

Economy of Salt in Chloralkali Manufacture

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Impurities in salt are costly. Impurities dissolve in electrolytic brine and need to be removed, employing expensive processes and chemicals. The cost of brine purification is high. Therefore, pure salt is more valuable. Chloralkali producers are willing to pay higher price for purer salt.

This paper deals with the technical aspects of the use of salt in the chloralkali industry, explains under what conditions the consumption of brine purification chemicals can safely be reduced and offers the economic rules that can be used for estimating the additional value of pure salt. The main principles of high quality solar salt production and the related economy are explained.

Advanced technologies, such as SOLARSAL saltworks design and operation, BIOSAL biological solar saltworks management and HYDROSAL salt purification process with hydroextraction of impurities facilitate profitable production of high quality solar salt for chloralkali industry, for human consumption and for exports.

Salt is a most important raw material for chemical industry

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

Salt type	World production
Solar salt	90,000,000 t/y
Rock salt	60,000,000 t/y
Brines and vacuum salt	80,000,000 t/y

The chemical industry is the largest salt consumer of salt using about 60% of the total production. This industry converts the salt mainly into chlorine, caustic soda and soda ash. Without these basic inorganic chemicals, the chemical industry, glass production, etc. would be unthinkable. The second largest user of salt is mankind itself. Humans need about 20% of the total salt produced to support their physiological functions and eating habits. About 20% of salt is needed for road de-icing, water treatment, production of cooling brines and many other, smaller applications.

Salt user	Salt consumption
Caustic / chlorine	90,000,000 t/y
Soda ash and other	50,000,000 t/y
Human consumption	50,000,000 t/y
Road de-icing	20,000,000 t/y
Other	20,000,000 t/y

Impurities in natural salts

Sodium chloride is the main component of natural common salt. Natural salt is never pure. It contains impurities, mainly originating from sea water. Solar sea salts are rather similar. Rock salts vary greatly in purity, colour, insolubles, etc. Lake salts contain components leached from the ground in variable quantities. Salt lake

chemistry is a science of its own. Calcium sulphate is always present in sodium chloride. In rock salt, it is present as anhydrite, hemihydrate or polyhalite. In sea salt and lake salt it is found as gypsum. Natural brines are usually saturated with calcium sulphate. Magnesium is always present in the sea salt as magnesium chloride and magnesium sulphate. In lake salts, also sodium sulphate, calcium chloride, potassium chloride, sodium bromide and iodide may be found in exceptionally high concentrations. Insolubles are present in natural salts of all origins.

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

Elements such as aluminium, barium, fluorine, iron, nitrogen, phosphorous, silica, strontium, etc., heavy metals such as cadmium, chromium, copper, manganese, molybdenum, nickel, vanadium, etc., and poisonous elements such as arsenic, mercury, lead, etc., are of interest in the chemical industry. Their content in the salt should be known when salt is used as feedstock in the chloralkali industry, particularly in the electrolysis using ion exchange membranes.

How does the chemical industry deal with impurities in salt?

In the chemical industry, salt is dissolved together with the impurities in water or brine. Prior to feeding to the process, the brine is purified. Failure to purify the brine may have serious, even lethal consequences.

In electrolytic cells, excessive magnesium causes hydrogen evolution on the anode. Hydrogen and chlorine form an explosive mixture. Explosion may damage the equipment and release chlorine to the environment. Chlorine gas is highly poisonous. The elimination of magnesium is of prime concern.

Erratic impurity content in salt may cause hardness breakthrough to the electrolytic cells. Impurities will damage the ion exchange membranes. Membranes cost a fortune, several hundred US dollars per square meter. The purer the salt, the more remote is the danger of membrane damage.

In soda ash production, excessive sulphate reduces the value of the product. Calcium accumulating in the process causes encrustations. Periodical scale removal is costly and leads to loss of production.

Therefore, in the chemical industry, impurities from salt dissolved in brine are precipitated with chemicals and removed by various processes. The cost associated with brine purification is the cost of chemical reagents and the investment and operating cost of the brine treatment plants. The cost of contaminated sludge disposal, purge decontamination and the loss of salt in purge also represent substantial costs.

Calcium, magnesium and sulphate precipitation

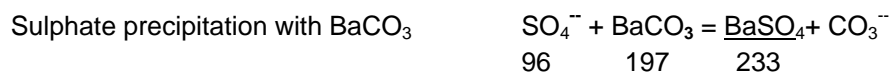
The precipitation of calcium, magnesium and sulphate from brine is described by the following chemical reactions:



This chemical reaction shows that each 40 kg of calcium impurity entering the chloralkali process with salt requires 108 kg of soda ash for precipitation and formation of 100 kg of calcium carbonate.



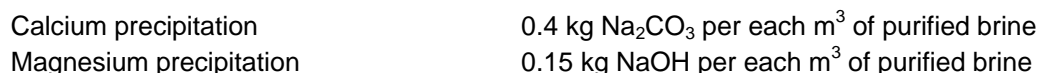
This chemical reaction shows that each 24 kg of magnesium impurity entering the chloralkali process with salt requires 82 kg of sodium hydroxide for precipitation and formation of 58 kg of magnesium hydroxide.



These chemical reactions show that each 96 kg of sulphate impurity entering the chloralkali process with salt requires either 197 kg of barium carbonate or 208 kg of barium chloride or 111 kg of calcium chloride for precipitation and formation of either 233 kg of barium sulphate or 136 kg of calcium sulphate.

Overdosing of brine purification chemicals

The above chemical reactions require that more than the stoichiometric quantity of the reagent is added to the brine to fully precipitate the impurity. This additional quantity is called overdosage. The overdosage requirements are as follows:



Sulphate precipitation with barium does not require overdosing of barium carbonate or chloride. On the contrary, a minimum sulphate concentration of approx. 5 g/l SO₄ (5 kg sulphate per each m³ of purified brine) is required to be maintained in the brine for barium to fully precipitate. This is particularly important in membrane cell electrolysis of brines made by dissolution of salt containing iodine.

Sulphate precipitation with calcium chloride requires overdosing of calcium chloride and extended time for the formation of gypsum crystals. The excess calcium from calcium chloride overdosing has to be removed from desulphated brine in a second process step by precipitation with soda ash.

Brine containing overdoses of soda ash and sodium hydroxide is alkaline. Brine in the electrolytic cells is acidic. The alkalinity of the treated brine is removed with hydrochloric acid. Thus the excess soda ash is decomposed forming carbon dioxide and sodium hydroxide is forming sodium chloride.

Maintenance of correct overdosage is an essential requirement in brine purification. If the overdosage is too low, the impurities will pass through the brine treatment, enter the cells and damage the membranes. If the overdosage is too high, the excess reagent is wasted, hydrochloric acid consumption for dealkalisation is too high, there is too much carbon dioxide in the chlorine gas and the overall cost is excessive.

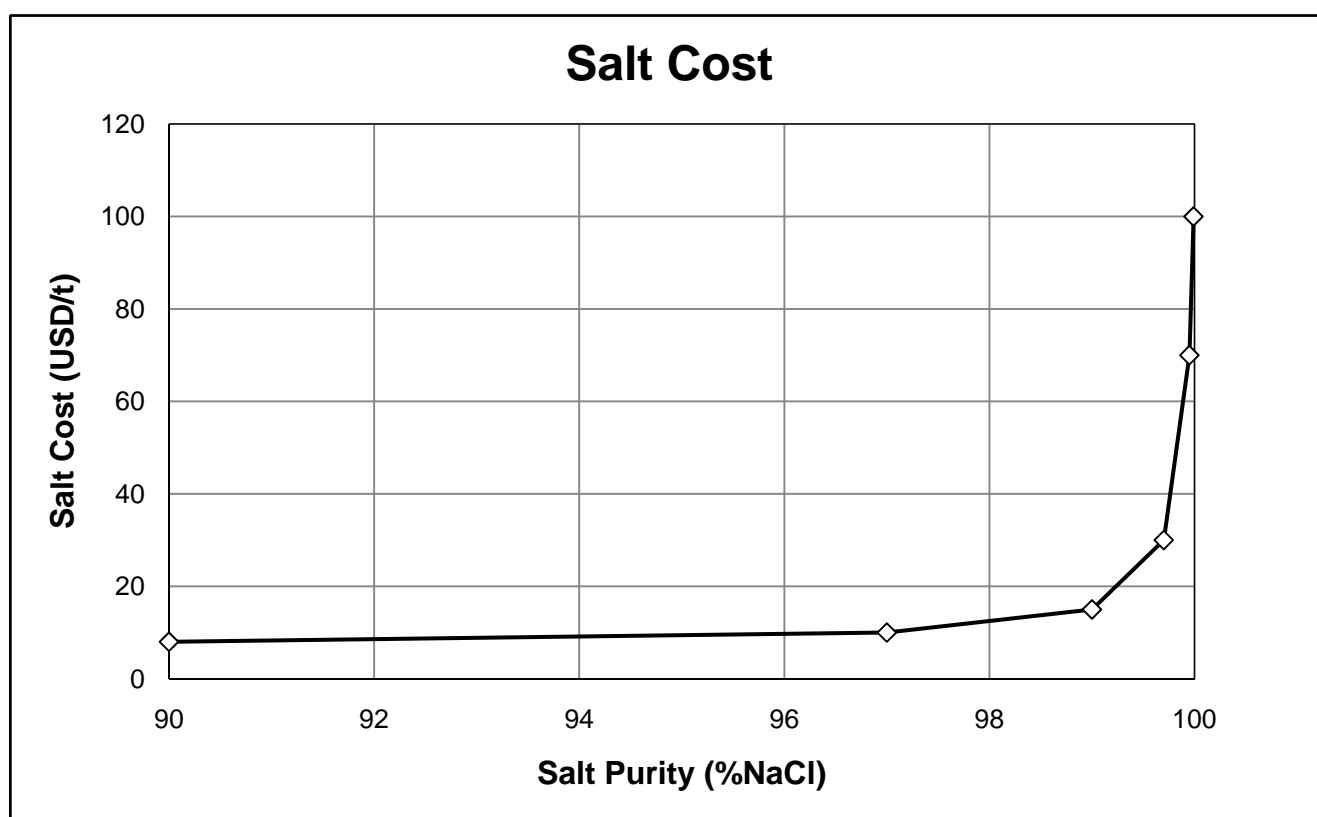
Why is constant salt quality important?

Overdosing of chemical reagents in brine purification can only be maintained at the correct level if the salt composition is constant. Brine residence time in the treatment plant is short. Within only few hours the brine passes from the saturator to the cells. If the salt composition changes suddenly, either the impurities or the excess overdosage can reach the cells before corrective action takes place.

Danger of suddenly changing salt composition is particularly high when chloralkali manufacturers are receiving salt of different quality. Although it might be theoretically possible to store each salt in a separate stockpile and to feed the chloralkali plant with each quality for a period of time, this is normally not practicable. In fact, salt is frequently stored on the same stockpile and the overdosage is maintained at an excessive level for safety reasons. It is less expensive to maintain higher dosage than to run the risk of impurity breakthrough, explosion or membrane damage. Necessity to maintain higher overdosage, however, limits the value of better quality salt. Lower consumption of reagents for precipitation does not compensate for higher consumption of reagents for overdosing. Demand for higher price for better quality salt thus cannot be satisfied.

Cost of salt

Salt prices vary depending on availability, method of production, transport cost and quality. The higher the purity, the higher is the cost of salt.



Cost of sodium chloride and brine treatment

The overall cost of salt and brine treatment in chloralkali manufacture is a sum of the following cost elements:

1. Cost of sodium chloride. This is equal to the price of salt divided by purity expressed as % NaCl content and divided by 100
2. Salt handling losses
3. Cost of stoichiometric calcium precipitation according to the chemical reaction of calcium with soda ash
4. Cost of soda ash overdosing
5. Cost of stoichiometric magnesium precipitation according to the chemical reaction of magnesium with sodium hydroxide
6. Cost of sodium hydroxide overdosing

7. Cost of stoichiometric sulphate precipitation according to the chemical reaction of sulphate with barium salt or cost of salt loss with brine purge
8. Cost of brine acidification
9. Cost of effluent decontamination
10. Cost of effluent disposal

In this list, cost of processing steps that are independent of the salt quality has been omitted.

Typical Salt Analyses

In the examples of calculation of the cost of salt and brine purification, the following typical salt qualities have been assumed:

	Ca	Mg	SO ₄	Insolubles
	%	%	%	%
Rock salt	1	0.05	2.5	2
Crude sea salt	0.2	0.1	0.6	1
Upgraded sea salt	0.04	0.02	0.12	0.03
Vacuum salt	0.001	0.0002	0.03	0.01

Typical brine purification cost

Calculated from typical salt composition and average prices of brine purification chemicals as given above, the cost of brine purification works out as follows:

	Brine Purification Process		
	BaCO ₃ (USD / t salt)	BaCl ₂ (USD / t salt)	CaCl ₂ (USD / t salt)
Rock salt	30	70	50
Crude sea salt	10	20	15
Upgraded sea salt	4	6	6
Vacuum salt	3	4	4

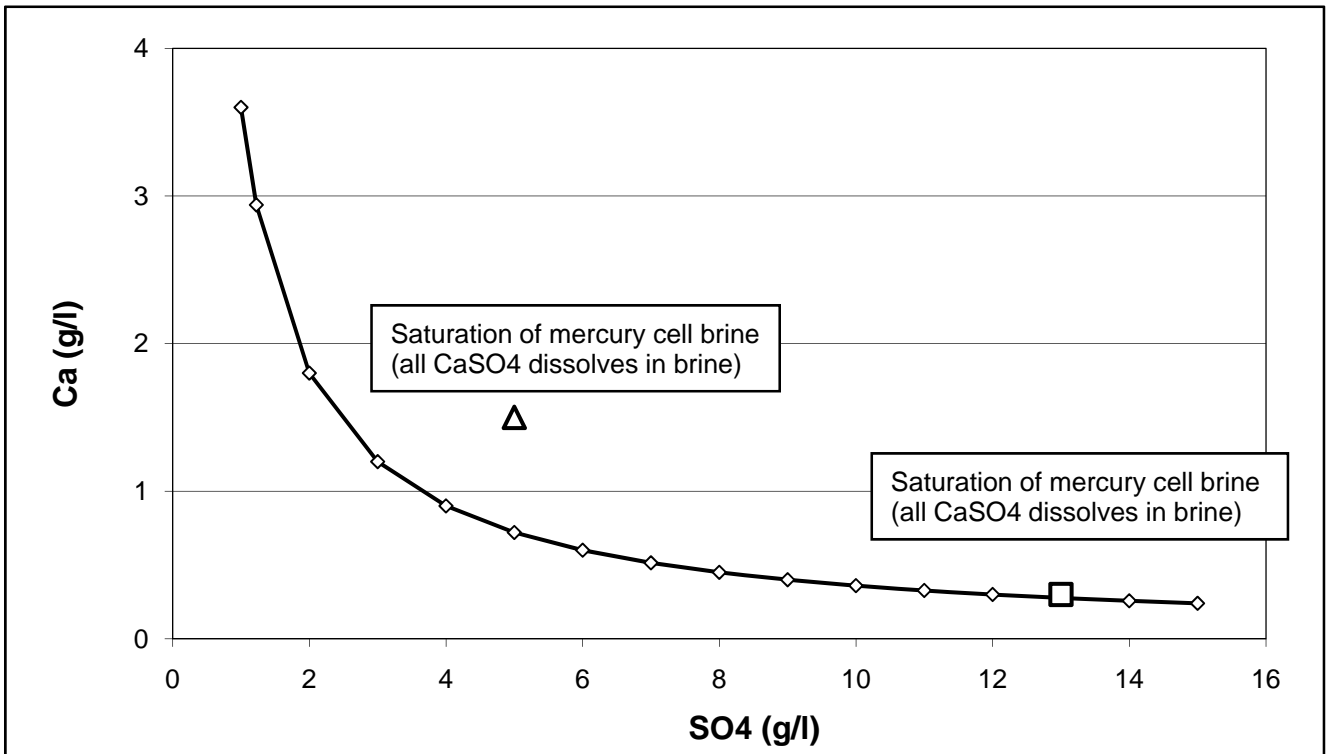
Brine saturation and salt dissolution in electrolytic brine

For calculation of the cost of chemical reagent overdosing, the following typical saturation, conversion and dissolution rates of salt in electrolytic brine have been assumed:

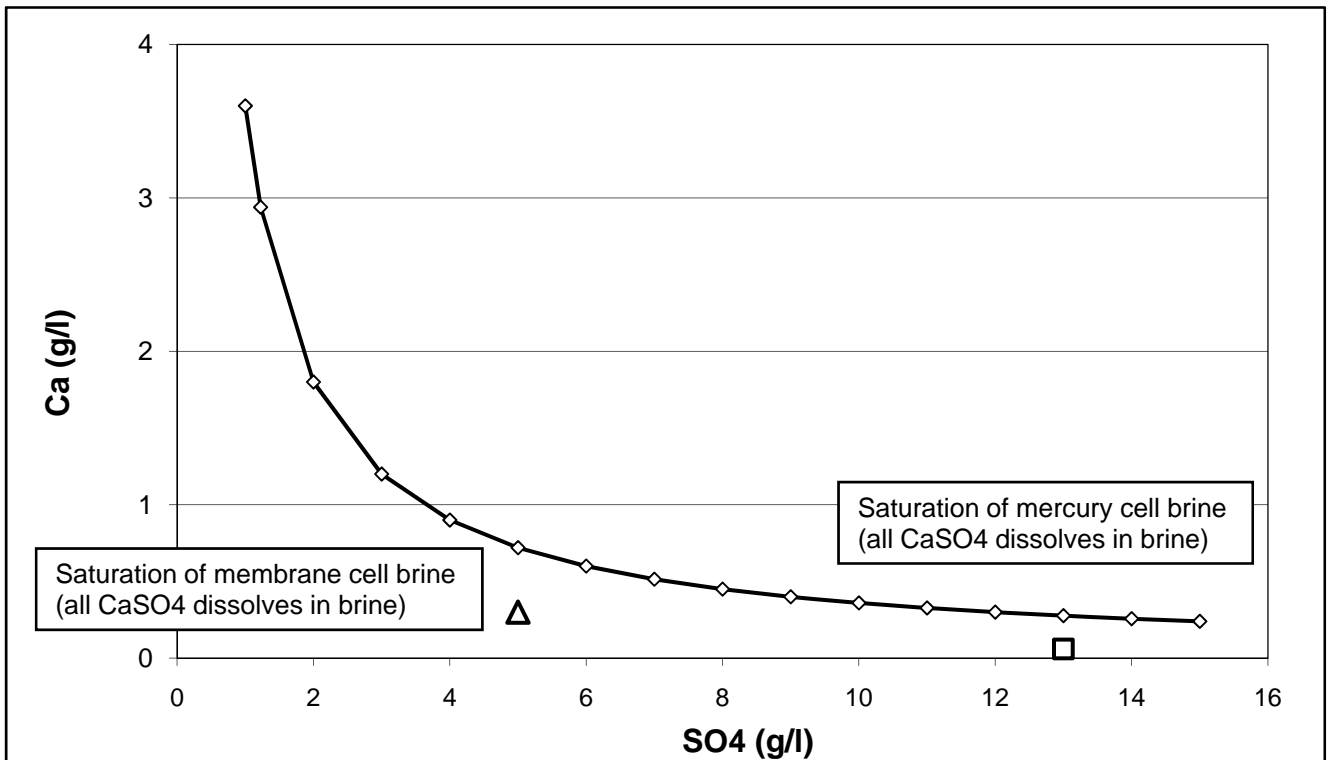
	Lean brine (g NaCl/l)	Saturated brine (g NaCl/l)	Salt dissolution (kg NaCl/m ³)	Ca in rock salt (kg Ca/m ³)	Ca in crude sea salt (kg Ca/m ³)
Mercury brine	270	300	30	0.3	0.06
Membrane brine	150	300	150	1.5 *)	0.3

*) In the above calculation, solubility of calcium sulphate in mercury electrolytic brine containing 13 g/l SO₄ and membrane electrolytic brine containing 5 g/l SO₄ has been assumed. Whereas all calcium sulphate from rock salt dissolves in mercury brine, only half of the calcium sulphate from rock salt dissolves in membrane brine. This is illustrated on the graphs below.

Rock salt dissolution in electrolytic brine



Solar salt dissolution in electrolytic brine



Contaminated effluent disposal

Effluents leave chloralkali plants either as excess brine or as solids from the precipitation of impurities. Quantity of both effluents depends on the amount of impurities in salt.

	Brine Effluent	Solids
Mercury brine disposal	Demercurization	Special depository (salt mines)
Membrane brine disposal	Neutralisation	Desalination and land fill

The relevant cost of effluent brine and solids from chloralkali circuits have been reported as follows:

	Brine disposal cost (USD / t of salt)	Solids disposal cost (USD / t of salt)
Minimum	0.05	0.20
Average	0.30	1.50
Maximum	0.60	4

Cost of salt and brine treatment

Summarising the cost of salt and brine treatment, as reported by the contributors to the cost surveys carried out by Salt Partners, the overall cost figures are as follows:

	Cost of brine treatment and disposal (USD / t salt)	Cost of salt, brine treatment and disposal (USD / t salt)
Minimum	1.50	10
Average	10	25
Maximum	30	50

The relative cost of brine treatment and effluent disposal, expressed as percentage of the cost of salt and as percentage of the cost of chloralkali production are as follows:

	Cost of brine treatment and disposal as percentage of salt cost (%)	Cost of salt, brine treatment and disposal as percentage of chloralkali production cost (%)
Minimum	100	3
Average	170	15
Maximum	300	40

It can be seen that both the absolute cost figures as well as the relative cost percentages vary greatly, depending on the local conditions. Decisions related to the selection of salt source and the related salt and brine processing must be examined from case to case, decided based on techno-economic analyses of the prevailing conditions and provision for changes that may occur in the future.

Whereas no generally valid predictions as to the economy of salt in chloralkali manufacture can be made, it is clear that the importance of salt cost and quality should receive the attention that it deserves.

Elements of high quality solar salt production

There are three main areas in the solar salt production where the quality of the salt and the production yield is determined. Firstly, it is the brine pre-concentration area. The main task there is to increase the concentration of

salts in the sea water from the starting density of 3.85°Bè to 26°Bè when NaCl begins to precipitate (1). In this process, several requirements should be fulfilled:

- The sea water should increase its concentration gradually, without back-mixing
- The sea water should not get lost due to seepage
- The bottom of the ponds should be impervious (2) and dark, to facilitate maximum absorption of solar radiation
- The sea water should remain clear, allowing solar radiation to reach the bottom of the ponds
- Impurities, such as calcium carbonate and calcium sulphate, should crystallise to maximum possible extent prior to the brine reaching density of 26°Bè when NaCl begins to precipitate
- Nutrients and biological material present in the feed sea water should be allowed to get consumed fully by succession of species whose life is supported by the respective salinity of the brine (2)
- The brine entering the crystallisers should be free of excessive organic material (2) that would negatively influence the salt crystallisation behaviour.

Secondly, it is the salt crystallisation area, where NaCl precipitates from brine progressing from density of 26°Bè to 28.5°Bè. The crystallisers should fulfil the following:

- The brine should not get lost due to seepage
- The brine should support the existence of *Halobacterium* that colours the brine red, increasing the absorption of solar radiation. *Halobacterium* also oxidises organic matter (2) that is detrimental to crystal growth, preventing large, clear crystals and causing formation of fine, impure crystals and agglomerates with impurities trapped inside
- The coloured brine layer should be thick enough to avoid reflection of solar radiation from the white salt crystals back to the atmosphere
- The brine should proceed through the crystallisers without back-mixing, so that only 28.5°Bè brine is drained, facilitating faster evaporation and avoiding contamination of salt with impurities, such as magnesium, sulphate, etc.
- The crystalliser dykes should prevent contamination of salt with insolubles
- The harvesting method should recover maximum percentage of crystallised salt avoiding contamination with insoluble material at the bottom of the crystallisers

Thirdly, it is the solar salt processing that purifies the salt prior to delivery. The purification process should fulfil the following requirements:

- Remove mother liquor from the salt crystals so that the salt crystal surface will be free of magnesium and sulphate impurities
- Remove gypsum crystals and insoluble impurities from the salt so that the salt crystal surface will be free of calcium sulphate and insolubles and the salt will be white
- Remove excess moisture from the salt so that no brine will drain from the salt during handling and storage
- Process the salt with minimum consumption of utilities, power and water and do so with minimum loss of sodium chloride.

Successful solar saltworks design, operation and salt processing

The above requirements can be satisfied by:

- Firstly, solar saltworks design and operation principles, such as the SOLARSAL technology, taking into account the climatic and geological conditions, brine quality, computerised operation control, etc. (5)
- Secondly, solar saltworks as an open environmental system having its own life and metabolism of nutrients must be understood and managed, according to the BIOSAL biological principles, to achieve the goals of production capacity and quality of salt crystals, being large, hard, clear and pure inside (3)

- Thirdly, a salt purification process should be employed, such as the HYDROSAL salt purification process with hydroextraction of impurities, that purifies the salt fully with minimum consumption of utilities and minimum of losses (10).

Application of advanced technologies in salt production and processing facilitate profitable production of high quality solar salt for chloralkali industry, for human consumption and for exports.

Salt Partners

Salt Partners are consultants and engineers, active in the field of salt production, processing and hypersaline biotechnology. Salt Partners' reputation is based on more than 35 years of experience gained in projects implemented around the world.

Salt Partners strive to develop innovative technologies that are inexpensive, yet achieve the highest levels of salt quality. Salt Partners technologies are applied to establish new salt production facilities, to improve the profitability of salt production and reduce the cost of salt use in the industry. Salt Partners supply technology and equipment and build salt plants world-wide.

References

1. Baseggio G., *Fourth International Symposium on Salt*, 351 – 358: The composition of Sea Water and Its Concentrates
2. Davis J. S., *Fourth International Symposium on Salt*, 369 – 372: Importance of Micro-organisms in Solar Salt Production
3. Davis J. S., *Fifth International Symposium on Salt*, 265 – 268: Biological Management of Solar Saltworks
4. Masuzawa T., *Fifth International Symposium on Salt*, 463 – 473: Impurities Contained Inside the Crystals of Solar and Vacuum Evaporated Salts
5. Mottershead R. A., *International Conference on Salt 2006, Ahmedabad January 2006*, Solar Salt – Optimising Production in India, China and Australia to Meet the Demand in Asia
6. Mottershead R. and Davidson P., 1st International Conference on the Ecological Importance of Solar Saltworks, Santorini, October 2006, The Yannarie Solar project: Design of a Solar Saltfield in Western Australia to safeguard the natural environment
7. Sedivy V. M., *International Seminar on Membrane Cell Technology, Vadodara 1988*, The Processing of Solar Salt Feedstock for Membrane Cell Chloralkali Plants
8. Sedivy V. M., *Industrial Minerals*, April 1996, Purification of salt for chemical and human consumption
9. Sedivy V. M., *The 7th Asian Chlor-Alkali Conference, Singapore, June 2002*, Economy of Salt in Chloralkali Production
10. Sedivy V. M., *International Conference on Salt 2006, Ahmedabad January 2006*, Upgrading and refining of salt for chemical and human consumption
11. Sedivy V. M., 1st International Conference on the Ecological Importance of Solar Saltworks, Santorini, October 2006, Environmental balance of salt production speaks in favour of solar saltworks