PROCESS OPTIMIZATION OF BRINE PURIFICATION AND EVAPORATION FOR COMBINED CRYSTALLIZATION OF NACL AND NA_2SO_4 BY MEANS OF MECHANICAL VAPOUR RECOMPRESSION

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General introduction

Raw brines from solution mining process contain not only dissolved Na^+ and Cl^- but also Mg^{2+}, Ca^{2+}, SO_4^{2-} and other ions like K^+ and Br^-. There are three different types of raw brine: 1) low concentration of SO_4^{2-} and other ions (Colombia, Thailand), 2) medium concentration of SO_4^{2-} and high concentration of other ions (Europe), 3) high concentration of SO_4^{2-} (China). The brines are normally treated with NaOH / Na_2CO_3 or CaO/ CO_2/ Na_2CO_3 to precipitate Ca^{2+} Mg^{2+} and SO_4^{2-}.
Most of the brines from Chinese brine wells contain higher concentrations of SO_4^{2-} and make the process of precipitation of SO_4^{2-} expensive. Therefore the combined process is used to crystallize not only NaCl but also Na_2SO_4 in the crystallization plant.
In the past all Chinese plants which are based on the combined process used multiple effect evaporation process with additional Na_2SO_4 loop. SEP Salt and Evaporation plants developed a new process which uses mechanical vapour recompression as main process step for NaCl crystallisation. The optimal configuration of the process was found after cost comparison for all process steps.
(1) brine purification with different options of mother liquor re-circulation to save operating costs
(2) crystallisation of NaCl by means of mechanical vapour recompression
(3) crystallisation of NaCl by means of multiple effect cooling of mother liquor and additional loop
for crystallisation of Na_2SO_4.
(4) Alternatively to (2) and (3) the above mentioned multiple effect evaporation concept was considered in the comparison

Composition of raw brine

In China raw brines contain high concentrations of Na_2SO_4.
We have used a typical composition as listed in table
Tab **1**.

Component	Concentration	Unit
Ca^{2+}	0.732	g/l
Mg^{2+}	0.020	g/l
K^+	0.100	g/l
Br^-	0.050	g/l
SO_4^{2-}	10.0	g/l
NaCl	300.0	g/l

Tab 1 composition of raw brine from well

Parameters used for the calculations and process simulations

Salt production 100 t/h
Mother liquor circulation to the first or second process step of brine purification process.
Prices and costs:

CaO 80 %	RMB 450 per ton,
Na_2CO_3	RMB 1'100 per ton,
NaOH 30%	RMB 720 per ton,
Flocculants	RMB 20 per kg,
Steam case 1	RMB 200 per ton,
Electricity case 1	RMB 500 per ton,
Steam case 2	RMB 130 per ton,
Electricity case 2	RMB 670 per ton,
Steam case 3	RMB 50 per ton,
Electricity case 3	RMB 800 per ton,

Brine purification

General remarks

An important step in the production process of salt is the treatment of raw brine. The so called "Brine Purification" process is used to remove earth alkaline ions like Ca^{2+}, Mg^{2+}, Sr^{2+} as well as potentially present heavy metal ions as far as possible.
The composition of the purified brine has an important impact on the evaporation process and especially on the salt quality.

The common way is the purification with NaOH and Na_2CO_3, but this method leads to high operating costs, because of the costs of the chemicals.
Alternatively the so called "Schweizerhalle" process can be used. The raw brine is treated with CaO / CO_2 / Na_2CO_3. This process normally is applied as batch process with 2 process steps, but also continuous operation of reactors is possible. The addition of CaO leads to lower operating costs and improves the economy of brine purification process. Even if the sulphate content in the brine is low, the purification with the CaO process could be more economic.
Many of the brines gained in China have high sodium sulphate content. If the brine purification concept is chosen properly no soda ash is required and therefore the purification process is rather cheap.

A short abstract of the "Schweizerhalle Process"

The process is performed in 2 steps:

Process step 1

- typical reactions:
- $MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaSO_4$
- $Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4 \downarrow$

Most of the brines produced from rock salt layers are saturated with $CaSO_4$. One important key figure is the solubility product of $Ca^{2+} \times SO_4^{2-}$.
The solubility of $CaSO_4$ depends on the NaCl content and the temperature of the brine.
In the first process quicklime or calcium hydroxide and mother liquor with a high SO_4 content is added. Magnesium hydroxide and gypsum precipitate.
With sodium sulphate and calcium hydroxide sodium hydroxide is produced.
The solubility of portlandite ($Ca(OH)_2$) in saturated brine limits the OH^- concentration.

Process step 2

- typical reactions:
- $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$
- $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$

After the precipitated sludge from process 1 is separated Ca^{2+} has to be removed. Ca^{2+} is precipitated as $CaCO_3$. CO_3^{2-} can be added as Na_2CO_3 or it can be produced by addition of CO_2. CO_2 reacts with OH^- to CO_3^{2-}. Addition of CO_2 has to be controlled carefully because chemical equilibrium between CO_2 and CO_3^{2-} depends on the concentration of OH^- (pH-value).

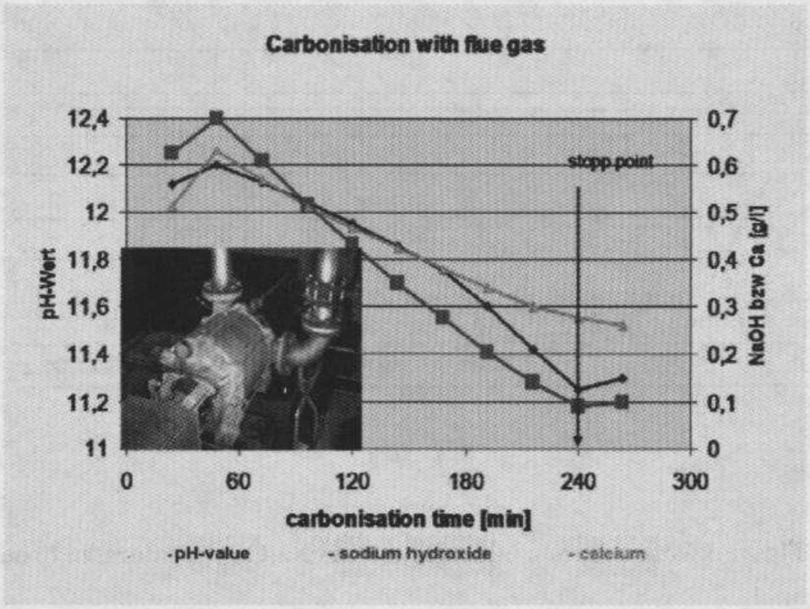


Figure 1 Carbonisation of brine in process step 2

To avoid the generation of sodium hydrogen carbonate ($NaHCO_3$) the flue gas compressor has to be stopped before the concentration of sodium hydroxide (NaOH) reaches it's critical value, (measurement of the pH).

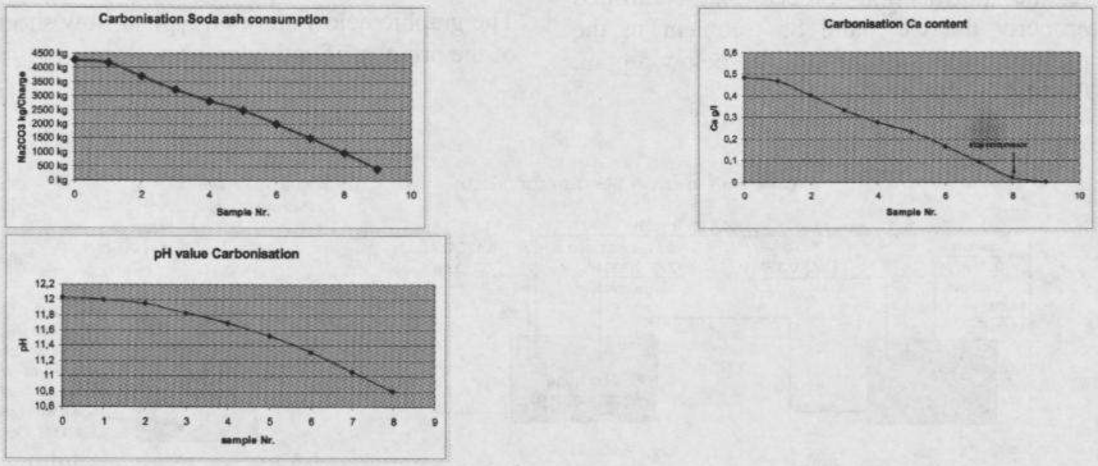


Figure 2 carbonisation results from start-up trial of a Chinese salt plant

If necessary some soda ash has to be added to achieve the required CO_3^{2-} concentration.

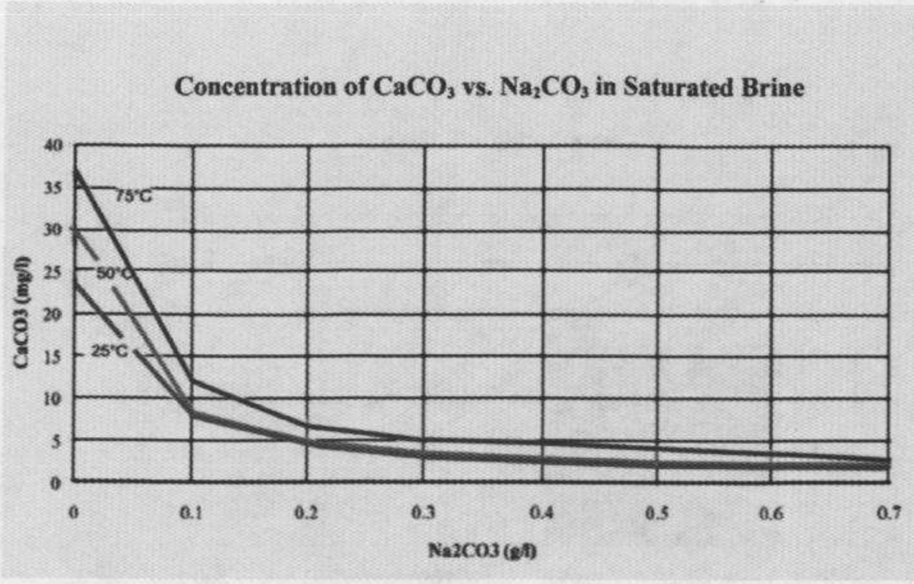


Figure 3 Concentration of $CaCO_3$ versus Na_2CO_3 in saturated brine

The purified brine should contain a soda ash excess. The remaining sodium hydroxide content should be high enough. But also temperature of the brine has an influence on the solubility of the Mg^{2+}, Ca^{2+} and Sr^{2+} ions. If the purification process is controlled properly the Ca^{2+} and Sr^{2+} content in the purified brine is expected to be below 5 ppm, the Mg^{2+} content below 1ppm.

Comparison of different process concepts of mother liquor recirculation

Mother liquor added to the first purification process:

The graphic below shows a typical flow sheet of the brine purification process.

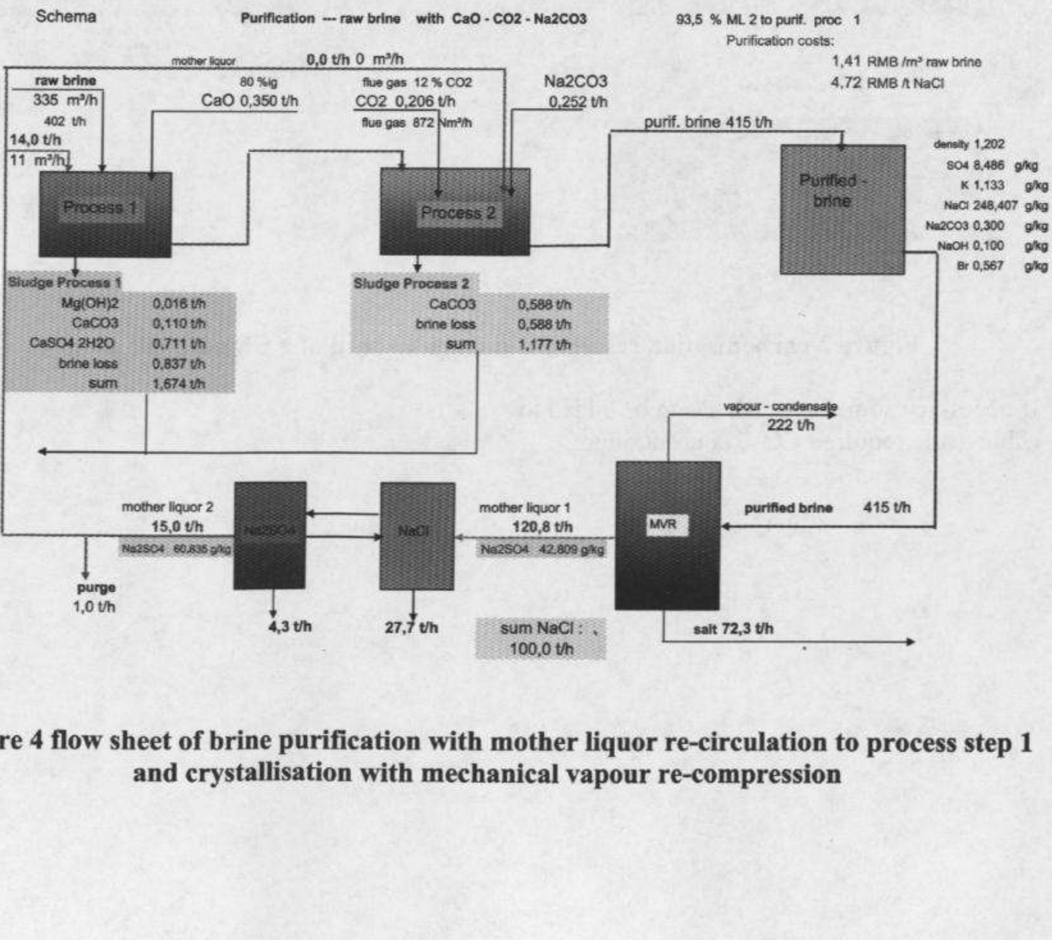


Figure 4 flow sheet of brine purification with mother liquor re-circulation to process step 1 and crystallisation with mechanical vapour re-compression

The diagrams below show the influence of the mother liquor circulation on the brine flows, chemical consumptions, brine quality and costs. Additionally the figures for brine purification by means of NaOH and Na_2CO_3 are indicated (red point).

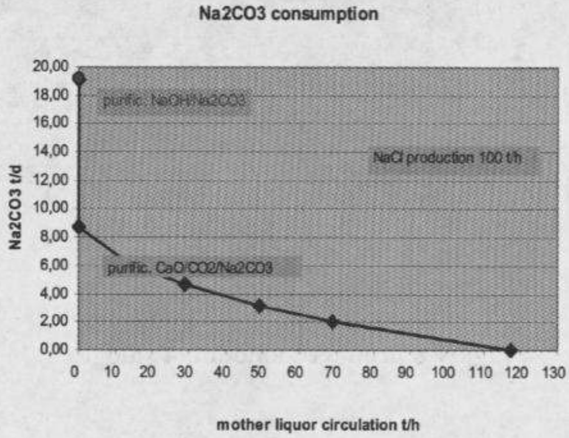


Figure 5 Na_2CO_3 consumption

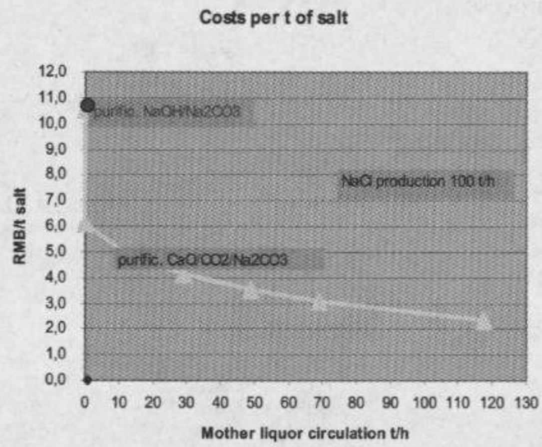


Figure 6 Costs of chemicals

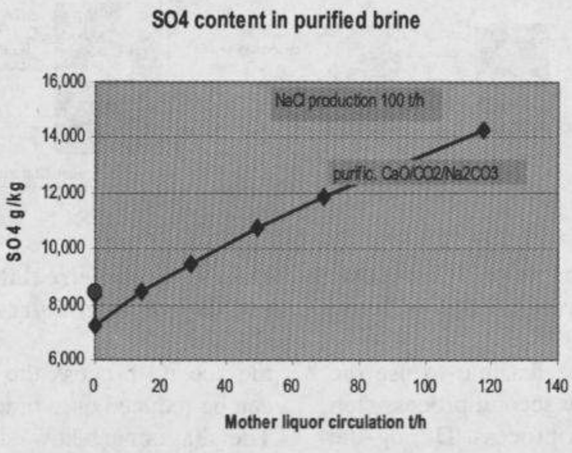


Figure 7 SO_4 content in purified brine

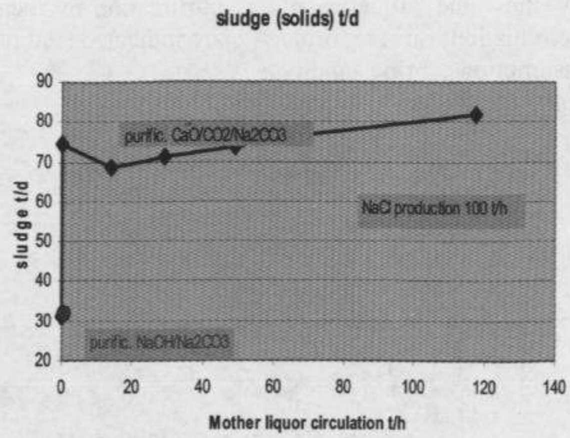


Figure 8 produced amount of sludge

Mother liquor added to the second purification process:

The graphic below shows a typical flow sheet of the brine purification process.

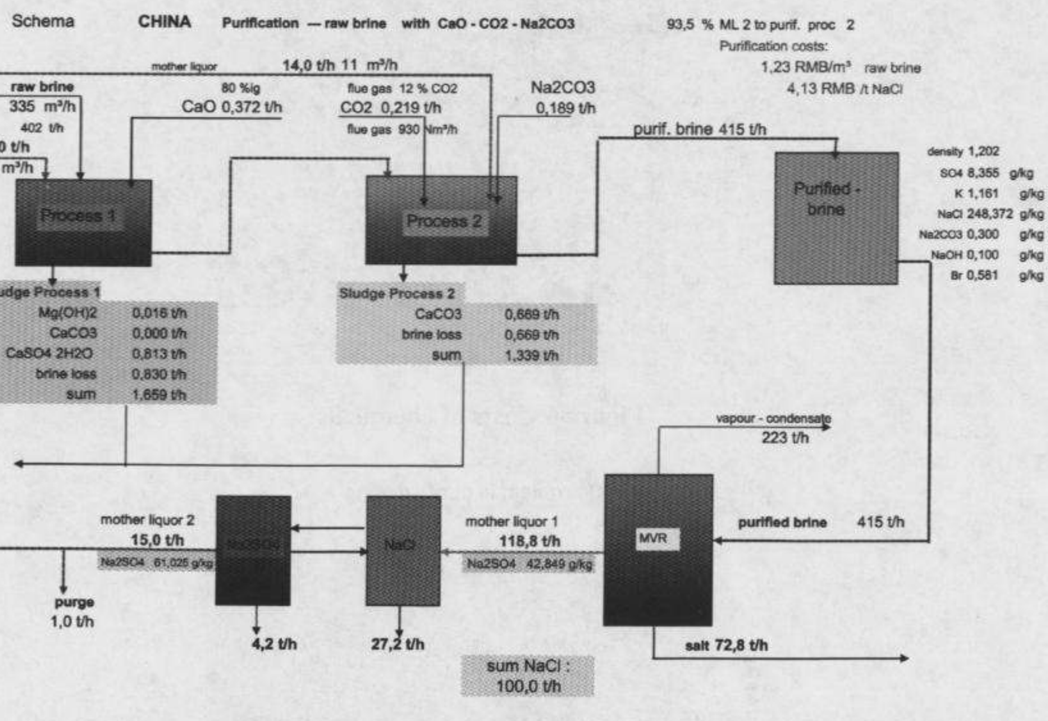
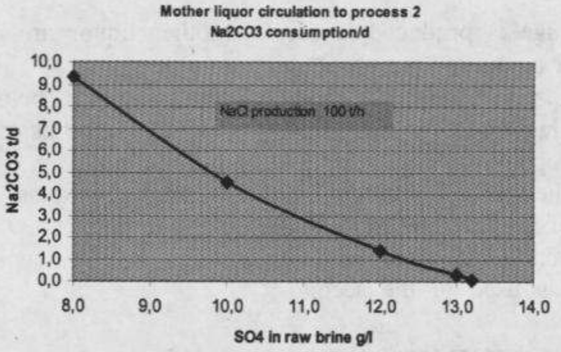


Figure 9 flow sheet of brine purification with mother liquor re-circulation to process step 2 and crystallisation with mechanical vapour re-compression

In some cases it is more feasible to use the mother liquor only in the second process step of the brine purification process. During the evaporation process Na_2CO_3 and NaOH are concentrated in the mother liquor. By returning a certain amount of mother liquor to the second process the addition of soda ash can be reduced or avoided completely.

The diagrams below show the influence of the SO_4^{2-} content of the raw brine on different consumption figures and costs. If the raw



brine contains about 14 g/l SO_4^{2-} soda ash addition is not necessary.

Figure 10 mother liquor re-circulation

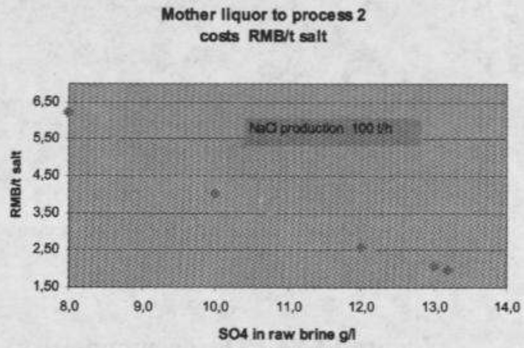


Figure 11 costs of chemicals

If the raw brine contains 10 g/l SO_4 and mother liquor is sent to the second process, (in this case 14 t/h mother-liquor) it would be required to circulate about 30 t/h of mother liquor to process 1 to get the same Na_2CO_3 consumption and costs. (See diagrams below). Also the SO_4^{2-} content in the purified brine (feed brine) is lower if the mother liquor is used in the second process, which is beneficial for the performance of MVR process in the crystallisation plant.

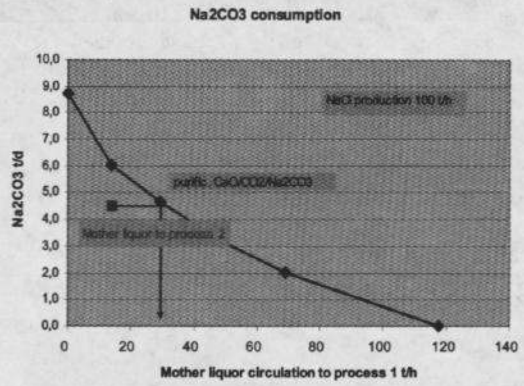


Figure 12 soda ash consumption

Additionally less sludge is produced if the mother liquor is used in the second process. The costs of sludge disposal have also to be considered in the evaluation of the results of different process concepts.
On the other hand the savings are limited, because the amount of Na_2CO_3 and NaOH in the mother liquor remains the same even if more mother liquor is used in the second process.
Savings will be higher if more than 30 m³/h mother liquor are re-circulated to the first process.
The diagrams below show the results if different amounts of mother liquor are added to
the second process. (SO_4^{2-} content in the raw brine 10 g/l)

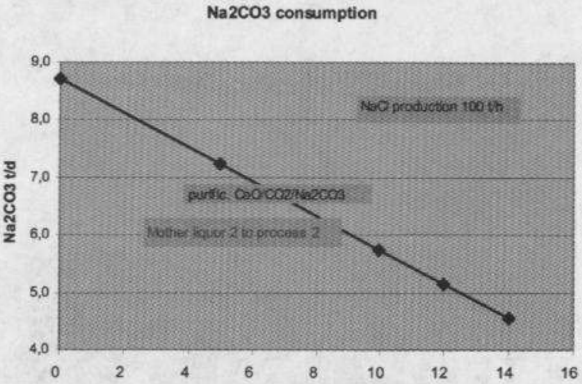


Figure 13 Na_2CO_3 consumption

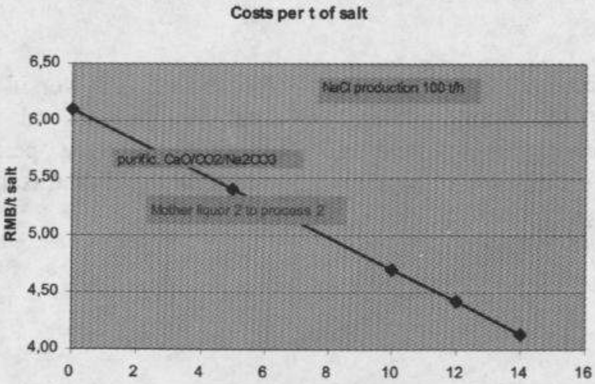


Figure 14 cost of chemicals

Consumption figures and costs of brine purification depending on the raw brine composition

Tab 2 Analysis of raw brines indicates composition of typical raw brines from different origin.

Raw brine	1 Zhig	2 Jin	3 Shu	4 Eb	
density	1,200	1,200	1,200	1,200	
HCO3	0,001	0,001	0,001	0,001	g/l
Ca	1,800	0,732	0,500	1,000	g/l
Mg	0,200	0,040	0,040	1,200	g/l
SO4	3,900	10,000	15,000	7,500	g/l
K	0,010	0,100	0,050	1,800	g/l
NaCl	300,000	300,000	300,000	300,000	g/l
Br	0,010	0,050	0,050	0,070	g/l

Tab 2 Analysis of raw brines

The first three brines are of Chinese origin, brine 4 Europe. The diagrams below show the consumption figures and costs for chemicals for different raw brine brine compositions and different purification concepts: purification with NaOH / Na_2CO_3, purification with CaO / CO_2 / Na_2CO_3 respectively.

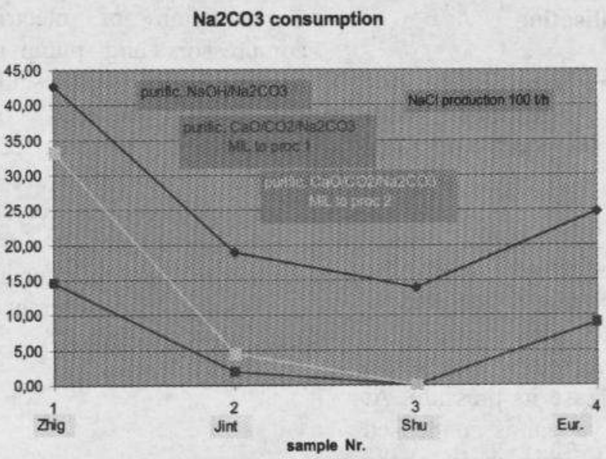


Figure 15 soda ash consumption

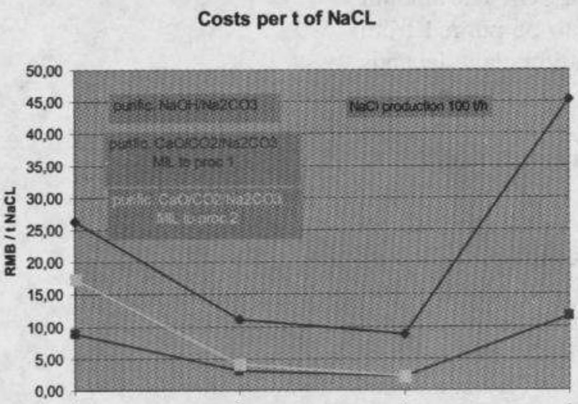


Figure 16 costs for chemicals

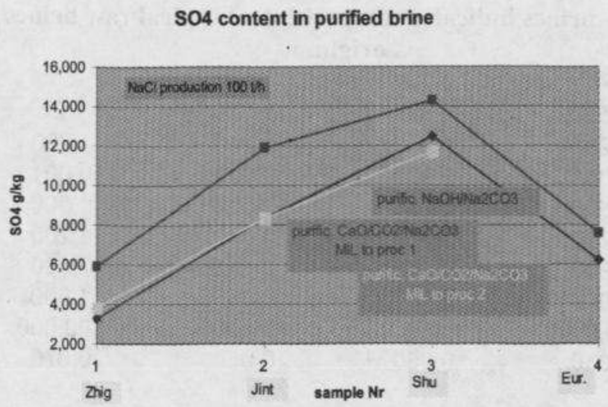


Figure 17 SO_4^{2-} concentration in purified brine

Process simulation of crystallisation part of the plant for two different process concepts and consideration of costs for brine purification and crystallisation

Mechanical vapour re-compression for NaCl crystallisation combined with crystallisation process for NaCl and pure Na_2SO_4

Process concept

Purified brine is preheated with hot condensate and fed to the mechanical vapour re-compression part of the plant. Evaporated water vapour is re-compressed by means of a turbo compressor to increase its pressure. At the higher pressure the vapour is condensed on the shell side of the heating chests of the evaporators and the condensation heat is used to heat the system. NaCl is crystallised and separated. Mother liquor is concentrated close to the saturation point of Na_2SO_4. The amount of mother liquor which is to be purged from MVR part of the crystallisation plant depends on the Na_2SO_4 çoncentration of the purified brine fed to the plant. The higher the Na_2SO_4 concentration the more mother liquor has to be purged.

The mother liquor from MVR process is introduced into the flash cooling cascade of the Na_2SO_4 crystallisation part of the plant. More NaCl is produced by further evaporation and cooling of the brine. From the coldest NaCl evaporator a certain amount of brine is sent to the Na_2SO_4 evaporator. A small amount of water is evaporated and pure Na_2SO_4 is produced. The more Na_2SO_4 has to be separated according to the total mass balance of combined brine purification and salt crystallisation process the more brine has to be sent to the Na_2SO_4 evaporator which is heated with steam. The ratio between Consumption of electrical power (for compressors and pumps) and steam (for heating the Na_2SO_4 crystalliser and other heat consumers) depends on the Na_2SO_4 concentration in the feed brine and the amount of mother liquor which is recycled from the coldest NaCl crystallizer to the brine purification plant. Additionally a small amount of mother liquor has to be purged to control the concentration of other dissolved salts like KCl and NaBr.

Consumption figures for high steam price and low price of electrical power (Case 1)

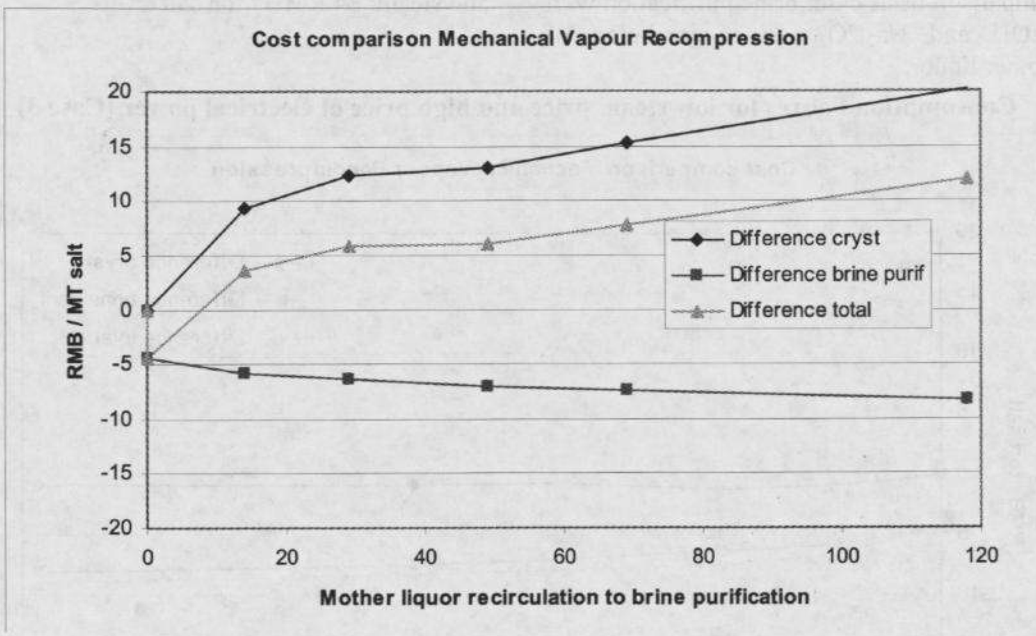


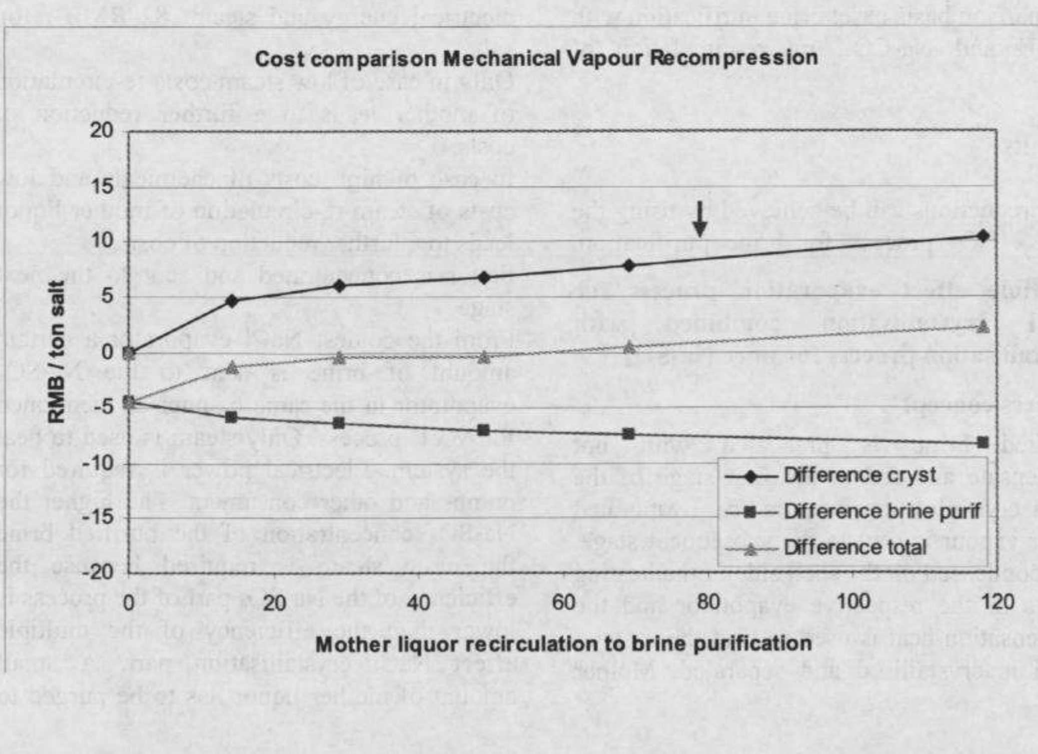
Figure 18 cost comparison MVR steam price low, electrical energy high

All cost differences are compared with the comparison basis case: brine purification with NaOH and Na_2CO_3, no re-circulation of mother liquor.

Consumption figures for medium steam price and medium price of electrical power (Case2)

Total costs of chemicals, electrical energy and steam: 79 RMB / ton salt

Figure 19 cost comparison MVR steam price medium, electrical energy medium



All cost differences are compared with the comparison basis case: brine purification with NaOH and Na_2CO_3, no re-circulation of mother liquor.

Total costs of chemicals, electrical energy and steam: 84 RMB / ton salt

Consumption figures for low steam price and high price of electrical power (Case 3)

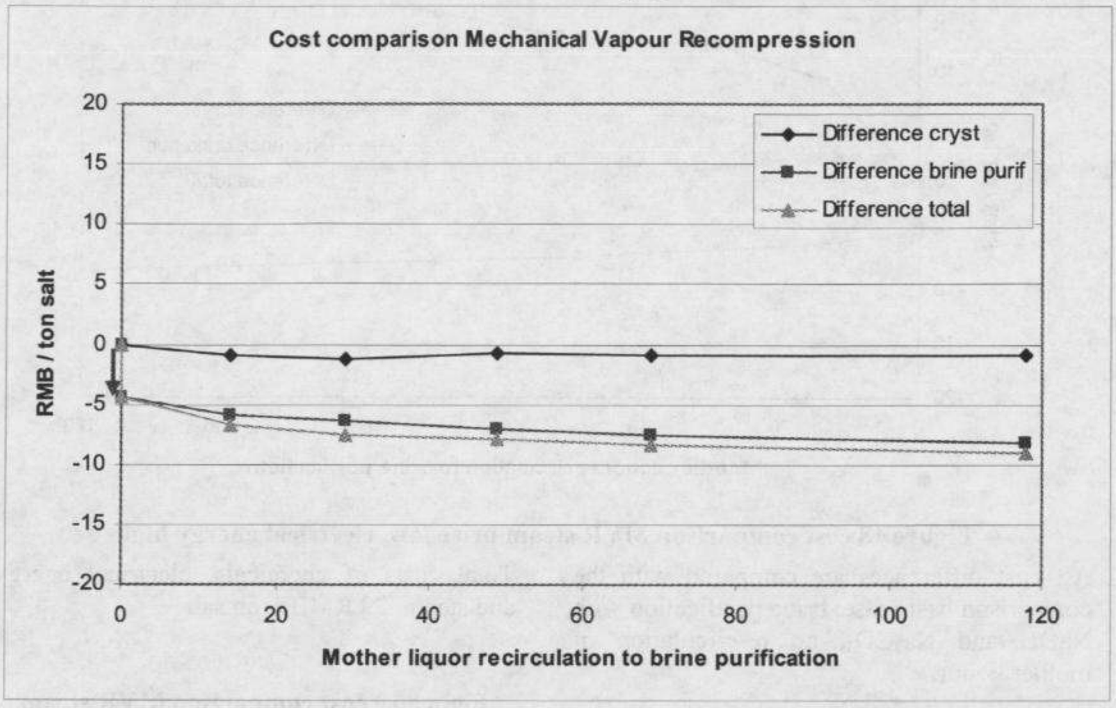


Figure 20 cost comparison MVR steam price high, electrical energy low

All cost differences are compared with the comparison basis case: brine purification with NaOH and Na_2CO_3, no re-circulation of mother liquor. Total costs of chemicals, electrical energy and steam: 82 RMB / ton salt

Only in case of low steam costs re-circulation of mother leads to a further reduction of costs.

In case of high costs of chemicals and low costs of steam re-circulation of mother liquor leads to a further reduction of costs.

Results

Cost reductions can be achieved by using the CaO / CO_2 process for brine purification.

Multiple effect evaporation process for NaCl crystallisation combined with crystallisation process for pure Na_2SO_4

Process concept

Purified brine is preheated with hot condensate and fed to the first stage of the NaCl crystallisation evaporators. Evaporated water vapour is sent to the subsequent stage. It is condensed on the shell side of the heating chests of the respective evaporator and the condensation heat is used to heat the system. NaCl is crystallised and separated. Mother liquor is concentrated and sent to the next stage

From the coldest NaCl evaporator a certain amount of brine is sent to the Na_2SO_4 evaporator in the same manner as mentioned for MVR process. Only steam is used to heat the system. Electrical power is required for pumps and other consumers. The higher the Na_2SO_4 concentration of the purified brine the more steam is required because the efficiency of the Na_2SO_4 part of the process is lower than the efficiency of the multiple effect NaCl crystallisation part. A small amount of mother liquor has to be purged to control the concentration of other dissolved salts like KCl and NaBr.

Consumption figures for high steam price and low price of electrical power (Case 1)

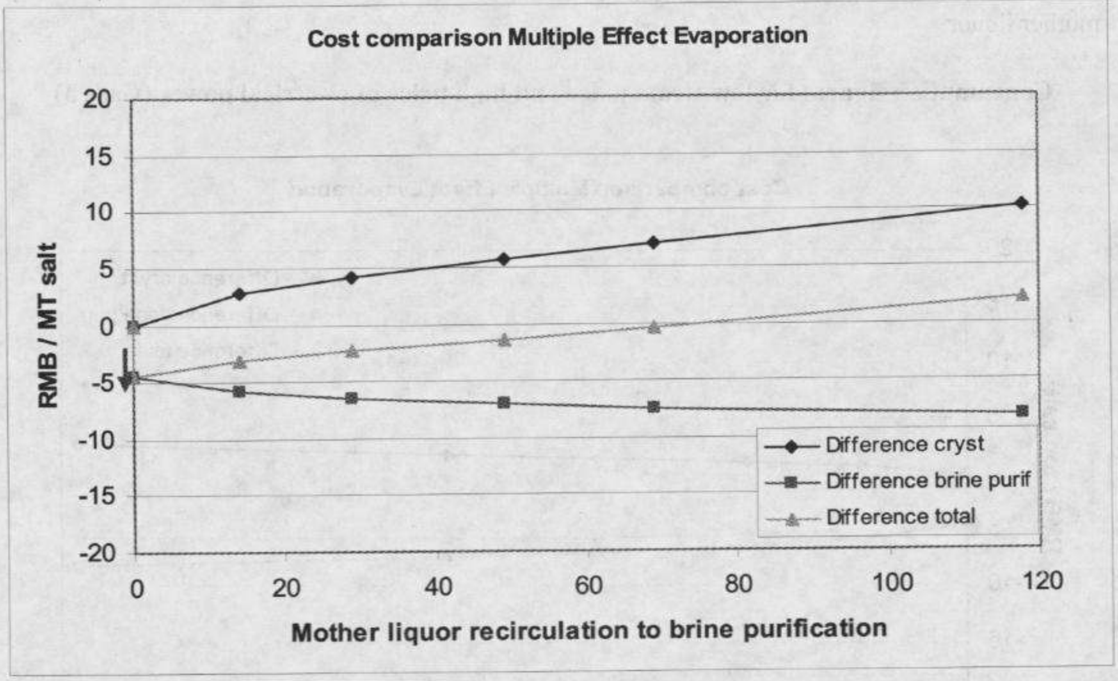


Figure 21 cost comparison MEV steam price low, electrical energy high

All cost differences are compared with the comparison basis case: brine purification with NaOH and Na_2CO_3, no re-circulation of mother liquor.

Total costs of chemicals and steam: 144 RMB / ton salt

Consumption figures for low steam price and high price of electrical power (Case 2)

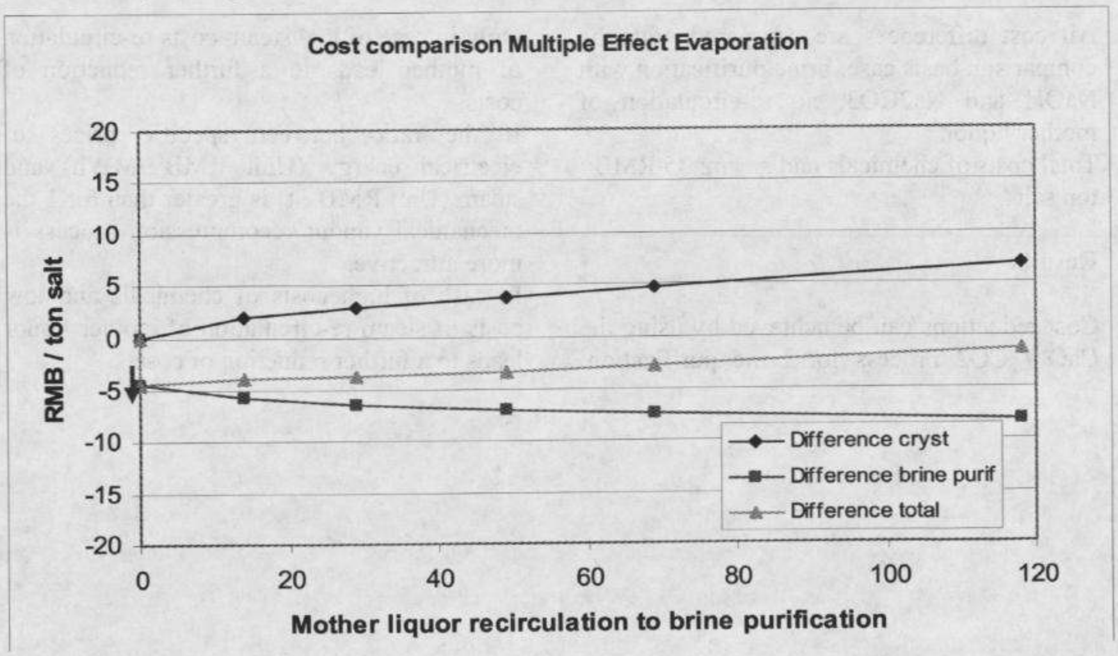


Figure 22 cost comparison MEV steam price medium, electrical energy medium

All cost differences are compared with the comparison basis case: brine purification with NaOH and Na_2CO_3, no re-circulation of mother liquor.

Total costs of chemicals and steam: 96 RMB / ton salt

Consumption figures for low steam price and high price of electrical power (Case 3)

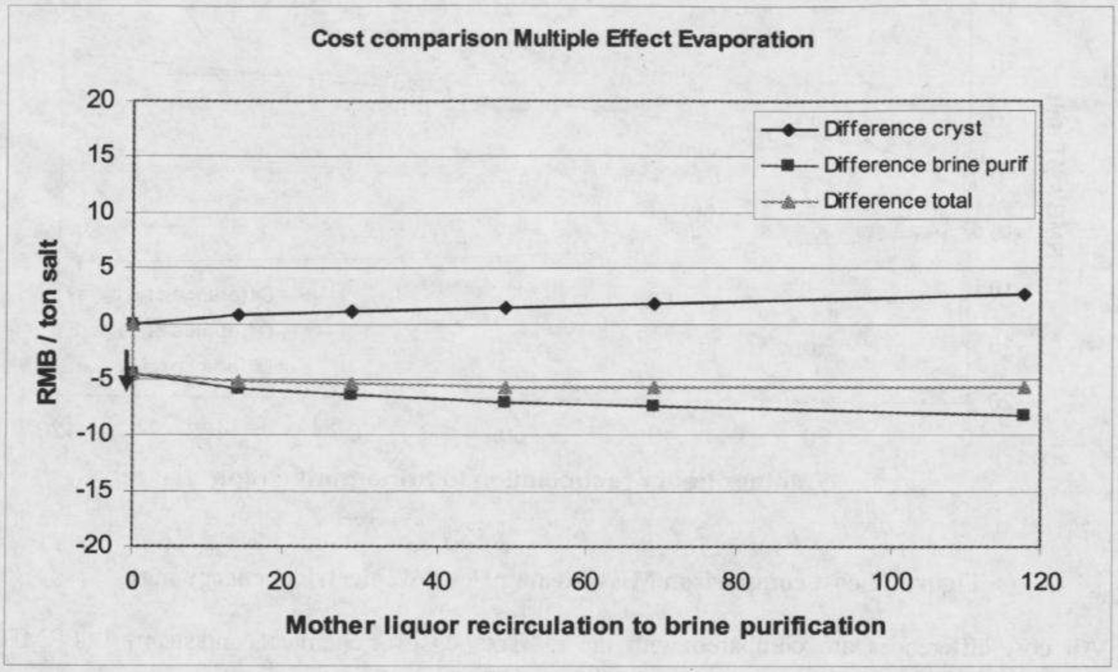


Figure 23 cost comparison MEV steam price medium, electrical energy medium

All cost differences are compared with the comparison basis case: brine purification with NaOH and Na2CO3, no re-circulation of mother liquor.
Total costs of chemicals and steam: 35 RMB / ton salt

Results

Cost reductions can be achieved by using the CaO / CO2 process for brine purification. Only in case of low steam costs re-circulation of mother leads to a further reduction of costs.
If the ratio between specific prices of electrical energy (Unit RMB /MWh) and steam (Unit RMB / t) is greater than 6 : 1 the mechanical vapour recompression process is more attractive.
In case of high costs of chemicals and low costs of steam re-circulation of mother liquor leads to a further reduction of costs.

Summary

Based on the composition of the raw brine different options of mother liquor recirculation from crystallisation to brine purification were investigated.
The use of CaO and CO_2 instead of NaOH and Na_2CO_3 can significantly reduce the costs of chemicals in the brine purification process. Additionally the circulation of mother liquor from crystallisation process can lead to savings. It has to be carefully evaluated whether these savings have a positive influence on the total costs of both brine purification and crystallisation process. The cost effect depends on the specific costs of electrical energy and steam.
Recirculation of mother liquor on one hand leads to savings in consumption of chemicals in the brine purification process. On the other hand the concentration of SO_4^{2-} in the purified brine is increased. Subsequently the brine can be concentrated less in the mechanical vapour recompression part of the crystallisation plant. Less electrical power but more steam has to be used to crystallise NaCl which has an impact on the utility costs in the crystallisation plant.
Depending on the composition of the raw brine and the costs of the utilities and chemicals the optimal configurations of the different process steps vary for each specific salt manufacturer. Detailed process studies are required to determine the most economic solution.
For the Jintan plant SEP and China Salt Company have chosen the improved brine purification process with CaO and CO_2 and a Mechanical Vapour Re-compression process combined with a Na_2SO_4 crystallisation process to minimise the total operating costs of the plant.