Carnallite and Potassium Chloride Crystallisation and Washing

P.A. Fokker[a]; J.R. Ipema[a]; P.V. Steeneken[a]; D. Verdoes[b]

a: NEDMAG INDUSTRIES Mining & Manufacturing B.V.
P.O. Box 241; NL9640AE Veendam; the Netherlands
Tel: +31 598651223 / ..911 ; p.fokker@nedmag.nl; p.v.steeneken@nedmag.nl; www.nedmag.nl

b: TNO Institute of Environmental Sciences, Energy Research and Process Innovation, dep. of Chem. Eng.
P.O.Box 342; NL 7300 AH Apeldoorn
Tel: +31 55 5493053; d.verdoes@mep.tno.nl

Nedmag Industries, a producer of magnesium chloride salts and Dead Burned Magnesia is investigating the production of carnallite and (via carnallite) of potassium chloride salt (sylvite) at their Mining site in the north of the Netherlands. Presently, they are testing the production and processing of pure carnallite ($KMgCl_3.6H_2O$) from (solution mined) brine, saturated with carnallite at 65 °C. Main goal is to recrystallise this carnallite to pure KCl (99- 99.5% KCl or 62% K_2O), though there exists a limited market for pure carnallite as well. Nedmag owns large caverns filled with 65 °C saturated carnallitic brine, according to ambient (1500 m depth) formation temperatures. The brine composition is about 27 % $MgCl_2$, 5% KCl, 2% NaCl and 1% $MgSO_4$. At cooling to 20 °C about half of the brine's KCl drops out as relatively pure carnallite (99% of $MgCl_2$, KCl and crystal water and max. 0.7% of NaCl and 0.2% $MgSO_4$).

Up to now, cooling has been performed by direct cooling over a cooling tower, which causes the brine to cool to 10-15 °C above the ambient temperature, with only limited salt crusting on the cooling surfaces themselves. Further (limited) crystal growth occurs in a stirred holding tank. This simple system already renders crystals with a D_{50} of 200 microns.

Dissolution recrystallisation of the relatively pure carnallite to KCl renders a low sodium and sulphate product. To reduce the magnesium compound, the separation of crystals and mother liquor can be done by a centrifuge with washing or alternatively by a Hydraulic Wash Column. This patented apparatus, developed by TNO research laboratories in the Netherlands, washes the crystals by a countercurrent flow of washing fluid, where washing fluids and mother liquor are removed halfway the crystal bed through a set of filters. It can therefore not only displace the (free or adhered) impure mother liquor, but has some salt dissolving capacity as well.

1. INTRODUCTION

NEDMAG INDUSTRIES Mining and Manufacturing have been solution mining magnesium chloride salts for almost 30 years. NEDMAG produce brine from thick layers of carnallite and bischofite in the Zechstein formation at a depth of 1500 metres. The brine has mainly been used as feed for NEDMAG's Magnesia plant, producing Dead Burned Magnesium Oxide, while an increasing quantity of brine is sold to third parties. NEDMAG are presently focussing on expanding into special products rather than on bulk magnesia production. They are a leading producer of high-grade calcium chloride brine, magnesium chloride brine and ~flakes, and magnesium hydroxide slurry.

After focussing on and mastering of the production of bischofitic brine (bischofite = $MgCl_2.6H_2O$), NEDMAG now focuses on the carnallitic brine (saturated with the salt carnallite $MgCl_2.KCl.6H_2O$ at 70 °C). This brine contains some 8% "impurities" (5% KCl, 2% NaCl, 1% $MgSO_4$) and is therefore not used as direct magnesium chloride source. However, experiments have demonstrated that very pure carnallite can be crystallised by cooling. A 99%-99.5% KCl product can be crystallised in a single step from the carnallite, provided that the residence time and washing are sufficient to remove the remaining impurities via the brine.

2. COOLING CRYSTALLISATION

Approximately 70 m^3/h of brine needs to be cooled from 65 °C to as low as is economically feasible (in practice ~ 20-25 °C as year's average), which requires some 4 MW of heat to be removed from the system. The decrease in salt solubility with temperature will cause carnallite to crystallise, provided that the $MgCl_2/KCl$ ratio is neither too high (resulting in bischofite precipitation) or too low (KCl precipitation). See Figure 1.

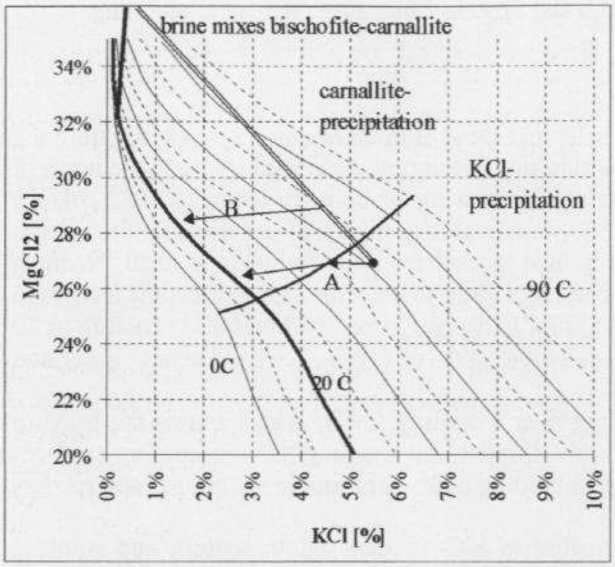

Fig. 1 Phase diagram KCl-$MgCl_2$ (saturated in NaCl). Slightly undersaturated brine follows line A: KCl precipitation, followed by carnallite precipitation. Mixed bischofitic-carnallitic brine could follow path B: only carnallite precipitation.

If the brine is slightly undersaturated in carnallite, KCl will precipitate until the carnallite saturation is reached (line A in Fig. 1). This will create a slurry of small KCl crystals (10-50 micron) and large carnallite crystals (150-250 micron), which is difficult to handle. Besides, KCl produced from carnallite contains 2-3 times less bromine than KCl crystallised directly form the mother liquor (80 versus 200 ppm). To obtain a low Br concentration in the KCl, 20-30% bischofite brine is added to the carnallite brine to prevent direct KCl precipitation. The KCl content of the brine (after precipitation) should remain above 1.5-2% however, to avoid large scale NaCl co-precipitation. Too much NaCl in the carnallite cannot be removed by a one-step dissolution process and thus will end up in the KCl or will require extra dissolution water and product loss.

Two systems are still under consideration for economical optimisation: (i) evaporation cooling by applying a vacuum evaporator, and (ii) direct cooling of brine over a cooling tower.

2.1 vacuum evaporator

Vacuum evaporation cooling combines two aspects: it cools down and concentrates simultaneously, the former being responsible for about 80% of the crystallisation. The 10 °C boiling point elevation limits the attainable cooling temperature when using plate condensors. This effect can be largely neutralised by spraying cold concentrated brine as a condensation medium.

2.2 cooling tower

The alternative system, much cheaper in investment and operation costs, has been tested on the NEDMAG Mining site. Carnallitic brine has been directly cooled over a cooling tower. The 300 m^3/h water capacity cooling tower has been subjected to a 40 m^3/h flow of saturated brine, in some tests with an additional recycle of 30 m^3/h. At least 90% of the salt precipitates as single crystals with a 150-250 micron diameter, even though the residence time must be low (less than 1 minute). The tower contains internal packs of plastic sheets to delay the brine flow and to increase evaporating surface. These sheets slowly encrust, especially at the lower side of the tower, from where the slurry falls on the bottom plate. Small stalactites form as well. The air flow up (and thus the tower's performance) decreases with encrustment. After a production period of 5-10 hours, the tower needs to be flushed with water or dilute brine to re-dissolve the carnallite. Usually a 5-10 minute flushing with 100 m^3/h was sufficient to clean the tower.

The fan-induced whirlwind in the cooling tower causes a vortex of the slurry on the tower's bottom plate, which takes all crystals towards the tower's exit automatically.

The efficiency of the cooling tower (in terms of kilograms of salt per cubic metre of brine) is estimated to be some 80-85% of that of the vacuum evaporation, including the flushing losses. The evaporation contribution to the cooling will be somewhat less than for vacuum cooling; the final temperature will be approximately 5°C higher. Employing at least two towers allows a time triggered flushing of one tower, while the other tower(s) takes a larger brine flow during the 10 minutes flushing time.

The thin slurry is pumped to a reactor vessel to allow further (limited) crystal growth and thickening through hydrocyclones.

3. CARNALLITE SEPARATION

The carnallite crystals need to be separated from the mother liquor, since the latter contains 90-99% of the sodium, sulphate, and iron impurities. First concentration will be performed by hydrocyclones, to concentrate the slurry from 5-wt% to 50-wt% solids. Two further separation methods have been tested: (i) a centrifuge and (ii) a wash column.

A centrifuge renders a 3% free water crystal product with only 0.2-0.3 wt% Na (0.5-0.8% NaCl) and 0.1 wt% SO_4.

Separation has been tested with a TNO Hydraulic Wash Column as well, discussed in more detail in chapter 5. After countercurrent washing, the remaining carnallite has 30%-50% lower sulphate and sodium levels than after centrifuging. Brine from the decomposition of carnallite (i.e. carnallitic brine with a low sodium and sulphate content compared to the cavern brine) has been used as washing liquid. The additional purification is not crucial for the production of 99% KCl, however. Once the column becomes an established and proven apparatus for the process industry, it may become economically attractive as a replacement for the centrifuge.

4. CARNALLITE DECOMPOSITION

To obtain potassium chloride from carnallite, decomposition is induced by adding water. The carnallite dissolves under precipitation of KCl. The solution will contain KCl as well, causing a loss of 20-35% of the KCl from the carnallite with the brine. Part of this loss can be regained by feeding the brine to the carnallite crystalliser.

The sodium chloride, magnesium sulphate and carnallite, should be given time to fully redissolve, The amount of water required for full dissolution of carnallite at say 50°C, (about 2 m^3 per 3 tons of carnallite) can dissolve a 3 wt% NaCl impurity of the carnallite, while only a 0.8 wt% needs to be removed. Even in NaCl-undersaturated brine not all NaCl will dissolve. Insufficient residence time or its presence as inclusions may cause a fraction to slip through the system. A 100% dissolution / separation is hence not attainable.

5. KCL WASHING AND SEPARATION

After decomposition, the KCl crystals should be separated from the brine to remove as much Mg, Na, SO_4 and water as possible before sending the crystals to a dryer. Preconcentration can be performed by a hydrocyclone. Especially the removal of $MgCl_2$ from the KCl slurry is difficult, since brine and remaining carnallite crystals are significant Mg carriers. With centrifuging or repeated filtering and washing it is difficult to get the $MgCl_2$ concentration below 1.5% (15000 ppm), whereas the aim is 500 ppm or less. Sodium and sulphate levels were already within the anticipated specification.

5.1 Wash column

A test has been performed with an experimental TNO Hydraulic Wash Column to further reduce impurity levels. The principle of this TNO-patented wash column is countercurrent washing of crystals in a continuous operation (see Figs. 2, 3). The experimental column is a glass cylinder of 15 cm diameter and 100 cm length. Six steel tubes of 2 cm diameter have been installed, having a 4 cm filter opening 15 cm above the tube's bottom. These filter(pipes) drain away the downward flowing brine and the upward flowing washing liquid, so that in principle only solids are pushed along the filters. Crystal slurry is injected into the column's top section. When reaching the crystal bed, the solids sediment, while the brine flows through the porous crystal bed towards the filters. The brine flow generates a hydraulic downward force on the bed, which is balanced by the pressure below the bed (the reslurry chamber) and the wall /filter pipe friction. At certain bed height and brine flow the bed is pushed downwards into the reslurry chamber. Here the bed is disintegrated by a rotating scraper knife and mixed with reslurry/washing fluid to allow pumping and pipeline transport of the slurry. The brine in the product slurry can be centrifuged and re-used as washing fluid, with additional makeup water to compensate for the washing flow losses.

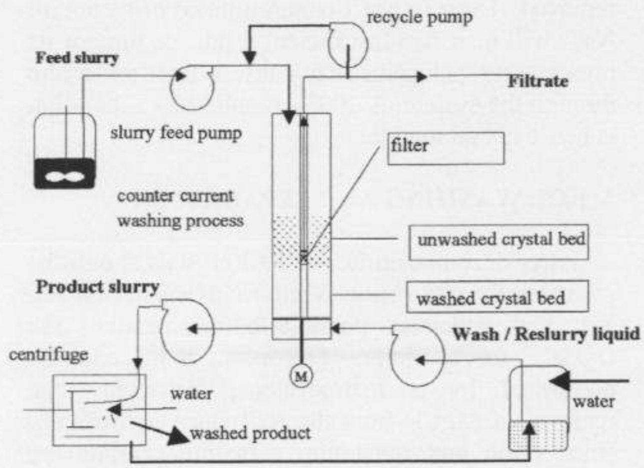

Fig.2 Hydraulic Wash Column schematic.

Part of the reslurry / washing fluid is flowing upwards through the bed towards the filters. To be sure that there exists an upward (countercurrent) flow the product and reslurry pumps should be controlled in flow, so that the incoming flow is just greater than the outgoing flow. Dependent on the bed speed (crystal flow per area), the crystals experience 30 to 100 seconds of countercurrent flow, by which not only the mother liquor will be displaced from the pores and crystal surface, but also actual dissolution of solid impurities can occur.

5.2 Operational test results

In many cases the column could be operated without great difficulties and a production of 100-200 kg/h of KCl could be achieved, 10% of the design commercial production. Assuming the use of two 70% capacity columns, a single column requires a 7 times larger cross sectional area, hence a 40 cm diameter column.

The column is somewhat more sensitive to process interruptions or changes than a centrifuge would be. Although the operation of the column is in principal simple requiring little steering, the actual operation needs to be controlled for stable operation. The friction on the wall and pipes should be kept reasonably low, which is a function of crystal matrix stresses, bed height and the injection pressure. Maximum (stable) operating pressures were 4-5 bars and a bed height of 20 cm above the filters. Otherwise high wall and pipe friction disallow the hydraulics to push the crystals through the column.

When the bed level rises for whatever reason (interruption, other crystals, etc) the injection pump should not react by increasing its pressure to push the crystals through the column, since the increased wall friction (as a result of higher pressures) may be counteractive. A recycle flow of filtrate brine should assist in lowering the bed without adding more crystals. The friction effects will be somewhat smaller for larger size columns (with relatively smaller friction surface)

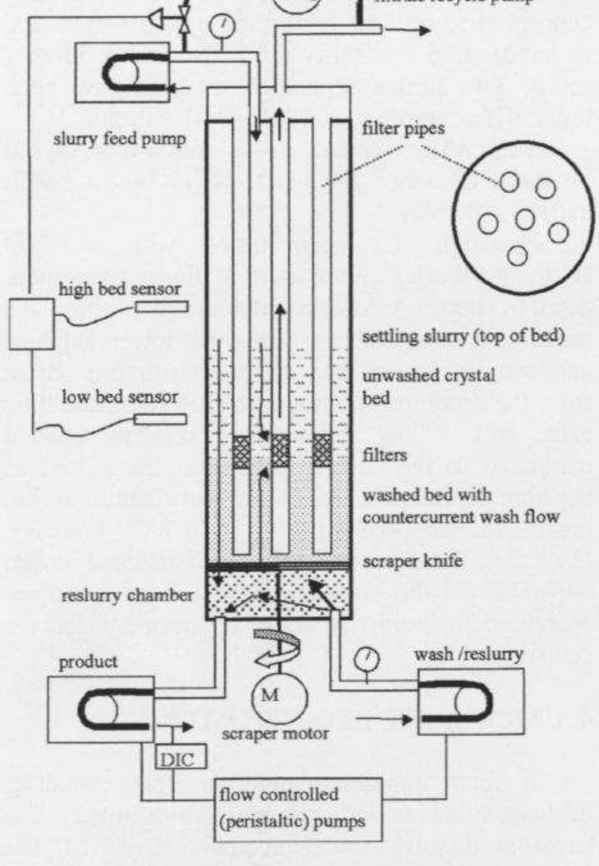

Fig. 3 Schematic diagram showing detail of Hydraulic Wash Column and pumps.

When the slurry is too thin, the permeability of the bed too low, or the crystals too variable in size, the brine or washing fluid may form channels towards the filters or interconnect the injection and reslurry chamber. The washing effect stops, by which serious pollution of the system may occur if undetected. A control on the bed height and pressures should be in place, for instance by applying PLC-connected pressure gauges and photocells, to adjust the pumping speed and pressure. TNO experimentally confirmed the applicability of various control principles for the bed height and the washing fluid flow.

5.3 Analytical Test Results

Table 1 shows the average product from the column and the most important impurities. A 99.5% purity has been reached (99.7% on dry basis). The wash efficiencies of the column are given as well.

KCl-impurities	KCl 99.5%	Wash efficiency
$MgCl_2$ ppm	1000	85-95%
$MgSO_4$ ppm	50	40-60%
NaCl ppm	600	10-20%
Br ppm	900	0-5%

Table 1. Typical KCl impurity level after applying the Hydraulic Wash Column and wash efficiencies of the column.

The wash efficiency is defined here as the reduction in impurity level from feed~ to product solids. The impurity level in the solids was determined by vacuum filtration of the feed slurry; the analysed solids hence still contained some adhered brine. Vacuum filtration, as separation step, would hence render 0% efficiency, where full elimination of the impurity would render 100% efficiency. The measured washing effect is high (85%-95%) for magnesium, intermediate for sulphate and low for sodium and bromine. The low bromine washing effect is to be expected, since most bromine atoms are incorporated as impurity atoms in the KCl crystal lattice.

6. CONCLUSIONS

Testwork has demonstrated that a 99-99.5% purity KCl can be produced from NEDMAG's cavern brine, by applying a TNO Hydraulic Wash Column. The KCl is produced from carnallite crystals, which in turn are crystallised from 65 °C cavern brine, applying direct cooling on a cooling tower. Whether or not direct cooling is an attractive option is a matter of economics (investment and operating costs in comparison with for instance vacuum evaporative cooling).

REFERENCES

Schneiders, L.H.J.M. (june 1998); Oriëntatie naar de mogelijkheden van de toepassing van de TNO-Thijssen waskolom bij de kristallisatie van carnalliet: TNO-rapport TNO-MEP-R 98/240;

Schneiders, L.H.J.M., Arkenbout, G.J. (april 1986) Developing a High-efficiency Wash Column.
paper at 4th world congress (KVIV), Ostend, Belgium. pp-304-306

Jansens, P.J. et al. (1995) The purification proccess in hydraulic packed wash columns
Chemical Engineering Science, Vol 50, No 17 pp 2717-2729