Purification and Refining of Salt for chemical and human consumptions

Serra Salt Engineers, 2005

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The presence of impurities in salt has serious economic and environmental consequences. Impurities increase the cost of brine treatment in chemical processes, may affect the problems of contaminated effluent disposal and necessitate costly refining of salt for human consumption. The classic approach to salt purification ranges from mechanical salt washing to vacuum salt recrystallization. SERRA has been engaged in developing unconventional and innovative processes that are inexpensive, yet achieve highest levels of salt purity. This article examines the nature of impurities in salt and explains the unit operation employed in the SERRA salt purification process. It describes the prediction methods of the process performance and reviews results obtained in industrial plants commissioned recently. Finally, it describes the latest developments in the field.

SALT PRODUCTION WORLD-WIDE

Recently, the annual world production of salt has reached 230 million tons. Approximately 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, mostly by solution mining. Brines can be used directly (for example in diaphragm electrolysis) or thermally evaporated to produce vacuum salt.

<table>
<thead>
<tr>
<th>Salt type</th>
<th>World production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar salt</td>
<td>88,000,000 t/y</td>
</tr>
<tr>
<td>Rock salt</td>
<td>70,000,000 t/y</td>
</tr>
<tr>
<td>Brines</td>
<td>70,000,000 t/y</td>
</tr>
</tbody>
</table>

The purity of washed solar salt can reach 98 - 99.5% (NaCl, dry basis) in Africa, America, India and China and 99.7% in Europe, Australia and Mexico. The purity of processed rock salt fluctuates between 97 and 99% - in the USA and Europe. Vacuum salt is usually 98.8 - 99.95% pure.

SALT CONSUMPTION WORLD-WIDE

The chemical industry is the largest salt consumer of salt using about 80% of the total production. This industry converts the salt mainly into chlorine, caustic and caustic soda without which petroleum refining, paper-pulp industry, organic synthesis, glass production, etc. would be impossible.

The second largest user of salt is mankind itself. Humans need about 30% of the total salt produced to support their physiological function 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 industrial salt for food production.

How to use 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.

IMPURITIES IN NATURAL SALTS

Sodium chloride in salt is always the same. It is "non-salt" in salt - the impurities that make the difference. In fact, the multiplicity of impurities in salt, their relative quantities and how they influence the salt properties 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. Salt contains a wide variety of metals or similar rock salts, as a rule just a 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. But lake chemistry is a science of its own.

Calcium sulphate is the most prevalent impurity of salt. In rock salt, calcium sulphate is sometimes found as anhydrite, hemihydrate or polyhydrate. gypsum is found both in sea salt and in lake salt. Natural brines are, as a rule, saturated with calcium sulphate. 

<table>
<thead>
<tr>
<th>Rock salt</th>
<th>Sea salt</th>
<th>Lake salts</th>
<th>Brines</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO4</td>
<td>0.5 - 2%</td>
<td>0.5 - 1%</td>
<td>0.5 - 2% saturated</td>
</tr>
<tr>
<td>MgSO4</td>
<td>Traces</td>
<td>0.2 - 0.6%</td>
<td>Traces</td>
</tr>
<tr>
<td>MgCl2</td>
<td>0.3 - 1%</td>
<td>Traces</td>
<td>Traces</td>
</tr>
<tr>
<td>CaCl2</td>
<td>Traces</td>
<td>Traces</td>
<td>Traces</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>Traces</td>
<td>Traces</td>
<td>Traces</td>
</tr>
<tr>
<td>KCl</td>
<td>Traces</td>
<td>Traces</td>
<td>Traces</td>
</tr>
<tr>
<td>NaCl</td>
<td>Traces</td>
<td>Traces</td>
<td>Traces</td>
</tr>
<tr>
<td>Insolubles</td>
<td>1 - 10%</td>
<td>0.1 - 1%</td>
<td>1 - 10%</td>
</tr>
</tbody>
</table>

Magnesium salts are always present in the sea salt, usually in a ratio of approx. One at a half weight units of magnesium chloride to one weight unit of magnesium sulphate. In lake salts, magnesium sulphate is usually accompanied by sodium chloride. For example in Tajikistan, India or Aral, Jordan. Magnesium chloride also occurs together with calcium chloride, for example in the Dead Sea where also potassium chloride and sodium bromide occur in exceptionally high concentrations. Insolubles are found in salts of all origins in greatly fluctuating quantities.

HOW DO 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 the brine to the process, it is purified. Failure to purify the brine adequately may have serious, even fatal consequences.

HYDROGEN EVOLUTION IS ELECTROLYTIC CELLS, EXCESSIVE MAGNESIUM WILL CAUSE HYDROGEN EVOLUTION ON THE ANODE.

Hydrogen and chlorine form an explosive mixture. Exposure to the moist air or the chlorine gas is highly dangerous and explosive. Stringent safety measures are taken in the metalworking industry to avoid this to happen but the elimination of magnesium is of prime concern.

MERCURY BUTTER

Impure brine in mercury cells will cause butter formation. Butter will disturbs mercury flow, causing slow circulates that turn the electrodes. Alternately, a large electrode gap must be maintained which will increase the power consumption. Butter remove will deposits works to mercury vapours that are damaging to health. Disposal of mercury butter is costly and undesirable for the environment.
CONTAMINATED SLUDGE
Sludge from brine purification in chloralkali plants permits cells is contaminated with 
mercury. Sludge decontamination by distillation requires high temperatures, is costly and 
energetically uneconomical. The disposal of mercury-contaminated sludge is environmentally objectionable and 
very costly. Avoiding the formation of sludge is better than trying to 
dispose of it. This requires salt of high purity.

MEMBRANE DAMAGE
Calcium and magnesium will damage the ion exchange membranes irreversibly. Starch impurity content in salt may cause hardness 
breakthrough in the membranes. Membranes cost a fortune. The fewer retards in the danger of membrane damage.

ENCRUSTATION
In soible salt production, excessive sulfates reduces the value of the product. Accumulating calcium in the process lowers crystallization. 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.

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 
manufactures. Sulfates are removed either by precipitation with barium or calcium or are controlled by 
putting the barium. The main cost associated with further purification is the cost of chemicals and 
their investigation and cutting cost of the brine treatment plant. In mercury cell plants, the cost of contaminated sludge disposal and 
pure decontamination is also substantial.

WHAT DO IMPURITIES IN SALT MEAN TO THE FOOD INDUSTRY?
Quality conscious consumers demand pure products. As one of the 
raw materials salt must fulfill stringent specifications, otherwise the 
product quality may get affected.

Crystal salt, whether stored or used in a shaker, must retain 
free flowing properties. Magnesium on the surface of the salt crystals 
always humidity from the air and moisten the salt damp. Slowly 
cannot be avoided and shaker boxes get filled. The salt loses weight until 
as well.

CONVENTIONAL SALT REFINING: VACUUM CRYSTALLIZATION
The highest standards of quality are set by vacuum salt. Usually, 
vacuum salt is produced from brine obtained by cavern mining of underground deposits and chemically purified.
Vacuum evaporating plants and their operation are a highly end to 
and the vacuum salt.

THE ECONOMICAL ALTERNATIVE: SALT UPGRADE?
If impurities are removed from salt directly, without dissolution and 
recrystallization, substantial cost savings can result. Simple washing 
and filtration 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 
and still do it with an enhanced overall economy?

SERRA developed three time and effort to this subject. As a result, they 
designed a process that removes more impurities from salt, uses less water and recovers the dissolved salt to reduce the losses. They also 
remove impurities that are inside the salt crystals — by selectively 
the crystals to free the suspended impurities, without breakdown of fines that increase the impurities. They achieve and exceed the purity of 
99.85% NaCl.

Examples of Middle East lake salt customers with different 
Washing/Upgrading processes:

<table>
<thead>
<tr>
<th>Salt Type</th>
<th>Raw Salt 1</th>
<th>Raw Salt 2</th>
<th>Raw Salt 3</th>
<th>Raw Salt 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>2.4%</td>
<td>2.1%</td>
<td>2.8%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.14%</td>
<td>0.04%</td>
<td>0.15%</td>
<td>0.03%</td>
</tr>
<tr>
<td>Boron</td>
<td>1.6%</td>
<td>0.6%</td>
<td>1.2%</td>
<td>0.9%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.2%</td>
<td>0.03%</td>
<td>0.4%</td>
<td>0.06%</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.2%</td>
<td>0.5%</td>
<td>0.2%</td>
<td>0.0%</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.7%</td>
<td>0.2%</td>
<td>0.5%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

HOW CAN CHEMICAL PLANTS TAKE ADVANTAGE OF SALT UPGRADE?
A plant that obtains salt from a simple source can upgrade the 
where it is produced. It is lighter to dispose of the rejected impurities. 
When the salt comes from many places, then the salt upgrading 
can be integrated into the brine circuit. Depending on the type of salt, 
SERRA process can be selected.

Salt upgrading helps solve the problem associated with contaminated 
salt and sludge disposal. The overall salt consumption, the initial 
investment and the operating cost are reduced. With pure salt of 
constant composition the brine plant operation becomes easier.
In modern and larger plants, the investment in a salt upgrading plant is invested from 
the savings in brine purification chemicals typically 
within a year or two, depending on the scale.

WHY CAN SOLAR SALTWORKS INCREASE PRODUCTIVITY WITH 
THE SERRA PROCESS?
In order saltworks, salt is harvested from crystallizing ponds as a mixture of salt, (or, and salt deposit forming solution impurities in high 
concentrations. During storage, the content of soluble impurities is 
reduced, until it becomes constant after some 6 months. 
During this period, the humidity of the salt on the stockpile is about 3%
but it drops down to approx. 1% thereafter. This phenomenon is known as "quartz washing" or "natural purification". This is a very unique 
description since the purification occurs also when there is no rain at all.

Bulk density of the salt is about 1.2 t/m³, specific gravity of salt crystal 
about 2.15 t/m³. Thus, the stockpile consists of half by salt per "by half 
of air. Magnesium chloride on the surface of the crystals absorbs 
moisture from the air that dissolves sodium chloride. Salt cannot hold 
more than 3% of moisture in equilibrium. The absorbed moisture with 
the dissolved impurities and with the dissolved sodium chloride slowly 
flows out of the stockpile and dissolves to the ground. The sodium 
hydroxide loss due to this amount to 10%.

Conventional salt washing protocols have typically an efficiency of 
80% and salt losses of 10%. If such salt washing is automated in the 
saltworks, the "natural purification" continues, leading to an additional 
loss of some 4% of NaCl on the stockpile. Thus, the overall salt losses can be up to 15%.
In addition, due to variations in the temperature and humidity, salt on the pedestal undergoes an irreversible precipitation of its crystal surface. Impurities on the crystal surface (likely to contain sodium chloride and the impurities in the salt) are gradually dissolved in the crystal, thus the impurities get washed away. When this phenomenon is detected, the salt is washed away to prevent it becoming insoluble. The water thus is exchanged against warm water, which is then discarded. This process is repeated until the impurities are removed.

The SERRIA process purifies the treated hypercarb salt completely. The typical purification effect of the mother salt is shown in the diagram. The crystal salt is visually inspected; all of the impurities and crystals are removed. The impurities are then washed away and discarded. The purified crystals are then dried to remove any moisture. This results in high-quality salt that is suitable for industrial use.

How to remove impurities from the inside of the salt crystals?

To remove impurities from the inside of the salt crystals, the following steps are taken:
1. The crystals are washed and conditioned to remove any moisture and impurities.
2. The crystals are then subjected to a high-temperature wash, which removes any remaining impurities.
3. The crystals are then dried to remove any moisture.

The resulting purified salt is then ready for use in various applications, such as food, pharmaceuticals, and agriculture.
From the n-tainment of the settlement, twelve g (120) to the inlet and weather where we mixed with the incoming salt.

As the weather, the whole term usually appears as the sunny field; until the fine mixture is under the overpass, it is required as the main part where the mixture is collected. Clarified brine is returned to the process. Water added to the process is heated to a temperature of 30°C and separation of pure brine leavse the plant for the next step.

In the complete water treatment process, the salt water is separated by a specific type of brine, using an electrolysis process, leaving a highly concentrated and a predominantly brine. The energy and raw salt content are somewhat higher but the product can be achieved with higher purity.

The process with addition of raw salt when reaching high salt recovery is required where the higher energy and raw salt consumptions are involved. This salt can be used in the chemical industry, but usually it is avoided because, conditioned with phosphates and added to contain the best appearance, clearness, brilliance whitens and insoluble free flowing properties qualified and used in the food market.

**HOW TO DETERMINE THE MOST ECONOMICAL PROCESS OPTION?**

The lower the salt is separated and the better the purity, the more it can be made. The purest salt should be the higher the energy and raw salt consumption and the more expensive is the plant. Obviously, the optimum exists where the salt is recovered at the minimum of cost.

The method is calculating the economy of the SERRA process and selection of the most economical operating option is simple. Savings are calculated as the difference in cost of brine purification chemicals with the existing salt and with the upgraded salt. The savings are compared with the investment cost and the minimum payback is determined. The process with the shortest payback is then recommended as the most economical one.

Further by the direct, more complex unit processes are eliminated, requiring no chemical treatment, components, engines. Combined production of upgraded salt in chemical processes and salted salt for human consumption, waste treatment, etc.

**HOW DOES THE SERRA PROCESS PERFORM WITH SALT OF VARIABLE QUALITY?**

Recently, a 330 kV grid was commissioned in the South America. The chemical plant in which the grid has been incorporated, receives salt of different quality. After the removing process the salt is upgraded from 9% to 37% purity. The upgradability of this salt varies widely. The plant processes this mixed feedstock to sell at about 30-37% purity.

**SERRA USED ON RECYCLATION IN OPEN PONDS WITH GENERATION OF ELECTRICITY FOR CHEMICAL SALT PRODUCTION.**

Currently, the process is the economical alternative to mining. Sometimes, the energy use is negligible, for example, for storage of natural gas, and the brine cannot be depleted off as liquid. Sometimes, the circumstances solar evaporation, or the evaporation should be accelerated. Solar arrays, direct solar salt should be made available. Conventionally, vacuum salt evaporation would be employed in such cases.

Recently, SERRA process associated with a project that was previously named the South American project. This project is unconventional, non-renewable and allows the unique opportunity to deliver brine to a wide range of industries that benefit from the use of brine. The production of high quality brine for salt and other activities below salt.

**SERRA REFINING AREAS USE THE MOST ADVANCED TECHNOLOGIES.**

16,000 power plant mills for salvaging and reclaiming mill of dewatering are used in the salt, for transformations from the initial properties and products clean free flowing salt for several years. The solution in order to replace and also for the process for the plant for different capacities.