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Potassium sulfate – A precious by-product for solar salt works

Dr. Heiner MARX¹, Stephan KAPS¹, Dr. Bernd SCHULTHEIS¹ and Dr. Markus PFÄNDER^{1*}

In salt production from sea water, water is evaporated in open ponds and common salt (NaCl) is crystallized and harvested. At the end of sea salt production usually large quantities of high salinity brines, so-called bittern remains. Discharge of that bittern can lead to significant environmental challenges. Furthermore, but not less important, bittern contains a large amount of valuable minerals. To describe how to process sea bittern further to recover and extract these valuable minerals and convert them into precious by-products is the prime objective of this paper. The present work will focus on the production of potassium fertilizers and in particular potassium sulfate as an especially attractive by-product of seasalt production. The paper describes all essential process steps required to produce potassium sulfate (K_2SO_4) and potentially other valuable downstream products. Finally, some project examples and an economic assessment are given to underline, that processing of bittern is not only getting more and more important because society and companies are focused increasingly on environmental protection. In fact, it is shown that extracting valuable by-products out of bittern can be a very economically attractive option to diversify production and create additional input streams for sea salt works with a production capacity of above one million tons of common salt per year.

Key Words : sea salt production, bittern, waste water treatment, potash, potassium sulfate, diversification, by-products

Introduction

Recovering common salt from seawater is usually done by natural evaporation of water using the sun's energy. Solar salt production is a simple, effective and well-known method that is suitable for arid regions with high evaporative rates and availability of land at affordable costs. Roughly 40 % of the current world wide salt production of approximately 280 million metric tons is produced by means of solar evaporation [1]. When seawater is evaporated gradually, brine concentration increases leading to the successive precipitation of different salts when their saturation points are reached. The least soluble salts in seawater as iron oxide and calcium carbonate start to crystallize first, followed by calcium sulfate known as gypsum and subsequently sodium chloride. The common salt is the main product of sea salt production and thus harvested and further processed and upgraded as required. As next mineral magnesium sulfate ($MgSO_4$) would start to precipitate along with sodium chloride so that salt production is usually stopped at this point to avoid impurities in the end product. This leads to vast amounts of reject brine that because of its bitter taste is also called bittern. In most cases sea bittern is currently still treated as waste water and discharged back to the sea, which can lead to significant environmental challenges by affecting the aquatic life. Furthermore, and not less important, sea bittern is a rich source for many chemicals particularly chlorides and sul-

fates of sodium, potassium and magnesium as well as bromine. Various precious by-products further to NaCl can thus be recovered from bittern, which gives good reasons to change the point of view and identify sea bittern as source of raw materials instead of wastewater. The following scheme gives an idea of the quantities of valuable raw materials which can be produced from bittern in order to increase the value chain in saltworks and generate additional income.

Not only because potassium containing minerals precipitate just after the magnesium sulfate mineral epsomite in the crystallization sequence of seawater, but also due to the relatively high prices and easy market access, potassium fertilizers make an economically attractive and interesting by-product of sea salt production.

Potassium fertilizers

Potassium that according to an early production technique is sometimes also called “potash” is required by all plant and animal life. For that reason, potash is the third major plant and crop nutrient after nitrogen and phosphorus. With approx. 90 % of the current potash production, potassium chloride (KCl), also called muriate of potash or MOP, is the most commonly used potassium fertilizer. However, there are some drawbacks to potassium chloride as at high levels of chloride in soil or irrigation water additional MOP can create toxicity. This is especially important for plants

¹ K-UTEC AG Salt Technologies, Am Petersenschacht 7 – D-99706 Sondershausen, Germany

* Corresponding author E-mail : Markus.Pfaender@k-utec.de Tel : +4936326100

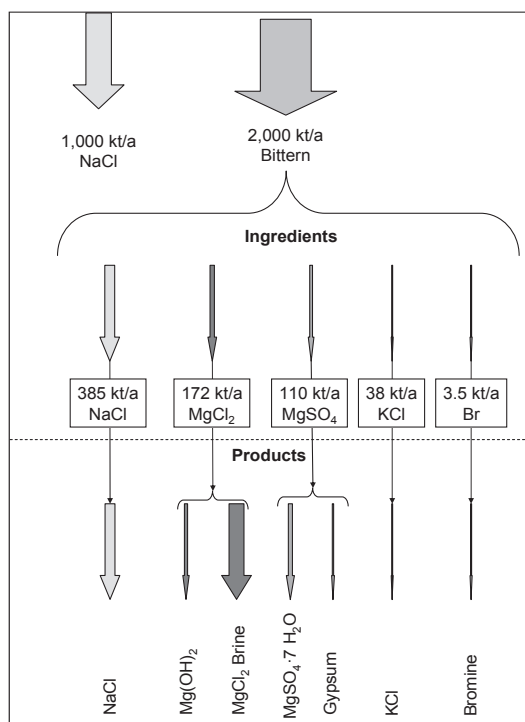


Figure 1 Valuable raw materials in bittern and related commercial products on the basis of a saltwork with a NaCl capacity of 1 Mt/a

that are sensible to chloride. Since potassium sulfate, also called “sulfate of potash” or SOP, does not contain chloride, it is the preferred choice for many high value crops as coffee and several fruits and vegetables. The latter together with the fact that it contains two key nutrients for growing crops, potassium and sulfate, are the main reasons why SOP is considered a premium-quality potash that is valued with currently almost 500 US\$ per metric ton with a premium of more than 250 US\$ per ton compared to MOP [3].

Potash is generally mined throughout the world from potassium deposits, either in underground or surface mines. However, unlike potassium chloride, which is found in many deposits, potassium sulfate is not a naturally occurring mineral and must thus be produced through a chemical reaction by potassium and sulfate carrying components. There are three primary methods for production: first of all, a reaction of potassium chloride with sulfuric acid according to the so-called Mannheim Process, secondly a reaction between potassium chloride and sulfate salts and last but not least and especially important in this context sulfate and potassium containing brine processing that can be applied to the treatment of sea salt bittern.

Process description

In principle, there are two main options for processing of

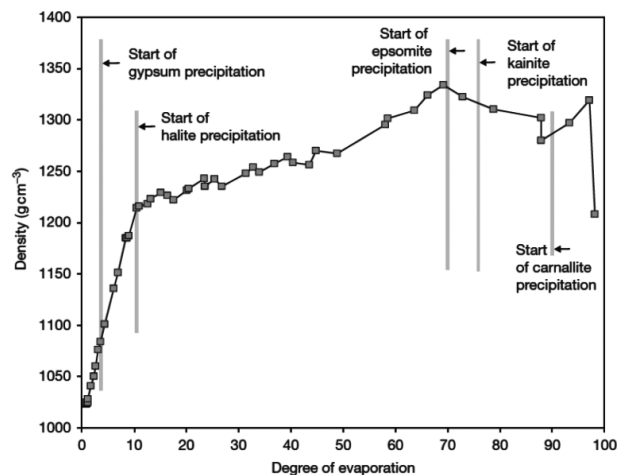


Figure 2 Typical major and minor ion concentrations and density rise in evaporating seawater, degree of evaporation based on Mg^{2+} and Li^+ [2], details may vary dependent on the location.

sea bittern, either the so-called MOP process route for production of potassium chloride and by-products or the SOP process route for production of potassium sulfate and by-products [4]. Because of the higher market prices of SOP and other process related advantages, the SOP process route leads to better techno-economic performance in most cases. Therefore, this paper will focus in the following on the SOP process based on the Kainite-Schoenite process route, which is usually the preferred choice for handling sea bittern.

A simplified scheme for processing of sea bittern with the aim to produce SOP and further saleable by-products is shown in **Figure 3**. As a first step water is removed by solar evaporation resulting in crystallization of a NaCl salt mixture with higher sulfate concentration than the common salt of the previous crystallizer ponds. The salt mixture can either be upgraded to NaCl for industrial use. A further possibility to recover the NaCl content of this salt mixture is a complete dissolution and recycling of the resulting brine to the previous ponds of the solar salt production, which leads to an increase of the total NaCl production.

After crystallization of the major part of NaCl, a Kainite Type Mixed Salt (KTMS) will precipitate by means of fractional crystallization. This KTMS is the input material for the production of SOP via the Kainite-Schoenite process route as explained in the following chapter.

The bittern resulting from the solar evaporation after the KTMS crystallization has a relatively high $MgSO_4$ concentration. Thus, a further treatment of the remaining bittern does usually make techno-economic sense depending however on the concrete boundary conditions of the project in

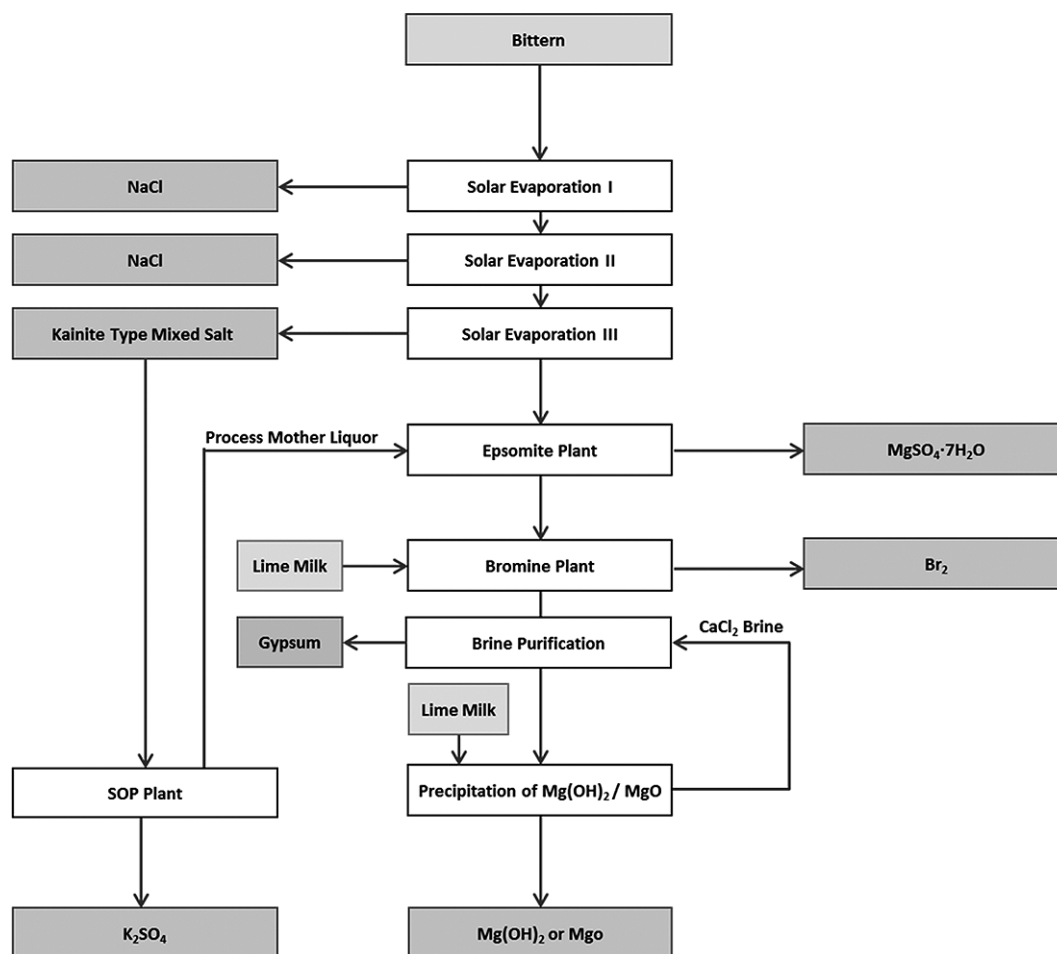


Figure 3 The sequence of process steps of the bittern processing with the aim to produce SOP and other valuable by-products

question as for example size, location and market access as well as prices that can be achieved for the Epsomite. The core process for the Epsomite production is based on cooling crystallization, which uses the strongly decreasing solubility of Epsomite with decreasing temperature.

After this, the partly desulphated brine can either be discharged or be used further for bromine production via oxidation of magnesium bromide (MgBr_2) to bromine (Br_2). Depending on the economics and market access, the resulting concentrated magnesium chloride (MgCl_2) solution could then be used as raw material for potential downstream products as per example Bischofite, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and/or magnesium oxide (MgO). The respective processing of the remaining bittern is based on further concentration of the brine in case of Bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), production and by precipitation and calcination in case of $\text{Mg}(\text{OH})_2$ and MgO production.

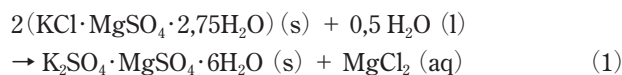
Kainite-Schoenite Process Route

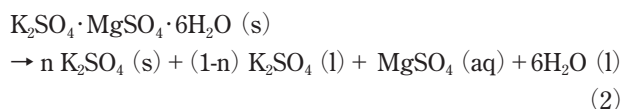
The so-called KTMS is a mixture of different salts and minerals. Beside Kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 2,75\text{H}_2\text{O}$) and NaCl ,

it usually contains Schoenite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), Leonite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) and Sylvine (KCl). In the first step, the KTMS is crushed (Section 100) and the KTMS is converted to primary Schoenite as an interim product by mixing the KTMS with water and cooled mother liquor from a subsequent processing step (Section 200). Although NaCl in the KTMS is generally maintained at the lowest possible level by careful fractional crystallization, an additional purification process step (section 300) might be required to eliminate most of the NaCl before the conversion of Schoenite to SOP. This purification can either be done by flotation or a leaching process respectively.

The purified Schoenite is then subsequently decomposed in water to the desired potassium sulfate while the dissolved magnesium sulfate remains in liquid phase (Section 400). After dewatering, the wet SOP is dried in a fluidized bed dryer and brought to the product storage.

The following gross chemical equations describe the two-stage process from Kainite to SOP.





The Schoenite decomposition liquor contains beside magnesium sulfate about the half of the potash. Making use of the temperature depending solubility of Schoenite a cooling crystallization is thus used to produce secondary Schoenite (Section 600) from the hot SOP mother liquor that is recycled to the Schoenite decomposition process. The cold mother liquor containing still potassium and sulfate as valuable chemicals is recycled back to section 200.

Apart of the product SOP, the only outlet of the process is the Schoenite End Liquor (SEL). Assuming that there are no substantial spilling losses, the primary recovery rate (without taking into account recirculation of SEL) of the SOP process is thus directly related to the amount of potash in the SEL and the corresponding quantity of produced SOP. Primary recovery rates of up to 70 % of potassium can be achieved, while the rest of the potassium is recycled to the pond system. The SEL is however evaporated in the solar ponds by a stage-wise recovery of sodium chloride and KTMS, which is then used again as input for the SOP process plant. Hence, the overall efficiency corresponding to the SOP process is much higher and determined mainly by the losses of the recirculated SEL during the evaporation

process in the solar pond system.

Practical experience and techno-economic assessment

There are several production facilities which operate with a production process for SOP via the Kainite-Schoenite route in Germany, USA, South America and India that work either with sea bittern, salt lake brine or mined mixed salts as raw material. All these SOP plants operate based on two principal steps similar to the presented process route for sea bittern processing: production of Schoenite as an interim product and conversion of Schoenite to K_2SO_4 . Although the process design has to be adapted for each project depending on raw material and concrete boundary conditions, the process technologies applied in the production of SOP and other valuable by-products for sea bittern are well known and considered as proven technology. K-UTEC has been involved in many SOP projects providing engineering and expert services during the whole lifetime of a project from exploration up to operation. Some of these projects have been realized in the meantime and are under operation, others are still in the financing or construction phases. On request an actualized reference list can be provided.

A techno-economic evaluation does always depend on the concrete boundary conditions of a project and has to be

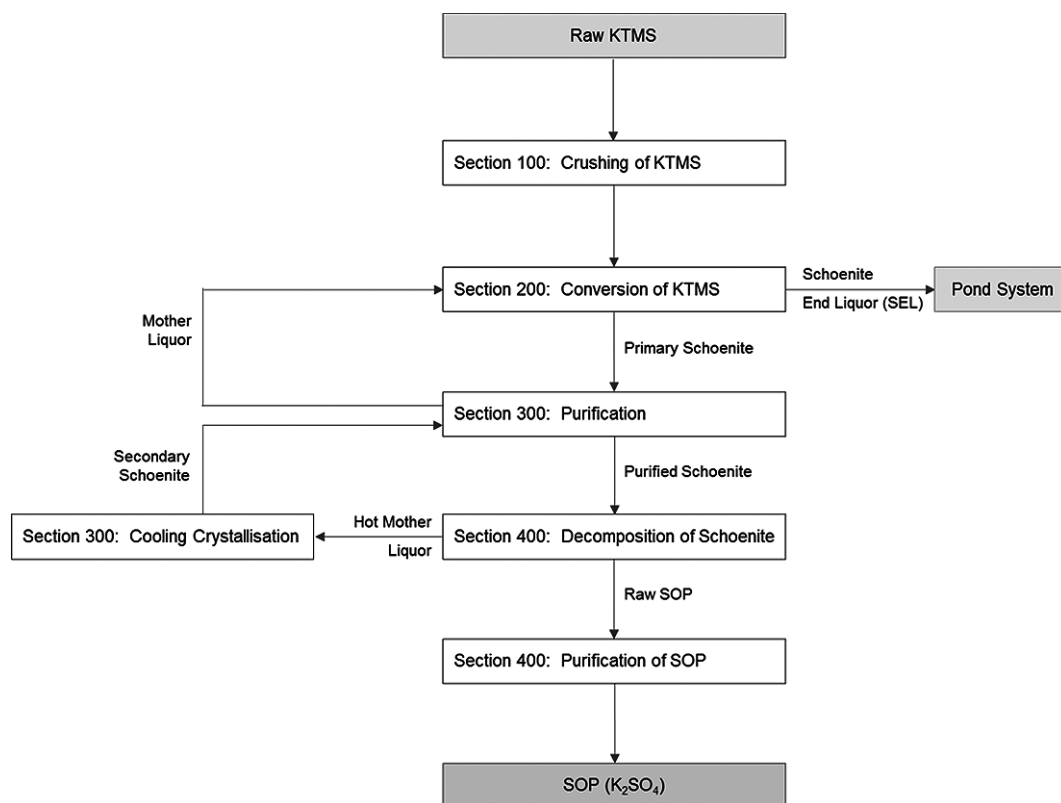


Figure 4 Simplified process scheme for production of SOP based on KTMS

done case by case. Of especial importance for the economic assessment are in that context land cost and soil quality due to land requirement of the additional solar evaporation as well as personal and energy costs affecting directly the OPEX of a project.

The experience of many case studies shows that for sea salt works with an annual production of above 1Mt/a common salt, the processing of bittern with the to produce SOP can reach very attractive paybacks of below 3 years under suitable conditions. In most cases a further treatment of the remaining bittern in an Epsomite plant does even increase profitability, while the economics of production of bromine and magnesium products depend significantly on the overall conditions of a project that have to be studied carefully case by case.

Conclusions

The further processing of bittern for SOP production can be an attractive expansion of solar salt works that is able to 'kill two birds with one stone'. On one hand environmental concerns on bittern discharge are solved with a positive effect on permitting and operation. On the other hand, and not less important, income streams are diversified with premium priced potassium and magnesium sulphate fertilizers of increasing demand and importance. Last but not least the

investment case for bittern processing in solar salt works of a capacity of more than 1MT/a of common salt production can be very attractive with payback times below 3 years under suitable conditions.

K-UTECH has more than 65 years of experience in the potash and salt industry and has demonstrated the capability to investigate, plan and manage the implementation of the Kainite-Schoenite process or similar processes for bittern treatment into existing saltworks. K-UTECH has always in its history been involved in development and operation of SOP processes. Whereas in the past these projects were based on mineral resources in the underground (German potash deposits), nowadays K-UTECH is increasingly working for SOP production from lake brine and seawater bitter.

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