# POTASSIUM COMPOUNDS

## 1. Introduction

Potassium as a mineral is essential for life. As a consequence, potassium compounds or potash have been regarded as articles of commerce since the days of antiquity. Historically, the term potash denoted an impure form of potassium carbonate mixed with other potassium salts obtained by leaching wood ashes. As of the late twentieth century, within the English-speaking world, potash refers to the whole group of water-soluble potassium salts that are easily accessed by growing crops (1). The majority of the world's potash-bearing salt deposits likely originated from the evaporation of seawater or of mixtures of brines and seawater (see Chemicals from brine) (2). Potassium carbonate, obtained as crystals from the evaporation of potash solutions in large iron pots, served as the main building block for the production of other potassium compounds. In Pompeii, potassium carbonate was converted to potassium hydroxide by reaction of lime and was subsequently used to make soap (qv).

Potash manufacture was the first chemical industry in North America (3) and, until the latter part of the nineteenth century, potash was essential to the manufacture of soap, glass (qv), dyed fabrics, and gunpowder. Approximately 85% of Canadian and U.S. potash production shipped to U.S. destinations is used in agriculture. Fertilizer potash is potassium chloride, potassium sulfate–magnesium sulfate, and potassium permanganate (see Fertilizers). The remaining 15% of the potash goes to the manufacture of glass, medicines, food, and soaps, as well as the polymerization of synthetic rubbers and plastics, and to export, mainly as potassium sulfate.

The very first patent issued by the U.S. government was for improving the "making of Pot ash and Pearl ash [a purer form of potassium carbonate] by a new Apparatus and Process." The said patent went to Samuel Hopkins on July 31, 1790, and was signed by both President George Washington and Attorney General William Randolph (3). Over 90,000 standard short tons of potash, selling for $200–300 a short ton, were exported from the United States during the 14-year life of that patent, at a time when coal sold for $8 a short ton. However, the production of less than 1 ton of potash required the consumption of approximately 400–500 standard tons of wood, and world demand was outstripping the supply of readily accessible forests. Close to the time when the Hopkins patent was issued, the invention of the sodium sulfate reduction process led to the general substitution of sodium carbonate for potassium carbonate as an alkali source.

Potassium nitrate, essential in the manufacture of black gun powder, was produced by the Chinese, who had developed gun powder by the tenth century AD. The process involved the leaching of soil in which nitrogen from urine had combined with mineral potassium. By the early 1800s, potassium nitrate had become a strategic military chemical and was still produced, primarily in India, by using the ancient Chinese method. The caliche deposits in Chile are the only natural source of potassium nitrate (2). These deposits are not a rich source of potassium nitrate, purifying only to about 14% as $K_2O$.

In 1840, potassium was recognized as an essential element for plant growth (6). This discovery and the invention in 1861 of a process to recover potassium

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chloride from rubbish salt, a waste in German salt mines, started the modern potassium chemical industry (5).

Between 1869 and the beginning of World War I, most of the world's supply of potassium salts came from the Stassfurt deposits in Germany. During World War I, U.S. production, measured as $K_2O$, rose from 1000 metric tons in 1914 to 41,500 t in 1919. Following the end of World War I, U.S. production declined as imports increased. By the time the United States entered World War II, however, production had expanded enough to meet domestic needs. Since then, production has fluctuated. Total annual U.S. demand peaked at $6.9 \times 10^6$ t in 1979 and had leveled off at approximately 5.1 to 5.5 million t. Demand in 2002 was $6.3 \times 10^6$ t and the projected demand for 2006 is $6.4 \times 10^6$ t (5). Canada is the principal potash exporter.

## 2. Occurrence

Potassium, one of the mineral nutrients (qv), is the seventh most abundant element, constituting about 2.4% by weight of the earth's crust. Commercial production of potassium compounds is generally limited to the extraction of ores from underground deposits containing significant concentrations of soluble potassium salts. Exceptions include commercial potassium chemical operations on the Dead Sea and the Great Salt Lake, where potassium sulfate production capacity has been increasing (see Chemicals from brine). These natural brine refining operations exploit the highly favorable climatic conditions at those locations for the utilization of solar energy (qv). Estimated world reserves and the production of potash are presented in Table 1.

Canada leads the world in both reserves and production, operating at about 57% of estimated production capacity (4). New Mexico is the primary source of potash in the United States, accounting for ca 80% of total marketable salts produced in 2003 (5). North American agricultural potash is delivered to every State in the Union. Illinois is the destination for more potash than any other state. More North American produced nonagricultural potash is shipped to Alabama than to any other state. Alabama receives approximately 2.5 times the amount received by Ohio, the second-place destination (7).

Four minerals are the principal commercial sources of potash (Table 2). In all ores, sodium chloride is the principal soluble contaminant. Extraneous water-insoluble material, eg, clay and silica, is a significant contaminant in some of the evaporates being mined from underground deposits. Some European potassium ores contain relatively large amounts of the mineral kieserite, $MgSO_4 \cdot H_2O$. It is recovered for captive use to produce potassium sulfate compounds or is marketed in relatively pure form as a water-soluble magnesium fertilizer.

There are two basic classes of potash-containing evaporites (2), those deposits that are rich in magnesium sulfate, such as polyhalite and kieserite, and those that are poor in magnesium sulfate. The primary source of potash in the magnesium-rich deposits is carnallite, whereas both carnallite and sylvite are found in the magnesium-poor deposits.

Approximately 98% of the potassium recovered in primary ore and natural brine refining operations is recovered as potassium chloride. The remaining 2%

consists of potassium recovered from a variety of sources. Potassium produced from these sources occurs as potassium sulfate combined with magnesium sulfate. From a practical point of view, the basic raw material for all of the potassium compounds discussed in this article, except potassium tartrate, is potassium chloride.

## 3. Properties

Physical properties of selected potassium compounds are listed in Table 3, solubilities in Table 4.

## 4. Potassium Chloride

Potassium chloride [7447-40-7], or muriate of potash (MOP) as it is known in the fertilizer industry (at about 97% purity), is the world's most commonly used potash. Chemical-grade potassium chloride (99.9%) is the basis for manufactured production of most potassium salts (10). It is used in aluminum recycling, in the production of potassium hydroxide, in metal electroplating, oil-well drilling mud, snow and ice melting, steel heat-treating and water softening (7).

**4.1. Mining.** Potassium chloride is produced mostly from solid ores occurring in underground deposits 300–1700-m deep. All New Mexico potash producers mine underground bedded ore zones and all except one mine sylvinite ore, a mixture of sylvite and halite, from which most muriate of potash originates (1). Conventional mining methods adapted from coal (qv) and hard-rock mining operations and machine mining are employed to mine ores to a depth of ca 1100 m. Solution mining is employed to recover potassium chloride from deposits exceeding ca 1100 m or from deposits that cannot be mined conventionally because of geological anomalies (see Mineral recovery and processing).

Although it is a relatively small source in terms of total world production of potassium chloride, significant tonnages of potassium chloride, ca 3% of world production, are produced by solar evaporation of natural brines. These sources are mined by pumping the brines to evaporating ponds for enrichment under controlled conditions. Natural ores being mined for potassium chloride are either a simple mixture of potassium chloride and sodium chloride (sylvinite [12174-64-0]) or complex salt mixtures that contain langbeinite [67320-08-5] and kainite [1318-72-5]. All ores contain sodium chloride as a principle contaminant. Extensive studies of the geology of potash deposits have been made in countries where extensive deposits are known to occur (2,11,12).

Descriptions of contemporary methods employed in potash salt mining are available (2,10,13). Because the evaporate beds are generally regular, tabular bodies, underground potash mining is a relatively clean and straightforward operation having few complications. One rare hazard is the existence of occasional pockets of gas under pressure that can cause explosions when the pressure is released. Water inflow problems have become a primary concern at some Canadian mine sites, prohibiting continued conventional mining. For the most

part, mining methods have been adapted from coal and salt mining and the equipment used is similar.

The room-and-pillar configuration has been used predominantly in underground mines in the United States and Canada and widely in the CIS and Europe. This results in a checkered pattern of mining areas separated by pillars. Timbering is not often used, but roof-bolting is commonly practiced by most operators. A funnel system, similar to sublevel stopping with waste fill, is used in many mines in Germany along with mechanical drilling and blasting, and particularly on the steeply dipping ore bodies of the Hannover district. In New Mexico, after the intended limit of the mining area is reached, the pillars are mined and the overlying strata are allowed to subside as mining retreats toward the shaft. Shaft depths are 233 to 575 m. Slight subsidence is noted on the surface. A total recovery of well over 80% is obtained. In other areas, notably Saskatchewan, the overlying strata are water-bearing and removal of pillars floods the mine. Recovery of ore therefore is only ca 35%. The lesser problem of water-bearing strata in New Mexico is controlled by grouting and concrete lining of the shafts.

A portion of the mining in New Mexico is conducted by conventional mining methods, that is, a cycle of undercutting, drilling, and blasting with an ammonium nitrate–fuel oil mixture and loaders, use of shuttle cars, and belt haulage. Such conventional methods are used, although not exclusively, in the CIS, Germany, France, Spain, and the United Kingdom.

Sylvinite ore is relatively soft and easily broken. Thus, continuous miners of the boring- or rotating drum-type can be used. These machines are modified continuous coal miners. This method is used in some of the mines in New Mexico, in all Canadian mines except the solution mines, and in many European mines. Ore is removed from the face by a number of methods, eg, with extensible belt conveyor ore-loading machines and shuttle cars to the main haulage line. To obtain maximum benefits from the continuous miners, the ore transport system must be as nearly continuous as possible.

Potash is removed by long-wall mining in the CIS and European countries such as France and Spain. One U.S. company has considered usage in its Canadian and domestic operations. In long-wall operation, material is removed in slices up to 76 cm thick and up to 183 m or more long. Upon completion of a cut, the shear-cutting system, the conveyor system, and the powered roof-support system are advanced a distance equivalent to one-cut thickness, thereby allowing a portion of the roof behind the system to fall. The rock structure must fit certain strength and fracture requirements to allow the use of the long-wall system. The main advantages of the system over room-and-pillar methods are essentially complete removal of the ore and the potential for more rapid removal of the ore.

The long-wall method is used to remove about half of the ore from the mines owned by the Byeloruskali combine. In one mine, two 1-m thick sylviniti beds, separated by a lone meter-thick sylvinite bed, and the upper face are mined ca 5.5 m in advance of the lower. This increased recovery from 45 to 70% and increased the $K_2O$ content of the ore from 26 to 36 wt % (21.6–29.9 wt % K). Approximately one-half of French ore production is by long-wall mining and occurs mainly in the Marie Louise mine. Long-wall mining is also used in the Potasas de Navarra mine in Spain.

Solution mining is used in North America to extract sylvinite from strata underlying the earth's surface at relatively great depths. Three producers in Utah evaporate saline brines, and the muriate and sulfate are produced at Searles Lake in California via solar evaporation and selective crystallization from underground brines. In the early 1970s, one firm in Utah abandoned conventional mining because of unfavorable geologic conditions (14). The mine was sealed, flooded with water, and the resulting saturated brine pumped to the surface where the sylvinite was recrystallized by solar evaporation. An injection well was used to add makeup water. Moab Salt, Inc. uses two-well solution mining and solar evaporation to recover muriate of potash in Utah. In Saskatchewan, Canada, which has the world's largest high grade sylvinite ore reserves, sylvinite is extracted by solution mining from an ore zone too deep to be mined conventionally (15). Brine recovered from the wells is processed in multiple-effect evaporators to recover the potassium chloride values dissolved in the brine.

**4.2. Refining.** Process selection for the separation of potassium chloride as a relatively pure product from other constituents is based on the physical and chemical characteristic of a given ore and the unique mineralogy of each potash mining area. Ores amenable to treatment by the physical separation methods commonly used in other nonmetallic minerals processing industries generally are chosen to recover the potassium chloride. These methods include heavy-media and froth-flotation separations. Physical separation processes are less energy-intensive than fractional crystallization (qv), which is the traditional method of producing potassium chloride. Mainly because of the cost of energy, conventional fractional crystallization is generally confined to ores that are not amenable to processing by physical separation methods. However, pond crystallization methods are receiving increased consideration owing to favorable energy costs. Fractional crystallization is included as a secondary operation in some physical separation plants for recovery of potassium chloride crystals that are trapped in the waste streams exciting the primary ore beneficiation plant.

Relatively pure potassium chloride is a product containing not less than 60 wt % $K_2O$ (49.8 wt % K or 95 wt % KCl equivalent). Contaminants making up the remaining 5 wt % are not objectionable. Some, such as magnesium sulfate salts, may enhance the agricultural value of the agricultural-grade muriate (chloride) products. In Europe, where the principal agricultural areas are near the mines and thus significantly reduce the importance of transportation as a cost element, potassium chloride products contain 40 wt % $K_2O$ (33.2 wt % K). Except for the presence of minor by-products, all production in North America must meet the 60 wt % $K_2O$ (49.8 wt % K) specification.

*Froth Flotation.* Froth flotation (qv) of potassium chloride from sylvinite ores accounts for ca 80% of the potassium chloride produced in North America and about 50% of the potassium chloride in Europe and the CIS. Fractional crystallization and heavy-media processing account for the remaining amounts produced. Froth flotation has been described (6,16,17).

Unlike some ores mined in Europe, sylvinite mined in North America consists of coarse crystals of potassium chloride and sodium chloride. When the mine-run ore is crushed to a grain size suitable for application of the froth flotation to separate the salts, the crystals of each must be reduced to individual grains (see Size reduction). This grain size is called the liberation grain size of

the ore. Sylvinite ores in New Mexico are liberated when crushed through a ca 2.4-mm (8-mesh) screen. Maximum grain size for efficient froth flotation is about this size. Consequently, liberation grain size and froth flotation are compatible for processing New Mexican ores. In contrast, sylvinite ores mined in Saskatchewan are composed of much coarser grains. These ores are liberated in a ca 9-mm screen. In conventional mining of sylvinite ore, the ore is crushed through a ca 2.3-mm screen before it is sent to the flotation plant. However, some Canadian mine operators produce a coarse crystalline product, called granular muriate of potash, by crushing the ore through a 9-mm screen followed by screening the crushed ore at 1.7 mm. Screen undersize ($<1.7$ mm (12 mesh)) is sent to froth flotation. Screen oversize, ie, the $9 \times 1.7-$cm fraction, is processed by heavy-medium separation to produce granular 60 wt % $K_2O$ muriate for the agricultural market. Basic unit operations of the flotation process are shown in Figure 1.

*Crushing.*   The ore is crushed through a ca 12.7-cm screen in the mine to facilitate conveying and hoisting. It is further reduced to an appropriate size for milling by multiple-stage dry crushing or by initial dry crushing in a rod mill. Gentle crushing is required because sylvinite ores are friable. Severe crushing causes excessive formation of fine particles. Because of mechanical entrainment, sodium chloride grains less than ca 0.2 mm in diameter tend to entrain with the KCl product recovered in the flotation cells. Contamination of the KCl in this manner interferes with product quality and potassium chloride recovery.

*Scrubbing and Desliming.*   Sylvinite ores in North America contain $1-6$ wt % water-insoluble clays. A significant portion of these clays is less than 0.002 mm in diameter. If not removed or controlled in some manner, clay bodies that are dispersed in the flotation solution, ie, brine saturated with KCl and NaCl, absorb the amine collector, which is added to effect flotation separation, and the collector is rendered ineffective. Clay is the most troublesome impurity encountered in the processing of sylvinite ore.

In North America flotation plants, $90-95$ wt % of the clay and other water-insoluble material, eg, silica particles, are removed by hydraulic desliming. This operation entails scrubbing the ore mixed with process brine in agitated tanks at a solids-to-brine weight ratio of ca 1:1. Residence time is ca 3 min. The scrubbers are frequently operated in series to ensure complete dispersion of the clay. Amorphous clay agglomerates and clay adhering to the crystal surfaces disperse into the brine as finely divided particles. Pulp from the scrubbers, which consists of ore grains, disseminated clay particles, and process brine, is separated by wet screening or mechanical classification into a coarse fraction ($>0.8$ mm (ca 20 mesh)) and a fine fraction ($<0.8$ mm). Each fraction is separately deslimed. The coarse fraction is mixed with clear brine to wash out entrained clay particles and is rescreened or reclassified to separate the wash ore from the muddy brine. The muddy brine stream is returned to the hydroseparators, which separate the clay particles from the fine fraction. Sylvanite ores containing more than ca 2 wt % clay require multiple-stage scrubbing for essentially complete removal of clay from the coarse fraction of the ore. Deslimed coarse ore advances to the coarse reagent conditioners. After desliming in a complex hydrocyclone–hydroseparator circuit for thorough cleansing, the fine fraction flows to the fine-ore reagent conditioners.

Clay exits the desliming circuit along with ore particles that are less than ca 0.07 mm (200 mesh) in diameter. Brine saturated with KCl and NaCl is the carrying medium. The solids content of the suspension is 3–5 wt %. Because of the KCl content (typically 10 wt %), and for water-conservation reasons, most of the process brine is recovered in conventional thickeners for recycling to the process as clarified brine. Underflow from the primary slime thickeners contains substantial quantities of process brine. A typical ratio is one part of solids per four parts of brine. Several methods are used for secondary recovery of brine. These include prolonged settling in sealed lagoons, multiple-stage countercurrent decantation, and filtration with sodium chloride residues as a filter aid (18).

*Reagent Conditioning.* This unit operation is carried out in two stages. Optimum pulp density in both stages is 50–60 wt %. The first stage involves agitating the deslimed ore with a clay depressant or slime blinder to deactivate clay particles that are entrained in the washed ore flowing from the hydraulic desliming operations. Suitable depressants include starches, guar gum, carboxymethyl cellulose, and polyacrylamides. Depending on the amount of entrained clay and the type of depressant used, dosage rates are 50–500 g of depressant per metric ton of ore processed. Cost-effectiveness is usually the sole criterion in selecting a depressant. After 1 or 2 min of conditioning, the pulp enters the second-stage conditioner.

Reagents, including a collector, required for the flotation separation are added in the second stage. Specially developed flotation oils called extenders are added if the ore contains relatively large percentages of coarse KCl crystals, ie, >15 wt % of 0.8–1.7-mm crystals. An extender makes the amine-coated surfaces more hydrophobic, thereby enabling the particles to float readily in the flotation cells. Retention time in second-stage conditioning is 1–2 min.

Potassium chloride collectors are primary amines derived from beef tallow. Commercially available amine is a homogeneous mixture of palmityl-, stearyl-, and oleylamines. Several years after the discovery that normal tallow amine has a specific affinity for KCl crystals only, it was realized that hydrogenation of normal amine greatly increases overall effectiveness of the collector. Hydrogenation converts the oleylamine to stearylamine, thereby bringing all alkyl groups to near saturation. Free-base amines are converted to salts with acetic or hydrochloric acid, the latter preferred by most operators. Consistent amine quality is mandatory. Some companies specify amine containing not less than 97 wt % amine. Others find that the normal commercial-grade, ie, not less than 96 wt % primary amine, is satisfactory. For homogeneous distribution of the salt with the crushed ore, the amine salt is prepared as an aqueous 4–5 wt % solution.

Longer-chain amines, ie, arachidyl–behenyl ($C_{20}$ to $C_{22}$) amines, are used in special cases in which brine temperatures exceed 35°C. At temperatures higher than ambient, normal tallow amine tends to dissolve and therefore is unavailable to coat the surfaces of the potassium chloride crystals. Amine consumption is from 50 g/t (ca 40 wt % KCl) of high grade ore, to 150 g/t (ca 20 wt % KCl) of low grade ore.

Pulp exiting the conditioners is diluted by using process brine to a solids content of 30–35 wt % for use as feed for the flotation cells. In some plants, the coarse- and fine-fraction flows are floated separately. In most plants, the

two fractions are recombined and the flotation is conducted in a common operation.

*Flotation.*   Tallow amines contain small amounts of short-chain compounds, eg, the octyl, lauryl, and myristyl ($C_{14}$) groups. These amines usually produce enough froth for the flotation. Small quantities of specialized synthetic alcohols, eg, Dowfroth P, are frequently added to the flotation system to supplement the natural frothers. The quantities of the reagents used in potash flotation plants are listed in Table 5.

Separation of amine-coated potassium chloride grains from sodium chloride grains requires about three minutes of retention time in the first bank of flotation cells and is referred to as the rougher operation. Froth impregnated with KCl grains and a small amount of entrained fine NaCl grains is screened at ca 0.8 mm (20 mesh). Oversized material meets agricultural-grade potassium specifications. Consequently, it is passed directly to the product debrining and drying operations. Undersize material, which is contaminated with sodium chloride, is sent to a second bank of flotation cells, called cleaner cells, for final separation of potassium chloride from sodium chloride grains. Froth from the cleaner cells flows to the product debrining and drying operations. Process brine saturated with sodium chloride and potassium chloride contains ca two parts of sodium chloride per one part of potassium chloride. Thus, product crystals from the debrining operation must contain less than ca 10 wt % process brine to meet the minimum standard $K_2O$ content of 60 wt %.

Underflow from the rougher cells consists of sodium chloride suspended in process brine and other salts in the ore. This waste stream or tailing is passed to debrining devices for separation of the solid material from the process brine. The separation must be efficient because it is essential that the brine is recovered for recycling to minimize potassium losses. Tailing salt from the debrining operation is rejected from the process. Underflow from the cleaner cells contains considerable quantities of potassium chloride grains that fail to float, and is recycled to the rougher cells.

*Product Debrining and Drying.*   Solid-bowl and pusher centrifuges are used to separate the product crystals from the process brine. The latter is recycled to the flotation circuit as dilution brine. Damp centrifuge cake is sent to the product dryers. Dryer temperature and the final moisture levels in the product vary. Potassium chloride having higher moisture content tends to cake during storage, especially when shipped to locations that are subject to high humidity. Amine remaining on the product is beneficial in that it acts as an anticaking reagent, thereby preventing pile set. Anticaking, which is added to the final product, is usually a mixture of oil (0.1–0.3 kg/t) and amine (0–6%) used for agricultural products. A straight-chain amine (0.1–0.3 kg/t) is used for high grade industrial products. Some industrial customers for the potassium chloride, eg, the chlor-alkali industries (see Alkali and chlorine products), require that no amine be present. In this case, granulation using compactors or loading into sparger cars is carried out.

*Sizing.*   In most flotation plants, flotation concentrates, after being dried, are sized into three fractions and each serves a specific agricultural market. The fractions are coarse-, standard-, and suspension-grades of muriate of potash.

Typical screen analyses are presented in Table 6; other physical characteristics are summarized in Table 7.

*Products.* Significant quantities of undersized potassium chloride particles, which make up 10–15% of total production, are generated in the flotation processes. These particles are collected by air-emission control devices (see Air pollution control methods) and are processed into completely water-soluble grades of muriate by single or double recrystallization. Potassium chloride produced by a single recrystallization is marketed in the fertilizer industry as a source of completely water-soluble potassium chloride. It is used to prepare specialty water-soluble fertilizer solutions containing nitrogen, phosphorus, and potassium plus other elements required for a specific agricultural use. If impurity concentrations of the process streams are controlled during single recrystallization, a grade of potassium chloride is produced of sufficient quality to be used as feedstock for the production of potassium chemicals. Refined potassium chloride, which is prepared by recrystallizing a portion of the first recrystallized potassium chloride crystal crop, is sold for applications requiring exceptionally pure potassium chloride.

An increasingly important segment of the complete fertilizer-formulation industry is called bulk blending and requires particles of potassium chloride that are compatible in size with other plant nutrients used to formulate the fertilizers. Size guide number (SGN) and uniformity index (UI) are two measurements employed when dealing with blending applications. These blended fertilizers usually contain the three primary elements essential for plant growth, ie, nitrogen, phosphorus, and potassium. Secondary elements, ie, magnesium, sulfur, zinc, iron, etc, that are deficient in the soil are also included in the blends. Potassium chloride destined for this important market is called granular muriate of potash. It is produced by compacting normal flotation concentrates.

Screen analyses vary but typical examples for granular and water-soluble agricultural-grade potassium chloride products are given in Table 8. Typical loose bulk densities of granular and agricultural white MOP are 1.056–1.088 g/cm$^3$ and 1.104–1.152 g/cm$^3$, respectively. The angles of repose for these two grades are 32–34$^\circ$ and 24–26$^\circ$, respectively. Chemical specifications are 49.8 wt % potassium for granular MOP and 51.5 wt % potassium for white soluble MOP.

Unlike agricultural potassium chloride products, grain-size distribution is not important for chemical grades of potassium chloride, as long as the products are free flowing and do not generate dust in materials handling operations. Chemical purity is of paramount importance. Typical specifications for chemical grades of KCl are given in Table 9. Typical bulk densities of the industrial and refined grades are 1.216–1.264 g/cm$^3$ and 1.28 g/cm$^3$, respectively. The angle of repose is the same for each, 24–26$^\circ$.

**4.3. Compaction.** A compacting machine consists of a set of two powered, inward-turning rolls (6). One roll has a fixed bearing, the other is floating in a slide and is arranged so that it can be forced toward the fixed roll by hydraulically actuated pistons acting on the bearing blocks. The potassium chloride is fed continuously into the nip of the rolls from above. High pressure can be exerted on the material as it is forced or drawn between the rolls where a momentary phase change to a plastic flow condition takes place. The potassium

chloride crystals are compressed into an almost continuous sheet of product, which is ejected beneath the rolls. The specific gravity of the sheet approaches the specific gravity of pure potassium chloride, $1.99\,\mathrm{g/cm^3}$. The sheet thickness is ca 3.18–12.70 mm, depending on the grain size of the feed and the pressure applied to the rolls. A simplified flow sheet for a compaction plant is shown in Figure 2.

*Feed Grain Size, Quality, and Temperature.*   The optimum particle-size distribution of the new feed to a compaction circuit is the size range within which ca 92% of the particles pass through a 1.2-mm (16-mesh) screen and less than 8% pass through a 0.07-mm (200-mesh) screen. The actual feed includes <1.4−mm (−14−mesh) material, which is recycled as undersize grains from the compacted sheet-crushing and sheet-screening operations. Excessively coarse feed results in a friable and grainy sheet. Excessive quantities of <0.07−mm (−200−mesh) particles decrease the specific gravity of the sheet and cause severe mechanical stresses on the drive gears of the compacting machine because of chattering, ie, vibration and slipping of the rolls under load.

Residual film of organic reagents on the grains inhibits fusing and results in poorly textured sheet. On crushing for granular muriate production, the flake tends to degrade to the original grain size of the compactor feed. Optimum feed temperature is 49–66°C. Higher temperatures can be employed at the expense of increased plant maintenance costs. Low temperatures result in poor quality sheet.

*Heavy-Media Separation.*   Heavy-media separation, depicted in Figure 3, can only be used for relatively rich sylvinite ores that consist of large crystals of KCl and NaCl, such as those mined in Saskatchewan (6,20). Crystals of the two salts in the Saskatchewan deposits are 6−9 mm in diameter. Mine ore that is crushed sufficiently to pass through 6−9-mm screens in this size range results in a mixture consisting of discrete grains of each salt.

The specific gravity of potassium chloride is 1.99; of sodium chloride, 2.17. A separation of the two species can be made by placing a mixture of the salts in a liquid or medium having an intermediate specific gravity of 2.08. The result is that the KCl crystals float to the surface of the medium and the NaCl crystals sink. In laboratory determinations of whether an ore is amenable to processing by gravity separation, brominated hydrocarbons of appropriate specific gravities are employed as the media. However, these liquids are not economical for commercial operation. Consequently, a mixture of pulverized magnetite (sp gr = 5.17) and saturated brine (sp gr = 1.25) is adjusted to an appropriate specific gravity and is used to make the separation. Time is a critical variable because the magnetite settles if the mixture is held too long in a static condition. Use of hydrocyclones makes possible the separation in a fraction of a minute (21). These devices impart centrifugal force to the system, thereby permitting a separation to be made at a specific gravity less than that required in static, heavy-liquid separations.

Heavy-medium separation of potash ores is restricted to processing of the coarse fraction of the crushed ore ($1.7 \times 8$ mm). After heavy-media separation, ashing the two products of the separation free of magnetite requires a relatively simple and inexpensive wet-screening operation. Permanent magnets are used to separate the magnetite recovered in this manner and it is recycled within the process. In contrast to grains of coarse ore and after separation into the two pro-

ducts, fine-ore particles (<1.7 mm) are difficult to wash free of magnetite. This is the main reason fine-ore products are excluded from the process. This processing barrier is reported to have been surmounted in coal (qv) processing (22). Mine-run ore, after being crushed through a 9-mm screen, is screened at 1.7 mm. Particles passing through the screen are sent to flotation. Coarse-ore particles that are retained on the screen are processed by heavy-media separation. A satisfactory separation cannot be made in a single-pass operation because a small quantity of salt is trapped as misplaced particles in the flowing stream of the other salt. In a sylvinite heavy-medium separation plant, an initial separation is made at an effective specific gravity of ca 2.10 to minimize the quantity of misplaced KCl particles in the sodium chloride fraction. A sufficient number of NaCl particles report to the KCl fraction as misplaced particles to cause the KCl fraction to contain less than 60 wt % $K_2O$.

After being washed to remove the magnetite, hydrocyclone underflow containing most of the NaCl is rejected from the process. Overflow containing KCl grains and misplaced NaCl grains is processed in a second stage of hydrocyclones at an effective specific gravity of 2.05. After being washed to remove the magnetite, the cyclone overflow contains KCl at ca 60 wt % $K_2O$. Underflow containing the misplaced NaCl grains and a small amount of misplaced KCl grains is recycled to the process feed.

A variation of the process is operated in New Mexico to separate a potash ore mixture consisting of langbeinite, $K_2SO_4 \cdot 2MgSO_4$; KCl; and NaCl. In this operation, langbeinite (sp gr = 2.38) is recovered as a product in the first stage of hydrocycloning. The chloride salt mixture is separated in the second-stage hydrocyclones into a sodium chloride waste and a potassium chloride–sodium chloride fraction, which is sufficiently concentrated with respect to KCl for recovery of the KCl by froth flotation.

*Fractional Crystallization.* Fractional crystallization is the traditional method for the refining of potassium chloride from underground ore deposits that contain KCl as the principal salt (Fig. 4) 23. It is a much more energy-intensive process compared with froth flotation and its use is often confined to ores that cannot be processed by froth flotation. Ores in this classification may have a fine grain structure, contain excessive amounts of clay, or have the potassium chloride chemically combined with magnesium chloride as the double salt carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$. Fractional crystallization is also used to produce high grade industrial or refined products in which the processing may involve double recrystallization and product leaching, as well as control of circuit brine chemistries to achieve the required product grade.

Fractional crystallization is based on favorable solubility relationships. Potassium chloride is much more soluble at elevated temperatures than at ambient temperatures in solutions that are saturated with sodium and potassium chlorides. Sodium chloride is slightly less soluble at elevated temperatures than at ambient temperatures in solutions that are saturated with KCl and NaCl. Working process temperatures are usually 30–110°C. The system, KCl–NaCl–H2O, within this range is presented in Table 10.

Some of the ores being mined, especially from the German deposits, contain soluble salt contaminants other than NaCl, eg, magnesium chloride, which occurs as carnallite. Process brines are bled from the process and contain quan-

tities of the contaminants equal to the quantities in the ore. The bleed or waste streams are retained in waste-storage lagoons or are pumped into deep, underground porous strata. The latter method was commonly used in the former FRG for reject brine disposal.

The fractional crystallization process is outlined in Figure 4. Essential steps are (*1*) heating the process-saturated solution remaining after separation of the product potassium chloride crystals from 30 to 100°C; (*2*) mixing the hot solution with ore containing sufficient KCl to saturate the solution with potassium chloride (sodium chloride is insoluble); (*3*) separating the sodium chloride from the hot saturated solution and rejecting it from the process; (*4*) cooling the solution to 30°C to recrystallize the potassium chloride dissolved from the ore; and (*5*) separating the potassium chloride crystals from the cool solution. The crystals are dried and, after screening into the specified products, sent to product storage. The cool solution is recycled to the ore dissolvers, ie, step (*1*). Appropriate adjustments are made to maintain a process water balance and to control the concentrations of water-soluble impurities.

To avoid generation of waste brines and the associated serious problem of brine disposal, the potash industry in the former FRG began converting some operations to electrostatic separation, a dry process for separating potassium salts from other soluble salts (24,25).

## 5. Potassium Sulfate

Compared to potassium chloride, potassium sulfate [7778-80-5], $K_2SO_4$, and its complexes with magnesium sulfate play a minor role as sources of potassium in agriculture. However, potassium sulfate in simple form or combined with $MgSO_4$ as a double salt is an essential source of potassium for crops that are chloride-sensitive. In arid parts of the world and places where saline water is used for irrigation, potassium sulfate must be used to provide potassium in order to avoid chloride toxicity. This undesirable characteristic of chloride and other undesirable soluble elements is called the salt index. Any soluble element not utilized by a growing plant contributes to the salt index.

Potassium sulfate is also a well-established source of soluble sulfur, an essential element for plant growth. Complexes with magnesium sulfate supply water-soluble magnesium, an agronomically essential element. Although much less significant than potassium in terms of tonnage consumption, magnesium and sulfur are becoming increasingly important as essential fertilizer elements (see Fertilizers). U.S. producers of potassium sulfate and their capacites are given in Table 11.
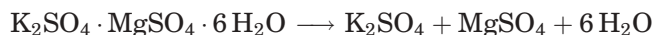
Quantities of potassium sulfate produced and consumed as potassium magnesium sulfate [13826-56-7], $K_2SO \cdot 2MgSO_4$, are omitted in the U.S. Department of the Interior reports as classified information. Consumption data for potassium compounds identified as other potassium salts imply that the amount of potassium magnesium sulfate consumed in the United States is about double that of $K_2SO_4$. This gap is expected to widen as soils become more depleted of natural magnesium- and sulfur-containing minerals.

Several types of chemical processes are used to produce potassium sulfate. The traditional Mannheim process is used in countries that produce KCl but lack a natural source of sulfate salts for converting the KCl to $K_2SO_4$. In this process, KCl reacts with sulfuric acid to yield $K_2SO_4$ and HCl as a co-product.

$$2\,KCL + H_2SO_4 \longrightarrow K_2SO_4 + 2\,HCL$$

This process or a variation called the Hargreaves process is also used in areas where sulfuric acid is available as a by-product or where co-product HCl is needed for the production of other chemicals.
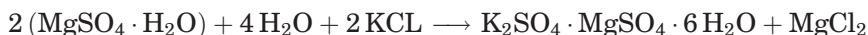
Potassium sulfate is produced in Sicily by controlled decomposition of the natural mineral kainite, $KCl \cdot MgSO_4 \cdot 2.75H_2O$ (27). This salt is first converted to schoenite in an aqueous solution from a potassium sulfate conversion step. A similar process is used in the United States. Kainite is obtained as the potassium feedstock by stage evaporation of Great Salt Lake bitterns (see Chemicals from brines).

$$4\,(KCL \cdot MgSO_4 \cdot 2.75\,H_2O)(aq) + H_2O \longrightarrow 2\,(K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O) + 2\,MgCl_2$$

$$K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O \longrightarrow K_2SO_4 + MgSO_4 + 6\,H_2O$$
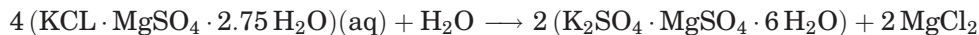
Water for the kainite conversion comes from the hydrated $MgSO_4$. This solution is saturated with $K_2SO_4$. Use of potassium sulfate mother liquor as a source of water for the reaction lowers the $K_2SO_4$ lost in the $MgCl_2$ solution, which is rejected as a waste stream from the process. It also is a solvent for sodium chloride that enters the process as a contaminant in kainite.

In Canada, ion-exchange (qv) technology has been used to produce potassium sulfate (28). Ion-exchange resins remove sulfate ions from lake water containing sodium sulfate. This is followed by a wash with aqueous solutions prepared from lower grade muriate of potash. High purity potassium sulfate is collected from the crystallizers into which the wash runs.

Approximately one-half of the world production of $K_2SO_4$ is obtained by the reaction of potassium chloride with magnesium sulfate as the double salt schoenite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ (29), or double salt langbeinite, $K_2SO_4 \cdot 2MgSO_4$. In Germany, kieserite, $MgSO_4 \cdot H_2O$, is the predominant soluble magnesium sulfate salt. This salt is converted to schoenite by the reaction of kieserite with the KCl that remains dissolved in the solution from the $K_2SO_4$ reaction step. Schoenite, after separation from the final $MgCl_2$ solution, reacts with KCl. The basic reactions are as follows:

$$2\,(MgSO_4 \cdot H_2O) + 4\,H_2O + 2\,KCL \longrightarrow K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O + MgCl_2$$

$$K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O + 2\,KCL \longrightarrow 2\,K_2SO_4 + MgCl_2(aq)$$

In contrast to sodium chloride, langbeinite has an extremely slow rate of solution. Upon control of agitation time, essentially all the sodium chloride dissolves but most of the langbeinite remains as a solid. Langbeinite is separated from the brine, dried, and then screened into granular, standard, and special-standard

particle sizes. These fractions are marketed directly. In one plant, the unsalable fines are used as the source of sulfate reactant for the production of potassium sulfate.

Kieserite is not present in U.S. potassium salt deposits in commercial quantities. Langbeinite is the predominant U.S. magnesium sulfate salt. The latter, a raw material for the production of potassium sulfate in New Mexico, reacts directly with potassium chloride:

$$K_2SO_4 \cdot 2\,MgSO_4 + 4\,KCL \longrightarrow 3\,K_2SO_4 + MgCl_2$$

A simplified flow sheet depicting the process used in New Mexico is presented in Figure 5.

The value of langbeinite as a fertilizer is enhanced because, in pure form, it contains 18.8 wt % potassium, 11.7 wt % magnesium, and 23.0 wt % sulfur. All three elements are essential nutrients for plant growth. Commercial grades contain ca 97 wt % mineral; the remaining 3 wt % consists of water-insoluble clays and residual sodium chloride.

Processes used to refine ores containing langbeinite are selected on the basis of the amount of langbeinite in the ores and the quantity of recoverable potassium chloride in the ores. In one potassium salt mineralized layer, identified as USGS (U.S. Geological Survey) Fourth Ore Zone, the ore contains relatively large amounts of langbeinite (30−45 wt %) and is generally lean in KCl. Except in areas where there are packets of ore containing significant amounts of KCl, ore from the Fourth Ore Zone is processed in a simple, freshwater washing process (31). Ore crushed through a 6-mm screen is agitated with fresh water in a ratio so as to produce an almost saturated NaCl brine.

Potassium ore in the USGS Fifth Ore Zone and pockets of ore in the Fourth Ore Zone contain commercially recoverable quantities of both langbeinite and KCl. Processing mixed KCl–langbeinite ore in the washing process to purify the langbeinite results in the solution and eventual loss of potassium chloride values. Operations to recover the potassium chloride must be conducted in brine saturated with potassium chloride. In commercial processing for KCl production, the process brine is also saturated with sodium chloride. A complex process used in New Mexico to recover KCl and langbeinite separately involves crushing the mine-run ore through a 6-mm screen (32). It is then wet-screened at 1 mm and oversize material is processed by heavy media to separate langbeinite from the chloride salts, KCl and NaCl. The recovered langbeinite is washed with brine to remove fine particles of magnetite. The washed langbeinite is then passed into the langbeinite product dryers. Undersize from the screens is processed by magnetic separation to recover the magnetite, which is recycled to the process.

Further upgrading of the potassium chloride content of the chloride salts recovered from the initial heavy-medium separation takes place in a second heavy-medium separation at a somewhat lower specific gravity than the first separation. Sodium chloride is discarded as a waste; the enriched KCl fraction is sent to a flotation process where a final separation of KCl from NaCl is made. Mine-run ore less than 1 mm that is not amenable to heavy-medium

separation is processed by amine flotation to separate KCl from NaCl and lang-beinite. The NaCl and langbeinite mixture, as tailings from the KCl flotation process, is treated by anionic flotation to recover the langbeinite.

Chemical fertilizer is the predominant market for langbeinite. Compara-tively small but increasing amounts of langbeinite are used by the animal feed ingredient industry (see Feeds and feed additives). Producers who supply this market must take special precautions to be sure that any langbeinite intended as an animal feed ingredient meets all USDA specifications for toxic heavy metals and other impurities.

Potassium sulfate and langbeinite may be screened into three different size ranges to serve all segments of the fertilizer industry. Typical screen analyses of the size products are presented in Table 12. Chemical analyses for the products are shown in Table 13.

## 6. Other Potassium Compounds

**6.1. Potassium Acetate.** Potassium acetate [127-08-2], $KC_2H_3O_2$, is usually made from carbonate and acetic acid as follows:

$$K_2CO_3 + 2\,HC_2H_3O_2 \longrightarrow 2\,KC_2H_3O_2 + H_2O + CO_2$$
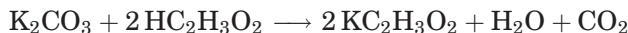
It is also made industrially by the simple reaction of acetic acid and potassium hydroxide:

$$HC_2H_3O_2 + KOH \longrightarrow KC_2H_3O_2 + H_2O$$
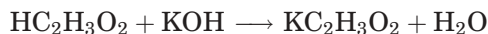
Potassium acetate is very soluble and is used in the manufacture of glass (qv), as a buffer (see Hydrogen-ion activity) or a dehydrating agent, and in medicine as a diuretic (see Diuretic agents). It is deliquescent and is used as a softening agent for papers and textiles.

**6.2. Potassium Bromide.** Potassium bromide [7758-02-3], KBr, can be prepared by a variation of the process by which bromine is absorbed from ocean water. Potassium carbonate is used instead of sodium carbonate:

$$3\,K_2CO_3 + 3\,Br_2 \longrightarrow KBrO_3 + 3\,CO_2 + 5\,KBr$$

Potassium bromate [7758-01-7] is much less soluble than the bromide and can mostly be removed by filtration; the remaining bromate is reduced with iron. After filtration of the iron oxide, the KBr is crystallized.

An alternative method, which does not involve the formation of bromate, is treatment of iron turnings with a 35 wt % aqueous solution of bromine. Ferroso-ferric bromide, $Fe_3Br_3 \cdot 16H_2O$, forms and can be crystallized. The iron bromide is heated to a boil with a slight excess of 15 wt % potassium carbonate solution.

$$Fe_3Br_8 \cdot 16\,H_2O + 4\,K_2CO_3 \longrightarrow 8\,KBr + 4\,CO_2 + Fe_3O_4 + 16\,H_2O$$
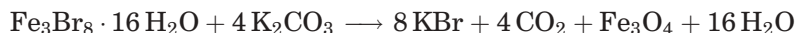
Ferrosoferric bromide effects formation of a precipitate that is readily filtered in the second step. No final purification should be necessary.

Potassium bromide is extensively used in photography (qv) and engraving. It is the usual source of bromine in organic synthesis. In medicine, it is a classic sedative.

**6.3. Potassium Carbonate.** Except for small amounts produced by obsolete processes, eg, the leaching of wood ashes and the Engel-Precht process, potassium carbonate is produced by the carbonation, ie, via reaction with carbon dioxide, of potassium hydroxide. Potassium carbonate is available commercially as a concentrated solution containing ca 47 wt % $K_2CO_3$ or in granular crystalline form containing 99.5 wt % $K_2CO_3$. Impurities are small amounts of sodium and chloride plus trace amounts (<2 ppm) of heavy metals such as lead. Heavy metals are a concern because potassium carbonate is used in the production of chocolate intended for human consumption.

A phase diagram depicting the solubility of potassium carbonate in water is shown in Figure 6. Solubilities in the system $KOH-K_2CO_3-KHCO_3-H_2O$ are shown in Figure 7.

In many heavy-chemical manufacturing operations requiring an intermediate alkaline metal carbonate reactant, potassium carbonate and sodium carbonate can be used with equal effectiveness. The cost of producing potassium carbonate is four to five times greater than that of producing sodium carbonate. Thus, sodium carbonate is almost always used for applications in which the two carbonates are equivalent chemically. Potassium carbonate possesses properties for some applications that preclude the substitution of sodium carbonate, eg, in television glass. Television glass accounts for a substantial portion of the consumption of potassium carbonate because the potassium salt is more compatible with the lead, barium, and strontium oxides contained in these glasses than is sodium carbonate. The properties of these specialty glasses include high electrical resistivity, high index of refraction, good brilliance or luster, low softening point, and wide temperature working range. In addition, potassium carbonate produces improved behavior of colorant in glass. Uses of potassium carbonate other than glass include applications in ceramics (qv), engraving processes, finishing leather (qv), chemical dyes and pigments, foods, cleaners, and gas purification, eg, $CO_2$ and $H_2S$ (33).

**6.4. Potassium Bicarbonate.** Potassium bicarbonate, $KHCO_3$, is made by absorption of $CO_2$ in a carbonate solution, ie, potassium hydroxide is carbonated to $K_2CO_3$, which in turn is carbonated to $KHCO_3$. The changes of solubility during carbonation are presented in Figure 7. Usually the carbonate is crystallized, washed, and redissolved before carbonation and crystallization of the bicarbonate. The solutions can also be filtered. Thus, the purest carbonate is made by calcining the bicarbonate. Potassium bicarbonate is more stable than $NaHCO_3$ at normal temperatures, but $KHCO_3$ decomposes at ca 190°C.

Potassium bicarbonate is used in foods and medicine. It is approximately twice as effective as $NaHCO_3$ in dry-powder fire extinguishers, perhaps because the potassium affects the free-radical mechanism of flame propagation. However, the material does not have good handling characteristics.

**6.5. Potassium Formate.** Potassium formate [590-29-4], HCOOK, is made by the following reaction (34):

$$CO + KOH \longrightarrow HCOOK$$
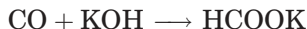
Carbon monoxide (qv), eg, by-product CO from phosphorus manufacture or extracted from synthesis gas, is freed of acidic gases and absorbed in $50-80 \, \text{wt}$ % KOH at $100-200°C$ at a partial pressure of $P_{CO} > 690 \, \text{kPa}$ ($>100 \, \text{psi}$). The reaction is fairly slow.

Potassium formate melts at $167°C$ and decomposes almost entirely to oxalate [583-52-8] at ca $360°C$. Above and below this temperature, different decomposition products form. Most of the formate produced is converted to oxalate.

**6.6. Potassium Hydroxide.** Potassium hydroxide [1310-58-3] is produced industrially by the electrolysis of potassium chloride. The electrolysis cells are similar to those used for $NaOH-Cl_2$ production (see Electrochemical processing, inorganic). In diaphragm cells, the product liquor contains $10-15 \, \text{wt}$ % KOH and ca $10 \, \text{wt}$ % KCl. Most of the KCl crystallizes during concentration by evaporation and subsequent cooling, which results in purification of the KOH solution. The concentrated $50 \, \text{wt}$ % KOH solution contains ca $0.6 \, \text{wt}$ % KCl. A phase diagram of the system $KOH-H_2O$ is given in Figure 8.

For purity and energy conservation reasons, mercury cells are used to produce most of the KOH in the United States. Feed to the cells consists of brine saturated with KCl at a moderate temperature. After purification to remove assorted metal impurities, the brine is fed into the cells, which operate on dc. These cells can be visualized as large batteries containing positive and negative terminals. The positive terminal or anode is constructed of titanium; the negative terminal or cathode is a flowing layer of metallic mercury. A potassium–mercury amalgam forms from the reaction of the potassium in the brine with the flowing layer of mercury, and the amalgam flows into the denuder. Water is added and reacts with the elemental potassium in the amalgam to form potassium hydroxide and hydrogen. The stripped mercury is recycled into the cells. Potassium is recovered as $50 \, \text{wt}$ % KOH solution. After purification to remove the mercury, the hydrogen (qv) is compressed to liquid hydrogen or is used to produce hydrochloric acid (see Hydrogen chloride).

Environmental awareness is a prime concern in all KOH plants. Safety precautions required in KOH and chlorine operations are well documented in operating manuals and sales brochures published by all commercial producers. Discharges of waste effluents containing mercury are strictly forbidden.

Principal uses of KOH include chemicals, particularly the production of potassium carbonate and potassium permanganate, pesticides (qv), fertilizers (qv), and other agricultural products; soaps and detergents; scrubbing and cleaning operations, eg, industrial gases; dyes and colorants; and rubber chemicals (qv) (10,36).

**6.7. Potassium Iodide.** Some potassium iodide [7681-11-0], KI, is made by the iron and carbonate process similar to that used for the bromide. However, most U.S. production involves absorption of iodine in KOH.

$$3 \, I_2 + 6 \, KOH \longrightarrow 5 \, KI + KIO_3 + 3 \, H_2O$$
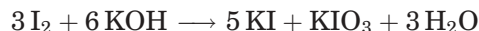
Approximately 80 wt % of the potassium iodate [7758-05-6], $KIO_3$, crystallizes from the reaction mixture and is separated for sale. Of the remainder, 90 wt % is removed by evaporation, fusion, and heating to ca $600°C$.

$$2 \, KIO_3 \longrightarrow 2 \, KI + 3 \, O_2$$
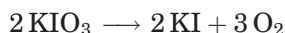
The iodate is a poison; potassium iodide, however, is used in foodstuffs. Thus the iodate must be completely removed frequently by a final reduction with carbon. After re-solution in water, further purification is carried out before recrystallization. Iron, barium, carbonate, and hydrogen sulfide are used to effect precipitation of sulfates and heavy metals.

Approximately half of the iodine consumed is used to make potassium iodide (see Iodine and iodine compounds). Its main uses are in animal and human food, particularly in iodized salt, pharmaceuticals (qv), and photography (qv).

**6.8. Potassium Nitrate.**   Potassium nitrate [7757-79-1], $KNO_3$, is produced commercially in the United States based on the reaction of potassium chloride and nitric acid (qv) (37). Ammonia (qv) oxidation is the source for the nitric acid and the reaction is manipulated chemically to yield chlorine as a co-product. The process is operated at an elevated temperature to drive the reaction to completion according to the following equation:

$$3 \, KCL + 4 \, HNO_3 \longrightarrow KNO_3 + NOCL + 2 \, H_2O$$

Nitrosyl chloride, a product of the basic reaction, has no commercial value and is converted to salable chlorine and to nitric acid for recycling.

$$2 \, NOCL + 4 \, HNO_3 \longrightarrow 6NO_2 + CL_2 + 2 \, H_2O$$

$$4 \, NO_2 + O_2 + 2 \, H_2O \longrightarrow 4 \, HNO_3$$
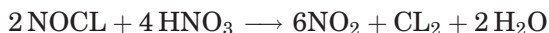
A simplified flow diagram of the process is presented in Figure 9.

Physicochemical relationships are such that solid potassium chloride can be converted to solid potassium nitrate in a one-stage operation of the simplest kind. The conversion takes place in a stirred reaction system (Fig. 10). The overall separation is analogous to a rectification and stripping operation in a distillation process.

A methathesis reaction between hot aqueous sodium nitrate and solid potassium chloride generates aqueous potassium nitrate and solid sodium chloride.

$$NaNO_3(aq) + KCL(s) + KNO_3(aq)$$

The hot potassium nitrate solution is drawn through the crystalline NaCl and the $KNO_3$ is isolated. Solubility data for $KNO_3$ in water are presented in Table 14.

Solvent extraction has been employed in Israel to produce $KNO_3$ according to the following equation (39).

$$KCL + HNO_3 \longrightarrow HCL + KNO_3$$

Among the properties sought in the solvent are low cost, availability, stability, low volatility at ambient temperature, limited miscibility in aqueous systems present in the process, no solvent capacity for the salts, good solvent capacity for the acids, and sufficient difference in distribution coefficient of the two acids to permit their separation in the solvent-extraction operation. Practical solvents are $C_4$, $C_5$, and $C_6$ alcohols. For industrial process, $C_5$ alcohols are the best choice (see Amyl alcohols). Small quantities of potassium nitrate continue to be produced from natural sources, eg, the caliche deposits in Chile.

Although no longer in great demand for the preparation of black gunpowder, potassium nitrate is used in the preparation of smokeless powder and slow-burning fuses (10). The main uses of potassium nitrate include fertilizer, fireworks, steel (qv) making, the food industry, and in a eutectic mixture with $NaNO_2$, service as a heat-transfer agent (see Heat-exchange technology) (10).

**6.9. Potassium Phosphates.**   Phosphoric acid is the source of phosphate for the production of potassium phosphates (see Phosporic acid and phosphates). Orthophosphates, ranging from monopotassium phosphate [7758-11-4], $KH_2PO_3$, to tripotassium phosphate [7758-53-2], $K_3PO_4$, are made by simple neutralization with KOH. Similar to the sodium analogues, potassium orthophosphates have buffering, complexation, and cleaning capabilities. Because of their significantly lower cost, the sodium compounds are much more widely used than potassium phosphates. The latter are generally limited to special applications where solubility is important, eg, the removal of $H_2S$ from gases in a process similar to that involving amines. In this case, the high solubility minimizes the heat requirements. A growing market has developed for specialty liquid fertilizers containing potassium orthophosphates, usually a mixture of $KH_2PO_4$ and $K_2HPO_4$, for pH control. Although these are expensive sources of phosphorus and potassium, the fertilizers do not increase the salt index of soil for house plants or the media used in greenhouse horticulture.

Devising an economical method of producing agricultural-grade potassium phosphates from potassium chloride and wet-process phosphoric acid has been the subject of intense agricultural–chemical research (39-41). Limited quantities have been produced industrially. The impact on the overall quantities of phosphorus and potassium compounds consumed by the fertilizer industry is small. Because potassium phosphates are an excellent source of two essential fertilizer elements, this research is expected to continue.

Condensed potassium phosphates have been used as builders in liquid detergents. The compound tetrapotassium pyrophosphate [7320-34-5], which forms by dehydrating $K_2HPO_4$ at 400°C, was used.

$$2\,K_2HPO_4 \longrightarrow K_4P_2O_7 + H_2O$$
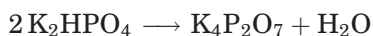
Potassium tripolyphosphate [13845-36-8], $K_5P_3O_{10}$, also used in detergents, is made by dehydrating an equimolar mixture of mono- and dipotassium phosphates.

$$KH_2PO_4 + 2\,K_2HPO_4 \longrightarrow K_5P_3O_{10} + 2\,H_2O$$
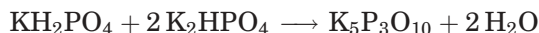
**6.10. Potassium Acid Tartrate.** The monopotassium salt of tartaric acid, $KHC_4H_4O_6$, also called potassium acid tartrate or cream of tartar, is a common ingredient in baking powders and leavening systems (see Bakery processes and leavening agents). It has limited solubility in cold water and therefore does not prematurely activate the leavening reactions during dough mixing processes. These reactions are accelerated during the baking process, partially owing to an increase in the solubility of cream of tartar at the higher temperature. Cream of tartar, tartaric acid, and its Rochelle salt are manufactured from the by-products of the wine (qv) industry, ie, press cakes, lees, and argols.

# 7. Economic Aspects

The fertilizer industry used about 85% of the U. S. potash sales and the chemical industry used the remainder in 2004. More than 60% of the produced potash was muriate of potash. Potassium magnesium sulfates, used for certain crops and soils, were also produced (4).

Inportant statistics for potash in the United States are listed in Table 15(4).

In 2003, potash imports into the United States increased and exports declined from the previous year (see Table 16 and 17). For 2003, apparent consumption rose by 3% owing to a 2% increase in imports and despite a more than 11% decrease in exports.

At present, with the U.S. dollar declining, increased exports sales of U. S. agricultural products are expected because the U.S. commodities are relatively cheaper. Worldwide stocks of grains have declined. There is a need to rebuild these stocks and if the U.S. can lead this effort then an increase in demand for fertilizer would occur, at least temporarily. The world demand, except for Western Europe and Japan, in expected to increase 1.5–2.5%. CIS, except for Russia, is expected to increase demand by 2.5% because of a demand for agricultural products by the larger, more affluent population. The Asia Pacific region will see stronger domestic growth, which should lead to increased imports of fertilizers, grains, and other foods (42).

# 8. Analytical Methods

Potassium is analyzed in chemicals that are used in the fertilizer industry and in finished fertilizers by flame photometric methods (43) or volumetric sodium tertraphenylboron methods (44) as approved by the AOAC. Gravimetric determination of potassium as $K_2PtCl_6$, known as the Lindo-Gladding method (44), and the wet-digestion determination of potassium (45) have been declared surplus methods by the AOAC. Other methods used for control purposes and special

analyses include atomic absorption spectrophotometry, inductively coupled plasma (icp) emission spectrophotometry, and a radiometric method based on measuring the radioactivity of the minute amount of the $^{40}$K isotope present in all potassium compounds (46).

## 9. Health and Safety Factors

Potash mining and refining operations in the United States are strictly regulated by appropriate federal and state agencies. Field studies conducted by NIOSH failed to disclose any evidence of predisposition of undergound miners to any of the diseases evaluated, including lung cancer (47). Exposure to dust, ie, of sodium and potassium salts, commonly encountered in the potash industry did not influence mortality for various medical conditions that are believed to be significant statistically in some nonmetallic mining and processing industries.

Potassium compounds listed as hazardous substances by the U.S. EPA are given in Table 17. The U.S. Department of Transportation (DOT) maintains a Hazardous Materials Table that designates the listed materials as hazardous for the purpose of transportation, packaging, and labeling (48). Potassium compound DOT hazard classifications are also listed in Table 18.

Potassium compounds commonly used in fertilizers, eg, KCl and $K_2SO_4$, are not considered to be hazardous substances. Detailed information concerning health and safety precautions recommended for a specific, industrially produced potassium chemical can be obtained by contacting a manufacturer directly. Principal potassium chemical producers are listed in buyers' guides published annually by chemical trade magazines (50).

## 10. Biological Role of Potassium

Potassium ions are essential to both plants and animals (see Mineral nutrients). Within cells, potassium serves the critical role as counterion for various carboxylates, phosphates, and sulfates, and stabilizes macromolecular structures. $K^+$ is the principal cation mediating the osmotic balance of the extra cellular fluids, and it is accumulated in cells in concert with the expulsion of $Na^+$ (51). If a cell dies or has its metabolism blocked, the concentration gradient for intracellular potassium to extracellular potassium disappears as potassium ions slowly diffuse out across the cell membrane. This implies that metabolic energy is expended in maintaining the gradient. The term sodium pump is used for the mechanism of active transport in rejection of sodium and accumulation of potassium by a cell. Energy for the sodium pump is provided by adenosine triphosphate (ATP) hydrolysis. This $K^+/Na^+$ separation has allowed the evolution of the reversible transmembrane electrical potentials essential for nerve and muscle action in animals. The $K^+/Na^+$ ratio for excitable membranes requires precise homeostatic control over internal electrolyte concentrations. Alkali metal ion levels in the circulating fluids are adjusted by the effect of thirst and salt-craving on intake and the influence of antidiuretic hormone and aldosterone on reabsorption in the kidney tubules.

Potassium transport through the hydrophobic interior of a membrane can be facilitated by a number of natural compounds that form lipid-soluble alkali metal cation complexes (51). For example, nonactin and valinomycin act as antibiotics by disrupting the essential $K^+/Na^+$ concentration gradient of bacteria. The natural ionophores are grouped as nigericins, macrotetrolides, depsipeptides, and cyclic peptides. Many of these organic ligands have a remarkably higher specificity for forming complexes with potassium over sodium. Selection of $K^+$ over $Na^+$ may be a size effect or may be the result of $Na^+$ being less easily stripped of coordinated water molecules. Ionophores have been synthesized primarily as cyclic polyethers generally called crown compounds, and as bicyclic polyether–diamine compounds generally known as kryptates.

Potassium is required for enzyme activity in a few special cases, the most widely studied example of which is the enzyme pyruvate kinase. In plants it is required for protein and starch synthesis. Potassium is also involved in water and nutrient transport within and into the plant, and has a role in photosynthesis. Although sodium and potassium are similar in their inorganic chemical behavior, these ions are different in their physiological activities. In fact, their functions are often mutually antagonistic. For example, $K^+$ increases both the respiration rate in muscle tissue and the rate of protein synthesis, whereas $Na^+$ inhibits both processes (53).

Information about a food's potassium content is required on the nutrition facts panel only if the food contains added potassium as a nutrient or if claims about it as a nutrient appear on the label. In all other cases, it is voluntary. The recommended daily value for potassium is 3500 mg. The following labels have been designated for foods: high potassium (700 mg or more per serving); good source of potassium (350–665 mg per serving); more or added potassium (at least 350 mg more per serving than the reference food) (54).

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Table 1. **World Mine Production, Reserves, and Reserve Base of Potash,**[a] $\times$ **10³ t K$_2$O equivalent**

| | Mine production 2003 | 2004[b] | Reserves | Reserve base |
|---|---|---|---|---|
| United States | 1,100[c] | 1,200[c] | 90,000 | 300,000 |
| Belarus | 4,200 | 4,650 | 750,000 | 1,000,000 |
| Brazil | 340 | 360 | 300,000 | 600,000 |
| Canada | 9,200 | 9,500 | 4,400,000 | 9,700,000 |
| Chile | 360 | 400 | 10,000 | 50,000 |
| China | 500 | 550 | 8,000 | 450,000 |
| Germany | 3,600 | 3,670 | 710,000 | 850,000 |
| Israel | 1,960 | 1,940 | 40,000[d] | 580,000[d] |
| Jordan | 1,200 | 1,130 | 40,000[d] | 580,000[a] |
| Russia | 4,700 | 5,400 | 1,800,000 | 2,200,000 |
| Spain | 510 | 600 | 20,000 | 35,000 |
| Ukraine | 60 | 60 | 25,000 | 30,000 |
| United Kingdom | 620 | 580 | 22,000 | 30,000 |
| other countries | 0 | 0 | 50,000 | 140,000 |
| *World total (rounded)* | *28,400* | *30,000* | *8,300,000* | *17,000,000* |

[a]Ref. 4.
[b]Estimated.
[c]Rounded to index $0.1 \times 10^6$ t.
[d]Total reserves and reserve base in Dead Sea arbitrarily divided equally between Israel and Jorden.

Table 2. **Principal Commercial Potash Minerals and Contaminants**

| Mineral | CAS Registry Number | Chemical formula | Pure mineral K, % | K$_2$O, % |
|---|---|---|---|---|
| | | *Ores* | | |
| sylvite | [14336-88-0] | KCl | 52.44 | 63.17 |
| carnallite | [1318-27-0] | KCl·MgCl$_2$·6H$_2$O | 14.07 | 16.95 |
| kainite | [1318-72-5] | KCl·MgSO$_4$·2.75H$_2$O | 16.00 | 19.27 |
| langbeinite | [67320-08-5] | K$_2$SO$_4$·2MgSO$_4$ | 18.84 | 22.69 |
| | | *Contaminants* | | |
| halite | [14336-88-0] | NaCl | | |
| polyhalite | | K$_2$SO$_4$·MgSO$_4$·2CaSO$_4$·H$_2$O | | 15.62 |
| leonite | | K$_2$SO$_4$·MgSO$_4$·4H$_2$O | | 25.68 |
| kieserite | | MgSO$_4$·H$_2$O | | |
| anhydrite | | CaSO$_4$ | | |

Table 3. **Physical Constants of Potassium Compounds**[a]

| Potassium compound | CAS Registry Number | Formula | Mol wt | Form | Specific gravity | Melting point, °C |
|---|---|---|---|---|---|---|
| acetate | [127-08-2] | $KC_2H_3O_2$ | 98.14 | white powder | 1.57 | 292 |
| bromide | [7758-02-3] | $KBr$ | 119.01 | cubic | 2.75 | 734 |
| carbonate | [584-08-7] | $K_2CO_3$ | 138.20 | monoclinic | 2.428 | 891 |
| bicarbonate | [298-14-6] | $KHCO_3$ | 100.11 | monoclinic | 2.17 | 100–200 dec |
| chlorate | [3811-04-9] | $KClO_3$ | 122.55 | monoclinic | 2.32 | 356 |
| chloride | [7447-40-7] | $KCl$ | 74.55 | cubic | 1.984 | 770 |
| formate | [590-29-4] | $KHCO_2$ | 84.11 | rhombic | 1.91 | 167.5 |
| hydroxide | [1310-58-3] | $KOH$ | 56.10 | rhombic | 2.044 | $300.4 \pm 0.7$ |
| iodide | [7681-11-0] | $KI$ | 166.02 | cubic | 3.13 | 681 |
| nitrate | [7757-79-1] | $KNO_3$ | 101.10 | rhombic, trigonal | 2.109 | 334 |
| nitrite | [7758-09-0] | $KNO_2$ | 85.10 | colorless, prism | 1.915 | 440 |
| orthophosphates | | | | | | |
| normal phosphate | [7758-53-2] | $K_3PO_4$ | 212.27 | rhombic | 2.564 | 1340 |
| monohydrogen phosphate | [7758-11-4] | $K_2HPO_4$ | 174.18 | amorphous | | dec |
| dihydrogen phosphate | [7778-77-0] | $KH_2PO_4$ | 136.09 | tetragonal | 2.338 | 252.6 |
| sulfate | [7778-80-5] | $K_2SO_4$ | 174.26 | rhombic or hexagonal | 2.662 | 1069 |
| bisulfate | [7646-93-7] | $KHSO_4$ | 136.17 | monoclinic rhombic | 2.24–2.61 2.322 | 210 214 |
| sulfite | [10117-38-1] | $K_2SO_3$ | 194.29 | monoclinic | | dec |
| acid tartrate | | $KHC_4H_4O_6$ | 188.1 | rhombic | 1.984 | |

[a]Ref. 8.

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Table 4. **Aqueous Solubility of Potassium Compounds, wt %**[a,b]

| Potassium compound | Temperature, °C | | |
| --- | --- | --- | --- |
| | 30 | 50 | 100 |
| acetate | 73.9 | 77.1 | |
| bromide | 41.4 | 44.7 | 51.0 |
| carbonate | 53.2 | 54.8 | 60.9 |
| bicarbonate | 28.1 | 34.2 | |
| chlorate | 9.2 | 15.0 | 36.0 |
| chloride | 27.1 | 30.0 | 36.0 |
| formate | | 80.7 | |
| hydroxide | 55.8 | 58.3 | 65.2 |
| iodide | 60.4 | 62.8 | 67.4 |
| nitrate | 31.3 | 46.0 | 71.0 |
| nitrite | 76.1 | 77.3 | 80.2 |
| sulfate | 11.5 | 14.2 | 19.4 |
| sulfite | 51.8 | | 55.5 |
| acid tartrate | 0.762 | 1.8[c] | 6.5[c] |

[a]Ref. 9.
[b]Values may be converted to solubilities, $S$, expressed as potassium salt g/100 g water, by $S = v/(100-v) \times 100$, where $v$ is the solubility in g as listed.
[c]Value may be too high.

Table 5. **Reagents Used in Potash Flotation**

| Reagent type | Ore, g/t |
| --- | --- |
| clay depressants | |
|    starches | 500−900 |
|    gums and others | 75−125 |
| amine collectors | 50−150 |
| amine extenders | 75−200 |
| frothers | 25−50 |

Table 6. **Screen Analysis of Muriate of Potash**[a]

| Coarse-grade | | Standard-grade | | Suspension-grade | |
|---|---|---|---|---|---|
| Screen aperture, mm (mesh) | Cumulative, %[b] | Screen aperture, mm (mesh) | Cumulative, %[b] | Screen aperture, mm (mesh) | Cumulative, %[b] |
| 2.38 (8) | 16 | 1.19 (16) | 4 | 0.42 (40) | 12 |
| 1.68 (12) | 45 | 0.84 (20) | 23 | 0.30 (50) | 35 |
| 1.19 (16) | 80 | 0.59 (30) | 55 | 0.21 (70) | 70 |
| 0.84 (20) | 95 | 0.42 (40) | 76 | 0.15 (100) | 86 |
| 0.59 (30) | 98 | 0.30 (50) | 90 | 0.11 (140) | 95 |
| | | 0.21 (70) | 96 | | |

[a]Ref. 19.
[b]Percentage of cumulative equals the percentage of MOP that is guaranteed not to pass through a given screen aperture.

Table 7. **Typical Characteristics of Muriate of Potash**[a]

| Grade | MOP, wt % | Density, loose bulk, g/cm$^3$ | Angle of repose, deg |
|---|---|---|---|
| coarse | 96.7 | 1.11–1.14 | 31–33 |
| standard | 96.3 | 1.07–1.15 | 29–31 |
| suspension | 95.9 | 1.07–1.12 | 28–30 |

[a]Ref. 20.

Table 8. **Screen Analyses for Agricultural-Grade Potassium Chloride Products**[a]

| Granular MOP | | Agriculural white MOP | |
|---|---|---|---|
| Screen aperture, mm (mesh) | Cumulative, %[b] | Screen aperture mm (mesh) | Cumulative, %[b] |
| 3.36 (6) | 7 | 0.420 (40) | 6 |
| 2.38 (8) | 45 | 0.297 (50) | 33 |
| 1.68 (12) | 80 | 0.210 (70) | 65 |
| 1.19 (16) | 96 | 0.149 (100) | 87 |
| 0.84 (20) | 98 | | |

[a]Ref. 19.
[b]Percentage of cumulative equals the percentage of MOP that is guaranteed not to pass through a given screen aperture.

Table 9. **Specifications for Chemical Grades of KCl**[a]

| | Guaranteed composition, wt % | |
|---|---|---|
| Component | Industrial | Refined[b] |
| KCl | 99.5 | 99.9[c] |
| Na | 0.18[b] | 0.0150 |
| Br | 0.09[b] | 0.0600 |
| $SO_4$ | 0.001[b] | 0.0010 |
| Ca | 0.0075 | |
| Ca + Mg | 0.0180 | 0.0030 |
| Pb | 0.0003 | 0.0003 |
| Fe | 0.0005 | 0.0005 |
| Cu, Ni | 0.0001 | 0.00005 |
| Cr, Mo, V, Ti | 0.00004 | 0.00001 |

[a]Ref. 19.
[b]Values given are maximum unless otherwise noted.
[c]Value given is minimum.

Table 10.  **Solubility Relationships KCl–NaCl–H$_2$O$^a$**

| Temperature, °C | Quantity, wt % | | | Quantity, t/100 t water | | |
|---|---|---|---|---|---|---|
| | KCl | NaCl | H$_2$O | KCl | NaCl | Total tonnage$^b$ |
| 30 | 11.70 | 20.25 | 68.05 | 17.19 | 29.76 | 146.95 |
| 40 | 13.16 | 19.66 | 67.18 | 19.59 | 29.26 | 148.85 |
| 50 | 14.70 | 19.02 | 66.28 | 22.18 | 28.70 | 150.88 |
| 60 | 16.07 | 18.57 | 65.36 | 24.59 | 28.42 | 153.01 |
| 70 | 17.59 | 18.05 | 64.36 | 27.33 | 28.04 | 155.37 |
| 80 | 19.03 | 17.59 | 63.38 | 30.02 | 27.76 | 157.78 |
| 90 | 20.32 | 17.24 | 62.44 | 32.54 | 27.61 | 160.15 |
| 100 | 21.68 | 16.90 | 61.42 | 35.29 | 27.51 | 162.80 |

$^a$Ref. 9.
$^b$Total $= t_{KCl} + t_{NaCl} + 100\, t H_2O$.

Table 11.  **U.S. Producers of Potassium Sulfate and their Capacities$^a$**

| producer | Capacity, $\times 10^3$ t |
|---|---|
| Basic Elements Manufacturing, Grantsville, Utah$^b$ | 41 |
| IMC Potash, Carisbad, N.M.$^b$ | 181 |
| IMC Potash, Carisbad, N.M.$^c$ | 998 |
| Great Salt Lake Minerals, Ogden, Utah $^b$ | 544 |
| *Total* | *1764* |

$^a$Ref. 26.
$^b$Potassium sulfate produced.
$^c$Potassium-magnesium sulfate produced.

Table 12. **Typical Screen Analyses of Potassium Sulfate and Langbeinite**[a]

| Screen aperture, mm (mesh) | Cumulative, %[b] | | |
|---|---|---|---|
| | Granular | Standard | Special standard |
| 3.36 (6) | 2 | | |
| 2.38 (8) | 20 | | |
| 1.68 (12) | 60 | | |
| 1.19 (16) | 90 | 10 | |
| 0.84 (20) | 97 | 35 | |
| 0.59 (30) | | 63 | |
| 0.42 (40) | | 90 | 8 |
| 0.30 (50) | | 95 | 40 |
| 0.21 (70) | | 98 | 60 |
| 0.15 (100) | | | 76 |
| 0.07 (200) | | | 94 |

[a]Ref. 19.
[b]Percentage of cumulative equals the percentage of MOP that is guaranteed not to pass through a given screen aperture.

Table 13. **Chemical Analyses of Potassium Sulfate and Langbeinite**[a]**, wt %**

| Component | $K_2SO_4$ | Langbeinite-grade | |
|---|---|---|---|
| | | Granular and standard | Special standard |
| K | 41.9 | 18.5 | 18.0 |
| Mg | 0.9 | 10.9 | 10.9 |
| Ca | 0.3 | 0.2 | 0.2 |
| Na | 0.2 | 0.8 | 0.8 |
| Cl | 1.5 | 1.5 | 1.5 |
| $SO_4$ | 51.5 | 67.4 | 67.4 |
| insoluble[b] | 1.0 | 0.3 | 0.3 |
| $H_2O$ | 0.1 | 0.1 | 0.1 |
| S | 17.5 | 22.4 | 22.4 |

[a]Ref. 19.
[b]For instance, clay.

Table 14. **Solubility of KNO$_3$ in Water**[a]

| Temperature, °C | KNO$_3$, g/100 g saturated solution | Temperature, °C | KNO$_3$, g/100 g saturated solution |
|---|---|---|---|
| 0 | 11.7 | 60 | 52.2 |
| 10 | 24.0 | 70 | 57.8 |
| 20 | 24.0 | 80 | 62.8 |
| 30 | 31.3 | 90 | 67.0 |
| 40 | 39.0 | 100 | 71.0 |
| 50 | 46.0 | 110 | 74.8 |

[a]Ref. 38.

Table 15. **Salient Statistics for Potash in the United States,** $\times 10^3$ t[a]

|  | 2000 | 2001 | 2002 | 2003 | 2004[a] |
|---|---|---|---|---|---|
| production, marketable[b] | 1,300 | 1,200 | 1,200 | 1,100 | 1,200 |
| imports for consumption | 4,600 | 4,540 | 4,620 | 4,720 | 4,900 |
| exports | 367 | 366 | 371 | 329 | 200 |
| consumption, apparent[b] | 5,600 | 5,300 | 5,300 | 5,400 | 5,800 |
| price, dollars per metric ton of K$_2$O, average, muriate, f.o.b. mine[c] | 155 | 155 | 155 | 160 | 170 |
| employment, number: |  |  |  |  |  |
| mine | 610 | 585 | 540 | 520 | 500 |
| mill | 665 | 670 | 645 | 620 | 630 |
| net import reliance[d] as a percentage of apparent consumption | 80 | 80 | 80 | 80 | 70 |

[a]Ref. 4.
[b]Rounded.
[c]Average prices based on actual sales.
[d]Defined as imports minus exports plus adjustments for government and industry stock changes.

Table 16. **U.S. Imports for Consumption of Potash, by Type**[a,b]

| | Approximate average $K_2O$ equivalent content (percentage) | Quantity, t | | Value, $\times 10^3$ | |
|---|---|---|---|---|---|
| | | Gross weight | $K_2O$ equivalent[c] | Customs | C.i.f.[d] |
| 2000: | | | | | |
| potassium chloride[e] | 61 | 7,380,000 | 4,500,000 | 559,000 | 590,000 |
| potassium sulfate | 51 | 132,000 | 67,500 | 23,800 | 26,500 |
| potassium nitrate | 45 | 101,000 | 45,300 | 27,900 | 31,800 |
| potassium sodium   nitrate mixture | 14 | 16,400 | 2,300 | 4,490 | 4,820 |
| *Total* | na[f] | *7,630,000* | *4,620,000* | *615,000* | *653,000* |
| 2003: | | | | | |
| potassium chloride[e] | 61 | 7,510,000 | 4,580,000 | 577,000 | 602,000 |
| potassium sulfate | 51 | 122,000 | 62,000 | 21,900 | 24,600 |
| potassium nitrate | 45 | 159,000 | 71,400 | 42,300 | 48,500 |
| potassium sodium   nitrate mixture | 14 | 22,200 | 3,110 | 4,170 | 4,870 |
| *Total* | na[f] | *7,810,000* | *4,720,000* | *646,000* | *679,000* |

[a]Ref. 7, Source: U.S. Census Bureau, adjusted by the U.S. Geological Survey.
[b]Data are rounded to no more than three significant digits; may not add to totals shown.
[c]Estimated.
[d]Cost, insurance, and freight.
[e]Contains imports listed undere Harmonized Tariff Schedule of the United States code 3104.10.0000.
[f]na=not applicable.

Table 17. **U.S. Exports of Potash, by Type**[a,b]

| | Approximate average $K_2O$ equivalent content (percentage) | Quantity, t | |
| --- | --- | --- | --- |
| | | Gross weight | $K_2O$ equivalent[c] |
| 2000: | | | |
| potassium chloride, all grades | 61 | 334,000 | 204,000 |
| potassium sulfate | 51 | 148,000 | 75,700 |
| potassium magnesium sulfate | 22 | 407,000 | 89,500 |
| potassium nitrate | 45 | 4,600 | 2,070 |
| *Total* | na[d] | *894,000* | *371,000* |
| 2003: | | | |
| potassium chloride, all grades | 61 | 268,000 | 163,000 |
| potassium sulfate | 51 | 162,000 | 82,400 |
| potassium magnesium sulfate | 22 | 365,000 | 80,300 |
| potassium nitrate | 45 | 6,020 | 2,710 |
| *Total* | na[d] | *801,000* | *329,000* |

[a]Ref. 7, Source: U. S. Census Bureau, adjusted by the U.S. Geological Survey.
[b]Data are rounded to no more than three significant digits; may not add to totals shown.
[c]Estimated.
[d]na = not available.

Table 18. **Hazardous Potassium Chemicals**

| DOT shipping name[a] | CAS Registry Number | DOT classification[a] | EPA reportable quantity[b], kg |
|---|---|---|---|
| potassium arsenate | [7784-41-0] | poison B | 0.454 |
| potassium arsenite | [10124-50-2] | poison B | 0.454 |
| potassium bromate | [7758-01-2] | oxidizer | |
| potassium chromate | [7789-00-6] | ORM-E[c] | 4.54 |
| potassium cyanide | [151-50-8] | poison B | 4.54 |
| potassium cyanide solution | [151-50-8] | poison B | 4.54 |
| potassium dichloro-*s*-triazinetrione | [2244-21-5] | oxidizer | |
| potassium dichromate | [7778-50-9] | ORM-A[c] | 4.5410 |
| potassium fluoride | [7789-23-3] | ORM-B[c] | |
| potassium fluoride solution | [7789-23-3] | corrosive material | |
| potassium hydrogen fluoride solution | [7789-29-9] | corrosive material | |
| potassium hydrogen sulfate | [7646-93-7] | ORM-B[c] | |
| potassium hydroxide | | | |
|    dry solid | [1310-58-3] | corrosive material | 454 |
|    liquid or solution | [1310-58-3] | corrosive material | |
| potassium metabisulfite | [16731-55-8] | ORM-B[c] | |
| potassium metal or metallic | [7440-09-7] | flammable solid | |
| potassium metal, liquid alloy | [7440-09-7] | flammable solid | |
| potassium nitrate | [7757-79-1] | oxidizer | |
| potassium perchlorate | [7778-74-7] | oxidizer | |
| potassium permanganate | [7722-64-7] | oxidizer | 45.4 |
| potassium peroxide | [17014-71-0] | oxidizer | |
| potassium superoxide | [12030-88-5] | oxidizer | |
| potassium sulfide | [1312-73-8] | flammable solid | |

[a]Ref. 48.
[b]Ref. 49.
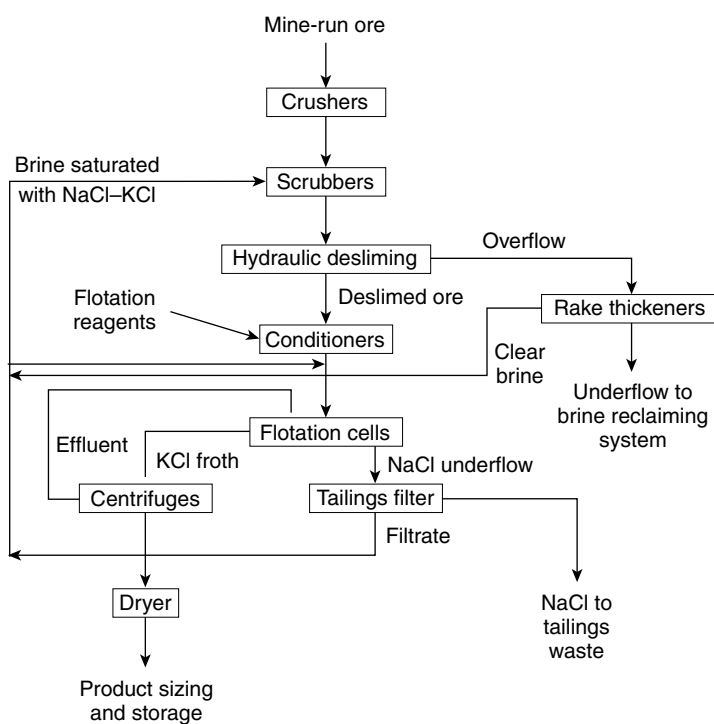[c]ORM = other regulated material.

**Fig. 1.** Flotation process for KCl production.
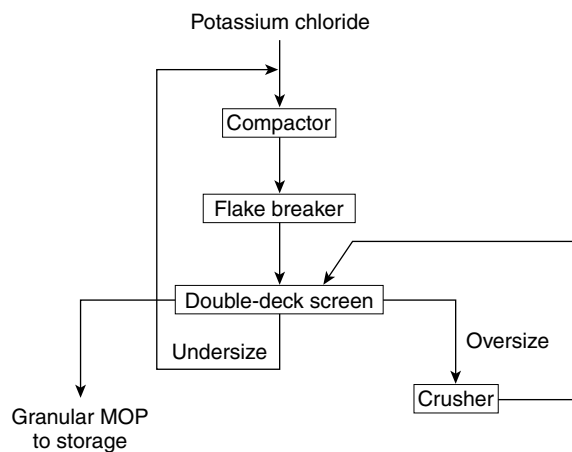


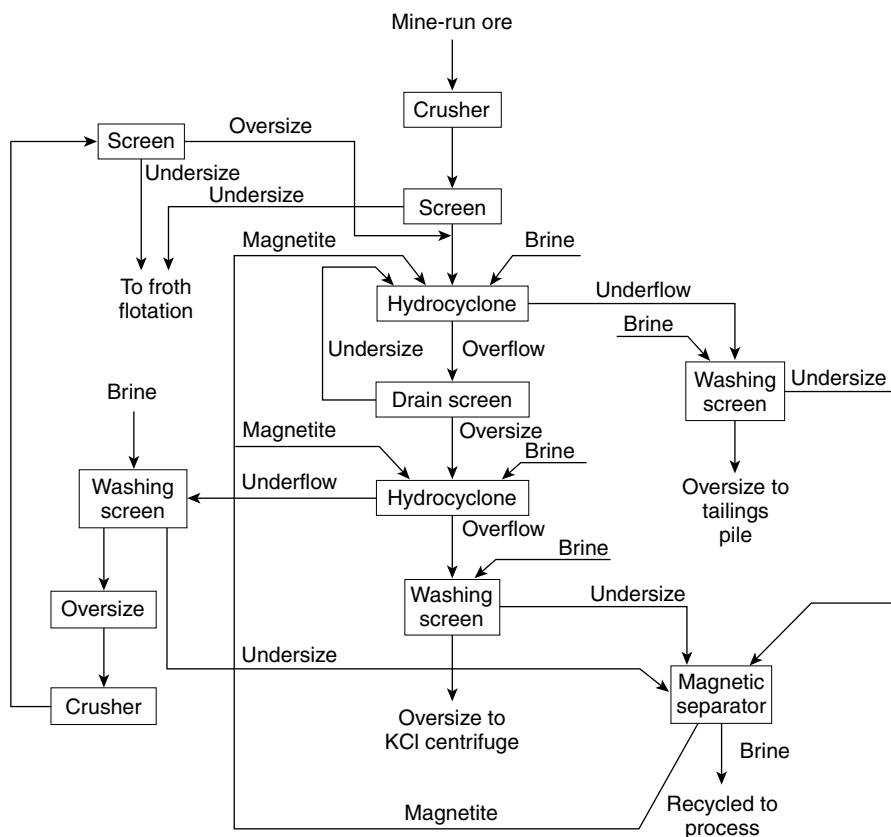**Fig. 2.** Simplified compaction plant operation.
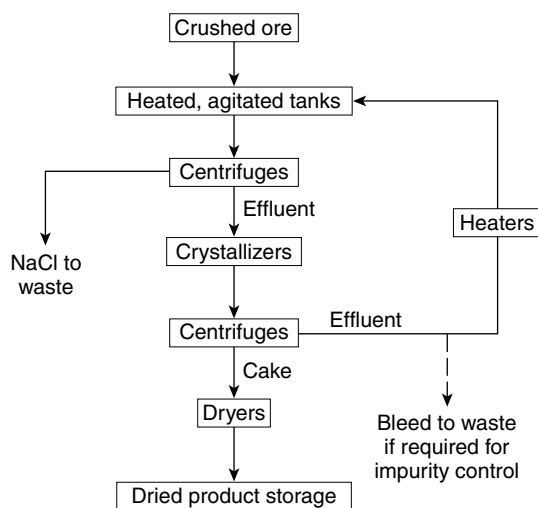
**Fig. 3.** Heavy-medium process.



**Fig. 4.** Fractional crystallization of potassium chloride ore.
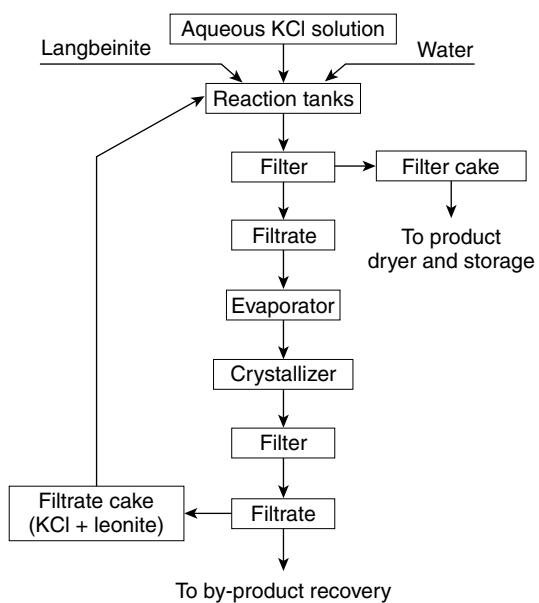
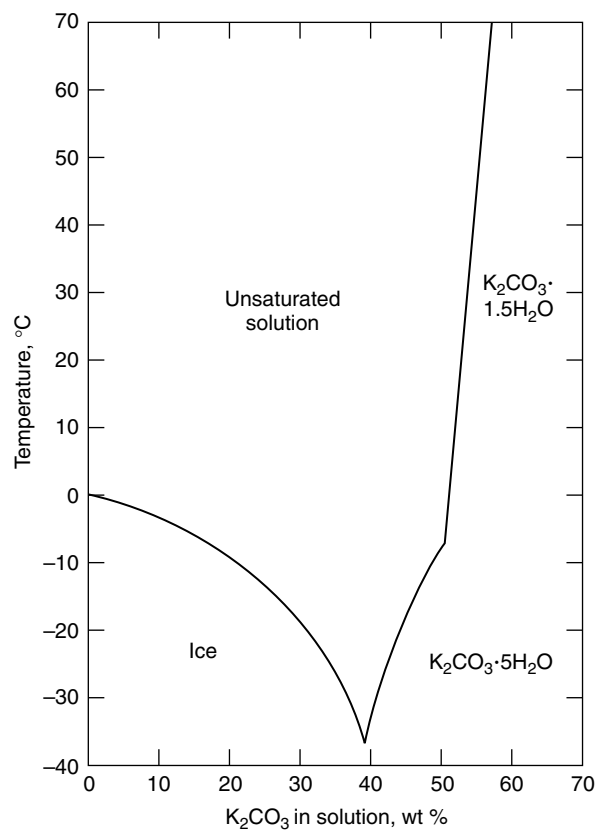**Fig. 5.** Process for the production of potassium sulfate (30).

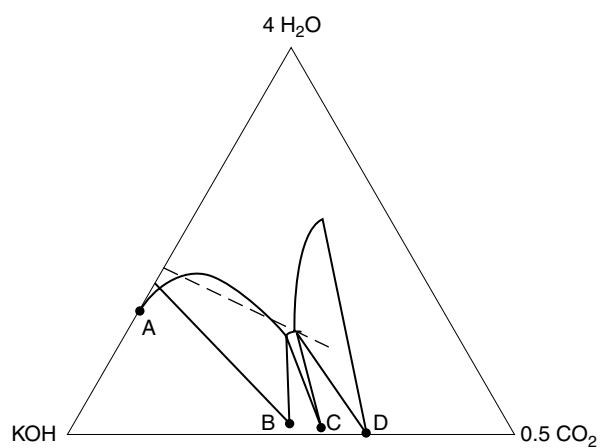**Fig. 6.** Solubility of potassium carbonate (33).



**Fig. 7.** Solubilities in the system $KOH-K_2CO_3-KHCO_3-H_2O$ at 25°C: A, $KOH·2H_2O$; B, $K_2CO_3·1.5H_2O$; C, $K_2CO_3·2KHCO_2·1.5H_2O$; and D, $KHCO_3$.
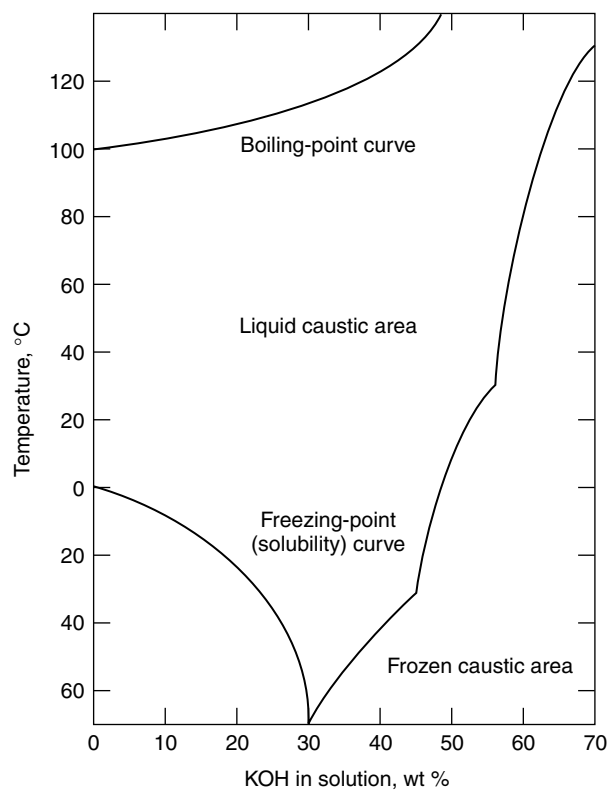
**Fig. 8.** Boiling and freezing temperatures of KOH solutions 35. The boiling point curve assumes a pressure of 101.3 kPa (760 mm Hg).
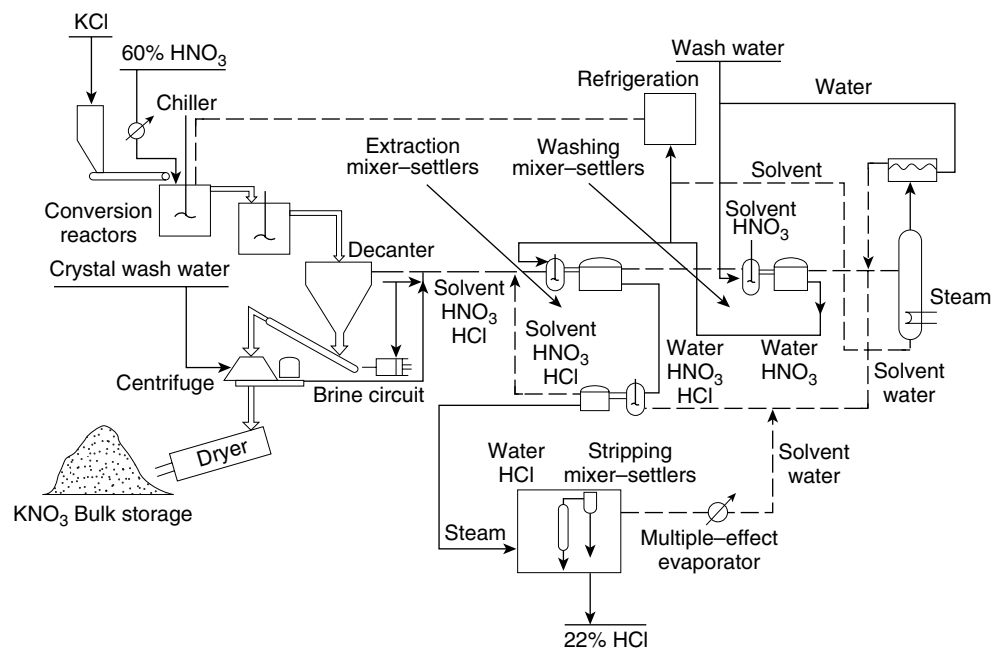
**Fig. 9.** Schematic of KNO$_2$ from NH$_2$ and KCl: A, KCl–HNO$_2$ reactor; B, NOCl oxidizer; C, acid eliminator; D, gas stripper; E, water stripper; F, H$_2$O–HNO$_2$ fractionator; G, evaporator–crystallizer; H, centrifuge; I, NO–NO$_2$ absorber; J, NH$_2$ burner; K, Cl$_2$ fractionator; and L, NO$_2$ fractionator.

**Fig. 10.** Flow sheet for the production of $KNO_3$–IMI process, where (—) represents the product stream; (– – –) the reaction solvent; and (– – –) aqueous streams 38.