

A General Overview of Chemical Brine Treatment for Salt Production Processes

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Main track 1: Salt Production

In many salt production processes, the implementation of a brine purification process is required in order to remove calcium and magnesium ions that are present in the raw brine and would disturb the salt production process in several ways. By utilizing a brine purification process, the operation of the salt plant is more reliable, with minimum interferences, and furthermore, a well controllable premium product quality for industrial salt can be produced. Furthermore, a significant reduction of liquid purge is possible depending upon the choice of process and the configuration of the brine purification with the salt production process. A reduction of sulphate ions in the feed brine will lead to higher concentration factors in the evaporation process, which reflects in a better process economy.

This article introduces a brine purification process based on caustic soda, as well as a modified process utilising lime, soda and flue gas. It will also be shown that there is an economical threshold for designing the process depending upon the sulphate content of the raw brine.

Furthermore, the practice of recycling the mother liquor from the evaporation process to the brine purification plant will be explained.

Key words: Brine Chemistry, Brine Disposal, Brine Purification, Salt Processing, Salt Properties, Scaling, Fouling

Introduction

In the last decades, the process of brine purification has been modified and improved in many ways. As the main target is to decrease the Ca^{2+} , Mg^{2+} and Sr^{2+} content as far as possible, some chemical investment has to be made in order to profit from the advantages that brine purification brings for the evaporation section of the salt production process.

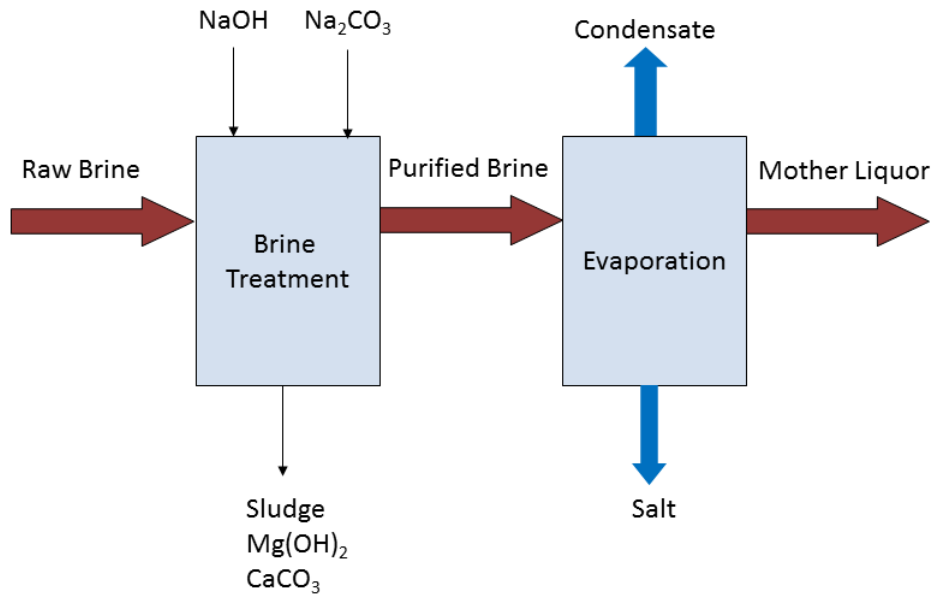
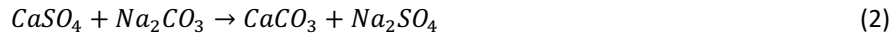
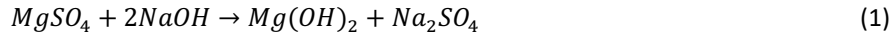
The decrease of Mg^{2+} , Ca^{2+} and also Sr^{2+} in the feed brine of salt production processes will lead to less scale formation in process piping and equipment. For example the performance of heat exchangers in the evaporation process is significantly improved. This leads to longer production times between regular cleaning intervals, savings in energy consumption and also the lifetime of the equipment itself is prolonged.

Another component to control is the SO_4^{2-} content of the brine. The sulfate content in most of the evaporation processes for salt production is the determining variable to the concentration factor and therefore influences the size of the plant significantly. The Na_2SO_4 solubility in the mother liquor of salt crystallization processes depends on the process temperature and also on the NaCl and KCl concentration. With a high Na_2SO_4 concentration in the feed brine, it will automatically lead to a bigger liquid volume to be processed in the evaporation plant and to a higher amount of mother liquor discharge.

Nevertheless, the impurities mentioned above can, if they are not removed from the feed brine or purged, lead to a decreased purity of the produced salt, which will exclude the usage of the salt product in high purity chemical applications such as membrane chlorine alkaline electrolysis etc.

Former Process

In order to eliminate Ca^{2+} and Mg^{2+} ions from the brine, the following precipitation reaction is used in the classic process of brine treatment:



Picture 1: Process Principle Former Process of Raw Brine Treatment

This precipitation reaction, with a small excess on NaOH and Na₂CO₃, leads almost to the total elimination of both ions.

The sludge that is created by the precipitation reaction can be handled separately by keeping each reaction step physically separated. The amount of caustic in the first process step and soda needed in the second process step is a significant factor influencing the economics of the entire salt production process. Slight modifications in this process lead to an improvement of the efficiency in terms of chemical usage. The return of mother liquor from the evaporation process is the most common one. Depending on the raw brine composition, the choice of returning the mother liquor either to the first reaction step or the second or even both is based on economic circumstances, such as the prices of raw materials.

Since this former process is mostly used for cases with low sulfate raw brine, a mother liquor return is in most cases only feasible if the sulfate is being removed from the mother liquor by precipitation with CaCl₂. This is not necessarily a measure to make the process more economic, but mainly to avoid as much liquid purge from the process as possible. The combination with a combined NaCl/Na₂SO₄ production process is also possible for this process.

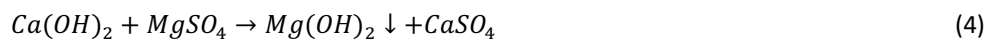
“Schweizerhalle” Process

A brine purification process that is in use in many salt production plants, is the so called “Schweizerhalle” process¹. For this process, the utilization of other chemicals is necessary, and this leads even with lower sulfate contents, in combination with mother liquor recirculation, to better process economics.

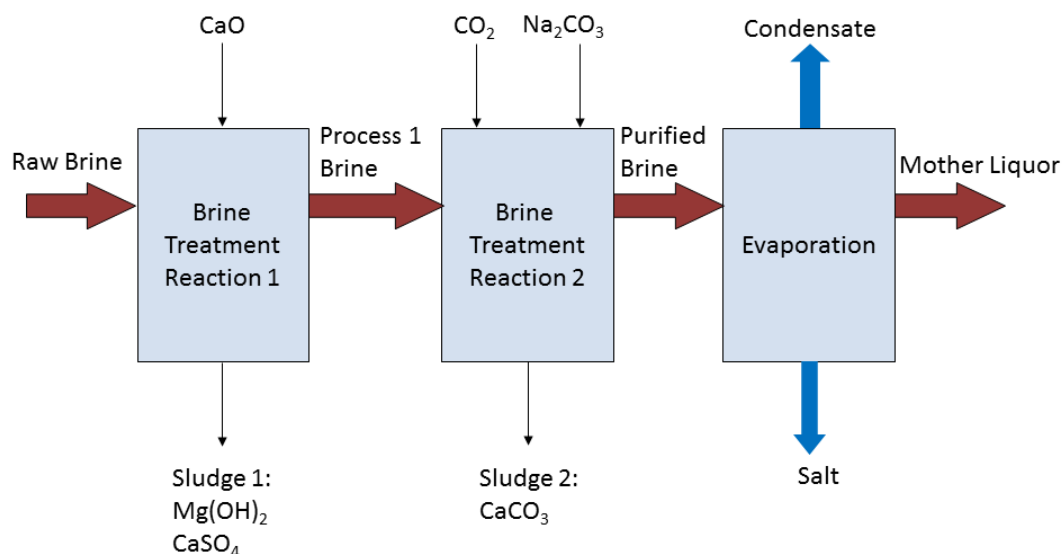
Instead of NaOH, CaO is used and the Na₂CO₃ consumption can be reduced by the additional use of flue gas CO₂ in the second process step. This process is not only very economic for raw brines with relatively high magnesium content, because of the substitution of caustic by lime, but also for raw brines with high sulfate concentrations. In those cases, the soda ash consumption can be reduced dramatically or even eliminated completely.

This process can be performed as a batch or continuous brine treatment process. The reaction is divided into two different process steps, in which also two different types of sludge result. Both process steps have to be kept strictly separate, which leads to more effort in terms of process equipment in comparison to the former process, where both reactions can also be performed in the same reactor when a mixed sludge can be tolerated.

First process step:



Second process step:



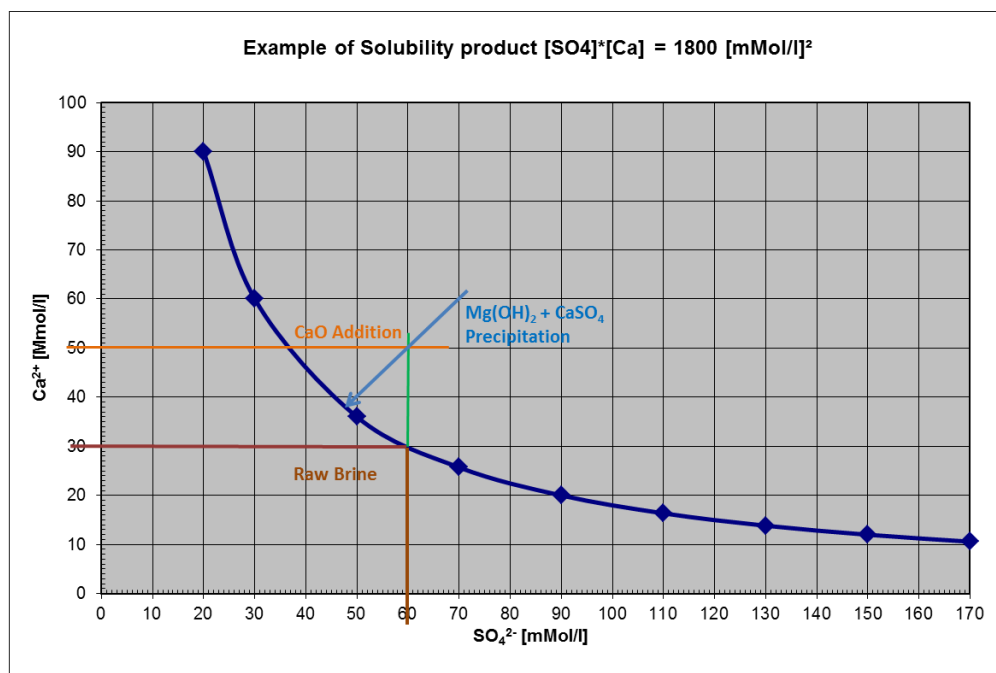
Picture 2: Process Principle “Schweizerhalle” Process of Raw Brine Treatment

For the first process step, the lime (CaO) has to be slaked to produce Ca(OH)_2 for the reaction. This slaking process is very often carried out with brine from the first reaction process in a separate process tank in order to control the exothermic reaction and optimize the conversion rate.

After the addition of the lime suspension, the precipitation reaction of Mg(OH)_2 takes place very fast. Whereas the Mg(OH)_2 particles are rather small and for the process design enough sedimentation time has to be considered.

Most of the different raw brines are close to saturation of CaSO_4 as they enter the brine treatment process. The addition of lime to the first process step causes two further effects, which help the brine purification to operate. The addition of excess Ca^{2+} to the first process step moves the amount of Ca^{2+} and SO_4^{2-} above the solubility of CaSO_4 . The solubility product ($\text{Ca}^{2+} \text{ mMol/l} \cdot \text{SO}_4^{2-} \text{ mMol/l}$), which can be in brine depending on the process conditions within a range of 1,500 to 2,500 ($\text{mMol/l})^2$, is exceeded and CaSO_4 precipitates. (See Picture 3)

This leads also to a decrease of SO_4^{2-} in the brine, which can, depending on the evaporation process chosen for the salt production, be an advantage for the process design.



Picture 3: Example of a Solubility Product of CaSO_4 of 1800 (mMol/l)^2 – First Process Precipitation without mother liquor recirculation

Depending on the brine composition and costs of available energy sources, different concepts for the salt production can be recommended. Raw brine, which contains high sulfate, can be very suitable for a combined NaCl and Na_2SO_4 production process. This process is a multiple effect evaporation and has the advantages of a very good steam economy and due to the temperature profile in the process and the inverse solubility of Na_2SO_4 in correlation to the

temperature, the sulfate content of the mother liquor is not as much a limiting factor as it is in a single stage MVR process.

Raw brine with a low sulfate content is very suitable for a single stage evaporation process which is driven by mechanical vapor compression. This process is recommendable for low sulfate brines and in the case of economic electricity prices.

In the following it is shown whether the brine treatment process is related to a combined NaCl and Na₂SO₄ process or to a process of solely NaCl production.

The second positive effect is the caustification reaction of Ca(OH)₂ coupled with the CaSO₄ precipitation reaction. As shown in the reaction equations above, hydroxide anions are released with the precipitation reaction and form NaOH. This reaction is only possible to a certain degree. As the formation of NaOH can be described by the p-value of the solution (measure for the alkalinity of a solution), the conversion of Ca(OH)₂ into NaOH is limited to a certain p-value. As the precipitation reaction is coupled to the SO₄²⁻ content of the raw brine, it is clear that the maximum reachable p-value is coupled indirectly to the sulfate content of the raw brine and is limited. The solubility of Ca(OH)₂ (portlandite) is additionally strongly depending on the NaCl concentration in the brine.

After the precipitation reaction is finished, the CaSO₄ and Mg(OH)₂ and also some small amount of Ca(OH)₂, which has been added in excess to ensure an optimum caustification reaction, sediments in the reactor and is collected and withdrawn after a certain period of time. The brine is then withdrawn and conveyed to the second process reactor.

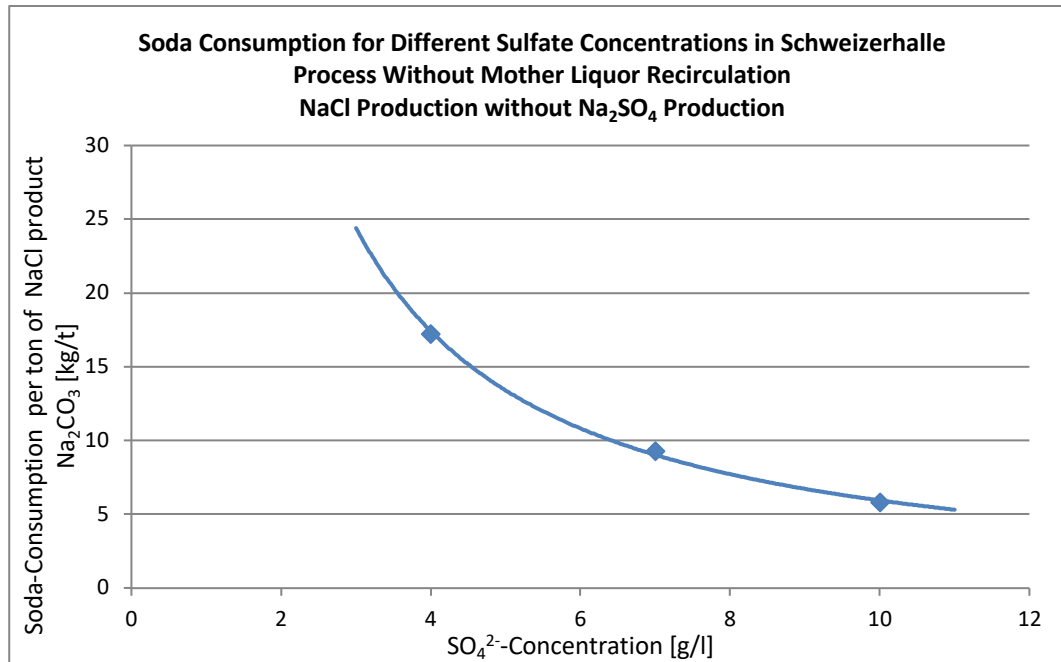
The second process step consists of two chemical reactions to precipitate the Ca²⁺ in the brine. The first reaction takes place with CO₂ taken from combustion processes (flue gas), which is in comparison to other chemicals in this process a cheaper additive. As shown in reaction equation (6), the NaOH reacts with the CO₂ to Soda. This soda then precipitates Ca²⁺.

The brine itself has only in some cases to be filtered before it enters the evaporation process to avoid any solids entering with the purified brine.

The precipitate of the second process reaction sediments in the reactor and is withdrawn subsequently.

The sludge coming from both process steps can be collected separately or both sludges combined. In some applications, the sludge can be disposed of in a disposal well. Diluting the sludge and discharging the slurry into lakes or the sea can lead to environmental problems and has to be investigated carefully. Some studies have been performed ² concerning the usage of the sludge as a lime fertilizer.

Diagram 4 depicts the correlation between the sulfate content of the raw brine and the resulting soda ash consumption for brine treatment without mother liquor recirculation. The soda ash consumption decreases significantly with increasing sulfate content. Although not shown in this diagram, the soda consumption can be totally eliminated, if the sulfate content is sufficient. Processes with high sulfate content can be very economic if chemicals brought into the process are limited to lime and flue gas.



Picture 4: Soda Consumption for Different Sulfate Concentrations in the “Schweizerhalle” Process Without Mother Liquor Recirculation

Mother Liquor Circulation in the 1. Process Step

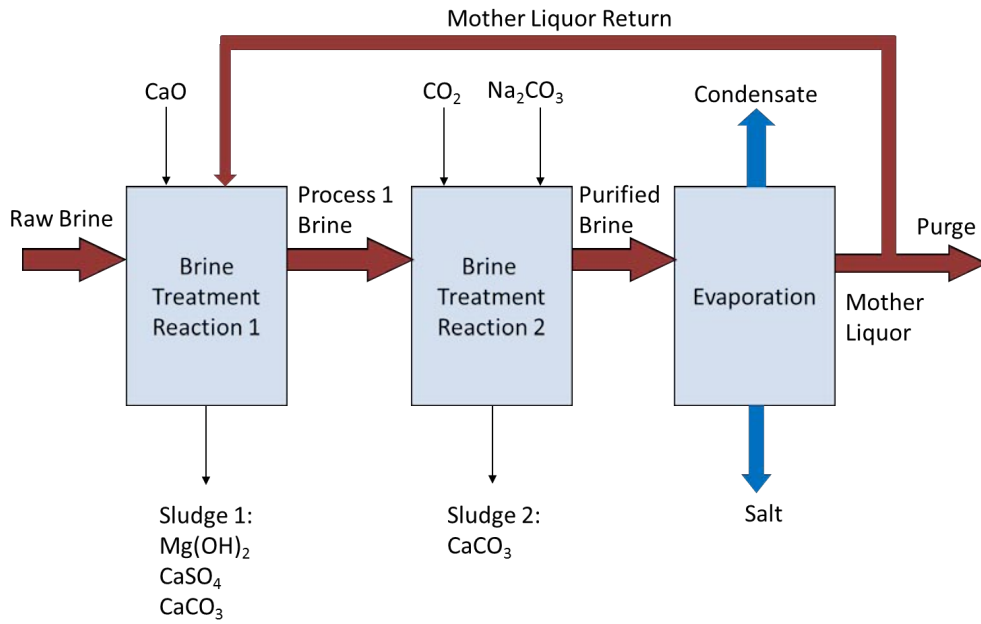
The correlation of the sulfate concentration in the raw brine and the expected caustification reaction and therefore the savings on soda in the second process step after carbonization can be used to optimize the process for raw brines with low sulfate content.

This is done by returning mother liquor from the evaporation process to the first reaction step of the brine purification process.

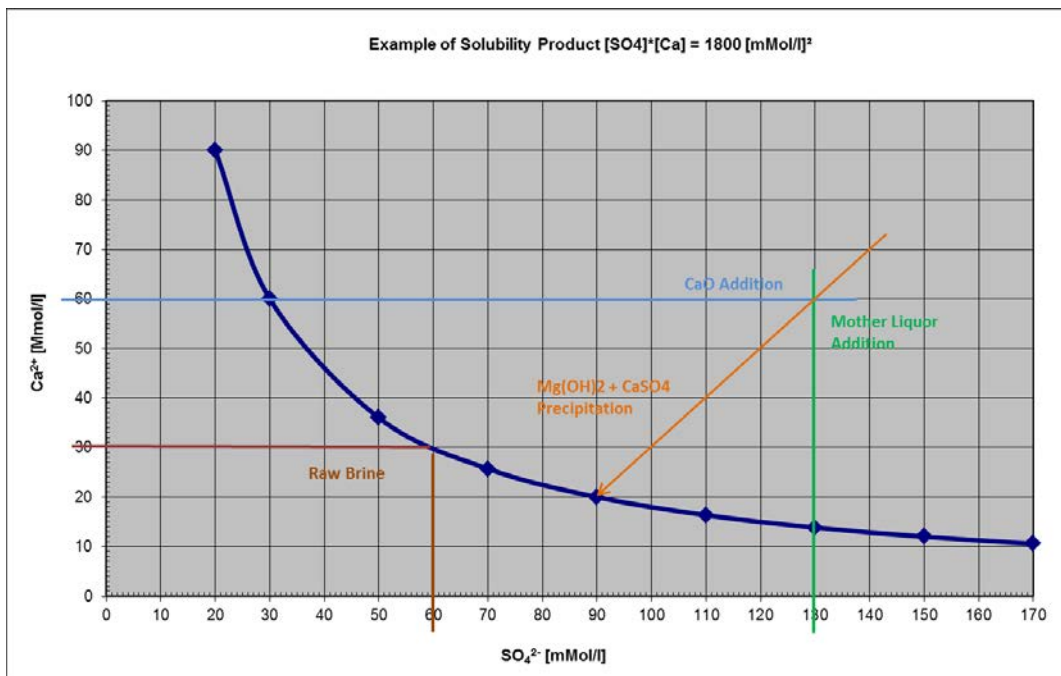
The mother liquor leaving the evaporation process has several favorable properties to support the brine treatment process when it is returned into the first process step, because it is saturated with sulfate. The evaporation process operates slightly under the saturation point of sulfate to produce NaCl in good purity. This is the case for both operating modes, with or without Na₂SO₄ production.

The second favorable condition is the concentration of caustic and soda ash in the mother liquor. The purified brine contains approximately 0.1 g/l of NaOH and 0.3 – 0.4 g/l Na₂CO₃ when entering the evaporation process. This is also concentrated by the same ratio as the sulfate and will support the first reaction step as caustic is needed in any case for the precipitation reaction.

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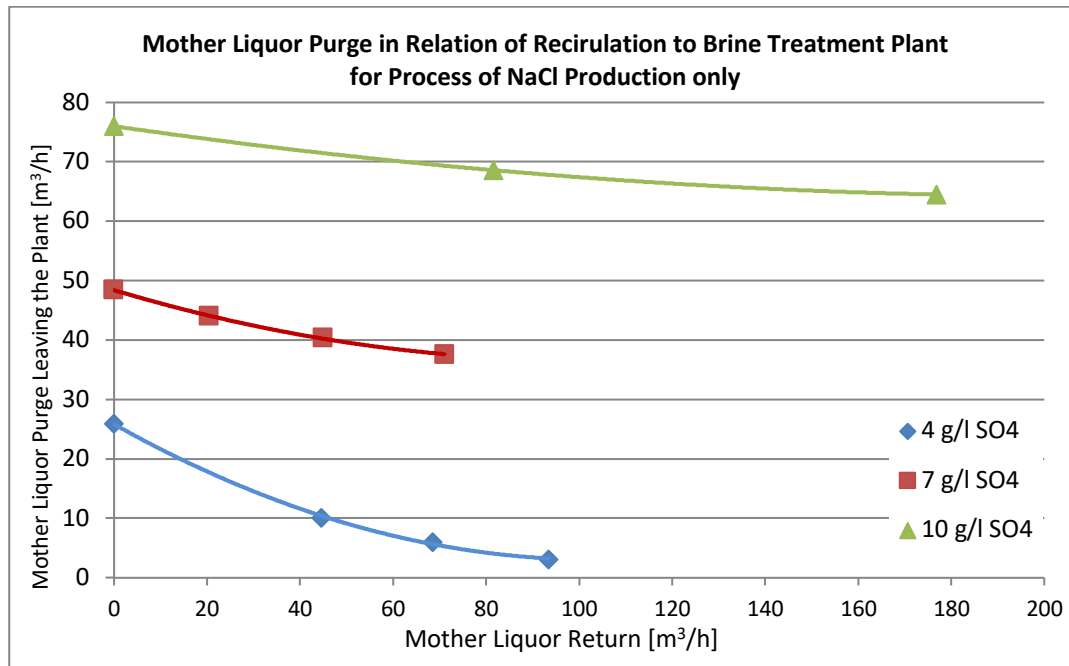
Picture 5: Process Principle "Schweizerhalle" Process of Raw Brine Treatment with Mother Liquor Return to Process Step 1



Picture 6: Example of a Solubility Product of CaSO₄ of 1800 (mMol/l)² – First Process Precipitation with mother liquor recirculation

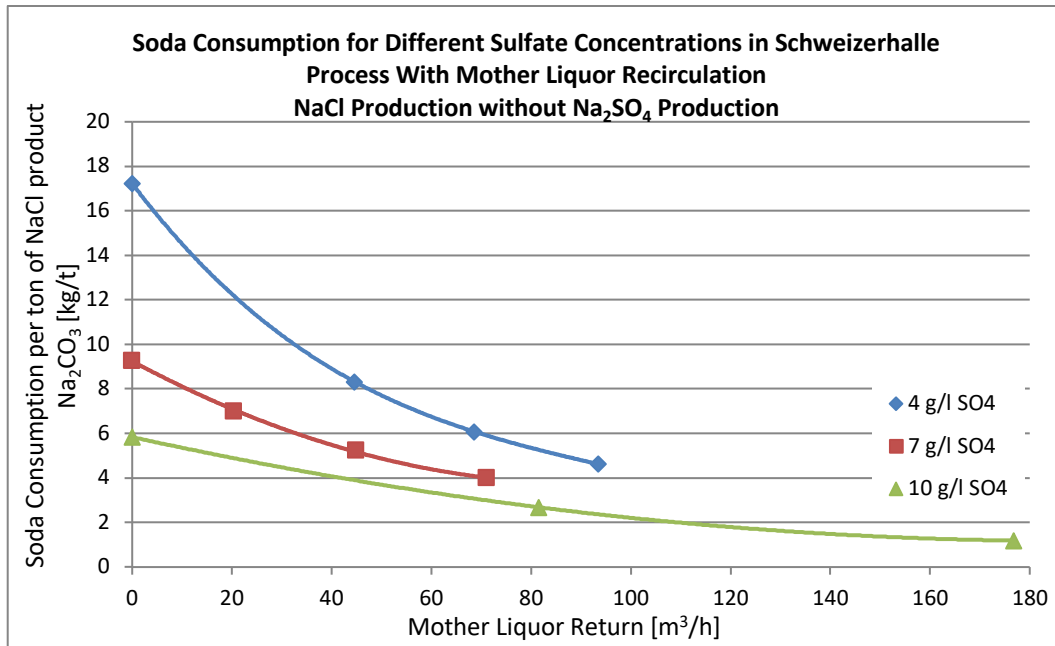
The addition of mother liquor into the first process step will lead to more effects. One of which is the creation of more sludge. Since the sulfate content is increased and therefore a precipitation reaction of more CaSO_4 results, also the question of sludge disposal has to be considered. (See Picture 6) Since the purified brine entering the evaporation process contains approximately 0.3 g/l Na_2CO_3 , this amount of soda will also be found at a corresponding higher concentration in the mother liquor purge.

Depending on the raw brine composition, the liquid purge of the complete system can be very low, which is another positive aspect for disposal issues to be considered. (See picture 7)

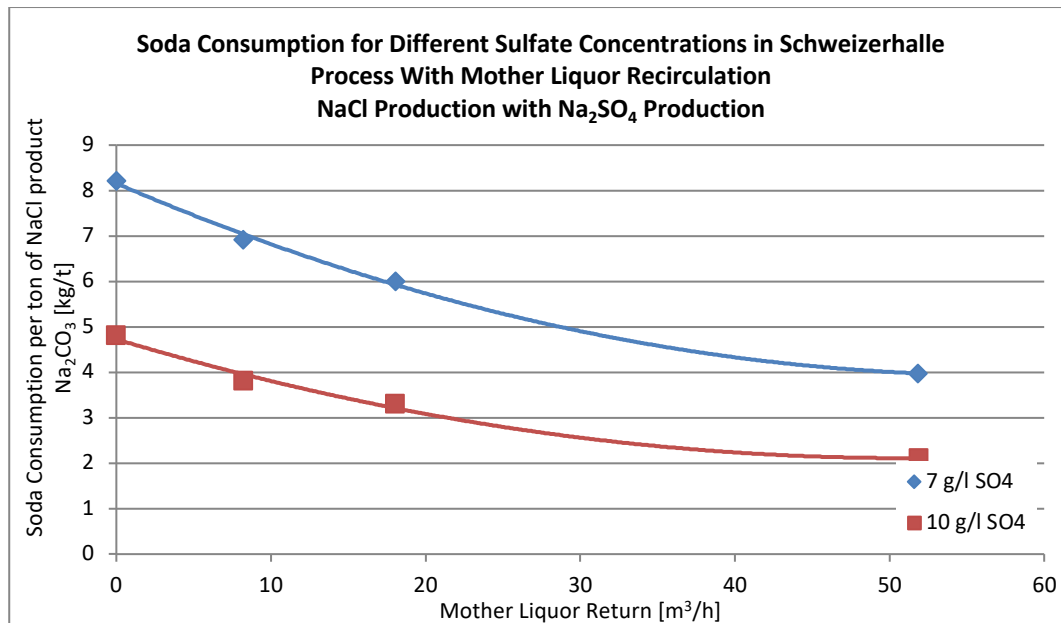


Picture 7: Reduction of Mother Liquor Purge Depending on the Amount of Mother Liquor Recirculation

As depicted in picture 8, the soda ash consumption is strongly influenced by the amount of mother liquor which is returned into the first process step. It is significant that the effect is strongest for low sulfate brine depicted with 4 g/l of SO_4^{2-} concentration in the raw brine. For this case, savings of 70% can be reached. The amount of mother liquor returned is still within feasible margins whereas the process equipment has to be enlarged by approximately 25%. In the above described case there is only a small amount of liquid purge to be expected of approximately 3 m³/h.



Picture 8: Soda Consumption for Different Sulfate Concentrations in the “Schweizerhalle” Process With Mother Liquor Recirculation and only NaCl Production



Picture 9: Soda Consumption for Different Sulfate Concentrations in the “Schweizerhalle” Process With Mother Liquor Recirculation and combined NaCl/Na₂SO₄ Production

Picture 9 depicts the soda ash consumption for different sulfate concentrations in the raw brine for a combined NaCl/Na₂SO₄ process. As already introduced, this process is usually favored for raw brines with high sulfate content. It is clear that the effect of soda saving is not as strong as for low sulfate brine, because the concentration factor of the evaporation process (amount of purified brine divided by the mother liquor discharge) is limited.

Still, savings up to 50% can be achieved easily, whereas also here, an enlargement of the equipment of 25% is the consequence.

The liquid purge of the entire system can be reduced to about 1m³/h, which is in terms of disposal costs and environmental requirements an economic solution.

Comparison and Conclusions

The former process (NaOH/Na₂CO₃) of brine purification is mainly economic for treating raw brines with a low magnesium and sulfate level before they enter the evaporation plant. It is however less suitable to handle brines with a high sulfate content.

It is also recommended for those salt producers, who have caustic soda available at low prices e.g. related to a chlorine-alkaline electrolysis process.

For cases of higher sulfate concentration in the raw brine it is better to use the “Schweizerhalle” process where the caustic is substituted by lime. This raw material is more economic and it will consequently lead to significant savings in soda ash in the second process step. In general the rule applies that the higher the sulfate content is the more soda that can be saved by the combined reaction of CaO caustification and flue gas turn over into soda.

Depending on the chosen salt production process it is also possible to make the “Schweizerhalle”-process economic for low sulfate raw brines. By returning the mother liquor from the evaporation process back into the first reaction step, the concentrated sulfate and caustic in the mother liquor increase the total sulfate level in the first process step and also increase the caustic concentration there. The process conditions are then shifted towards those of high sulfate brine and therefore the second process step turns out to be more economic by significant soda savings.

This is mainly feasible for evaporation processes which are either multiple effect evaporation plants or combined NaCl/Na₂SO₄ production processes, which are both less sensitive to elevated sulfate levels.

Summarizing, it can be concluded that raw brine treatment is a very important process step to make the entire salt production process as economic as possible. There is not only one solution, but different concepts have to be studied carefully for different specific needs to customize the process concept for the salt producer to its best environmental and economic conditions.

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² Steinhauser, G.: Split-Precipitation – an Ecological Alternative in the Purification of Crude Sodium Chloride Brine, BHM 150 (2005), H.8, pp. 283-286

³ Test results from salt plant Austrian Salt Works, Ebensee, A