New potassium-projects as a source for sodium chloride products with a high purity

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New potassium-projects in Central Asia are connected with a coupled production of 2-20 tons sodium chloride per ton potassium fertilizer. This expects a further increase of the sodium chloride production in Asia. Respective to the raw material– brines from "solution mining process" or natural brines - the by-product sodium chloride results in a vacuum salt grade or as a NaCl crop with a high purity.
Studies and examinations have shown that a high grade sodium chloride as by-product to potassium chloride is possible. The NaCl- crop is easy to purify, because of the little amount of insoluble components and the absence of gypsum as pollutant.

1. Introduction

Potash salts of a natural origin are always an association of potash minerals with rock-salt. Thereby rock-salt (NaCl) is nearly always the dominant mineral regarding the quantity and the portions.

Typical compositions of the raw-salt of sylvinite used by mining are shown in table 1 [1].

Table 1: Composition of sylvinite raw-salts (specifications in percent)

Component	Canada	Germany	GUS	
	Saskatchewan	K+S	Soligorsk	Ural
KCl	40	20-25	23-26	15-20
others	8-10	2	4-9	3-6
NaCl	50	75	65-75	75-80

Despite the dominance in quantity of the raw material component sodium chloride potash plants work usually without the utilization of the NaCl given in the raw salt as a by-product. On the contrary this is heaped up as huge salt dumps.

The reason of the non-utilization of the rock-salt produced together with the potash raw salt as an independent product are the problems and the associated costs of a cleaning, as well as logistical questions, because most of all there is no conformity between the locations of potash plant sites and the ones of important NaCl consumers, i.e. the chemical industry. This results in not inconsiderable transport costs for the NaCl production on a potash plant site. Additionally there are often cheaper possibilities for the production of very clean NaCl industrial salts due to carefully specific directed mining exploitations of pure rock salt seams in Europe, for example in the plants of Bernburg, Borth, Grasleben or Heilbronn.

The situation of the potash producers that manufacture potash fertilizer salts of natural sources or by means of solution mining of potassium bearing brines, is similar. Also in the case of a natural brine deposit sodium chloride is therein contained in higher proportions than potassium chloride. Therefore it would be obvious that of potassium including brines at least not only potassium chloride but two products are manufactured. Fig. 1 shows the bulk proportion of brine contents of different potassium containing natural brine deposits expressed as a percentage compared with seawater [2], [7].

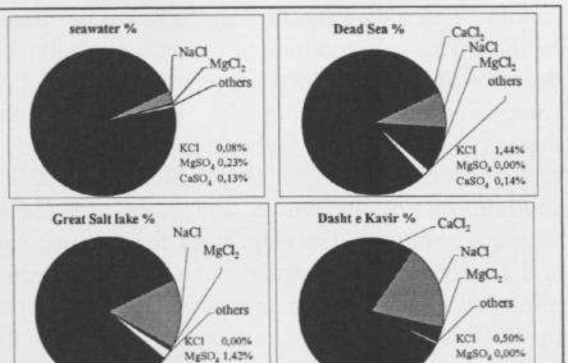

Fig. 1. The composition of seawater in comparison to the brines from Dead Sea, Great Salt Lake, and Dasht e Kavir

2. Possibilities of the production of common salt in the frame of the potash-project in Central Asia.

In the recent time further potential potash producers are occupied with the development of potash deposits, which are not already exploited and that similarly to the case of the Dead Sea should not be conventionally mined with a subsequent beneficiation of the potash raw-material, but recovered by means of a potassium chloride bearing brine.

In central Asia in the region of the so called Tadshikistan valley an extensive Evaporite-Formation is known, which contains potash deposits in an economically exploitable extent in the areas around Gaurdak (Turkmenistan) and Tjubegatan (Uzbekistan). The potassium salts are placed in low depths and are skilled in the west of the mountain chain of Kugitang in the immediate borderland of Uzbekistan (Tjubegatan) and Turkmenistan (Gaurdak) as the highest part of a mighty salt sequence formed in four stratigrafic horizons. The potassium salts exist as red sylvinite, which partly contain small amounts of carnallite [3].

Fig. 2 shows the profile of these salt deposits. This potash deposit should be won according to the method of solution mining after extensive comparison of different mining processes. Despite the usual manner of the solution mining for mighty rock salt deposits the solution mining of this deposit should be executed by an adapted solution mining method. This solution mining procedure is based on the state of art of doubled caverns for the carnallite solution mining [4]. For the conditions of the deposit of the location Tjubegatan a special kind of a solution mining cavern is functional. In fig. 3 a solution mining cavern is shown schematically, which adapts on the caving in on the salt deposits and consists of a vertical drilling and a deflected one. This novel type of procedure was developed by KBB enterprises, Hannover. By means of the solution mining process a concentrated KCl, NaCl brine is formed, which contains by the components KCl and NaCl approximately in the relation 1 part KCl to 2-2.5 parts NaCl and that is to benefit to two product ranges.

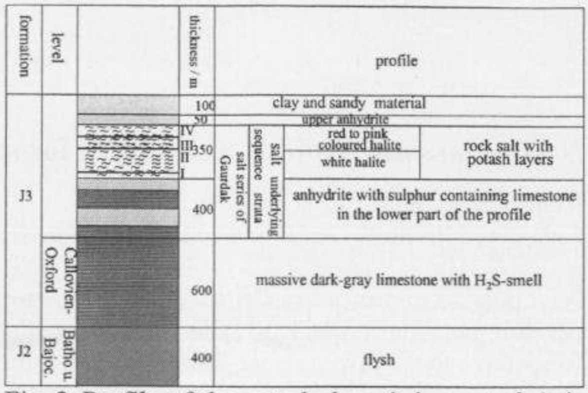

Fig. 2. Profile of the potash deposit in central Asia (Fiweg 1961)

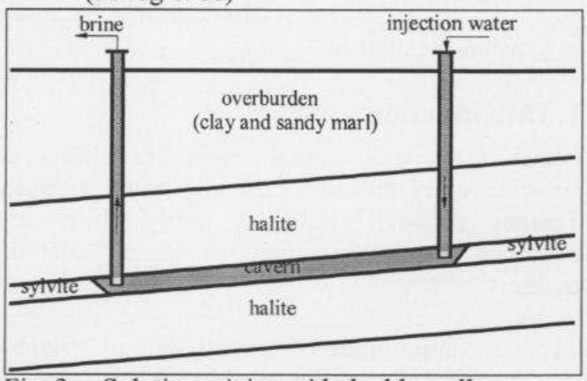

Fig. 3: Solution mining with double wells

For the technology of treatment of this KCl, NaCl brine different basic procedures can be taken into consideration. Fig. 4 shows the known equilibrium diagram of the system $KCl-NaCl-H_2O$ with the concentration given in " grams contained salt per 1000 grams H_2O". The representing point of the brine saturated with KCl and NaCl is reported as point P1 on the 25 °C isotherm. P2 is also reported for the brine saturated with both salts on the 95°C isotherm.

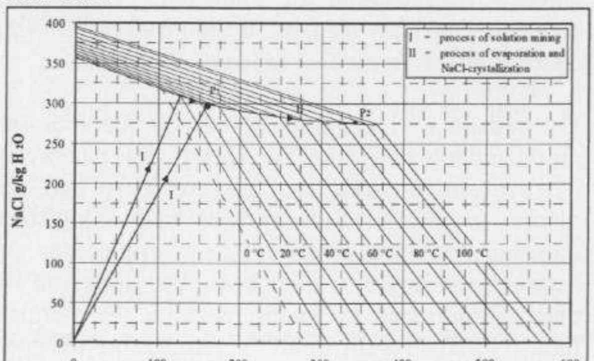

Fig. 4. Equilibrium system $KCl-NaCl-H_2O$

This ternary system forms the frame of a possible technical winning procedure for the separation of the salts KCl and NaCl in a technical process. Per 1 bulk proportion KCl there must be separated 2 up to 2.5 bulk proportions NaCl and approximately 8.5 volume shares of water.

In fig. 5 the possible treatment procedures are shown schematically. For the process-selection the procedure called A can be chosen, which is characterized by the evaporation of water on a temperature that is as high as possible, the NaCl crystallization and the separation of the NaCl-crystalline crop at temperature given in the evaporation process as well as the subsequent crystallization of KCl by means of cooling the solution.

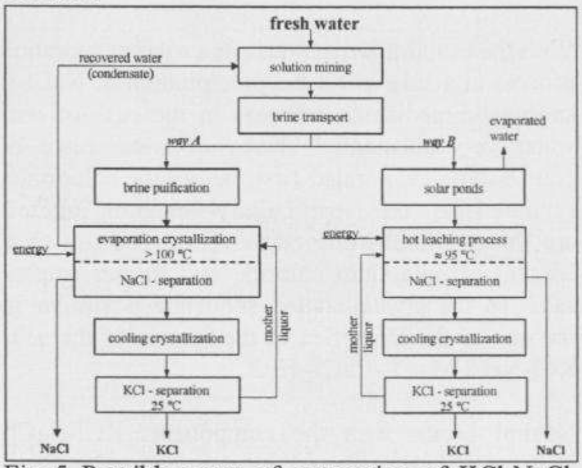

Fig. 5. Possible ways of processing of KCl-NaCl-H_2O brine

The procedure B is based on the evaporation process of water in a solar pond as a first step, the harvest of the KCl-NaCl-crystalline crop and on the separation of KCl and NaCl in a hot leaching and crystallization process in a second step. Due to a decision for a thermal method in accordance with method A a process known from the salt technology can be taken into consideration. Therefore the NaCl crystallization is effected in an evaporation apparatus. If the KCl-saturation-concentration of the solution is reached it is treated by cooling it down to crystallize the nearly pure potassium chloride. In fig. 6 the most important elements of the evaporation process are shown

An alternative for this technology is the KCl/NaCl production by solar evaporation and the production of saleable NaCl KCl products. This technology is shown simplified in fig. 7. The procedure of the

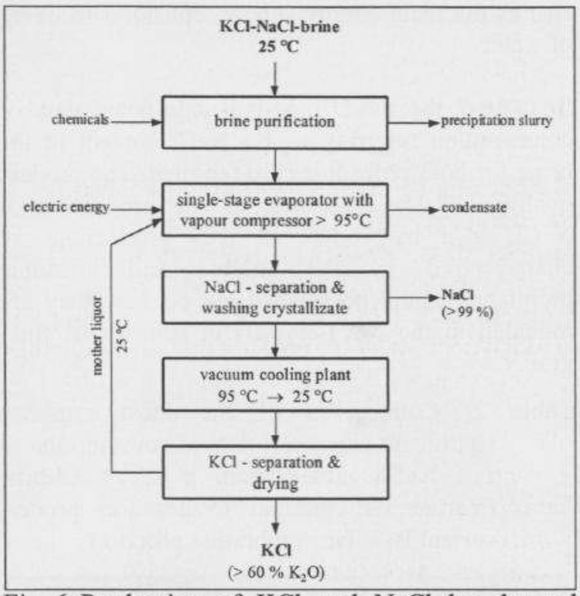

Fig. 6. Production of KCl and NaCl by thermal evaporation of brine (route A)

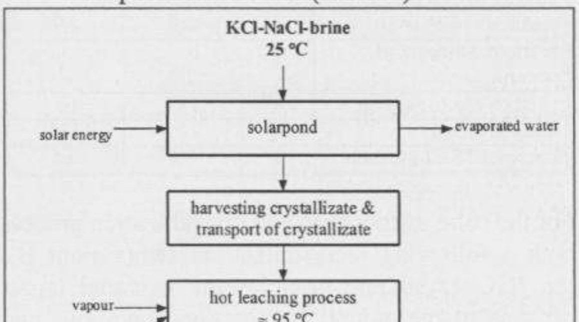

Fig. 7. Production of KCl and NaCl by solar evaporation and hot leaching process of KCl-NaCl-crystallizate (route B)

thermo-compression-evaporation-plant needs an electrical power supply and recovers next to KCl and NaCl in a good saleable quality the water contained within the KCl/NaCl-brine. The method with the solar evaporation and re-crystallization of the KCl-NaCl-crystalline crop uses solar energy for free as the main energy supply, but not a recovery of water.

In table 2 the most important significant data of consumption referring to 1 t NaCl content in the brine for both procedures are reported. The product qualities of NaCl reached by the production of NaCl as a by-product of KCl production are characterized by the soluble and insoluble pollutants cannot be washed out because they are included in the NaCl-crystals in spite of its fine-grainy.

Table 2. Comparison of the most important significant parameter data of consumption for 1 t NaCl gained from a KCl/NaCl-brine (Variant A: thermal evaporation process; variant B: solar evaporation process)

significant parameter		Variant A	Variant B
amount of brine	m^3	3.4	3.4
amount of evaporated water	t	2.9	2.9
recovered amount of water	t	2.7	-
need on electric energy	kWh	165	60
need on steam	kg	-	230
amount of KCl-product	t	0.4	0.4

For the solar evaporation and crystallization process with a following recrystallization step(variant B), the NaCl-crystalline granules are essential larger because of the natural evaporation conditions and pollutants can be removed partially by means of crushing of the NaCl-crystals.

The quality of the produced NaCl crystalline crop as a by-product is different for both methods as table 3 shows.

Table 3 Reachable product quality on the production of NaCl of the KCl-NaCl brine according to different production methods (Variant A: thermal evaporation process; variant B: solar evaporation process)

parameters of quality		Variant A	Variant B
content of NaCl	%	>99.5	>99.0
content of KCl	%	<0.4	<0.4
content of soluble by-components ($MgCl_2$)	%	<0.05	<0.1
content of $CaSO_4$	%	<0.1	<0.3
content insoluble components	%	<0.01	<0.2
grain size	mm	<0.8	0.5-5

3 Possibilities of the production of common salt in the framework of the potash production of natural brines in Middle East

The very substantial deposits of of natural brines in the form of salt-lakes or recent salt lakes represent a not insignificant natural NaCl resource. The Middle East region possesses a nearly inexhaustible NaCl resource. The utilization of salt lakes for the NaCl production has already started [5]. Particularly the recent salt lakes contain very large quantities of NaCl in a dissolved form. The naturally existing salt solution, the so-called Playas always contain the component NaCl at the saturation-concentration.

With the evaporation of water in a solar evaporation process in a solar pond the precipitation of NaCl is starting immediately, whereas in the case of sea-water very substantial shares of water have of course to be evaporated first, before the solution is saturated [7]. Of a particularly economic interest are these natural brine occurrences, because their content of potassium chloride and further soluble salts, so the crystallization sequence is similar to the one of the Dead Sea in the system of the salts $KCl-NaCl-MgCl_2-CaCl_2-H_2O$.

Natural brines with the components $KCl-NaCl-MgCl_2-CaCl_2-H_2O$ should not only be used at Dead Sea but also by using the brine-deposits of the Playas for the potassium chloride as well as for the sodium chloride production.

In such natural brines the concentration of potassium chloride amounts considerable less then its saturation-concentration, whereas the brine is practically saturated on the component NaCl and the concentration of NaCl is only determined by the concentrations of concentrations of the alkaline earth chlorides $CaCl_2$ and $MgCl_2$.

If such natural brines are evaporated under natural conditions of solar evaporation to her maximum possible final concentrations concerning $MgCl_2$ and $CaCl_2$, a course of the KCl concentration during the evaporation process results like the course of the KCl concentration is shown in fig. 8.

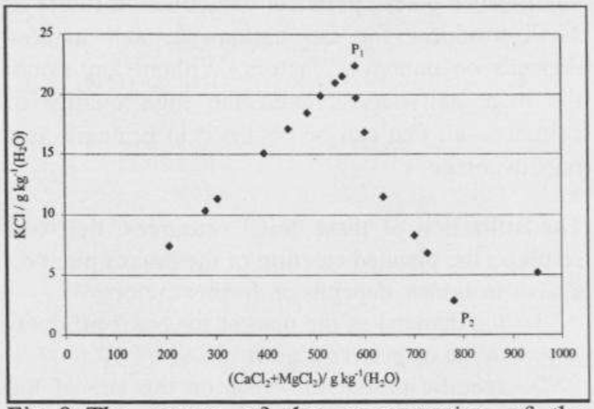

Fig. 8. The course of the concentration of the component KCl in dependency on the increasing total concentration $CaCl_2$+$MgCl_2$ during the evaporation process. P1 represents the maximum and P2 represents the minimum values of KCl

Until the concentration on point P1 KCl does not crystallize as a KCl deposit and its concentration increases to a maximum possible value. If the concentration of $CaCl_2$+$MgCl_2$ at P1 passes over the KCl concentration decreases steeply and carnallite $KCl{\approx}MgCl_2{\approx}6H_2O$ precipitates. The lowest potassium chloride concentration is reached in point P2. On further evaporation the KCl concentration increases, so that the evaporation process has to be terminated on Point P2.

Much more simpler is the course of the concentration of the component NaCl as the fig. 9 shows. Until the point P1 pure NaCl crystallizes, from P1 to P2 NaCl and carnallite crystallize simultaneously. The NaCl saturation concentration of advanced NaCl crystallization process depends essentially on the total concentration of $CaCl_2$+$MgCl_2$ and the ratio of $CaCl_2$:$MgCl_2$ [8].

Typical natural brines have a ratio NaCl:KCl more then 20:1. The consequence of this special feature is that until the carnallite saturation point P1 more then 95% of NaCl dissolved in the origin brine have precipitated.

Per 1 000 t KCl result more then 20 000 t NaCl as a compulsion additional bulk what represents an importable usable resource if the NaCl crystalline crop is harvested and cleaned by a salt washing process, analogous to the treatment of crude sea salt.

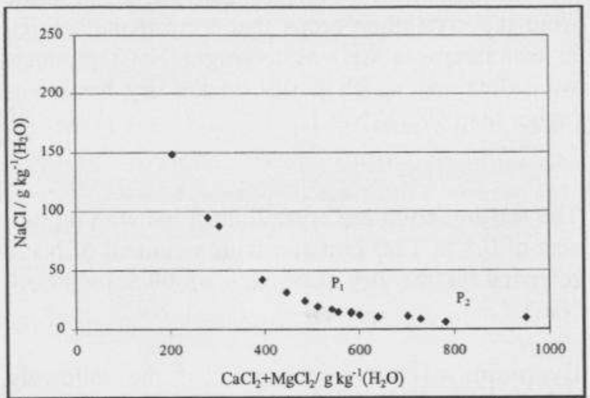

Fig. 9. The course of the concentration of component NaCl in dependency on the increasing total concentration $CaCl_2$+$MgCl_2$ during the evaporation process. P1 represents the maximum and P2 represents the minimum values of KCl

The study of the crystallization processes of such natural brines was effected by commissioning of the fractional crystallization process by solar evaporation of the brine in a small scale pilot plant which is shown in fig. 10. This experimental arrangement allows the modeling of nearly all influential natural parameters of a solar pond complex, like the incidence of radiation and its intensity, effect of wind modeling the day-night and seasonal rhythm as well as the quasi continuos operation conditions with quantities of brines of several cubic meters for several months within a brine density range of 1.20 to 1.45 g/cm^3. The compositions of the solutions obtained, amounts of crystalline crop as well as the morphological and physical properties if the crystalline crops are very similar to crystalline crops, which are obtained under natural evaporation conditions at the location.

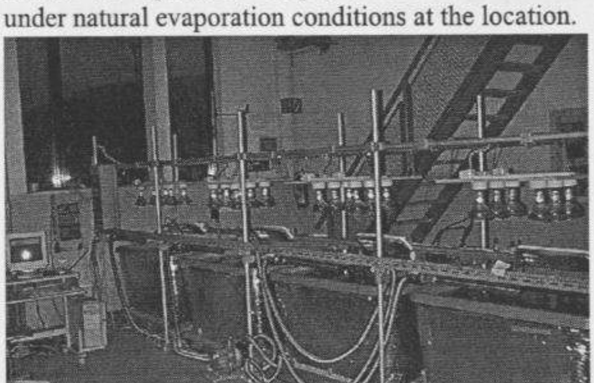

Fig. 10. The small plant for modelling the solar evaporation of brines

By washing with water respectively NaCl brine from the crystalline crops that were manufactured in technicum as well as in origin NaCl products were obtained which purity on the dry basis was higher than 99.5% NaCl.

The starting point are crystalline crops with a grain size of 0.1 to 10.0 mm and with a content of NaCl referring to the dry substance of 98.5 to 99.0% NaCl.

By means of the combination of the following process steps

- elution and displacement of the adhering mother liquor
- crushing and sieving
- filtration and washing of the crystalline crop with a NaCl brine

NaCl solution refined crystalline product qualities were obtained, that reached the following quality characteristic values: Fig. 11 shows the graphical illustration of the results for a chemical analysis.

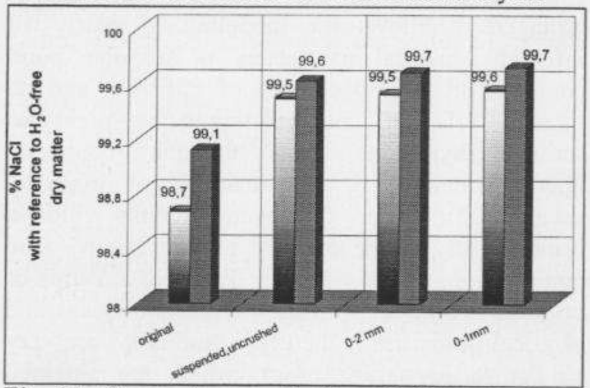

Fig. 11. Comparison of the NaCl-content of original crystalline crop (hatched columns) and washed products (gray columns)

4 Conclusions

With the results that were obtained the possible quality of common salt is proofed as equal until better in comparison with the product qualities won of seawater crystalline crops [9]. Thereby it must be considered that per 1 t of the target product potassium chloride until 20 t of cleaned NaCl-product could be generated to some extent incidentally. Important quantities of superior common salt can be manufactured as a by-product of the expected potash fertilizer production. The significance potash producer can obtain in future as NaCl producer for the nationwide salt marked depends on numerous factors. Without any doubt the huge salt deposits and the high quality of common salt that can be obtained in principle is a big advantage.

The utilization of these NaCl resources, that will result on the planned erection of the potash plant on a basis of brines, depends on further factors:

1. the demand of the market for NaCl-products in the respective region
2. specific production-costs on the site of the potash-plant
3. specific transport costs for the transport between the potash plant-site to the location of the consumer
4. production- and transport-costs of competing NaCl products within the respective region.

Altogether the possible production of NaCl products of future potash-plants on a brine basis is an very important quantitative resource that can be made available in a comparative high product quality and for low production costs on the site and can quantitatively as well as temporarily nearly unlimited placed for disposal. Decisive for its utilization will be to solve the logistical problems and the warranty of acceptable transportation costs, because potash resources are rarely situated on the yet situated consumption points of emphasis and therefore transport costs are not inconsiderable.

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