Novel Technology Makes Entry into Salt and Chemical Industry

Summary

In late 1987, Krebs Swiss was awarded a contract to supply a Salex-C¹ salt upgrading plant to Gujarat Alkalies and Chemicals who operate a chlorine plant at Vadodara, India. In early 1989, this first Indian salt-upgrading plant went on-stream.

As a consequence of employing the Salex-C process to upgrade their salt feedstock, Gujarat Alkalies and Chemicals, who use barium carbonate, caustic lye and soda ash for treatment of the brine required for their chloralkali cells, can reduce the cost of brine purification chemicals by more than a half. Discharge of mercury-contaminated sludge can be reduced by almost 70%. The project, estimated at 1.8 crores Rupee (approx US\$1.2m), has a payback of less than two years. Already during the construction period, further contracts have been awarded to Krebs Swiss by other clients who suffer from poor quality of local salt.

The Salex process is an advanced salt purification technology engineered for high efficiency removal of impurities with exceptionally low losses of salt, low consumption of energy and high return on investment. The first commercial plant employing the Salex salt upgrading technology went into operation in Olhao, Portugal in 1983 to produce refined salt. Today, the various versions of the Salex process find application in solar saltworks, in chloralkali and soda ash manufacture, in table salt production and in purification of rock and by-product salt.

Traditional sources and quality of salt

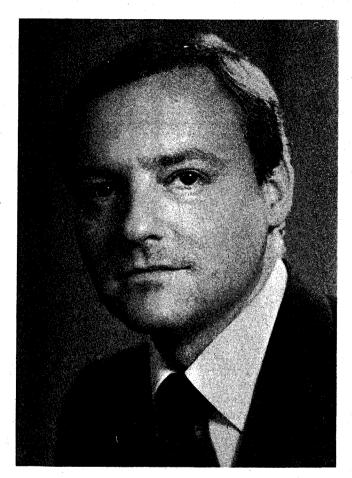
The salt-based industries in the US and Northern Europe have been obtaining their salt feedstocks by mining of high-quality rock salt deposits and by vacuum crystallization of brines from solution mining. In recent years, new salt-based industries have been established around the world, many in the developing countries. Excessive cost of importing the traditional grades of 'vacuum crystallized' or other high-quality salts has led to utilization of local sources of salt with higher and different levels of impurities, often originating from local salt mines, lakes and solar saltworks.

Fig 1 compares the range of impurities in the traditional refined or high-quality rock salt available in Europe or North America with that of solar salt.

Impurities in salt have costly consequences

Worldwide, some 180,000,000 t/y of salt is produced as rock salt, solar salt and solution mined brine for direct use. Of this, an estimated 100,000,000 t/y of salt is purified by

²SALEX is the Registered Trademark of KREBS SWISS, Zurich, Switzerland for its salt upgrading process with hydroextraction of impurities.



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Fig 1 Salt analysis comparison

Analysis	Traditional Salt (%)	Solar Salt (%) 0.1–0.3	
Ca	0.0004-0.04		
Mg	0.0001-0.01	0.1-0.8	
SO ₄	0.005-0.2 0.4-2		
Insolubles	0.0-0.1	0.5-2	
NaCl	99.6–99.99	9399	

various methods. The balance is used in its crude state with the impurities present in the natural salt deposits.

As a consequence of magnesium impurities in solar sea salts, some US\$100,000,000/year worth of losses is incurred in washing and stockpiling operations in solar saltworks around the world.

To deal with impurities in brine feed to chemical and electrochemical manufacturing plants, the chloralkali industry spends an estimated US\$1,000,000,000/year for

brine purification chemicals and disposal of mercury-contaminated sludge.

The salt-refining industry as a whole spends some US\$5,000,000,000/year in converting natural salt into refined product.

Apart from incurring costs, impurities in salt cause operational difficulties in industrial processes and reduce the value of the salt in the market-place. Cost-effective salt purification has a worldwide economic and environmental relevance.

Fig 2 shows the main solid and liquid impurities present in crude solar salts.

Fig 2 Impurities in solar salt solids and liquids

Impurity	Solid/Crystal	Liquid/Solution	
CaCO ₃	Calcium Carbonate		
CaSO ₄	Gypsum	Low Concentration	
MgSO ₄	Astrakanite	Magnesium Sulphate	
3,7	Bitter Salt		
$MgCl_2$	<u> </u>	Magnesium Chloride	
Insolubles	Clay, Sand etc		

Traditional methods of salt purification

Salt can be purified, in general, by one of the following two techniques:

- Mechanical washing
- Vacuum crystallization

Mechanical washing purifies salt to about 98%–99.5% NaCl. Salt losses are around 10%–20%.

Vacuum crystallization produces salt with NaCl content in the range of 99.7%–99.99%. Vacuum crystallization investment and operating costs are many times higher than those for salt washing.

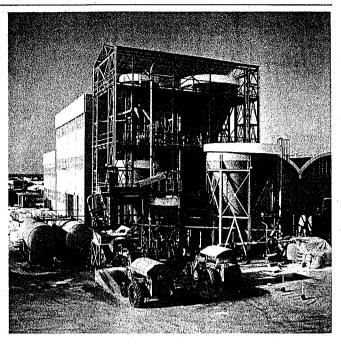
Development of Salex salt-upgrading process

Generally, it is possible to remove much higher levels of impurities from salt than by washing even without costly dissolution and recrystallization; salt purities in the range of 99%–99.95% NaCl are achievable.

With the objective of utilizing this basic physical behaviour of natural salt in developing a more efficient salt-purification process, the principles of formation and removal of impurities were scientifically researched by Krebs Swiss.

Earliest work was directed towards technical advancement of salt washing. Soon it became clear that the intrinsic weaknesses of mechanical processing leave insufficient scope for improvement. However, when countercurrent hydroextraction, hydroclassification and elutriation were employed, a dramatic rise in purification efficiency resulted. The process was given the name Salex.

The second phase of work by Krebs Swiss led to the development of a computerized modular design of Salex plants, engineered for various applications, with a range of processing alternatives for adequate economy. The Salex technology provides substantial technical advance



Salex Salt Upgrading Plant.

over inefficient salt washing and high-cost vacuum crystallization.

Fig 3 shows the various chemical engineering unit operations employed in the Salex process.

Saltwork productivity and salt marketability is improved with Salex-B process

In solar saltworks, salt is harvested from the crystallizing ponds as a mixture of salt crystals and mother liquor containing magnesium salts in a high concentration. During storage, the salt quality improves, until it becomes constant after about six months. This effect is commonly known as 'rain washing'. It is also known as 'natural purification' which is the more accurate description, since it also occurs in places where there is no rain.

Magnesium salts are highly hygroscopic. They absorb moisture from the air which dilutes them and facilitates their slow flow out of the stockpile. In this process, sodium chloride dissolves and dissipates, together with the magnesium, to the ground. The sodium chloride losses due to this phenomenon amount to 10%–15%.

In some saltworks, salt is washed before it is stockpiled. If, however, the salt is washed imperfectly, which is the

Fig 3 Unit operations employed in Salex salt upgrading process

Hydroextraction
Agitation
Elutriation
Hydroclassification
Options:

Selective Dissolution
Centrifuging
Sedimentation
Screening

Crushing
Hydromilling

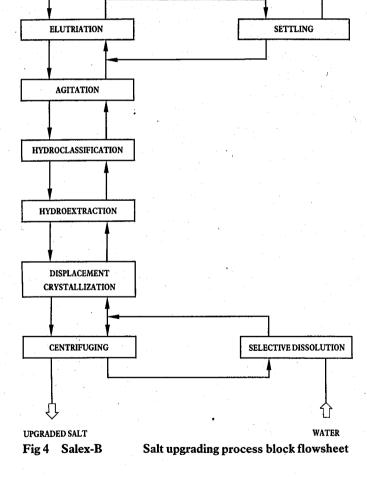
case with most conventional salt-washing methods, the 'natural purification' continues and the overall salt losses are even higher than without washing.

When employed in the solar saltworks, the Salex-B process purifies the salt completely, so that the 'natural purification' effect and the related salt losses are eliminated. The sodium chloride losses in the Salex-B process are only 1%–2%. Therefore, the Salex-B process substantially increases the effective salt production of solar saltworks. In addition, the Salex-B process markedly improves salt purity and value, particularly when the salt is supplied to the chloralkali industry or for exports.

Fig 4 shows the design configuration of the Salex-B process.

RAW SALT

PURGE



Brine treatment cost in chloralkali plants is reduced with Salex-C process

In the chloralkali industry, salt together with impurities is dissolved in the electrolytic brine. Prior to the electrolysis, the brine must be purified using various chemicals. The consumption of chemicals is directly proportional to the content of impurities in salt.

If impurities are removed in the Salex-C process prior to salt dissolution, the consumption of brine purification chemicals is reduced accordingly. Experience has shown that an investment in a Salex-C plant can be paid back within a year or two just by resultant savings in brine purification chemicals.

Fig 5 shows the savings in the cost of brine treatment chemicals at Gujarat Alkalies and Chemicals resulting from the use of Salex-C upgraded salt instead of mechanically-washed salt.

Fig 5 Brine treatment chemicals cost with Dahej washed and Salex-C upgraded salt

Analysis	Dahej Washed (%)	Dahej Salex-C (%)	
Ca	0.174	0.055	
Mg	0.067	0.048	
SO_4	0.553	0.18	
Insolubles	0.33	0.16	
NaCl	98.8	99.5	
Chemicals cost	(\$/ton salt)	(\$/ton salt)	
NaOH (\$300/t)	1.0	0.7	
BaCO ₃ (\$400/t)	5.0	1.4	
Na ₂ CO ₃ (\$200/t)	0.2	0.4	
Total	6.2	2.5	

Salt refiners boost profits with Salex-M process

Traditional salt processing consists of washing, drying, crushing and screening. Salt processed in this way is, at the best, dark-white. The crystals are irregular sharpedged splinters, so that the salt has limited free-flowing properties. It is hygroscopic, so that its initial free-flowing ability is quickly lost, despite use of additives.

Salt washing removes surface impurities and drying removes surface moisture. But salt cyrstals contain impurities enclosed inside. When salt is crushed after drying, the impurities are freed. The solid impurities, such as dust, spoil the salt's white colour. Magnesium containing mother liquor spills out from fractured cavities, freeing its hygroscopic power, so that the salt begins to absorb moisture from the air and becomes damp and sticky. With rising quality standards all around the world, manufacturers of such 'refined' salt find it increasingly difficult to sell their product.

In the Salex-M process, hydromilling selectively ruptures the salt crystals where the impurities are embedded and provides the ruptured crystals with regular, rounded form. Subsequently, the impurities are separated. Purities of refined solar sea salt of up to 99.92%–99.96% have been reached.

The Salex-M process is employed as the first stage of the Salex-R salt refining process where it is followed by drying, screening, conditioning and packaging. In the market, Salex-R refined salt matches the quality of vacuum salt at substantially lower production cost, leaving a healthy profit margin for the producer.

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Crude Salt	Process	Process Characteristics	
Product purity: 99.3		Increases solar saltwork productivity Product purity: 99.3–99.8% NaCl Salt losses: 1–2% NaCl	
Solar salt	Salex-C	Improves brine treatment economy Product purity: 99.5–99.9% NaCl Salt losses: 2–4% NaCl	
Solar sea salt	Salex-M	Salt refining Product purity: 99.7–99.95% NaCl Salt losses: 3–6% NaCl	
Rock salt, by-product salt	Salex-F	Enhanced removal of insolubles Product purity: 99–99.9% NaCl	
Solar sea salt	Salex-R	Refined table salt production Product purity: 99.7–99.95% NaCl Salt losses: 3–6% NaCl	

Salt from rock and by-product deposits becomes more valuable with Salex-F process

Rock salt is, as a rule, much cheaper than solar salt. However, salt deposits in mines frequently consist of sub-standard grades, such as 'red', 'brown', 'gray' or 'black' with a high percentage of anhydrite and clay. The market for such salt is limited to a few industrial users.

By-product salt deposits from sylvinite production often contain millions of tons of NaCl. The high content of impurities in such salt deters potential buyers.

Many such low-value salts can be upgraded with remarkable results. The separation properties of the salt and impurities are modified in the Salex-F process using special processing techniques. Up to 95% of impurities can be removed and dark salt can be turned into almost-white. Extensive testing and optimization of the operating conditions is required to determine the performance of the Salex-F process for each particular salt. Krebs Swiss has facilities to analyse and test the upgradability of any type of salt.

Krebs Swiss

Krebs Swiss (CH-8022 Zurich, Switzerland; Tlx: 815 348; Tel: 01/202 69 05) is an internationally-renowned company of chemical engineering consultants and process plant contractors serving the salt, chemical and electrochemical industries. Its reputation is founded on an impressive record of projects completed in most parts of the world.