

Why not turn your solar salt into gold with Certified Emission Reductions?

Vladimir M. Sedivy MSc (Hons) Chem Eng, IMD
President, Salt Partners Ltd, Zurich, Switzerland
Email: vladimir.m.sedivy@salt-partners.com

Extended Abstract

Production of vacuum salt requires energy, mostly obtained by burning coal, oil or natural gas, releasing carbon dioxide. Under the Kyoto protocol, commitments to reduce the carbon dioxide emissions and schemes that facilitate emission compensations across country borders exist.

Solar saltworks are the most efficient collectors of environmental energy converting it directly into salt, an essential inorganic commodity. Conversion rate of solar radiation and removal of water vapour from the brine to the open atmosphere take place with record efficiency. Only brine pumping, salt harvesting, processing and conveying is accompanied with consumption of electric power and man made energy inherent to burning fossil fuel for salt handling and transport. Implementation of solar salt projects that replace vacuum salt with solar salt can earn Certified Emission Reductions (CER) or Joint Implementation (JI) certificates. The value of these marketable certificates may reach or even exceed the value of solar salt. Considerable expertise is required to establish environmentally friendly solar salt projects qualifying for registration under the CDM and JI schemes.

The general perception that vacuum salt is of higher quality and, though more expensive, is more economical to use, particularly in chemical applications such as chloralkali and soda ash manufacture, is misleading. With employment of advanced technologies for biological management and brine control in solar saltworks, harvesting techniques and salt processing, it is possible to produce salt of very high quality with very low losses. Advanced technologies, such as BIOSAL biological solar saltworks management and HYDROSAL salt purification process with hydroextraction of impurities, facilitate economic production of high quality solar salt, comparable with vacuum salt.

About 60% of salt produced worldwide is consumed by the chemical industry. In chloralkali manufacture, the use of high quality salt is essential to save chemicals and prevent formation of contaminated effluents. High quality solar salt requires comparably low amount of brine purification chemicals for treatment as vacuum salt and the difficult to remove trace elements that may cause membrane damage, such as iodine, or those elements that are critical to chlorine purity, such as bromine, are present in smaller quantities in solar salt than in many salts originating from rock salt deposits.

Key words: thermal energy, vacuum salt, carbon dioxide emissions, Certified Emission Reductions (CER), Clean Development Mechanism (CDM), Joint Implementation (JI), solar saltworks, solar energy, biological management, impurity inclusions, salt crystal growth, salt upgrading, salt losses, membrane cell, brine purification.

1. Salt production world-wide

Recently, the annual world production of salt exceeded 200 million tons. More than one third of the total is produced by solar evaporation of sea water or inland brines. Another 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 | 80,000,000 t/y |
| Rock salt | 60,000,000 t/y |
| Brines | 70,000,000 t/y |

The purity of washed solar salt produced in India and China reach 99 - 99.5% (NaCl, dry bases) but solar salt produced in Australia and Mexico is 99.7 – 99.8% pure. Vacuum salt is usually 99.8 - 99.95% pure.

2. Salt consumption world-wide

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 needed for petroleum refining, petrochemistry, organic synthesis, glass production, etc.

The second largest user of salt is mankind itself. Humans need about 30% of the total salt produced to support their physiological functions and eating habits. Salt for food is the most "taken for granted" commodity, available from thousands of sources in hundreds of qualities as table, cooking and salt for food production.

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

| Salt user | Salt consumption |
|-------------------|------------------|
| Chemical industry | 60% |
| Food | 30% |
| Other | 10% |

Whatever the use of salt, it is the sodium chloride in the salt that is required and not the impurities. The purer the salt, the more valuable it is.

3. Impurities in natural salts and in solar salts

Sodium chloride in salt is always the same. It is the "non-salt" in salt - the impurities - that make the difference. In fact, the multiplicity of impurities in salt and their relative quantities are so variable that every salt needs to be considered on its own merits.

Except for insolubles, the origin of impurities is the sea water. Solar sea salts, as a rule just few months old, are rather similar. Rock salts, millions of years old, may vary greatly, from pure to dirty, from white to black. Lake salts contain components leached from the ground of the surrounding rocks in variable quantities. Salt lake chemistry is a science of its own.

Calcium sulphate is the most persistent companion of salt. In rock salt, calcium sulphate is found as anhydrite, hemihydrate or polyhalite. Gypsum is found both in sea salt and in lake salt. Natural brines are, as a rule, saturated with calcium sulphate. Magnesium salts are always present in the sea salt, usually at a ratio of approx. one and a half weight units of magnesium chloride to one weight unit of

magnesium sulphate. In lake salts, magnesium sulphate is usually accompanied by sodium sulphate, for example in Sambhar Lake salts from Rajasthan in India or in Azraq salts from Jordan.

| | 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 | Traces | Traces | Traces |
| NaBr | Traces | Traces | Traces | Traces |
| Insolubles | 1 - 10% | 0.1 - 1% | 1 - 10% | |

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

4. Salt production from brine by vacuum crystallisation

The highest standards of quality are set by vacuum salt. Usually, vacuum salt is produced from brine obtained by solution mining of underground deposits and chemically purified. Such brines are almost saturated, containing approx. 25% NaCl. Thus, to crystallise 1 tonne of salt, 3 tonnes of water need to be evaporated. In a six effect evaporation plant, 0.62 tonnes of live steam used six times do the job (4). Assuming 10 bar steam, the heat transferred through steam condensation into the system is 390 kWh/t of salt. Assuming further that the steam boiler is generating steam with 75% efficiency, 450 kWh of prime energy per tonne of salt is required.

5. Salt production from brine by mechanical vapour recompression

Provided that electrical power is cheap, recompression of vapour from the evaporator in a radial compressor can be employed. The compressor elevates the vapour temperature to such a level that the vapour can condense in a heat exchanger against the circulating brine, bringing it to boil. This system uses about 160 kWh of electricity per tonne of salt. Assuming 35% power generating efficiency, also approx. 450 kWh of prime energy per tonne of salt is required in this system (4).

Thermal evaporating plants (vacuum plants) and their operation are costly and so is the vacuum salt. Because it is crystallized from brine containing up to 4% of sulphate, vacuum salt always contains sodium sulphate, frequently some 200 - 500 ppm or more. Despite the low calcium and magnesium content in the 1 - 10 ppm range, vacuum salt will seldom exceed 99.95% purity.

6. Carbon Dioxide Emissions with Thermal Evaporated Salt

Recent Bench Marking Study (5) showed that thermal evaporation of solution mined brines practised world-wide requires 150 - 1'250 kWh/t of salt, depending on technology employed. Most advanced plants consume 150 kWh of hydraulic power, causing almost zero carbon dioxide emissions. Many other salt plants, however, consume in excess of 1'000 kWh of thermal energy per ton of salt, burning black coal and discharging carbon dioxide to the atmosphere.

1 kg CO₂ is generated when producing 1 kWh power in a modern, super or ultra critical power station reaching highest 45% thermal efficiency, fired with high quality black coal having heat of combustion of 7'000 kcal/kg.

Chloralkali industry is fast growing. The related additional demand for salt is estimated to grow at a rate of 2 - 5% per annum (7). If this additional demand for salt is met by coal fired evaporation, addi-

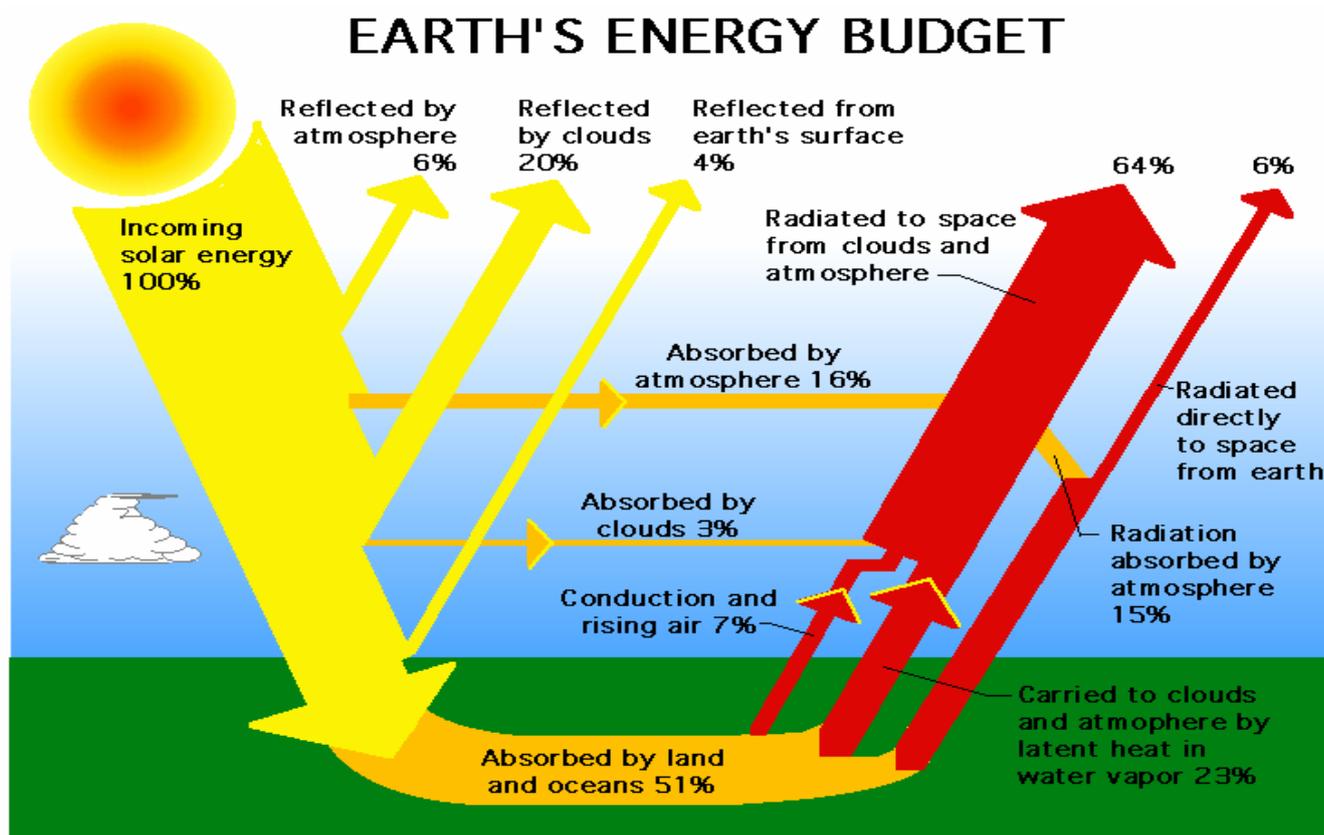
tional millions of tonnes of CO₂ will be discharged. If, however, met by supply of solar salt, the producers could earn CO₂ emission certificates. These could be used to close power supply gap elsewhere, fulfil CO₂ emission reduction targets under the Kyoto protocol or sold. At present price of USD 15.-/t CO₂, this represents a value comparable with the value of solar salt itself. Equally attractive is the perspective to replace present vacuum salt supplies with solar salt.

7. Salt production by solar evaporation of sea water

Sea water having density of 3.85°Bè contains 30.09 kg NaCl / m³ and 998.64 kg of water (1). 89.9% of this water needs to be evaporated before the first crystals of NaCl can crystallise. Further 6.16% of water is evaporated before the brine becomes so concentrated that the evaporation slows down considerably, further evaporation would spoil the salt quality and therefore the brine (bitterns) need to be discarded, still containing 8.37 kg NaCl per original 1 m³ of sea water. Thus 21.72 kg of NaCl can be recovered from 1 m³ of sea water by solar evaporation. Per each 1 kg of NaCl crystallised, 43.74 kg of water needs to be evaporated compared with 3 kg of water in thermal evaporation processes starting from almost saturated brine. Fortunately, solar energy is free of charge.

8. Earth's solar energy budget

Virtually all energy available on the planet Earth originates from the sun (8). 26% of the incoming solar energy is reflected by atmosphere and by clouds back to space, 16% is absorbed by atmosphere, 3% absorbed by clouds and 4% is reflected from the surface. Thus 51% of the incoming solar energy reaches the surface and is absorbed by land, oceans and solar saltworks. 23% is converted into water vapour and is carried to atmosphere and to clouds in the form of latent heat of evaporation. The balance is returned to atmosphere by conduction and radiation and finally, all of the solar energy received from the sun is radiated back to space.



Relevant for the operation of solar saltworks is the 51% of the incoming solar energy that reaches the surface (surface insolation). It amounts to 51% of 1'366 W/m² +/- 3.4% or 674 – 719 W/m² when the sun stands in zenith. Averaged over 24 hours per day in sub-tropical zones where most of the solar saltworks are located, it corresponds to 200 – 300 W/m² daily radiation average. The absorbed solar energy is thus 5 – 7 kWh/m²/day.

Latent heat of water evaporation at 30°C is 0.675 kWh/kg. Thus, 5 – 7 kWh/m²/day of surface insolation, if absorbed completely, could evaporate 7 – 10 mm of water per day. However, winds not only carry away the water vapour from the saltworks area, they also cool the brine by heat conduction. This phenomena accounts for 7% of the absorbed heat. Another 15% is radiated to the atmosphere and 6% to the space. The balance, 23% of the insolation is converted into latent heat of water evaporation from brine, the ultimate driving force behind solar salt production. Thus, instead of 7 – 10 mm of water per day, only 3 – 5 mm/d or 1.1 – 1.8 m/y is actually evaporated in average solar saltworks, resulting in production of 27 – 44 kg NaCl/m²/y. In terms of salt layer in crystallisers, which represent about 10% of productive saltworks area, 270 – 440 kg NaCl/m²/y having a density of about 2 t/m³, forms a layer about 13 – 22 cm thick. Exceptions to this average are known to exist in areas with very high wind temperature, for example near deserts, when the hot air actually heats the brine by conduction, instead of cooling it. In those places, salt layer thickness of half a meter or so in a year can be formed.

Comparing the efficiency of solar energy conversion into final product, 23% out of 51% surface insolation is directly converted into salt, representing 45% conversion efficiency. This compares favourably with 8 – 15% conversion efficiency of photovoltaic cells, 30% conversion efficiency of solar collectors with stirling engine (15) and even with 40 – 45% efficiency of super critical steam power plants burning fossil fuels that incur additional 4 - 12% losses in the existing power distribution grids.

It is no exaggeration to claim that solar salt production is one of the most efficient uses of solar energy, just next to agriculture and forestry. Salt is mainly a basic inorganic chemical raw material. In the field of inorganic chemistry, solar salt production is truly a remarkable and uniquely efficient process.

9. Prejudice about solar salt

Although several solar saltworks exist around the globe that produce excellent salt, many more produce salt having quality that leaves much to be desired. Thus, the general perception is that solar salt is cheap but dirty, impure, containing compounds that are detrimental to most of the uses, whether in the chemical industry, as food or anything else. Particularly in the chemical industry, in chlorine and caustic electrolysis or in soda ash manufacture, impurities in salt are costly and can be even dangerous.

10. Impurities in salt effect the chemical industry

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

10.1. Hydrogen evolution

In electrolytic cells, excessive magnesium causes hydrogen evolution on the anode. Hydrogen and chlorine form an explosive mixture. Explosion in the cells or in the chlorine liquefaction may damage the equipment and release chlorine to the environment. Chlorine gas is highly poisonous. Stringent safety measures are taken in the chloralkali industry to avoid this to happen. The elimination of magnesium is of prime concern.

10.2. Mercury butter

Impure brine in mercury cells will cause butter formation. Butter will disturb mercury flow, causing short circuits that burn the electrodes. Alternatively, a large electrode gap must be maintained which will increase the power consumption. Butter removal will expose workers to mercury vapours that are damaging to health. Disposal of mercury butter is costly and undesirable for the environment.

10.3. Contaminated sludge

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

10.4. Membrane damage

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

10.5. Encrustation

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

Salt may be a cheap commodity. But impurities in salt and their removal cost in many cases more than the salt itself.

11. How does the chemical industry deal with impurities in brine?

In the chemical industry, impurities in brine such as calcium and magnesium are precipitated with chemicals. In the chloralkali plants, sulphates are removed either by precipitation with barium or calcium or are controlled by purging the brine.

The main cost associated with brine purification is the cost of chemical reagents and the investment and operating cost of the brine treatment plants. In mercury cell plants, the cost of contaminated sludge disposal and purge decontamination is also substantial. In the membrane cell plants, the loss of salt in purge is much higher than in the mercury cell plants, reaching 30% with a salt feedstock containing some 0.7% of sulphate.

12. Three steps to produce high quality solar sea salt

There are three main areas in the solar salt production process 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. 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.

13. Three components of successful solar saltworks design and operation

The above requirements can be satisfied by:

- Firstly, correct solar saltworks design, taking into account the climatic and geological conditions, sea water quality and the mechanical design and operation of the saltworks (7)
- Secondly, solar saltworks as an open environmental system having its own life and metabolism of nutrients must be understood and correctly managed 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 that purifies the salt fully with minimum consumption of utilities and minimum of losses (13).

14. Comparison of high quality solar salt and vacuum salt

Although there are solar saltworks around the globe that produce better salt than the famous saltworks in Australia, such as the one presented in Figure 1, Australian salt is the best known and its quality is generally used as a standard. Australian salt compares with vacuum salt, for example the salt produced in Switzerland, as follows:

| | | Solar salt according to "Australian Standard" | Vacuum salt from Switzerland |
|-----------------|-----|--|---------------------------------|
| Ca | ppm | 400 | 5 |
| Mg | ppm | 200 | 1 |
| SO ₄ | ppm | 1200 | 300 |
| Insolubles | ppm | 20 | 20 |
| NaCl | % | 99.7% | 99.95% |

15. Solar salt upgrading

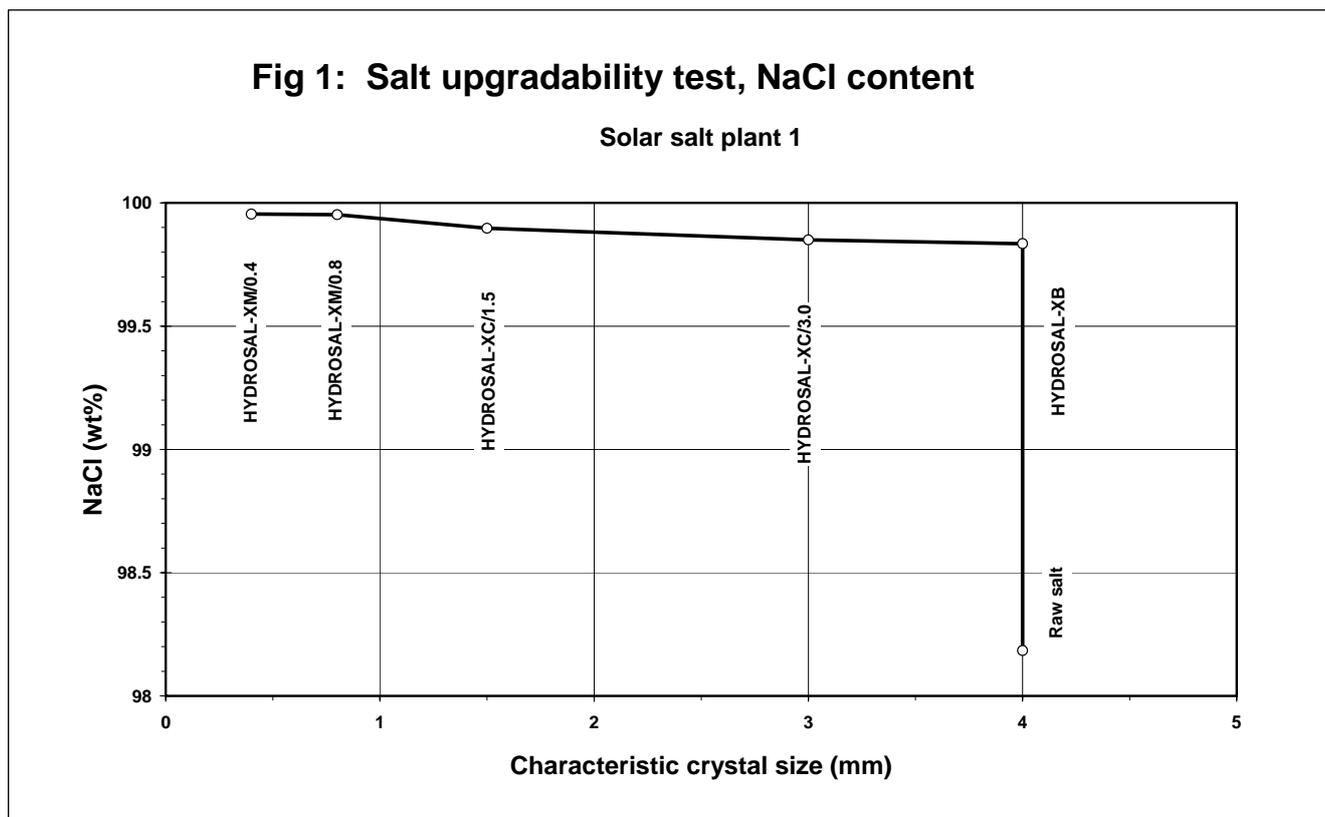
Simple salt washing will remove some of the impurities. But the more you wash, the more you lose. So the question is: How to get higher purity with less losses? And still do it with enhanced overall economy?

Salt Partners devoted much time and effort to this subject (10, 11). As a result, they developed a process that removes more impurities from salt, uses less water and recovers the dissolved salt to reduce the losses. If the salt is of poor quality and contains impurities inside the crystals, the process also removes them - by selectively cracking the crystals to free the enclosed impurities, with little formation of fines that increase the losses. The process achieves very high purity of NaCl. It is known as the **HYDROSAL** salt upgrading process with **HYDROEXTRACTION** of impurities from **SALT**.

16. Prediction of salt purity achievable with the HYDROSAL process

Even the best understanding of the principles of impurity formation and removal from salt cannot be transformed into a quantitative prediction of the achievable purity. This is only possible by testing the salt in the laboratory, using a sequence of unit operations that is identical to the sequence employed in the relevant process. Salt Partners have developed and standardized such procedure and used it to investigate hundreds of salt samples.

1. First, the raw salt is analysed. The raw salt analysis represents the sum of two unknown values: the surface impurities that are removable and those that are not. It is obvious that the raw salt analysis alone cannot give the information how much impurity can be removed and to what degree of purity the salt can be treated.
2. The next step is to find out, how much impurity can be removed without any change of the salt granulometry. This is called the HYDROSAL-XP upgradeability test.
3. Then we find out how much of the impurities enclosed inside the crystals can be removed if the salt is subjected to dry selective rupturing. Two characteristic crystal sizes, 1.5 and 3 mm, have been established as a standard (HYDROSAL-XC/1.5 and HYDROSAL-XC/3 upgradeability test).
4. This is followed by a test with hydromilling (HYDROSAL-XM test). Here, 0.4 and 0.8 mm characteristic crystal sizes are used as a standard (HYDROSAL-XM/0.4 and HYDROSAL-XM/0.8 refinability test).
5. If table salt production is intended, the HYDROSAL-XM salt is specially treated to produce salt that is blended with additives and analysed with respect to whiteness and free flowing characteristics. This is then called the HYDROSAL-XRT refined table salt test.



The analytical results are plotted against the characteristic crystal size. The resulting graphs are called the upgradability curves, such as the one shown in Figure 1 above. The curves are produced separately for calcium, magnesium, sulphate and insolubles. The analysed impurities are stoichiometrically combined to calculate the sodium chloride content. Potassium chloride and sodium bromide are usually not considered as impurities. The results are summarized in a report. Samples from all tests are sent to the client and a second set is kept by Salt Partners for records.

The test procedures and the analytical methods are given to clients who are encouraged to use them for control of their salt quality and the performance of their HYDROSAL plants. Thus, Salt Partners and their clients are able to refer to salt qualities and upgradabilities determined using consistent methodology over the years for the purpose of records, development or determination of plant performance guarantees.

17. performance of the HYDROSAL process

Several salt upgrading plants with hydroextraction of impurities were built in Europe, in the Middle East and in India, many of them integrated in chloralkali plants. These plants process salt from solar saltworks, having 96 - 99% NaCl content. The upgradability of these salts varies widely. There are some excellent solar salts produced, but also some rather poor salts that are difficult to upgrade. The best upgradeable salts, such as the salt having upgradability curve presented in Figure 1 above, are purified in the salt upgrading plants with hydroextraction of impurities to up to 99.8% purity. The best upgradeable salts are obtained in a THERMOSAL process (12) and upgraded to 99.988% purity, which is believed to be the record industrial salt purity ever achieved in Europe. The corresponding plant with hydroextraction of impurities works with certified efficiency of up to 97.4% and salt losses of less than 4%.

18. 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. Kondorosy E., *International Conference on Salt 2006, Ahmedabad January 2006*, Vacuum Salt Production by Using Various Processes
5. Kondorosy P., *Bench Marking Study of the Salt Plants World-wide June 2001*, Report for the Government of Netherlands
6. Masuzawa T., *Fifth International Symposium on Salt*, 463 – 473: Impurities Contained Inside the Crystals of Solar and Vacuum Evaporated Salts
7. 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
8. 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
9. NASA Homepage <http://asd-www.larc.nasa.gov>
10. Sedivy V. M., *International Seminar on Membrane Cell Technology, Vadodara 1988*, The Processing of Solar Salt Feedstock for Membrane Cell Chloralkali Plants
11. Sedivy V. M., *Industrial Minerals, April 1996*, Purification of salt for chemical and human consumption
12. Sedivy V. M., *Industrial Minerals, September 2000*, Salt from hot air
13. Sedivy V. M., *International Conference on Salt 2006, Ahmedabad January 2006*, Upgrading and refining of salt for chemical and human consumption
14. 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
15. Solar Stirling system ready for production (www.wapa.gov/es/pubs/esb/1998/98Aug/at_solargen.htm)