CHAPTER 12.31

Potash

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The term *potash* originated from the practice of burning seacoast plants or hardwoods to ashes in iron pots and then leaching the potassium salts, primarily potassium carbonate, from the residue to provide a usable form of potassium. Until about the 1950s, this term referred to potassium carbonate, but today potash is a generic term used to describe various potassium salts used in agriculture and industry. Potassium chloride, potassium sulfate, potassium-magnesium sulfate, and potassium nitrate are the most common of these salts. As potassium is usually the element of interest, potash is measured as the oxide of potassium, K_2O, and the potassium content of ores and products is stated as the weight percent of K_2O present. Its salts are commonly referred to as muriate of potash (MOP), sulfate of potash (SOP), nitrate of potash (NOP), and so on.

HISTORY

Early uses for potash included soap making, glass making, dyeing, baking, and manufacturing of gunpowder. Prior to the late 1800s, the majority of potash was produced by burning hardwood trees and by leaching kelp, with the first U.S. patent issued in 1790 for producing potash from the ash of hardwood trees. In 1840 Justus von Liebig, a German chemist, determined that the addition of minerals to soils was necessary to provide healthy plant life and could significantly improve crop yields. This recognition triggered a surge in demand for potassium. Potash ore was initially discovered in 1857 in Germany, with additional discoveries found in German-controlled Alsace in the early 1900s. The first potash mine and refinery began operating in Strassfurt, Germany, producing both crude salts and chemically refined potash from carnallite ores.

Germany and France supplied nearly the full world demand, with Germany dominating the market until almost World War II. During the potash shortages of World War I, the United States produced potash from lake water in Nebraska, brines in California, kelp beds on the Pacific Coast, waste from molasses distilleries, and alunite ores in Utah. After the war, many nations recognized the strategic significance of potash, and potash mining and processing began in Spain, Russia, and Palestine, with the United States starting mine production in 1931. Prior to 1931, the U.S. potash production was limited to production from Searles Lake in California and other small brine operations, but by 1941, domestic self-sufficiency was achieved when production from underground mines in New Mexico began to exceed all the U.S. potash consumption.

Increased demand, driven by the benefits of higher fertilization, was supported by the addition of production from Russia and Belarusia and, most notably, new Canadian production in the 1960s. Potash production rose steadily from just under 3.0 Mt (million metric tons) of K_2O just after World War II to 31.8 Mt K_2O in 1988. With the collapse of the former Union of Soviet Socialist Republics, Soviet potash entered the global market and created market destruction that extended into the following years. Global potash production ultimately decreased due to oversupply, and after finding a new bottom in 1993, it resumed a slightly lower average annual growth rate of approximately 4% over the next two decades, reaching a value of 40.7 Mt K_2O in 2015 (Figure 1).

OCCURRENCE

Potassium is the seventh most abundant element in the earth's crust and in seawater. It is estimated to constitute approximately 2.6% of the lithosphere and is found in soluble forms in our oceans, lakes, rivers, and subsurface waters. Potassium is also an important constituent of plant and animal life and the seventh most abundant element in the human body. Potash belongs to a family of minerals characterized as evaporites, and its origin is similar to that of salt, gypsum, and soda ash (Warren 2006). Commercially significant accumulations of potassium salts occur in underground deposits formed in past geologic times by the evaporation of ancient bodies of saltwater, inland drainage basins, and shallow sea lagoons. The concentrations of potassium salts in the natural brines of some lakes in the arid and semiarid regions of the continents are also important as sources of potash, for example, the brines of the Dead Sea in Asia Minor, the Great Salt Lake in Utah (United States), and Qarhan (Chaerhan) Lake in China.

The U.S. Geological Survey (USGS) completed a Global Mineral Resource Assessment for potash identifying more than 980 sites with evaporite-related potash mineral occurrences or potassium-enriched brines (Orris et al. 2014). Sites were

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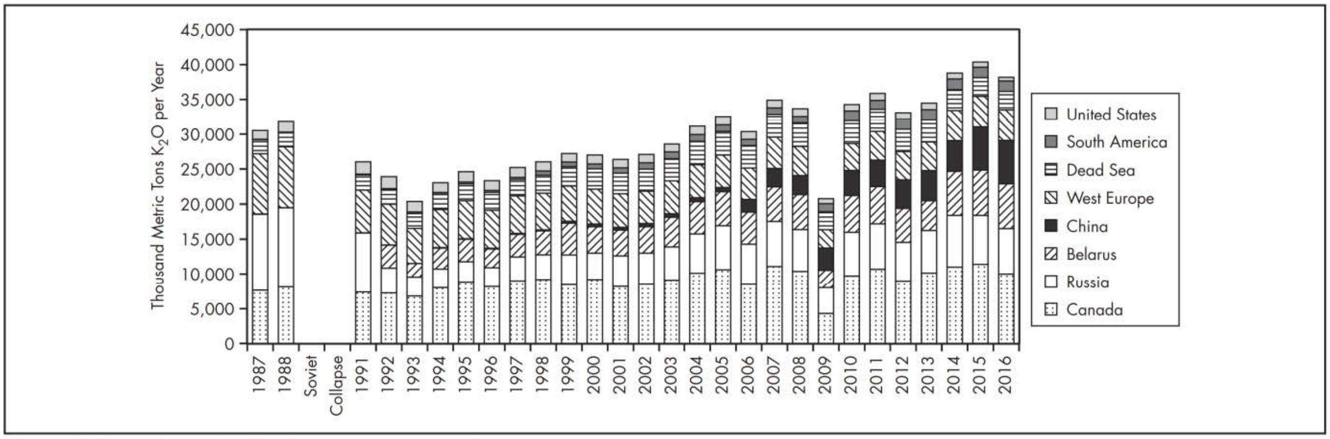


Figure 1 Potash production by country or region

classified by the nature of their occurrence, and the majority of the sites were identified as either stratabound deposits or halokinetic deposits. These two types of deposits represented about 40% each of the total sites inventoried. Stratabound deposits are described as thick, laterally continuous strata with minimal if any deformity. Seventy-five percent of the world potash production comes from this type of deposit. The Elk Point Basin in Canada, the Pripyat Basin in Belarusia, the Solikamsk Basin in Russia, and the Permian Basin in New Mexico are typical of this type of deposit. Halokinetic deposits result from differential loading of stratabound deposits or post-depositional folding, creating complex deformed or altered strata or beds. The halokinetic deposits are made up of salt structures such as anticlines, domes, and diapirs that were created from stratabound deposits. Between 10% and 15% of the world's production comes from this type of deposit. The Carpathian Subbasin of Poland and Ukraine and the Paradox Basin of Utah are typical of this type of deposit. Surface brines represent 7% of the sites, and the balance of the remaining deposits was classified as either a mixture of stratabound and halokinetic or as unclassified.

In general, the stratabound deposits are much larger deposits, typically an order of magnitude larger than halokinetic type deposits and much more uniform. Therefore, stratabound deposits are more conducive to less-expensive bulk mining methods. Where the grades of stratabound deposits vary regionally and may range from 11% to 25% K_2O, the grades of halokinetic deposits are highly variable and contain less than 20% K_2O. The vertical heights of the two deposit types vary significantly, again influencing the mining methods selected for extraction. The stratabound deposits may vary from one to several meters in seam thickness, whereas the potash seam thickness for halokinetic deposits can range from less than a meter to several tens of meters.

In addition to cataloging the location of known potash resources, the USGS highlighted 19 potash-producing areas, or tracts, including surface brine production, from fewer than 20 producing countries; they are listed in Table 1.

POTASH MINERALS

Because of its high chemical reactivity, potassium is never found in nature in its elemental form, and all potash deposits contain a variety of potassium compounds in both soluble and insoluble forms. The most common potash mineralizations are chloride salts, sylvite, and carnallite; the most common sulfate-containing potash mineral is polyhalite. The temporal differences in the chemistry of pre-depositional seawater, primarily magnesium sulfate content, influenced the nature of potash minerals contained in marine deposits (Hardie 1996). Seawater rich in magnesium sulfate resulted in sulfate-enriched deposits typically composed of halite, carnallite, and lesser sylvite, with varied amounts of polyhalite, kieserite, kainite, and langbeinite. Seawaters richer in magnesium sulfate resulted in sulfate-enriched deposits with little to no sylvite composed of halite, polyhalite, kieserite, and carnallite. Seawater low in magnesium sulfate resulted in sulfate-depleted deposits composed of halite, sylvite, and carnallite. More than 60% of potash production comes from the sulfate-depleted deposits (Hardie 1991). A list of common potash and potash-associated minerals is provided in Table 2.

POTASH ORES AND WORLD RESERVES

The principal sources of potash production are from potash ores found as bedded underground deposits. The most important type of ore is sylvinite, a mixture of sylvite and halite. Another important type of ore is carnallitite, a mixture of carnallite and halite. These two types of ores may contain varied amounts of the other primary potassium salts, carnallite and sylvite, respectively, and exist concurrently in some deposits. These ores are typically lower in sulfates but, in addition to clays, may contain minor amounts of anhydrite and occasionally potassium complexes such as polyhalite, kainite, kieserite, langbeinite, and leonite. Frequently, iron oxides occluded within the crystals tend to color sylvinite and carnallitite ores red, while clays contribute to gray or yellow colorations. Sylvinite ores are noted for their relative abundance, high potassium chloride (KCl) content, and ease of beneficiation. The high production rates from Canada, Russia, and Belarusia are predominantly from such ores. Carnallitite ores, however, are less abundant than sylvinite ores, contain less K_2O, and are more involved to beneficiate. Carnallitite ores have been mined since the discovery of potash ores in Germany. They are also typically the primary ore associated with the solar evaporation of some natural brines, such as the brines from the Dead Sea and Qarhan Lake.

The hard salts make up another type of ore, which contains increased sulfate mineralization. *Hartsalz*, a term used in Germany, applies to a mixture which is unique to Germany of

Table 1 Known resources exceeding 0.5 billion t of potash ore

Countries	Potash Tract	Resources, billion t	Deposit Type	Nature of Production*
Canada	Elk Point	>5	Stratabound	Active
Canada	Maritimes	1–5	Mixed	Active
United States	Permian Salado	1–5	Stratabound	Active
United States	Permian Rustler	0.5–1	Halokinetic	No
United States	Bonneville	Brine	Brine	Active
United States	Paradox	1–5	Halokinetic	Active
United States	Holbrook	0.5–1	Stratabound	No
United States	Michigan†	—	Stratabound	Active
Brazil	Sergipe	1–5	Stratabound	Active
Brazil	Amazonas	1–5	Stratabound	No
Argentina	Neuquén	1–5	Stratabound	Suspended
Chile	Atacama	Brine	Brine	Active
United Kingdom	Zechstein, UK	0.5–1	Stratabound	Active
Germany	Zechstein	1–5	Mixed	Active
Spain	South Pyrenean	0.5–1	Mixed	Active
Belarus, Ukraine	Pripyat	1–5	Stratabound	Active
Russia	Solikamsk	>5	Stratabound	Active
Russia	East Siberian	1–5	Stratabound	No
Ukraine, Poland, Romania	Carpathian	1–5	Halokinetic	Active
Kazakhstan, Russia	Cisuralian South	1–5	Halokinetic	No
Kazakhstan, Russia	Pricaspian‡	>5	Halokinetic	Yes
Uzbekistan, Afghanistan Tajikistan, Turkmenistan	Gissar	>5	Mixed	Active
Israel, Jordan	Dead Sea	Brine	Brine	Active
China	Tarim	Brine	Brine	Active
China	Qaidam	0.5–1	Brine	Active
China, Laos	Simoa	—	Halokinetic	Active
Laos, Vietnam	Lao	0.5–1	Mixed	Development
Thailand	Sakon Nakhon	1–5	Mixed	Development
Thailand	Khorat	1–5	Mixed	No
India, Pakistan	Nagaur	1–5	Mixed	No
Eritrea, Ethiopia	Danakil	1–5	Stratabound	Development
Congo, Angola Gabon, Zaire	Lower Congo	0.5–1	Stratabound	No

Adapted from Orris et al. 2014
*Assessment through 2012.
†Classified as active in report, no longer in production.
‡Not highlighted as active in report but listed as mining.

sylvite, halite, anhydrite, kieserite, and sometimes carnallite. Polyhalite, a polymineral, is currently experiencing renewed interest as a source of fertilizer with several new projects in development. Another polymineral, langbeinite, has notable mineralization located in the Carpathian Mountains of Ukraine and in New Mexico and is found in horizontal beds mixed with halite and varying amounts of sylvite. Kainite ore is another type of mixed salt that was commercially exploited in Sicily and Ethiopia and is being reconsidered in the Danakil Depression of Eritrea and Ethiopia.

Known world reserves of potash are estimated to be in excess of 4.3 billion t of K_2O as detailed in Table 3 (Jasinski 2017). The majority of the reserves are located in Canada, Russia, and Belarusia. At the current global consumption rate, more than a century of known potash reserves is identified. The USGS estimates resources at 250 billion t of K_2O.

POTASH PRODUCTS AND THEIR USES

The primary products of the potash industry are MOP, SOP, and sulfate of potassium magnesia recovered from sylvite, carnallite, langbeinite, kieserite, and kainite ores. Muriate of potash makes up 90%–95% of the global potash products and 60% of the domestic potash products. The final products are compatible with current agricultural products, namely granular, standard, fine standard, and the soluble (fine white product for liquid application) grades. The potassium and potassium-magnesium sulfates are also available to the agricultural sector as granular, standard, and fine standard grades.

Agricultural fertilizers account for 85% of the domestic potash consumption and 90%–95% of the global potash consumption. Potash is generally applied to the soil as muriate mixed with phosphorus and nitrogen materials in specific proportions, depending on the needs of the soil. Some crops, such

Table 2 Potash-related minerals and ores

Mineral or Ore	Composition	Percent K_2O	Specific Gravity
Primary Potash Minerals			
Sylvite	KCl	63.2	2.00
Langbeinite	$K_2SO_4 \cdot 2MgSO_4$	22.7	2.83
Kainite	$KCl \cdot MgSO_4 \cdot 3H_2O$	19.3	2.10
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$	16.9	1.60
Polyhalite	$K_2SO_4 \cdot 2CaSO_4 \cdot MgSO_4 \cdot 2H_2O$	15.6	2.77
Accessory Potash Minerals			
Arcanite	K_2SO_4	54.1	2.66
Niter (saltpeter)	KNO_3	44.0	2.10
Aphthitalite (glaserite)	$(K,Na)_3Na(SO_4)_2$	42.5	2.69
Leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	25.7	2.20
Picromerite (schoenite)	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$	23.4	2.03
Accessory Non-Potash Minerals			
Anhydrite	$CaSO_4$	0.0	2.98
Gypsum	$CaSO_4 \cdot 2H_2O$	0.0	2.30
Halite	$NaCl$	0.0	2.17
Kieserite	$MgSO_4 \cdot H_2O$	0.0	2.57
Primary Potash Ores			
Brine	Potassium-enriched brine	>0.5	—
Carnallitite	Halite and carnallite	<15	—
Hartsalz	Halite, sylvite, anhydrite, and kieserite	Typically <15	—
Sylvinitite	Halite and sylvite	Typically <25	—

Adapted from Orris at al. 2014

Table 3 World potash reserves, in million metric tons of K_2O

Country	2016	%
Belarus	750	17.4
Brazil	13	0.3
Canada	1,000	23.3
Chile	150	3.5
China	360	8.4
Germany	150	3.5
Israel	270	6.3
Jordan	270	6.3
Russia	860	20.0
Spain	20	0.5
United Kingdom	70	1.6
United States	270	6.3
Other countries	90	2.1
Total	4,300	100.0

Source: Jasinski 2017

as tobacco, citrus fruit, coffee, and nuts, have low chloride tolerances and require other forms of potassium, such as potassium sulfate, potassium-magnesium sulfate, or potassium nitrate. Potassium chloride is also used in the conditioning of drilling muds and completion fluids, producing potassium hydroxide, refining aluminum, heat treating steel, electroplating, melting snow and ice, and treating water. The secondary potassium products are potassium hydroxide, potassium carbonate, potassium nitrate, and other miscellaneous potassium salts that are produced in small quantities for special agricultural or industrial uses. The MOP is converted to potassium hydroxide by electrolysis, then to potassium carbonate and a variety of other salts. Potassium carbonate is used in animal food supplements, cement, fire extinguishers, pharmaceuticals, textiles, and high-quality glass, and as a catalyst for synthetic rubber manufacturing.

WORLD PRODUCTION AND CONSUMPTION

Potash production and consumption are generally reported as either metric tons of K_2O or equivalent metric tons of MOP. Generally, potash consumption increases with population growth or, more importantly, the affordability of the growing population (Williams-Stroud et al. 1994). Until recently, potash sales volumes and pricing were closely controlled through two major cartels and the oligarchy of potash producers, but with the breakup of the Belarusian Potash Company in 2013, Canpotex (headquartered in Canada) remains the sole potash cartel. In response to demand, potash production typically varied from 70% to 80% of installed productive capacity. Global potash production was 39.0 Mt K_2O in 2016. This equals about 64.5 Mt MOP. The world potash production statistics for the last 10 years are displayed by country in Table 4. Increased levels of production from China, Belarus, Russia, and Chile are evident in the production trends, while the levels of production from the Dead Sea, Europe, and the United States are declining. Canada remains the top potash producing country at 29% of the total world production, followed by Russia, 17%, Belarusia, 17%, and China, 13% (Natural Resources Canada 2016). These four countries represent 76% of world potash production. The contributions of the major potash producing companies are displayed in Figure 2.

Because of capital investments and increased productive capacity, potash is currently in an oversupply situation. The Food and Agricultural Organization of the United Nations (FAO 2015) estimated 2014 potash demand at 34.87 Mt K_2O, about 58.12 Mt MOP. The four primary potash consuming nations are China, Brazil, the United States, and India, representing 65% of the world consumption. Significant capital was invested to increase productive capacity over the last decade, with major projects in Canada, Russia, China, and Belarusia; many of these projects are still in progress. The FAO forecasted a compound annual rate of growth (CARG) of 4.6% for potash capacity between 2014 and 2018 because of these investments. This compares to a projected CARG of 2.6% for potash consumption over the same period. The projected volume of demand over this period is distributed as follows: 56% Asia (23% China, 17% India), 27% Americas (18% Brazil), 11% Europe, 6% Africa, and 0.4% Oceania. The current oversupply situation is expected to be exacerbated by these relative projections.

MINING

As described earlier, many potash deposits are found in nearly horizontal strata of various thicknesses and at depths ranging from 300 m to 3,000 m below the surface. In some localities, however, the beds or portions of beds may be folded, faulted, or tilted. The predominant mining methods for potash

Table 4 World potash production, thousand metric tons of K_2O

Country	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016 (estimated)	2016 vs. 2007	Increase (Decrease)
Belarus	4,972	4,968	2,485	5,223	5,306	4,840	4,243	6,290	6,470	6,400	127%	1,318
Brazil	424	383	453	448	424	425	430	311	293	300	73%	(113)
Canada	11,085	10,455	4,297	9,700	10,686	8,976	10,140	11,000	11,400	10,000	99%	(85)
Chile	515	559	691	964	861	1,053	1,050	1,200	1,200	1,200	233%	685
China	2,600	2,750	3,200	3,600	3,800	4,100	4,300	4,400	6,200	6,200	169%	1,800
Germany	3,637	3,280	1,825	3,024	3,215	3,149	3,200	3,000	3,100	3,100	82%	(637)
Israel	2,182	2,170	1,900	2,080	1,820	2,100	2,100	1,770	1,260	1,260	81%	(412)
Jordan	1,096	1,223	683	1,185	1,378	1,092	1,080	1,260	1,410	1,400	115%	164
Russia	6,429	5,992	3,727	6,283	6,498	5,563	6,100	7,380	6,990	6,500	115%	951
Spain	427	435	400	415	420	420	420	715	690	700	167%	288
United Kingdom	427	411	411	427	470	470	470	610	610	600	143%	183
United States	1,100	1,100	715	930	1,000	900	960	850	740	520	77%	(250)
Total	34,900	33,700	20,800	34,300	35,900	33,100	34,500	38,800	40,700	39,000	111%	3,900

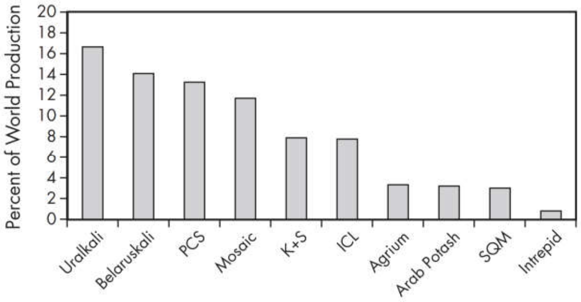
Adapted from Jasinski 2012–2017

Note: World totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not add to totals shown.

have been adopted from the coal mining industry; the modified room-and-pillar and the longwall methods. Some potash mines employ conventional coal mining sequences of undercutting, drilling, blasting, mucking, and transport to hoisting stations. Most modern mines are highly mechanized and use heavy-duty mechanical cutting and boring machines, automatic belt conveyors for ore transport, and high-capacity automated skips for hoisting. Conventional mining depths are limited by the plasticity of salt, and the deepest conventional potash mining occurs at depths of 1,300–1,500 m in Germany (e.g., Niedersachsen-Riedel, Sigmundshall, and Zielitz) and to 1,400 m in Great Britain (e.g., Boulby). Conventional mines in Saskatchewan (Canada) are operating at depths of approximately 1,000–1,100 m, and due to the characteristics of the salts, solution mining is preferred for deposits with depths greater than 1,100 m.

Potash can be extracted from deeper deposits by utilizing solution mining techniques. Typically, solution mines extract potash from depths beyond the reach of practical conventional salt mining, such as Mosaic's Belle Plaine mine (Saskatchewan) and Intrepid Potash's Moab (Utah) mine at 1,600 and 1,400 m deep, respectively. Potash is also extracted when unintentional or intentional flooding of prior mine workings takes place, which happened at Potash Corporation of Saskatchewan's (PCS's) Patience Lake (Saskatchewan) and Intrepid's Moab and HB (Utah and New Mexico, respectively) mines. Solution mining of carnallite occurs at shallower depths in Germany. Solution mining of kainite is being developed in east Africa at depths of 1,400–1,800 m.

Lake deposits may exist as brine, crystallized salts, or a mixture of the two phases. The extraction of these materials is usually accomplished by dredging and pumping or by draining ponds and mechanically harvesting the crystals with scrapers or similar earthmoving equipment. The Dead Sea operators, Israeli Chemicals Ltd. (ICL) and Arab Potash Company, Qinghai Salt Lake Potash Company Ltd. (QSL) in China, and Sociedad Quimica y Minera (SQM) in Chile represent the larger producers of potash from brines. Domestically, Compass Minerals and Intrepid Potash extract potash from the Great Salt Lake and Bonneville (Utah), respectively.



Note: Does not include China at 17% combined. PCS production does not include ICL, Arab Potash, or SQM production.

Figure 2 Potash production by company

BENEFICIATION

Every mineral has distinct physical and chemical properties that may be exploited to separate it from other minerals or substances. A key difference for many evaporites is mineral solubility. High solubility in water presents both opportunities and challenges. The increased solubility of sylvite relative to halite as a function of temperature provides a significant opportunity to separate the two minerals. Leaching with single saturated brines allows the removal of halite from sylvite and an upgrade of sylvite concentrates with minimal sylvite losses. However, all wet processing must be conducted in at least a doubly saturated brine, sodium chloride and potassium chloride, to avoid the loss of sylvite. The high solubilities of potash minerals create a series of challenges less common in the processing of most other minerals. Some such challenges are as follows:

- The higher specific gravity and increased viscosities of brines relative to fresh or mill water slurry systems have different impacts on hydraulic separations, sedimentation, bubble formation, and so on.
- The pseudo-phase equilibrium with normal temperature fluctuations can result in dissolution and recrystallization

of fine crystals dissolving targeted minerals or changing the surface chemistry of mineral particles.
- The unintended salting of screen openings, orifices, venturis, and other air–brine interfaces creates operational issues.
- The hygroscopic nature of sylvite may result in the development of salt bridges at higher relative humidity and create screen blinding, baghouse blinding, and materials handling difficulties.
- Covered storage is required due to product solubility, and a lower relative humidity is important to sustain the quality of inventoried potash products.
- The high ionic strength of the brines impacts the selection and effectiveness of surface modifying reagents, and the high ionic strength creates an environment where fine halite and sylvite will self-agglomerate due to opposite surface charges and make the recovery of minus 0.1 mm particles impractical.
- The high ionic strength of the brines also creates a corrosive process environment due to the higher chloride content of the brines, thus the sustaining capital requirements for a salt plant are higher than for other conventional mineral processing plants.

Sylvinite Ores

Most potash production comes from sylvinite ores, primarily in Canada, Russia, and Belarusia. Flotation and crystallization are the two principal processes for the beneficiation of sylvinite ores. Flotation is the lower-cost alternative due to the higher energy and maintenance costs associated with hot dissolution of sylvite prior to crystallization. Dense media separation, a third process, is minimally used to scalp coarse potash ahead of flotation and has been limited to ores with coarser liberation sizes.

The flotation process for the recovery of KCl from sylvinite ores was first commercially implemented at Carlsbad, New Mexico, in the early 1930s. A fatty acid flotation of halite from sylvite using a lead chloride activator was initially used. The differential flotation of the sylvite in preference to halite was initially used at Carlsbad in 1940 and is the universal practice in processing of sylvinite ores today. The development and use of the primary aliphatic amines as KCl collectors was critical to the development of this process. The larger potash-producing plants use flotation, several plants between 2 to 3 Mt MOP/yr. Brownfield expansions at Saskatchewan (Canada) plants Rocanville and Esterhazy project annual average production of 6.0 Mt and 7.1 Mt MOP/yr, respectively.

Hot leach/crystallization was the first commercial process for refining potash; it was developed in Germany and became the standard method for early European producers. Crystallization was adopted in 1916 for commercial production of KCl from the complex brines of Searles Lake, California, and the first vacuum cooling was introduced in 1918 (Schultz et al. 2005). The second crystallization plant in North America was erected in 1931 near Carlsbad, New Mexico. Crystallization of KCl yields a white, higher purity product with a more uniform particle-size distribution than that obtained by flotation. The process is normally selected for recovery of KCl when elevated levels of insoluble materials prevent reasonable recovery by desliming and flotation or when higher grade, 62% K_2O (98% KCl), product is preferred for market reasons. Many operators may use small crystallization plants to augment production or to produce quality potash from low-grade dusts, fines, or brines. Stand-alone crystallization plants are less common for potash recovery; however, Mosaic's Belle Plaine, Belaruskali's Soligorsk No. 4 (Belarus), and Uralkali's Solikamsk No. 1 and Berezniki No. 4 (Russia) are such examples. These plants produce from 1–2 Mt MOP/yr.

Plant recoveries usually are 85%–90% for flotation, with the losses of KCl occurring in separated slimes, flotation tailings, and necessary makeup of process brine to compensate for the brine lost as moisture in filtration and drying. Some plants combine flotation and crystallization to overcome variations in liberation characteristics of the ore. These plants diversify their muriate sales by marketing agricultural, soluble, and chemical grades of KCl. The major component of plant production, however, is a flotation concentrate that is sized and converted into granular and standard muriates.

Crushing and Grinding

Potash ores are friable and require careful selection of size-reduction equipment to minimize production of undesirable fines. Depending on the process and the market preference for final products, sizing is as important as size reduction in flotation or gravity plants. The first stage of crushing takes place underground usually by portable breakers near the mine face. The maximum size of ore hoisted is 100–125 mm. A somewhat recent trend in North America is to improve skip factors and feed sizing by utilizing underground roll crushers to deliver –50-mm material to the skips. Handling of the hoisted ore on the surface requires secondary crushing, usually a hammer-type rotary crusher preceded by a suitable grizzly typically delivering a –9.5-mm product to the final stage of size reduction, either wet milling using a KCl-saturated brine or tertiary dry crushing. Conventional rod mills in closed circuit with screens or cyclones are used for the wet milling option. In North America, many of the rod mills have been replaced by cage mills for this stage of size reduction. Most rod mills used for the regrind of rougher tails have also been replaced with cage mills to better control the generation of fines prior to flotation. The tertiary dry crushing stage, when employed, is accomplished by impact crushers in closed circuit with vibrating screens.

KCl crystals larger than 6 mesh cannot be floated efficiently. Therefore, the largest particle size of flotation feed is –6 mesh even for ores that have coarse liberation sizes. Potash particles float best between 0.1 and 1.2 mm; Canadian ores are typically reduced to passing 6–8 mesh, 3.35–2.36 mm (Strathdee et al. 2007). New Mexico limits ores to the maximum size of 2.4 mm and usually less than 1 mm, while German sylvinite ores are ground to a maximum particle size of 0.8–1.0 mm (Schultz et al. 2005). For crystallization, ore is crushed to 4 mesh, 4.75 mm, or finer.

Scrubbing

The slurried mill feed is subjected to a vigorous scrubbing, in either agitated tanks or rotating tumblers to remove insoluble particles from the crystal surfaces, to break up amorphous clay agglomerates, and to disperse freed clay slime in the brine medium. The ores are usually scrubbed in stages, with each stage followed by a screening step to remove the slime-laden brine from the scrubbing circuit. The screen oversize is repulped with clear brine at each succeeding stage. Pulp densities are critical in scrubbing, and densities of 60%–70% solids are preferred.

Mechanical desliming is the most common method of desliming. The usual practice is to separate the scrubbed ore into the coarse (+20 mesh, 0.85 mm) and fine (–20 mesh) portions and deslime these separately. Sieve-bend screens, cyclones, or mechanical classifiers serve equally well in desliming coarse fractions. Hydraulic classifiers (e.g., the CrossFlow classifier) have recently gained popularity in desliming and classifying coarser sized feeds prior to coarse flotation or in the reprocessing of rougher tails. Good desliming of the fine fractions requires efficient removal of –270 mesh, 0.05-mm solids. Mechanical classifiers, hydroseparators, cyclones, or combinations thereof are used. Desliming can be aided by the use of dispersants. A typical flow sheet of a scrubbing and mechanical desliming circuit is displayed in Figure 3. Desliming typically reduces insoluble levels in flotation feed to 0.8%–1.5% insoluble residue. Clay depressants generally work best between 1.5% and 2.0% insoluble residue.

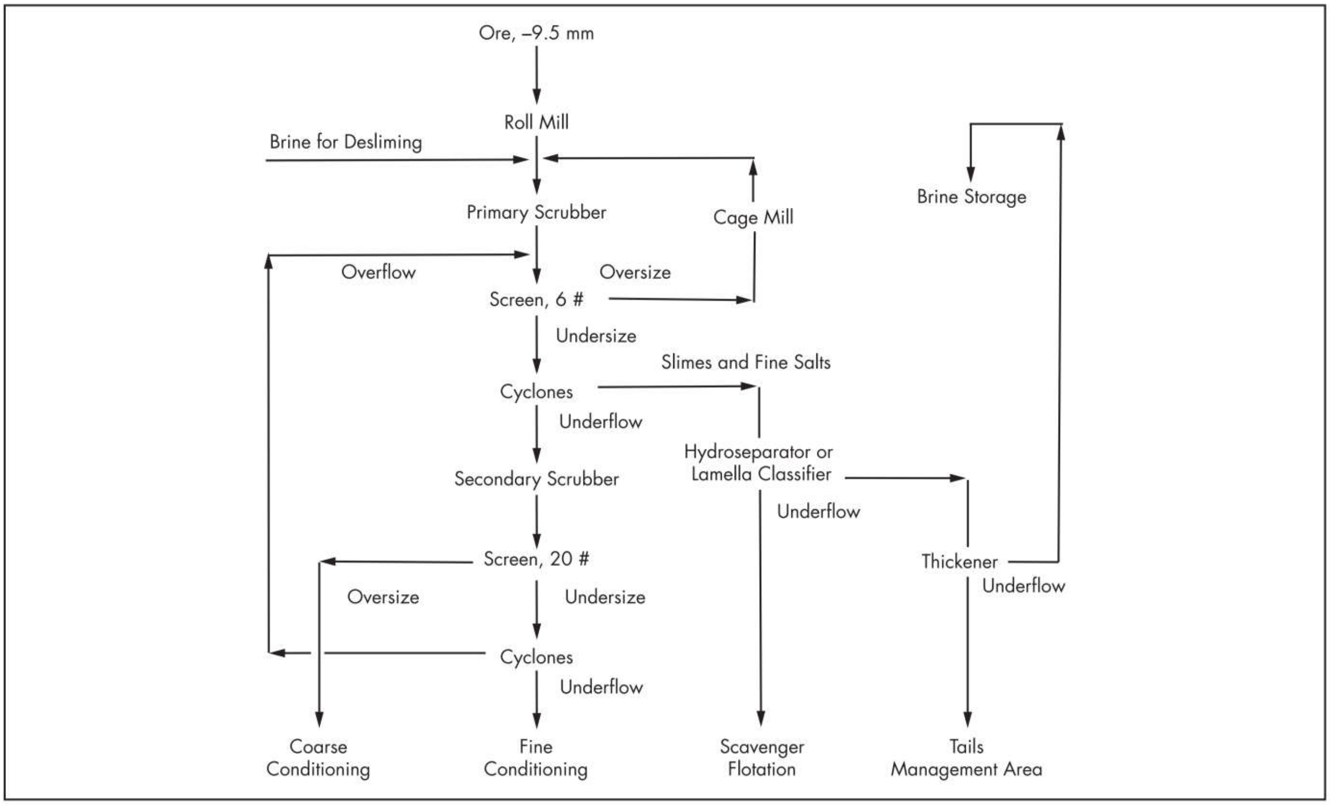
At insoluble concentrations >4%–5%, mechanical desliming becomes less effective and potash recoveries suffer. Flocculation and insoluble flotation or hot leach and crystallization are used for ores with higher insoluble contents. For flotation, two stages of flotation are usually utilized with reagent conditioning prior to each stage as the agitation in flotation liberates additional insolubles. Typically, an ether amine is utilized as a collector for the flocculated insoluble minerals. The Russian plants in Berezniki and Solikamsk, which may contain as much as 8% insoluble, utilize this process as did the original Vanscoy and Rocanville plants in Canada.

The presence of carnallite in sylvinite ores produces changes in scrubbed ore and plant brine composition. Carnallite is dissolved, introducing magnesium chloride to the brine and causing partial crystallization of KCl and sodium chloride (NaCl) from the brine. At magnesium chloride ($MgCl_2$) concentrations as low as 1%, sylvite recoveries begin to be adversely affected, especially for particles larger than 0.5 mm or at higher temperatures (Konoplev et al. 2014). Because of increased brine viscosity, increased reagent consumption, and decreased recoveries, magnesium concentrations are limited to <2.5% magnesium chloride in the brine. The negative impact of insoluble materials is exacerbated by increasing $MgCl_2$ concentrations. Due to a combination of geotechnical issues underground and increased magnesium concentrations in plant brines, ore is usually limited to less than 6% K_2O as carnallite.

Potash Flotation Reagents

A significant body of work has been generated in an attempt to understand the fundamentals of potash and soluble salt flotation. Summaries of the evolution of potash flotation can be found in Miller et al. (2007), Laskowski (2013), and Ozdemir et al. (2011).

Initial potash collectors were primary aliphatic amines produced from beef tallow, either saturated or unsaturated, containing predominantly C_{16} to C_{18} amines. The secondary, tertiary, or quaternary amines do not support hydrogen bonding at the mineral surface and therefore do not float sylvite. In response to coarser flotation and temperature variations, the inclusion of fish-based amines and other longer chain amines may make collector blends ranging from C_{16} to C_{26} amines. Sylvite flotation is affected by temperature, and it is typical



Adapted from Strathdee et al. 2007

Figure 3 Typical desliming flow sheet

Table 5 Reagent consumption ranges, in grams per ton processed

	Strathdee (1982)		Zandon (1985)		Schultz (2005)		Miller (2007)	
For Potash Ores	**Low**	**High**	**Low**	**High**	**Low**	**High**	**Low**	**High**
Depressant, starches	—	510	500	900	—	—	—	—
Depressant, others	20	70	75	125	—	—	200	300
Collectors, amines	40	100	50	150	40	80	50	60
Flotation aids, oils	10	85	75	200	40	—	30	40
Flotation aids, others	—	—	20	50	—	—	—	—
Frothers	20	23	25	50	20	—	20	0
Flocculants, brine recovery	—	—	40	75	—	—	—	—
Flocculants, filters	—	—	50	125	—	—	—	—
Anticaking, amines, etc.	30	100	15	60	12	75	—	—
Dust control	150	400	150	375	75	1,250	—	—

Source: Strathdee et al. 1982; Zandon 1985; Schultz et al. 2005; Miller and Nalaskowski 2007

for operators to alternate to longer chain amines during the warmer summer months. The flotation of coarse particles is difficult and is improved with the support of a promoter such as extender oil, especially when the oil is emulsified with the amine.

Slime depressants include starches, guar gum, dextrins, and synthetic polymers, such as polyglycols and polyacrylamides. Urea formaldehyde resin is also used as an effective cost-competitive alternative to guar, and a reduction of 25%–40% in amine consumption may result with its use (Titkov et al. 2005).

Flotation amines have frothing characteristics, and as a result, frother reagents often act more as a dispersant for the collector than as a frother. Methylisobutylcarbinol (MIBC) is employed mainly as a froth modifier in potash flotation, inhibiting the formation of excessive amine froth. In consideration of health and safety issues, hexanol or polyglycols may be preferred to manage froths. Glycol ethers, pine oil, and dioxane alcohols are used in Russia with a preference for higher dosing of the more dispersive type frothers, the glycol ethers. Guar and polyacrylamides are employed as flocculants in slime thickeners, in clarification of liquors for crystallization, and as internal flocculants in slime centrifuges.

The application of reagents in potash processing merits special attention. A slimes depressant, collector, and modifier are added to the slurry prior to flotation and preferably in the order given. Emulsifying the amine, modifier, and some frother prior to addition to conditioning improves flotation and reagent dosage. The fines require less collector but more depressant, and there is considerable advantage in separate conditioning systems for the coarse and fine fractions of the ore. Conditioning at high density is favored. Conditioning in drums, screw conveyor mixers, or launders is suggested for coarse flotation feed. Ranges of reagent usages in potash flotation plants are reported in Table 5.

Flotation Systems

Flotation kinetics are inversely related to particle size. Potash flotation systems generally consist of roughing, cleaning, and scavenger circuits. Some ores require two to three stages of cleaning. There is an emphasis on the capability of the circuit to float and recover coarse KCl. General experience is that only the intermediate and fine fractions of the rougher concentrate are readily refloated in the cleaner. The coarse KCl crystals, 6 × 14 mesh, fail to float efficiently for a second time unless appropriately debrined and conditioned anew. These particles are recovered after classification, utilizing either regrind or coarse fraction flotation (Figures 4 and 5). Recent developments with teeter bed, or hydrodynamic flow-assisted, flotation provides a highly efficient alternative to successfully recover coarse particles from either a rougher feed or rougher tail.

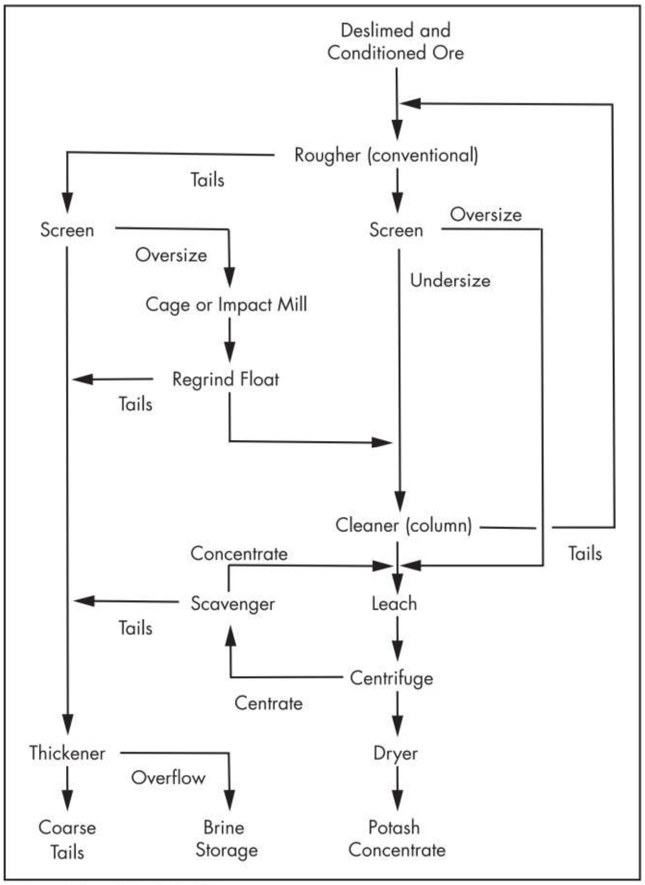
Ores containing sizable amounts of free coarse KCl may have their coarse and fine fractions floated separately as in Figure 5. The coarse circuit may be augmented with scavenging flotation where the rougher tail is screened and the oversize is conditioned and floated. The scavenger concentrate may be combined with the rougher concentrate or used as crystallizer feed while the scavenger tails report to tails. Scavenger flotation is also used for deslimed fines or centrate from centrifuges generating a dirty concentrate for brine makeup or crystallizer feed.

Final flotation concentrates contain minor amounts of middlings, fine NaCl, and traces of insolubles; grades of 90%–92% KCl are common.

Flotation Equipment

The Denver DR 300 has been a workhorse in the industry because of its ability to recover coarser potash particles. Until recently, it was the preferred machine for coarse flotation and is still the preferred equipment for coarser mixed flotation. In Canada, Fairbanks Morse and Gallagher cells are also used. Agitair and Mechanobr cells are commonly used in eastern Europe (Schultz et al. 2005). When a coarser, more uniform process stream can be created by preclassification, especially hydraulic preclassification, Eriez's HydroFloat has been used to recover coarser potash particles, 1–4 mm, from plant feed or rougher tails.

Mechanical or column cells are used for the flotation of intermediate-sized and fine-sized particles, 0.1–1.2 mm, and newer facilities or modernized plants are using column cells in the cleaning and recleaning circuits. Pneumatic flotation cells, such as the Imhof cell, have become common for cleaner flotation in Belarusia and are being used in Germany (Imhof et al. 2002; Fertilizer International 2010). The Jameson cell has successfully replaced mechanical cells for slimes and cleaner flotation, initially at Boulby (United Kingdom) and sequentially at the Dead Sea Works (Israel) and in Canada (Hall and Harrison 1995).



Adapted from Hatch 2012

Figure 4 Typical flotation option

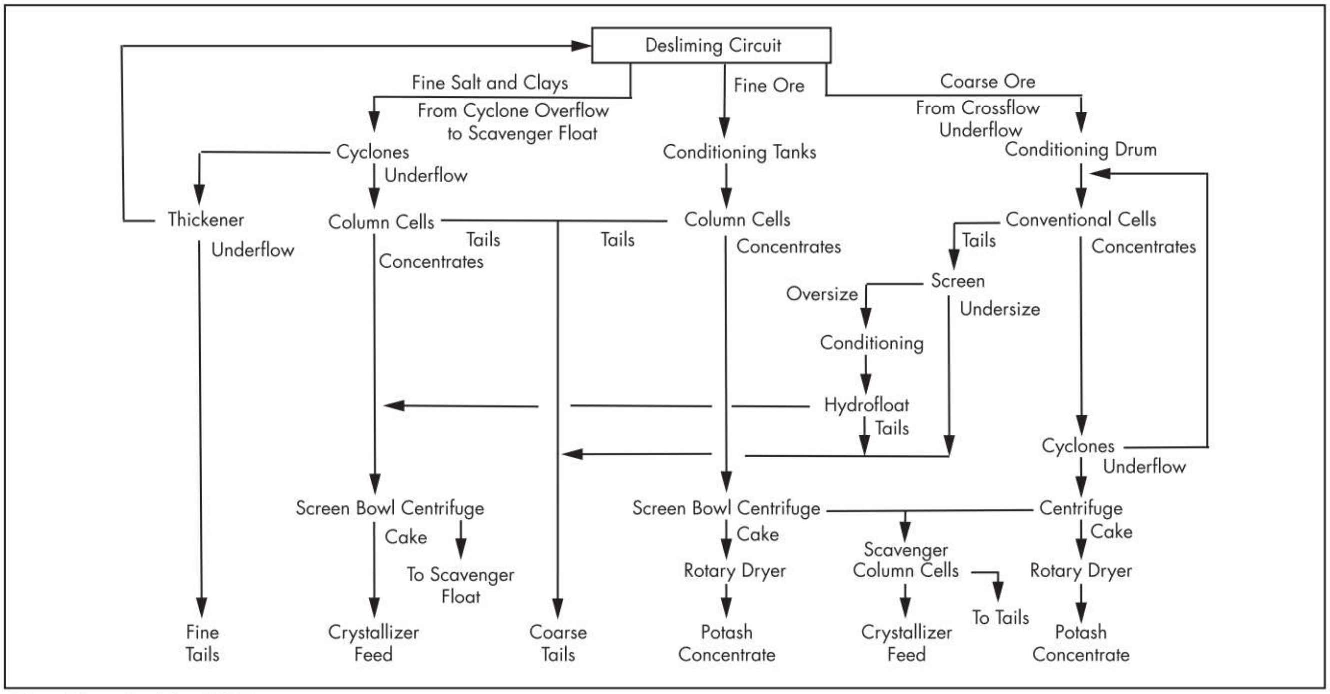
Flotation–Crystallization System

As was noted previously, many potash plants find it necessary to combine flotation and crystallization methods in treatment of their ores for optimum KCl recoveries and acceptable grades of all products. In some cases, coarse deslimed ore reports to flotation and the fines report directly to crystallization. Crystallizer feed may vary (e.g., hot rinse brines from tails and slimes, scavenger flotation concentrates, flotation concentrates from product centrate brines, potash dusts, and product losses from materials handling losses).

Crystallization

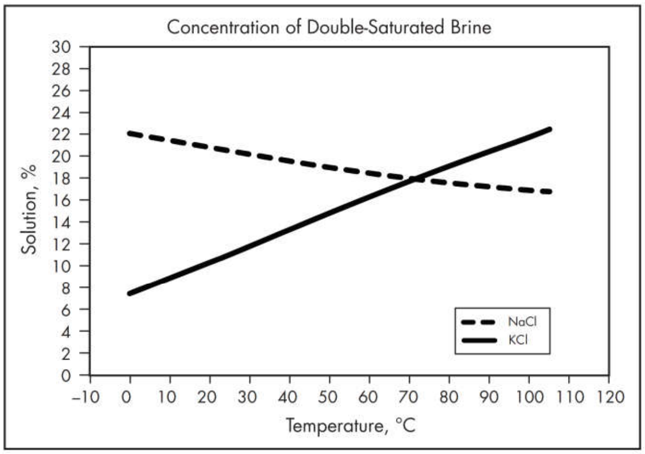
The crystallization of KCl from hot saturated brines is governed by equilibrium solubilities of KCl, NaCl, and other brine components, if any, in cooled solutions. The principle is demonstrated by the solubility–temperature relationship for a simple KCl-NaCl-H_2O system (Figure 6). The solubility of KCl increases rapidly with the increase in temperature, while that of NaCl decreases. Conversely, the solubility of KCl decreases sharply as the temperature is lowered, whereas the concentration of NaCl changes very little. This differential solubility of the two chlorides at lower temperatures produces supersaturation of the solution with respect to KCl which allows its separation and recovery by fractional crystallization.

The presence of other salts in the system alters the solubility of KCl and NaCl and therefore the equilibrium solubilities of all the salts present in the feed brine to crystallizers. The rate of crystallization of KCl from the complex mixture of salts must be considered in the design and operation of the crystallizer plant. Solubility data for a wide range of concentrations of KCl, NaCl, Mg, SO_4, and Ca are available in reference literature. A classic solubility reference for many salt systems has been written by D'Ans (1933).



Adapted from Strathdee 2007

Figure 5 Potash flotation with separate coarse and fine flotation



Source: Garrett 1996; Siedel 1919

Figure 6 Solubilities in a NaCl–KCl system

Crystallizers

The majority of modern potash operations use continuous vacuum crystallizers, which develop the needed degree of supersaturation by cooling the hot saturated brines. The cooling is produced by the evaporation of water from the hot brines and is governed by a vacuum in the crystallizing vessel. The decrease in brine temperature reduces the solubility of KCl, and its excess crystallizes out as fine nuclei that subsequently grow to the crystal size desired. After crystallization, the brine reverts to a saturated state, and the cycle is repeated with fresh hot feed. Uncontrollable formation of fine seed crystals or spontaneous nucleation takes place when supersaturation is maintained at too high a level, reaching into the labile field of supersaturation. The resulting crystal crop will be confined to extremely fine sizes, which are undesirable. Production of larger crystals requires operation of the crystallizer at a lower level of supersaturation, the metastable field in which a limited formation of new nuclei occurs and conditions are favorable to the growth of existing crystals.

The continuous crystallizing plants contain several cooling stages in series, usually between four to eight stages. The last stage will have the highest vacuum and the coolest brine. In some designs the entire crystallizer body may be under vacuum; other designs favor a separate vacuum or "flash" vessel directly above the crystal suspension chamber of the crystallizer body proper. Such vaporizer discharges through a seal leg into the lower chamber, which is at atmospheric pressure. The vapor released in the crystallizing vessels is condensed in either barometric or surface condensers; in either case a significant quantity of heat is recovered when recycle brine is used as a coolant prior to its return to the dissolvers.

Typical Crystallizer System

A simplified flow sheet for a crystallization circuit for the basic case of a sylvinite ore is shown in Figure 7. Hot recycle brine between 95° and 105°C is used to dissolve the solid KCl into a liquor that is clarified and reports to crystallization. The undissolved solids in the clarifier underflow, primarily NaCl and insoluble materials, are debrined and discarded. Depending on the level of insolubles in the ore, multiple stages of thickening and countercurrent decantation may be utilized to minimize soluble KCl losses to the tails. The filtrates from both debrining operations are recycled to the system. Recycling of the brine may lead to a buildup in the concentration of undesirable ions in solution, which can be detrimental to crystallization. General plant practice is to minimize the buildup of harmful impurities by a controlled bleeding of brine from the system.

When chemical-grade KCl is desired, the concentration of NaCl and other impurities in the brine must be limited. This is usually accomplished by redissolving the commercial grade of KCl in water to remove the objectionable impurities and recrystallizing the purified brine in a separate circuit

Hot leaching and crystallization is employed with sylvinitic, carnallitic, and hartsalz ores. Operational leach and brine management practices are significantly different between the different ore types as magnesium concentrations must be closely managed in the case of carnallite and hartsalz ores. Schultz et al. (2005) provide a good reference on crystallization with a relatively detailed description of the impacts of other ions, especially magnesium. Crystallization is also utilized to recover other potassium salts, such as potassium sulfate, from schoenite and kieserite.

Other Methods of Concentration

The dense media process has been successfully employed to recover coarser KCl crystals less suited to flotation, such as at Mosaic's Esterhazy operation where the ores are known for their relatively coarser liberation size compared to the other Saskatchewan ore zones, 9.5 mm versus 1.5 mm, respectively (Perucca 2003).

The separation is favored by the difference in specific gravities of the ore components (i.e., 2.17 for halite and 1.98 for sylvite). The crushed middlings and –10 mesh product from the screen undersize are combined and proceed to flotation.

Several other methods were used or considered for the concentration of potash ores, such as tabling and electrostatic separation (LeBaron and Knopf 1958).

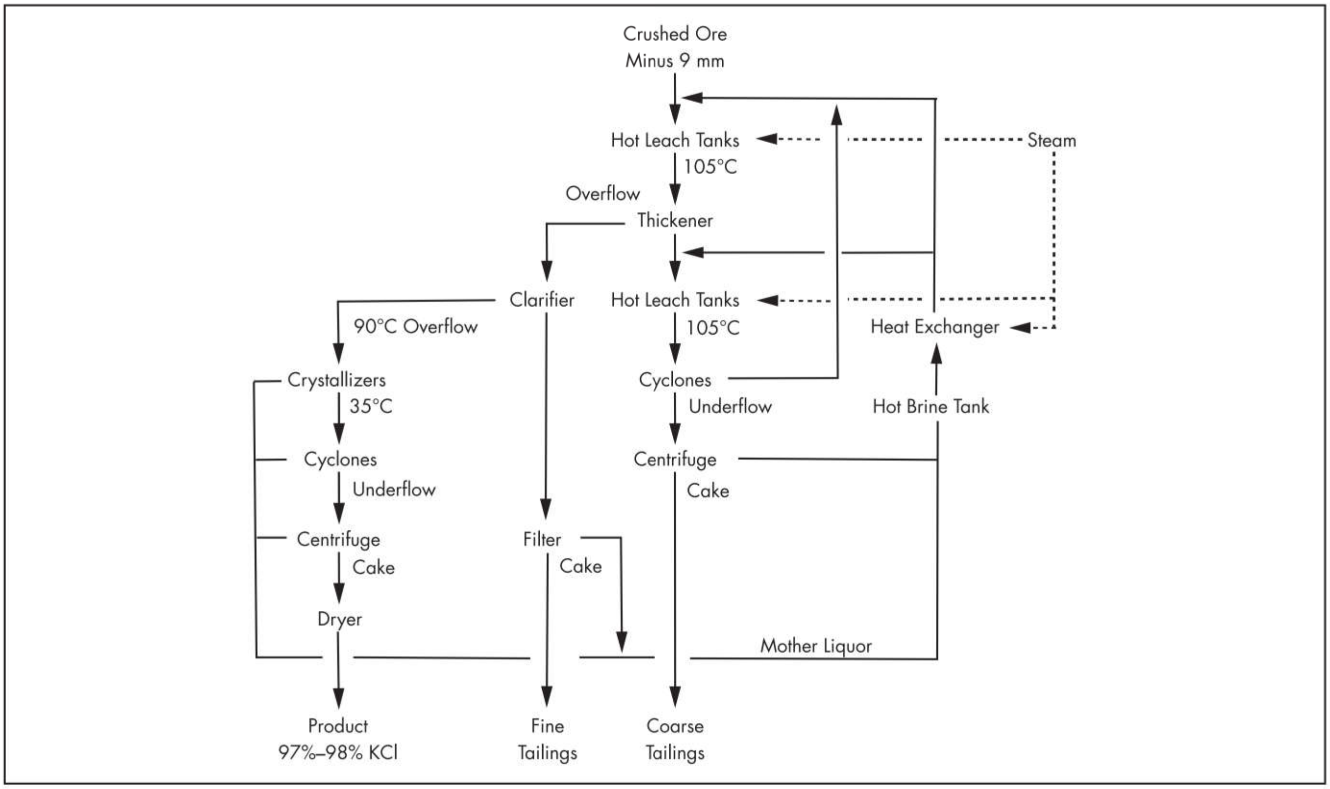
Carnallitic Ores

Carnallite is considered a minor impurity in North American sylvinite ores, but it is a major potassium-bearing mineral in several European deposits, notably in Germany and Solikamsk in Russia, and evaporative products from lake brines of the Dead Sea and the Qarhan Lake in China's Qaidam Basin. ICL's Dead Sea Works has been extracting potash from carnallite salts since 1955 and currently produces around 2 Mt MOP/yr. APC (Jordan) produces at almost the same level of production.

Carnallite was the first potash ore refined at Strassfurt, Germany, in 1861. Following hand sorting as the primary form of beneficiation, leaching and crystallization were used to obtain a purer product, initially up to 80% KCl. Commercial flotation of carnallite was not introduced until the 1980s. Today several processes are combined in the recovery of KCl from carnallitic ores or raw salts. Generally, some combination of selective decomposition of carnallite, hot leach and crystallization, cold crystallization, sylvite flotation with alkylamines, and reverse flotation of halite with alkylmorpholines is used.

Elevated magnesium levels in the flotation brine activate insoluble materials relative to alkylmorpholines, and therefore the Russian operations in Perm favor desliming by flotation where both halite and insolubles can be removed from carnallite (Titkov et al. 2014).

The known German practice for processing carnallite–sylvite ores employs hot leaching of the ore and recovery of the low-grade KCl product (80% KCl or lower) by vacuum



Source: Zandon 1985

Figure 7 Hot leach/crystallization of sylvinite ores

crystallization. The essential feature of this particular process is the control of $MgCl_2$ concentration of the brine below the point at which crystallization of carnallite might occur. Such control is usually achieved by a bleed of the lean circuit brine containing $MgCl_2$ relative to the amount of carnallite in the ore.

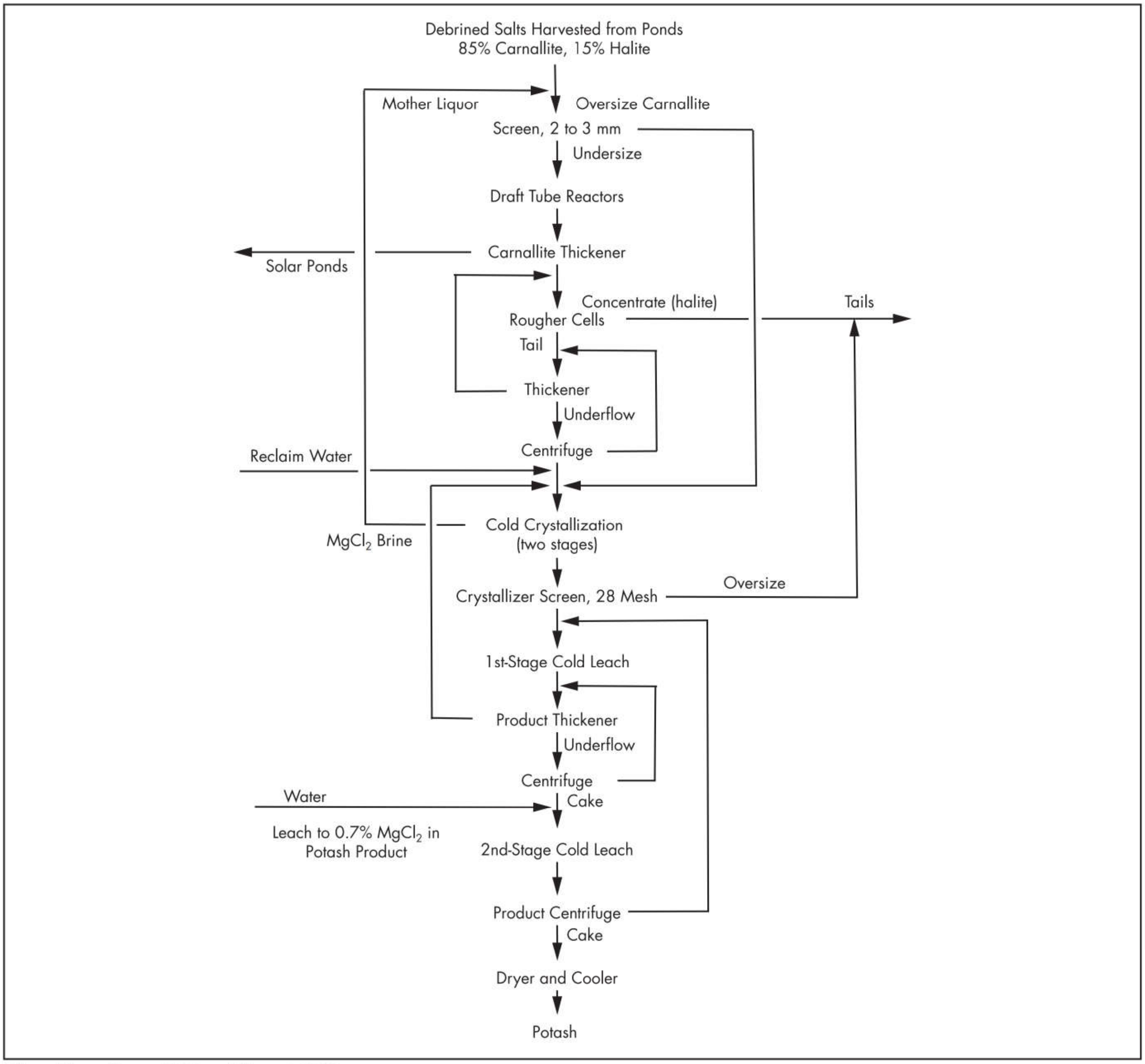
Raw carnallite salts are recovered from the solar evaporation of Dead Sea brines. Israel began recovering potash from these carnallite salts by utilizing selective decomposition of carnallite followed by hot leaching and crystallization of sylvite to remove the potash from halite. This became the standard approach for recovering potash in the region until the development of the cold crystallization process (Alamer 2009; Garrett 1996; Wisniak 2002; Zbranek 2013). In hot crystallization, raw carnallite salts containing about 16% halite are recovered from the solar ponds, debrined, and mixed with weak brine. The more soluble $MgCl_2$ is selectively dissolved from the carnallite double salt while undissolved potassium and sodium salts remain or recrystallize as sylvinite. The washed sylvinite is hot leached at 105°C with mother liquor from crystallization and thickened. Sylvite is recovered from the thickener overflow in multiple stages of crystallization. Including pond losses, regionally about 50% of the KCl that is introduced to the solar ponds is recovered as product (Zbranek 2013).

A cold crystallization process was developed by the Israelis to lower costs. The carnallite crystals from the evaporation of Dead Sea brines are coarser than the halite crystals. By exploiting this fact, about 25% of the raw carnallite is removed as a high-grade carnallite oversize and bypasses halite flotation prior to cold crystallization, as detailed in Figure 8. A sylvite cake containing less than 0.7% $MgCl_2$ is produced from the process.

Almost all MOP production in China is extracted from carnallite salts evaporated from lake brines at Lake Qarhan in the Qinghai Province. These carnallite crystals are smaller than the carnallite crystals produced from Dead Sea brines and therefore influence the Chinese processing options. Two main methods are used to recover muriate from these carnallite salts: selective decomposition–flotation and reverse flotation–selective decomposition. Due to better product quality, coarser product size, improved debrining properties, and higher recoveries, the industry is migrating from the older selective decomposition–flotation process to reverse flotation-selective decomposition. QSL is the largest producer and uses the reverse flotation process (Wang et al. 2014; Zhang et al. 2009). Although there may be as many as 50 smaller operators producing small quantities of MOP from the lake (Zhang et al. 2009), many of these smaller operators use cold decomposition–flotation. A comparison of the two processes is provided in Table 6.

Hard Salts and Polymineral Ores

The production of potash from hartsalz represents some of the earliest potash production techniques. The product mix from hartsalz can vary depending on the composition of the ore and the selection of the processing methods. Potash products are generally MOP, SOP, kieserite, and epsomite. Since the first commercial introduction of flotation in 1953 and electrostatic separation in 1974, crystallization, electrostatic separation, and flotation typically have been used in the recovery of products. For ore containing greater than 15%–20% carnallite,



Adapted from Alamer 2009 and Zbranek 2013

Figure 8 Cold crystallization for Dead Sea salts

Table 6 Comparison of Chinese process options at Qinghai Province

Production Attributes	Decomposition and Sylvite Flotation	Halite Flotation and Decomposition
Product grade, % KCl	86–92	90–95
Overall recovery, %	40–50	59–62
Particle size distribution, mm	P_{80} of 0.088	D_{50} of 0.2
Temperature sensitivity	High	Low
Collector dosage, g/t	450–500	50
Product moisture, %	6	3
Production, t/yr in mm	0.5	2.5

Adapted from Wang et al. 2014 and Zhang et al. 2009

cold decomposition is typically used to initially remove higher levels of magnesium.

The hot leach crystallization process for ores containing carnallite requires close control of magnesium content in the mother liquor and yet still produces lower quality MOP. By using a quick hot leach, the solids to liquid ratio, and coarser particle sizes, sylvite and carnallite can be selectively leached from the slower leaching kieserite. A liquor bleed is used to control $MgCl_2$ concentrations, or the production of a 60% K_2O product is not possible without excessive leaching. The flotation of kieserite from the hot leach residue results in a final halite residue.

Electrostatic separation is successfully used at particle sizes >0.1 mm. One processing sequence is to remove the halite and then separate and upgrade kieserite from the potassium salts. A variety of other mineral separation sequences are utilized depending on the product preference. Schultz et al. (2005) provide a more detailed reference for the processing of hartsalz using electrostatic separation. MOP, kieserite, epsomite, KCl brine, and $MgCl_2$ brines are produced for sales or the creation of other products. For instance, epsomite or kieserite are reacted with a KCl brine to form intermediates leonite ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) or schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), respectively, and $MgCl_2$ brine. These intermediates are further reacted with KCl brine to form SOP and additional $MgCl_2$ brine.

Schoenite produced as raw salts from evaporation ponds is reacted in a similar fashion. Halite has a negative impact on this conversion and therefore is generally removed by flotation ahead of schoenite decomposition. Schoenite can also be floated from halite.

Kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) often appears as minor quantities in potash ores. Kainite is usually upgraded by flotation, reacted with excess sulfate brines to form a crystalline schoenite intermediate and $MgCl_2$ brine. The schoenite is further converted to form SOP and additional $MgCl_2$brine. Raw salts with higher levels of kainite are reacted with sulfate brines to convert the kainite to schoenite prior to flotation.

Langbeinite is another polymineral, a twin salt ($K_2SO_4 \cdot 2MgSO_4$) that is currently produced and marketed as sulfate of potash magnesia by Mosaic and Intrepid Potash. The ore is crushed, ground, and screened and the denser langbeinite sink is removed from a lighter, predominantly halite, float using dense media cyclones (Harrison 1972; Garrett 1996). The screen undersize is water leached to remove the fine salt from the fine langbeinite. The recovery of langbeinite in the dense media circuit is high (90%–95% langbeinite), while the overall recovery is 70%–80%.

Another polymineral, polyhalite, with a lower potassium content, 15.6% K_2O, is used as a lower grade fertilizer or soil amendment. Cleveland's Boulby mine in the United Kingdom, owned by ICL mines, crushes, screens, and direct sells the unrefined ore as a fertilizer with two products sizes, granular or powder. Two greenfield projects, one in New Mexico and the other near the Boulby mine, are in the financing phase.

About half of the SOP production is obtained from sulfate containing ores or brines. The other half of production is as a secondary product created by reacting MOP with sulfuric acid or sulfate brines. The majority of secondary SOP is produced in the Mannheim process in which KCl and sulfuric acid are reacted in Mannheim furnaces at 600°C to produce SOP and hydrochloric acid. A less common method is to react sodium sulfate with MOP to produce glaserite ($Na_2SO_4 \cdot 3K_2SO_4$). The glaserite is further reacted with MOP to produce SOP and salt brine.

Alunite, an aluminum potash sulfate mineral ($KAl_3(SO_4)_2(OH)_6$), has also been processed to produce SOP, primarily from ores in Russia, and historically from ores in Italy and for a brief period during World War I from ores in Utah. Processes vary, but after either a soda roast or a reduction roast, the calcine is hot leached and SOP is crystallized from resulting liquors.

Nitrate Ores

No natural form of potassium nitrate, NOP, is mined or harvested from brines, and therefore its production is all secondary. Sodium nitrate is mined from natural sources, caliche ores, in Chile and reacted with MOP from solar brine operations to produce NOP and NaCl brine.

BRINE SOURCES AND SOLUTION MINING

Between 20% and 25% of the global potash production originates from brine sources. As these brine sources are predominantly located in arid environments, the potash minerals are recovered from the brines through solar evaporation in the form of raw salts creating a synthetic ore. The nature of the evaporated raw salts depends on the composition of the brine, and the management of brine chemistry by advancing concentrated brines through successive ponds to selectively deposit different salts (Table 7). Low-sulfate brines will deposit halite first and sylvinite next, for example, Bonneville, Utah, and the Salar de Atacama, Chile. The Atacama brines contain higher sulfate levels, and schoenite and kainite will deposit later in the sequence; therefore the production of MOP and SOP are possible from the same region. For low-sulfate brines with increased magnesium levels, the raw salts are carnallitic with little if any sylvinite, for example, the Dead Sea (Israel) and the Qarhan Salt Lake (China). The raw salts from brines with increased magnesium and sulfate levels contain halite, schoenite, and kainite (e.g., Lop Nur Salt Lake in China and Great Salt Lake [Utah]). Processing of sylvinitic, carnallitic, and potassium sulfate raw salts was described earlier.

Solution mining of sylvite beds was first used in 1964 at Belle Plaine in Saskatchewan; it is the largest solution mining operation and is still producing at about 2 Mt MOP/yr. K+S produces MOP from the Bethune solution mine in Saskatchewan. At three sites in North America (Patience Lake, Moab, and Carlsbad HB), brines are injected and extracted from old mine workings. Patience Lake is operated seasonally, taking advantage of the cold winters with sylvite depositing in the cooling ponds. At Moab and HB, a raw sylvinitic salt is deposited from the extraction brine in solar evaporation ponds. Direct flotation of potash from the harvested salts produces the final MOP product. MOP and $MgCl_2$are recovered from carnallite brines at DEUSA International's Bleicherode, Germany, solution mine by the careful management of brine temperatures and brine magnesium levels. In all cases the processing of brines or salts from solution mining is simplified due to the absence of insoluble materials, which remain underground.

PREPARATION FOR MARKET

The fertilizer market is diverse, and the application of product will vary with crop type and location. As potassium products are generally blended with nitrogen and phosphate, the nature and quantity of contained impurities and the size of the final product are targeted to meet the needs of specific markets. Value-added steps are required to prepare potash concentrates for the diverse needs of the market.

Debrining and Drying

Whether recovered by flotation or crystallization, the recovered potash is a suspension of solids in brine. It must be debrined, dried, sized, stored, and, finally, shipped to the customers. Potash concentrates can be debrined either by centrifuges or vacuum filters. Centrifuges are favored because of their ability to lower the concentrate moisture to a level of 2%–4% versus the range of 6% to 8% moisture obtainable with vacuum filters. Lower cake moistures are preferred as the

Table 7 Chemical composition of commercially extracted brines

	Concentration, g/L					Mass Ratios		
Brine Source	Na	K	Mg	Cl	SO_4	$\frac{K}{Mg}$	$\frac{SO_4}{Cl+SO_4}$	Potash Salts
Dead Sea	35	7	35	190	<1	0.2	0.01	Carnallite
Qarhan Salt Lake	14	22	75	250	5	0.3	0.02	Carnallite
Bonneville	118	7	5	202	4	1.4	0.02	Sylvite
Salar de Atacama	90	22	12	190	23	1.8	0.11	Sylvite, schoenite, kainite
Great Salt Lake	95	7	10	155	20	0.7	0.11	Schoenite, kainite
Lop Nur Salt Lake	—	10	17	180	45	0.6	0.20	Schoenite, kainite

Adapted from Garrett 1996; Fertilizer International 2015

crystallization of soluble salts from the entrained brine will decrease the K_2O grade of the dried product.

Drying of the filtered concentrates is conducted at relatively low temperatures ranging from 150° to 200°C. Product moisture levels are generally less than 0.1% H_2O. Product leaching, brine management, and cake washing are used to control the final product grade. An elevated presence of $MgCl_2$ in brine leads to some deterioration in the free-flowing quality of the dried product. Potash operations use both direct-flow rotary dryers and fluid bed dryers.

Product Sizing and Compaction

Prior to 1957, MOP was sold on the basis of K_2O content only. The fertilizer trade adopted sophisticated practices in the formulation of complete plant foods during this time. With the majority of MOP usage as fertilizer, either applied separately or blended with nitrogen or phosphate products, a standard uniform size was preferred. The product, known as granular muriate, has a firmly established position in bulk blending or dry mixing of nitrogen, phosphorus, and potassium (NPK) fertilizers for direct application to soils.

Because of plasticity, fine particles of potash can be fused together with the application of pressure and without the use of binders and then subsequently broken into granules. Compaction can be an important means of salvaging non-contaminated dusts and fine products by converting them to a readily saleable granular product. Granulation by compaction started in the 1950s and has proven to be an economic size-enlargement process for MOP and other potassium salts (Figure 9). Granular sales in the United States have grown from 8% of total, or 300,000 t, in 1962 to 70%, almost 7,200,000 t in 2013. Granular consumption is greatest in the more mature fertilizer markets such as in the United States and Brazil, and overall represents about 45% of the global market.

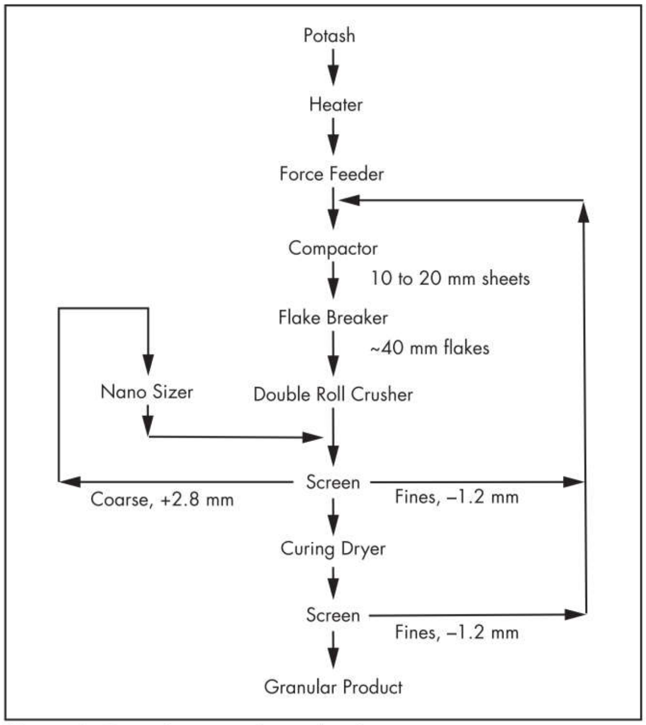


Figure 9 Granular potash production

Storage and Loadout

Since 90%–95% of all potash production is used in agricultural applications, the peak sales and shipping demands occur during the spring and fall crop-planting seasons. The logistics involved in production and movement of millions of tons of potash from mines to market under such conditions suggest the need for large storage facilities at the plant sites. In practice, however, the product storage capacity is limited to about 10%–30% of the annual production by individual plants. The practice is supported with long-term sales contracts calling for steady shipments during the year, off-season export sales, seasonally adjusted price schedules stimulating extra domestic sales in slack periods, and rentals of warehouse space at some marine terminals and strategic inland locations. Fertilizer application rates have dramatically increased due the modernization of farm equipment, and therefore application seasons have been compressed. The establishment of large wholesaler-owned storage and load-out facilities at transportation hubs and warehouse contracts are used to meet just-in-time farm demands.

Normal warehousing practice is to store each product separately, but some producers store several grades in one large structure. Warehouse storage capacity can be comprised of a single structure or multiple structures. With the average size of current operations, most producers have at least 100,000 t of on-site storage. Individual warehouses can range from 60,000 t to 300,000 t. The 526,000-t product warehouse at PCS Rocanville's Scissors Creek is one of the largest reported warehouses. Stored materials can be reclaimed through multiple draw points in the floor slab, partly by gravity, but mostly with the aid of slushers, front-end loaders, or bulldozers. Newer warehouses have eliminated reclaim tunnels and utilize stacker/reclaimers to manage warehouse inventories.

SUPPORT SYSTEMS

In addition to the processing of potash ores, other infrastructural needs and support systems are required in the production of potash. The materials handling and deposition of the nonpotash materials must be appropriately managed, and water, brine, and energy systems must also be managed to minimize costs and to optimize stewardship.

Potash Tailings

In practice, potash tailings are managed in three forms: coarse slurry, fine slurry, and excess brine. The composition of slurries varies depending on the ore type processed and the recovery processes selected. Local regulations, proximity to communities, and climate are major factors that influence the choice in management of tails. Tailings may be slurried to impounded piles, dry stacked in heaps, backfilled in underground cavities, or slurried with fresh or seawater prior to riverine or marine deposition. Excess brines are injected through deep wells into deeper underlying strata or in some cases pumped into rivers or seas. The coarse and intermediate fractions are usually debrined by centrifuges, horizontal rotary filters, or belt filters.

In Saskatchewan, coarse and fine tails are dewatered separately, slurried, and pumped onto separate tailings piles. Slurry transport and deposition is preferred to conveyors. Well injection is used for excess brines that predominantly contain NaCl and $MgCl_2$. German operations have been backfilling underground cavities since 1908. Surface storage of tails is also used in Germany; filtered tails are combined with the dry tails from electrostatic separation and dry stacked in piles using conveyors. Increased pile heights are possible with dry stacking, and Monte Kali, the largest of the salt piles at the time of writing, produced by K+S, is approximately 240 m high. The Belarusian operations also use conveyors to dry stack tails. To manage subsidence, Russian operations backfill tails as slurry; dry stacking of tails is also used. The Boulby mine in England uses a combination of methods for tailing management. Centrifuged coarse tails are repulped with seawater and discharged in the North Sea; the finer tails are slurry backfilled underground.

Brine Systems

Unwarranted losses of brine are detrimental to efficiency of the plant, and the optimum recovery of brine for reuse is of paramount importance. Thickeners or lamella-type settlers are utilized in the recovery and clarification of brine. Producing a high clarity overflow is one of the most important functions in potash operation as a flotation circuit may experience 2%–5% lower recoveries by using brines with higher suspended solids. The thickener underflow usually contains most of the clay, a high proportion of fine NaCl, some fine KCl, and a substantial volume of brine.

Temperature is an important factor in the brine system; cooling of the brine produces partial recrystallization of its components, whereas at high temperatures the brine dissolves additional minerals, decreases flotation efficiency, and increases consumption of reagents. Several methods are used to regulate brine temperatures, such as enclosure in heated buildings, cooling towers, and crystallization–refrigeration systems.

Process Control

Process control and control variables for potash flotation plants are common to other branches of the mineral processing industry. The soluble nature of the ore and its sensitivity to temperature makes online density and mass measurements difficult and complicates accurate mass balances. On-line ^{40}K analyzers are successfully used to determine the potassium content of process streams and readily integrated into process control strategies. In Russia, laser-induced breakdown spectroscopy has been successfully utilized to measure the grade of final product and control product leaching (Groisman and Gaft 2010). Flotation controls such as optical froth monitoring systems to identify bubble properties and mass pull rates are finding a home in several potash operations. Special design considerations should be given to the location, installation and long-term operation and serviceability of belt weightometers as accurate measurements will be required to complete mass balances and to manage product inventories. Process control automation, integrated with recording, reporting, data analysis and data storage has found wide application in potash plants.

Energy

Several energy studies reviewed Canadian potash operations such as Natural Resources Canada through the Canadian Industry Program for Energy Conservation (CIPEC) (Natural Resources Canada 2003) and Canadian Industry Energy End-Use Data and Analysis Center (Nyboer and Bennett 2015). Total energy consumption ranges from 1.1 to 2.3 GJ/t MOP product depending on the scale of the operation, the nature of the process, the age of the plant, and the plant utilization. Natural gas generally makes up about 75% of the energy used. Russian operations report similar rates and distributions. CIPEC reported that nearly 70% of the energy is used in the surface operation, whereas 30% is used underground. Solution mines and plants with thermal leach crystallization are about 2.5–3.5 times more energy intensive and range from 3.0–6.0 GJ/t.

Water

The water requirement for a potash plant also varies, primarily based on the ore mineralogy and process selection. For sylvinite ores, water consumption will increase with carnallite and insoluble content. The efficiency of the brine recovery system and water management practices will also influence water requirements. In a conventional operation the total water requirement is in the range of 2.0–6.0 m^3/t MOP, typically between 3.4 and 4.0 m^3/t. Most operations reclaim the clarified tailings pond brine from transporting slurried tailings, from process use, and from plant housekeeping purposes. Such practices reduce fresh water makeup requirements to 1.5–2.0 m^3/t.

CAPITAL AND OPERATING COSTS

Potash is a capital-intensive business, and the general rule of thumb states that it requires between US$500 and US$1,000 of capitalization per metric ton of annual MOP production to develop brownfields and approximately US$2,000/t for greenfield site costs. PCS regularly reports that a 2.0 Mt MOP/yr greenfield project will require from US$4–$6 billion of capitalization for site costs and support infrastructure (Potash Corporation of Saskatchewan 2014; Fortney 2013). Operating costs are reported by most potash producers, potash analysts, or potash development projects. Significant levels of capitalization were invested over the last decade, significantly reducing operating costs. As with any mineral operation, operating costs vary with ore grades, the scale and nature

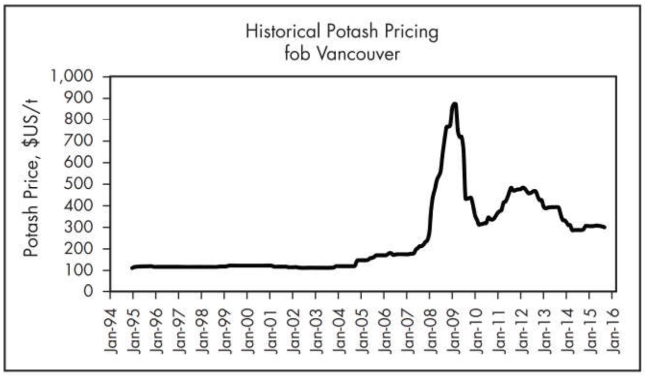


Figure 10 Price for North American potash

of the operation, and by-product credits. Cash operating costs, including royalties and selling, general, and administrative expenses, currently range, in U.S. dollars, from $55/t to $200/t MOP product for approximately 90% of the market. The cash costs for several smaller producers ranges from $200–$330/t.

PRODUCT PRICING

A 10-year pricing trend is presented in Figure 10. Potash products are sold by the ton, either short ton or metric ton, depending on the location of the sale. Sale prices for muriate, sulfates, and sulfates magnesia will depend on the product grade and size. Per-ton pricing is tied to the producers' product specification. Generally, an increased price is commanded for coarser products, such as granular or pellet products, and for increased potassium content. Prices are quoted per short ton or metric ton of product based on a minimum potassium content. This minimum is 60% K_2O for muriate and 50% K_2O for potassium sulfate. Price quotations are usually free-on-board plant sites for domestic shipments or specific ports for export sales. Large volume pricing contracts are annually negotiated with major potash consumers such as China, Brazil, and India, setting the tone for pricing in the rest of the market.

Average potash prices are published in trade publications such as Green Markets, Fertecon, and Argus. The individual potash producers in North America publish their own price schedules and distribute them to their customers. These schedules usually cover the so-called fertilizer year, a period beginning on or about July 1 of one year and ending on June 30 of the following year. Schedules state price differentials for various grades available and include seasonal price adjustments.

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