

The Processing of Solar Salt Feedstock for Membrane Cell Chloralkali Plants

presented to

**The Indian Institution of Chemical
Engineers'
International Seminar on
'Membrane Cell Technology for the
Chloralkali Industry'
at Vadodara, 12th March 1988**

by

KREBS SWISS
Krebs & Co Ltd
Chemical and Electrochemical Plants
Claridenstrasse 20
CH - 8022 Zurich / Switzerland
Phone (01) 202 69 05 Telex 815 348
Telefax (01) 201 41 61

The Processing of Solar Salt Feedstock for Membrane Cell Chloralkali Plants

The use of solar salt as feedstock for chloralkali plants leads to higher brine treatment costs and to reduction in the operational efficiency of the brine plant. The higher brine purity requirements of membrane cells accentuate these problems. The paper reviews processing options for removal of the impurities and the structural formation of the impurities in the salt. Development, successful operation and operational benefits are presented for the SALEX-C (1) salt upgrading process developed by KREBS SWISS to provide a cost effective means to improve chloralkali plant operation when solar salt feedstocks are employed. Such improvement is particularly relevant to membrane cell operation.

Conventional Chloralkali Industry Feedstock Practises.

Since the early days of its development in the last century, the chloralkali industry in North America and Europe, has drawn its industrial salt feedstock by solution mining of salt deposits, for direct use in diaphragm cells or for processing by vacuum salt crystallisation for mercury cells as well as for the new membrane cell plants or by drawing on high quality rock salt deposits. Because of the low impurity content of such feedstocks, suitable brine quality for the chloralkali electrolysis could most readily be obtained by relatively simple chemical treatment of the brine. With the small amount of treatment required the cost of the treatment chemicals was insignificant. Clarification after the treatment was relatively simple and the amount of sludges was small.

Recent Changes in Brine Demand and Salt Source.

During this century, chloralkali production has extended around the world as developing countries have established their own basic chemical industry. Many of the newer production plants, particularly among those built in the last 2-3 decades have been located in the "sun belt" countries, where most if not all of local salt production is by solar evaporation of sea water. High costs of importing the traditional grades of "vacuum crystallised" or other high purity salt and restrictions on importation have induced chloralkali producers in such countries to use the locally available solar salt as feedstock for their plants. In practice this has meant feeding the plants with higher and different levels of impurities than

Fig 1 - SALT ANALYSIS COMPARISON
CHLORALKALI PLANT FEEDSTOCK

Analysis	Traditional Salt (%)	Solar Salt (%)
Ca	0.0004 - 0.04	0.1 - 0.3
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	93 - 99

those for which the primary brine processing was originally conceived.

Fig 1 compares the range of impurity content applicable to the traditional feedstock employed in European or North American chloralkali plants with that for solar salt sources.

Over the last 10-15 years, changes in the chloralkali production processing - firstly through introduction of dimensionally stable metal anodes and secondly, through introduction of the membrane cell process - have demanded higher standards of purified brine. As a result, most attention in the development of improved methods of brine purification has been directed towards meeting these higher purification requirements and little progress has been made in facing the problems specific to the use of solar salt.

Higher Treatment Costs for Solar Salt Brine

Use of the conventional chemical treatment methods for the "primary purification" of brines obtained from solar salt feedstocks has resulted in ex-

(1) SALEX is the Registered Trademark of KREBS SWISS for its salt upgrading process with hydroextraction of impurities

Fig 2 - TREATMENT CHEMICALS
COST COMPARISON

Analysis	Typical High Purity (%)	Typical Solar (%)
Ca	0.03	0.25
Mg	0.01	0.35
SO ₄	0.1	1.0
Insolubles	0.06	0.5
NaCl	99.8	97.2
Chemicals Cost (\$/ton salt)		
NaOH (\$300/t)	0.4	4.0
BaCO ₃ (\$400/t)	0.6	9.4
Na ₂ CO ₃ (\$200/t)	0.5	-
Total	1.5	13.4

cessive costs caused by the increased requirement for treatment chemicals for removal of the higher content of impurities contained in the solar salt.

Fig 2 compares the cost of treatment chemicals for the typical high purity salt feedstock employed in a North European chloralkali plant with that for a typical feedstock based on locally produced solar salt.

With a high purity salt source, treatment chemical costs represent only a small proportion of the value of the salt, but with solar salt, chemical costs for treatment can be significant. Considering a typical delivered price of \$20/ton for raw salt, the treatment cost shown in Fig 2 would represent approx. 8% supplementary charge when processing high grade salt but 65% for the solar salt. In some locations where the solar salt is of inferior quality and where imported barium chemicals have a higher value, the cost of treatment chemicals can be higher than the cost of the salt itself.

For brine treatment, the caustic soda requirement is met by recycle from the chloralkali plant's production. At some plants, soda ash is also provided internally by carbonation of caustic soda product. In such cases, true cost of treatment chemicals may be understated. Cost of barium chemicals is nevertheless a useful indicator, since this is purchased from outside and in some cases may have to be imported.

Impact of Membrane Cells.

One of the first relevant problems to be faced with membrane cells, is the lower tolerance limits for sulphate in the purified brine feed to the cells. For membrane cells, the sulphate limit is reduced from 13 gpl for metal anode mercury cells, to a maximum of 5 gpl. Adherence to this limit is important because it has been demonstrated that with higher sulphate levels crystallisation occurs in the membrane, with a consequent deterioration in performance and reduction of membrane working life. In some mercury cell plants the lime-soda process is used to control sulphate contamination but this is not desirable with membrane cells and even with mercury cells has the undesirable side-effect of increasing the formation of cell "butter" and neces-

sitating more frequent cell cleaning. Brine purging can also be used to reduce the sulphate content in the circulating brine system, but with membrane cells, the effectiveness of the purge is reduced, because of the lower sulphate level in the brine. At the same time, the salt losses resulting from brine purging become significant. The extent of sulphate removal required from the brine system is directly dependent on the level of sulphate contamination in the salt feed. Hence, reduction in the sulphate contamination of the salt directly reduces the sulphate removal cost in the brine treatment plant.

Although tight tolerance limits are imposed on hardness metals content of brine feed for membrane cell operation, the required levels upstream of the secondary brine purification plant are generally unchanged. However, uniform operation with consistent quality of primary purified brine is essential if the secondary treatment plant is to work effectively and efficiently. In the primary treatment plant efficient clarifier performance requires that the Ca : Mg ratio should be greater than 1.0. With traditional salt feedstocks, there is usually no problem in meeting this requirement. With the higher magnesium content of solar salt, the ratio is often less than 1.0, with resulting problems in clarifier performance. The disturbance to primary treatment caused by the higher impurity levels of solar salt, particularly in respect of higher magnesium content and the related deterioration of clarifier performance, can lead to irregularities in brine purity at inlet to the secondary treatment. This puts a greater burden on the secondary treatment plant, requiring increased frequency of regeneration of the ion-exchange resin and increasing the risk of break-throughs and consequent damage to the membranes.

A further problem with use of solar salt as feedstock to a membrane chloralkali plant is its propensity to cause "magnesium peaks" in the brine plant. When the brine saturators are charged with salt intermittently, the concentration of magnesium in the brine increases abnormally because of the higher concentration of the magnesium salts on the surface of the solar salt crystals. Such peaks will further upset performance of the secondary brine treatment and increase the risk of break-throughs and membrane damage. Even with mercury cells, magnesium breakthroughs are harmful in causing an excess of hydrogen in the chlorine cell gas.

Options for Improved Operation with Solar Salt.

Although the manner in which solar salt is crystallised and harvested can have an important influence on the level and types of impurities present in the raw salt, the industrial user has little or no control over the quality of the salt acquired from a particular source. Hence processing techniques to be

Fig 3 - PROCESSING OPTIONS
FOR BRINE TREATMENT

Chemical Treatment	Precipitation	Absorption
Clarification	Polishing	Ion Exchange
Filtration	Purging	Dechlorination
Flocculation	Sludge Dewatering	CaSO ₄ Precipit'n

employed by the user must be based on either or both of the following -

- Removal of impurities from the salt before dissolution or by selective dissolution during the dissolving process

- Removal of impurities from the fresh brine prepared as feedstock for the chloralkali plant and prior to any secondary brine purification process.

Fig 3 lists unit operations employed as processing options for impurity removal from the brine system, either by treatment of the fresh brine after dissolution of the salt or from the recycle after the electrolysis.

These are the techniques that are most commonly practised in chloralkali plants. They represent the simplest approach for the non-specialist designer. However, they suffer economic and operational deficiencies when employed with raw solar salt. This imposes restrictions on options available for achieving improved performance with these brine processing operations.

Techniques have been developed for certain rock salts with high gypsum or anhydrite content, for selective dissolution by suppression of the dissolution of the specific impurity during the salt dissolving operation. However, these have found limited success in application to solar salt.

This leaves the apparently more difficult option of removing impurities directly from the crystalline salt or "upgrading" of the salt prior to its dissolution. Earliest attempts to remove impurities from raw solar salt were based on the use of water washing to physically remove dirt and some of the surface contamination. This approach has been practised in some solar saltworks. Although marginal improvement in the salt quality can be achieved, the washing operates at low efficiency and the quality improvement is achieved at the expense of high salt losses, generally in the range of 10-20%. When mechanical washing plants are employed, involving moving parts exposed to air and seawater, they suffer excessive corrosion, and their operation and maintenance is expensive and not cost effective.

Formation of Impurities in Solar Salt.

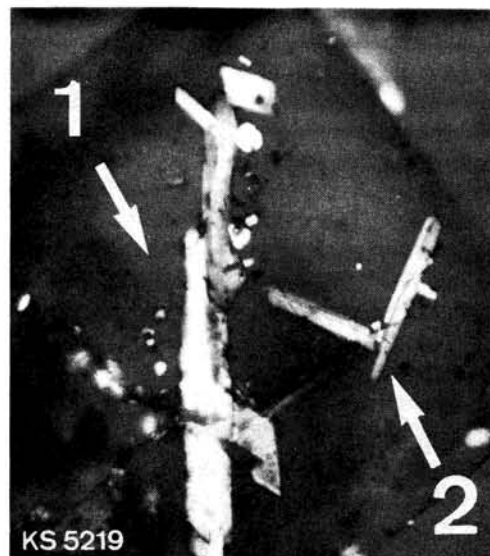
Although impurity levels in solar salts are high, the range of impurities is limited. The primary impurities are the calcium and magnesium salts present in the seawater. With solar salt the form, location and structure of the impurities in the salt

crystals is dependent on the manner in which the salt has been crystallised and harvested. In devising techniques for efficient and effective removal of these impurities, an understanding is required of the mechanisms involved in their formation during the solar salt production process.

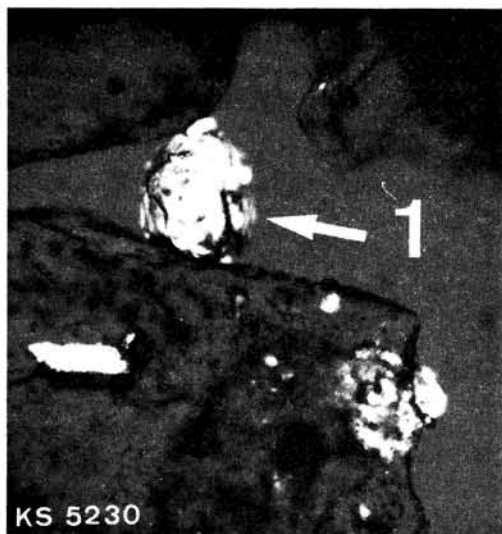
When sea water evaporates, the first component to precipitate is calcium carbonate. At 16.5 °Be, the seawater becomes saturated with calcium sulphate, which eventually precipitates as gypsum in the form of long needle shaped crystals. At 25.5 °Be, the sodium chloride reaches saturation and halite begins to crystallise with the remainder of the gypsum. If the brine is oversaturated with calcium sulphate, as it is frequently the case in solar saltworks, the amount of gypsum precipitated together with the halite is increased. The needle like gypsum crystals become enclosed within the growing halite crystals and entrapped between them so that their further growth is impeded. The gypsum crystals will not normally exceed 0.3 mm in length. Fig 4 is a high resolution salt crystal photograph in phase shifted polarised light showing two gypsum crystals, one on the surface and the other grown inside a halite crystal.

By the time the seawater's density has reached 29 °Be, about 80% of the sodium chloride content will have crystallised. At this density, the evaporation rate slows down and the bitterns are discharged prior to the harvesting of the crystallised salt. Draining of the bitterns takes time and is incomplete. During the draining operation, further evaporation takes place and the magnesium components also reach saturation and begin to crystallise out of bitterns. First magnesium component to crystallise is astrakanite ($\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$), see Fig 5, followed by bitter salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$),

Fig 4 - IMPURITIES IN SOLAR SALT
BITTER SALT AND GYPSUM



1. Bitter salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) precipitated on halite
2. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) occluded on and imbedded in halite

Fig 5 - IMPURITIES IN SOLAR SALT
ASTRAKANITE

1. Astrakanite ($\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$) attached to halite

Fig 6 - IMPURITIES IN SOLAR SALT
SOLIDS AND LIQUIDS

Impurity	Solid/Crystal	Liquid/Solution
CaCO_3	Calcium Carbonate	-
CaSO_4	Gypsum	Low Concentration
MgSO_4	Astrakanite Bitter Salt	Magnesium Sulphate
MgCl_2	-	Magnesium Chloride
Insolubles	Clay, Sand etc	-

Fig 4, and other complex salts containing trace impurity components.

Fig 6 shows the main solid and liquid impurities present in solar salt. A high proportion of the gypsum crystals is present in the salt crust that is disintegrated during the harvesting operation and in consequence can be separated physically from the larger halite crystals. Astrakanite and bitter salt - the main solid magnesium containing impurities in dry solar salt - are found partly loose or adhering to the surface of the halite crystals and partly embedded inside crevices in the halite. The remainder of the magnesium contamination remains dissolved in the salt's own moisture and is found occluded on the surface and in crevices and fissures on the surface of the halite crystals such as are shown on the photograph Fig 7. Apart from calcium and magnesium impurities, solar salt may contain windborn dust, clay and sand from the bottom of the crystalliser pans, shells and remnants of algae, together comprising the insolubles component of the raw salt.

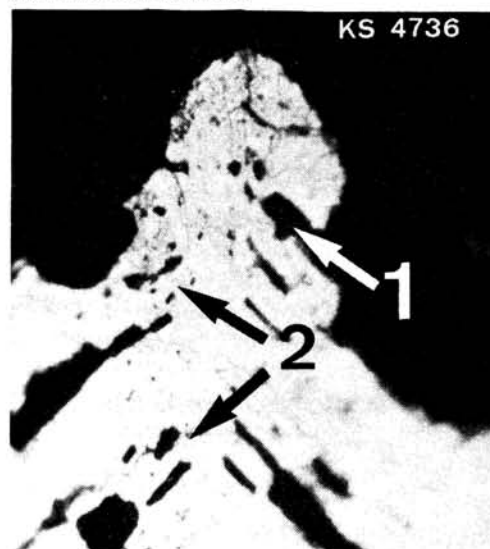
Development of an Upgrading Process

Removal of impurities from crystalline salt before its dissolution in brine is a subject that has

been studied by KREBS SWISS for more than a decade. Earliest work was directed towards technical advancement of the mechanical salt washing techniques, with the aim of seeking improvement in their inherent low efficiency and high loss of salt. This work showed that the intrinsic weaknesses in such mechanical processing leave insufficient scope for improvement to achieve appropriate economy. Additionally, the exposure to air and seawater in such plants, demands corrosion resistant materials, which pose a further obstacle to commercial viability. This initial work and parallel investigations on the characteristics and structural formation of the impurities in solar salt, indicated that development of a commercially viable purification process demanded a chemical engineering solution that would selectively make use of the applicable unit operations to match the precise characterisation and form of the impurities within the salt crystals. This second phase of development work by KREBS SWISS led to the conception of a fully continuous closed multi-stage upgrading process, designed and engineered for application with a range of processing alternatives and which was first put into commercial operation as the SALEX salt upgrading process in 1982.

The SALEX-C Upgrading Process

The SALEX-C process is the design configuration among the various Salex processes that is best suited to the requirements of industrial salt users for the upgrading of solar salt as feedstock for chloralkali plants. The process makes use of the unit operations shown in Fig 8, with the exception of the option for hydromilling that is not economical for this particular application, but which are incorporated in other versions of the SALEX process,

Fig 7 - SOLAR SALT CRYSTAL
CREVICES AND CAVITIES

1. Crevices opened to crystal surface
2. Cavities containing enclosed impurities

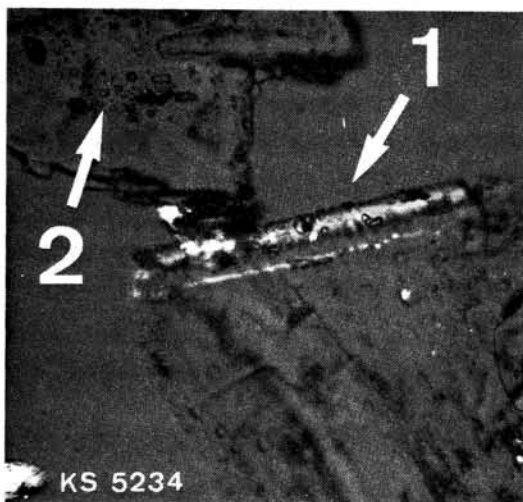
Fig 8 - UNIT OPERATIONS
EMPLOYED IN SALEX SALT UPGRADING PROCESS

Hydroextraction	Selective Dissolution
Agitation	Centrifuging
Elutriation	Sedimentation
Hydroclassification	Screening

Options:

Crushing
Hydromilling

Fig 9 - SELECTIVE RUPTURING OF SOLAR SALT
EXPOSING EMBEDDED GYPSUM

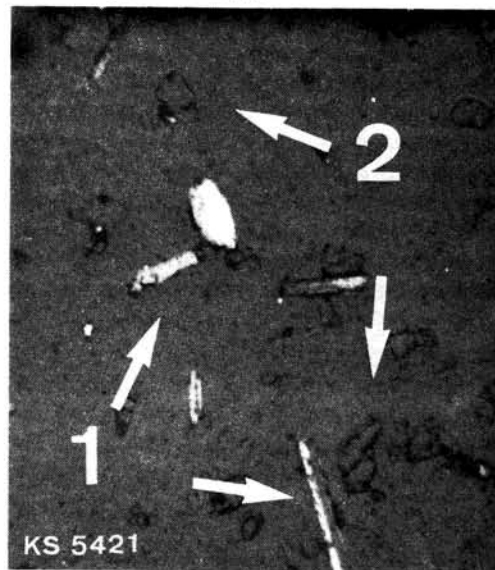


1. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) imbedded in halite,
exposed by selective rupturing
2. Cavities containing enclosed bitterns

developed for related salt processing applications. The SALEX-C process employs a combination of selective rupturing, elutriation, agitation and hydroclassification for separation and removal of the fine, needle shaped crystals of gypsum together with other fine, insoluble contaminants.

Halite crystals break preferentially along the planes weakened by the presence of enclosures. This physical property of salt is being made use of in the SALEX-C process for removal of a substantial part of the enclosed impurities. Fig 9 shows a photograph of a solar salt crystal selectively ruptured along the plane containing embedded gypsum crystal which has thus been exposed to removal. Followed by agitation, hydroclassification and elutriation, the gypsum crystals are removed from the process in the stream of circulating brine. This processing combination makes use of the particular shape of gypsum crystals which causes their sedimentation velocity to be equal to that of halite splinters much smaller in size. Fig 10 shows a photograph of solids removed from the process and illustrates that the largest halite splinter is only about one third of the size of gypsum. As the particular rupturing technique employed in the SALEX-

Fig 10 - GYPSUM REMOVAL BY ELUTRIATION WITH
COUNTERCURRENT BRINE



1. Gypsum crystals (0.1 - 0.3 mm)
2. Halite splinters (0.01 - 0.1 mm)

C process produces a very limited amount of such small fines, the losses of solid halite from the process are reduced to less than 1%. Magnesium salts are removed in a continuous countercurrent extraction or hydroextraction with a pure saturated brine solution. Selective brine displacement technique is employed to achieve a high concentration gradient across the hydroextraction stage of the process to achieve maximum magnesium removal and minimum loss of sodium chloride by dissolution. Near equilibrium conditions of the solubility system $\text{MgSO}_4\text{-MgCl}_2\text{-NaCl-H}_2\text{O}$ are maintained in the hydroextraction stage to achieve sodium chloride recovery from the pure make-up brine to the salt crystals which is required to minimise the salt losses by dissolution in the SALEX-C process down to 1-2%. Retention time for the various processing phases has been carefully designed to optimise the removal of magnesium salts not merely from the surface of the salt crystals, but also from the occluded mother liquor retained within the crevices in the halite crystals. Sedimentation is employed for separation of insolubles and crystals of gypsum from the brine circuit. The process employs novel techniques for optimising the effectiveness of the small quantity of water employed and for use of undesired salt fines for saturated brine make-up.

Cost Benefits of Salt Upgrading

In the chemical treatment of brine, precipitation of impurities takes place according to stoichiometric reactions. Apart from the need for excess dosing, consumption of treatment chemicals is directly proportional to the content of impurities in the salt fed to the brine system. When impurities are removed by the SALEX upgrading process prior

to dissolution of the salt in the brine, the consumption of brine treatment chemicals is reduced proportionally.

When raw solar salt is continuously charged to the saturators of the brine plant, it is necessary to dose the primary treatment chemicals in excess of the stoichiometric requirements including the over-dosage, in order to accommodate for the variation in impurity content which is a characteristic of raw solar salts. With membrane cells which require 60-80% less brine than the mercury cells, the problem of salt quality fluctuations is accentuated in proportion. The excess of caustic soda demands additional hydrochloric acid in the subsequent acidification of the brine prior to feeding it to the membrane cells which increases the cost of both reagents. The SALEX-C process produces a uniform product that is hardly effected by the fluctuations in quality of the raw salt supply. Hence, the excess dosing of chemicals in the primary treatment can be reduced accordingly. This further reduces treatment chemicals requirements and reduces the risk of excess barium reaching the membrane cells. It also reduces formation of CO₂ in the chloralkali cell gas caused by the excess of soda ash.

Depending on the raw solar salt quality, the SALEX-C process will generally remove between 60 and 90% of the impurities present in the raw salt.

This is illustrated in Fig 11, which shows the percentage removal effected for each of the contaminants in various raw solar salts investigated recently by KREBS SWISS.

Fig 11 - IMPURITY REMOVAL FROM INDIAN SOLAR SALTS WITH SALEX-C SALT UPGRADING PROCESS

Impurity	Dahej Washed (%)	Impurity Removal (%)
Ca	0.174	68
Mg	0.067	28
SO ₄	0.553	67
Insolubles	0.33	52
Kutch Raw		
Ca	0.041	90
Mg	0.233	91
SO ₄	0.405	91
Insolubles	0.048	90

Fig 12 - 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)		
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

Fig 13 - BRINE TREATMENT CHEMICALS COST WITH KUTCH RAW AND SALEX-C UPGRADED SALT

Analysis	Kutch Raw (%)	Kutch SALEX-C (%)
Ca	0.041	0.004
Mg	0.233	0.022
SO ₄	0.405	0.038
Insolubles	0.048	0.005
NaCl	98.82	99.89
Chemicals Cost (\$/ton salt)		
NaOH (\$300/t)	2.7	0.5
BaCl ₂ (\$400/t)	3.4	0.1
Na ₂ CO ₃ (\$200/t)	0.7	0.4
Total	6.8	1.0

Fig 14 - BENEFITS OF SALT UPGRADING FOR CHLORALKALI MANUFACTURE

- Uniform feed for brine plant
- Improved brine plant performance
- Reduced sulphate treatment
- Reduced brine losses
- Increase in NaOH production
- Saving in treatment chemicals
- Elimination of Mg peaks
- Reduced brine sludges

Fig 12 shows a comparison of analyses for the same type of raw solar salt and the equivalent upgraded salt obtained by SALEX-C processing. Also shown in Fig 12 and 13 are the comparative costs for the respective treatment chemicals required in the primary brine treatment.

The saving in cost of the treatment chemicals is substantial. In respect to a typical \$20/ton delivered cost for raw solar salt this saving represents around 30% of the cost of the brine feed for the chloralkali operation. Such savings, together with savings from reduction of salt losses in the clarifier underflow and the cost of sludge disposal provide a rapid pay-back on the investment in the SALEX-C plant.

Operational Benefits of Salt Upgrading

Fig 14 lists the key operational benefits of upgrading of solar salt with the SALEX-C process before charging the salt as feedstock to a chloralkali brine plant. Of major significance is the provision of feed uniformity and the reduction in the amount of impurity charged to the brine plant. These improvements permit the primary brine plant to operate efficiently and in a stable and reliable manner. This in turn provides downstream benefits in respect of a uniform quality of brine to the secondary treatment

plant and reduced risk of breakthroughs and contamination of membranes.

As explained above, sulphate contamination is a particular problem with membrane cells. The typical 60-80% removal of sulphates achieved in the SALEX-C salt upgrading process considerably reduces the problem of sulphate removal and provides further insurance against damage of the membranes by sulphate contamination.

Magnesium peaks were discussed above. They are a source of operational instability in a primary brine purification plant operating with solar salt feed. Their elimination is a further contribution to assurance of reliability and uniformity of brine quality that is an essential requirement of successful membrane cell operation.

Brine losses are reduced by the reduction in the brine sludges and the reduced brine retention characteristics of the sludges, resulting from the improved Ca : Mg ratio. Brine conservation is also improved by the improvement in sulphate contamination and the consequent reduction in purging requirements.

A subsidiary benefit of upgrading is the potential for increasing the chloralkali production by reduction in usage of caustic soda product for treatment of magnesium salts. This improvement arises not only from the reduction in magnesium contamination, but from the ability to reduce the excess dosage - which also conserves recycle hydrochloric acid.

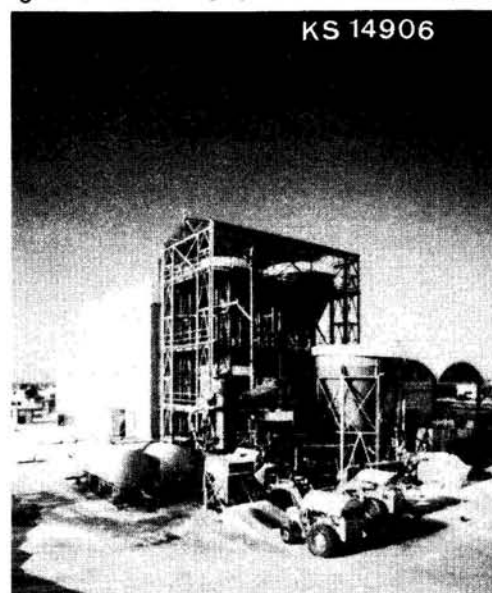
Indirect practical benefits of solar salt upgrading extend to such factors as reduced frequency for brine saturator cleanouts and brine filter backwashing.

The above benefits have been referred to membrane cell operation and although some of the benefits discussed are not as significant for mercury cell operation, the reduction in brine sludges is of prime importance to mercury cell plant operators because of the strict environmental regulations for mercury contaminated waste materials.

Ease of Operation and Maintenance

The equipment required for the SALEX-C upgrading process is incorporated in a compact structure that can be installed out-of-doors. Fig 15 shows a typical operating plant. The structure is installed immediately adjacent to the brine plant so that upgraded salt can be discharged directly from the unit to the brine saturators to provide continuous, automatic and uniform feed to the brine circuit, without any additional handling of the salt. The raw solar salt is delivered to the feed section of the upgrading plant from where it is automatically transported through the various processing operations to discharge from the final centrifuge stage

Fig 15 - SALEX SALT UPGRADING PLANT



Salexpor Ltd., Portugal, 15 t/h SALEX Plant

into the brine saturators. Because of its simplicity and continuous automated flow, the upgrading plant can be operated by the normal operating staff of the brine plant without need for staff increase. Because the plant equipment operates submerged, air-brine interfaces are avoided in most parts of the plant. Hence corrosion is effectively controlled without need for special materials of construction for those parts of the plant. This has the benefit of significant reduction in capital cost and in permitting local fabrication of the major part of the plant.

Related Salt Upgrading Applications

So successful has the SALEX upgrading process been in meeting the design objectives for removal of impurities from solar salt, that it has been possible to extend the processing approach to develop a design variant with additional processing steps able to produce a quality of salt suitable for edible or "table" salt requirements and comparable with refined salt grades produced by vacuum recrystallisation.