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POTASH BENEFICIATION "FROM HOT TO COLD CRYSTALLIZATION"

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RESUME

L'Arab Potash Company produit de la potasse à partir de saumure de la Mer Morte par évaporation solaire suivie d'un processus de lessivage à chaud depuis 1982. Le processus de lessivage à chaud est considéré comme un processus classique pour la récupération de potasse de grande qualité à partir de minerais de carnallite ou de sylvinite. Le procédé de lessivage à chaud repose sur l'emploi d'une saumure chaude non saturée pour récupérer la potasse à partir du minerai extrait ou des bouillies recueillies des bacs d'évaporation solaire. Ce procédé tout en produisant du chlorure de potassium avec une granulométrie et une pureté satisfaisantes n'est pas sans inconvénient. Le lessivage à chaud exige des installations complexes, permettant en particulier la cristallisation par refroidissement dans des cristallisoirs où l'eau est évaporée sous vide, cependant que la consommation d'énergie calorifique demeure très élevée, ainsi que la consommation d'eau nécessaire au refroidissement des derniers stades de cristallisation.

Un procédé tout à fait nouveau a été considéré, qui n'exige pas le chauffage et le refroidissement de la saumure avec tous les aspects indésirables. Ce procédé est habituellement appelé procédé de cristallisation froide.

Cette invention emploie un procédé d'enrichissement appliqué à la carnallite elle-même qui donne avant la phase de décomposition la pureté nécessaire pour garantir au chlorure de potassium obtenu une pureté égale ou supérieure à 95 % KCl. A cette fin, la pureté exigée pour la carnallite ne doit pas être inférieure à 95 % avec 5 % de NaCl au maximum.

L'invention consiste à introduire la carnallite brute, contenant la proportion naturelle de chlorure de sodium dans un processus de purification par flottation afin d'éliminer une partie considérable du chlorure de sodium qu'elle contient.

La pureté de la fraction granulométrique supérieure à 2,5 ou 3 mm est suffisamment élevée pour ne pas exiger de purification ou même que l'addition de NaCl par cette fraction a peu d'importance si l'on considère l'addition par la fraction granulométrique inférieure à cette dimension limite. Dans le premier stade, il suffit en conséquence de séparer la fraction granulométrique la plus élevée en tamisant la carnallite brute avec un tamis choisi judicieusement pour avoir une granulométrie qui se prête à l'opération de flottation : ceci est déterminé par la nature de la carnallite à traiter normalement qui a une dimension de 0 à 3 mm.

Le deuxième stade du procédé consiste à soumettre les fines de carnallite ainsi obtenues à une opération de flottation en utilisant un réactif approprié dans le but de séparer une fraction appelée "flottante" (qui sera entraînée à la surface par le réactif dû au piégeage sélectif des bulles d'air et qui contient une grande partie du chlorure de sodium présent), d'une deuxième fraction appelée "coulée" qui reste au fond de la cuve d'attaque et qui contient la partie principale de la carnallite. Un rapport saumure/carnallite judicieusement choisi en fonction de la qualité de la carnallite, de la configuration des cellules de flottation et de la nature du réactif employé doit être appliqué afin d'assurer une bonne opération physique de la flottation.

Dans le troisième stade, les particules sur-dimensionnées des tamis à côté de la carnallite enrichie obtenue de la flottation qui contient une quantité minime de NaCl sont ensuite envoyées vers la phase de décomposition qui peut être avantageusement effectuée par le processus de croissance artificielle des grains de KCl produits et ainsi conduire directement au chlorure de potassium de qualité commerciale satisfaisant au point de vue teneur et granulométrie.



INTRODUCTION

The Arab Potash Company is located at the south end of the Dead Sea in Jordan 178 km south of the Jordanian capital of Amman. The company utilizes two of Jordan's most abundant natural resources: solar energy and the mineral rich brine of the Dead Sea.

Carnallite is a mineral of the following chemical formula: $MgCl_2 \cdot KCl \cdot 6H_2O$ which exists in the natural state in many countries of the world. It may exist more or less pure, or mixed with sodium chloride and other natural salts. The essential interest of carnallite resides in the potassium chloride that it contains, with a theoretical content of 26.83% of the pure product.

The chemical content of the Dead Sea brine which has a density of 1.230 g/cc holds a unique assemblage of salts. It is rich in calcium, magnesium, potassium, sodium, and bromine with an average salinity of 350 grams of salt per kilogram of water. The estimated total amount of these salts is over 43 billion ton. The typical composition by weight is:

Sodium chloride	7.8	%
Potassium chloride	1.21	%
Magnesium chloride	14.48	%
Magnesium bromide	0.48	%
Calcium chloride%	3.75	%
Water	72.28	%

In solar evaporation system (which is the most important), Dead Sea brine is pumped into a series of large pans enclosed by man-made dykes. The resulting deposits of the potash rich ore carnallite are then harvested by sophisticated floating harvesters.

When it is desired to extract potassium chloride, the carnallite is subjected to a selective dissolution in a well determined quantity in order to remove magnesium chloride by making use of the equilibrium which exists between carnallite, potassium chloride and sodium chloride in its saturated solution, a so-called operation of "decomposition".

The decomposition of carnallite is an example of incongruent dissolution. When water is brought into contact with the carnallite, the rhombic crystals dissolve and, because of the common ion effect, small cubic potassium chloride crystals form in a vicinity of the dissolving carnallite.

The resulting solids from the decomposition are potassium chloride and sodium chloride, the mixture being called sylvinite.

Two processes are industrially applied in order to obtain pure potassium chloride from sylvinite:

1. The process of hot leaching, which employs the difference in solubility, hot and cold, of the potassium chloride, consists in treating the two minerals in a hot mother liquor, and in cooling it. During the first phase, only the potassium chloride dissolves; during the second phase, after filtration of the undissolved NaCl, only the potassium chloride crystallizes from the solution; it is consequently easy to obtain it in a satisfactory state of purity, and with a granularity complying with current standards.
2. The process of flotation, in which the choice of appropriate reagents prompts the affinity of the crystals of potassium chloride with the air bubbles injected into a suspension of KCl and of NaCl in saturated water. These air bubbles selectively entrain the potassium chloride towards the surface of the liquid where it can then be separated, but this process can yield only a potassium chloride with fine granularity besides a supplementary stage of washing is necessary to obtain higher purity.

Hot leaching process which is the main process in the Arab Potash Company, although yields potassium chloride with standard granularity and satisfactory state of purity is not without drawbacks. Hot leaching requires complex installations, allowing, in particular crystallization by cooling-in crystallizers where the water is evaporated under vacuum. Besides that, the consumption of heat energy remains very high, as well as the consumption of water necessary for cooling the last stages of crystallization.

This is why the best process consists in enriching the carnallite in priority, to remove therefrom the maximum NaCl that it contains by flotation, and then in decomposing this carnallite under conditions where the size of the grains of KCl produced is artificially enlarged. Consequently, a product is obtained which complies with the required standards concerning both the content and the granularity.

This is actually the new process to produce KCl in Arab Potash Company expansion a so-called "Cold Crystallization Plant".

The crystallization of potassium chloride proceeds in two separate steps, i.e. dissolution of carnallite and crystallization of the potassium chloride, and is therefore difficult to control. When the carnallite crystals are small, dissolution is faster than crystallization. On the other hand, when the carnallite crystals are large, dissolution is slower than crystallization. Thus the decomposition of small carnallite crystals usually gives rise to higher supersaturation and, consequently, to more nucleation and finer potassium chloride crystals. Because of both mechanical and marketing reasons, potassium chloride crystals, obtained by the decomposition of large slowly dissolving carnallite crystals, are preferred.

SOLAR EVAPORATION METHOD

The salt pans are considered to be the key element in the potash recovery process. Due to high evaporation rate, most of the sodium chloride is deposited and the water content of the brine reduced bringing the density to 1.290 g/cc.

At the end of the salt pans, the brine is transferred to the pre-carnallite pan (PC2) by gravity flow. This pan, acting as a control measure, facilitates the control of the brine composition at the "Carnallite Point". This is the concentration at which the brine is saturated with carnallite but no carnallite has yet precipitated. The density of the brine is further increased at this stage reaching 1.295 to 1.310 g/cc in PC2.

The last six pans finalize the evaporation process by the precipitation of the carnallite double salt, through series flow from Pan C-3 to Pan C-2, to Pan C-1, to Pan C-5, to Pan C-6, and finally to Pan C-7 (Figure 1).

Brine from Pan C-7 which now contains little potassium chloride and has a density of 1.340 g/cc is then discharged into the flood channel and flows back to the Dead Sea.

The precipitated carnallite in these pans which contains 84% pure carnallite and 16% sodium chloride is harvested as a slurry from beneath the brine by four floating tracked harvesters, and delivered to booster pumps on the dykes via a floating line. The carnallite slurry is then pumped to the refinery through steel pipes.

EXISTING HOT LEACHING REFINERY

The APC's plant is now operating at a production rate equivalent to 1.4 MMTPY utilizing the hot leach process as described below.

The carnallite slurry is received, dewatered and decomposed with water in two stages of agitated tanks (Figure 2). The resulting solids from the decomposition are potassium chloride and sodium chloride, the mixture being called sylvinite. The sylvinite is dewatered and washed. The resulting sylvinite cake is leached using four agitated tanks in a two stage process. Heated brine, returned from the crystallization process, is used for leaching potassium chloride from the sylvinite. The potassium chloride is dissolved leaving the sodium chloride solids. The hot brine, now saturated with potassium chloride, is clarified in a thickener.

The thickener underflow slurry containing sodium chloride crystals is dewatered, repulped with waste brine and pumped to tailing.

The hot brine from the thickener overflow, which is saturated with sodium and potassium chlorides, is cooled successively in a five-stage draft tube baffle vacuum crystallizer system from 93°C to 49°C. Upon cooling, potassium chloride (KCl) decreases in solubility, and crystallizes under controlled conditions. Potash slurry from the last stage crystallizer is directed to the product hydrocyclones where partial dewatering takes place. The underflow of the cyclone is sent to centrifuges for further dewatering.

The cake from the centrifuges is conveyed to an oil-fired co-current rotary dryer to remove the last traces of moisture entrained with the crystals. Product from the dryer is sent to the screening system, while the dust is collected using cyclones and an electrostatic precipitator.

The product discharged by the dryer goes to the screening section where it is segregated into two product grades: standard and fine. Granular product is obtained by compaction of fine and/or standard fraction.

An anti-caking agent is added to all products in carefully controlled amounts to minimize the natural tendency of potash to agglomerate during storage and shipment. Free flowing properties are thus insured to facilitate handling of these products by the customer.

COLD CRYSTALLIZATION PROCESS

The present innovation employs a process of beneficiation applied to the carnallite itself, which gives it, before the decomposition phase, the required purity to guarantee for the potassium chloride obtained by the subsequent composition a purity equal to or greater than 95% of KCl. To that end, the purity required for the carnallite must be no less than 95% with a complement of 5% maximum amount of NaCl.

The innovation consists in engaging the crude carnallite, containing the naturally present proportion of sodium chloride in a process of purification by flotation in order to remove therefrom a considerable part of the sodium chloride that it contains.

The purity of the granulometric fraction above 2.5 or 3 millimeters is sufficiently high in order not to require a purification, or even that the addition of NaCl by this fraction is of little significance having regard to the addition by granulometric fraction less than this separating size. In the first stage, it is consequently sufficient to separate the higher granulometric fraction by sieving the crude carnallite with a mesh of judiciously chosen cut to have a granularity which lends itself well to the flotation operation; this granularity is determined by the nature of the carnallite to be treated, currently within the range of 0 to 3 millimeters.

The second stage of the process consists in subjecting the undersize carnallite thus prepared to an operation of flotation by using an appropriate reagent for the purpose of separating a so-called "floating" fraction (which will be entrained to the surface of the reaction medium thanks to the selective catching of air bubbles, and which contains major part of the sodium chloride present), from a second so-called "sunken" fraction which remains at the bottom of the reaction medium and which contains the major part of the carnallite. A brine/carnallite ratio judiciously chosen as a function of the quality of the carnallite, the configuration of the flotation cells and the nature of the reagent employed should be applied, in order best to promote physical operation of the flotation.

In the third stage, the oversize from sieving besides the enriched carnallite obtained from flotation which contains minimum amount of NaCl is then conveyed towards the decomposition phase, which may advantageously be carried out by the process with artificial growth of the grains of KCl produced and thus lead directly to a potassium chloride of commercial quality, satisfactory in content and in granularity.

A pilot plant was designed and constructed by APC in 1989 at the site to determine the parameters necessary for the design of a commercial plant. The pilot plant was operated for two years. During this time a suitable method was developed to upgrade the carnallite feed to acceptable carnallite purity, and a draft tube crystallizer was designed to decompose carnallite with water and form KCl crystals of suitable grade and size (Figure 3). The commercial plant was then designed based on the knowledge gained from the pilot plant operation.

COMMERCIAL PROCESS FLOW DIAGRAM DESCRIPTION

The APC is in the process of producing 400,000 TPY of potash at the 1st stage expansion by cold crystallization process. Commissioning and start up had already been started in May 1994, crude carnallite is delivered from any harvester and the process description is as follows.

The large carnallite sizes are separated as oversize by two carnallite screens and stored in a livebottom 2 hour surge bin located directly below the screens to accommodate large changes in harvester slurry. After densifying in the carnallite thickener to 45% solids, the screen undersize is suspended in an agitated tank with a 2 hours maximum surge capacity (Figure 4).

Oversize solids from the carnallite screen are low in sodium chloride solids which are removed later in the process by screening. The screen undersize must be beneficiated by sodium chloride flotation before it can be used in the cold crystallization process. In the flotation process 45% slurry from the carnallite surge tank is treated with a small amount of flotation reagent, in a series of two agitated tanks for a period of 3 minutes. As the reagentized slurry is fed to the bank of flotation cells, it is diluted with brine from the downstream flotation thickener overflow, to give a slurry containing about 23% solids.

In the flotation cells, air is dispersed into the slurry. The reagent, which has coated the salt particles, causes them to adhere to the air bubbles and float to the surface where they are continuously skimmed off by the froth paddles. The carnallite, which is not coated with the flotation reagent, passes through the series of 5 flotation cells and is withdrawn as a slurry at the end of the bank. The carnallite, after passing through flotation is upgraded to minimum amount of sodium chloride. About 95% of the carnallite entering the cell bank is recovered in the sink.

The sodium chloride contained in the flotation cell froth flows by gravity to the agitated tails disposal tank and then pumped to the tailing area.

Carnallite slurry in the flotation underflow (sink) must be dewatered before it is fed to the cold crystallization process. The first step in dewatering is densification in the flotation thickener to 45% solids. The final dewatering down to 4% brine is achieved in worm-screen centrifuge.

The centrifuge screens require a minimum of 40% solids in the feed slurry to effectively contain the solids and dewater the slurry. The agitated fine carnallite surge tank provides a maximum of 1 hour surge before the final carnallite dewatering step by the carnallite centrifuges. Ten centrifuges are provided, one or two being a spare. Feed slurry is distributed to the centrifuges from a single agitated feed tank.

The effluent flows by gravity to the feed launder of the flotation thickener. The centrifuge cake is collected on a belt conveyor and fed into the downstream crystallizers.

Most of the flotation thickener overflow brine is used for diluting the feed to the flotation cell bank and, therefore, constitutes a recirculating brine around the flotation cells. The excess is pumped to the carnallite thickener.

Carnallite feed to the cold crystallizers consists of carnallite screen oversize (which is stored in the coarse carnallite storage bin) and the carnallite centrifuge cake. The coarse carnallite bin discharges the solids, at a controlled rate, into the carnallite repulp sump. The carnallite centrifuge cake (fines) is distributed between the 1st stage and the 2nd stage crystallizer in any proportion desired. For the flowsheet material balance, fines to the first stage crystallizer was set to give 60% of the total carnallite feed to the 1st stage, which required 29% of the fines split off the 1st stage. Crystallizer piping has been designed so that the crystallizers may operate independently of each other so one may be taken out of service for maintenance.

For maximum recovery in the crystallizer system, the 1st stage crystallizer, where brine is discharged from the crystallizer system, must be kept saturated with carnallite at its triple point (saturated with carnallite, KCl and NaCl). If unsaturated with carnallite, more KCl and NaCl will be dissolved in the brine and thus will be lost from the crystallizer system. To ensure that the 1st stage crystallizer brine is saturated with carnallite, water to the 1st stage is adjusted so that about 10% carnallite remains in the slurry. Too much water addition to this stage will result in lower recovery, and too little could cause unsatisfactory carnallite dissolution in the 2nd stage. The addition of water to the carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) causes it to be dissociated into its components. If the MgCl_2 concentration in the brine is at or near the triple point, the potassium chloride solubility is suppressed to the point where most of it will precipitate.

It is of the utmost importance to promote growth of KCl crystals in the crystallizer. To minimize nucleation leading to undesirable fines, the fines destruction system is designed to destroy fines by removing them in a brine stream followed by dissolution with water.

Slurry from the 1st stage crystallizer at 25% solids is pumped to the 2nd stage crystallizer where the remaining carnallite cake is also added. Excess water is added to the 2nd stage to dissolve all the carnallite as well as to make the brine slightly unsaturated with carnallite. Overflow brine from the 2 stages overflows to the product thickener. Clarified product thickener overflow brine is distributed to the 1st and 2nd stage crystallizers. Consistent quantity and quality of carnallite feeds and water addition to the crystallizers are important. For instance, a change in carnallite or water addition could cause an increase in magnesium chloride concentration in the 2nd stage crystallizer brine. This will cause precipitation of sodium chloride (if the brine is already saturated with NaCl) and product contamination will occur unless corrective measures are taken.

Slurry discharged from the 2nd stage crystallizer will contain all the KCl precipitated from both crystallizers and any undissolved NaCl and carnallite. The slurry is pumped to the crystallizer screen where the plus 600 micron solids are screened off and fall into the tails disposal tank located directly below the screen. Most of the sodium chloride crystals fed to the 1st stage crystallizer from the coarse carnallite storage bin are expected to be screened out here, plus a small amount of the largest carnallite particles remaining undissolved.

Crystallizer screen undersize slurry passes through a series of 2 agitated tanks giving 15 minutes retention. Effluent of product centrifuges is added to the 1st tank for dissolution of fine carnallite and as much NaCl solids as necessary to maintain product grade.

Slurry from the product leach tank flows to the product thickener by gravity. Here, the slurry is thickened to 45% by weight solids prior to being fed to the worm-screen product centrifuges.

Product thickener underflow slurry is pumped to the 1st stage product centrifuge splitter box. From here, it flows by gravity into the three 1st stage product centrifuges. 2nd stage product leaching is provided in 20 min leach tank for the centrifuge cake to remove as much of the high magnesium chloride from the product cake as particle. Slurry from the product leach tank stored in 30 min surge tank prior to being fed to the worm-screen centrifuges.

Product slurry is pumped to the 2nd stage splitter box. From here, it flows by gravity into the three 2nd stage product centrifuges.

The product centrifuge cake is conveyed to the product dryer which is co-current rotary, direct fired type. The solids exit the dryer at 150°C, and enter the rotary cooler. In the cooler, the product is cooled to 90°C (the maximum temperature desirable for shipments) by direct contact with atmospheric air flowing counter-current to the solids. A screw conveyor between the dryer and cooler serves as an air lock.

Cooler discharge solids will be conveyed to a bucket elevator in the product screening section of the plant. Lumps created in the dryer together with any material larger than 2.4 mm are removed by vibrating scalping screen. Oversize falls into a hammermill crusher after which it flows by gravity back to boot of product elevator.

Scalping screen undersize is distributed to five high frequency vibrating product screens by a vibrating pan conveyor. Any product remaining at the end of the conveyor is returned to the boot of the product elevator to be redistributed to the product screen.

Product screen oversize and undersize are conveyed to the appropriate 250 ton standard and fines bins to await dispatching. The bins have activated bottoms to aid in trouble free discharging.

Each of the dispatch bins are discharged at a constant volumetric rate of about 300 TPH by a screw feeder. After the material has been conveyed from beneath the bin discharge, the flights are changed so that the screw is only partially filled hereafter. This is done so that anti-caking material can be applied and mixed thoroughly with product before it is discharged onto the downstream belt conveyor.

The product is conveyed to above the existing shipping bins with inclined belt conveyors. From here standard product will usually be transferred into the existing bins and fines product transferred into the product storage building.

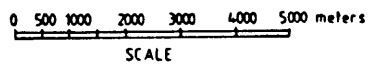
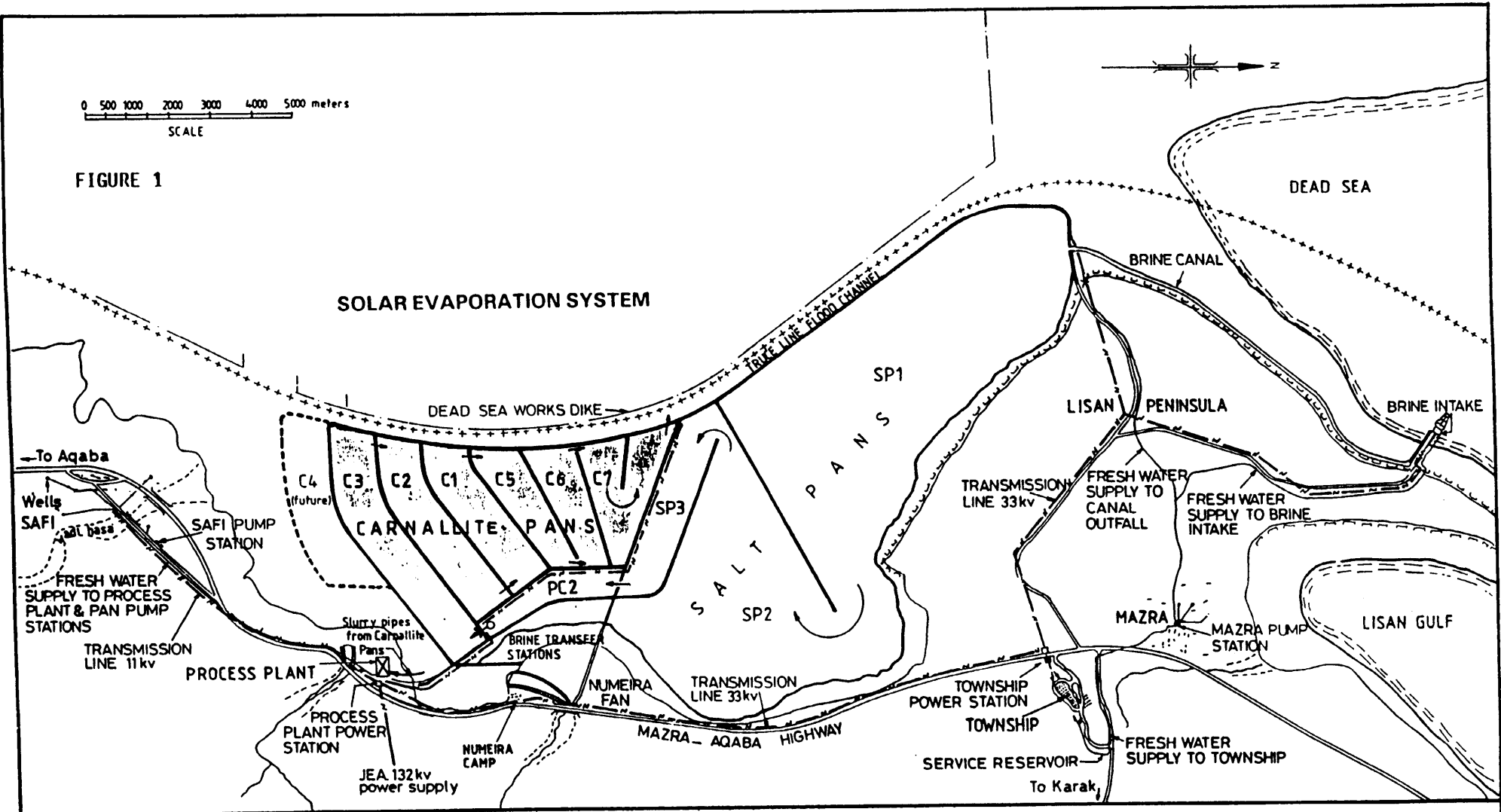
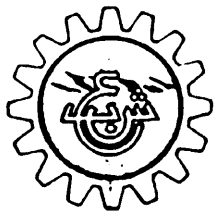


FIGURE 1

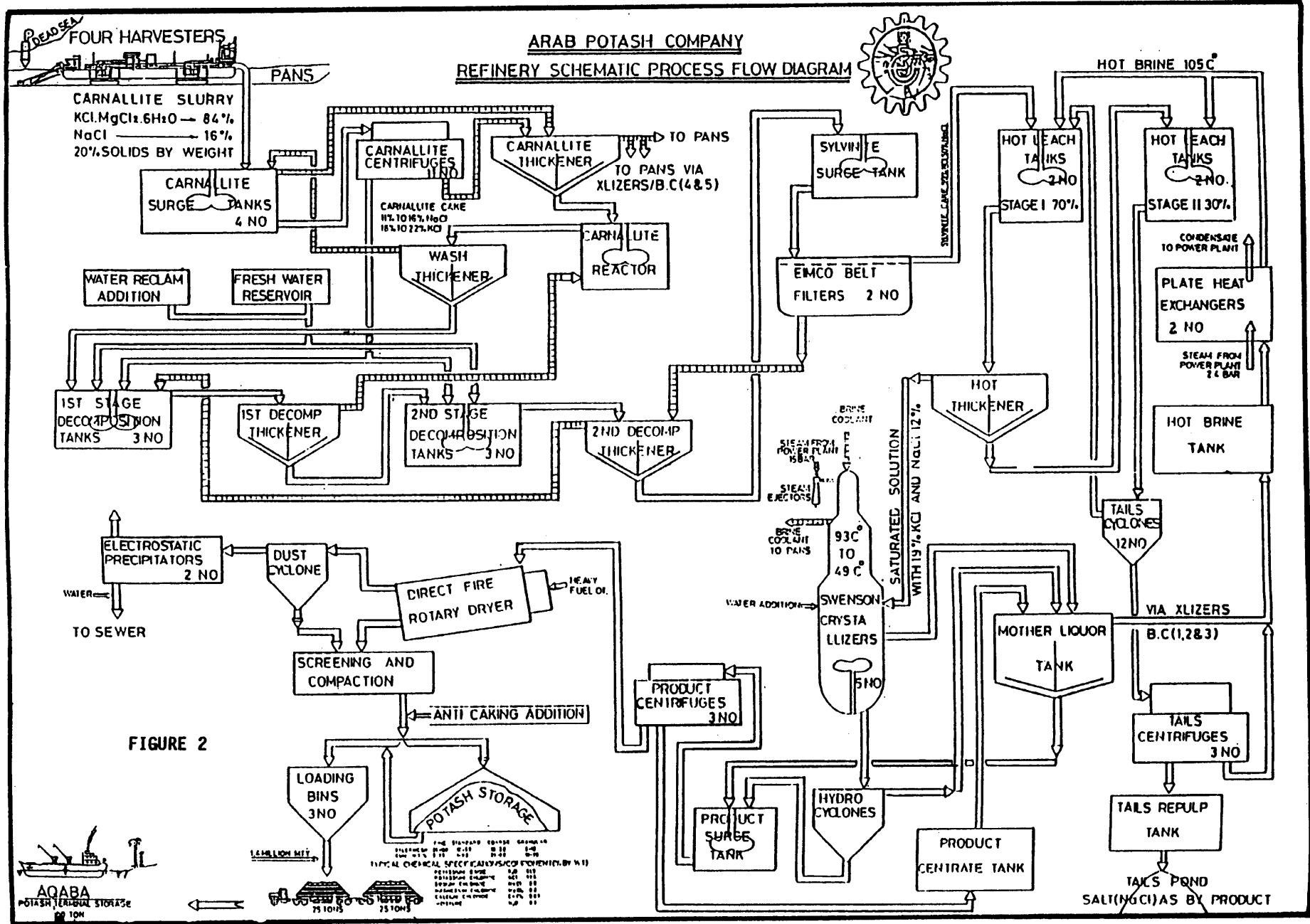


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THE ARAB POTASH COMPANY LTD.

THE HASHEMITE KINGDOM OF JORDAN



COLD CRYSTALLIZATION PLANT

PROCESS FLOW DIAGRAM

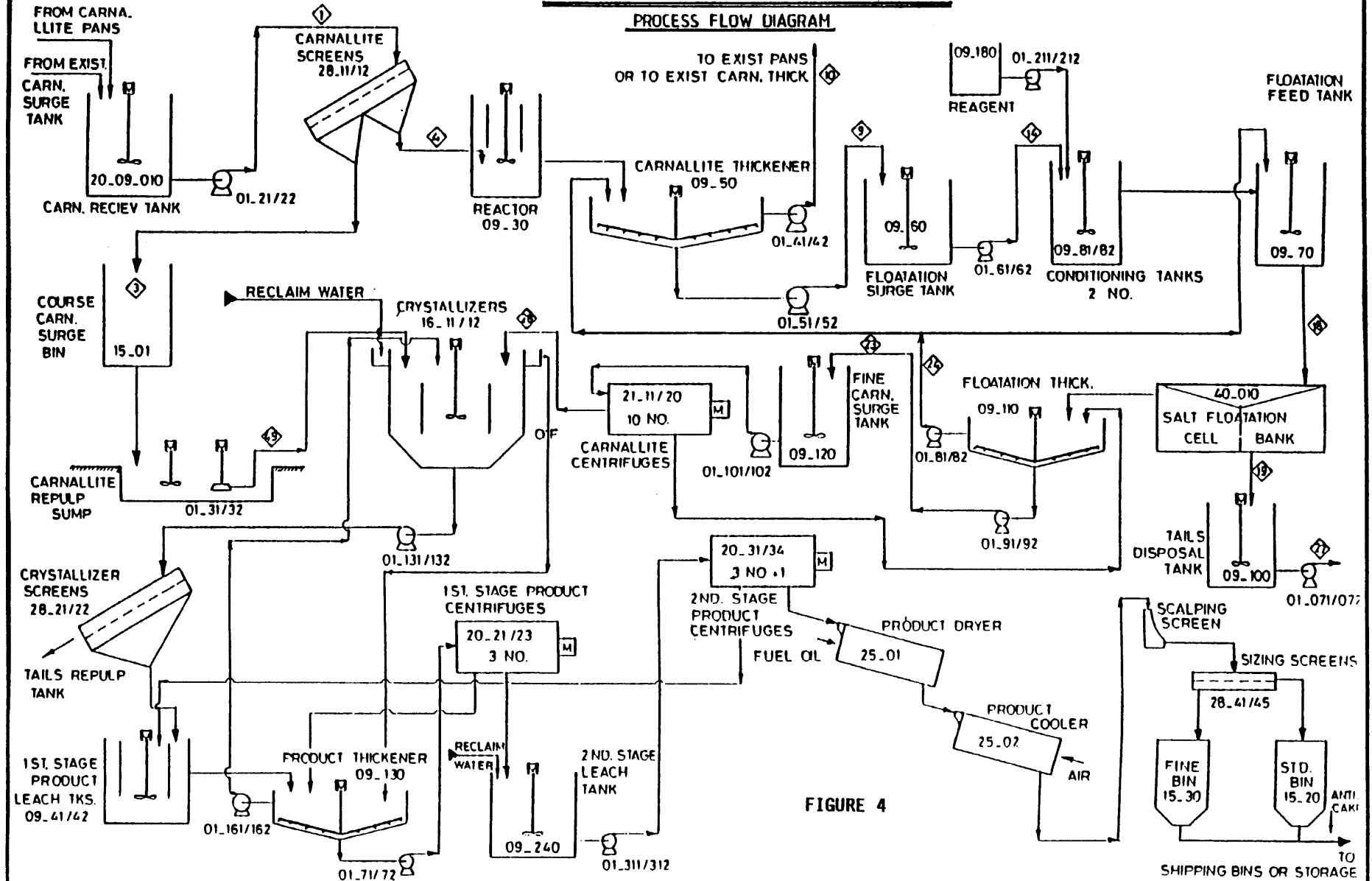


FIGURE 4