

## PURIFICATION OF ROCKSALT BY A NEW PROCESS AT LOW TEMPERATURE

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Rocksalt is a major raw material source for salt; industrial use of rocksalt requires a purification of the major impurities such as Ca, Mg,  $\text{SO}_4$  and sometimes of some minor impurities like K, Br. Washing of rocksalt (fine or coarse) is usually not enough for purification; a known purification process comprises dissolution of salt, chemical epuration of concentrated brine, and evaporation of water to crystallize a purified salt.

A new process has been investigated to purify rock salt without evaporation, thus saving the energy needed for evaporation in a classical vacuum crystallization process.

This new process consists of the following steps: (1) fine grinding of rocksalt, (2) dispersion of this fine salt in a saturated cold brine to make a slurry, (3) cooling this slurry below  $0^\circ\text{C}$ , (4) heating this cold slurry to  $5^\circ\text{C}$ , (5) epuration of the fine insoluble impurities by hydraulic classification, (6) separation of the purified recrystallized salt, (7) recycling to step 2 the saturated brine.

During step 3, all salt in suspension dissolves and recrystallizes as dihydrate crystal and all impurities are set free; some impurities dissolve, some recrystallise.

During step 4 purified salt is recrystallized at the desired particle size; separation of fine insoluble impurities and purified salt is made in step 5. Soluble impurities can be eliminated by the classical techniques from the recycled brine.

This process has been investigated on a lab and a small scale pilot plant; a few rocksalt sources have been tested; with a typical rocksalt of 98% initial purity, a final purity higher than 99.9% could be reached; more than 95% of impurities were removed. Several types of crystallizers and agitators have been tested. The major energy consumption is for grinding of rocksalt and for a heat pump between  $-5^\circ\text{C}$  and  $+5^\circ\text{C}$ ; investments should be lower than for the vacuum salt process.

Development and optimisation of this process is not finished; the product quality can still be improved and vacuum salt quality could be reached.

### 1. SOURCES OF SALT

Salt is a well distributed resource throughout the world; it is available in large deposits and in large water volumes of seasalt. The processes to obtain this salt can vary greatly.

#### 1.1. ROCKSALT

Rocksalt is found in large deposits; the usual techniques are mechanical mining; salt is obtained in different sizes which can be separated by usual sieving technology. Depending on the morphology of salt and the impurities, dry separations are sometimes used to partially purify salt: magnetic and electrostatic technologies have been reported in some mining of salt. No crystallization is involved in refining rocksalt and epuration is limited

#### 1.2. SOLAR SALT

Seawater is concentrated in large ponds heated by solar energy; evaporation occurs by the effect of wind combined with heating by solar energy. Supersaturation results from evaporation and salt crystallizes at the surface of the brine and later in the brine body.

Concentration of the seawater up to saturation can require most of the ponds surfaces, sometimes more than eighty percent. Crystallization of salt and the impurities may occur sequentially and it is the know-how of the seasalt producers to manage the crystallisation ponds efficiently in order to reach the best purity of salt. In order to improve the productivity of the ponds, feeding of the ponds with saturated brines resulting from another source of salt, like brine from solution mining has been reported.

To enhance the evaporation rate, heating of the brines with waste heat has also been reported (1)

and patents have been published. In this case the layer of salt harvested is larger than the usual thickness of salt obtained in the normal seasalt production.

### 1.3. SOLUTION MINING

Solution mining is an operation of dissolution of the underground salt deposit; water injected in the salt layer saturates in contact with salt and a saturated brine is pumped to the surface for treatment. Solution mining carried out in isolated cavities or in series of cavities connected together.

During dissolution, all impurities trapped in the rocksalt are freed and insolubles fall at the bottom of the cavity; soluble impurities dissolve and concentration of these impurities increase, sometimes up to saturation (calcium sulfate).

Saturated brine usually contains calcium, magnesium, potassium, sulfate, and bromide.

Brine epuration removes some impurities; classical epuration of brine precipitates calcium and magnesium; potassium, sulfate and bromide remain in solution and can accumulate during the evaporation and crystallization process.

For some processes like membrane electrolysis, a super epuration of brine is needed to avoid difficulties with membranes.

## 2. CHARACTERISTICS OF THESE SALTS

### 2.1. ROCKSALT

Rocksalt usually is not very pure; when this salt is used in deicing, this is not a major problem; however, rocksalt is also sold for industrial uses and with several percents impurities, a purification is often needed during the process; there is considerable pressure to improve the quality of rocksalt for some industrial applications and to decrease the costs of usage for customers.

Rocksalt can obviously be dissolved in water to prepare saturated brine; this solution is similar to the brine epuration of the brine from solution mining and all water must be evaporated.

There is a need for a process that is able to improve the quality of rocksalt but is cheaper in investment and energy than the usual vacuum evaporation process.

### 2.2 SOLAR SALT

Solar salt can be obtained at a rather good quality depending on the management of the crystallization

ponds; when harvested, special care is taken to avoid contamination by soil and other impurities. Some impurities can be trapped inside the crystals or between the crystals; washing is done to improve the quality; in some cases, washing can be preceded by intense mixing or mild grinding to free some of the impurities; these impurities can be separated by washing or washing plus hydraulic classification (1).

### 2.3. VACUUM SALT

Usually, salt from solution mining, after an epuration of calcium and magnesium, is crystallized by evaporation in a vacuum crystallizer; salt resulting from this operation is very pure provided that impurities not eliminated in the epuration of brine do not accumulate. A purge is necessary to decrease or limit the level of the following impurities (potassium, sulfate, bromide) in the mother liquor.

If a significant purge of mother liquor can't be disposed of, a treatment of mother liquor is required: one technique consists of precipitating the excess of sulfate with calcium in the form of gypsum or other mixed sulfate salt. Usual purge of 10 to 20 % can then be reduced to a few percent of the inlet feed.

Purity of this vacuum salt can satisfy the specifications of food grade and in some cases specifications of the pharmaceutical salt.

## 3. EVAPORATIVE CRYSTALLIZATION

### 3.1 DESCRIPTION

Several processes have been described and are used to obtain vacuum salt by evaporation and crystallization. The basic crystallizer to obtain a salt of 100 to 800 microns in size is a vacuum evaporation crystallizer: it is operated with an external circulation loop of magma of crystal and mother liquor. Heat is supplied to the magma by an external shell and tubes heat exchanger. Some deviations of this basic configuration are possible like the internal circulation with an internal heat exchanger or calandria. Steam removed from the boiling zone can be reused in two different ways: either this steam is recompressed and reused again in the same equipment (mechanical recompression steam evaporator) or it is used in another evaporative crystallizer (this is the multi-stage evaporation crystallizer).

When large particle sizes are needed, removal of fines is applied in some special crystallizers; particles of 500 to 1000 microns can be obtained.

When very large particles are needed (1 to 5 mm) the evaporative crystallizer is of the OSLO type: a clear saturated brine is heated to produce supersaturation by evaporation; supersaturated brine is desupersaturated in a liquid-solid fluid bed of large crystals. Supersaturation must be carefully monitored in the metastable zone and supersaturated brine is handled carefully to avoid uncontrolled crystallization before contacting the growing crystals in the fluid bed.

### 3.2. BASIC STUDIES IN EVAPORATION CRYSTALLIZATION OF SALT

Most of the basic studies in crystallization have been made for the evaporation crystallization processes.

Some basic papers, books or theses have been published (2,3,4).

The tools used in these studies are mainly:

- Mass balance in crystallizers
- Concept of saturation and supersaturation: diagram of solubility gives the equilibrium between the solid and the saturated solution. Supersaturation is created by heating and evaporation; supersaturated solution results from this operation; if this supersaturation remains in a zone called 'metastable', this solution does not precipitate crystal and can be handled. Some publications (7) have determined this metastable zone in the temperature range of 50 to 120 °C: width of this zone is in the range of 1 g/kg of solution. Experimental system used are described in publication (7). Comparison of the low value of supersaturation with solubility values of 270 g/kg means that supersaturation is difficult to reach by direct measurements (Density measurement can be used in lab). The experiments consist of lab tests to measure the rate of growth of crystals versus a supersaturation created by a change of temperature of a saturated solution. In pilot or industrially, the rate of growth can be reached by mass balance of the process and the total crystallization area of the solid; so, this data allows to reach the real supersaturation prevailing inside the crystalliser.

- Mechanisms and sources of nucleation: primary nucleation and secondary
- Rate of growth of crystals. Detailed mechanisms are described in literature; the overall rate of growth has been measured in publication of Rumford and Bain (6). At about 100 °C, salt has a very high rate of growth when supersaturation is of the order of 0.5 g/kg.
- Population balance concept. This problem has been studied by Randolph and Larson (5). The population density concept and the moments of the distribution are powerful tools to investigate the process of crystallization: ideal crystallizers and deviations from ideality in real crystallizers can be examined. Analysis of particle size distribution in MSMR crystalliser, can give the rate of growth of crystals and the rate of birth of the distribution.

## 4. PURIFICATION OF ROCKSALT BY A NEW PROCESS

For a long time, a process to purify rocksalt has been needed.

### 4.1. NEED FOR A NEW PROCESS

Rocksalt is extracted at very large volumes; the purity is often not high enough for industrial applications; there is always the possibility to produce refined salt by dissolution and recrystallisation of salt by the usual vacuum evaporation crystallization process. However, the costs of the total operation would be penalized by the initial costs of rocksalt that are usually higher than cost of salt obtained by solution mining. A process that can refine rocksalt at a total cost (cost of rocksalt plus cost of evaporation) lower or equal to the total cost of vacuum salt (cost of brine plus cost of vacuum crystallization) would be of interest for a number of applications. This need has been expressed many times; several preliminary studies were made internally inside Solvay.

This publication reports some results on a new promising process investigated in lab work and in limited pilot plant tests.



#### 4.2. PRINCIPLES OF NEW PROCESS

- ◆ Several principles are necessary to reach the objectives of a new process. Evaporation has to be avoided: as rocksalt is already solid, it would be a waste of energy if we had to dissolve it in water and evaporate again this water. This leads to the change of phase at low temperature: below 0 °C, the solid phase in equilibrium with saturated brine is sodium chloride dihydrate  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ . At this low temperature, rocksalt in suspension in a saturated brine should dissolve and recrystallize into the hydrate form; all impurities should be set free. All the impurities freed are of two types: soluble impurities and insoluble impurities. Soluble impurities accumulate in the liquid and in some cases can reach another limit of solubility. Insolubles will remain in suspension at their initial size. To make sure that insoluble and soluble impurities could be separated later, initial rocksalt has to be ground at a size smaller than a preset value compatible with final separation.
- ◆ To reconvert the dihydrate into the anhydrous salt, temperature of the suspension must be increased: solid dihydrate salt will recrystallise as sodium chloride and care must be taken to obtain the required particle size despite the presence of solid impurities.
- ◆ Classification of insolubles must be made to eliminate these insoluble in order to achieve a suspension of sodium chloride of a good purity.
- ◆ After mechanical separation of refined salt, the mother liquid could be treated, if needed, to limit the build-up of some soluble impurities in the recycled mother liquor stream.

#### 4.3. DESCRIPTION OF NEW PROCESS

The pilot is described in figure 1. This process involves the following steps:

- 1) Fine grinding of rocksalt at a size smaller than 100 microns
- 2) Dispersion of this fine salt in a saturated cold brine to make a slurry at about 5°C
- 3) Cooling this slurry below 0 °C. During this cooling step, all salt in suspension dissolves and recrystallizes as dihydrate crystals; all

impurities are set free; some dissolve (polyhalites are not the stable form in the saturated brine) and some recrystallize (calcium and sulfate can reach the gypsum limit of solubility); some insolubles remain solid.

- 4.) Heating up the suspension to 5 °C. During this step, purified salt is recrystallized in the presence of some fine insoluble materials. One key to this process is to have a good control of heterogeneous nucleation.
- 5.) Separation of the purified salt.
- 6.) Recycling of separated brine to step 2. This is the only place in the process where clear brine is available. So, if treatment is needed to limit some build-up of soluble impurities, it has to be done on this clear mother liquor.
- 7.) Provisional treatment of this liquid to limit some impurities: magnesium, bromide, .... Some brine with low calcium and low sulfate can also be generated if very pure brine is needed for a specific washing of salt.

#### 5. RESULTS FROM LAB EXPERIMENTS

Lab experiments have been performed on several topics: grinding of salt, rate of growth of sodium chloride crystals at low temperature, batch experiments of all steps of the process with several compositions of mother liquors, and batch experiments of additional epuration to improve final purity.

##### 5.1 RATE OF GROWTH IN LAB

We have been using the same principle of measurement as described by RUMFORD and BAIN (7). We have extended the range of measures to the low temperatures. Table 1 gives the rate of growth of crystal at a supersaturation of 1 g/kg of mother liquor

Table 1 Rate of growth

Supersaturation = 1.0 g/kg

Rate of growth is expressed in g per hour and  $\text{cm}^2$  of external surface area of cubic crystals (7)

Rate of growth, $\text{g}/\text{cm}^2 \cdot \text{h}$		
Temp, °C	Rumford	Solvay
73	0.060	0.075
38-40	0.010	0.035-0.043
12	-	0.0073
5	-	0.0021

## 5.2. METASTABLE ZONE

The metastable zone was extended till more than 3 g/kg at 5 °C

## 5.3. BATCH EXPERIMENTS OF PROCESS

### 5.3.1. EPURATION OF SALT IN LAB

The lab scale consists of a reactor of 3.5 l with a jacket and a draft tube, a pH meter, a thermostat and a classification column of 25 mm internal diameter and 1m height.

The methods of analysis are classical: calcium by complexometry with EDTA, calcium + magnesium by complexometry with EDTA, sulfate by gravimetry and potassium by ICP.

Total analysis of salts are made first by alkaline fusion followed by analysis.

A stock of brine is prepared, stored for 1 day, filtered and then analysed.

In some experiments this brine is enriched in soluble impurities in order to simulate accumulation of soluble impurities in mother liquors; the impurities tested have been sulfate, magnesium, calcium, potassium and in some cases bromide.

Rocksalt is grinded, and then suspended in the brine in the reactor.

The crystallization tests are made batch wise: first cooling of the slurry to a temperature below 0 °C (-8, -5, -2 °C); exothermal crystallization is observed. Hydrated salt appears in the form of hexagonal particles; density of suspension has to be limited at this stage.

Slurry is heated to reach a temperature slightly above 0 °C (2 to 5 °C); cubic crystals replace progressively the dihydrate sodium chloride. The slurry can be filtered, and then dried for analysis; alternatively a slurry sample can be put through an elutriation or classification step to improve purity; product can be improved through a final washing.

The insoluble impurities separated in the classification step are removed from the brine by decantation, if needed, with flocculation.

### 5.3.2. RESULTS FROM LAB TESTS: FIRST TESTS BEFORE PILOT PLANT TESTS

Rocksalt used in most of experiments was a salt from a German mine; limited experiments were performed also with rocksalts commercially available and residual salts from different origins. Rocksalt has a purity of 98 % and most of Ca, Mg

and SO<sub>4</sub> are present in the form of polyhalite (MgSO<sub>4</sub>.K<sub>2</sub>SO<sub>4</sub>.2CaSO<sub>4</sub>).

- Crystals of NaCl obtained in lab had a small particle size (50 to 250 microns); analysis have been performed on the salt larger than 100 microns
- Without enrichment of the liquor, and without epuration treatment, refined salt has a good quality (99.8 %).
- Addition of CaCl<sub>2</sub>, MgCl<sub>2</sub> and Ca(OH)<sub>2</sub> have been tested in several points in the process
- Ca(OH)<sub>2</sub> added to the clear liquid precipitates Mg(OH)<sub>2</sub> that can be separated by decantation; the level of magnesium can be maintained low.
- MgCl<sub>2</sub> has been added to look for limits of coprecipitation in the sodium chloride crystals.
- CaCl<sub>2</sub> has been added to modify the balance of Ca and SO<sub>4</sub> in order to precipitate CaSO<sub>4</sub>.

### 5.3.3. RESULTS FROM LAB: LAST TEST AFTER PILOT TEST

After the pilot plant tests, additional treatment of the salt obtained in the pilot have been made in order to explore the limits of the epuration.

Operation of additional washing and additional classification have been tested

The best results obtained in these tests are:

Salt from pilot	ASTM purity	: 99.8 %
Salt after additional treatment		: 99.95 %

## 6. RESULTS FROM PILOT EXPERIMENTS

Two campaigns of pilot tests have been made: one with a MSMR crystalliser and one with a well mixed crystalliser plus a removal of fines

### 6.1. WELL MIXED CRYSTALLISER: TYPE MSMR

First the flowsheet of pilot was identical to the one on lab scale as described in figure 1.

The first campaign allowed to test the various types of crystallisers and miscellaneous types of equipment.

The first dihydrate crystallizer is of the MSMR type with an external circulation loop to cool down the suspension to the desired level. Due to higher than expected thermal losses, heat had to be extracted at a higher rate to reach the required process temperature.

The second crystallizer is of the MSMR type also without a draft tube. The quality of the crystals was

not high enough :the smaller than expected size of the crystals was probably caused by an uncontrolled nucleation with the presence of impurities in this crystallizer .Crystals were not cubic .

Despite these problems ,the purity of the salt reached the same level as obtained in the bench scale experiments .

It soon became clear that the crystalliser and the agitator had to be modified.

## 6.2 WELL MIXED CRYSTALLISER + FINES REMOVAL

### 6.2.1. DESCRIPTION

The description of final configuration of pilot is given in [figure 2](#).The equipment consists of :

- Condux grinder :maximum production = 40 kg/h
- Slurry reservoir :Volume = 100 l --Density of suspension= 20 % -Temperature = 10 °c
- Dihydrate crystalliser :Well mixed reactor -- Temperature = -2 to - 5 °c--Density of suspension = 40° %--Volume = 100 l-- External loop of slurry through a multitube cooling heat exchanger
- Sodium Chloride final reactor :  
Well mixed reactor circulation type with a draft tube and an agitator . Design production = 15 kg/h . Initial density of suspension = 20 % increased later to 40 % . Annular zone to remove fines by fluidisation and hydraulic classification .Theoretical cutoff diameter of particles entrained = 50 to 70 microns .This withdrawal of fines with liquid allows to increase the density of suspension and reduce the level of supersaturation .  
External loop for sodium chloride slurry reheating to a temperature of 5 to 10 °C .
- Hydraulic classification in a column of 100 mm diameter
- Slurry of fines particles from crystallizer annular zone and from classification column are treated in a reservoir : fines are separated by decantation or filtration ; mother liquor is returned to a storage tank .
- Separation and washing of salt is made in a continuous pusher centrifuge ; liquid from centrifuge goes to the storage tank .
- Mother liquor from crystalliser , classification and centrifuge go also to the storage tank .

### 6.2.2. MAIN PROCESS PARAMETERS

We will report only one typical set of conditions leading to good results and stable operations .

- Purge = 3 % leading to an equilibrium for highly soluble impurities like K and Br being used as tracers .
- .Higher value of purge gives lower equilibrium values for K and Br and higher purity of salt in K and Br
- No addition of calcium chloride to precipitate sulfate , or no addition of calcium hydroxide to keep the Mg concentration.at low level in circulating liquor.
- Salt separated on centrifuge can be washed to improve the purity by washing off the mother liquor ; inclusions are not separated by washing.
- Production pushed to 35 kg/h
- Temperatures in dihydrate and anhydrous sodium chloride crystallizers are respectively -5°C and + 5 °C
- During the start-up of the pilot campaigns , spiking mother liquor with some impurities can reduce time to reach steady state conditions .

### 6.2.3. RESULTS

#### (a) Purity of salt

- An example of purity of NaCl obtained is reported in [table 2](#) at a production rate of 35 kg/h . In this test ,the mother liquor has been enriched in K and Br . Total purity is close to 99.95 % . In some tests , purity of 99.99 % has been attained temporarily .
- Epuration of calcium and sulfate is very effective due to limitation of calcium sulfate and glauberite solubility ; epuration of Ca and SO<sub>4</sub> is larger than 90 % .
- Epuration of magnesium is very good and limited by the efficiency of washing mother liquor ; little Mg salt is included in NaCl crystals.
- Epuration of potassium is limited at 70 % in most tests
- Epuration in bromide is a split between the purge and the salt ; some Br is occluded in the crystals ; in order to reach a low level of Br in the final salt below 30 ppm , a high purge would be needed or a treatment of the clear recycled mother liquor should be performed. Some such processes have been reported in



literature ( 6 ) .These processes are based on oxidation of bromide to bromine by chlorine ; they are usual in chlor-alkali industry and bear the risk of generating traces of chlorate .At the low temperature of this dihydrate process , epuration of bromide is possible because the risk of equipment corrosion is very low .

#### ( b)Particle size

The operation of the crystalliser with fines removal allowed to reach an average particle size of 350 microns ( D 50) ; the particle size is very sensitive to fines removal within crystallizer ; particle population balances have been made regularly . Before the fines removal system was installed , the population balances were in agreement with MSMR model ( straight relationship  $\ln(n)$  versus  $L$  ) . After installation of a fines removal loop, the PSD showed clearly a change in slope for sizes close to 80 to 100 microns ; a second change appears also at large size diameters ,and can be attributed to segregation of large particles

#### c)Stability

Stable operation of the crystallisers was reached in the last trials . Limited dynamic fluctuations were experienced .

### 7. ECONOMICS

Preliminary economic evaluations show that for a 500 kt/y industrial plant , capital investment could be about half of that of a vacuum evaporation plant. In operations , less energy is consumed ; without drying , the only significant energy consumed ,is the electrical energy for heat pump compressor ( temperature between +10 °C and -5°C ) and for grinding rocksalt ; savings are also possible in chemicals for epuration of brine : no sodium carbonate and no caustic in some cases .

It remains to be seen ,case by case, if these savings in capital , energy and chemicals costs can balance the additionnal cost for rocksalt mining compared to cost of salt made from brine in a vacuum salt plant.

### 8. FUTURE DEVELOPMENTS

The knowledge and performances of this new process can probably be improved in different ways :

- A better knowledge of impurities species and their solubility will help to improve the purity of salt .
- Evaluate process alternatives
- Optimize process and equipment
- Apply this process to a large diversity of salts

### 9. CONCLUSIONS

A new process working at low temperature has been tested on a lab and on a pilot scale ; the purity and particle size of salt are good and can be compared to vacuum salt from a multi stage evaporative process .

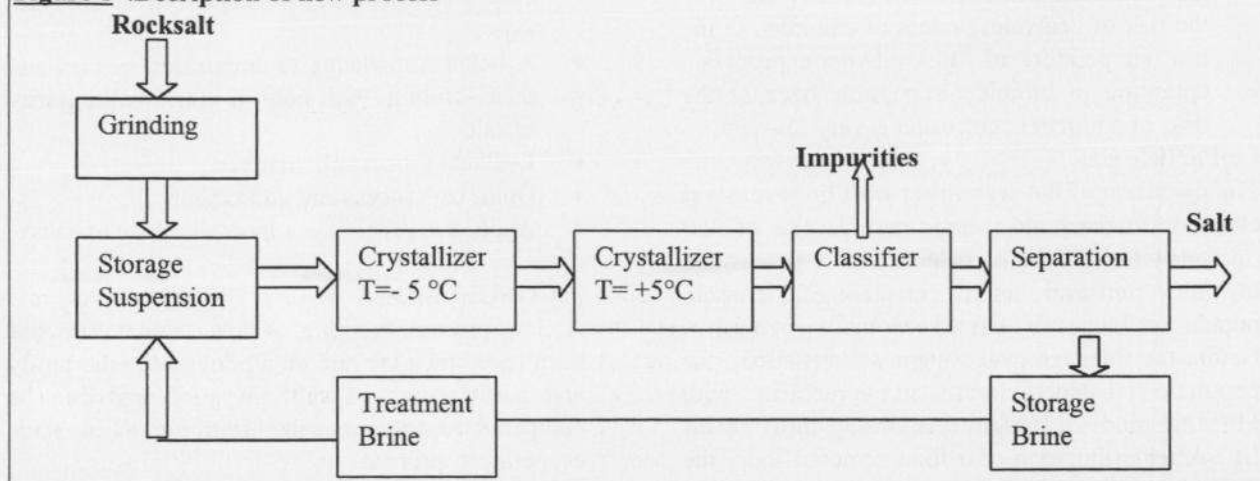
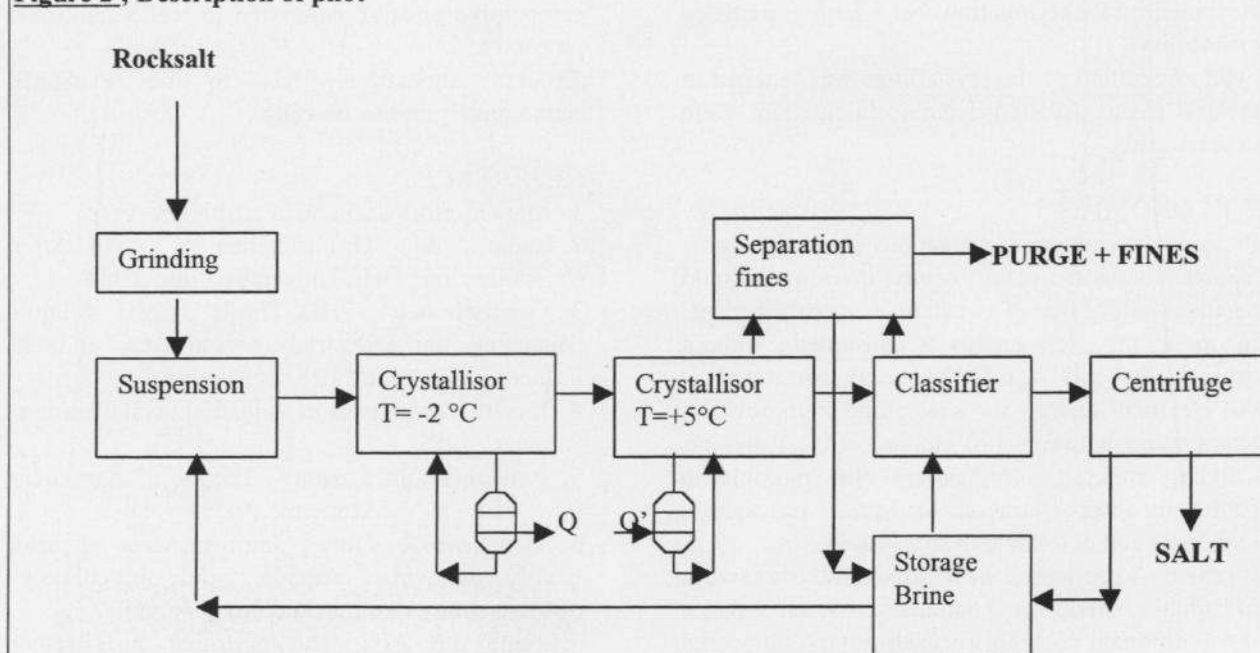
Salt purity achieved is 99.95 % and can still improve

Further developments are still needed to reach a competitive position compared to well established processes .

Process alternatives has to be evaluated economically and technically .

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**Figure 1** .Decription of new process**Figure 2 ; Description of pilot****Table 2**

Results from pilot test , g/kg

	Calcium	Sulfate	Magnesium	Potassium
Rocksalt	3	9.2	0.2	0.9
Salt	0.12	0.4	0.07	0.28
Washed salt	0.1	0.4	<0.05	0.27