

Potassium Chloride Crystallization

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ABSTRACT

Paper covers refining processes, industrial and chemical quality, types of crystallizers, size of crystals, growth type of crystallizer operations, crystal modification agents, KCl overgrowth in NaCl, impurity build up in solutions and phase diagrams for the ions commonly found in KCl ores and solutions.

INTRODUCTION

The paper describes the two grades and various marketable sizes of potassium chloride (KCl). It provides a brief history of KCl processing techniques, including the development of vacuum and growth type crystallizers. Processing techniques and controls, as well as brief equipment descriptions, are included to provide the reader with an overall picture of KCl crystallization. Discussions on phase diagrams, crystal modification, crystal overgrowth, and impurity buildup are also included.

There are two basic methods currently used to produce marketable KCl. These are flotation and crystallization. Various combinations of these two methods are also used to improve recovery. This paper is concerned with the commercial practice of crystallization.

Potassium chloride crystallization techniques were used in the early development of KCl processing, but the use of crystallizers diminished with the advent of flotation. However, with the development of growth-type crystallizers, crystallization has again reached prominence for preparing marketable KCl or processing potash ores that cannot reach market grade by flotation.

Crystallization is capable of producing a higher purity product than flotation. The flotation process is limited, since certain impurities within the ore cannot be removed without solution. Two grades of KCl are commonly produced for the market. These are industrial grade (98.5 to 99% KCl) and chemical grade (99.95% KCl).

INDUSTRIAL GRADE KCl

A typical chemical analysis of industrial grade KCl is shown in Figure 1. (1)

Industrial grade KCl is used primarily for potash fertilizers. It is prepared in three general size

Potassium Chloride	98.85 %
Sodium Chloride	0.939
Magnesium Chloride	0.03
Magnesium Sulfate	0.03
Potassium Bromide	0.04
Anhydrous Boric Acid	0.001.
Insoluble	0.01
Moisture	0.10

Figure 1. Typical chemical analyses of industrial KCl.

ranges. These are: (1) granular, in -6 + 14 mesh size, (2) coarse, in -10 328 mesh size and, (3) standard, in -28 + 48 mesh size. Markets also exist for a -35 + 100 mesh size which is used for solu-

tion fertilizer and in other industrial applications, such as making industrial grades of various potassium chemicals. Figure 2 shows the size ranges in these classifications. The ranges vary with each

	Granular	Coarse	Standard
-6+8	14		
-8+10	30		
-10+14	34	2	
-14+20	17	34	
-20+28	4	42	2
-28+35	1	17	35
-35+48		4	45
-48+65		1	15
-65			3

Figure 2. Typical screen size ranges of industrial KCl.

producer. The product is usually treated with an anti-caking agent such as primary fatty amine acetates.

CHEMICAL GRADE KCl

Chemical grade KCl is prepared either by recrystallization of industrial grade or by crystallization of flotation grade having a sodium chloride content low enough to produce a crystallization liquor having less than two parts NaCl per 100 parts of water.

Figure 3 shows the brine-free KCl content of crystals grown in various concentrations of NaCl. The major impurity that occurs is in the form of sodium chloride, which results from the occlusion of brine in the druse or cavities in the KCl crystals. The druse can be readily seen under a microscope. Additional treatments may also be required to reduce such impurities as clay, bromine, heavy metals, copper, magnesium, calcium, or sulfates to fractional parts per million, depending on the user's particular requirement. One of the most exacting specifications is for the manufacture of caustic potash used in mercury cells, since many ions poison the electrodes or cause an explosive combination. A typical chemical grade analysis of KCl is shown in Figure 4. (2)

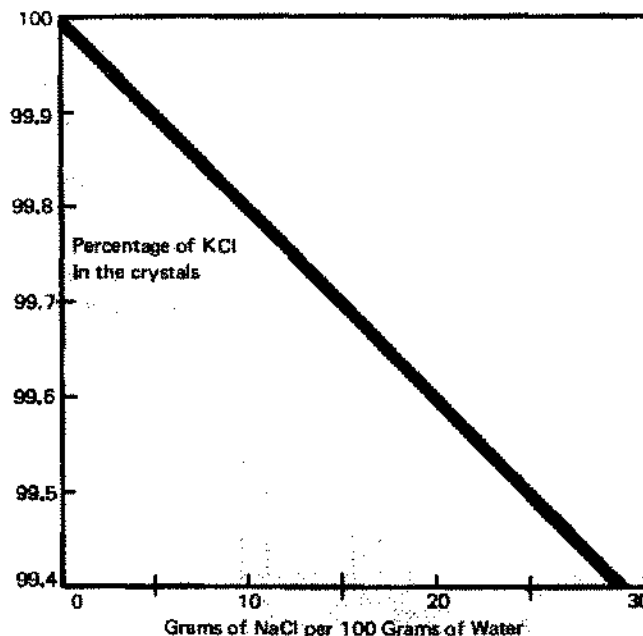


Figure 3. Purity of KCl crystals grown in various concentrations of NaCl.

EARLY CRYSTALLIZERS

The batch crystallizers used for producing potash in the early days consisted of tanks that were filled with hot brine and allowed to cool. The

Potassium Chloride	99.947 %
Potassium Bromide	.03
Sodium	.008
Sulfate	.0015
Boron	.0003
Calcium	.0005
Magnesium	.0005
Iron	.0005
Arsenic	.0001
Silicon	.0001
Heavy Metals (as Pb)	.0005
Alkalinity (as CO ₂)	.001
Water	.02

Figure 4. Typical chemical grade analysis of KCl.

crystals formed were either dendritic or hopper shaped. The initial nucleus, supported by surface tension, floated on the surface of the motionless solution. In this condition, the nucleus grew until some mechanical movement or its own weight caused it to sink to the bottom of the tank. Here it formed a loose mat with other individual hopper-shaped crystals and an occasional long rectangular-shaped crystal. When the tank cooled, the brine was drained and the crystals removed. Figure 5 shows various crystal forms.

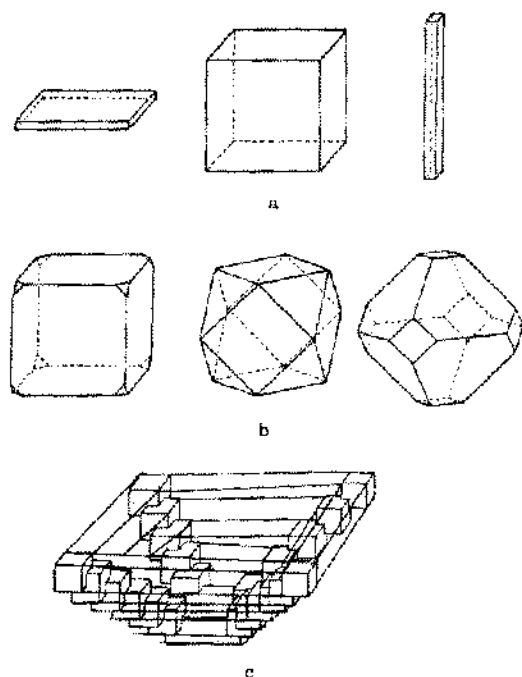


Figure 5. Various crystal forms of KCl: (a) Normal, (b) Modified, (c) Dendritic.

The use of cooling surfaces, such as coils in the tanks or trough walls of screw conveyors, to accelerate the crystallization process proved unsatisfactory because of the low heat transfer rate caused by crystal buildup on the heat exchange surface. Further attempts to improve the process were also unsatisfactory. For example, the heat exchange surface was eliminated by spraying hot solutions into huge evaporation towers, where the solution dropped by gravity against an upflow of air. The disadvantages of this system were: (1) the crystals produced were too small, (2) buildup occurred on

the walls and floor of the tower, and (3) the heat exchanges were inefficient.

The development of the flash-type vacuum crystallizers, which cool by boiling under reduced pressure, overcame many of the disadvantages of heat exchange surface cooling. The vacuum crystallizer system used was a high capacity, continuous production unit. The vacuum is provided by the cooling of the vapors in the heat-exchanger condenser. With this system there was still crystal buildup on the walls, but this did not interfere with the heat exchange rate. The crystals were still small but had the advantage of being cubical.

Several expedients were tried to improve crystal size. One system was to make a long series of units with only a few degrees drop between each. An installation with over twenty units in series was tried in Germany for a period. Another attempt to increase crystal size was made by using an external circulation loop to which the feed was added. But even these changes did not increase the crystal size sufficiently to meet requirements established by the change to coarse-granule fertilizer mixture in 1956.

OSLO CRYSTALLIZER

The first major breakthrough was the development of the Oslo growth-type crystallizer. A modern unit is shown in Figure 6. This unit is

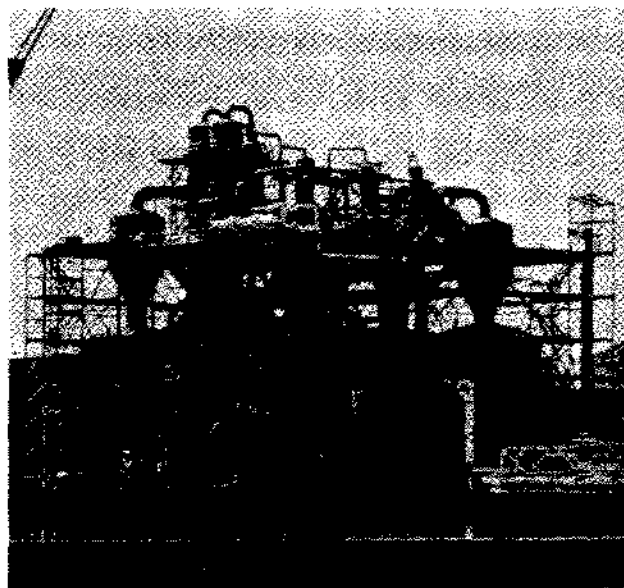


Figure 6. Modern Oslo-type crystallizer.

composed of two tanks. The top vessel is the vaporizer unit where vacuum is applied. Warm feed is added to a large amount of cooled brine recycled from the retention tank. The combined solution is cooled a few degrees until it is in a supersaturated state. This solution flows down through a downcomer pipe to the bottom of the lower cone-shaped retention vessel containing the crystals formed in the process. In theory, the flow of brine classifies the crystals and the larger remain in suspension at the bottom of the vaporizer where they are in contact with the supersaturated brine. In this process growth takes place initially just on the larger crystals, then more slowly on the smaller crystals (in suspension higher in the vessel); the finest crystals overflow to the next unit and into the circulation system which usually then contains a small amount of very fine crystals. As the crystals grow, they work down to the bottom of the unit. The coarser crystals remain at the bottom of the vessel, growing in size until they are removed through a drawoff near the bottom.

The small crystals are cubical when less than 35 mesh size. Above 35 mesh, the cubical edges show rounding from attrition of the corners. Above 20 mesh, the crystals are almost round. Figure 7 shows representative crystals.

At this stage of development, the crystallizer units still had the disadvantage of crystal buildup,

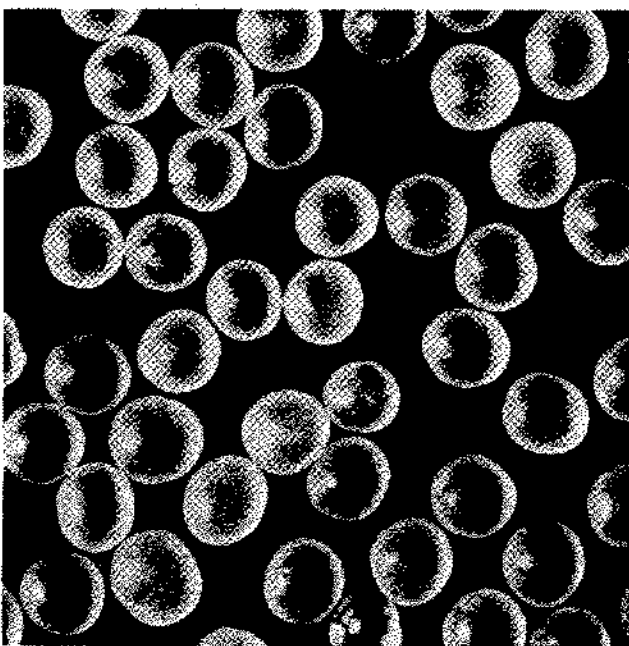


Figure 7. Representative crystals from growth-type crystallizers.

particularly on the bottom of the crystal suspension vessel at the downcomer discharge. However, washout intervals had been extended from days to weeks.

DRAFT TUBE BAFFLE (DTB) CRYSTALLIZER

The next growth-type crystallizer developed was the Draft Tube Baffle (DTB). A modern DTB unit is shown in Figure 8. This unit is a single vessel

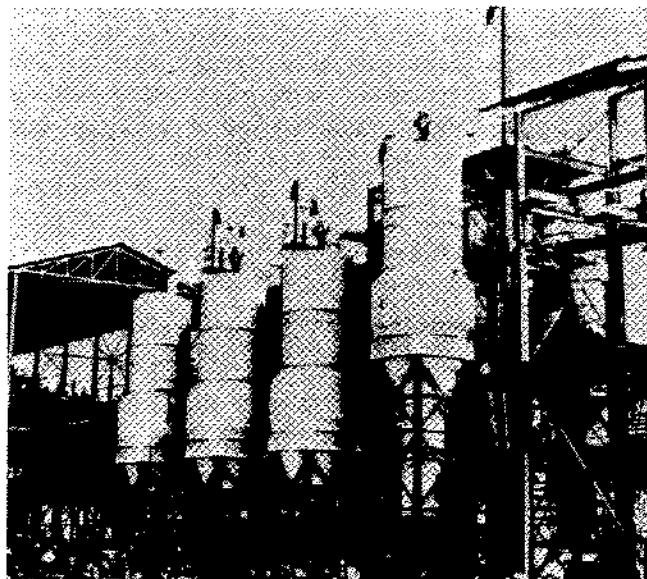


Figure 8. Modern DTB crystallizers.

with an inner draft tube and a screw propeller. The screw propeller forces circulation up the draft tube to the evaporation surface and down the outside of the draft tube past the baffle discharge outlet. The baffle section is built into the outer wall to selectively draw out the overflow brine and very small size crystals from the downflowing crystal magma. The crystallizer feed is introduced into the magma. The crystallizer feed is introduced into the draft tube just below the impeller. The large crystals are drawn off at an opening in the bottom. These crystals are also gradually rounded by attrition and by impact with the mixing impeller. Theoretically, the mixture of the coarser retained crystals with a large quantity of cooled solution is circulated up to the evaporation surface, where growth takes place directly on the crystals with only a few degrees of

temperature drop. There is practically no supersaturation, so buildup is reduced and operation time between washouts might be several months.

DTB, Oslo, and flash-type vacuum crystallizer design is performed and guaranteed by vendors who have considerable experience. All three are built to perform in accordance with the requirements of the purchaser's specifications for quantity, size, purity, and special conditions imposed by the solutions used. Figure 9 is a general sketch of each of these three types. In recent times the flexibility of the Oslo and DTB types has almost eliminated the use of the flash-type vacuum crystallizer.

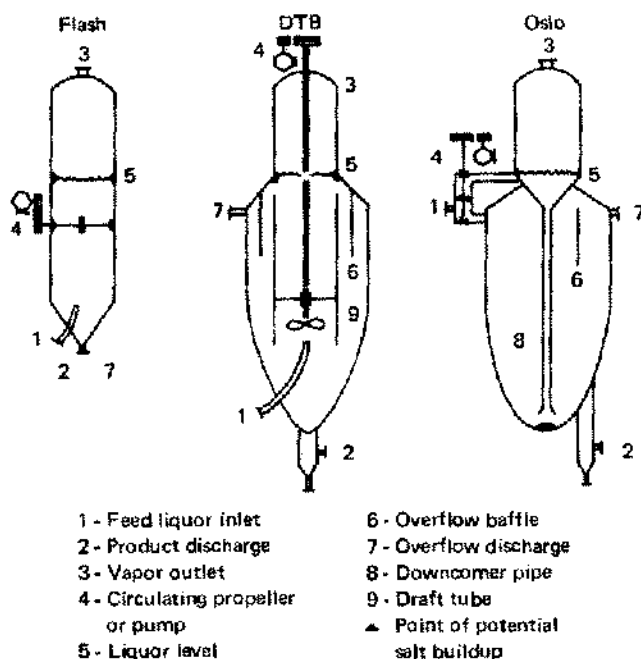


Figure 9. Vacuum crystallizers used in KCl manufacture.

CRYSTALLIZER ACCESSORIES

Vacuum crystallizers employ a number of auxiliary pieces of equipment; these are specialized condensers, instrumentation, and mechanical units that facilitate product drawoff.

Condensers are used to remove the water from the vapor discharge. The two types of condensers in use are barometric and surface. The barometric condenser is a vessel in which the water vapor is condensed by contact with a spray or curtain of

colder water. The condensing point of the vapor is lower than the temperature of the crystallizer by twelve to eighteen degrees. This is caused by a vapor pressure phenomenon called boiling point rise (BPR). The BPR varies with the concentration of the various salts in solution in the crystallizer. These values can be calculated from published tables. (3) Figure 10 shows BPR variation with KCl brines. The BPR change is significant with the increase in solubility of KCl as the temperature is raised. The BPR effect can be considerably reduced by using brines instead of water as coolant in barometric condensers, if dilution of the brine is acceptable.

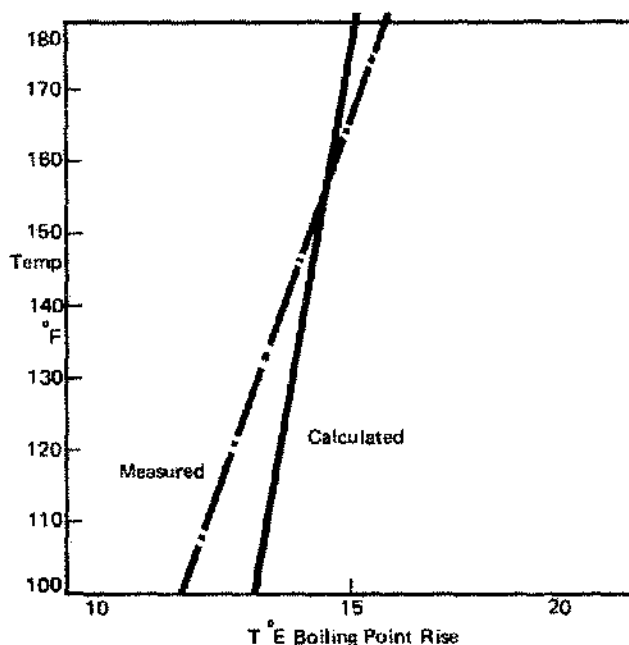


Figure 10. Boiling point rise variation with KCl brines.

The heat released in a barometric condenser is usually not recovered. A cooling tower or a refrigeration unit is used to re-cool the barometric condenser water, unless large volumes of cold water are available. The barometric condenser must be provided with a water-sealed barometric leg.

Surface condensers used to condense water vapor are shell and tube heat exchangers. This type of condenser is used to recover the water from the crystallizer for use as boiler water or plant makeup

water. The outside of the tube is usually used for the vapors. The inside of the tube is used for heat recovery by circulating plant brines. Here again, the BPR must be added to the temperature approach factor in the condenser design. The temperature approach factor for surface condensers is approximately 10° F, while the approach factor for barometric condensers is approximately 5° F.

If the condensate purity is significant, the crystallizer is equipped with a demister pad. Conductivity cells are used on the condensate discharge lines to monitor the purity and operate bypass valves at the required purity limits. The vacuum on most crystallizers is augmented by steam jet ejectors pulling out the non-condensable gases after the vapor passes through either the surface or barometric condenser. Slightly more vacuum is pulled than required. The vacuum is held constant by an absolute pressure controller which opens a valve to let air in to hold the desired pressure and temperature.

Other instrumentation consists of a feed flow meter and control valve; a level control and overflow valve; a dilution water flow meter and control valve; temperature indicators on feed, overflow, and body; and a device to measure slurry density in the suspension tank.

The product drawoff system of crystallizers growing coarse crystals is usually improved by an elutriation leg. This is a cylindrical attachment to the bottom of the crystallizer body and is used to collect the coarse crystals. A stream of final brine is injected near the bottom to sweep the finer sized crystals back into the body. The coarser crystals are drawn off from a side or other opening near the bottom of the leg.

Product crystals contain occasional lumps that are three or four inches in diameter by a half inch thick. These lumps form on sight glasses or at the solution level. This makes the product difficult to withdraw through a small opening at a low rate of flow. To overcome this problem, wide-opening, fast-operating, timer-controlled valves or slow-moving, wide-faced rotary valves are used. These valves discharge by gravity into a screen-topped sump with auxiliary brine added to aid suspension into a discharge slurry pump. (4)

Another auxiliary item that may be used is a special fines removal drawoff unit and fines dissolver tank. The dilution water for a following unit and heat are often added to a fines dissolver system. Heat is an aid to solution since KCl has a negative heat of solution of 106 Btu per pound.

OPERATIONAL FACTORS

In actual operation the major problem with the growth-type crystallizer is in obtaining the maximum quantity of the largest size crystals. Among the control factors are feed rate, brine level in the vaporizer section, operating temperature, correct crystal density, a steady crystal product removal, and the removal and disposal of fine crystals generated in the process. Most of these factors are inter-related.

Feed rate is limited by the circulation rate design. However, too high a feed rate will raise the degree of supersaturation to the point where nucleation takes place forming many fine crystals. In KCl crystallization, three degrees F is about the maximum supersaturation allowable. The differential temperature between the circulation and final brine is measured and used as a control. Even within this prescribed range, the feed rate may have to be limited to keep from producing soft crystals. Crystal hardness is measured by a comparison test. (5) This is gaged by mechanical breakdown of given sized crystals into a smaller size. This may be accomplished by screening the crystals through a selected screen and the following screen size in the series, then adding a definite weight of steel balls to a definite amount of the retained crystals and vibrating the mixture prescribed on the retaining screen for a period of time. The weight percentage passed through the retaining screen is used as a measure of hardness. When the percentage breakdown increases significantly, a five percent cutback in feed rate will help restore crystal hardness to an acceptable value.

Brine level in the crystallizer is critical. In the Oslo type, flashing may occur when the evaporation area is reduced by the brine level falling to within the conical downcomer section. Further rise in the brine level will increase retention time so there is more buildup in the downcomer. In the DTB crystallizer, high and low levels adversely affect the circulation, since a low head impeller is used. In both types a high brine level increases buildup on the demister pad and vapor piping, and may increase the salt concentration of the condensate, thus making it less acceptable for use as boiler water.

A constant operating temperature is necessary in order to avoid sudden flashing of the unit (as may happen if the vacuum increases, lowering the boiling point), or to prevent dissolving of the crystal bed (which occurs if the temperature in the crystal-

lizer increases). It may be necessary to adjust the body temperature to fit a change in profile caused by taking a unit out of service or bringing a unit on stream. In this case the vacuum is slowly adjusted with a change in body temperature of a few degrees each hour.

The density of the slurry in the bottom section of the crystallizer is used as an indication of the retention time in the body. This is usually measured by a DP (differential pressure) cell using one tap near the bottom and another in the range of ten feet or more above. Water purge is used on the two taps to keep the taps from salting shut. The instrument is calibrated against a mercury column to read direct in specific gravity over a range of 1.2 to 1.4 and can also be checked when the unit is full of brine with no crystals in suspension. The proper slurry density to produce a certain crystal size is found by actual operation. Air bubbles in the water, lack of water to displace all the brine from the column, or improper protection from freezing will give false readings.

A steady crystal withdrawal rate is imperative to produce maximum crystal size. This means holding the slurry operation density as near to plus or minus .001 specific gravity as possible. This is impossible if the drawoff is too rapid or plugged up often. Too low a density will cause nucleation and introduce fines which will take 10 to 12 hours to rebuild to size. Too high a density distributes the growth over too many particles and also causes crystal size to fall off.

Nucleation may occur if a sufficient distance exists between crystals. Beaker seeding tests have shown that nucleation will occur if there are fewer than 1,000,000 crystals per liter of solution. The crystal population of a pound of KCl is estimated to be 100,000,000 crystals of 100 mesh size, 10,000,000 crystals of 50 mesh size, 1,000,000 of 30 mesh size, and 100,000 of 14 mesh size. The distance between crystals at 37 percent solids and 30 mesh is about .003 inch. After nucleation, each particle grows in several minutes to the 100 mesh size but takes three to four hours to grow to 8 mesh size.

Crystal growth is influenced by temperature with the larger crystals being grown at the higher temperatures. This may be due to the higher KCl solution concentration at the higher temperatures.

During the startup period, individual sizes between screens should be plotted in the size range of particular interest with body density plotted on the same sheet to establish correlation of density

and crystal size, as shown in Figure 11. This illustration shows typical size and density patterns.

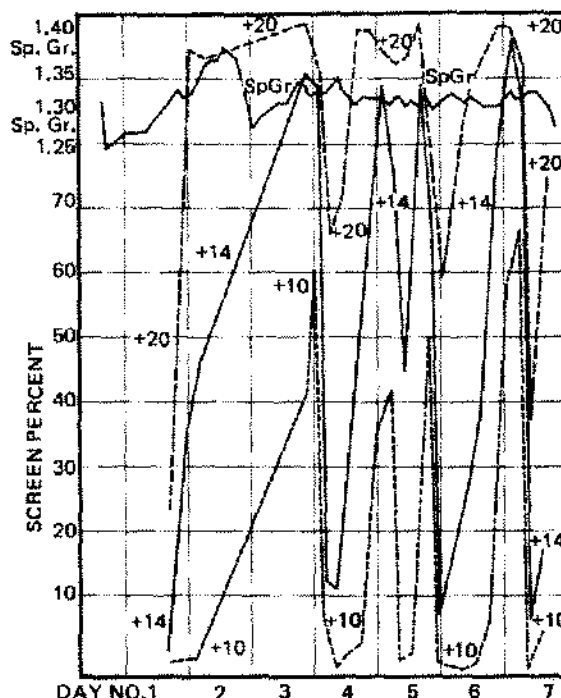


Figure 11. Correlations of density and crystal size.

Evidence that an excess of fines is being produced is found in the quantity of fines occurring in the circulation system in the case of the Oslo unit, or in the overflow of the DTB unit. Over one percent of fines is considered excessive, and immediate steps need to be taken to reduce the fines by increasing the drawoff.

Fines drawoff on the Oslo unit is made by a special baffle or a dip tube that can be lowered into the bed to the fines level. Accumulation of excess fines can be seen in sight glasses provided on the sides of the unit. The appearance of fines usually follows an upset in steady operating conditions or results from the need of the unit for wash out.

On the DTB unit, fines drawoff is increased by reducing the baffle area. This is achieved by building the overflow baffle in several sections which can be shut off individually to increase the flow rate in those remaining in service.

Seeding a unit at startup has never been significantly successful in making large crystals of KCl.

This is probably due to the fact that crystals cannot be drawn off without having gaps in the succession of crystal sizes or without creating fines. The general experience in a number of attempts has been to have the bed go completely fine and then have to rebuild from a generally worse condition than if the unit were brought on stream with barren brine.

PHASE DIAGRAMS

The solubility data for KCl in a saturated solution with NaCl, $MgCl_2$, $MgSO_4$, Na_2SO_4 , $CaCl_2$, and $CaSO_4$ is well documented in the tables of D'Ans, Van't Hoff, Autenrieth, Teeple and the International Critical Tables; (the last reference contains some errors, however). These data are published showing mols per 1000 mols of water and parts per 100 parts of water. They can be arranged in various phase diagrams for specific temperatures. The diagrams are often expressed as mol percent of part of the ions such as the triangular Jenecke diagram leaving out Na and Cl, or the rectangular Jenecke diagram leaving out NaCl with the statement that the solution is saturated (6) in NaCl. There are groups of diagrams that give the quantities of each single salt, two salts, or a single ion with a temperature range from 0 to 100°C. These groups show the solid salts that are in equilibrium with the brine.

A relatively simple method of plotting used by Autenrieth, (7) giving mols per 1000 mols of water shows $MgCl_2$ as the right horizontal coordinate and $MgSO_4$ as the vertical coordinate, with KCl, NaCl, and other salt solubilities as transverse dotted lines. It is even more convenient when the values are expressed in parts per 100 (or per 1000) parts of water at specified temperatures. The value of this type of system is that complete data for all the salts are present at a particular point. To extend the information into those fields, values of sodium sulfate or potassium sulfate are plotted as the horizontal left coordinate. The five component systems generally covering the KCl field are K, Na, Mg, Cl, and SO_4 . These can be expressed in four salts: KCl, NaCl, $MgCl_2$, $MgSO_4$; or KCl, NaCl, $MgSO_4$, Na_2SO_4 at specific temperatures.

This quinary system type diagram is shown in Figure 12. Extrapolation curves for NaCl and KCl can be plotted against a range of temperatures at a particular $MgCl_2$ and $MgSO_4$ concentration. Figure 13 shows a comparison of $MgSO_4$ and $MgCl_2$ in two potash ores.

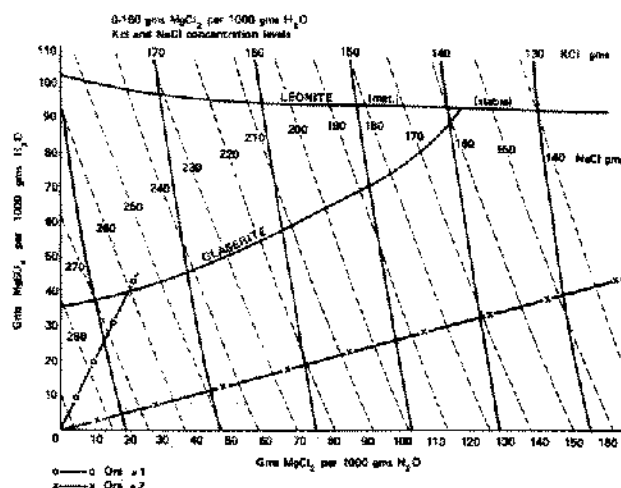


Figure 12. Phase diagram-KCl and NaCl on $MgCl_2$ - $MgSO_4$ grid at 95°.

ANALYSIS	ORE #1	ORE #2
Ca	0.32	0.26
SO_4	3.05	1.44
Mg	0.64	0.36
CALCULATED AS POLYHALITE		
SO_4	1.54	1.25
Mg	0.09	0.08
CALCULATED AVAILABLE		
$MgSO_4$	1.89	0.23
$MgCl_2$	0.67	1.25
ACTUAL AVAILABLE		
$MgSO_4$	1.76	0.23
$MgCl_2$	0.83	0.86

Figure 13. Comparison of $MgSO_4$ and $MgCl_2$ in two potash ores.

CRYSTAL MODIFICATION

Potassium chloride belongs to the simple cubic lattice system. Growth in a static condition on a liquid surface is dendritic or hopper shaped. Under

the surface, the crystals grow into cubes or elongated cubes. KCl crystals formed while in motion are cubes, except for the larger growth type which are rounded by attrition. In some cases, where flotation agents or clay slimes are present, the large crystals become flattened into a disc shape. (See Fig. 5 for various crystal forms.)

The KCl cube has voids in it that contain the saturated brine. The voids or druse can be seen under a microscope. This is the major source of the impurity in the industrial grade KCl.

A number of dyes listed by Buckley (8) cause modification in growth on a microscope slide but do not modify the cubic shape if prepared while stirring.

Three modification agents are known that modify the simple cubic KCl to the cesium chloride octahedra type lattice, while growing during stirring. These are lead, stannous tin, and Leonil SA. The two metal ions are absorbed to give a clear crystal with a metal content in the range of 0.01 to 0.04 percent in the brine-free crystal. The cesium chloride type lattice is more compact than the simple cubic lattice and does not contain pockets of brine in the crystal. The industrial crystal grown in this way has higher KCl purity, but contains the metal impurity which may be undesirable for agricultural or industrial use.

The Leonil SA modification produces a similar type cesium chloride lattice. The crystal is cloudy or opaque. The brine free analysis is lower in KCl than the simple cubic lattice with its brine pockets. Some ions are preferentially absorbed by KCl. Among these are bromine, lead, tin, and copper. This property is used in analysis to accumulate trace elements. (9) This property also makes it difficult to eliminate trace elements in preparing chemical grade KCl.

KCl OVERGROWTH

The property of overgrowth is well known and described by Royer. (10) Where fine NaCl crystals are present, the NaCl crystals appear under the microscope to be absorbed in the large KCl crystals. In other cases, KCl growth occurs on large NaCl crystals and likewise NaCl growth occurs on large KCl crystals, when the dilution water is below requirement or has been low during a stage of growth.

This phenomenon is particularly likely to occur in a first stage crystallizer unit that receives feed brine from improper leach conditions, e.g., where insufficient KCl is present from the leach brine,

and growth rates are fastest. This condition often occurs when the ore supply fails and the leach brine is continued in anticipation that the ore supply problem will soon be solved. This can also happen in the early startup where the leach plant is recycling to a thickener to bring the system up to saturation and operating temperature.

Dilution water is added in KCl crystallization to replace water evaporated by the brine boiling under vacuum. Sufficient water is added to ensure complete NaCl solution so NaCl will not crystallize with the KCl.

IMPURITY BUILDUP

In KCl crystallization the major salts in the system are KCl and NaCl. These have definite solubilities. The other salts common to this system are Na_2SO_4 , MgCl_2 , MgSO_4 , CaCl_2 and CaSO_4 . CaSO_4 is only slightly soluble in water, in the range of one percent. It is about one tenth as soluble in saturated KCl-NaCl brine. As the system builds up in sulfate, the CaSO_4 is even further depressed by the common ion effect to approximately 0.01 percent. Calcium does not come into solution directly in the leach system except in counter-current washing of waste salts or thickener slimes with water. In this case syngenite, a double salt potassium and calcium sulfate, will form in the washing system as saturation in chloride and sulfate increases. Microcrystalline gypsum has formed on heat exchanger tubes where soluble calcium salts occur in the dilution water.

The KCl solid-phase field on a grid of MgCl_2 , MgSO_4 and Na_2SO_4 is bounded at 20°F and below by Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), schoenite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), and carnallite ($\text{MgKCl}_3 \cdot 6\text{H}_2\text{O}$). At higher temperatures, from 77 to 131°F , the KCl field is bounded by glaserite ($\text{K}_3\text{Na}(\text{SO}_4)_2$), schoenite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), leonite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), kainite ($\text{MgSO}_4 \cdot \text{KCl} \cdot 2.75 \text{H}_2\text{O}$), and carnallite ($\text{MgKCl}_3 \cdot 6\text{H}_2\text{O}$). Above 55°C the KCl field is bounded by glaserite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$), leonite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{H}_2\text{O}$), kainite ($\text{MgSO}_4 \cdot \text{KCl} \cdot 2.75 \text{H}_2\text{O}$), carnallite ($\text{MgKCl}_3 \cdot 6\text{H}_2\text{O}$), and langbeinite ($2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$).

Crystallizers are generally operated in the range of 95°F to 185°F because of the economical advantage of using a cooling tower instead of a refrigeration system for auxiliary cooling. In this range the major impurity buildup is glaserite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$) and langbeinite ($2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$), which are due to sulfates, and carnallite ($\text{MgKCl}_3 \cdot 6\text{H}_2\text{O}$)

due to high amounts of $MgCl_2$. Figure 13 shows the sulfate field most commonly encountered. Glaserite is found in the final stage crystallizer feed pipes and final liquor discharge pipes all the way to the initial heating system which is probably the first surface condenser in the heat recovery stages of operation. Langbeinite may be found in the hot feed liquor tank and piping.

All the double sulfates have a degree of supersaturation which requires seeding to start. Glaserite supersaturation appears to extend about 20 percent higher than the indicated field boundary established with solid phase present unless seed crystals are present. The relative rates of crystallization KCl, NaCl, schoenite, leonite, and glaserite are given as 1:2:600:3,000:30,000. On a time basis they are KCl and NaCl in seconds, schoenite in minutes, leonite in hours, and glaserite in months.⁽¹¹⁾ However, once glaserite has started forming, it is very pernicious and difficult to remove although it is soluble in water. Syngenite is even worse as it is practically insoluble in water.

Figure 13 shows several types of ore and resulting buildup in solution. Figure 12 shows these values plotted on a typical phase diagram.

The solubility of NaCl in NaCl-KCl brine at low $MgCl_2$ concentration is less in hot solution than in cold. This requires less dilution water to hold the NaCl in solution. As the $MgCl_2$ concentration increases, the difference in solubility becomes less, and finally, more water has to be added than is removed in the vacuum cooling as the carnallite field boundary is approached, or when carnallite is used for preparing the crystallizer brine.

When the impurities reach the point of continuous interference with operation, a bleed system may be required to remove and separately treat a portion of the brine. The brine can be used to prepare other valuable salts such as K_2SO_4 ,

Na_2SO_4 , $MgCl_2$, MgO , and HCl, depending on economic feasibility.

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