

# Purification of salt for chemical and human consumption

by V.M.Sedivy\*

The presence of impurities in salt has serious economic and environmental consequences. Impurities increase the cost of brine treatment in chemical processes, magnify 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. Krebs Swiss has been engaged in developing unconventional and innovative processes that are inexpensive, yet achieve the highest levels of salt purity. This article examines the nature of impurities in salt and explains the unit operations employed in the Krebs Swiss SALEX salt purification process. It describes the prediction methods of the process performance and presents 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 200 m. tonnes. Approximately one third of the total is produced by solar evaporation of seawater 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.

### World salt production

<i>Salt type</i>	<i>Production (m. tpa)</i>
Solar salt	70
Rock salt	60
Brines	70

The purity of washed solar salt can reach 99 - 99.5% (NaCl, dry base) in India and China, and 99.7% in Australia and Mexico. The purity of processed rock salt fluctuates between 97 and 99%+ in the USA and Europe. Vacuum salt is usually 99.8 - 99.95% pure.

## Salt consumption world-wide

The chemical industry is the largest consumer of salt using about 60% of total production. This industry converts the salt mainly into chlorine, caustic, and soda ash without which petroleum refining, petrochemistry, organic synthesis, glass production, etc. would be unthinkable.

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 industrial salt for food production.

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

### World salt market

<i>Sector</i>	<i>Salt consumption</i>
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.

## Impurities in natural salts

Sodium chloride in salt is always the same. It is the "non-salt" in salt — the impurities — which makes 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 seawater. Solar sea salts, as a rule just a few months old, are rather similar. Rock salts, millions of years old, may vary greatly,

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**Typical salt analyses**

	<i>Rock salt</i>	<i>Sea salt</i>	<i>Lake salts</i>	<i>Brines</i> Saturated Traces
CaSO <sub>4</sub>	0.5-2.0%	0.5 - 1%	0.5 - 2%	
MgSO <sub>4</sub>	Traces	0.2 - 0.6%	Traces	
MgCl <sub>2</sub>		0.3 - 1%	Traces	
CaCl <sub>2</sub>			Traces	
Na <sub>2</sub> SO <sub>4</sub>			Traces	
KCl			Traces	
NaBr			Traces	
Insolubles	1 - 10%	0.1 - 1%	1 - 10%	

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 sometimes 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.

**Typical salt analyses**

Magnesium salts are always present in the sea salt, usually in a ratio of approximately 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 Rajasthan, India or in Azraq, 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 lethal consequences.

**Hydrogen evolution**

In electrolytic cells, excessive magnesium will cause 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 and dangerous. Stringent safety measures are taken in the chloralkali 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 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.

**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.

**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.

**Encrustation**

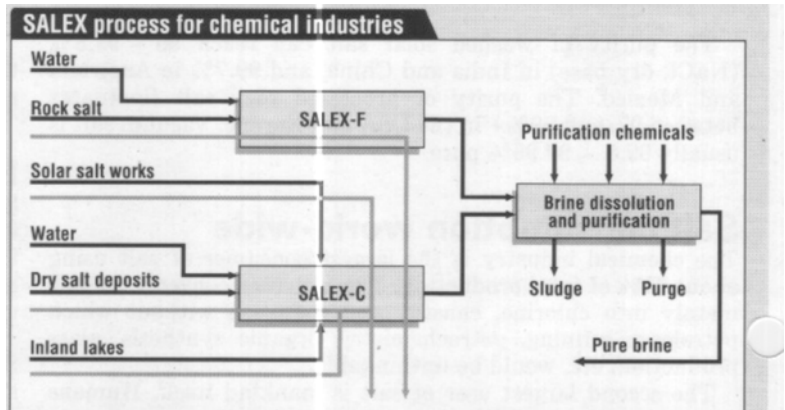
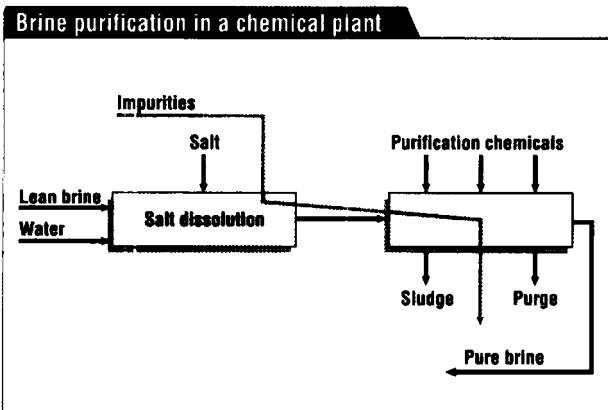
In soda ash production, excessive sulphate reduces the value of the product. Accumulating calcium in the process causes encrustation. Periodical scale removal is costly and leads to loss of production.

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 chemicals. 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 chemicals and the investment and operating cost of the brine treatment plant. 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.

### What do impurities in salt mean to the food

#### industry?

Quality conscious consumers demand pure products. As one of the raw materials salt must fulfil stringent specifications, otherwise the product quality may get effected.

Crystal salt, whether stored in silos or used in a shaker, must retain its free flowing properties. Magnesium on the surface of the salt crystals absorbs humidity from the air and makes the salt damp. Silos cannot be emptied and shaker holes get blocked. The salt loses market and value.

### Conventional salt refining: vacuum crystallisation

The highest standards of quality are set by vacuum salt. Usually, vacuum salt is produced from brine obtained by cavity mining of underground deposits and chemically purified. Vacuum evaporating plants and their operation are costly and so is the vacuum salt. Since vacuum salt is crystallized from brine containing up to 4% of sulphate, it always contains sodium sulphate, frequently some 400 - 500ppm or more. Despite the low calcium and magnesium content in the 1 - 10ppm range, vacuum salt will seldom exceed 99.95% purity.

### The economical alternative: SALEX

If impurities are removed from salt directly, without dissolution and recrystallisation, substantial cost savings can result. Simple 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?

Krebs Swiss devoted much time and effort to this subject. As a result, the company designed a process that removes more impurities from salt, uses less water and recovers the dissolved salt to reduce the losses. It also removes impurities that are inside the salt crystals — by selectively cracking the crystals to free the enclosed impurities, without formation of fines that increase the losses. The process achieves and exceeds the purity of 99.95% NaCl.

The name of the unique process is the SALEX salt upgrading process for EXtraction of impurities from SALt.

### How can chemical plants take advantage of salt upgrading?

A plant that obtains salt from a single source can upgrade the salt where it is produced — it is easier to dispose of the separated impurities there. When the salt comes from many sources, then the salt upgrading can be integrated in the brine circuit.

Depending on the type of salt, either the SALEX-C or the SALEX-F process can be selected. The SALEX-C process is usually more economical for upgrading of low quality solar salt, for dry salt deposits or for lake salts. The SALEX-F process is required for upgrading of rock salts.

Salt upgrading helps to solve the problems associated with contaminated sludge and purge disposal. The overall salt consumption, the total investment and the operating cost are reduced. With pure salt of constant composition the brine plant operation becomes easier. In medium and larger plants, the investment in a salt upgrading plant is financed from the savings in brine purification chemicals typically within a year or two.

### Increasing productivity with the SALEX process

In solar saltworks, salt is harvested from crystallizing ponds as a mixture of salt crystals and mother liquor containing soluble 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 "rain washing" or as "natural purification". This is the more accurate description since the purification occurs also when there is no rain at all.

Bulk density of the salt is about 1.2 t/m<sup>3</sup>, specific gravity of salt crystals about 2.15 t/m<sup>3</sup>. Thus the stockpile consists by half of salt and 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 diluted impurities and with the dissolved sodium chloride slowly flows out of the stockpile and dissipates to the ground. The sodium chloride losses due to this amount to 10 - 12%.

Conventional salt washing processes have typically an efficiency of 60% and salt losses of 10%. If such salt washing is employed in the saltworks, the "natural purification" continues, leading to an additional loss of some 5% of NaCl on the stockpile. Thus, the overall salt losses can be as high as 15%.

In addition, due to variations in the temperature and humidity, salt on the stockpile undergoes micro-recrystallisation of the crystal surface. Impurities on the crystal surface become covered with solid sodium chloride and the crevices in the crystals, full of impure mother liquor, will get closed. Many of the impurities, originally accessible to purification, will become imbedded inside the crystals. This phenomenon is well known: "Old salt is more difficult to wash than fresh one".

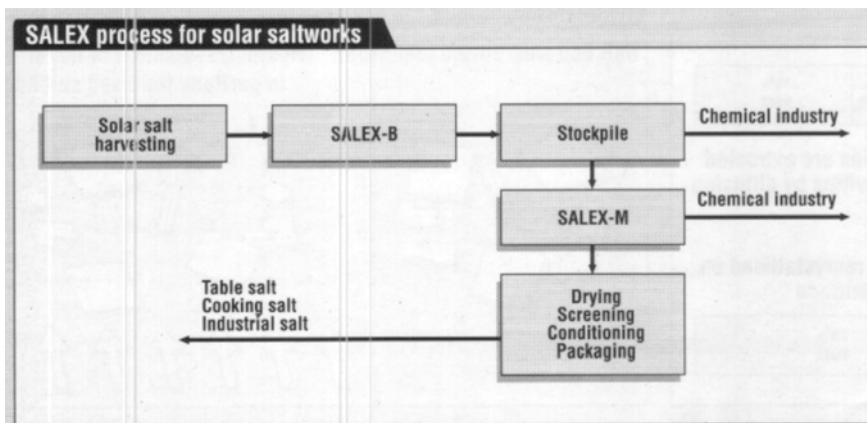
The SALEX-B process purifies the freshly harvested salt completely. The "natural purification" effect and the related salt losses are eliminated. Since the sodium chloride losses in the SALEX-B process are only 1 - 2%, the effective salt

production of the saltwork is increased. Salt of higher purity and value is available on the stockpile from the time of the harvest which matters when the salt is supplied to the chloralkali industry or for exports.

### Salt refinery benefits with the SALEX process

Solar salt is frequently used as a feedstock in salt refining plants. Traditional salt processing in mechanical refineries consists of washing, drying, crushing and screening. Salt washing removes surface impurities and drying removes surface moisture. But salt crystals contain impurities enclosed inside.

When salt is crushed after drying, the



impurities are set free. The solid impurities spoil the whiteness of the salt. Magnesium containing mother liquor spills out of fractured cavities, freeing its hygroscopic power. The salt begins to absorb moisture from the air and becomes damp and sticky.

In the SALEX-M process, hydromilling selectively ruptures the salt crystals where the impurities are embedded so that they become exposed to purification. Purities of 99.97% have been reached with natural solar salt. Hydromilling also provides the crystals with rounded form resulting in superior free flowing properties of the product. Hydromilling remarkably improves the whiteness of the salt.

SALEX-M process followed by drying, screening, additive blending and packaging is known as the SALEX-RT (Refined Table salt) process. In the market, SALEX-RT refined salt matches the quality of vacuum salt at substantially lower production cost.

### Unit operations for removal of soluble impurities

The most obvious and simple way of removing soluble impurities from salt is spraying of brine or water over a layer of salt — on a heap, on a screen, on a wire mesh belt or screw conveyor. The disadvantage is that the brine will flow downwards through a path of least resistance, forming channels. Washing takes place within the channels but not between them. Downwards flowing brine cannot displace the air between the crystals. Where there is air, there is no brine and thus no washing. That is why the spraying methods have a limited efficiency.

Salt needs to be completely submerged in the brine to dilute the magnesium containing bitters. Sufficient time is needed for the magnesium to leave the crevices in the crystals by diffusion. Obviously, very pure brine is needed to get the best purification. But pure brine is obtained by dissolution of salt in water and this leads to losses. The losses can be reduced with brine recycling, but then the purity is not achieved. This is the well-known problem of co-current salt washing.

Here is how the SALEX process solves the problem: it takes the least valuable salt fraction, the fines, and dissolves them in a small amount of water, forming pure saturated brine. Then it allows the brine to flow — slowly and upwards, counter-currently — through a layer of downwards moving salt crystals. Each salt crystal is completely encompassed by the pure brine so that every soluble solid impurity has the opportunity and time to dissolve. Also, the impurities entrapped in the crevices have enough time to leave.

As the brine is progressing upwards, it picks up more and more magnesium and its density goes up. Just as the density of brine in the saltworks increases with the progress of crystallisation, the salt crystallises from the upwards flowing brine on the surface of the downward moving crystals.

This benefits the product purity because the crystal surface

of the processed salt consists of pure, recrystallised sodium chloride. The salt losses in the process are reduced because the dissolved salt fines are thus recovered. It is called hydroextraction with displacement crystallisation. It is simple and it makes sense.

### Removal of insoluble impurities

Fortunately, most of the insolubles consist of fine dust from the air or clay from the bottom of the crystallisation ponds. Also gypsum crystals are fine needles, just a fraction of a millimetre long. Brine sprayed over a salt layer could wash the fine insolubles down but the salt layer acts as a filter, holding the fines back, particularly when the salt is rather fine. That is why the content of calcium and insoluble matter in the salt washed on a heap is almost the same before and after the washing.

In the SALEX process, brine is forced to flow upwards against the downwards moving salt crystals, fluidising them and pushing them apart so that the fine particles are free to float upwards out of the salt and to the overflow of the process vessels. The brine velocity is precisely controlled to remove just the right size of particles containing as much impurities as possible but very little salt. This is called elutriation and hydroclassification.

### Removal of impurities from the inside of salt crystals

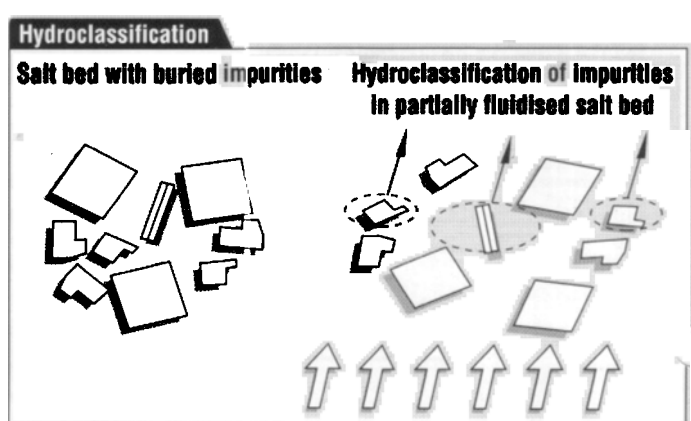
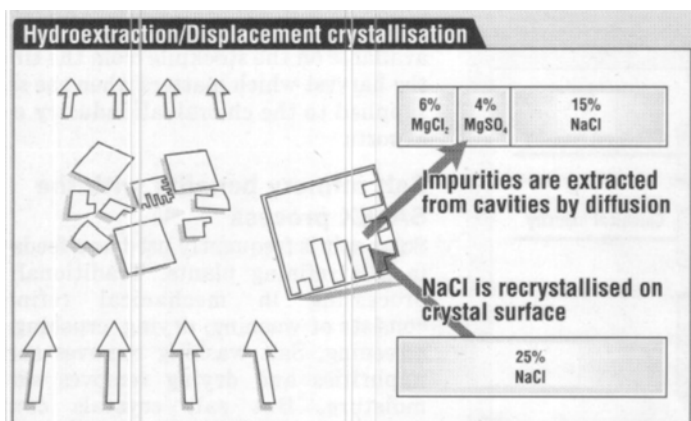
It is obvious that we have to break the crystals. But how? If the crystals are crushed with a hammer, they break in thousands of pieces. The fines formation is high and the salt losses are heavy.

But if we apply a shear force to the crystal, it will break gently along the planes where it is weakest. It is weak where the impurities disturb the crystal structure. In this way we access the inclusions selectively without an excessive loss of salt. This is called selective rupturing. Depending on the application, the salt is ruptured dry in the SALEX-C process or as a mixture of salt and brine in the hydromill of a SALEX-M plant.

### Organisation of unit operations in the SALEX process

Let us begin at the end. The last step of any salt purification process must be the separation of the purified salt from the brine. This happens best in a centrifuge. The centrifuge of a vibrating resonance type gives salt with an economic minimum of moisture and recovers the maximum of the valuable pure brine. Centrifuges produce salt fines by mechanical abrasion.

In the SALEX process the fines are utilised for production of pure brine in a dissolving vessel. From there the pure brine is returned to the vessel from which the salt and brine flow to the centrifuge. This vessel is called the hydroextractor. The lower part of the hydroextractor is called the hydroextraction zone.



Performance comparison of SALEX

	Upgraded salt with co-current flow	Efficiency with co-current flow	Upgraded salt with counter-current flow	Efficiency with counter-current flow
Ca	0.092%	69%	0.06%	96%
SO <sub>4</sub>	0.31%	65%	0.21%	92%

Above it the hydroclassification zone is located.

From the overflow of the hydroextractor the brine flows to the elutriator where it is mixed with the incoming salt. The mixture of salt and brine is pumped to the top of the hydroextractor. Pumping helps to separate impurities attached to the surface of the salt crystals.

In the elutriator, the brine flows upwards against the freely falling salt and carries the fine insoluble impurities to the overflow. Overflowing brine is directed to a settling pond where the insolubles are collected. Clarified brine is returned to the process. Water added to the process for dissolution of fines and formation of pure brine leaves the process carrying soluble impurities. This sequence of unit operations is called the SALEX-B (Basic) process and is common to all the SALEX process variants.

In the SALEX-C process (with Crushing, for the Chemical industries) the salt is selectively ruptured in a special type of shear force dry rupturing equipment operating with a precisely defined gap and a predetermined differential velocity. The energy and raw salt consumption are somewhat higher but the SALEX-C salt can achieve much higher purity.

The SALEX-M process (with hydroMilling) is employed where quality reaching vacuum salt standards is required and where the higher energy and raw salt consumptions are justified. The salt is first treated in a sequence corresponding to the SALEX-B or SALEX-C process, then passed through the hydromill of special design and purified again in a process similar to the SALEX-B sequence.

Since the salt product is very fine, another type of centrifuge (pusher type) must be used. The SALEX-M salt can be used in the chloralkali industry, but usually it is dried, screened, conditioned with additives and packed to ensure the best appearance, cleanliness, brilliant whiteness and excellent free flowing properties appreciated in the food market.

**SALEX compared with conventional processes**

In one of the first SALEX plants incorporated in a membrane cell chloralkali plant, Krebs Swiss had the opportunity to compare the process efficiency with the same salt but once with conventional co-current and then with counter-current flow of brine.

With co-current flow of brine, the hydroextraction and hydroclassification stages were out of operation. When the

counter-current flow was established, the hydroextraction and hydroclassification became operative and the performance of the plant has markedly improved. The results illustrate the effectiveness of the unit operations hydroextraction and hydroclassification that are inherent to the SALEX process.

**Performance comparison of SALEX**

One of the largest SALEX plants ever built, a 130 tph SALEX-B plant in Spain, has undergone a rigorous commissioning test. During the test, the water input and the distribution of water in various injection points were optimised. Whereas at the beginning of the test the plant efficiency was fluctuating around 90%, it has reached 98 - 99.5% when the optimum operating parameters were found.

The plant operates only during the salt harvesting season. Still, the investment in the plant has been paid back in 2 1/2 years with the savings on brine purification chemicals and with the reduction of salt losses compared to the previously employed conventional salt washing plant.

Recently, a 40th SALEX-C plant was commissioned in the south of India. The chloralkali plant in which the SALEX-C plant has been incorporated, buys salt along the eastern and southern coast of India. The salt is washed in the saltworks by spraying water on the heaps. After the washing the salt is 99.0 - 99.4% pure.

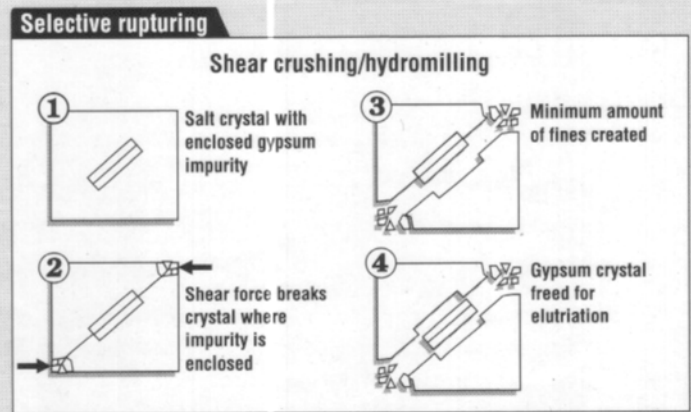
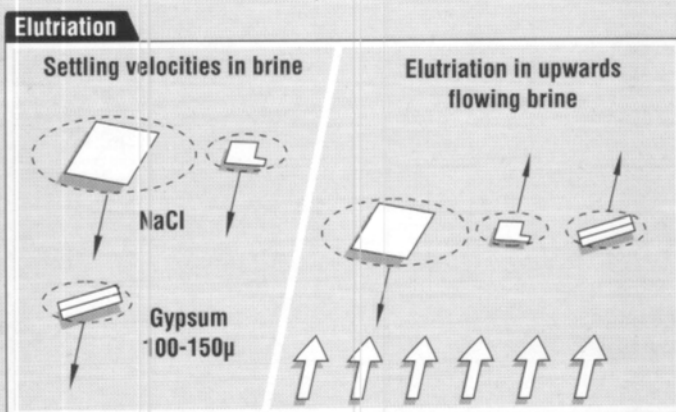
The upgradability of these salts varies widely. There are some excellent salts available from the Tuticorin area but some rather poor salts produced near Madras. The SALEX-C plant purifies this mixed feedstock to up to about 99.7% purity.

**SALEX salt for human consumption compared with vacuum salt**

Refined salt for human consumption should be pure and white. The purity of SALEX refined salt matches, or even exceeds, the purity of vacuum salt, although there are differences. Whereas the impurities in the SALEX salt consist of CaSO<sub>4</sub>, MgSO<sub>4</sub> and MgCl<sub>2</sub> in the natural proportions, the main impurity in the vacuum salt is Na<sub>2</sub>SO<sub>4</sub>, the residuum of the chemical brine purification.

**SALEX/vacuum salt comparison**

The whiteness of SALEX refined salt often exceeds the whiteness of vacuum salt quite substantially. The special



	<i>SALEX-M/0.4 salt Plant 1</i>	<i>Vacuum salt from Switzerland</i>
CaSO <sub>4</sub> (ppm)	136	17
MgSO <sub>4</sub> (ppm)	55	5
MgCl <sub>2</sub> (ppm)	74	
Na <sub>2</sub> SO <sub>4</sub> (ppm)		420
Insolubles (ppm)	20	20
NaCl (%)	99.972	99.954

Krebs Swiss hydromill has the unique capability to remove yellow colour from salt and give it a blue tinge that makes the salt to appear even whiter.

#### **SALEX-F under development**

Many types of rock salt contain impurities (anhydrite, insolubles) dispersed throughout the crystalline salt. Such salts can be upgraded in the SALEX-M process, for example, from 95% to 99% purity. In many cases, such performance would not be interesting. However, if the salt could be upgraded to say 99.7% or better, upgrading would become attractive.

A review of processes based on differences in certain properties of sodium chloride and calcium sulphate, such as density, colour, and electrostatic and magnetic properties have shown that the purity achievable with such processes is insufficient. Other disadvantages, such as limited applicability (not all impurities are heavy or dark) or high energy

consumption, decided against these processes.

Flotation was the only unit operation that was promising. Flotation takes place in the SALEX process naturally. Krebs Swiss only had to enhance the natural flotation with suitable reagents. In search for reagents, they came across a potash mine with a plant for salt flotation. The floated salt was used by chloralkali producers using mercury and membrane cells.

The discouraging aspect was that the salt purity achieved in that plant did not even reach 99%. However, combining the flotation with the SALEX-M process provided the answer. With the same salt and the same reagents, but with the Krebs Swiss hydromill and hydroextraction, purity of 99.7 - 99.8% NaCl became achievable. The process is called the SALEX-F process (with Flotation).

Chloralkali producers using mercury cells and rock salt are interested in the SALEX-F process. They are presently discharging up to 40kg of mercury contaminated sludge per tonne of caustic. The sludge disposal may cost up to DM 1,000/t. Environmentalists press them hard for reduction of contaminated output. The economy of the alternatives — SALEX-F salt versus vacuum salt — speaks clearly for SALEX-F.

#### **Acknowledgement**

The author thanks Mr Peter Chromec, marketing and process manager of the salt technology department of Krebs Swiss, for collection and presentation of the data published in this article.