CHAPTER 1

WHAT IS POTASSIUM CHLORIDE?

Potassium is the seventh most abundant element and makes up about 2.6% of the Earth's crust. Potassium metal is far too reactive to be found uncombined in nature, so it exists as compounds in minerals. Examples of compounds are potassium silicate, potassium nitrate, potassium sulfate, potassium hydroxide, and, of course, potassium chloride. Potassium silicate, or feldspar [$KAlSi_3O_8$], is the most abundant compound of potassium on Earth, but feldspar minerals are very stable, so extraction of K^+ from feldspars is not industrially viable. Potassium chloride (KCl), which is also abundant in nature, is better suited to separation and concentration of potassium on an industrial scale. In industry, KCl is used as a feedstock for the production of many other potassium compounds. Potassium chloride is also the most important compound for supplying potassium to the fertilizer industry.

Potassium deposits are spread throughout the world in minerals such as sylvite (KCl), sylvinite (KCl/NaCl), langbeinite [$K_2Mg_2\ (SO_4)_3$], and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). These deposits are found in ancient, shallow saline lake and sea beds.

The world's largest reserve of potassium is located in west-central Canada, primarily in the province of Saskatchewan. The potash deposits formed over 380 million years ago as a result of the final stage of

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Water Softening with Potassium Chloride: Process, Health, and Environmental Benefits,
by William Wist, Jay H. Lehr, and Rod McEachern

evaporative concentration of seawater in the Middle Devonian Sea. This shallow, inland sea extended from the southern part of the Northwest Territories southeast through Alberta, through southern Saskatchewan into Manitoba and southeast into North Dakota. Potash salts are concentrated in the southeastern extent of this basin, underlying much of southern Saskatchewan. The average depth of these deposits is ~1 kilometer or 3300 feet. The mineral name for the predominant potash ore is sylvinite, which is a mixture of halite ~60% (sodium chloride or NaCl), sylvite ~35% (potassium chloride or KCl), and clay (and other water-insoluble minerals) ~5%. The concentration of the minerals in sylvinite can vary significantly depending on the location of the potash ore.

SASKATCHEWAN POTASH HISTORY

The discovery of the potash deposits in Saskatchewan occurred in 1943 from an exploratory oil well in southern Saskatchewan. The first core sample was at a depth of 2 kilometers or 6600 feet. Another core sample from an exploratory oil well northwest of the first core in west central Saskatchewan discovered a high-grade potassium ore at a depth of 1 kilometer. Exploration was expanded over the next few years, and in the 1950s it was determined that a vast (probably the world's largest) potash deposit was below the surface of most of southern Saskatchewan.

By conservative estimates, potash mineralization in Saskatchewan could supply the world potassium demand for several hundred years.

The first potash mine in Saskatchewan was completed in 1958. However, the shaft was flooded the same year by a high-pressure sand- and water-bearing formation above the potash zone, and the mine did not return to production until 1965. The ~100-meter-thick layer of water-bearing sands of the Lower Cretaceous Mannville Group occurs about halfway between the surface and the potash zone; within the Saskatchewan potash industry the common name for this unit is the Blairmore Formation. The water pressure in this formation is proportional to burial depth, so it can be as high as 500 psi. To successfully sink a shaft to the potash zone, Blairmore sands had to be sealed. A successful technique was developed in the 1960s in which the Blairmore formation was frozen until the shaft was dug and sealed with concrete and iron-ring tubbing segments to form a permanent watertight shaft lining. The second potash mine began production of potash mining 1000 meters below the surface in 1962. By 1974 there were 10 potash

TABLE 1-1: Production capacity (in millions of metric tons per year, as KCl) of Saskatchewan potash mines, as of 2006

Producer	Location	Mining Method	Nameplate Capacity (MTPY)
Agrium	Vanscoy	Conventional	1.750
Mosaic	Belle Plaine	Solution	2.533
Mosaic	Colonsay	Conventional	1.485
Mosaic	Esterhazy K1/K2	Conventional	3.928
PotashCorp	Allan	Conventional	1.885
PotashCorp	Cory	Conventional	1.361
PotashCorp	Lanigan	Conventional	3.828
PotashCorp	Patience Lake	Solution	1.033
PotashCorp	Rocanville	Conventional	3.044

mines operating in Saskatchewan, with a total annual production capacity of 13 million tons of potassium chloride. Nine of the mines used conventional mining techniques, and one used a solution mining technique that does not require the sinking of a shaft.

The original 10 mines built in Saskatchewan in the 1960s were privately owned by nine separate companies. At present, all 10 mines are still operating, but there are only three separate companies. The original mine built at Patience Lake in 1958 was flooded in 1988 and has since been converted to a solution mine. Many expansions have taken place over the years, so that annual production capacity currently exceeds 20 million tons.

The Saskatchewan potash industry is currently expanding rapidly in an effort to meet rising world demand. Production from the Saskatchewan potash mines exceeds 20 million tons annually (Table 1-1) and provides over 30% of the worlds potash. Data shown in Table 1-1 apply to Saskatchewan mines only; some of the producers have potash capacity elsewhere in the world, but these other facilities are excluded from this table.

POTASH MINING

The deposits in Saskatchewan are typical of many potash deposits around the world, that is, they were formed millions of years ago by evaporation of an inland sea. When an inland sea is isolated from the ocean, the sea salts in the water will become more concentrated (saturated) because of evaporation. If the climate is warm and dry, then the sea salts will over time become saturated, so that further evaporation results in precipitation (crystallization) of the salts. Sodium chloride is the least soluble of the common salts in ocean water, so it crystallizes out from the solution first. Other salts, including potash (KCl) crystallize out later as they too achieve saturation. As the various sea salts crystallize out and fall to the bottom of the inland sea, a layer of these salts is built. The various salts crystallize in sequence (according to their quantity and solubility), so there are discrete layers of KCl-rich salts that can be mined economically. Potash deposits, formed by crystallization of ancient seas, can be covered by sediment and other material over geological time, so that the potash deposits in modern times can be buried at substantial depths. The Saskatchewan deposits vary in depth below surface. Most of the mines in the province are conventional mines, located near the northern (shallow) end of the potash deposit; for these mines the potash is located approximately 1 kilometer (3300 feet) below the surface. Once the potash ore is mined and hoisted to the surface, the KCl is then separated from the other salts and sold, primarily as a plant nutrient (fertilizer). Potash production is therefore the recovery and purification of material from sea salts!

The potash deposits in Saskatchewan were formed at the bottom of an ancient inland sea 380 million years ago, and therefore the salts were deposited over a large area, in a relatively flat, thick layer of salt-rich material. Many such deposits were formed around the world in a similar way. In some cases the potash deposit became tilted or folded over time because of geological processes. In Saskatchewan, fortunately, the potash deposits remain relatively undisturbed and flat, which makes it easier to recover the potash ore safely and efficiently.

Potash ore is a mixture of KCl (sylvite) and NaCl (halite) along with minor amounts of $KCl \cdot MgCl_2 \cdot 6H_2O$ (carnallite) and water-insoluble minerals. The mixture of sylvite and halite is given the mineralogical name "sylvinite." Sylvinite, like sodium chloride, is a fairly hard, but brittle material. Therefore, mining equipment has been developed to efficiently extract the ore by taking advantage of this characteristic. Most of the potash mining is done with large continuous boring equipment, originally developed for coal mining. A typical continuous borer consists of large rotors mounted on a powerful track-driven tractor (Figs. 1-1 and 1-2). The tractor pushes the rotors against the mining face (ore body), and the rotors scrape the potash ore from the face. The particle size of the ore extracted in this manner will vary from 1-foot diameter all the way down to dust-sized particles. The potash falls to the ground, where it is scooped up by the mining machine and deposited onto a conveyor belt. The circular motion of the rotors leaves a pattern of characteristic circular grooves on the ore face (Fig. 1-3).

FIGURE 1-1 A potash miner inspects the front of a continuous boring machine. Machines such as this unit will cut up to 700 metric tons of ore per hour from the ore body and deposit it on a conveyor belt for transport to the shaft.

The ore cut by the boring machine is deposited directly onto a movable (extensible) conveyor belt, which delivers it to a permanent belt. There can be as many as 25 miles of underground conveyor belts in the larger mines, transporting up to 2000 tons per hour of ore to the shaft. Inside the shaft is equipment that loads the ore into specially designed containers ("skips"). Each skip holds 20–30 tons of ore, which is rapidly hoisted to the surface. The skips make many cycles from underground to surface each hour; the total capacity for hoisting ore is approximately 1000 to 2000 tons per hour. Once on the surface, the ore is transported to the refinery for processing, as described in the following sections.

In a typical conventional potash mine the majority of the ore is extracted with continuous boring machines as described above. Many

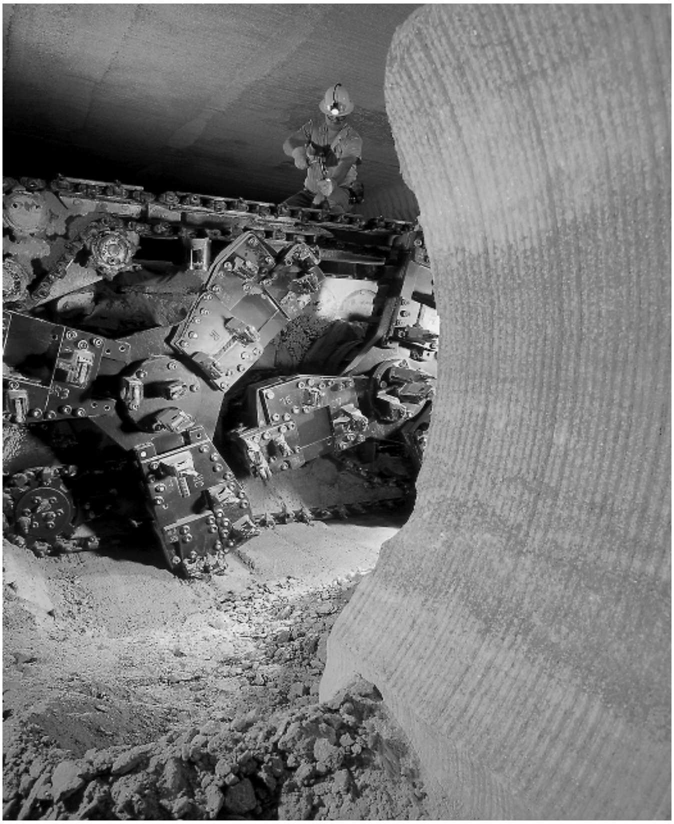

FIGURE 1-2 A mechanic making repairs and adjustments to the front end of a continuous boring machine in potash service.

other types of equipment are also required as part of the mining operation. Some equipment is used to install rock bolts, which provide stability to the roof of the mine and thereby reduce the risk of falling rocks. Other equipment consists of boom-mounted rotating cutting heads (Fig. 1-4), which are used to trim irregular surfaces in the mine workings. The equipment in an underground mining operation requires repair from time to time, and so each mine has underground shops with teams of welders, mechanics, and electricians (Fig. 1-5).

Many conventional underground potash mines in Saskatchewan use some variation of long room and pillar mining. The long room and pillar technique involves cutting a series of rooms, which can be 4000 to 6000 feet long and 40 to 80 feet wide. Along with conservative extraction ratios, this provides enough support to prevent the mine

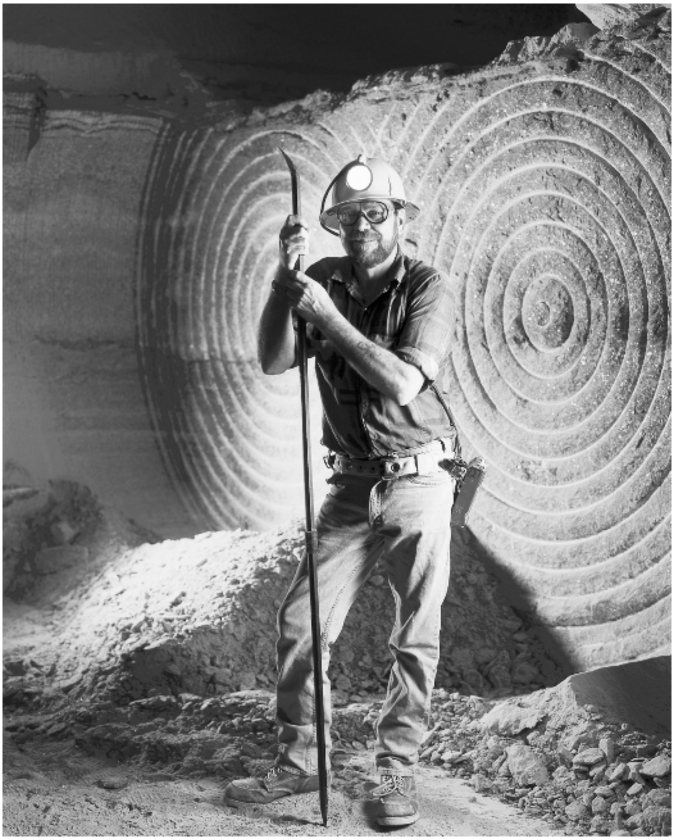

FIGURE 1-3 A potash miner stands in front of the sylvinite ore face, which shows the characteristic circular grooves cut into the ore by the tungsten carbide bits on the mining machine rotors. The miner is holding a scaling bar, which is used to inspect the roof for loose rocks and safely remove them. Mounds of potash ore, recently extracted from the face, lie on the floor behind the miner.

rooms from collapsing. This mining pattern is illustrated in Figures 1-6 and 1-7. Stress-relief mining methods are used to alleviate risk in Saskatoon-area mines, where clay layers in the mine roof could render room-and-pillar methods unsafe in the absence of proper safe mining techniques. Stress-relief mining involves cutting underground openings in a pattern that creates areas of ground failure in order to deflect rock pressure away from other mine rooms, keeping these safe for extended time periods. The resulting stress-relief mining pattern is often called the herringbone pattern, for obvious reasons (see Fig. 1-8). The overall extraction ratio for either mining method ranges from 35% to 45%.

FIGURE 1-4 A mining machine with a boom-mounted cutting head. Machines such as this are use often used in potash mining to trim irregularities in the mine workings to ensure a safe working environment.

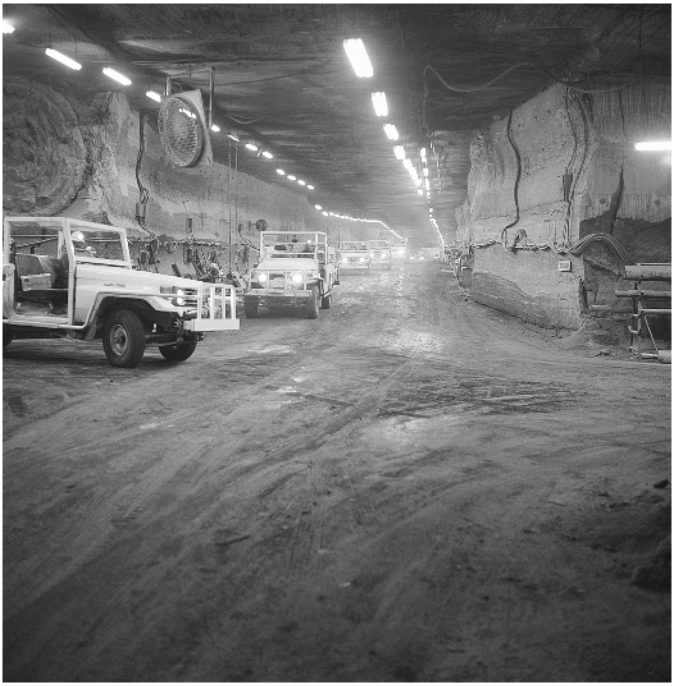

FIGURE 1-5 Underground shops where welders, mechanics, and electricians work to repair damaged equipment, so that it can be quickly returned to mining service. The shops shown in this photograph are 3200 feet (~1 kilometer) below the Earth's surface.

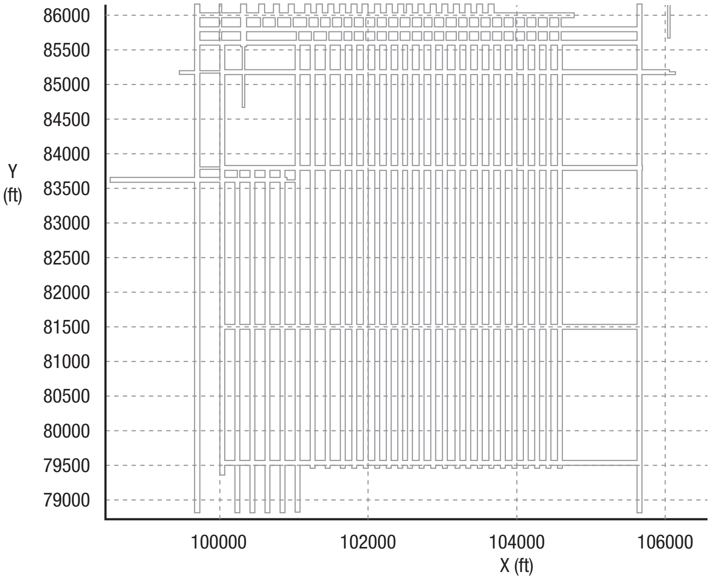

FIGURE 1-6 Example of a long room and pillar cutting pattern at the PCS Potash, Rocanville Division in southeast Saskatchewan. Coordinate axes are in mine coordinates (feet), and *X* is east and *Y* is north. Overall extraction for this panel is just under 40%.

These conservative extractions are strictly adhered to in order to minimize the likelihood of mine flooding from overlying water-bearing formations.

SOLUTION MINING

The depth of the potash ore in Saskatchewan varies. At the northern side of the deposit, the ore is found approximately 3300 feet (~1 kilometer) below the surface. However, the depth of the potash deposit is greater in the southern part of the ore body. When the ore is located significantly greater than 1 kilometer below the surface, shaft sinking and mining become more difficult and costly. Fortunately, the deeper deposits are also warmer, so it is possible to extract potash from the deeper deposits by solution mine. One such mine was built deliberately as a solution mine in the southern part of Saskatchewan, near Belle Plaine, at an ore depth greater than 1500 meters. A second mine near Saskatoon was converted to a solution mine in 1991 after it was forced to shut down because of uncontrolled flooding in 1988.

FIGURE 1-7 Photo of a 4-rotor continuous mining machine at PCS Potash, Lanigan. The long room-and-pillar mining method is utilized at Lanigan; completed 4-pass mine rooms are 42′ wide and 16′ high. An extensible conveyor belt is located behind the mining machine; the ore is transported back to the shaft by conveyor belt and then hoisted to the surface.

Solution mining for potash is based on the temperature dependence of the solubility of KCl and NaCl in water. The solubility of KCl in water or brine increases as the temperature of the solution increases, but the solubility of NaCl slightly decreases (see Fig. 1-9). This is the basis for both crystallization and solution mining.

In a solution potash mine, a number of bore holes are drilled from surface down into the potash ore zone. Hot brine saturated with NaCl but unsaturated with KCl is pumped into the bore holes and into the potash bed. Since the brine is saturated with NaCl it will only dissolve KCl. The solution eventually saturates with KCl and is pumped to the surface for processing. Solution mining uses large volumes of high-

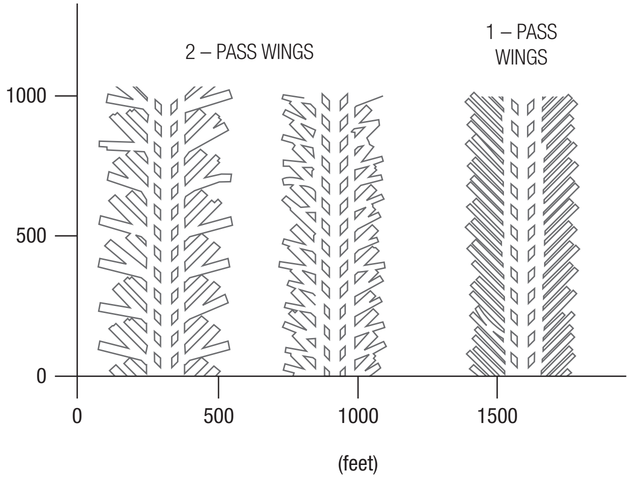

FIGURE 1-8 Examples of "herringbone" stress-relief cutting patterns employed at the PCS Potash, Allan Division in central Saskatchewan (near Saskatoon). Coordinate axes are in feet. At the present time (2008), the "1-pass wing" cutting pattern is the most common mining pattern at Allan.

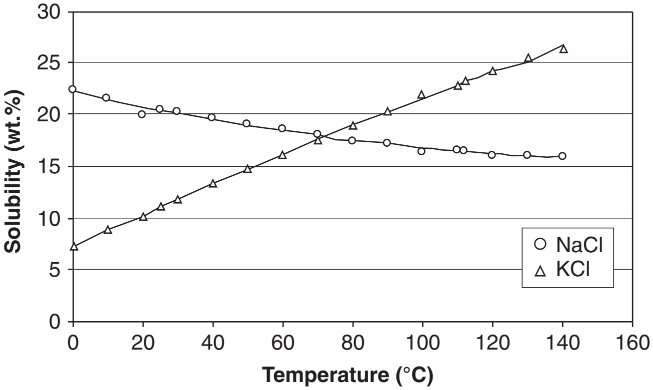

FIGURE 1-9 Solubility of KCl (—Δ—) and NaCl (—O—) as a function of temperature, for solutions that are saturated with respect to both salts.

temperature brine, and therefore energy consumption (and costs) can be high. The two solution mines in Saskatchewan rely on natural gas as their source of energy.

The hot brine returned to surface from a solution mine has a high content of KCl. To recover the KCl, one needs only to cool the brine and KCl crystals will precipitate (Fig. 1-9). Cooling of the brine is achieved by processing in a set of crystallizers, as described in detail in

FIGURE 1-10 Harvesting KCl from the bottom of a cooling pond using a dredge, at the PCS Patience Lake mine.

the section "Crystallization." The spent brine from crystallization remains warm (approximately 30–40 °C) and still contains a significant amount of KCl in solution. Producers therefore take advantage of the cool Saskatchewan winters, and allow the spent brine to flow through a series of specially designed open-air cooling ponds. As the brine flows through the ponds it is cooled further, and additional KCl crystallization occurs. A layer of KCl crystals grows on the bottom of the pond over time, and KCl is harvested from this layer by a dredge (Fig. 1-10) and pumped to the mill for processing. This product contains almost no clay and is white in color.

The solution mining process discussed above is used at the one mine deliberately built as a solution mine. The second solution mine in Saskatchewan is PCS Patience Lake, which was originally built as a conventional mine but was abandoned because of an uncontrolled inflow of fresh water in 1988. Production of KCl from this mine resumed in 1991 as a solution mine. The Patience Lake mine applies technology slightly different from that of a typical solution mine. In the Patience Lake process, the brine is injected warm (not hot) to reduce energy costs. The warm, KCl-rich brine returned to surface is not sent to a series of crystallizers, but instead it flows directly to a set of cooling ponds, from which KCl is recovered by dredge. The Patience Lake process allows for the recovery of KCl from a mine otherwise lost because of flooding, and it has lower energy consumption, per ton of product, than a conventional solution mine. The plant throughput from a Patience Lake type of process, however, will be lower than for a typical solution mine.

PROCESSING POTASH ORE

The ore received from underground mining consists of a mixture of KCl (30–40%), NaCl (52–69%), and water-insoluble minerals (1–8%). The basic processing requirement is removal of the NaCl and some of the insoluble material from the KCl. In the ores, the KCl and NaCl crystals are formed as discrete, single crystals of the pure compounds, rather than as a solid solution of KCl/NaCl. The individual crystals of KCl and NaCl are, however, agglomerated into a complex mechanical mixture, with clays and other insolubles located interstitially (between crystals). The one exception to this behavior is iron oxide, which is found in very low levels (parts per million) dispersed as inclusions throughout many of the KCl crystals, and imparts the characteristic rusty red colour to potash fertilizer.

Worldwide, there are many different mineral processing techniques for processing potash ore, but the most common are flotation and crystallization. Many plants rely on both of these separation techniques. For example, many plants will process the ore by flotation to produce a concentrate containing 95% KCl (suitable for sale as a fertilizer) and then process a portion of the product further, by crystallization, to produce a higher-purity product for sale as an industrial chemical. In the present discussion, we shall therefore follow the basic process for a “typical” potash refinery, treating crystallization as one of the methods of further processing the low-grade fines. It should be recognized that some plants rely solely on crystallization as their method of upgrading potash ore; in such a case the process would be different, but many of the basic concepts would be the same.

In the following sections, we examine briefly each of the key steps in the production of potash.

Ore Handling

The potash ore is hoisted to the surface in “small” (20–30 ton) containers, known as skips, as described in the section on mining. The skips will carry numerous loads from underground each hour, so that the total hoisting capacities of the plants are typically in the range of 1000 to 2000 tons per hour. The ore is dispatched from the skips onto conveyor belts (Fig. 1-11), which transport the ore to storage bins. Surface storage of ore will vary but will be in the range of 1000 to 8000 tons typically. Since potash ore is predominantly a mixture of two salts (KCl and NaCl), it is not surprising that moisture in the ore can lead to caking or setup in the storage bins (similar to what happens to the salt in a salt shaker on humid summer days). To reduce the risk of setup,

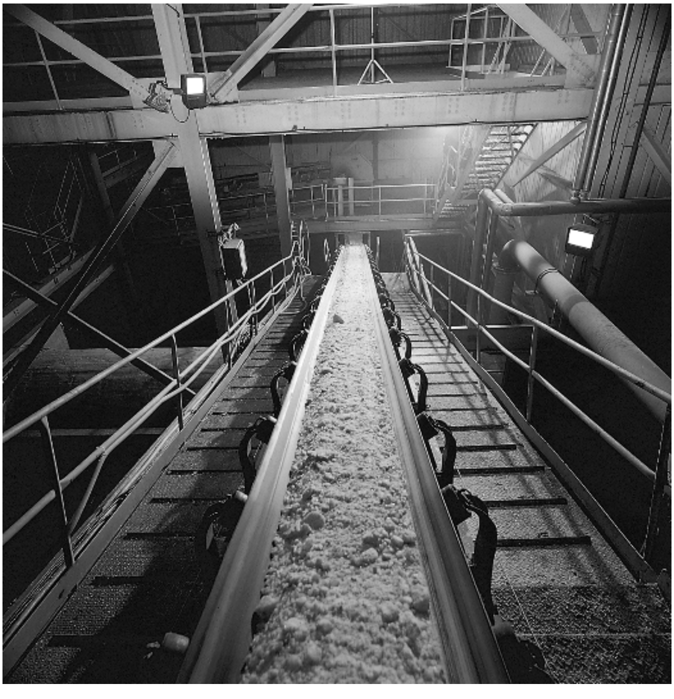

FIGURE 1-11 Transportation of potash ore from the skips (hoist) to the ore storage bin. Processing potash ore involves moving hundreds (or thousands) of tons of material from one part of the process to the next; conveyor belts are one of the common pieces of equipment used for material handling.

plant operators ensure that the contents of the storage bin are "live" or continuously moving—setup in an 8000 ton storage building is a bigger problem than in a salt shaker!

Comminution

The first task in processing potash ore is to crush the ore to the point where KCl crystals are free from NaCl and other minerals in the host rock. At this point, the KCl can be separated efficiently—in mineral processing language, one would say that the ore has been crushed to its "liberation size." The liberation size will vary for different ores. Mines in the southeast part of Saskatchewan produce an ore in which the majority of the potash crystals are liberated when crushed to less than ½ inch (12.5 mm), while in other parts of the province the ore must be crushed considerably finer.

Potash ore is moderately hard, but brittle, so it is relatively easy to crush. The first stage of crushing was traditionally done with impactors, in which the ore flows through the crusher past a series of rapidly rotating steel hammers. In recent years, there has been a tendency to replace impactors with cage mills, in which the ore is impacted with rotating steel cages rather than hammers.

The primary crushing circuit can be either open or closed. In an open circuit, the ore is screened at approximately ½-inch size, and the oversize material is fed to the crusher. The crusher discharge is then recombined with the screen undersize. In contrast, in a closed circuit, the crusher discharge is recycled back to the screen. Open circuits have the advantage of being simpler processes to operate, with less material-handling equipment. However, they lack the control on the upper particle size that a closed circuit has—a small number of particles as large as ½ inch will pass through the crushing circuit, so the downstream equipment needs to be able to process such material.

The secondary stage of comminution is generally done as a wet process. The crushed ore from the primary circuit is slurried in a brine saturated with both KCl and NaCl salts. The brine is in chemical equilibrium with the ore at the process temperatures and has a composition of approximately 10% KCl, 20% NaCl, and 70% water. The secondary stage of comminution has traditionally been done with rod mills. A rod mill is a large steel cylinder (10–15 feet in diameter and 15–20 feet long) with a large number of steel rods inside (Fig. 1-12). As the potash ore slurry flows through the rod mill, the mill turns rapidly, causing the rods to tumble. The result is a fairly gentle crush that reduces the particle size of the ore without excessive generation of fine particles (which

FIGURE 1-12 A potash plant operator standing beside a rod mill, used for the secondary comminution of potash ores.

are more difficult to process). Ore slurry from the rod mill is sent to a set of screens with ~3–4-mm openings. The ore particles with less than 3–4-mm size flow on to the next stage of the process (desliming), while the oversize (>3–4 mm) are returned to the rod mill for further size reduction.

In recent years there has been a shift away from rod mills, which are large and expensive and can be difficult to maintain. In their place, plants are installing cage mills or impactors.

Desliming

Potash ores in Saskatchewan contain 1–8% water-insoluble minerals; mines in the southeast part of the province tend toward the lower end of the range, while Saskatoon-area mines are higher. The insoluble minerals originated as suspended solids, or mud, in the ancient sea that evaporated to create the potash ore. There are a number of different minerals in the "insolubles" group, including:

— Dolomite
— Quartz
— Anhydrite
— Gypsum
— Hematite
— Illite
— Chlorite

The insoluble minerals tend to have a very small particle size of approximately 10-micron diameter. They therefore have a very large surface area that tends to adsorb the organic chemicals used later in the process, in flotation. As a consequence, it is important to do a thorough job of removing the insolubles from the potash ore, in a process known as "desliming."

The insoluble minerals are generally located interstitially in the potash ore. They are generally scrubbed free from the KCl and NaCl crystals in attrition scrubbers, in which the ore slurry is agitated vigorously for several minutes. At this point in the process, the insolubles have a very small particle size (~10 micron) while the KCl and NaCl particles are much larger (30–3000 micron). Many different methods for desliming, based on the differences in particle size, are in use, including:

— Hydrocyclones, in which the ore slurry is pumped through a specially designed conical device that collects the coarse particles from the bottom (underflow) while allowing the majority of the brine to report to the top (overflow). In a hydrocyclone the majority of the very fine materials (i.e., the insolubles) are carried along with the brine and report to the overflow, while the coarser KCl and NaCl crystals report to the underflow. A set of cyclones being used to deslime potash ore is illustrated in Figure 1-13.

— Hydroseparators, in which the fine solids (in a brine slurry) are sent to a device that allows the heavy particles (relatively large KCl and NaCl particles) to settle and be recovered from the bottom. Hydroseparators are designed so that a

FIGURE 1-13 A set of hydrocyclones, which is used for effective desliming, i.e., removal of insoluble particles, from potash ore.

substantial portion of the fluid overflows a weir at the top of the unit. The upward flow of brine carries the smallest particles (predominantly the insolubles) over the top. Thus a reasonable separation of coarse KCl/NaCl from the fine insolubles can be achieved.

— Fluidized-bed separators, in which the ore slurry is fed into a unit in which the particles are fluidized by an upward flow of clean brine. The coarse KCl/NaCl particles are recovered from the bottom of the unit, while the fine insoluble particles are recovered from the overflow.

— Slimes flotation, in which the fine solids are flocculated and then conditioned with a collector (Brogiotti and Horwald, 1975). The ore slurry then reports to a flotation cell in which the insoluble particles adhere to air bubbles and are thus transported to the top of the flotation cell, from where they are collected and removed from the ore.

The majority of the insoluble minerals have been removed from the potash ore once it has been processed in desliming. The ore is then ready for the key separation—removal of the KCl from NaCl, which is achieved in flotation.

Flotation

Froth flotation is a widely used technique for separating a wide range of valuable minerals (copper, nickel, gold, zinc, etc.) from their respective ores. The technique is based on the chemical properties of the mineral surfaces. If a mixture of minerals is slurried in a tank and air bubbles are injected, the air bubbles will adhere to those minerals that are hydrophobic (nonpolar, air-wetted), but not to the minerals that are hydrophilic (polar, water-wetted). The air bubbles will drag the desired mineral to the top of the tank, and it can be collected, separate from the undesired minerals. The process engineer can thus achieve good separation of the desired mineral by selecting appropriate conditions and surface treatment so that only the desired mineral is air-wetted.

In many industries, the surface of the desired mineral is naturally air-wetted, that is, hydrophobic. In such cases the flotation process will work with no special surface treatment. Some examples of such naturally hydrophobic materials include bitumen, graphite, sulfur, and talc. In many cases, however, like potash processing, careful surface treatment is required so that the surface of the desired mineral becomes hydrophobic (air-wetted) while the other minerals remain hydrophilic (water-wetted). A compound added to a flotation system to render the surface of the desired mineral hydrophobic is known as a *collector.* In potash processing the most common collector is a long-chain amine molecule.

The long-chain amine used in potash processing, like all common collectors, is a surfactant, that is, it has both polar and nonpolar components to the molecule. The collectors work because the polar portion of the molecule attaches to the surface of the desired mineral (KCl). When uniform (monolayer) coverage of the surface has been achieved, the nonpolar part of the collector is on the outside surface, exposed to the solution (Fig. 1-14). Once the KCl surface is coated with a monolayer of the collector, the surface has been effectively rendered hydrophobic, and air bubbles will adhere to the surface. The amine will not adhere to NaCl because of some subtle differences in the surface chemistry of these two salts; as a result, the NaCl surfaces remain hydrophilic and will not be collected by flotation.

In potash processing, the deslimed ore slurry will be conditioned with a very small quantity (e.g., 50 grams of amine per ton of ore) of the collector by mixing in a tank, launder, or drum. Small amounts of several other chemicals are added to improve the flotation process, including those described below.

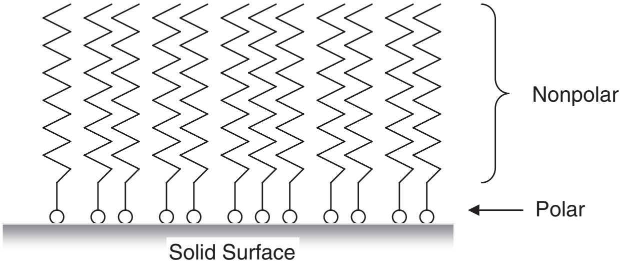

FIGURE 1-14 Monolayer coverage of the amine collector on the surface of a KCl crystal, showing both polar (amine functional group) and nonpolar (long-chain hydrocarbon) parts of the collector molecule. Alignment of collector molecules as shown in this figure results in a hydrophobic layer on the surface of the KCl, but not on the NaCl.

Depressants. Chemicals added to a flotation system to depress (inhibit) the flotation of undesired minerals are known as depressants. In potash, depressants are added to inhibit flotation of any residual insoluble material that was not removed in desliming. In potash flotation, clays are particularly problematic, as they have a very large surface area, so they would adsorb large amounts of the collector. The clays are therefore depressed with inexpensive reagents such as carboxymethylcellulose and guar. These polymeric species are added to the ore slurry before the addition of collector. The polymeric depressants adsorb onto the clay surfaces through hydrogen bonding and coat the surface, thus preventing adsorption of the collector.

Frothers. The flotation process would not work if the air bubbles (with attached particles) rose to the top of the cell and promptly burst—leaving the solids to settle back to the bottom of the cell. Frothers are therefore added to the flotation slurry; they stabilize the air bubbles so that they do not burst when they reach the top of the cell. Instead, the air bubbles form a layer of KCl-enriched foam that is skimmed from the top of the cell. Frothers are usually alcohols that reduce air-water interfacial tension by coating the air bubbles, leaving the polar hydroxyl groups exposed to the solution. In potash, the frothers in use are typically C_6 to C_{10} aliphatic alcohols.

Extenders. Nonpolar chemicals added to the flotation circuit to improve recovery of the desired mineral are known as extenders. The mechanism by which extenders work is unknown. Two proposed theories are that the extender collects near the bubble-solid interface, thus strengthening the bond between them, and that the extender binds to the hydrophobic part of the collector molecules, thus making the surface of the desired mineral more hydrophobic.

Once the ore slurry has been properly conditioned with the collector, and other necessary reagents, it is pumped to the flotation cells, in which the KCl is collected from the top of the cell while the NaCl flows through. In flotation, the ore slurry is agitated in a series of flotation cells, and air bubbles are injected into the mixture at the cell bottom. As the air bubbles rise to the top of the cell, collector-coated KCl particles adhere to the air bubbles and are dragged to the top of the cell, where they are skimmed off into a collection launder.

Each flotation bank is commonly a large rectangular steel tank, subdivided into a number of square cells. Each cell has a large agitator to slurry the ore and provision for the injection of air bubbles. The KCl concentrate froth is collected from the top of each cell by a paddle wheel, which scoops the product from the top of the cell and deposits it into a collection launder. A typical potash flotation circuit is illustrated in Figure 1-15. Flotation concentrate is typically close to the 95% KCl grade that is required for fertilizer, and can be sold after debrining, drying, and sizing.

Product Debrining and Drying

The product obtained from flotation is a slurry, consisting of solids that are a minimum of 95% KCl, and a cosaturated KCl/NaCl brine. The brine must be recovered and recycled for efficient plant operation. The slurry is therefore processed through screen-bowl centrifuges (Fig. 1-16). In a screen-bowl centrifuge the solids are transported past a screen section before they are discharged as a damp cake. The screen section results in a drier cake, and also allows the operators the opportunity to displace some of the KCl/NaCl brine in the product. One of the goals in centrifuging is to reduce the cake moisture as much as possible, because high moisture leads to high drying costs, and because the NaCl in the brine salts dilutes the concentrate grade. The moisture content of the damp cake varies with particle size of the product, and will be in the range of 3–6% moisture. All the brine from the centrifuges is recovered, cleaned (of insolubles) in a thickener, and recirculated to the front of the flotation circuit.

Centrifuge cake is then rigorously dried in cocurrent rotary kiln or fluidized bed dryers. The final product moisture is less than 0.1%, since damp product will cake during storage and shipping. Potash dryers are fired with natural gas.

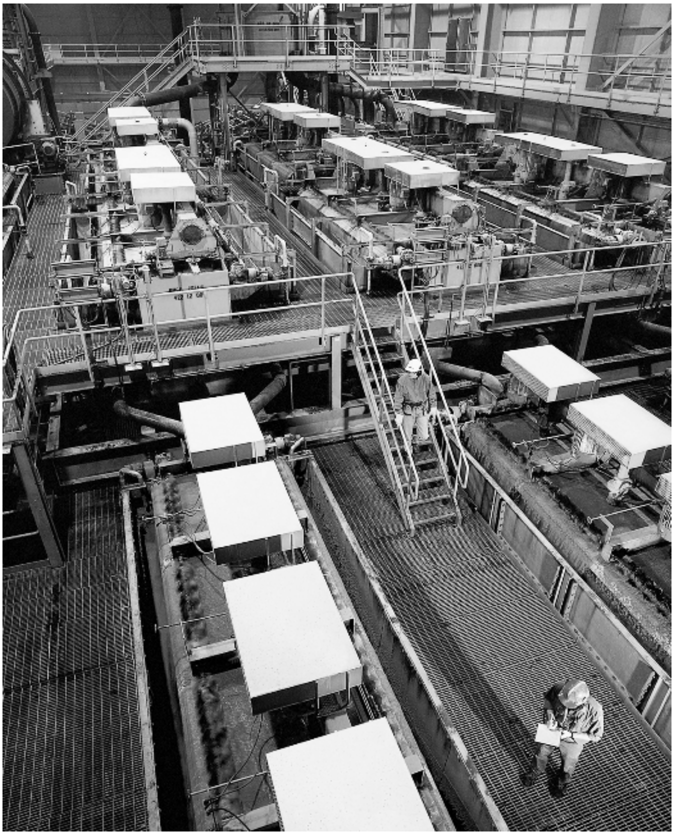

FIGURE 1-15 Banks of flotation cells used for the production of potash concentrate.

Dryer exhaust gases contain a significant amount of fine particulate, and therefore these off-gases must be cleaned before release to the environment. Many different types of gas cleaning equipment are in use in the potash industry, including wet scrubbers, baghouses, and electrostatic precipitators (Fig. 1-17).

Product Screening and Compaction

The dried product will be on grade (>95% KCl) but with a wide range in particle sizes, varying from 3 mm to dust of less than 30 microns. Such a wide range of sizes is not acceptable to customers. Farmers usually purchase fertilizers that are a blend of all three plant nutrients (N, P, K), and it is important that the sizing of each of the three nutri-

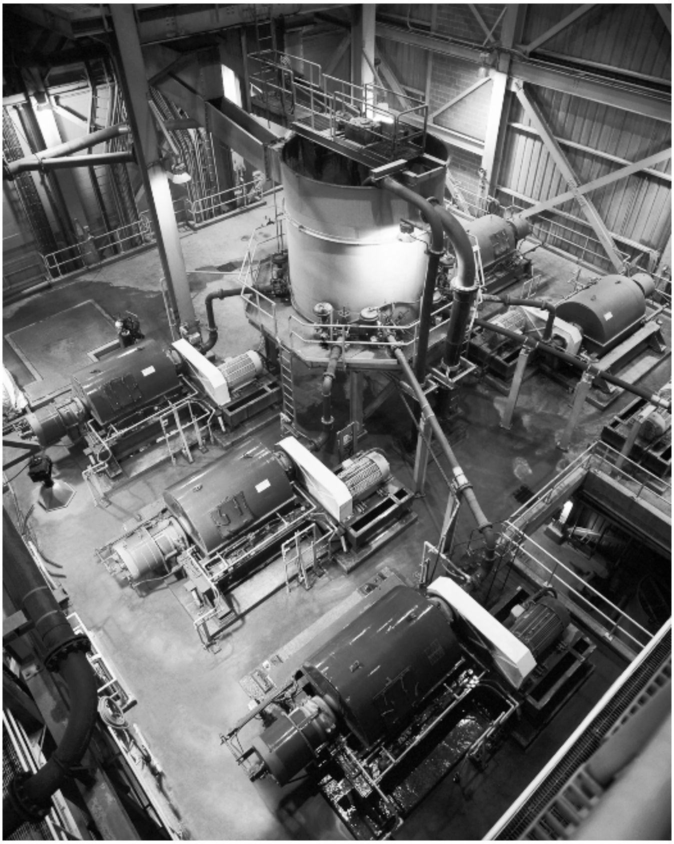

FIGURE 1-16 A set of screen-bowl centrifuges used for debrining potash product. The tank in the central part of the picture is a feed distributor, which accepts the concentrate from flotation and directs a portion of the slurry to each of the centrifuges.

ents is the same; otherwise, segregation of the fertilizer components will occur during storage and transportation, resulting in inhomogeneous distribution of nutrients on the crops.

Potash product is therefore screened into carefully controlled size fractions and sold accordingly. The most common sizes of potash fertilizer are Granular (~1.7–4.0 mm) and Standard (~0.2–1.7 mm). Product screens achieve a separation by allowing the dryer product to flow by gravity over an inclined screen deck. Undersize material is collected from beneath the screen, while oversize material flows off the end of the screen. Modern plants rely on multideck, high-efficiency screens which have high throughput and good screening efficiency (i.e., minimal contamination with off-size material).

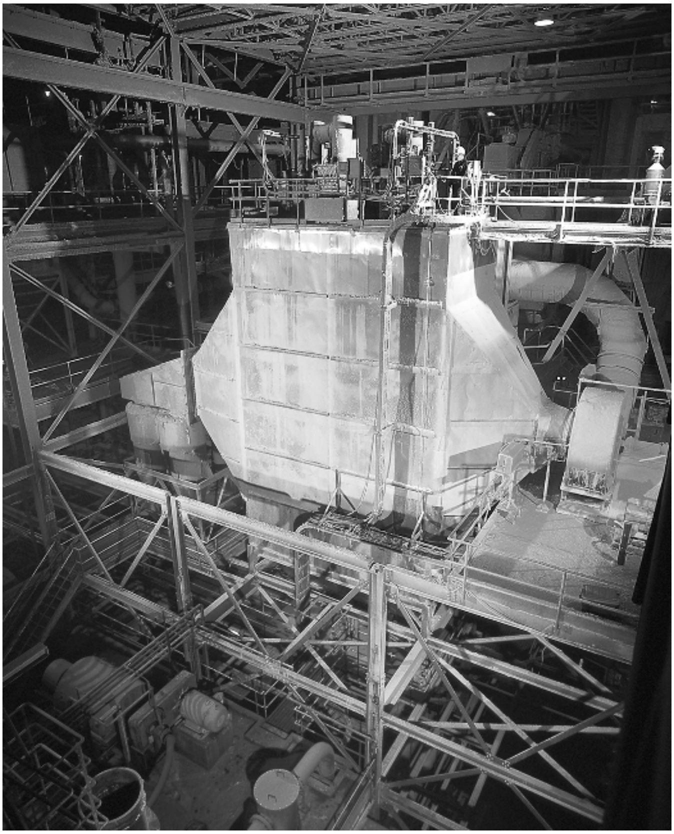

FIGURE 1-17 An electrostatic precipitator, which is used to remove fine particulate matter from the exhaust gases from a potash dryer.

After standard and granular products have been collected from the dyer discharge, the plant operator is left with a large portion of undersize potash dust, which is rich in KCl but too small to be sold as product. Producers have two options for dealing with this dust—compaction or crystallization. The compaction process is described in the following paragraphs, while a discussion on crystallization is presented in the next section.

Compaction is a process by which producers convert potash dust into additional granular product by using mechanical roll presses. Dust is fed into the compactor, either by gravity or by a system of mechanical screws known as a "force feeder." Inside the compactor, the dust is compressed under a high pressure of ~12 tons per inch of roll width. Roll sizes in the potash industry vary from 24 to 39 inches, with larger machines becoming the norm. The compactors discharge a sintered "board" that has a high (99.5% of theoretical) density.

The board produced by compactors is very brittle and can easily be crushed in a roll crusher. The crushed board is then screened, and additional granular product is recovered. Oversize from the screens is crushed and rescreened, etc., until all the board is converted to granular product.

Crystallization

There are two principal applications for the crystallization technique in potash processing. In a conventional flotation mill, crystallization is one option for processing the KCl-rich fines collected from the screening plant, as described above. These excess KCl fines can be dissolved in a hot brine to produce a KCl-rich (pregnant) solution, which is then recrystallized to produce a purified (value-added) product. In several plants, however, crystallization is the primary process for production of potash. In the two solution mines, a warm, undersaturated brine is injected into the potash ore zone and pumped back to the surface (some distance away) as a near-saturated brine. The KCl-rich brine is then cooled in a pond or in a series of crystallizers (or both) to produce potash.

The crystallization process utilizes the difference in solubility between KCl and NaCl. In a cosaturated brine (i.e., saturated with respect to both KCl and NaCl) the solubility of KCl in water increases, and the solubility of NaCl decreases, with increasing temperature (Fig. 1-9). Therefore, if a hot (e.g., 100 °C) brine is saturated with both KCl and NaCl and then subsequently allowed to cool (e.g., to 40 °C), it will precipitate KCl from the solution. In practice, the brine is often not cosaturated with both KCl and NaCl; rather, the sodium content of the brine is controlled to somewhat lower levels, and thus the purity of the resulting KCl product can be regulated.

The cooling of hot brines to precipitate KCl is performed in a series of vessels known as crystallizers. A typical crystallizer is shown in Figure 1-18. Crystallizers are sealed vessels in which a vacuum is maintained, causing the surface of the liquor to undergo vigorous boiling. The hot brine is continuously circulated either by an agitator and draft tube (Fig. 1-18) or by an external pump. As a result of the boiling and the constant circulation, the brine undergoes uniform cooling. The KCl crystals that precipitate as a result of the cooling settle to the bottom of the vessel. At the bottom, some crystallizers have an elutriating leg. Brine is circulated into the bottom of the

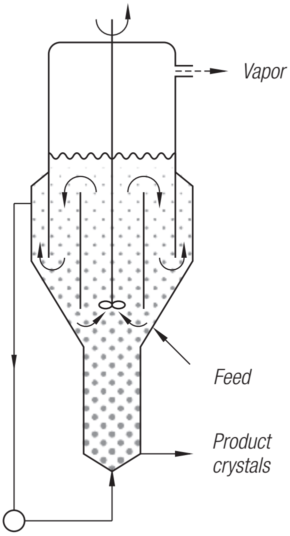

FIGURE 1-18 A draft-tube baffle (DTB) crystallizer used in the potash industry. Variations on this design include the use of a bottom-entry agitator drive and the lack of an elutriating leg.

elutriating leg so that the product crystals are kept fluidized. In such a state, the crystals grow larger and they can also be pumped out of the crystallizer. Other crystallizers simply pump the product slurry from the bottom of the vessel.

The steam that is produced at the top of the crystallizer must be collapsed, or the vigorous boiling (necessary for good cooling) would cease. The steam vapors are generally collapsed in a barometric condenser in which the steam vapors flow countercurrent to a spray of a cooler fluid. Crystallizer circuits are generally arranged in series with the first crystallizer containing the hottest brine; each subsequent stage then cools the brine to a lower temperature. The coolest brine (from the final stage) is then used as the cooling fluid for the second-last crystallizer's condenser (Fig. 1-19). After flowing through this condenser, the cooling fluid is pumped to the third-last condenser, and so on, until the (reheated) cooling fluid exits from the first-stage condenser. Thus, the cooling fluid and the pregnant liquor flow countercurrent to each other through the series of crystallizers. Such an arrangement is useful because it optimizes heat recovery of the crystallizer circuit, since the reheated cooling fluid can then be heated further, resaturated with potash, and recirculated back to the first stage of crystallizers as pregnant liquor.

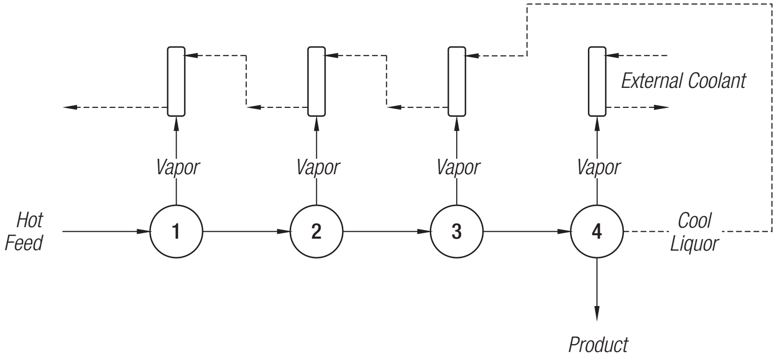

FIGURE 1-19 Typical flows in a four-stage crystallization circuit. Note that the flow of the cooling liquor (------) through the barometric condensers is countercurrent to the flow of the feed (———).

STORAGE, TRANSPORTATION, AND DISTRIBUTION OF POTASH

Production rates from modern potash plants are several hundreds of tons per hour. The demand for potash product varies according to the season and demand from various parts of the world. As a consequence, producers need to install substantial storage and shipping capability.

Storage of finished potash product is generally done in covered buildings up to 200 feet wide and 1600 feet long. Potash, being a salt, will absorb moisture and cake into lumps, much like salt cakes in a salt shaker on a humid day. As a result, it is important that the finished product be protected from rain and snow.

The finished product is transported to storage by conveyor belt, and each product is dispatched into its own storage area by an overhead tripper. On-site storage capacity varies, but is typically in the range of 200,000 tons.

When orders are received, product is reclaimed from storage, usually with a loader or a dozer (Fig. 1-20) that transports the material to a conveyor belt. The conveyor moves the product to the loading facility, where it is screened to remove any remaining dust. The finished product is then conditioned by addition of small quantities of reagents designed to suppress dust and to eliminate caking. Finally, the potash is loaded into trucks or railcars for delivery to customers.

Transportation of 20+ million tons of potash product to customers around the world is a difficult task. A small fraction of the product is

FIGURE 1-20 A storage facility containing potash product. In the foreground is a loader, which is used for moving the product to a reclaim conveyor, which transports the product to the loading facility.

shipped by truck, usually to customers relatively close to the producing plant. The majority of the product, however, is shipped by rail.

Distribution of product within North America is generally achieved by shipping 124-car “unit trains” that carry potash only. The unit trains deliver the product to holding tracks in the Midwest. The unit trains are then separated according to the types of product and customer demand, and the railcars are fanned out to in-market warehouses or potash distribution centers. Individual railcars then fan out to dealers. In-market warehouses vary in size from 1,000 to 60,000 tons and reduce the dealers’ need for warehouse space.

Shipment overseas is typically accomplished by delivering unit trains of product to ports. Several different ports are used, with the largest being Vancouver, Canada. Product is received at the port, where it can

FIGURE 1-21 Marine terminal for loading potash product, located at St. John, New Brunswick, Canada.

then be placed into storage. The terminal at Vancouver has storage capacity for 300,000 tons of potash. Storage of such large volumes of potash is a challenge, with many different types of product received from various mines. In some cases, the product is not directed to storage, but rather is directly loaded into waiting vessels (Figs. 1-21 and 1-22). The loading rate for oceangoing vessels is 3000 tons per hour. Once loaded into oceangoing vessels, the finished product is ready for delivery to countries around the world.

POTASH PRODUCTS

Most granular and standard potash is produced for sale as a fertilizer, which must meet a minimum of 95% purity of KCl. Remaining impurities in the final product include low levels of sodium chloride and insoluble minerals such as dolomite, anhydrite, and quartz. The fertilizer-grade material is screened so that it meets exacting standards of particle size, so that it will be easy for the farmer to handle, and so that it can

FIGURE 1-22 An oceangoing vessel being loaded with potash for delivery to offshore customers.

be blended with other nutrients such as nitrogen and phosphorus. Standard product is shipped predominantly to India and China, while granular material is the preferred product in most other countries. Potash fertilizer is then sold as a crop nutrient throughout the world (Fig. 1-23).

Crystallized products, either from a solution mine or from crystallization of the KCl dust generated from a flotation plant, are typically sold for use as an industrial chemical. This purified KCl is used in the manufacture of KOH for glassmaking, potassium carbonate, and many

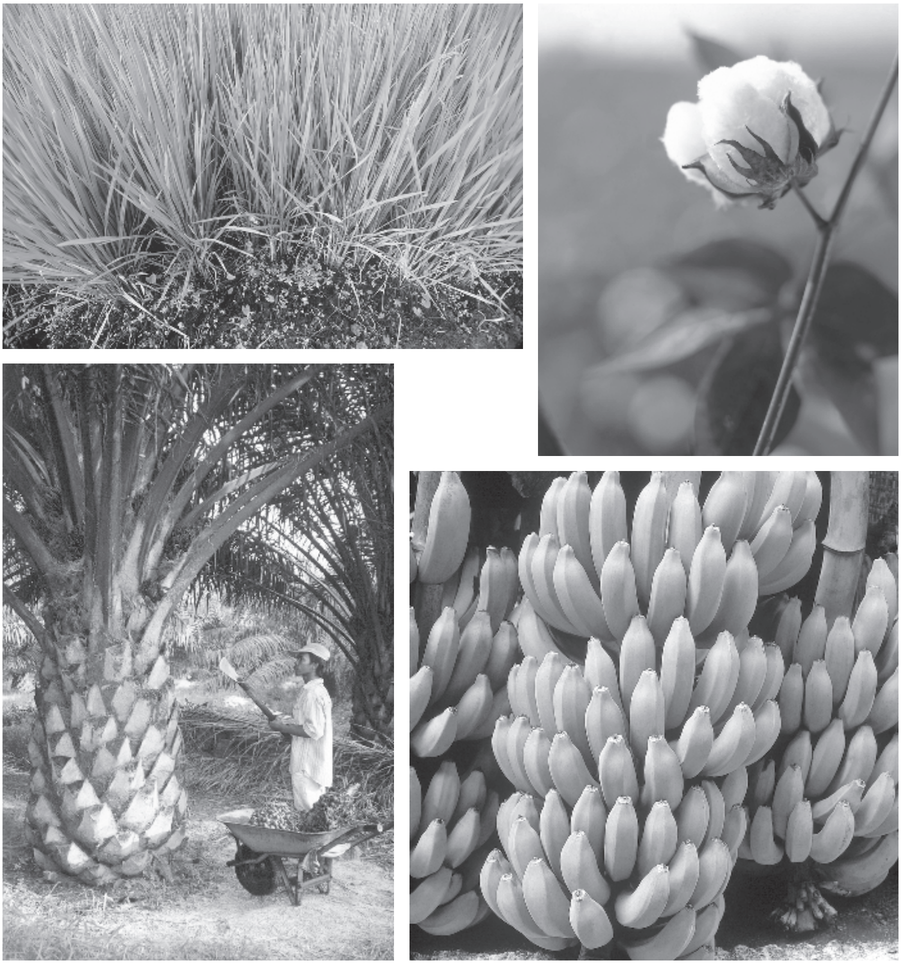

FIGURE 1-23 A selection of crops fertilized with potash. Clockwise from the upper left: rice, cotton, bananas, and oil palm.

other chemicals. Some of the industrial-grade KCl is processed through a roll press (“compactor”) using equipment similar to that described in the section “Product Screening and Compaction.” The compactor fuses the industrial-grade product into large (1 inch) pieces, which can be easily handled and stored without the addition of any conditioning chemicals; such large pieces of purified potash are sold for use in water softening applications. One of the largest North American producers of KCl for water softening is the PotashCorp Cory plant, shown in Figure 1-24.

FIGURE 1-24 PotashCorp Cory Division, which produces fertilizer-grade potash, along with KCl sold for use as a water softening regenerant under the trade name Softouch.

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