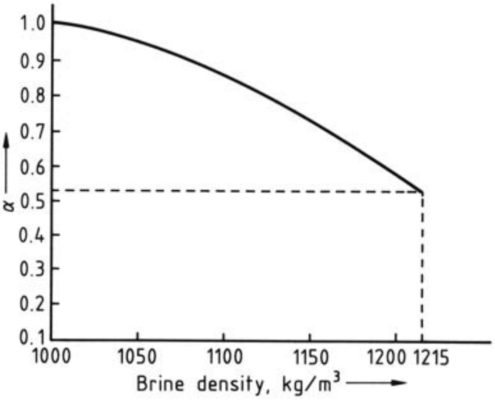

Figure 13. Evaporation coefficient α as a function of density

These conditions are often satisfied in the deltas of large rivers. The Rhône delta in France's Camargue is one example, and is the location of two large salt fields: Aigues-Mortes and Salin de Giraud.

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 from 28 g/L to roughly 260 g/L, corresponding to an increase in relative density from 1.026 to 1.215. At this point, the brine begins to deposit its salt. Most of the calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4 \cdot 2\,H_2O$) has already crystallized before this point, as shown in Figure 14, while the magnesium salts continue to become concentrated without crystallizing. Salt workers use the empirical Baumé (°Bé) scale, to measure the concentration of brines. According to that scale the seawater concentration is 3.5 °Bé. The crystallization of $CaCO_3$ begins at 4.6 °Bé and that of $CaSO_4$ at 13.2 °Bé. NaCl crystallizes at 25.7 °Bé, followed by the more soluble Mg salts at 30 °Bé.

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 [89]. Surprisingly, despite rising salinity, life in the

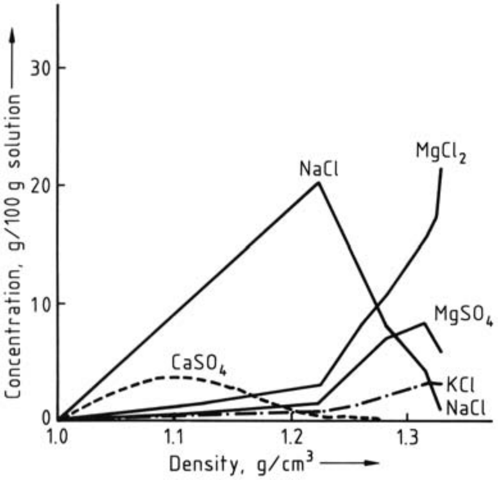

Figure 14. Brine composition as a function of density [88] Values for $CaSO_4$ concentration are multiplied by a factor of ten.

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 [90]:

- 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 colors 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 colorless salt bed. The red color of the brines in the crystallizers 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, low in Ca^{2+} (0.03–0.06%), Mg^{2+} (0.003–0.05 %), SO_4^{2-} (0.10–1.2%), and admixtures of soil (0.01–0.02%).

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. The floors of the crystallizers must first be carefully prepared by compacting and leveling to ensure easy separation of the salt from the ground and a uniform layer of brine. The surface area of these crystallizers generally represents ca. 10% of the total area of the salt field.

From this point on, the salt worker's job is to monitor the brine strengths and purge the bitterns from the ponds when the concentration of secondary salts, particularly magnesium salts, is liable to lower the quality of the salt. The ponds are then filled with fresh or pure brine with a low magnesium salt content.

The salt is produced in the form of a layer of tangled crystals whose density and grain size depend on the characteristics of the bittern and, especially, on the turbidity or cloudiness. If the brine is turbid, the suspended fine particles act as seed crystals. If, however, the brine is clear and well settled, the number of seed crystals is greatly reduced, and crystal growth occurs in preference to germination.

The thickness of the salt layer varies from one site to another, and also, at a given site, from one year to another, depending on weather conditions. In the South of France where the production period runs from May to September, the thickness at the end of the season averages

10 cm. At other latitudes, layers may be over 20 cm thick.

The Margherita di Savoia saltworks, located in Apulia (Southern Italy), since the mid-1980s has used a new method of deposited salt production, known as long-term production and designed to significantly reduce operating costs. In this process, the salt produced during the salt-extraction campaign (May to September) is not collected, but left as a deposit on the bottom of the saltpans. This process is repeated for 4–5 years. At the end of the cycle, there are several superimposed layers, with a total thickness that varies from 50 to 60 cm. The saltpans are harvested on a six-monthly basis using the "big beam" harvesting method. In fact, the thickness of the crust of salt deposited in the salt pans allows a certain number of diggers (three or four) to descend directly into the salt pan and form roads of salt (the so-called big beams). The thickness of these roads is twice that of the crust. A scraper then compacts the beams, enabling trucks to descend directly into the saltpan for loading by the diggers. Several advantages have become apparent by adoption of long-term production und beam harvesting; in particular the harvest is separated from the production phase. The harvest can therefore be scheduled on the basis of market requirements or quieter times of year at the plant, such as March and October [91].

4.4.1.2. Production Stages in a Modern Salt Field

Figure 15 shows the main components of the infrastructure of a modern salt field, from seawater intake to the production facilities for processing and packaging the salt.

The production process features the following stages:

1. Seawater pumping: the salt field is supplied with seawater by a pumping station. In some parts of the world, such as Australia, the salt fields are gravity fed with seawater in accordance with the tides. Several million cubic meters of seawater are required annually to produce several hundred thousand tonnes of sodium chloride (the Aigues-Mortes salt field in France pumps 50 × 10^6 m^3 of seawater for an average annual output of 400 000 t).
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: for a salt field with a single production season during the year, the crystallizers are first filled

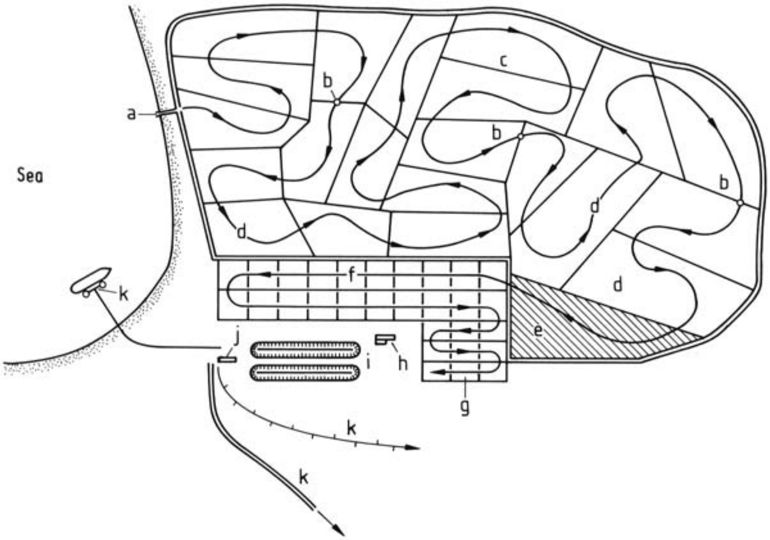

Figure 15. Modern salt field [86] a) Sea water intake; b) Pumping station; c) Dikes; d) Condensers; e) Brine storage tanks; f) Crystallizers; g) Bitterns area; h) Washing plant; i) Salt storage areas; j) Packaging plant; k) Dispatch

with brine kept from the previous year, which has been protected from rain dilution in deep storage ponds. A few weeks later, the old brine is replaced by the new concentrated brine leaving the ponds.

By the time the relative density of the brine reaches 1.215 g/L, when NaCl crystals start to form, the brine has already precipitated 80% of the calcium sulfate in the form of gypsum. The high-magnesium brine, called bittern, because of its bitter taste, is then removed before the relative density reaches 1.260 to avoid codeposition of magnesium salts.

4. Salt harvesting: in batch-operated salt fields, salt harvesting begins at the end of the salt production period. For continuous salt fields, harvesting is performed at regular intervals to ensure that the level of the salt does not exceed the operating height of the harvesting machines. The harvester is generally carried by a tractor of the type often used for civil engineering projects. The salt is first scooped off the floor of the crystallizer by a large blade up to 3.6 m wide pushed along by the tractor. It is then lifted by slotted or bucket conveyors. The salt is then evacuated and poured into trailers by a conveyor belt.
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.
6. Processing and packaging: The salt reclaimed from the salt stockpile may be washed a second time, which increases the sodium chloride content to 99%. The salt is then generally dried, crushed, and screened, and anticaking agents are added. Other substances added at this stage include iodide or fluoride in salt for human consumption. The salt is then packaged in various containers (e.g., boxes, polyethylene bags), as required by the consumer.

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”.

The washing process immediately after harvesting ensures high salt quality, as it minimizes the impurity levels and moisture content. The design of the wash plant and location of the salt stockpiles have an important bearing on the quality of the end product. Proper salt washing improves the color of the salt and removes some impurities, both soluble and insoluble. In one such method, the crude salt is fed into an agitated tank where it is mixed with saturated brine from the crystallizers to form a slurry, which is pumped into a screw classifier. The wash liquor overflows. The salt then passes through a dewatering screen for further removal of impurities. Hydromilling selectively ruptures the salt crystals in which the impurities are embedded so that they become exposed to purification [92].

In Mexico a unique process for refining salt was developed [93]. By redissolving high-quality solar salt and using a “salting out” process to precipitate out trace amounts of calcium, magnesium, and sulfate, it is possible to produce a solar sea salt exceeding 99% purity.

The best solar salt qualities achieve 99.80% NaCl content (Table 11).

Table 11. Typical solar salt qualities

Component	Guerrero Negro, Mexico (unwashed grade) [94]	Port Hedland, Australia (washed grade) [95]
NaCl (dry basis), %	98.54*	99.70–99.80
Moisture, %		1.80–2.80
Calcium, %	0.16	0.03–0.05
Magnesium, %	0.20	0.02–0.03
Potassium, %		0.01–0.02
Sulfate, %	0.68	0.10–0.15
Iodine, ppm		< 0.5
Insolubles, %	0.07	0.01–0.03

*Washed: average 99.70%.

Byproducts. In most commercial operations, the bittern often is disposed in the sea. Where bitterns are present in sufficiently large quantities, an adequate market exists and if the climate allows, the bitterns can be concentrated on a bittern salt field to extract the magnesium bromide, magnesium sulfate, and even magnesium chloride (→ Magnesium Compounds) [96, 97].

When the salt concentration in the salt marshes reaches 50 g/L, *Artemia salina* (brine shrimp) starts to develop. This tiny crustacean, measuring just a few tenths of a millimeter, reaches an adult size of 1 cm and weighs approximately 2 mg. Artemia is an important source of food for fish and crustaceans. Rich in proteins, polyunsaturated fatty acids, vitamins, and carotenoids, it is suitable for fresh and seawater aquarium fish. Artemia is also the main source of food for larvae and adult fish and crustaceans bred in fish farms. In some salt works, like Aigues-Mortes in France, *Artemia salina* is bred as a secondary activity to salt extraction.

4.4.2. Crystallization from Mined Brine

The salinity of brines from solution mining is much higher than that of seawater. In consequence there is no need for ponds in which the brine is concentrated.

The composition of underground brines varies widely. In certain inland underground brines, potassium and magnesium salts are absent and calcium sulfate is the only constituent other than sodium chloride. In such cases an 8 m deep brine pond is used for intermediate brine storage before entering the crystallization ponds. During six-month intermediate storage gypsum precipitates from the 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. The estimated annual solar salt production is 200–250 kg/m^2.

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 co-generation the brine from solution mining caverns is heated to ca. 80°C before entering the crystallization ponds. The evaporation rate at that temperature is ten times higher than at 30 °C. As a result, the ponds required are much smaller than solar evaporation ponds and the salt layer is much thicker [98].

4.4.3. 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 Great Salt Lake in Utah has a NaCl content of 15.11%. It does not contain any bromide, unlike seawater, and the content of Glauber's salt is higher than that of magnesium sulfate. The NaCl concentration in the Dead Sea is 7.93% (Table 12).

Products from lakes such as the Dead Sea, the Salar de Atacama, and the Great Salt Lake, in addition to halite, include magnesium and potassium salts, bromine, iodine, and boron, lithium, and nitrate salts. These salts, including halite, are converted to a number of other chemicals. The production of salt from salt lakes occurs in

Table 12. Comparison of composition of saline waters [99]

Component (g/L)	Seawater	Great Salt Lake	Dead Sea	Salar de Atacama
Sodium	10.56	80.1	39.15	93.18
Potassium	0.38	5.22	7.26	21.95
Magnesium	1.27	5.19	39.15	12.26
Calcium	0.40	NR*	16.86	0.30
Sulfate	2.65	18.74	0.47	23.29
Chloride	18.98	139.12	212.40	192.0
Bicarbonate	0.14	NR	0.22	NR
Bromide	65×10^{-3}	NR	5.12	NR
Boron	4.6×10^{-3}	NR	40×10^{-3}	0.84
Lithium	0.17×10^{-3}	NR	18×10^{-3}	1.96
Total	34.38	248.37	320.63	345.78
SG**	1.02–1.04	1.164	1.220	1.226

[*] Not reported.

[**] Ratio of the weight of the liquor to that of an equal volume of water at 4 °C.

similar way to that of seawater by evaporation with solar energy.

4.4.4. Seawater Desalination

In water-poor regions the shortage of drinking water led increasingly to the installation of seawater desalination plants, in which salt can be produced as a byproduct. In numerous countries stationary installations for seawater desalination are in use. These operate according to the principle of the multistage flash process (MSF) or are multiple-effect desalination plants (MED). In tropical and subtropical regions solar energy is also used for seawater distillation.

A method for the production of salt from seawater is the freezing process, in which the water is cooled until salt is produced. The salt crystals occur as dihydrate in the temperature range below 0.1 °C. The process did not get practical importance.

Other processes for the separation of NaCl from seawater are electrodialysis and reverse osmosis. The MSF process has the highest share in installed capacities, followed by reverse osmosis. Processes which are useful for the production of salt from seawater are described in Section 4.3.8.

5. Salt Standards

Salt produced worldwide normally varies in purity from 90% NaCl for rock salt to 99.99% for vacuum salt. Vacuum salt made from purified brine or by recrystallization generally has the highest purity, and rock salt the lowest. Several mandatory and voluntary standards apply to salt to ensure appropriate quality, purity, and gradation for particular salt uses (Table 13).

The important Codex Alimentarius Standard for food-grade salt applies to salt used as an ingredient of food, both for direct sale to the consumer and for food processing. Essential quality factors are the content of NaCl, which must not be less than 97% on a dry matter basis, exclusion of additives, and maximum limits for contaminants.

6. Analytical Methods

Sampling is just as important as the analysis itself. Particularly in bulk salt where during

Table 13. Salt standards

Type of standard	Title	Designation	Jurisdiction
Food	Standard for Food Grade Salt	Stan 150	Codex Alimentarius Commission (FAO)
	Sodium Chloride Monograph	Food Chemicals Codex (FCC)	Food and Nutrition Board, Academy of Sciences
Deicing	Standard Specification for Sodium Chloride	ASTM-D-632	ASTM
	Standard Specification for Sodium Chloride	AASHTO-M-143	American Association of State Highway Transportation Officials
	Technische Lieferbedingungen für Streustoffe	TL-Streu	Forschungsgesellschaft für Straßen- und Verkehrswesen e.V. (FGSV), Germany
	Specification for Salt for Spreading on Highways for Winter Maintenance	BS 3247	British Standards Institution (BSI), UK
	Chlorure de sodium solide utilisé comme fondant routier	NF P98-180	Association Francaise de Normalisation (AFNOR), France
Pharmaceutical		Ph. Eur.	European Directorate for the Quality of Medicines & HealthCare
		U.S.P.	U.S. Phamacopeia Convention
		JP	Society of Japanese Pharmacopoeia
Water treatment	AWWA Standard for Sodium Chloride	ANSI/AWWA B200	American National Standards Institute/American Water Works Association
	Sodium chloride for regeneration of ion exchangers	EN 973	European Committee for Standardization (CEN)
	Sodium chloride for on site electrochlorination using nonmembrane technology	EN 14805	CEN

Table 14. Analytical methods for salt

Organization	Analytical method	Designation
ISO	Determination of loss of mass at 110°C	ISO 2483
	Determination of insoluble matter	ISO 2479
	Determination of sulfate content—barium sulfate gravimetric method	ISO 2480
	Determination of halogens, expressed as chlorine—mercurimetric method	ISO 2481
	Determination of calcium and magnesium contents—EDTA complexometric methods	ISO 2482
Codex Alimentarius Commission	Method for sampling of food grade salt for determination of sodium chloride	STAN 150
ASTM	Standard Methods for Chemical Analysis for Sodium Chloride	ASTM E534
AOAC International, Official Methods for Analysis	Salt	AOAC 925.55
European Salt Producers' Association (EuSalt)	*Cations:*	EuSalt/AS 01-18
	AAS: Cd, Ca + Mg, Pb, Hg, K	
	ICP-OES: several cations	
	Photometry: Fe	
	Titration, mercurimetric: K	
	Anions:	
	HPLC: several anions	
	Titration: Br^-, I^- (iodometric), NO_2, Hexacyanoferrate(II)	
	Potentiometry: Cl^-, F^-	

handling, storage, and shipment a tendency exists for the various-sized salt particles to segregate, a detailed sampling plan is necessary. A method for sampling of food-grade salt for determination of sodium chloride is included in the Codex Standard 150 for Food Grade Salt. Many other salt standards include sampling methods and methods for chemical analysis and determination of grading by sieve analysis. An overview of official standard methods for chemical analysis is given in Table 14.

7. Uses

Salt has more than 14 000 known uses. The salt industry generally classifies salt uses by the five principal use categories and then lumps the remaining uses in the miscellaneous classification: Table salt and food processing, agriculture, water treatment, chemical, anti-icing and de-icing, and miscellaneous [70].

7.1. Table Salt and Food Processing

Salt is added to food by the food processor or by the consumer through free choice, as a flavor enhancer, preservative, binder, fermentation-control additive, texture-control agent, and color developer. This major category is subdivided, in descending order of salt consumption, into other food processing, meat packing, canning, baking, dairy, and grain mill products [100]. Of the millions of tonnes of dry salt produced annually in the world, a very small percentage finds its way to dining tables either in commercially processed foods, in home preparations, or in the saltshaker.

Functional Salts. Salt enjoys unique advantages as a vehicle for micronutrient fortification in most parts of the world in terms of universal access, uniformity of consumption, and low cost of fortification (Table 15).

Iodine deficiency is one of the world's most important nutritional deficiencies, and produces a spectrum of disorders—impaired cognitive development and function, hypothyroidism, congenital abnormalities, cretinism, and endemic goiter—known as IDD [101]. These disorders are endemic in many countries around the world. Iodine deficiency affects one-third of the global population, including 260×10^6 school-age children. Iodine deficiency is the result of insufficient dietary iodine intake. The prevention of IDD is possible with the addition of iodine to the diet. Of the various methods used to add iodine to the diet, fortification of salt with iodine for human and animal consumption has been recommended and is implemented worldwide [102, 103].

Iodine may be added to salt as iodides or iodates. Potassium iodide is unstable under con-

Table 15. Table salts with micronutrients (examples) [106, 107]

	Iodine, ppm	Fluoride, ppm	Folic acid, ppm	Iron, ppm
Salt with fluoride[a]		250		
Iodized salt with fluoride and folic acid[b]	15–25	212.5–287.5	100	
Iodized salt with iron[c]	30			850–1100

[a] France: Fluoride as potassium fluoride.

[b] Germany: Iodine as potassium iodate, fluoride as sodium fluoride.

[c] India: Iodine as potassium iodate and iron as encapsulated ferrous fumarate.

ditions of extreme moisture and temperature, particularly in an acid environment. Sodium carbonate or sodium bicarbonate is added to increase alkalinity, and sodium thiosulfate or dextrose is added to stabilize potassium iodide. Without a stabilizer, potassium iodide is oxidized to iodine and lost by volatilization from the salt.

Oral disease is a significant burden to all countries of the world and is the fourth most expensive disease to treat. Although dental health has improved dramatically across many of the world's populations, there are still huge problems with dental caries in many sections of society, particularly the underprivileged. While steps can be taken to improve general education about oral care and hygiene, research and practical experience have shown that dental caries can be prevented most effectively through the establishment of fluoride programmes. Salt fluoridation should be considered where water fluoridation is not feasible for technical, financial, or sociocultural reasons.

Iron deficiency is one of the top ten most serious health problems in the modern world. Iron deficiency anemia (IDA) impairs the mental development of over 40% of the developing world's infants and reduces their chances of attending or finishing primary school. IDA decreases the health and energy of pregnant women and contributes to approximately 50 000 deaths in childbirth each year. IDA is complex because it requires increased iron intake at critical stages of the life cycle: before and during pregnancy and throughout early childhood. The solution is double fortified salt with iodine and iron, which is on stream in India, one of the world's most iron-deficient countries [104].

Folic acid deficiency can lead to neural tube closure defects (NTDs) and anemia. Fortification of cereal flours with vitamin and mineral premixes containing folic acid and other essential micronutrients, as well as salt fortification with folic acid, help adolescent girls and women of childbearing age prevent anemia and NTDs [105].

Iodization is performed by spraying a concentrated solution of sodium or potassium iodide or iodate over crystalline sodium chloride and thorough mixing. This process can be carried out continuously or as a batch operation. Usually drying is not necessary, since one tonne of salt is sprayed with only about one liter of solution. Fluorides are added to salt is by wet or dry methods [108].

Folic acid is added as dry vitamin to the iodized salt. Double fortified salt with 30 ppm iodine and 850–1100 ppm iron contains potassium iodate and encapsulated ferrous fumarate containing soy stearin, titanium dioxide, hydroxypropyl methyl cellulose, and sodium hexametaphosphate [106].

Nitrited Salt. In cured products, salt acts in combination with nitrite to effect preservation. It improves product safety and stability, prevents botulism, and has positive effects on the sensory properties (curing color, curing aroma). In most cases a nitrite content of 0.5% in the salt is sufficient. The production of iodized meat products is possible if the nitrite is added to salt with potassium iodate.

Dendritic Salt. For the production of dendritic vacuum salt, sodium or potassium ferrocyanide is added to the brine before the crystallization process. This crystal modifier prevents a normal crystallization and leads to an open, porous crystalline structure with a large surface. This salt is readily compactable, has strong adhesive ability, e.g., for seasoning chips, peanuts, and other snacks, and its high adsorption capacity makes it suitable as a carrier for natural and artificial flavors. The low density of ca. 0.7 kg/L and an increased content of ferrocyanide (20 ppm, calculated as potassium ferrocyanide) are characteristic of dendritic salt.

Encapsulated Salt. Sodium chloride which is coated with fat or oils is used in food processing applications where controlled release of sodium chloride is needed. Coating occurs in a fluidized bed of salt by spraying with the coating material. An example of an encapsulated product has 80–90% of salt; the rest is a mixture of vegetable oils with a melting point of 58–62 °C.

Salt Replacers and Enhancers. As a result of concern about the relationship between dietary sodium and hypertension, low sodium products and salt substitutes are used. Mixtures of sodium chloride and potassium chloride, herbs and spices, as well as modified salt crystals of lower density are marketed in response to a limited consumer demand for reduced-sodium products. Salt enhancers are substances, like monosodium glutamate and L-arginine, which themselves do not have a salty taste, but enhance a salty taste when used in combination with sodium chloride. Salt replacers are substances like potassium chloride and magnesium sulfate, which themselves have a salty taste [109].

7.2. Agriculture

The mineral sodium is a vital element for animals, just as for humans. Sodium is involved, like potassium and chloride, mainly in physiological functions. It is needed particularly for maintaining the osmotic pressure of the body liquids and for the acid–base-balance. Chloride is involved in enzymatic reactions as a cofactor of α-amylase in the pancreas. Chloride ions are needed further for the formation of the hydrochloric acid in the stomach. Most forage provides insufficient sodium for animal feeding and may lack adequate chloride. Therefore, salt supplementation is a necessary and critical part of a nutritionally balanced diet for animals.

Salt can be mixed with commercially feed or fed free-choice. It is produced plain or as trace mineralized salt, in blocks, and as loose salt. Salt acts as an excellent carrier for trace elements and vitamins not found in the vegetation consumed by grazing livestock. Some of the salt additives are zinc, manganese, copper, iodine, cobalt, selenium, and vitamins such as A and D. Magnesium, calcium, phosphorus, and sulfur are frequently added to salt blocks for free-choice feeding as well.

7.3. Water Treatment

Water Softening. Many areas have hard water, which contains excessive calcium and magnesium ions that contribute to the buildup of a scale or film of alkaline mineral deposits in household and industrial equipment. Commercial and residential water-softening units use salt to remove the ions causing the hardness. The sodium ions are captured on a resin bed and exchanged for the calcium and magnesium ions. Periodically, the water-softening units must be recharged because the sodium ions become depleted. Salt is added and dissolved, and the brine replenishes the lost sodium ions. The same process is used in smaller water-softening units mounted in dishwashers.

Water Disinfection. Disinfection of water can be performed centrally with chlorine and hypochlorite. Beside this, however, sodium chloride can be electrolyzed on-site near swimming pools. Simple tube cells or installations which work according to the membrane procedure are used for electrolysis. In tube-cell electrolysis salty swimming pool water flows directly through the equipment. Membrane electrolysis produces hypochlorite that is dosed into the swimming pool water. On-site salt electrolysis can be used also for the disinfection of drinking water.

A variety of sodium chloride salt grades are useful for water softening and water disinfection. These include higher purity rock salt, solar salt, and evaporated salt. Rock and solar grades may require more frequent cleaning of the brine tank to remove insoluble sediment naturally present in the salt. Evaporated salt is mostly used in compressed form, as granulates, briquettes, tablets, and blocks [110].

7.4. Chemical Uses

The greatest single use for salt is as a feedstock for the production of chemicals. The chlor-alkali sector is the main consumer of salt for manufacturing chlorine (→ Chlorine), sodium hydroxide (→ Sodium Hydroxide), and synthetic soda ash (→ Sodium Carbonates, Section 1.4.1.2.). Salt electrolysis using the three cell technologies (diaphragm, membrane, mercury) is fed with salt in the form of brine,

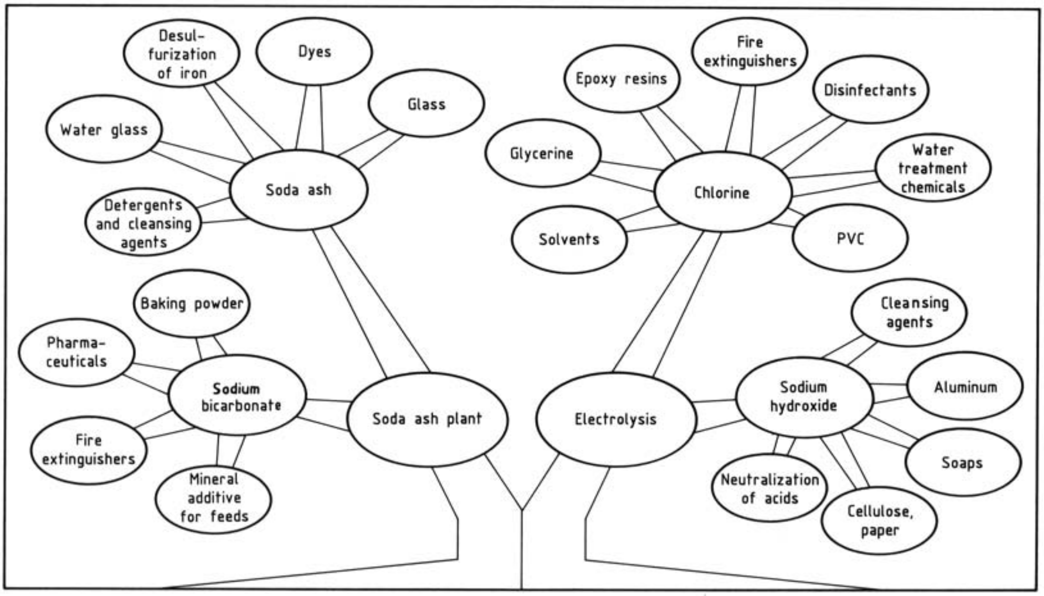

Figure 16. Family tree of salt chemistry [111]

low-sulfate rock salt, evaporated salt, and solar salt. It takes about 1.75 t of salt to make 1.0 t of chlorine and 1.1 t of coproduct caustic soda. These two chemicals are further used to manufacture other materials (Fig. 16).

The Solvay process is the most widely used method for the production of synthetic soda ash. The raw materials for the process are captive or purchased salt in the form of brine and limestone. Soda ash is made by saturating purified brine with ammonia gas and then carbonating the solution with carbon dioxide gas to form a sodium bicarbonate precipitate, leaving ammonium chloride in solution. The sodium bicarbonate is calcined to soda ash, and the ammonium chloride is treated with milk of lime to recover the ammonia and to produce the byproduct calcium chloride.

The ammonium chloride coproduction process for synthetic soda ash, is essentially a variation of the conventional Solvay process, where instead of treating the ammonium chloride with milk of lime, the ammonium chloride is crystallized and the mother liquor is recycled. The process requires the use of solid raw salt. The ammonium chloride can be used as food additive in liquorice and for manufacturing dry batteries.

Salt is also used as a feedstock in chemical plants that make sodium chlorate by the electrolysis of acidified brine, metallic sodium by the electrolysis of a molten salt mixture containing 33% sodium chloride and 67% calcium chloride, and other downstream chemical operations. It is also used with sulfuric acid to produce sodium sulfate and hydrochloric acid.

7.5. De-icing and Anti-icing

The second largest use of salt is for highway de-icing. Rock salt, solar salt, and in some cases, evaporated salt are used to maintain traffic safety and mobility during snow and ice conditions in snow belt regions throughout the world. Sodium chloride melts ice at temperatures down to its eutectic point of −21.12 °C. For de-icing on highways dry salt, nearly saturated brine or prewetted salt is used, depending on the road and weather conditions. Salt is prewetted with 20 to 30% of brine or solutions of calcium and magnesium chloride. In anti-icing near 0 °C, where salt is very effective, prior to the beginning of snowfall or frost, brine is sprayed onto the dry or wet pavement, where it prevents a bond forming between the snow or ice and the pavement. Anti-icing allows savings in salt consumption on highways to be achieved.

Salt is an inexpensive, widely available and effective ice control agent. However, it becomes less effective as the temperature decreases below about −10 °C. At lower temperatures, more salt would have to be applied to maintain a higher brine concentration in order to provide the same degree of melting.

7.6. Other Industrial Uses

Salt is used to fix and standardize dye batches in the textile industry; it is used in metal processing and secondary aluminum making to remove impurities; rubber manufacturers use salt to separate rubber from latex; salt is used as a filler and grinding agent in pigment and dry-detergent processes; ceramics manufacturers use salt for vitrifying the surface of heated clays; soap makers separate soap from water and glycerol with salt; oil and gas drillers use salt in well drilling muds to inhibit fermentation, increase density and to stabilize drilling in rock salt formations; hide processors and leather tanners use salt to cure, preserve and tan hides.

Dry-compacted salt cores are used in foundries for mass production of cast aluminum pistons. Core removal is simple, because the salt is completely water-soluble.

In the pharmaceutical industry, salt is used for preparation of saline solutions for injection, and for manufacturing hemodialysis and peritoneal dialysis solutions used in kidney machines. Oral rehydration therapy is a simple, cheap, and effective treatment for dehydration associated with diarrhea, particularly gastroenteritis, such as that caused by cholera or rotavirus. Oral rehydration solutions (ORS) consist of a solution of salts and sugars which is taken by mouth. UNICEF recommends a ORS formulation with 2.6 g/L sodium chloride, 13.5 g/L anhydrous glucose, 1.5 g/L potassium chloride, 2.9 g/L and trisodium citrate dihydrate [112].

8. Anticaking and Free-Flow Additives

Sodium chloride is hygroscopic above 75% relative humidity (critical humidity). Therefore, salt crystals can absorb enough moisture during storage to form a brine film on their surfaces. Subsequent water evaporation due to changes in temperature or air humidity causes recrystallization of the brine film and the crystals bond together. Also the presence of small quantities of brine included in the crystals can contribute to caking. Especially evaporated salt that exits the salt dryer at higher temperatures tends to undergo increased caking during cooling in silos. To prevent caking, free-flow additives or anticaking agents are added to salt.

Water-insoluble adsorbents such as calcium carbonate, magnesium carbonate, magnesium hydroxide carbonate, tricalcium phosphate, calcium silicate, and silicon dioxide are used as free-flow additives. These additives are finely distributed in concentrations of 0.1–3% in the salt. Free-flow additives are not suitable for every application since they become suspended in solution, for example, in a saline solution for vegetable preservation. In deicing salt free-flow additives would delay the start of the melting process.

Most effective are water-soluble crystal modifiers such as yellow prussiate of soda (YPS, sodium ferrocyanide decahydrate). These are sprayed as aqueous solutions onto the salt. In general 2–20 ppm of YPS is sufficient to prevent caking. For deicing salts which are stored for a longer time under changing weather conditions, YPS and Prussian blue (ferric ferrocyanide) are most commonly added. Concentrations of YPS and Prussian blue in deicing salt vary, typically in the range of 20–100 ppm.

Alternatives to ferrocyanides include *meso*-tartrate derivatives, for example, an iron complex of *meso*-tartaric acid, which is used with an approximate concentration of < 40 ppm on salt [113].

9. Health Aspects

Sodium chloride is an essential nutrient for the normal functioning of the body. It is important for nerve conduction, muscle contraction, correct osmotic balance of extracellular fluid, and absorption of other nutrients.

Sodium, together with potassium, is an essential mineral for regulating body fluid balance. Sodium is the most abundant cation in the extracellular fluid, and sodium salts account for more than 90% of the osmotically active solute in the plasma and interstitial fluid. Sodium is the principal cation of the plasma. Consequently, sodium load is the major determinant of extracellular volume. Chloride is also important in maintaining the fluid balance and is an essential component of the gastric and intestinal secretions.

The total body store of sodium in healthy humans is 100 g or 60 mmol/kg body weight, 95% of which is found in the extracellular and 5% in the intracellular space. Around one-third is stored in bound form in bones as a reserve, which means that around 70% of body sodium, corresponding to approximately 40 mmol/kg body weight, can be quickly exchanged. The sodium concentration in blood plasma is normally between 135 and 145 mmol/L, corresponding to 3105–3335 mg/L [114–117].

Renal excretion of sodium in urine is highly regulated, through the complex interaction of hormonal, nervous and other systems that enable tight homeostatic control. In this way urinary sodium excretion can be adjusted over a very wide range to achieve sodium balance, from virtually zero when sodium needs to be retained in the body, to 1100 mmol/d when intake is high [118].

Sodium Intake. Sodium is added to foods, commonly as sodium chloride, during processing, cooking, and immediately prior to consumption, but also in other forms, for example as sodium glutamate. The amount of sodium c-onsumed, varies widely between populations, within populations, and within individuals with time. In the Intersalt study of 52 centers in 32 countries, 24-h specimens of urine were collected from 10 079 men and women 20–59 years of age [119].

Twenty centers from 12 countries in Western Europe participated, providing data from 3942 men and women. In this group median sodium excretion varied from 135 to 180 mmol/d (equivalent to 3.1–4.1 g Na or 7.9–10.5 g NaCl).

The main source of sodium in the diet is processed foods, and it is estimated that this nondiscretionary consumption accounts for about 70–75% of the total intake in most European countries. Naturally occurring sodium in unprocessed foods contributes about 10–15% of total sodium intake. Discretionary sources of sodium added during cooking and at the table make up about 10–15% of total intake [120].

Sodium Restriction. The major adverse effect of increased sodium intake is elevated blood pressure. Higher blood pressure is an acknowledged risk factor for ischaemic heart disease, stroke, and renal disease. For groups of individuals there is strong evidence of a dose-dependent rise in blood pressure with increased consumption of sodium as sodium chloride [121].

Individuals with hypertension, diabetes, and chronic kidney disease, as well as older-age persons, tend to be more sensitive to the hypertensive effects of sodium intake. Blood-pressure response to sodium can be modulated by a range of factors that include other components of the diet (e.g., potassium), relative body weight and level of physical activity, as well as fixed factors that include age, gender, and genetic factors [122].

Current recommendations of WHO/FAO indicate that in order to prevent chronic diseases, the population average consumption of salt should be less than 5 g/d [123].

Possible risk groups for a purely dietary sodium deficiency are pregnant women and elderly people. During pregnancy and breastfeeding (because of the sodium content in human milk), it is assumed that there is an increased need. It is suggested that polypathia (a multiplicity of illnesses) in the elderly is frequently associated with an inadequate supply of sodium [124].

In healthy individuals there may be cases of higher sodium losses through sweat as a consequence of intense physical activity or periods spent at high temperatures which can lead to a critical nutritional status.

A sodium deficiency normally only occurs in conjunction with congenital (e.g., mucoviscidosis) or acquired diseases as a consequence of elevated losses if no corresponding substitution occurs [125].

Recent discoveries by studying salt and fluid homeostasis in weightlessness indicate that a so far unknown low-affinity, high-capacity osmotically inactive sodium storage mechanism appears to be present in humans that acts through sodium/hydrogen exchange on glycosaminoglycans and might explain the pathophysiology, e.g., of salt-sensitive hypertension [126].

Toxicity. Sodium chloride is not a hazardous material. The FDA regards NaCl as GRAS for its intended use as a food additive. Although rare, acute toxicity may be caused by ingestion of 0.5–1 g sodium chloride per kilogram body weight. Symptoms include vomiting, ulceration of the gastrointestinal tract, muscle weakness, and renal damage, leading to dehydration, metabolic acidosis, and severe peripheral and central neural effects. The acute lethal dose for humans is given as 0.75–3 g/kg body weight.

Oral toxicity for mammals is reported in mg/kg [127]: human, TDLo: 12 357; mouse, LD_{50}: 4000; rat, LD_{50}: 3000; rabbits, LDLo: 8000.

Aquatic toxicity in mg/L: *Pimephales promealas* (fathead minnow), 69-h LC_{50}: 7650 [128]; *Daphnia magna* (water flea), 48-h EC_{50}: 3310 [129]; *Myriophyllum spicatum* (water milfoil), phytotoxicity (EC_{50} for growth): 5962 [130]; and for *Rana breviceps* (frog), NOEC: 400 [131]. Further toxicity and ecotoxicity data are available from the IUCLID dataset for sodium chloride [132].

The ferrocyanides which are used as anticaking agents are not toxic; they are chemically stable metal complexes and completely nontoxic. YPS is approved by the FDA and Joint FAO/WHO Expert Committee on Food Additives (JECFA) for use in food-grade salt.

10. Environmental Aspects

During rock salt production by blasting attention must be paid to the gaseous reaction products (CO, NO_x), 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. Fully grown caverns must plugged well, filled with saturated brine.

In evaporated-salt production sludges from chemical brine purification and the purged mother liquor enter the environment. Depending on the local situation, the sludges and mother liquor are purged into caverns or mines as backfill, into rivers, or into the sea. Some treated sludge can be used for agricultural applications and dam construction.

Solar salt works need a series of connected ponds through which seawater flows, evaporates, and deposits sodium chloride. Compared with the other production methods, the production of solar salts requires considerably more land. Aigues Mortes with a total capacity of 1.2 t of sea salt uses solar ponds with an area of 10 800 ha [133]. The waste product (bittern) from solar salt works is returned to the sea in diluted form, used to produce fertilizers and other products, or they retained permanently on the property. The volume of the bittern is about 2–3% of the volume of the intake seawater. Calcium sulfate, which forms deposits in the last-stage condensers, must be periodically scraped off and is retained on the property. 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 [134].

For rock salt energy savings compared with evaporated salt can be up to 70% [135].

A German study showed that sodium chloride (rock salt) consumes less energy for production and distribution than other spreading materials for winter road service (Fig. 17).

Impact of Salt Use. In highway deicing, salt has been associated with corrosion of motor vehicles, bridge decks, unprotected steel structures, and reinforcement bar and wire, used in road construction. Surface runoff, vehicle spraying, and windblown actions also affect roadside vegetation, soil, and local surface and ground water supplies. Although evidence of environmental impact of salt has been found during peak usage, the spring rains and thaws usually dilute the concentrations of sodium in the area where

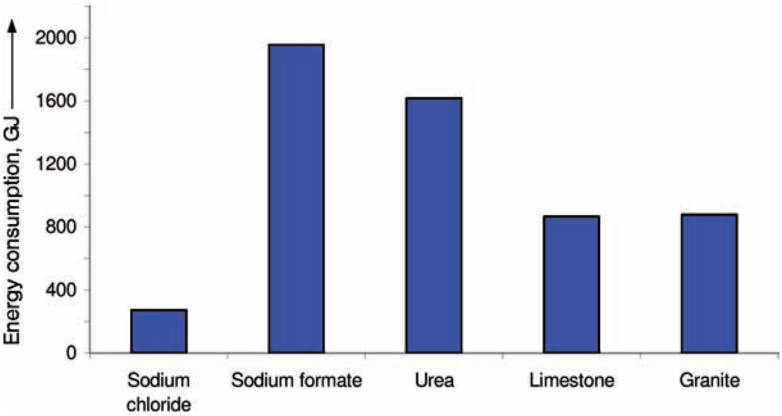

Figure 17. Energy consumption for production and distribution of spreading materials on 1000 km (4 km^2) of road [136]

salt was applied. Fortunately, through sensible salting, the environmental downside can be mitigated while preserving the social and economic benefits of proper winter road service. Use of road salt is cost-effective and environmentally acceptable at current levels [137–139].

The electrolysis of salt and use of chlorine bear risks for human health and the environment. Matters of concern include the use of mercury, asbestos, chemicals having an ozone-depletion potential, and chlorine-containing materials which are persistent, toxic, and liable to bioaccumulate. Regarding the principles of Responsible Care and of Sustainable Development the chemical industry is managing this challenge [140]. One of the consequences is the phasing out of mercury cell technology.

Water softeners must be regenerated periodically with salt and the resulting discharge stream returns the minerals calcium, magnesium, sodium and chloride to the environment. These require proper management to avoid impairing drinking water quality, potential for water reuse, and the efficient functioning of home on-site wastewater recycling (septic) systems [141].

11. Economic Aspects

The world reserves of salt are very large. Economic and subeconomic deposits of salt are substantial in principal salt producing countries. The oceans contain an estimated amount of 5×10^{16} t of mineral salts [142], which is a practically inexhaustible supply of salt. In 2008, world salt production was estimated at 245×10^6 t. Up to 2005, the USA was the leading producer of salt. In 2006, China overtook the USA in salt production with an estimated annual production of 12×10^6 t. In 2008, China accounted for 23% of global production, and the USA for 18 %.

Table 16. Production of sodium chloride in Europe (in 10^3 t), [143, 144]

Country	2000	2002	2004	2006	2008e
Albania	20	23	25	50	50
Austria	641	643	747	750	850
Belarus	437	1 369	1 883	1 900	1 900
Bosnia	325	400	260	260	260
Bulgaria	1 700	1 800	1 900	1 900	1 900
Croatia	34	30	33	40	40
Denmark	587	590	600	600	600
France	6 823	7 894	7 612	8 448	7 800
Georgia	30	30	30	30	30
Germany	15 054	15 633	18 696	17 470	16 000
Greece	245	126	188	200	200
Iceland	4	5	5	5	5
Italy	3 933	3 943	3 476	3 500	3 500
Netherlands	5 564	5 773	5 896	5 900	5 900
Poland	3 493	3 558	4 150	4 000	4 000
Portugal	659	645	737	750	750
Romania	2 308	2 258	2 398	2 400	2 400
Russia	3 170	2 800	2 800	2 800	2 800
Serbia	42	17	33	40	40
Slovakia	122	97	122	110	100
Slovenia	99	128	125	120	125
Spain	3 869	3 893	3 944	3 850	3 850
Switzerland	452	400	486	575	420
Turkey	2 116	2 197	2 158	1 750	1 750
Ukraine	2 287	2 300	4 393	4 800	4 800
United Kingdom	5 800	5 700	5 800	5 800	5 800
Europe total	**59 814**	**62 252**	**68 497**	**68 048**	**65 870**

Table 17. World production of sodium chloride (in 10^3 t) [143]

Region	2000	2002	2004	2006
Asia	58 370	61 459	60 130	77 963
Europe	59 814	62 252	68 497	68 048
North America	66 614	60 843	68 696	68 838
South America	13 654	11 943	14 178	16 367
Oceania	8 977	10 092	11 182	12 490
Africa	4 024	4 766	5 487	5 455
Middle East	3 122	2 994	3 118	3 131
Central America	2 044	2 173	2 380	2 396
World total	**216 619**	**216 522**	**233 668**	**254 688**

Table 18. Global consumption of sodium chloride in major application areas in 2008 and forecast for 2013 (in 10^6 t) [144]

	North America	Central and South America	Europe	CIS	Africa and Middle East	China	Other Asia and Oceania	Total	Total 2013
Chemical production									
Chlorine and caustic soda	24.2	3.1	18.8	2.6	3.8	25.3	20.9	98.6	111.5
Sodium carbonate	0.5	0.3	9.7	3.6	2.7	21.6	3.2	41.6	48.6
Sodium chlorate	1.0	0.1	0.4			0.1	0.1	1.7	2.0
Other			1.2			0.2	1.2	2.6	2.9
Total	25.7	3.4	30.1	6.2	6.5	47.2	25.4	144.6	164.9
De-icing	22.9	0	8.0	0.1	0	0.5	1.0	32.5	34.1
Food processing									
Slaughterhouses			1.5	0.3	0.7			2.4	2.7
Dairy industry			0.7	0.1	0.4			1.2	1.4
Household salt			0.8	0.1	0.6			1.5	1.6
Bakeries			0.4	0.1	0.3			0.8	0.9
Miscellaneous			0.3	0.1	0.2			0.5	0.6
Total food	2.3	2.5	3.7	1.1	2.1	7.6	7.0	26.3	31.7
Water softening	3.5	0.8	1.8	0.2	0.5	0.3	2.0	9.0	10.0
Medicine/chemical/technical use	2.5	1.9	1.3	0.1	0.2	0.3	1.5	7.8	8.8
Mineral fodder blends	1.9	1.9	1.5	0.1	0.8	1.0	2.0	9.2	9.5
Other technical industries	3.6	3.2	2.0	0.1	1.7	0.5	4.1	15.1	17.8
Total	**62.5**	**13.7**	**48.4**	**7.8**	**11.7**	**57.4**	**43.0**	**244.5**	**276.8**

Other major producing countries include Germany, India, Canada, Australia, Mexico, and Brazil.

The capacities of the main salt suppliers worldwide for crystallized salt and salt in brine are as follows (in 10^6 t, excluding captive use):

K + S (Germany/USA)	29.8
China National Salt Industry (China)	18.7
Compass Minerals (USA)	14.4
Cargill (USA)	14.0
Dampier Salt (Australia)	9.0
Artyomsol (Ukraine)	7.5
Exportadora del Sal (Mexico)	7.0
Südsalz (Germany)	5.3
Salins (France)	4.1
Mitsui (Australia)	3.8
Akzo Nobel (Netherlands)	3.6

Table 16 shows the development of salt production in Europe, and Table 17 lists world production figures. Breakdown of worldwide consumption by end-use is summarized in Table 18.

References

1 M. J. Schleiden: *Das Salz, seine Geschichte, seine Symbolik und seine Bedeutung im Menschenleben*, Verlag Wilhelm Engelmann, Leipzig 1875.

2 R. P. Multhauf: *Neptune's Gift*, The Johns Hopkins University Press, Baltimore 1978.

3 H.-H. Emons, H.-H. Walter: *Mit dem Salz durch die Jahrtausende*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1984.

4 J.-C. Hocquet: *Le sel et le pouvoir - de l'an mil à la Révolution*, Editions Albin Michel S.A., Paris 1985.

5 J.-F. Bergier: *Die Geschichte vom Salz*, Campus Verlag, Frankfurt, New York 1989.

6 B. Moinier: *Sel et Société — Une affaire de métier*, Editions Nathan, Maxéville 1997.

7 M. Kurlansky: *Salt — A World History*, Walker & Company, New York 2002.

8 D. W. Kaufmann: *Sodium Chloride*, Reinhold Publ. Co., New York 1960, pp. 587 ff.

9 *J. Phys. Chem. Ref. Data* **11** (1982) 15 – 81; **13** (1984) 1 – 102. *Gmelin's Handbook of Inorganic Chemistry*, 8th ed., System No. 21, Springer, Heidelberg, pp. 309 ff. *Landolt-Börnstein*, 6th ed., vol. 2, part 8, Springer, Heidelberg 1962, p. 46 ff.

10 S. K. Coburn, *Corrosion* **10** (1954) no. 5, 1.

11 W. W. Bradley, *Corrosion (Houston)* **11** (1955) 383.

12 DECHEMA-Werkstofftabelle, Blatt Nr. DWT 1043 ff, 3. Bearbeitung, DECHEMA, Frankfurt/Main 1962.

13 S. J. Lefond: *Handbook of World Salt Resources*, Plenum Press, New York 1969.

14 H. A. Rabitz, W. Arnold: "Rock Salt Beneficiation with Heavy Media Cyclones", *World Mining* (1973) no. 6.

15 R. J. Brison, O. F. Tangel: "Development of a New Dry Method for Mineral Separation", *Mining Eng.* **12** (1959) 1229.

16 P. Ambatiello, *Felsbau* **8** (1990) 180 – 184.

17 G. Feder, M. Hoscher, *Felsbau* **5** (1987) 114 – 149.

18 P. W. Harben, M. Kuzvart: *Global Geology*, Industrial Mineral Information Ltd., Worcester Park, UK, 1996, p. 343.

19 O. Schauberger: *Archiv für Lagerstättenforschung*, Band 7, Geologische Bundesanstalt Wien, 1986.

20 O. Fukuta, N. Fujii: "Japanese Iodine — Production, Geology, and Geochemistry", *Ind. Miner.* **175** (1982) 101 – 115.

21 K. Schmidt, *Tech. Mitt.* **68** (1975) 363 – 368.

22 H. Gomm, J. Hieblinger, G. Kühn, *Erdöl Erdgas Z.* **93** (1977) 83 – 90.

23 H. K. Röhr, *Erdöl Kohle Erdgas Petrochem.* **22** (1969) 670 – 679, 734 – 741.

24 S. Meister, G. Kuhr, *Erdöl Erdgas Z.* **88** (1972) 248 – 257.

25 H. Borchert, W. Dreyer: Gutachten über die Standfestigkeit und Konvergenz von Kavernen im Salzstock, Mineralog.-petrograph. Institut der TU Clausthal, 10 Dec. 1967.

26 W. Dreyer, *Kali Steinsalz* **5** (1971) 473 – 478.

27 S. Serata in J. L. Rau (ed.): "Continuum Theory and Model of Rock Salt Structures," 2nd Symposium on Salt, Northern Ohio Geological Society, Cleveland 1965.

28 R. W. Durie, F. W. Jessen, *Soc. Pet. Eng. J.* 1964, 183 – 190.

29 W. Dreyer: *Gebirgsmechanik im Salz*, Enke Verlag, Stuttgart 1974.

30 K.-H. Lux: *Gebirgsmechanischer Entwurf und Felderfahrungen im Salzkavernenbau*, Enke Verlag, Stuttgart 1984.

31 F. Schober, A. Sroka: "Die Berechnung von Bodenbewegungen über Kavernen unter Berücksichtigung des zeitlichen Konvergenz- und Gebirgsverhaltens, " *Kali Steinsalz* **8** (1983) no. 10.

32 A. Sroka, F. Schober: "Die Berechnung der maximalen Bodenbewegungen über kavernenartigen Hohlräumen unter Berücksichtigung der Hohlraumgeometrie, " *Kali Steinsalz* **8** (1982) no. 8.

33 A. Sroka: "Abschätzung einiger zeitlicher Prozesse im Gebirge, " *Schriftenreihe Lagerstättenerfassung und -darstellung, Bodenbewegungen und Bergschäden Ingenieurvermessung*, Leoben, Austria, 15 – 16 Nov. 1984.

34 A. Sroka, A. Hartmann: "Die Überwachung von Speicherkavernen mittels geodätischer und physikalischer Beobachtungen, " *Proceedings 5th International Congress, International Society of Mine Surveying*, Harrogate, UK, 9 – 13 Sept. 1985.

35 H. von Schonfeldt, L. Remoline in A. H. Coogan (ed.): "Mechanism of Solution and Cavity Control in a Two-Well-System with Emphasis on Jetting," *4th Symp. on Salt*, vol. 2, Northern Ohio Geol. Soc. Inc., Cleveland 1974, pp. 189 – 202.

36 K. Henderson: "Methods of Joining Two or More Wells for Brine Production," in [40], pp. 211 – 218.

37 Hagan Chemicals & Controls Inc., US 2906599 (A), 1959 (R. T. Charles).

38 Jamestown Chemical Company Inc., Material Safety Data Sheet of Sulfate Solubility Inhibitor SSI-200 West Haven, CT, USA.

39 F. Crotogino: "Compressed Air Storage", *Internationale Konferenz "Energieautonomie durch Speicherung erneuerbarer Energien*", RWTH Aachen, Germany, 30 – 31 October 2006.

40 Argonne National Laboratory, *Oil and Gas Technology Feasibility Studies*, http://www.ead.anl.gov/project/dsp_topicdetail.cfm?topicid=18 (accessed 28 May 2009) .

41 H. Rischmüller, *Erdöl Erdgas Z.* **88** (1972) 240 – 248.

42 H.-G. Haddenhorst *et al.*, *Erdöl Erdgas Z.* **90** (1974) 154 – 161, 197 – 204.

43 H. Bresson, *Rev. fr. énerg.* **26** (1969) 527 – 543.

44 M. Klafki, H.-J. Kretzschmar, W. Menzel, W. Schreiner: "Aussolung von Gasspeicher-Kavernen in mächtigen Salzlagerstätten," *Neue Bergbautech.* **20** (1991) no. 3.

45 Solution Mining Research Institute, Clarks Summit, PA 18411, USA (www.solutionmining.org).

46 K. Thomanek, *BHM Berg Hüttenmänn. Monatsh.* **127** (1982) 381 – 389.

47 M. Hoscher, *BHM Berg Hüttenmänn. Monatsh.* **126** (1981) 234 – 238.

48 O. Schauberger, *Arch. f. Lagerstforsch. Geol. B.-A.* **7** (1986) 217 – 254.

49 M. Hoscher, *BHM Berg Hüttenmänn. Monatsh.* **134** (1989) 230 – 234.

50 Morton Salt, Chicago, USA, personal communication, 2004.

51 S. J. Lefond: *Handbook of World Salt Resources*, Plenum Press, New York 1969.

52 The Canadian Salt Company Limited, Quebec, Canada, personal communication, 2004.

53 A. Hiltscher, C. Heinrich, *Kali Steinsalz* **11** (1994) no. 7, 211 – 217.

54 J. D'Ans, D. Bredtschneider, H. Eick, H.-E. Freund, *Kali Steinsalz* **1** (1955) no. 9, 17 – 38.

55 H. Schwaiger, *BHM Berg Hüttenmänn. Monatsh.* **143** (1998) 128 – 132.

56 Solvay Österreich GmbH, Ebensee, Austria, personal communication, 2002.

57 Wacker-Chemie GmbH, Burghausen, Germany, personal communication, 2004.

58 G. Guibert, M. Viard: "Physical and Chemical Phenomena Accompanying Thermal Evaporation of Raw Brine", *5th International Symposium on Salt*, Hamburg, Germany, 1978, pp. 295 – 300.

59 P. Jongema: "Production of Low Bromine-Containing Evaporated Salt", *7th Symposium on Salt*, vol. II, Kyoto, Japan, 1993, pp. 159 – 163.

60 Akzo N.V., EP 0492727, 1992 (P. Jongema).

61 Chemetics International Company Ltd., US 5587083, 1996 (Z. Twardowski).

62 W.M. Samhaber, K. Krenn: "Potential of Membrane Technology for Improving the Brine Purification Process", *8th World Salt Symposium*, vol. 2, The Hague, The Netherlands, 2000, pp. 1209 – 1210.

63 T. Altmann, A. Attenborough, C. Kenny, GB 2395946, 200.

64 Esco - European Salt Company, EP 1826179 A1, 2007 (T. Kopp, H.-J. Barge).

65 H. Flachberger, K. Krenn, *BHM Berg Hüttenmänn. Monatsh.* **144** (1999) 234 – 240.

66 H. Flachberger, K. Krenn, *BHM Berg Hüttenmänn. Monatsh.* **149** (2004) 138 – 143.

67 J. A. Lee, B. Greenwood, *Biol. Conserv.* **10** (1976) 131 – 149.

68 Vsesojuznyi nautschno-issledovatelskij I proektnyj institute galurgii, Leningrad, DE 2820445, 1979 (I.D. Sokolov, V. A. Ostania, J. S. Safrygin, T.I. Rutkovskaja, N.V. Antonova, R.E. Naginskaja).

69 R. Katzlinger, H. Flachberger: "Saline Ebensee – Statusbericht und Ausblick", *BHM Berg Hüttenmänn. Monatsh.* **152** (2007) no. 4, 92 – 96.

70 S. Feldmann: "Sodium Chloride" in *Kirk-Othmer*, 5th ed., vol. 22, Wiley, New York 2006, pp. 797 – 822.

71 K. Krenn: "Vorstellung einer modernen Eindampfanlage", *BHM Berg Hüttenmänn. Monatsh.* **143** (1998) no. 4, 124 – 127.

72 R. Winkler: *Seit 150 Jahren Wärmepumpen in der Salzproduktion*, Kupper-Bücher, Meilen, Switzerland, 2006.

73 *Mechanische Brüdenkompression, Informationsschrift der VDI-Gesellschaft Energietechnik, Düsseldorf 1988.*

74 HPD Selected to Supply the Second Salt Production and Caustic Facility for Shintech Inc. on U.S. Gulf Coast, www.hpdsystems.com (accessed 28 May 2009) .

75 R. Winkler, *Escher-Wyss-Mitteilungen* **34** (1961) nos. 2–3, 10 – 12.

76 R. O. Walter, P. Kondorosy, *Escher-Wyss-Mitteilungen* **48** (1975) no. 2, 3 – 9.

77 F. Götzfried, E. Kondorosy: "Recrystallization Process for the Upgrading of Rock- and Solar Salts", *9th International Symposium on Salt*, Beijing, China, 2009.

78 International Salt Company, Watkins Glen, N.Y., US2555340, 1951 (C.M. Hopper, R.B. Richards).

79 Société Industrielle & Commerciale de la Compagnie des Salins du Midi, FR 977.397, 1951 (H.-L.-M. Guinaudy).

80 K. Krenn, *BHM Berg Hüttenmänn. Monatsh.* **143** (1998) 124 – 127.

81 A. Leckzik, F. Götzfried, L. Ninane: "Natriumchlorid und Alkalicarbonate", in *Winnacker-Küchler, Chemische Technik*, vol. 3, Wiley-VCH, Weinheim 2005, pp. 545 – 597.

82 H. Bauschlicher, W. Wöhlk: "Production of Vacuum Salt Based on Seawater as Raw Material", in B. Ch Schreiber (ed.): *6th International Symposium on Salt*, vol. 2, Toronto, Canada, May 24–28, 1983, pp. 495 – 497.

83 M. Ohno: "Technical Progress of the Salt Production in Japan", *7th International Symposium on Salt*, vol. I, Elsevier, Amsterdam 1993, pp. 13 – 19.

84 J. Sikora, K. Szyndler, R. Ludlum: "Desalination Plant at Debiensko, Poland: Mine Drainage Treatment for Zero Liquid Discharge", *International Water Conference*, Pittsburgh, Pennsylvania, 1993.

85 E. F. Armstrong, L. M. Miall: *Raw Materials from the Sea*, Chemical Publishing Co., Brooklyn 1946.

86 A. Colas: *Le Sel*, Presses Universitaires de France, Paris 1985.

87 Laboratoire C.S.M.E., Aigues-Mortes, France, personal communication.

88 Central Research Institute, Japan Monopoly Corporation, Figures for Salt Production, Tokyo 1954.

89 N.A. Korovessis, Th.D. Lekkas: "Solar Saltworks Production Process Evolution – Wetland Function", in *Post Conference Symposium Proceedings: Saltworks: Preserving Saline Coastal Ecosystems*, Pythagorion, Samos 1999, pp. 11 – 30.

90 J.S. Davis: "Biological and Physical Management Information for Commercial Solar Saltworks", *1st International Conference on the Ecological Importance of Solar Saltworks*, Santorini, Greece, October 2006, pp. 5 – 14.

91 C. Zeno: "The Ecological Importance of the Margherita di Savoia Saltworks", *1st International Conference on the Ecological Importance of Solar Saltworks*, Santorini, Greece, October 2006, pp. 15 – 24.

92 V. M. Sedivy: "Upgrading and Refining of Salt for Chemical and Human Consumption", *International Conference on Salt*, Ahmedabad, India, January 2006, pp. 78 – 90.

93 Exportadora de Sal SACV, US 5447543, 1995 (A. Sadan).

94 J.I.G. Bremer: "Solar Salt Production at Exportadora de Sal", *6th International Symposium on Salt*, vol. 2, Toronto, Canada, May 24–28, 1983, pp. 401 – 406.

95 Dampier Salt Limited: Typical Chemical Salt Analysis, www.dampiersalt.com.au/tnpn002785/prod/dsl/dslhome.nsf (accessed 28 May 2009) .

96 H. Kakihana, H.R. Hardy, Jr., T. Hoshi, K. Toyokura (eds.): *7th International Symposium on Salt*, Kyoto, Japan, April 6–9 1992, Elsevier, Amsterdam 1993.

97 R. M. Gaertman (ed.): *8th World Salt Symposium*, The Hague, The Netherlands, May 7–11 2000.

98 V.M. Sedivy: "Salt from Hot Air", *Ind. Miner.* 2000, no. 9, 40 – 45.

99 H. Aral, B.D. Hill, G.J. Sparrow: "Value Adding to Salts Recovered from Saline Waters" in *Disposed Basins in the Murray-Darling Basin – Appendix 2: Production of Salts from Brines and Bitterns*, Murray-Darling Basin Commission, Canberra 2004 (ISBN 1921038268).

100 D.S. Kostick: *Salt*, U.S. Geological Survey, Washington, D.C., 2002.

101 M. Andersson, B. de Benoist, I. Darnton-Hill, F. Delange (eds.): *Iodine Deficiency in Europe: A Continuing Public Health Problem*, World Health Organization (WHO), Geneva 2007.

102 World Health Organization (WHO), The United Nations Children Fund (UNICEF), International Council for the Control of Iodine Deficiency Disorders (ICCIDD): Assessment of Iodine Deficiency Disorders and Monitoring their Elimination: a Guide for Programme Managers, 3rd ed. (updated 1st September 2008), WHO, Geneva 2007.

103 World Health Organization (WHO): Salt as a Vehicle for Fortification, Report of a WHO Expert Consultation, Luxembourg, 21-22 March 2007, WHO, Geneva 2008.

104 Tamil Nadu Salt Corporation Limited, India, www.tnsalt.com/schemes.htm (accessed June 2009) .

105 Arbeitskreis Folsäure & Gesundheit, Frankfurt, Germany, www.ak-folsaeure.de (accessed June 2009) .

106 The Micronutrient Intitiative: "Double Fortified Salt: Product Description", www.micronutrient.org/english/View.asp?x=584, (accessed 28 May 2009) .

107 F. Götzfried: "Spezialsalze für die Lebensmittelherstellung", *Le Cahiers du Sel* **16** (2003) 45 – 54.

108 F. Götzfried: "Production of Fluoridated Salt", *Schweiz Monatssch. Zahnmed.* **116** (2006) no. 4, 367 – 370.

109 D. Kilcast, F. Angus: *Reducing Salt in Foods: Practical Strategies*, CRC Press, Boca Raton, FL 2007.

110 S.R. Feldmann: "A Consumer's Guide for Selecting the Right Water Softener Salt", *Water Treatment Dealer* 2003, no. 9–10, 24 – 26.

111 Deutsche Solvay-Werke: *Das Salz der Chemie*, Solingen 1983, pp. 28 – 29.

112 UNICEF: "Improved Formula for Oral Rehydration Salts to Save Childrens' Lives", News Note, March 20, New York, Geneva 2006 www.unicef.org/media/media_31825.html (accessed 28 May 2009) .

113 Akzo Nobel, WO 00/59828, 2000 (H.F. Boon).

114 DGE (ed.): *Ernährungsbericht 1996*, Frankfurt/Main 1996.

115 J. Falbe, M. Regitz (eds.): *Römpp Lexikon, Chemie*, 10th ed., vol. 4, Georg Thieme Verlag, Stuttgart 1996.

116 R.W. Grunewald: "Wasser und Mengenelemente. 4.2 Natrium", in P. Schauder, G. Ollenschläger (eds.): *Ernährungsmedizin: Prävention und Therapie*, 2nd ed., Elsevier, Urban & Fischer Verlag, Munich 2006.

117 G. Löffler, P.E. Petrides (eds.): *Biochemie und Pathobiochemie*, 7th ed., Springer Verlag, Heidelberg 2006, p. 934 ff.

118 J.C. Roos, H.A. Koomans, E.J. Dorhout Mees, M. Delawi: "Renal Sodium Handling in Normal Humans Subjected to Low, Normal and Extremely High Sodium Supplies", *Am J Physiol* **249** (1985) 941 – 947.

119 Intersalt Cooperative Research Group: "Intersalt: An International Study of Electrolyte Excretion and Blood Pressure. Results for 24 Hour Urinary Sodium and Potassium Excretion", *Br. Med. J.* **297** (1988) 319 – 328.

120 C.P. Sanchez-Castillo, S. Warrender, T.P. Whitehead, W.P. James: "An Assessment of the Sources of Dietary Salt in the British Population", *Clin Sci* **72** (1987) 95 – 102.

121 M. Ducher, J.-P. Fauvel, M. Maurin, M. Laville, P. Maire, Ch. Z. Paultre, C. Cerutti: "Sodium Intake and Blood Pressure in Healthy Individuals", *J. Hypertension* **21** (2003) no. 2, 289 – 294.

122 European Food Safety Agency: "Opinion of the Scientific Panel on Dietetic Products, Nutrition and Allergies on a request from the Commission related to the Tolerable Upper Intake Level of Sodium", *EFSA J.* **209** (2005) 1 – 26.

123 WHO/FAO (World Health Organization/Food and Agriculture Organisation): Diet, Nutrition and the Prevention of Chronic Diseases, WHO Technical Report Series 916, Geneva 2003.

124 I. Füsgen: "Disorders of Water and Sodium Metabolism in Older Patients", *Eur. J. Geriatr.* **5** (2003) 162 – 165.

125 A. Domke, R. Großklaus, B. Niemann, H. Przyrembel, K. Richter, E. Schmidt, A. Weißenborn, B. Wörner, R. Ziegenhagen: *Use of Minerals in Foods — Toxicological and Nutritional-Physiological Aspects*, Federal Institute for Risk Assessment, Berlin 2005 (ISSN 1614-3795).

126 R. Gerzer, M. Heer: "Regulation of Body Fluid and Salt Homeostasis — From Observations in Space to New Concepts on Earth", *Curr. Pharm. Biotechnol.* **6** (2005) no. 4, 299 – 304.

127 Registry of Toxic Effects of Chemical Substances, DHHS (NIOSH), Publication No. 97–119, p. 4433.

128 *Fisheries Res. Bd. Can.* **33** (1976) no. 2, 209.

129 U.S. EPA, Ambient Water Quality Criteria for Chloride, 1988.

130 *Arch. Environ. Contam. Toxicol.* **2** (1974) no. 4, 331.

131 *Ind. J. Exp. Biol.* **127** (1979) no. 11, 1244.

132 European Inventory of Existing Commercial chemical Substances (EINECS), http://ecb.jrc.ec.europa.eu/ (accessed 31 May 2009) .

133 B. Moinier: "The Appropriate size of Saltworks to meet Environmental and Production Requirements", *Post*

Conference Symposium Proceedings Saltworks: Preserving Saline Coastal Ecosystems, Pythagorion, Samos, 1 September 1999, pp. 49 – 65.

134 A. Marques, R. Teixeira, A. Lorena, V. del Pino, Y. del Valle-Inclan, J. Navalho, T. Domingos: "Sustainability Assessment of Traditional Solar Salt", *2nd International Conference on the Ecological Importance of Solar Saltworks (CEISSA 2009)*, Merida, Yucatan, Mexico, 26–29 March 2009, pp. 88 – 97.

135 F. Götzfried: *Industrial Salt for Chlor-Alkali Electrolysis*, Südwestdeutsche Salzwerke AG, Heilbronn 2000.

136 S. Gartiser, C.-O. Gensch, R. Reuther: Machbarkeitsstudie zur Formulierung von Anforderungen für ein neues Umweltzeichen für Enteisungsmittel für Straßen und Wege, in Anlehnung an DIN EN ISO 14024, Umweltbundesamt-Forschungsbericht 000404, UBA-Text 09/03, Berlin 2003.

137 Salt Institute: *Highway Salt and our Environment*, Alexandria, Virginia 2004.

138 European Cooperation in the field of Scientific and Technical Research (COST): *Project 344 – Improvements to Snow and Ice Control on European Roads and Bridges*, Documentation for the Final Seminar, Ljubljana, Slovenia, December 2002.

139 European Cooperation in the field of Scientific and Technical Research (COST): *Project 353 – Winter Service Strategies for Increased European Road Safety*, Final Report 2008 and Proceedings of the Final Conference, Dresden, Germany, May 2008.

140 P. Schmittinger (ed.): *Chlorine*, Wiley-VCH, Weinheim 2000.

141 Salt Institute: Water Softener Discharges, http://www.saltinstitute.org/Issues-in-focus/Water-softener-discharges (accessed 31 May 2009) .

142 K. H. Wedepohl, *Kali Steinsalz* **11** (1995) no. 10, 311 – 315.

143 *The Economics of Salt*, 12th ed., Roskill Information Services Ltd., London 2007.

144 S. Schlag, J. Glauser; K. Yokose: *Sodium Chloride Report*, Chemical Economics Handbook, SRI, Menlo Park 2008.

Further Reading

G. Kreysa, M. Schütze (eds.): *Corrosion Handbook*, 2nd ed., Wiley-VCH, Weinheim 2007.