





Plant Nutrients & Plant Nutrient Products

In this section:

Overview

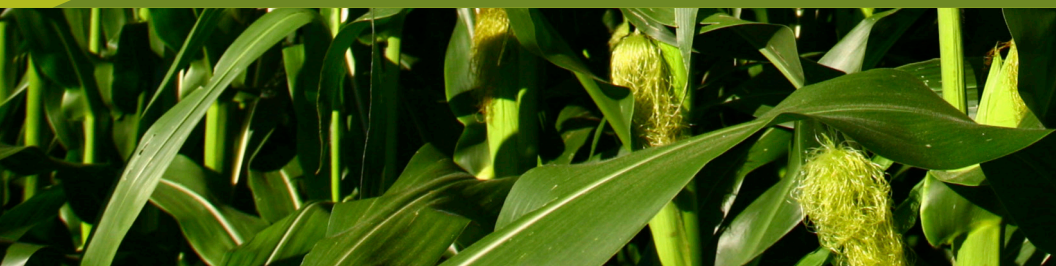
Nitrogen

Phosphate

Potash



Overview



The 17 Elements Required for Plant Growth

1 H																	2 He															
3 Li	4 Be																	10 Ne														
11 Na	12 Mg																	18 Ar														
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr															
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe															
55 Cs	56 Ba																	86 Rn														
87 Fr	88 Ra																	118 Og														
																		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
																		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
																		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Non-Mineral Elements	Macronutrients		Micronutrients	
	Primary	Secondary		
C - Carbon	K - Potassium	Ca - Calcium	B - Boron	Mn - Manganese
H - Hydrogen	N - Nitrogen	Mg - Magnesium	Cl - Chlorine	Mo - Molybdenum
O - Oxygen	P - Phosphate	S - Sulphur	Cu - Copper	Ni - Nickel
			Fe - Iron	Zn - Zinc

Plant nutrients simply are plant food. Just like feed provides the carbohydrates, protein, fat, vitamins and trace minerals required to nourish animals, plant nutrient products deliver the essential nutrients needed to nourish plants.

Plants require seventeen nutrients for optimum growth and development. Each of these nutrients is a chemical element found on the periodic table. Three of the seventeen elements – carbon, hydrogen and oxygen – are non-mineral elements that are available from the atmosphere or water. The other fourteen are classified as primary nutrients, secondary nutrients and micronutrients.

The three primary nutrients – nitrogen (N), phosphorus (P) and potassium (K) – are the carbohydrates, protein and fat of plant diets. Plants remove large amounts of the primary nutrients during the growing season and soils become depleted if these nutrients are not replenished after each harvest.

Calcium (Ca), magnesium (Mg) and sulphur (S) are classified as secondary nutrients while the eight micronutrients include boron (B), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), nickel (Ni), and chlorine (Cl). A deficiency of any one of the 17 nutrients will limit plant growth

The Law of the Minimum

Justus von Liebig, the famous 19th century German chemist who is recognized as the father of plant nutrition, discovered that plants absorb nitrogen and several other elements through their roots. Liebig's Law – also known as The Law of the Minimum – establishes that a deficiency of any one of these nutrients will limit plant growth.

The Law of the Minimum often is illustrated by Liebig's Barrel. This graphic shows that the shortest stave determines the maximum volume of liquid in a barrel. Similarly, a deficiency of a single nutrient will limit plant development and result in suboptimum yields or crop quality. Primary nutrient deficiencies are the most common, but secondary nutrient and micronutrient deficiencies are on the rise.

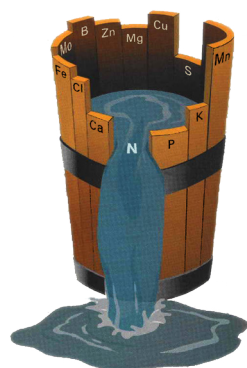
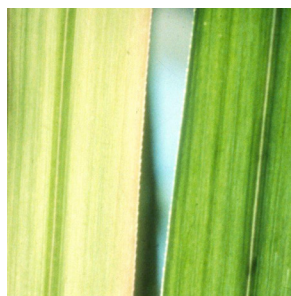


Image: TFI

The Growing Importance of Secondary and Micronutrients

Secondary nutrient and micronutrient deficiencies are occurring more frequently for several reasons. For example, sulphur deficiencies are occurring in many regions due to higher crop yields and thus greater plant uptake, lower sulphur dioxide emissions (acid rain deposited sulphur on soils), and a switch from low-analysis products that contain large amounts of sulphur (e.g. single superphosphate) to high-analysis products that contain little or no sulphur (e.g. diammonium phosphate).

Zinc deficiencies also are occurring more frequently, especially in the developing world. Recent studies indicate that as many as one-fourth to one-third of the world's population is at risk of hypozincemia – a debilitating disease caused by insufficient amounts of zinc in the diet. One way to increase dietary zinc, particularly in the developing world, is to apply zinc to deficient soils in order to boost the amount of this nutrient in the edible portion of food crops such as wheat, rice and legumes



Sulphur Deficiency (Left)

Maintaining Soil Fertility

Most of the 17 nutrients required for optimum plant growth are absorbed from the reservoir of nutrients in the soil or from what agronomists call the soil solution. Crops remove large amounts of nutrients over the course of a growing season. For example, corn that yields 200 bushels per acre removes 310 pounds of primary nutrients per acre just in the grain that is hauled from the field. Wheat that yields 80 bushels per acre removes 195 pounds of primary nutrients per acre in the grain taken off the field. Farmers at a minimum must replace these nutrients in order to keep the reservoir charged and maintain soil fertility.

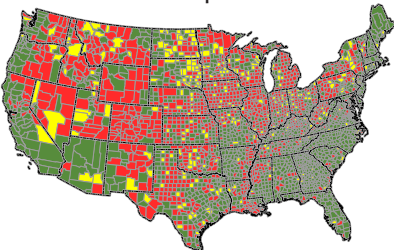
Steady yield increases mean that crops are removing more nutrients from soils each year. Yet many farmers continue to apply nutrients, especially phosphorus and potassium, at recommended rates that were developed years ago. A comprehensive analysis by the International Plant Nutrition Institute (IPNI) concludes that crops have removed more phosphorus and potassium than were applied to soils in the form of plant nutrient products and manure in many parts of the United States during the past several years. Nutrient management practices no doubt have improved over time due to advances such as the development of precision agriculture technologies, but this study indicates that U.S. farmers are mining phosphate and potash from their soils in many parts of the country.

Nutrient Removal by Crop

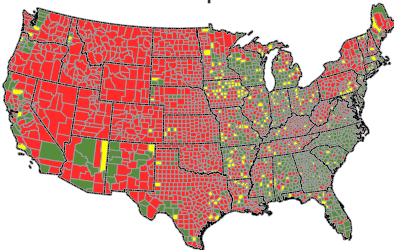
lbs Acre	N	P ₂ O ₅	K ₂ O	S
Corn - 200 Bu Acre Yield				
Grain	180	76	54	16
Stalks	90	32	220	14
Total	270	108	274	30
Soybeans - 70 Bu Acre Yield				
Grain	266	59	91	13
Stover	77	17	70	12
Total	343	76	161	25
Wheat - 80 Bu Acre Yield				
Grain	120	48	27	8
Straw	56	13	96	11
Total	176	61	123	19

Source: IPNI

P Nutrient Balance Map



K Nutrient Balance Map



Nutrient inputs for 2007

Nutrient removal average of 2006 - 2008

Source: IPNI and PAQ - NuGIS Project

- Removal less than nutrient replacement
- Removal approx. equal to replacement
- Removal exceeds nutrient replacement

Safeguarding the Environment

Managing nutrients in the soil solution is not an easy task thanks to the vagaries of Mother Nature. Farmers seek both to keep the soil solution charged with enough nutrients to optimize yields as well as to guard against losses of costly nutrients due to leaching and run-off – all without knowing what Mother Nature might deliver in terms of rainfall and other conditions that impact nutrient losses.

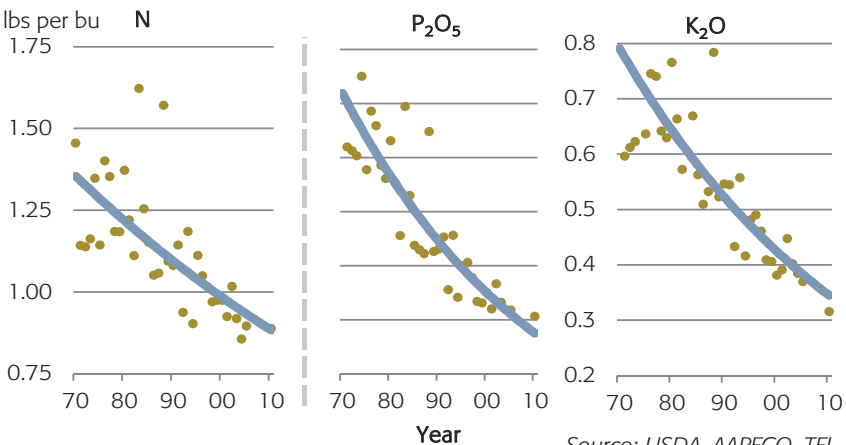


IPNI has developed a program to help farmers maintain soil fertilizer and safeguard the environment by ensuring that the soil solution is charged with nutrients from the right source, at the right rate, in the right place and at the right time. IPNI has labeled these the 4-Rs of nutrient stewardship. Execution of the 4-Rs includes best practices such as regular soil testing, accurate estimates of nutrients removed by crops, a full accounting of nutrients added by crop rotations or manure applications, balanced nutrient use, variable rate application, split applications and the use of nitrogen inhibitors or slow-release products.

The efficacy of plant nutrient use has increased significantly in the United States during the last few decades. For example, U.S. Department of Agriculture (USDA) data show that U.S. corn yields nearly doubled from 79 bushels per acre in 1970 to 157 bushels per acre in 2010. Yet primary nutrient application rates remained flat at 230 pounds per acre during the same period.

Nitrogen use per bushel of corn harvested has declined one-third from roughly 1.35 pounds in the first half of the 1970s to less than 0.9 pounds in 2010. Phosphorus and potash use per bushel of corn dropped nearly 60% from about 0.7 pounds to 0.3 pounds during the same period. The use of animal manure and other recycled materials has increased during this period, but U.S. farmers today are harvesting twice as much corn per acre using approximately the same amount of plant nutrients as in 1970.

U.S. Nutrient Use Efficiency on Corn



Source: USDA, AAPFCO, TFI

Vital Role of Plant Nutrients in Feeding the World

Modern plant nutrient products play a vital role in food production. In fact, agronomists estimate that plant nutrients account for 40% to 60% of crop yields. Plant nutrient products are a key component of a bundle of increasingly sophisticated inputs required to achieve the higher yields needed to feed the world.

No one understood this better or communicated it more effectively than Dr. Norman Borlaug. Borlaug, widely acclaimed as the Father of the Green Revolution, developed disease resistant and high yielding wheat varieties that are credited with saving hundreds of millions of people from starvation in the 1960s and 1970s. Beginning in 1944, Borlaug labored for 10 years breeding rust resistant cultivars at a research institute in Mexico. He then crossed these strains with a Japanese dwarf variety to produce hardy wheat varieties that, given sufficient water and plant nutrients, boosted yields almost three-fold.



Norman Borlaug
(1914 - 2009)

"Farmers can feed the world. Better seeds and fertilizer, not romantic myths, will let them do it."

Wall Street Journal
July 30, 2009

"This is a basic problem – to feed 6.6 billion people. Without chemical fertilizer, forget it. The game is over."

New York Times
April 30, 2008

Dr. Norman Borlaug
Nobel Peace Prize Laureate

The new varieties saved wheat production in Mexico and spawned the Green Revolution in Asia. India's wheat output doubled from 12 million tonnes in 1965 to 24 million tonnes in 1975. Wheat production in Pakistan also doubled during this period. Both countries had suffered deadly famines in the early 1960s and veterans of the Green Revolution joyfully recount how the countries frequently ran out of jute bags to store the bountiful harvests.

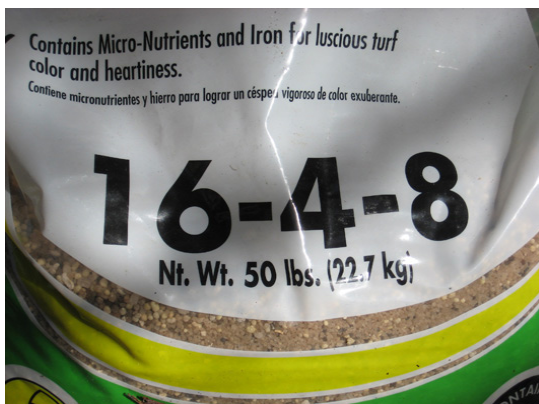
Borlaug, the strong farm boy (and accomplished wrestler) from Cresco, Iowa and a proud graduate of the University of Minnesota, won the Nobel Peace Prize in 1970 for the development of these new varieties as well as his tireless efforts to convince farmers to adopt this new technology. Time magazine named him one of the top 100 influential minds of the 20th century. Borlaug was driven by his strong conviction that it is impossible to build a peaceful world on empty stomachs.

Photo Source: Patrick O'Leary and University of Minnesota

Plant Nutrient Products

The three primary nutrients are contained in more than a dozen widely used commercial products just like carbohydrates, protein and fat are found in a variety of animal feeds. These commercial products contain one or more of the three primary nutrients. In fact, plant nutrient products are uniquely identified by three numbers that indicate the analysis or percentages of each primary nutrient in a unit of the product. For example, a bag of lawn fertilizer may show an analysis of 16-4-8 on its label. These numbers indicate that the product contains 16% nitrogen (N), 4% phosphorus expressed as available phosphorus pentoxide (P_2O_5) and 8% potassium expressed as soluble potassium oxide (K_2O).

So, this 50 lb. bag contains 8 pounds of N, 2 pounds of P_2O_5 and 4 pounds of K_2O . If a homeowner spreads the contents of this bag on a lawn that is one-tenth of an acre then the application rates are 80 pounds of N, 20 pounds of P_2O_5 and 40 pounds of K_2O per acre. By comparison, farmers in the Corn Belt apply roughly 150 pounds of N, 70 pounds of P_2O_5 and 60 pounds of K_2O on an acre of corn.



Some of the most widely used commercial plant nutrient products are anhydrous ammonia (82-0-0), urea (46-0-0), ammonium nitrate (34-0-0), urea-ammonium nitrate solution or UAN solution (28-0-0 to 32-0-0) ammonium sulphate (21-0-0), diammonium phosphate or DAP (18-46-0), monoammonium phosphate or MAP (11-52-0), ammonium polyphosphate solution or APS (10-34-0), single superphosphate or SSP (0-20-0), NPK compounds (numerous analyses such as 15-15-15) and muriate of potash or MOP (0-0-60).

The physical characteristics of these products differ greatly. For example, anhydrous ammonia is a gas at normal temperatures and pressures. UAN solution and APS are liquids. Urea, ammonium nitrate, ammonium sulphate, DAP, MAP, SSP and MOP are solid granules. A few of these solid products likely were physically blended together to make the lawn fertilizer.

Distribution and Application



The distribution and application of plant nutrient products vary around the world. For example, in India, nearly all plant nutrient products are distributed in 50 kilogram polypropylene-lined bags. We estimate that Indian plant nutrient shipments totaled about 54 million tonnes in 2012/13, so that means almost 1.1 billion bags of plant nutrient products moved from domestic production and port facilities through tens of thousands of wholesale and retail distributors to Indian farmers.

A small-scale Indian farmer typically buys several bags of urea, DAP, MOP or NPK compounds and applies these products either by hand or with a small mechanical spreader. By contrast, a large-scale U.S. farmer typically buys several hundred tonnes of bulk products and hires the retail dealer to custom apply these materials with large and sophisticated application equipment.

The distribution and application of plant nutrient products generally evolves as the agricultural sector develops, land holdings consolidate and plant nutrient use increases. First, high-analysis products replace low-analysis products. This shift reduces the cost of storage, shipping and handling. For example, a high-analysis product such as MAP (11-52-0) contains three times more nutrients than SSP (0-20-0), so distributors can transport and store almost two-thirds less product and still deliver the same amount of primary nutrients (SSP contains significant amounts of sulphur, however). Second, large one-tonne bags and then bulk distribution typically replace 50 kilogram bags resulting in significant logistics and transportation cost savings. Third, custom application by retail crop input dealers using large scale and sophisticated equipment replaces application by the farm operator using small scale and less sophisticated equipment. Finally, variable rate replaces constant rate application. Brazil provides the best example of a country undergoing this transition today.



Nitrogen



Nitrogen and Plant Nutrition

Nitrogen plays a vital role in plant development. This element is a key component of chlorophyll – the green compound that powers photosynthesis and enables a plant to absorb light energy and convert carbon, hydrogen and oxygen into the simple sugars needed for growth. Nitrogen also is an essential constituent of amino acids, the building blocks of protein. Grain formation depends on achieving threshold levels of protein within a plant, so yield and grain quality are closely tied to nitrogen availability.

Given the vital role of nitrogen, it is no surprise that the dry organic matter of most plants contain roughly three times more nitrogen than any other mineral element except potassium, and the grain of most crops contains more nitrogen than all of the other mineral elements combined. Symptoms of nitrogen deficiency include stunted growth and pale green or yellow leaves due to low chlorophyll levels. Nitrogen deficiencies result in low yields and low protein content in grain. There are no substitutes for nitrogen in a plant's diet.



Ammonia Tank



Granular Urea



Nitrogen Deficiency

Plants absorb nitrogen through their roots mostly in the form of ammonium (NH_4^+) or nitrate (NO_3^-) ions. Soil microorganisms convert nitrogen from plant nutrient products as well as other sources into these forms if the nutrient is not initially available as ammonium or nitrate. This conversion occurs quickly, and these ions are highly mobile in the soil solution.

Nitrogen Soil Science

This soil chemistry has several important implications. First, it helps to diffuse the “organic” versus “chemical” debate – at least with respect to plant nutrition. Plants are agnostic – they cannot distinguish whether an ammonium or nitrate ion came from soil organic matter, hog manure or a commercial product such as anhydrous ammonia, urea or urea-ammonium nitrate solution.

Second, in the case of these two highly mobile ions, plants must “use ‘em” or “lose ‘em” over the course of a growing season. As a result, farmers must apply nitrogen to crops every growing season.

Third, soils are susceptible to nitrogen losses due to extreme environmental conditions or poor management practices. For example, excessive rainfall can cause nitrates to leach into the subsoil and out of the plant’s root zone, or the failure to properly incorporate nitrogen products into the soil may result in volatilization into the atmosphere.

Finally, one of the most important objectives of best management practices (BMPs) is to make sure nitrogen is available from the right source, at the right rate, in the right place and at the right time in order to adequately nourish the plant yet minimize losses to the environment. Those practices may include split or multiple applications and the use of inhibitors or controlled release products that provide a steady supply of nitrogen to the plant throughout the entire growing season.



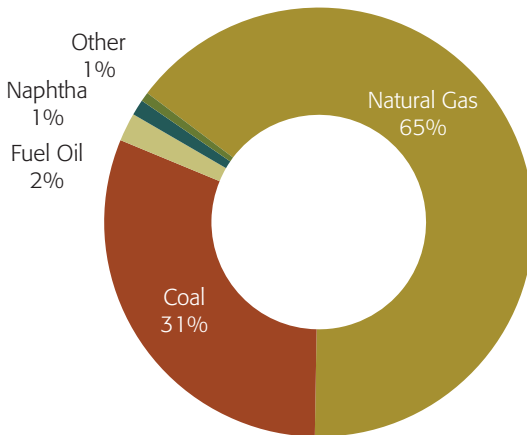
An Overview of Nitrogen Production

Nitrogen is abundant in the atmosphere. In fact, the atmosphere is about 78% nitrogen, and that means approximately 37,000 tons of nitrogen hover over each acre of the earth's surface. Unfortunately, plants cannot utilize tightly bonded inert nitrogen (N_2) from the atmosphere. Rather, nitrogen must be fixed to another element – usually hydrogen – and then applied to the soil in order for plants to absorb this vital nutrient from the soil solution.

The production of nearly all nitrogen products begins with the synthesis of ammonia (NH_3) from atmospheric nitrogen and hydrogen. The synthesis of ammonia was first achieved by Fritz Haber in 1909 and commercialized by Carl Bosch in 1913.

The production of ammonia is energy intensive because hydrocarbons are used both as a feedstock as well as a source of the considerable energy needed in the process. The production of synthesis gas as well as the synthesis of ammonia occurs at extremely high temperatures and pressures using iron, nickel and other catalysts. Natural gas is the most widely used hydrocarbon, but coal, naphtha and fuel oil are utilized in some regions such as China and India where these resources are more abundant and cost less than natural gas.

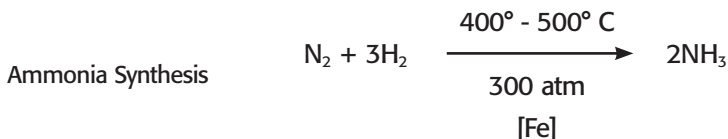
Ammonia Feedstock



Source: IFA
Average 2009-2013

Ammonia Production from Natural Gas

About two-thirds of global ammonia output is produced from natural gas. This process involves two stages – the production of synthesis gas and the synthesis of ammonia. The first stage utilizes natural gas, steam, air and several catalysts to yield a purified stream of hydrogen and nitrogen gas – or synthesis gas – that is fed into the ammonia synthesis loop where the Haber-Bosch reaction takes place. Frankly, the first stage is more complicated than the second and accounts for the bulk of the physical plant and capital investment in an ammonia plant.



The production of synthesis gas involves several steps. First, traces of sulphur are removed from the natural gas (CH_4 or methane) because sulphur poisons or renders catalysts ineffective.

Second, the de-sulphurized methane is fed into the primary reformer where it is mixed with steam (H_2O) that is pre-heated to temperatures in the 315°C to 425°C range. This mixture then moves through long vertical tubes in the primary reformer that contain nickel catalysts. Chemical reactions in the primary reformer occur at temperatures as high as $1,400^\circ\text{C}$ and convert the gas and steam into hydrogen (H), carbon monoxide (CO) and carbon dioxide (CO_2). However, chemical reactions here are not complete so the effluent gas from the primary reformer still contains unconverted methane.

Third, the effluent gas from the primary reformer then moves into the secondary reformer where compressed air is injected into this stream. Here oxygen combines with some of the hydrogen and this exothermic reaction provides the heat needed to power the breakdown of the remaining methane. The effluent gas from the secondary reformer now contains nitrogen (N) and steam in addition to hydrogen, carbon monoxide and carbon dioxide.

The final step is to purify the gas stream from the secondary reformer by removing the carbon monoxide and carbon dioxide. This is achieved by first converting carbon monoxide to carbon dioxide through low and high temperature shift conversions and then removing the carbon dioxide via standard scrubbing processes.

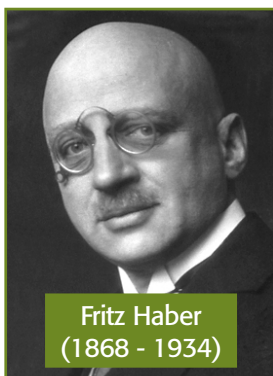
This purified stream or synthesis gas consists of three moles of hydrogen and one mole of nitrogen and is ready for the ammonia synthesis loop where the Haber-Bosch reaction takes place. The second stage of this process – the synthesis of ammonia – is almost anti-climactic. Nevertheless, ammonia is produced by circulating the gas around the synthesis loop that is charged with iron oxide catalysts. The reaction occurs under extremely high pressures and temperatures, but the chemistry is exactly the same as that discovered by Fritz Haber in 1909.

The Haber-Bosch Process

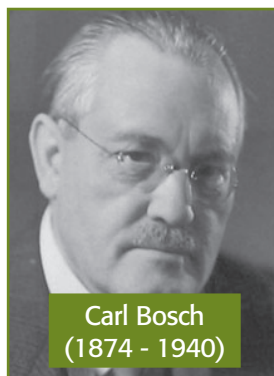
The scientific community has hailed the Haber-Bosch process for the synthesis of ammonia as one of the most important discoveries of the 20th century. The process was developed and commercialized by two German chemists, Fritz Haber and Carl Bosch, during the early decades of the last century. Haber is credited with developing

the theory and achieving the first synthesis of ammonia in a laboratory in 1909. He was awarded the Nobel Prize in Chemistry in 1918 for this discovery.

BASF, the large German company and mainly a producer of dyes at the time, purchased the rights to this new process and charged Bosch with the formidable task of commercializing it. Bosch's biggest challenge was developing the high pressure vessels required for large scale and continuous production of ammonia. He and his team succeeded, and the first commercial production took place at Oppau, Germany in 1913. The plant produced about 30 tonnes of ammonia per day, but unlike modern facilities that use a hydrocarbon feedstock, this plant utilized the electrolysis of water as the source of hydrogen. Bosch shared the Nobel Prize in Chemistry in 1931 for his work on developing high pressure vessels that are widely used in several chemical processes today.



Fritz Haber
(1868 - 1934)



Carl Bosch
(1874 - 1940)

"Without ammonia, there would be no inorganic fertilizers, and nearly half the world would go hungry. Of all the century's technological marvels, the Haber-Bosch process has made the most difference to our survival."

Vaclav Smil
Nature
July 29, 1999

If Haber and Bosch were the fathers of this important invention, necessity was its mother. At the time, saltpeter (potassium nitrate) was the leading plant nutrient product as well as the main ingredient in gun powder. The world relied on dwindling supplies from Chile's Atacama Desert. British scientists had warned of the consequences of an impending shortage on wheat yields, and Allies had cut off Germany from this important raw material for the production of munitions during World War I. The oxidation of ammonia provided

a new source of both nitrogen fertilizer and explosives. In fact, most of the output from the Oppau plant was used to produce munitions during World War I. Some historians argue that without this new source of firepower, Germany would have had to surrender as early as 1916 rather than in 1918.

The Haber-Bosch process has produced nearly all of the nitrogen used by farmers during the last 100 years as well as many of the explosives used by the military and mining industries. Haber and Bosch are credited with discovering and commercializing a process that has enabled the world to feed more than 7.0 billion people today and also has resulted in the loss of millions of lives.



2

3

4

1

Control Room

Faustina Ammonia
Plant
St. James, LA

1. Gas De-sulphurization
2. Primary Reformer
3. Secondary Reformer
4. Shift Conversion
5. CO₂ Removal
6. Ammonia Synthesis

Compressor
Building

5

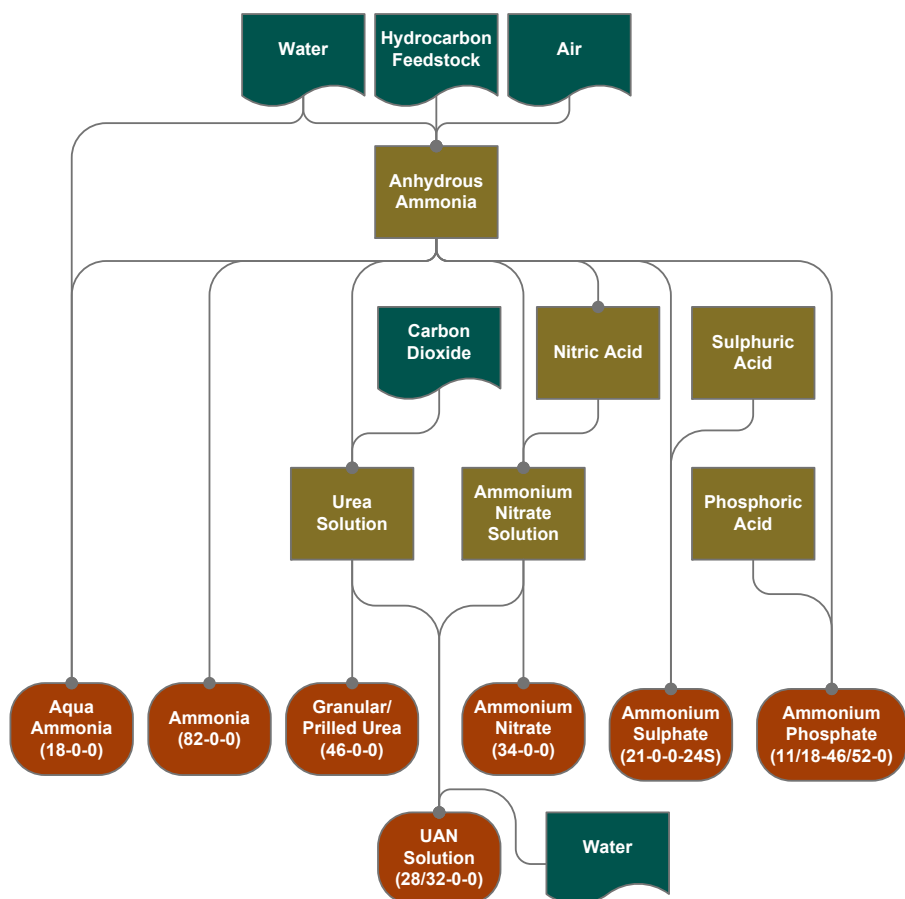
6

How Energy Intensive is Ammonia Production?

The Fertilizer Institute's 2012 annual cost of production survey shows that the average large-scale U.S. ammonia plant produced more than 566,000 tons of anhydrous ammonia and used 33.0 million Btu of natural gas per ton of ammonia. Of this total, approximately 21.5 million Btu or almost two-thirds were used as a feedstock and the rest were used to run the process.

The typical U.S. ammonia plant used about 18.7 billion cubic feet (BCF) of gas in 2012 (one million Btu equals one thousand cubic feet of natural gas). A typical home in Minneapolis burns about 140 thousand cubic feet of gas per year. Thus, the annual gas usage by an average U.S. ammonia plant could supply nearly 134,000 homes in Minneapolis with natural gas for a year. Alternatively, the annual amount of gas burned by a single home in Minneapolis would produce 4.2 tons of ammonia – or enough to fertilize about 46 acres of corn in Southern Minnesota.

Nitrogen Production Process Flow



The nitrogen content of plant nutrient products is measured in units of nitrogen (N).

Ammonia is the building block for nearly all other nitrogen products, but it is also used as a direct application product and for the production of a variety of industrial products. In fact, more than 80% of global gross ammonia output is utilized for the production of downstream nitrogen products. About 15% moves into the industrial market, and less than 5% is used as a direct application product. Just a few countries use anhydrous ammonia as a direct application material due to the specialized equipment required to transport, store and apply it.

Anhydrous Ammonia (82-0-0) Anhydrous ammonia is a high-analysis nitrogen product that is used as a direct application material mainly in North America. Ammonia is a gas at normal temperatures and pressures, and it is stored and transported as a liquid either under pressure or in refrigerated vessels. Farmers utilize specialized applicators to knife ammonia deep into the soil where it then turns into gas. Losses are minimal as long as soil temperatures are less than 50°F and soil moisture is

adequate to seal application cuts. Ammonia is a low cost source of nitrogen in markets with specialized distribution infrastructure and application equipment. For example, underground pipelines connect nitrogen plants in the southern United States to ammonia terminals in the heart of the Corn Belt. Its 82% nitrogen content more than offsets the higher costs of storage, transportation and application in areas near production facilities or distribution terminals. However, rapidly escalating costs for freight, regulatory compliance and liability insurance have eroded its advantage over other nitrogen products during the past several years in North America.

Urea (46-0-0) Solid urea is the most widely used nitrogen product in the world. Urea solution first is produced by reacting anhydrous ammonia with carbon dioxide (CO_2) at high pressures. Solid urea then is formed by using standard prilling or granulation processes. Granular urea granules are larger and harder than prilled urea granules. Granular urea often is mixed with phosphate and potash products to make blends that are tailored to meet specific soil and crop requirements. Prilled urea typically is applied directly on crops such as rice and wheat that often require multiple doses of nitrogen during the growing season in order to achieve optimum yields.

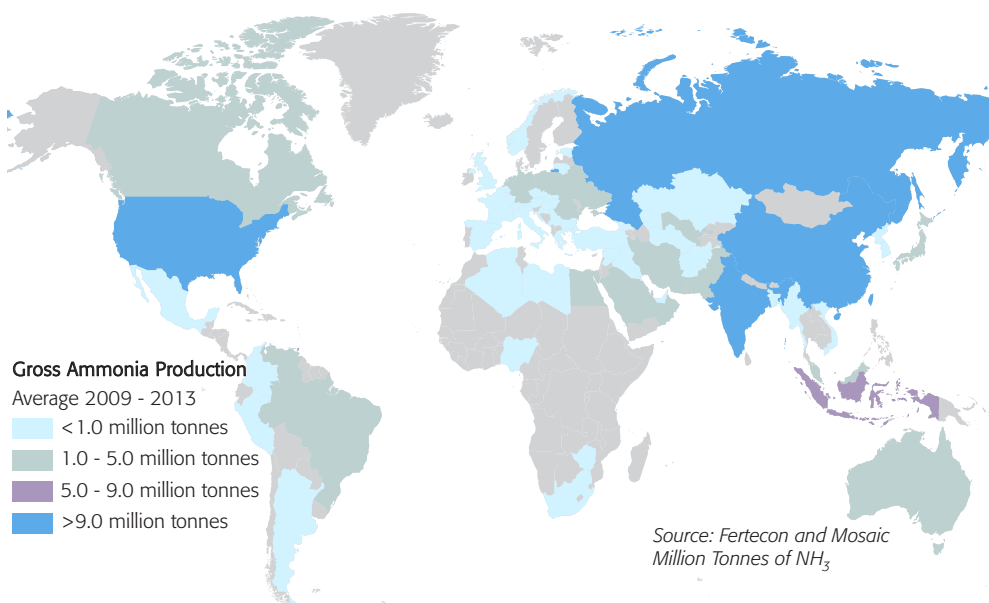
Ammonium Nitrate (34-0-0) Ammonium nitrate solution is produced by reacting anhydrous ammonia with nitric acid. Nitric acid is manufactured by oxidizing ammonia at high temperatures and in the presence of a platinum catalyst. The resulting gas is absorbed in water to form nitric acid. Solid ammonium nitrate also is produced using standard prilling or granulation processes. High-density grade is used as a plant nutrient product, while low-density grade, one that is porous and can absorb more fuel oil, is utilized as an explosive.

Urea Ammonium Nitrate (UAN) Solution (28/32-0-0) UAN solution is the most widely used liquid fertilizer worldwide. UAN solution is produced by combining urea solution, ammonium nitrate solution and water. It contains 28% to 32% nitrogen. UAN solution is an ideal fertilizer for no-till or reduced tillage operations as well as for irrigation systems. UAN solution also provides a good medium for the application of secondary and micronutrients. The distribution of UAN solution also requires specialized infrastructure and equipment for the storage, transportation and application of a product that contains 68% to 72% water.

Ammonium Sulphate (21-0-0-24S) Ammonium sulphate is produced by reacting anhydrous ammonia with sulphuric acid. Nearly all of the ammonium sulphate produced today is a by-product of caprolactum production, coal coke ovens or smokestack scrubbing processes. The nitrogen content of ammonium sulphate is relatively low at just 21%, but the product typically contains 24% sulphur, an important and increasingly deficient secondary nutrient in many regions.

Ammonium Phosphate & Nitrophosphate Compounds Ammonium phosphate products such as diammonium phosphate (DAP) and monoammonium phosphate (MAP) are produced by reacting anhydrous ammonia with phosphoric acid. Nitrophosphate compounds are produced by reacting nitric acid and phosphate rock. These products account for a significant percentage of nitrogen use worldwide, but they are described in more detail in the phosphate section.

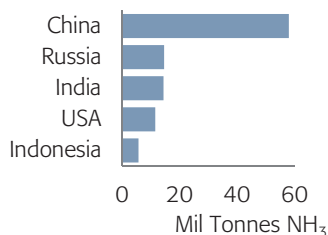
Global Gross Ammonia Production



The importance of nitrogen is evident in plant nutrient statistics. For example, global nitrogen use for agricultural purposes is almost three times greater than phosphorus use and nearly four times greater than potassium use.

Nitrogen is produced in many countries due to the widespread availability of hydrocarbon feedstock. In fact, ammonia was produced in nearly 70 countries, and gross output exceeded 175 million tonnes NH_3 in 2013, according to statistics from Fertecon.

Ammonia Production 2013

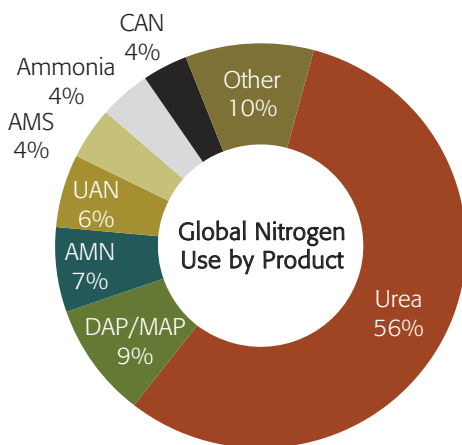


Source: Fertecon and Mosaic

China is the largest nitrogen producer by a wide margin and accounted for 33% of global ammonia output in 2013. At least 60% of China's ammonia is produced from coal, mostly in hundreds of small to medium scale facilities scattered throughout the country. Russia ranked second and accounted for 8% of world production. India (8%), the United States (7%) and Indonesia (3%) rounded out the top five producing countries in 2013.

U.S. gross ammonia production in 2013 was just two-thirds of its peak in 1998. About two dozen nitrogen facilities closed during the last 15 years due to the increase in the relative cost of domestic natural gas. Today, the United States relies on imports for about two-thirds of its agricultural and industrial nitrogen needs. However, the recent development of large shale gas supplies has lowered U.S. natural gas costs relative to other producers and has spawned a renaissance of the U.S. nitrogen industry.

The Leading Nitrogen Products



Source: Fertecon, CRU and Mosaic
Average 2009-2013

Urea is the most widely used nitrogen product in the world, accounting for 56% of global nitrogen use from 2009 through 2013.

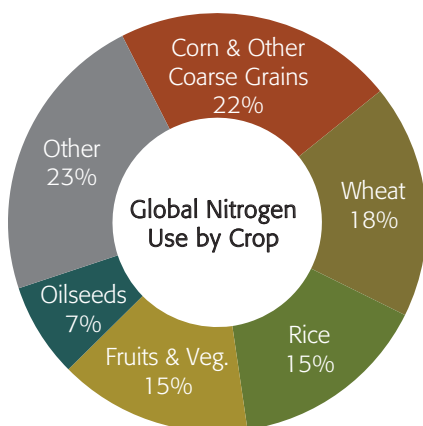
All of the remaining nitrogen products registered single digit percentages during this period, but some of these products are much more important in certain countries or regions. For example, direct application ammonia and UAN solution account for roughly one-quarter and one-third of U.S. nitrogen use, respectively, and are dominant sources of nitrogen in the Corn Belt.

Nitrogen Use by Crop

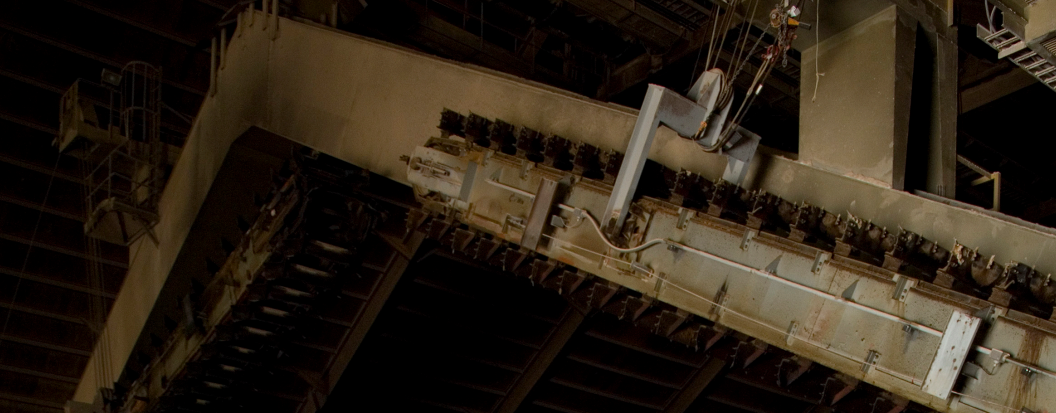
Grains including wheat, rice and corn account for 55% of global nitrogen use, according to the most recent estimates by the International Fertilizer Industry Association (IFA). Fruits and vegetables account for another 15% of world use.

These percentages differ significantly by country based on crop mix. For example, fruits and vegetables claim 30% of total nitrogen use in China. Rice and wheat combined account for more than one-half of nitrogen use in India, while corn captures almost one-half of nitrogen use in the United States.

The amount of nitrogen needed for optimum growth also varies by crop. For example, corn requires about 0.9 pounds of nitrogen per bushel, while wheat and canola require 1.5 and 1.9 pounds per bushel, respectively.



Source: IFA
Use in 2010/11



Phosphate



Phosphorus and Plant Nutrition

Phosphorus often is called The Energizer because it is a critical component of several “battery packs” that power plant growth and development. For example, phosphorus is an important compound in enzymes that control the production, transfer and storage of sugars throughout a plant. As a result, phosphorus is essential for the delivery of the large amounts of sugars required for early root development and seed formation. Phosphorus also is an important component of nucleic acids. These make up the DNA and RNA that direct complex processes such as cell division and protein synthesis.

Symptoms of phosphorus deficiency in plants include stunted growth, fewer or smaller leaves, overly green or purple leaves, delayed maturity and a lack of flowers or fruit. Purple leaves are a common symptom and indicate a build-up of sugars at the point of photosynthesis. There are no substitutes for phosphorus in a plant's diet.



Dragline Bucket



Granular DAP

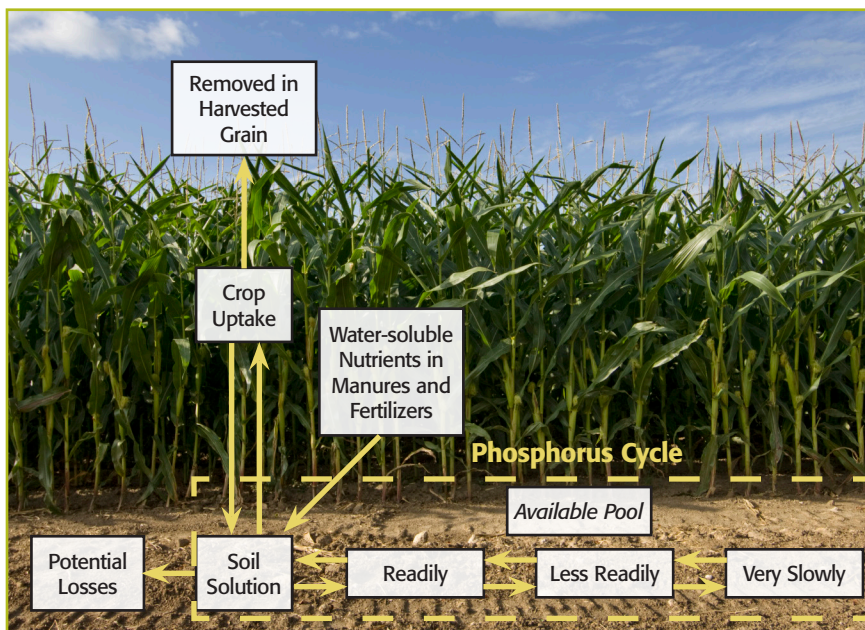


Phosphorus Deficiency

The soil chemistry of phosphorus is more complex than that of nitrogen and other mineral elements. Plants absorb phosphorus from the soil solution in the form of orthophosphate ions, and dihydrogen phosphate (H_2PO_4^-) is the common form in most soils. Several reactions occur when phosphorus is applied to a soil. Water soluble phosphorus from plant nutrient products initially breaks down into orthophosphate ions in the soil solution and is readily available to plants.

Orthophosphate ions, however, differ from ammonium and nitrate ions in two important ways. First, orthophosphate ions typically are immobile in the soil solution. Once applied, phosphorus stays in the field as long as the soil remains there. As a result, phosphorus will carry over from one growing season to the next if not taken up by a plant. Most phosphorus losses occur as a result of soil erosion, so best management practices include the use of reduced or minimum tillage and buffer strips to reduce soil losses.

The Phosphorus Cycle



Second, orthophosphate ions are highly social creatures. While they may not move far in the soil, these ions bond quickly with other minerals such as aluminum, calcium and iron or with organic matter to form compounds that are less soluble and eventually less available to a plant. The chemical and physical characteristics of soil such as its pH, organic matter, moisture, temperature and compaction determine how much, how quickly and how tightly phosphorus will bond with other elements and become unavailable to a plant.

Fortunately, these bonds do not last forever, and the compounds eventually release phosphorus back into the soil solution as a result of other chemical reactions over time. This cycling of phosphorus from readily available to less available to unavailable and back occurs over several years.

Best management practices include frequent soil testing to measure available phosphorus, maintaining proper soil pH, building up soil organic matter and using sound tillage and application methods. Many farmers build available phosphorus to adequate levels in their soils and then simply replace the amount removed by the crop each year in order to keep the cycle intact. Skipping phosphorus application for a year or two may not greatly jeopardize yields if there is sufficient phosphorus that will become available from past applications. However, skipping an application or two breaks this cycle and will reduce available phosphorus in future years. As a result, larger applications may be required at that time in order to supply the amount of available phosphorus needed by a crop.

Phosphate Production - It Begins with Rock

Phosphorus is produced from phosphate rock, a mineral ore found in both marine sedimentary deposits as well as igneous formations. Large deposits of economically recoverable rock are found in a small number of regions such as North Africa, Western China, Central Florida and the Kola Peninsula of Russia.

Sedimentary ores are mostly horizontal deposits near the earth's surface. These deposits are mined with large draglines using traditional surface-mining methods. Igneous formations are mostly vertical deposits formed by ancient volcanic activity and are mined using conventional open-pit or underground mining techniques. Sedimentary deposits are more common and account for about 90% of global phosphate rock production today.



Cockpit of Dragline - South Fort Meade, FL

In Florida, the mining of sedimentary ore begins by removing 30 to 40 feet of overburden. Massive electric-powered draglines then scoop the soft ore and dump it into an earthen sump where it is blasted with water cannons to form a slurry. The slurry then is pumped through above ground pipelines to a beneficiation plant.

Sedimentary ores contain a mix of sand, clay and phosphate rock. The beneficiation process separates the sand and clay from the phosphate rock. For some ores, phosphate rock is separated by simple and low cost washing and screening processes. For most ores, however, in addition to washing and screening more complicated but widely used flotation processes are needed to separate fine clay and sand particles from the phosphate rock. The sand is pumped back to the mining area where it is put into the mine cut. The clay is pumped to a settling pond where it settles to the bottom over time. Beneficiated rock is then sent to chemical plants for processing into finished phosphate products.

Before the First Bucket

The mining of surface ores with large draglines disturbs the land and creates unsightly landscapes. In the United States, long before the first bucket of ore is scooped out of the earth, a reclamation plan is in place that details how the mining company will restore the land to a state as good as or better than its original use.

The mining company works with regulatory authorities at local, state and federal levels to develop the reclamation plan. This plan documents land conditions prior to mining such as its topography, watershed, vegetative cover, wildlife populations and commercial uses and prescribes the programs and timeline to reclaim the land after it is mined.

The reclamation plan is one of the critical pieces required to obtain a mining permit and may take several years to complete. For example, vegetation may need to be documented or wildlife populations may need to be counted and tracked over multiple years.

In Florida, phosphate companies have restored mined areas to a variety of uses such as wetlands, wildlife habitats, citrus groves, pastureland, pine tree plantations, parks, golf courses and housing developments. In some cases, reclamation has rectified environmental damage that occurred prior to mining through the restoration of wetlands or the elimination of invasive species.



A Mud Business

The production of phosphate is more complex than the production of nitrogen or potash. In fact, some engineers refer to phosphate as a “mud business” because what comes out of flotation cells at the beneficiation plant or what goes into a granulation plant looks a lot like a mixture of dirt and water!

The comparison to nitrogen is stark. Nitrogen production is energy intensive and requires highly sophisticated equipment, but the chemistry is simple and precise. That is not the case with phosphate. The chemical reaction that strips calcium from phosphorus is greatly impacted by the characteristics of the mineral ore, and phosphate rock even from the same mine may vary significantly in terms of its phosphate content and amounts of trace minerals such as aluminum, magnesium and iron. Processing it efficiently or getting the recipe right is a bit of art as well as science. Human capital often is just as important as physical capital in this “mud business.”

Phosphate Production – Stripping the Calcium

Oil refineries “crack” the petroleum molecule. Soybean processors “crush” the oilseed. Phosphate chemical plants “strip” calcium from phosphate rock. That is because the phosphorus in the beneficiated ore is bonded tightly to calcium, making it water insoluble and therefore unavailable to plants. So, the simplest non-technical description of what takes place at these sprawling complexes is that the bond between calcium and phosphorus is broken in order to make plant nutrient products that contain water soluble phosphate.

The most widely used method of breaking this bond or stripping calcium from phosphorus is to grind the rock into a powder-like consistency and then attack it with either sulphuric or nitric acid. With the exception of a few plants mainly in Europe and Russia, most processes utilize sulphuric acid.

Sulphuric acid “strips” calcium from the phosphate rock. This reaction produces phosphoric acid, an intermediate product used to manufacture nearly all high-analysis phosphate products, and calcium sulphate. The calcium sulphate is an impure form of gypsum (called phosphogypsum) that has no economic value today and is stacked at production sites in the United States.

Phosphogypsum is considered a byproduct, but in reality the main chemical reaction is the crystallization of phosphogypsum during this process. So, the chemistry makes phosphoric acid look more like the byproduct of the crystallization of phosphogypsum!

High-analysis or concentrated phosphate products such as DAP, MAP, and TSP are manufactured by neutralizing phosphoric acid with anhydrous ammonia or additional high-grade phosphate rock. High-analysis products manufactured using this process account for approximately two-thirds of global phosphate production today.

The remaining one-third is made up mostly of SSP and NPK compounds. SSP also is produced by first attacking ground rock with sulphuric acid, but rather than removing the calcium sulphate, this slurry is granulated to make a lower analysis product that contains about one-third of the nutrients of a high-analysis product. As a result, SSP contains the calcium and sulphur that end up on a phosphogypsum stack when high-analysis products are made.

Most phosphate producers make sulphuric acid on-site by burning elemental sulphur. The production of sulphuric acid is exothermic and generates large amounts of heat that typically are captured to run plant processes as well as to generate electricity on site.

Wet vs. Thermal Process

The process for producing phosphoric acid described here is referred to as the wet process. Nearly all phosphoric acid operations utilize this method today. The thermal process is another method for producing phosphoric acid. This process roasts phosphate rock along with petroleum coke and silica in an electric arc furnace to produce elemental phosphorus. Elemental phosphorus then is burned to make a pure form of phosphoric acid that is used almost exclusively for food and industrial applications. The thermal process is energy intensive, and the combination of higher energy costs and technological advances in the purification of wet process acid during the last 20 years has resulted in the closure of nearly all thermal process facilities in the United States.

Phosphogypsum - Another Side of the Story



Phosphogypsum Stack #2 and Cooling Ponds - Riverview, FL

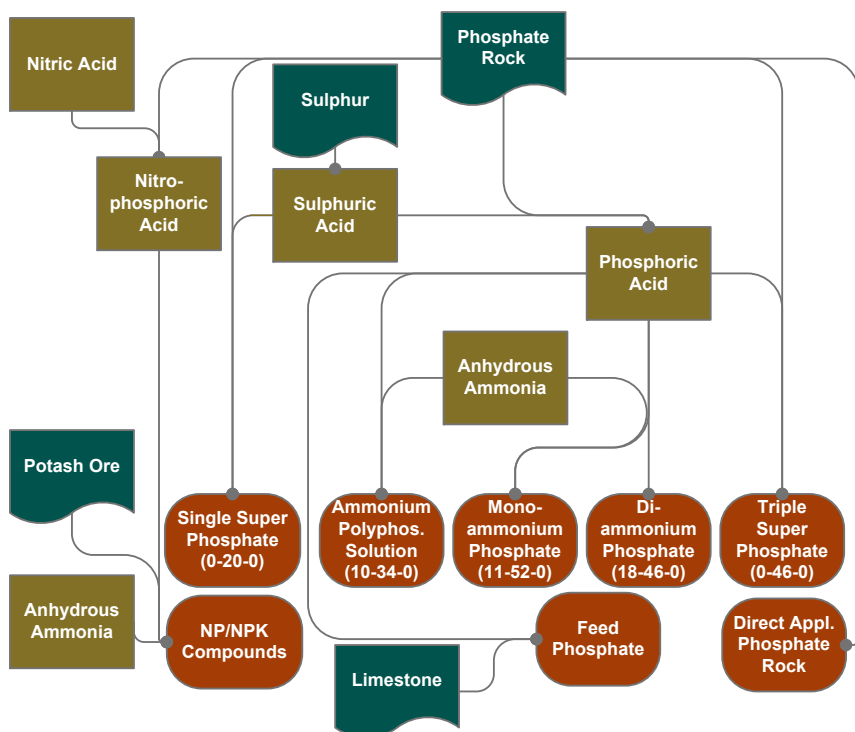
If you have ever driven through or flown over central Florida you can't help but notice the large phosphogypsum stacks that dot the landscape. The calcium sulphate byproduct produced at these facilities is an impure form of gypsum that has no economic use today and is stored at the plant site. These stacks are regulated and closely monitored in the United States.

Phosphogypsum storage is a costly part of the phosphate business, but there is another side of the story. Florida phosphate producers buy sulphur mainly from oil and gas refineries around the Gulf of Mexico. Refiners remove sulphur from oil and gas in order to comply with environmental standards for clean burning fuels. If refiners couldn't sell recovered sulphur to phosphate producers, they would have to store much of it at refineries because the phosphate industry uses about 50% of the sulphur recovered or mined in the world today.

Phosphate producers burn the sulphur to make sulphuric acid. This generates a large amount of heat and steam that is captured to run production processes as well as to generate "green" electricity at co-generation plants that are tied into the sulphuric acid units (there are no carbon emissions from this process). The sulphuric acid is used to make phosphate products that are vital to the world's food supply. The calcium sulphate byproduct then is pumped to a phosphogypsum stack where it is stored in compliance with strict environmental regulations and monitored on a regular basis.

That, we think, is a compelling story about the recycling and waste disposal of recovered sulphur.

Phosphate Production Process Flow



The phosphorus content of products is measured in units of phosphorus pentoxide (P_2O_5).

Diammonium Phosphate (18-46-0) Diammonium phosphate (DAP) is the most widely used high-analysis phosphate product worldwide. DAP is produced by first combining phosphoric acid with anhydrous ammonia in a reaction vessel. This initial reaction creates a slurry that is then pumped into a granulation plant where it is reacted with additional ammonia to produce DAP. DAP is a solid phosphate product that is applied directly or blended with other solid plant nutrient products such as urea and potassium chloride.

Monoammonium Phosphate (11-52-0) Monoammonium phosphate (MAP) is the second most widely used high-analysis phosphate product and the fastest growing phosphate product worldwide. MAP also is produced by first combining phosphoric acid with anhydrous ammonia in a reaction vessel. The resulting slurry is then pumped into the granulation plant where it is reacted with additional phosphoric acid to produce MAP. Some granulation plants can switch from DAP to MAP production simply by replacing the ammonia sparger with a phosphoric acid sparger. MAP also is a solid phosphate product that is applied directly or blended with other solid plant nutrient products.

Triple Superphosphate (0-46-0) Triple superphosphate (TSP) is the third most widely used high-analysis phosphate product. TSP contains only phosphate because

it is produced by reacting phosphoric acid with additional high-grade phosphate rock. TSP also is a solid plant nutrient product, but it is hygroscopic or absorbs moisture and therefore cannot be blended with some products such as urea.

Superphosphoric Acid (0-72-0) & Ammonium Polyphosphate Solution (10-34-0)

Superphosphoric acid (SPA) is produced by concentrating or removing additional water from phosphoric acid in order to boost its phosphate content to 68% to 72% P_2O_5 . This gel-like product primarily is reacted with ammonia to produce ammonium polyphosphate solution (APS). APS is commonly referred to by its analysis – 10-34-0 solution. This liquid product is used as a direct application material and also as the base for several solution or suspension products. 10-34-0 solution often is mixed with other liquid products such as UAN solution to make products tailored to specific crops or phases of the growing season (e.g. starter fertilizers). Solid products, particularly potash, also are dissolved in to make suspension blends that deliver all three primary nutrients. 10-34-0 solution typically is produced in smaller regional plants by distributors who source SPA and ammonia and utilize cross-pipe reactor technology to manufacture the product on site.

Nitrophosphate & NPK Compounds (several analyses such as 17-17-17)

Nitrophosphate compounds are produced by reacting phosphate rock with nitric acid rather than sulphuric acid. This process produces a variety of NP or NPK compounds containing different amounts of nitrogen, phosphorus and potassium (also added in the process). The process also produces calcium ammonium nitrate (CAN), an important nitrogen product in some regions such as Europe.

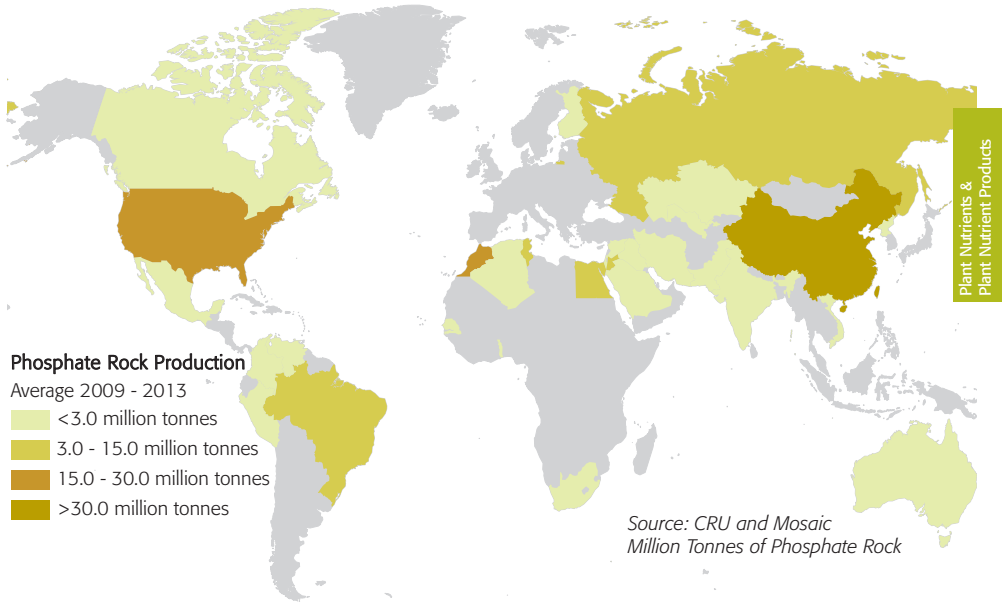
Single Superphosphate (0-20-0) Single superphosphate (SSP) is a low-analysis phosphate product that is produced by reacting ground rock with sulphuric acid. The resulting slurry is granulated into a solid that typically contains 18% to 22% P_2O_5 . The phosphate content depends largely on rock quality. SSP contains the sulphur and calcium that are removed in the processes used to make high-analysis products.

Feed Phosphate Feed phosphate products are produced by neutralizing defluorinated phosphoric acid with limestone. The first step in the process is to reduce the fluorine-to-phosphorus ratio of the phosphoric acid to less than 1:100. That is achieved by adding diatomaceous earth (or activated silica) to phosphoric acid in order to “strip” fluorine from the acid. This defluorinated acid is neutralized with different quantities of limestone to produce the two most widely used feed phosphate products – dicalcium phosphate (Dical) and monocalcium phosphate (Monocal). Dical contains 18.5% P or 42.4% P_2O_5 . Monocal is 21.0% P or 48.1% P_2O_5 . In 2011, Mosaic launched Nexfos®, a granulated feed-grade monocalcium phosphate that is a substitute for defluorinated phosphate rock. Nexfos contains 19.0% P or 43.5% P_2O_5 .

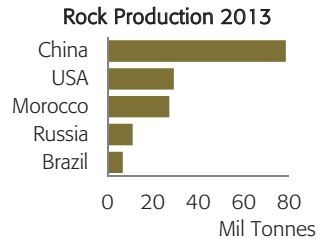
John Lawes: Father of the Plant Nutrient Industry

John Lawes is considered the father of the plant nutrient industry. Lawes was an agronomist who established the now legendary agricultural experiment farm at his family's estate in Rothamsted England in the 1840s. Among his many experiments and discoveries was the production of single superphosphate (SSP) from the reaction of sulphuric acid and phosphate rock. Lawes constructed the first simple production facility on the Rothamsted estate and patented the process in 1842. SSP became the first commercial plant nutrient product. It was wildly successful. In the UK alone, more than a dozen plants were operating within 10 years and about 80 facilities were producing SSP by 1870. SSP was the dominant phosphate product used by farmers worldwide for the next 100 years and is still a popular product in several countries such as Brazil, China and India.

Global Phosphate Rock Production



Phosphorus production begins with rock. Approximately 88% of global rock production is used to produce plant nutrients, and about 6% is used for the production of animal feed supplements. Industrial materials (mainly detergents and cleaning products) and food ingredients (largely purified acid for soft drinks) account for the remaining 6% of rock production.

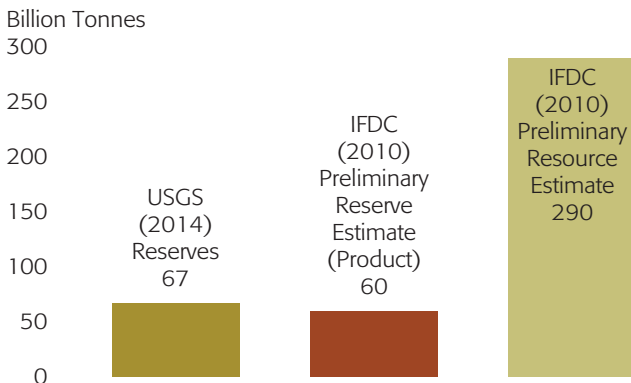


Phosphate rock was mined in more than 30 countries, and global production reached 195 million tonnes in 2013, according to CRU statistics. However, only 14 countries mined more than two million tonnes of phosphate rock, and just six countries mined more than five million tonnes (the equivalent of one world scale mine). The top five countries accounted for over three-quarters of world production, and the top ten countries accounted for more than 85% of global output in 2013.

As with nitrogen, China ranks as the largest phosphate rock producer in the world by a significant margin. China mined more than 78 million tonnes of rock in 2013 or 40% of global output. This country alone has accounted for nearly all of the growth in global rock production so far this century, and the increase in Chinese production during the last decade exceeded the annual output of the next largest country. The United States (15%), Morocco (14%), Russia (6%) and Brazil (3%) rounded out the top five rock producing countries in 2013. Phosphate rock production outside of China has remained flat since 1995 with increases in some countries such as Morocco offset by decreases in other countries such as the United States.

Peak Phosphorus

Peak phosphorus is a hot research topic in academic circles today. Following the model of Hubbert's Peak Oil, a few recent studies have concluded that phosphate rock production will peak during the next 20 to 40 years and then decline sharply during the last half of this century. Proponents warn that depletion of phosphorus resources will imperil food supplies and concentrate economic and political power in countries such as Morocco that possess the largest remaining reserves. Researchers recommend more strict regulation of phosphorus production, use and recycling.

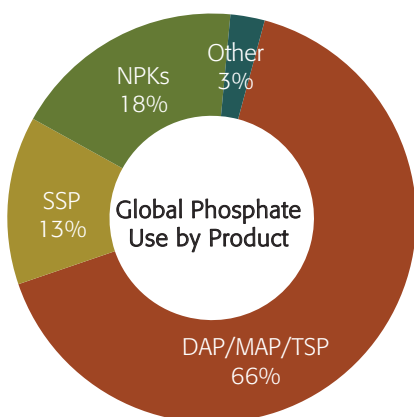


Source: USGS and IFDC

Critics of these studies acknowledge that phosphate rock is a finite and nonrenewable resource and support on-going efforts to further improve the efficacy of production, use and recycling. However, they contend that peak phosphorus studies utilize outdated estimates of rock reserves and fail to fully account for the impact of higher market prices and new technologies on resource estimates. They conclude that global phosphate rock reserves exceed estimates used in these studies by a wide margin and, as a consequence, see no threat of peak phosphorus production later this century.

That view is supported by recent estimates of global phosphate rock reserves and resources made by the U.S. Geological Survey (USGS) and the International Fertilizer Development Center (IFDC). Reserves are deposits that are economically recoverable based on expected market prices and current technology. Resources include reserves as well as deposits that likely will become economically viable as a result of higher market prices and likely advances in mining and beneficiation technologies. Based on a detailed review of global phosphate rock deposits, the IFDC and USGS estimate that reserves total 60 to 67 billion tonnes or roughly 310 to 340 years of production, and phosphate rock resources total 290 billion tonnes or more than 1,485 years of production at current rates.

The Leading Phosphate Products



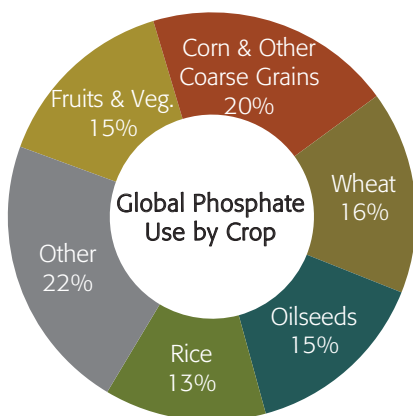
Source: CRU and Mosaic
Average 2009-2013

are still produced and used in China, India and Brazil. SSP remains a popular product especially on sulphur deficient soils in these countries.

DAP, MAP and TSP are the most widely used phosphate products in the world, accounting for about two-thirds of global use from 2009 through 2013. These high-analysis products are used for direct application, blended with other solid nitrogen and potash products, or utilized in the production of some types of NP and NPK compounds. They also are the most widely traded phosphate products.

The next most commonly used phosphate products are NP/NPK compounds and SSP. The production and use of these products are concentrated in certain regions. For example, many producers in Europe and the former Soviet Union manufacture nitric acid based NP/NPK compounds, and large amounts of SSP

Phosphate Use by Crop



Source: IFA
Use in 2010/11

Like with nitrogen, corn and other coarse grains account for the largest share of global phosphate use (20%), according to the most recent estimates from the International Fertilizer Industry Association (IFA). Wheat consumes another 16% of the total. Nutrient intensive fruit and vegetable crops account for 15% of global phosphate use. Oilseed crops and rice account for another 15% and 13% of total use, respectively.

Use by crop differs significantly by country based on crop mix. For example, fruit and vegetable production claims 29% of total phosphate use in China or roughly 3.5 million tonnes P_2O_5 . In fact, China's use of phosphate on just fruits and vegetables exceeds total phosphate consumption of all but two other countries today. In India, rice accounts for just under one-quarter of total phosphate use. Corn accounts for one-half of U.S. phosphate use, while soybeans consume nearly the same percentage in Brazil.

Potash



Potassium and Plant Nutrition

Agronomists have labeled potassium The Regulator because of the key role it plays in controlling critical plant processes such as photosynthesis, protein formation, enzyme activation and starch formation. For example, potassium helps to regulate nitrogen uptake and therefore plays a key role in controlling photosynthesis and protein formation. Potassium is vital for healthy plant metabolism. Potassium promotes the development of strong roots, stalks and stems as well as improves a plant's ability to utilize water. As a consequence, potassium increases the resilience of a plant to weather stressors such as variable temperatures, drought and high winds. Potassium also boosts disease and pest resistance and often is called the quality nutrient because it enhances the appearance, taste, nutritional value and shelf life of the harvested crop.



Potash Mine Shaft Headframe



Granular MOP



Potassium Deficiency

Symptoms of a potassium deficiency show up primarily on the leaves of most plants. Leaves become necrotic and turn yellow or brown along their edges and at their tips yet remain green in the middle. Plants require more potassium than any other nutrient except nitrogen. There are no substitutes for potassium in a plant's or animal's diet.

Plants absorb potassium in the form of a potassium cation (K^+). The soil chemistry of potassium is much less complex than that of phosphate and nitrogen. Many soils contain large amounts of potassium, but only a small percentage is available in the soil solution. Most of it is held tightly by soil colloids, the tiny particles that make up soil organic matter, and only a small percentage is released into the soil solution each year. As a consequence, the application of potassium is required to ensure that adequate amounts are available in the soil solution to meet plant needs. Potassium cations are more mobile than orthophosphate ions but much less mobile than ammonium or nitrate ions. As a result, potassium carries over from one growing season to the next.

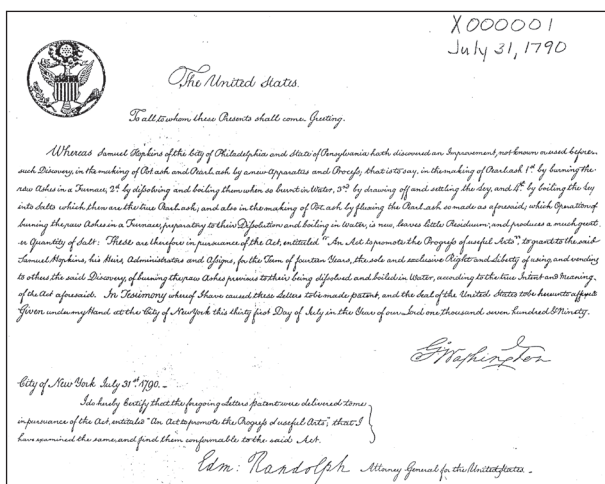
K for Potassium?

Why is potassium – the 19th element on the periodic table – represented by the letter K? Well, P was already taken by the 15th element, namely phosphorus, but the selection of K was not random. K stands for kalium, the German word for potassium.

Potash Production - The First U.S. Patent!

Farmers have long recognized the importance of potassium to plant health and have applied potassium to their soils since at least the 18th century. The first potassium product was extracted by leaching potassium salts from wood ashes. The solution of water and wood ashes was evaporated in large pots and yielded a residue made up mostly of potassium carbonate.

In fact, the very first patent issued by the U.S. Patent and Trademark Office and signed by President George Washington on July 31, 1790 was granted to Samuel Hopkins for "an improvement in the making of Pot ash and Pearl ash by a new Apparatus and Process." So, the process of making the first potassium product is the origin of the term potash or the commonly used name for potassium.



Whereas Samuel Hopkins of the City of Philadelphia and State of Pennsylvania hath discovered an Improvement, not known or used before, such Discovery, in the making of Pot ash and Pearl ash by a new Apparatus and Process; that is to say, in the making of Pearl ash 1st. by burning the raw Ashes in a Furnace, 2nd. by dissolving and boiling them when so burnt in Water, 3rd. by drawing off and settling the Ley, and 4th. by boiling the Ley into Salts which then are the true Pearl ash; and also in the making of Pot ash by fluxing the Pearl ash so made as aforesaid; which Operation of burning the raw Ashes in a Furnace, preparatory to their Dissolution and boiling in Water, is new, leaves little Residuum; and produces a much greater Quantity of Salt: These are therefore in pursuance of the Act, entitled "An Act to promote the Progress of useful Arts," to grant to the said Samuel Hopkins, his Heirs, Administrators and Assigns, for the Term of fourteen Years, the sole and exclusive Right and Liberty of using, and vending to others the said Discovery, of burning the raw Ashes previous to their being dissolved and boiled in Water, according to the true Intent and Meaning, of the Act aforesaid. In Testimony whereof I have caused these Letters to be made patent, and the Seal of the United States to be hereunto affixed. Given under my Hand at the City of New York this thirty first Day of July in the Year of our Lord one thousand seven hundred & Ninety.

Source: United States Patent and Trademark Office

Potassium Ores

Potassium is a mineral ore that typically is found in deep underground deposits or in natural brines such as those from the Dead Sea, Qinghai Salt Lake and the Great Salt Lake. Approximately 80% of global potash production today is mined from underground deposits, while the remaining 20% is evaporated from surface brines.

Underground ores were formed millions of years ago during the Paleozoic Era when sea and lake waters evaporated and potassium chloride (KCl) and sodium chloride (NaCl) crystallized to form deposits in sedimentary rock basins. Even mineral rich surface brines are remnants of larger ancient lakes from this era.

There are several types of potassium-bearing ores, but sylvinite is the most common. Sylvinite ore is made up of halite (sodium chloride), sylvite (potassium chloride) and small amounts of clay and other minerals. Because of its importance, this overview will describe the mining and milling of sylvinite ore. Similar processes, however, also are used to extract and refine other ores.

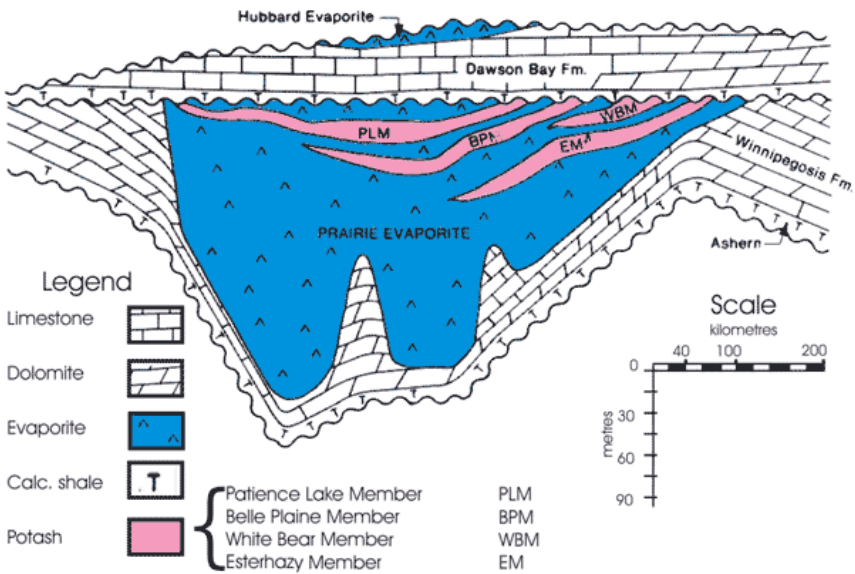
Other Potassium Ores

There are several other potassium-bearing ores, but two are noteworthy – carnallite and langbeinite. Carnallite ore contains magnesium chloride in addition to potassium chloride and sodium chloride. Deposits of carnallite are found in several parts of the world. This ore typically contains less potassium and is more costly to refine than sylvinite ore.

Deposits of langbeinite are much less common, but this ore contains soluble sulphate in addition to potassium and magnesium. Langbeinite contains no chloride, so the refined product is ideal for chlorine sensitive crops such as fruits and vegetables. Because this product delivers three important nutrients – potassium, sulphur and magnesium – farmers also use it on major field crops especially where soils are deficient in sulphur or magnesium. Mosaic mines langbeinite ore at its operations in Carlsbad, NM and markets this product under the brand name K-Mag®.

Saskatchewan's Rich Ore Deposit

Saskatchewan possesses the largest and some of the highest quality sylvinite deposits in the world. The deposit, known as the Prairie Evaporate Deposit, extends throughout the southern plains of Saskatchewan and dips into western Manitoba, northeastern Montana and northwestern North Dakota. The Saskatchewan government estimates that reserves and resources in the province total more than 105 billion tonnes or several thousand years of production. Ore is found in different layers or what are termed members of the Prairie Evaporate Deposit. The three main members in production today include the Patience Lake member (at depths of up to 800 meters), the Belle Plaine member (at depths of up to 1,000 meters) and the Esterhazy member (at depths of up to 1,500 meters). Saskatchewan deposits typically are characterized by thick flat beds of sylvinite ore that contain up to 40% potassium chloride.



Source: Saskatchewan Geological Survey

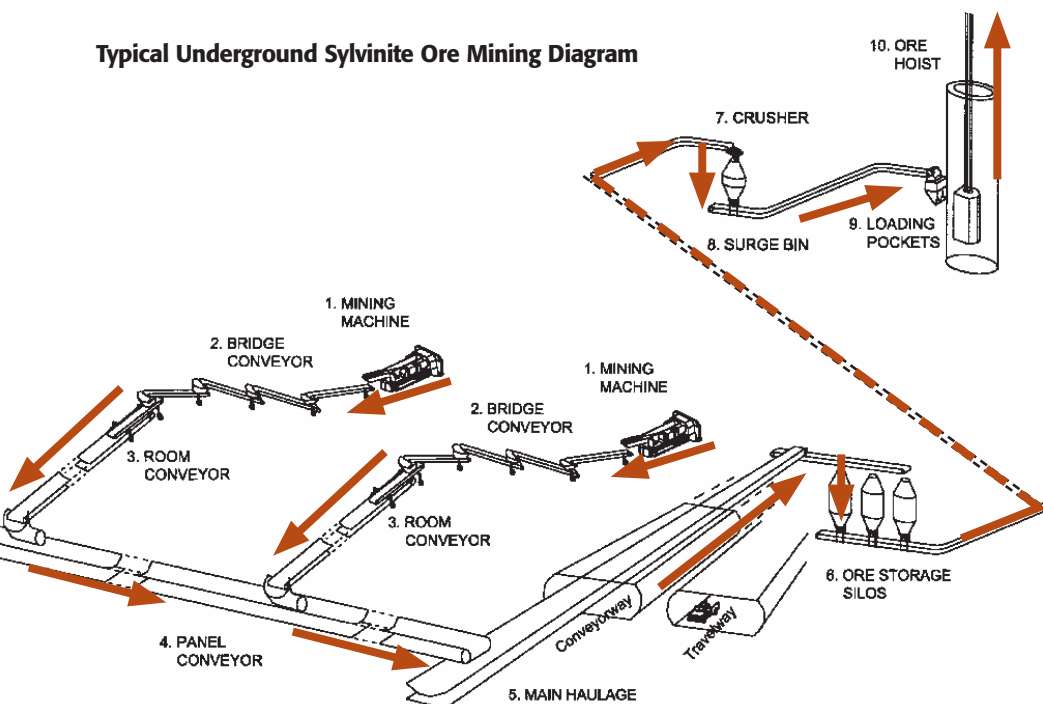
Underground Ore Deposits and Mining Techniques

Underground ore beds vary in terms of depth, grade, thickness and undulation – characteristics that are key cost drivers of a mining operation. Sylvinitic ore typically contains more potassium than other ores with grades ranging from about 10% to 50% potassium chloride.

Underground deposits are mined using either deep shaft or solution mining techniques. Deep shaft mining operations are the most common and currently account for over 90% of the potash extracted from underground deposits and more than three-fourths of total potash production worldwide. Deep shaft mining techniques typically are utilized to extract relatively thick and flat deposits at depths from about 250 meters to slightly more than 1,000 meters.

Solution mining operations account for the remaining production from underground deposits and slightly more than 5% of total potash production worldwide. Solution mining techniques typically are used to extract undulating or deeper deposits. Mosaic operates the largest solution mine in the world at Belle Plaine, Saskatchewan. This operation extracts ore from deposits as deep as 1,500 meters below ground.

Typical Underground Sylvinitic Ore Mining Diagram



Source: Mosaic

Deep Shaft Mining Operations

Deep shaft mining is the most widely used method for extracting potassium from underground ore deposits. A deep shaft mine utilizes mining machines, a system of conveyors or fleet of specialized vehicles

and a powerful hoist to extract, transport and lift ore from deep underground deposits to the surface. Most operations include two shafts – a production shaft and a service shaft. The production shaft contains the guides, cables and skips that are used to hoist ore as well as a cage that transports workers and some supplies into and out of the mine. The service shaft typically is used to ventilate the mine, deliver electricity and transport larger equipment as well as workers and supplies into and out of the mine.

The head frame over a shaft houses a large electric motor that turns a hoist drum to lift skips from the bottom of the mine to the surface. A skip is a long narrow vessel that carries 25 to 50 tons of ore from the mine to the surface. Two are used in this process. The skips are attached at the ends of a long and large cable. The hoist drum alternates first rotating clockwise and then counterclockwise so one skip loads at the bottom of the shaft while the other discharges in the ore dump in the head frame.

Most underground operations utilize room and pillar mining techniques. Because sylvinite ore is a soft rock, it typically is extracted using continuous mining machines that cut into the face of the deposit. Bridge conveyors transport the ore from mining machines to room conveyors that deliver it to panel conveyors. Panel conveyors run across several rooms or mine cuts and move ore to the main haulage conveyor. This large conveyor then transports the ore often long distances to storage bins near the production shaft. The ore moves from a storage bin to a surge bin, through a crusher and finally to the loading pocket. From the loading pocket the ore is dumped into the skip and then hoisted to the surface for processing.

Finely Tuned Hoisting Operations

Hoisting operations are finely tuned processes. For example, at our Esterhazy K2 mine each 75-foot skip carries 50 tons of ore. The skips load and discharge in about 23 seconds, and the 11,000 horse power electric motor propels the skips up and down the shaft at a maximum speed of 65 kilometers per hour! Cycle time from loading to discharge of a skip is about 106 seconds.



Flooding Risk

Sinking a mine shaft through aquifers and ancient seas is a risky endeavor. Several early attempts at sinking shafts in Saskatchewan were unsuccessful due to flooding, and the table lists potash mines that were lost to flooding during the last three decades.

Flooded Mines

Mine	Country	Capacity	Year Closed
Berezniki III	Russia	1.8 million tonnes	1986
Patience Lake (converted to solution mine in 1988)	Canada	1.0 million tonnes	1987
Cassidy Lake	Canada	1.3 million tonnes	1997
Berezniki I	Russia	1.3 million tonnes	2006

Source: Company Reports, Mosaic

One of the Greatest Engineering Feats of the 1960s

Deep shaft mining of potash sounds simple enough, but there is nothing simple about sinking a shaft one kilometer straight down into the belly of the earth. In Saskatchewan, a shaft must pass through flowing aquifers, the Blairmore quicksand formation and Dawson Bay before reaching the ore deposit. The technique used to reach deep potash deposits includes freezing the area around the shaft, then boring through these formations, and finally sealing the shaft with steel and concrete casing. This technique was used in the 1960s to sink nearly all of the deep shafts in operation today in the province. The first shaft completed in Saskatchewan using this technique was the K1 shaft at our Esterhazy mine in 1962. The sinking of the K1 shaft was hailed as one of the greatest engineering feats of its day. The Esterhazy mine celebrated its 50th year of operation in 2012. Today, its underground mining footprint is approximately 30 kilometers long by 18 kilometers wide and there are more than 4,700 kilometers of mine cuts or tunnels!

The last shaft sunk in Saskatchewan was at PotashCorp's Rocanville mine in 1970. However, three new shafts are under development in the province today – two at familiar sites at Rocanville and Esterhazy.

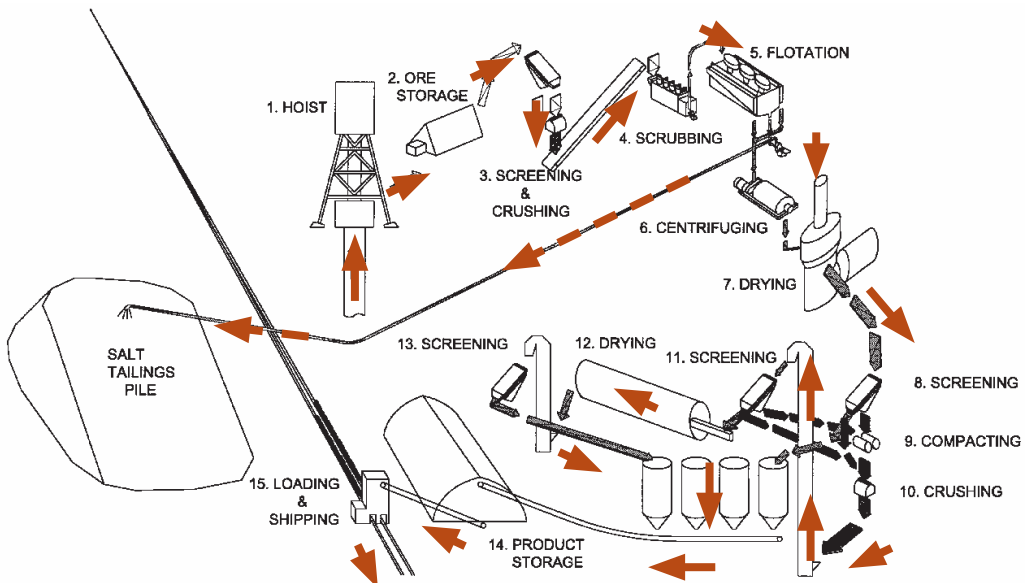
Deep Shaft Mine Milling Operations

Unlike the synthesis of ammonia or the stripping of calcium from phosphate rock, the refining of sylvinite ore requires no chemical reactions but just the physical separation of the potassium chloride from the sodium chloride and other materials in the ore.

For ore extracted by deep shaft mining operations, the most widely used separation technology is a flotation process that is similar to the one used to separate sand and clay from phosphate rock. The sylvinite ore first is crushed in order to liberate sylvite crystals (potassium chloride) from halite crystals (sodium chloride). The crushed ore is mixed with saturated brine and then flotation agents are added to this slurry. Sylvite crystals attach to these agents, float to the top of the slurry and are paddled off and separated from halite crystals that sink to the bottom of the slurry. Halite crystals are pumped to a salt tailings area where they are de-watered and stored. The sylvite ore is fed through a centrifuge or cyclones where insoluble materials or slimes are separated from the ore. The ore then is dried, screened and compacted to produce different grades of potassium chloride.

This milling process yields red products that contain 60% to 61% K_2O . The red color is caused by iron oxide impurities in the ore.

Typical Above-ground Sylvinite Ore Milling Diagram



Source: Mosaic

Solution Mining and Refinery Operations



Surface Operation and Evaporation Ponds - Belle Plaine, SK

Solution mining is a less widely used method for extracting potassium from underground ore deposits. The process is straightforward. Hot water initially is pumped through a series of bore holes or “clusters” in the ore. Because sylvinite is soluble, the hot water dissolves the ore and a cavity or cavern forms in the deposit. Once the cavity is formed, hot brine (salt water) is pumped into the cavity. Brine will selectively dissolve the potassium chloride resulting in less sodium chloride in the solution.

The life of a typical cavity is about 20 years, but production peaks from year four to year eight and then declines steadily. Production around year 20 typically drops to 10% to 20% of peak volume before the cavity is abandoned.

The potassium rich solution is pumped from several cavities to the refinery for processing. Again, no chemical reactions take place during this process. Potassium chloride simply is separated from sodium chloride in the saturated brine. The most widely used separation technology in solution mining operations is selective crystallization. Potash can be separated from salt because the solubility of potassium chloride declines more quickly than the solubility of sodium chloride as the saturated brine cools. In short, potassium chloride crystals form sooner than sodium chloride crystals as the temperature of the brine falls.

I Have How Many Cavities?

Cavities are bad when you go to the dentist, but they are good if you operate the world's largest potash solution mine. At any point in time, Mosaic's large scale Belle Plaine operation typically is pumping solution from 75 to 100 cavities to feed its refinery. Needless to say, a key part of this operation is a continuous drilling and cavity development program required to maintain production.

There is an indoor and outdoor version of selective crystallization. The indoor version takes place in vessels called crystallization circuits. In this case, the saturated brine is heated to 80° to 100°C to vaporize water.

The highly concentrated brine then is fed into the crystallizer where potassium chloride is precipitated and harvested. The brine containing sodium chloride is pumped to a salt tailings pile where it is dewatered and stored. In this case, both the mining and refining processes require significant amounts of energy – mostly natural gas – to heat water and brine. This process often is referred to as hot leaching.

The outdoor version of this process works on the same principle, but the beginning and ending temperatures are much lower, and it takes more time to crystallize potassium chloride from the brine. This technique is employed by companies that operate solution mines in cold climates. In this case, the brine from the cavities is pumped into large cooling ponds. Potassium chloride crystallizes as the solution temperature declines and then is harvested with floating dredges. This process, often referred to as cold crystallization, is particularly efficient during frigid winter months. At our Belle Plaine operation in Saskatchewan, about one million tonnes or roughly 40% of current production is harvested from ponds each year.

The potassium chloride from either process is dewatered, dried, cooled, screened and compacted to make finished potash products for agricultural and industrial uses. Because iron oxide is not water soluble, it remains in the cavity rather than the solution. As a result, the higher purity products from solution mining operations are white rather than red and typically contain more than 62% K₂O.

Shaft or Solution Mining?

Solution mining and refining operations are energy intensive, but these technologies have advantages over deep shaft mining in certain circumstances. This technology is better suited to mine deep deposits that are more difficult, costly and unsafe to mine with underground mining machines. The technology also is better suited to mine and process some types of ore such as carnallite. The development of a solution mine requires less capital and time than a deep shaft mine. There are no flooding risks, and solution mining yields less sodium chloride tailings. This technology is well suited to regions where labor is scarce and energy is abundant.

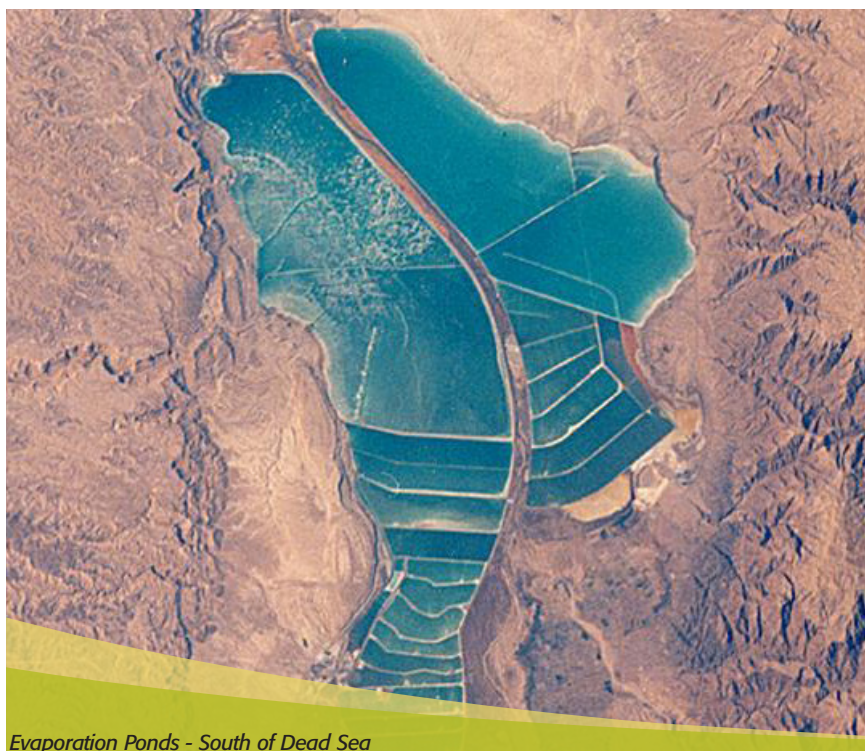
Several proposed greenfield projects such as the Legacy project in Saskatchewan, the Mengo project in the Republic of Congo, and the now dormant Potassio Rio Colorado project in Argentina plan to use solution mining technologies.

Brine Evaporation and Milling Operations

Almost one out of every five tonnes of potash produced today is from the solar evaporation of surface brines. The largest operations are in the Mideast (Dead Sea), China (Qinghai Salt Lake), the United States (Great Salt Lake) and Chile (Salar de Atacama).

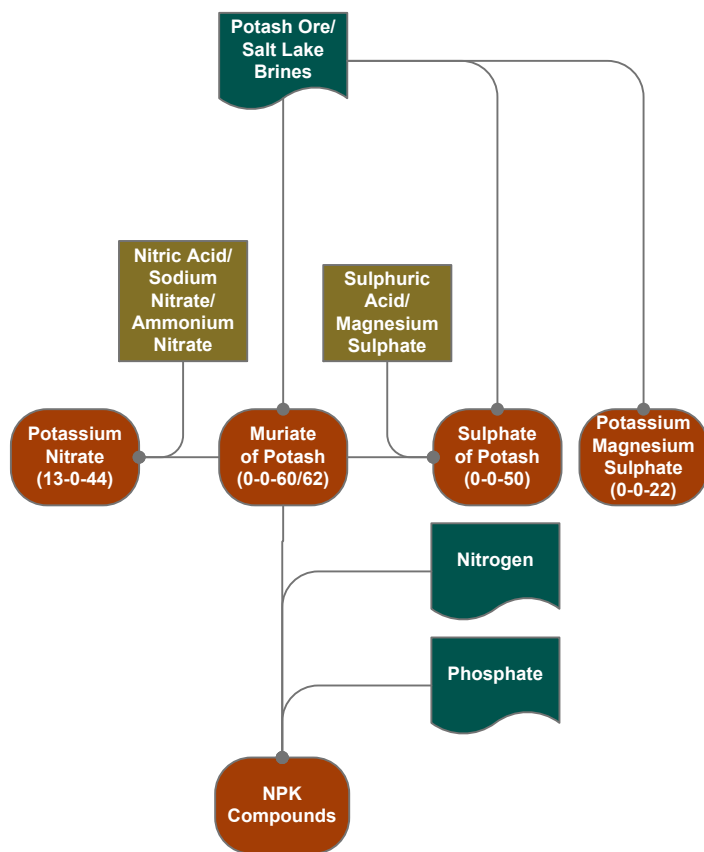
This process begins by pumping nutrient rich lake brine into solar evaporation ponds. The brine is moved through a network of ponds and becomes increasingly concentrated until potassium ore crystallizes. The ore then is harvested by floating dredges or by other heavy equipment if the remaining brine is drained. This process is ideally suited for sunny, hot and dry climates like the desert surrounding the Dead Sea. However, some brine evaporation facilities such as those at Qinghai Salt Lake in China operate in less ideal climates and shut down during the winter.

The type of ore harvested and the type of refining operation depend on the make-up of the surface brine. Sylvinite ore requires little further processing but carnallite ore needs to be refined. For example, the two large operations in the Mideast harvest mostly carnallite ore from Dead Sea brine. The operations around Qinghai Salt Lake in China also harvest mostly carnallite ore. Carnallite ore contains magnesium chloride in addition to potassium chloride and sodium chloride and typically is refined into potassium chloride products through hot leaching or cold crystallization.



Evaporation Ponds - South of Dead Sea

Potash Production Process Flow



The potassium content of products is measured in units of potassium oxide (K_2O).

Potassium Chloride (0-0-60/62) Potassium chloride is commonly referred to as muriate of potash (MOP). MOP contains 60% to 62% K_2O and is refined primarily from sylvinit and carnallite ores.

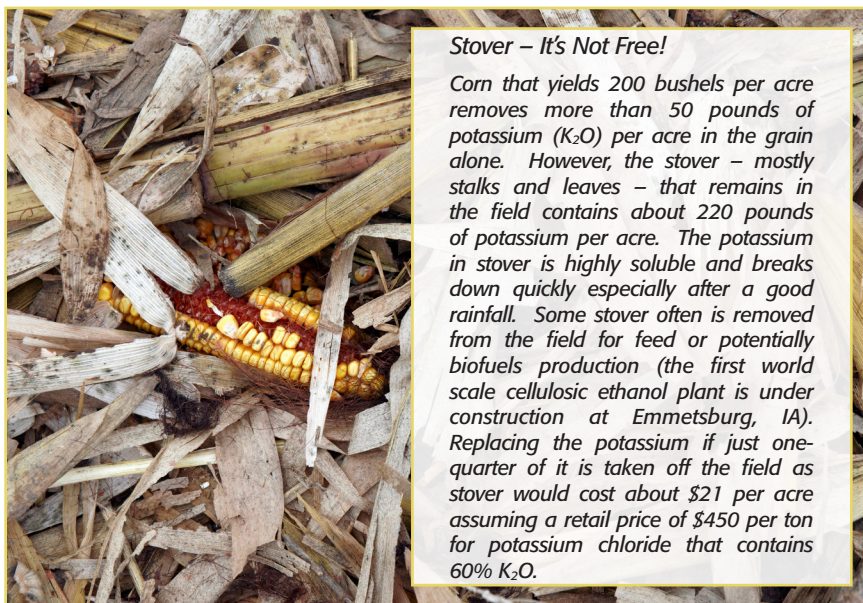
Potassium Sulphate (0-0-50) Potassium sulphate is commonly referred to as sulphate of potash (SOP). SOP typically contains 50% K_2O and 18% sulphur. Primary SOP is produced from kainite or other rare ores in surface brines or underground mineral deposits. Secondary SOP is produced by reacting potassium chloride and sulphuric acid. SOP is applied primarily to chlorine sensitive crops such as fruits, vegetables and tobacco.

Potassium Magnesium Sulphate (0-0-22) Potassium magnesium sulphate typically contains 22% to 30% K_2O , 17% to 22% sulphur and 10% to 11% magnesium. This product is refined from langbeinite ore. It is an ideal product for chlorine sensitive crops as well as for soils deficient in these important secondary nutrients.

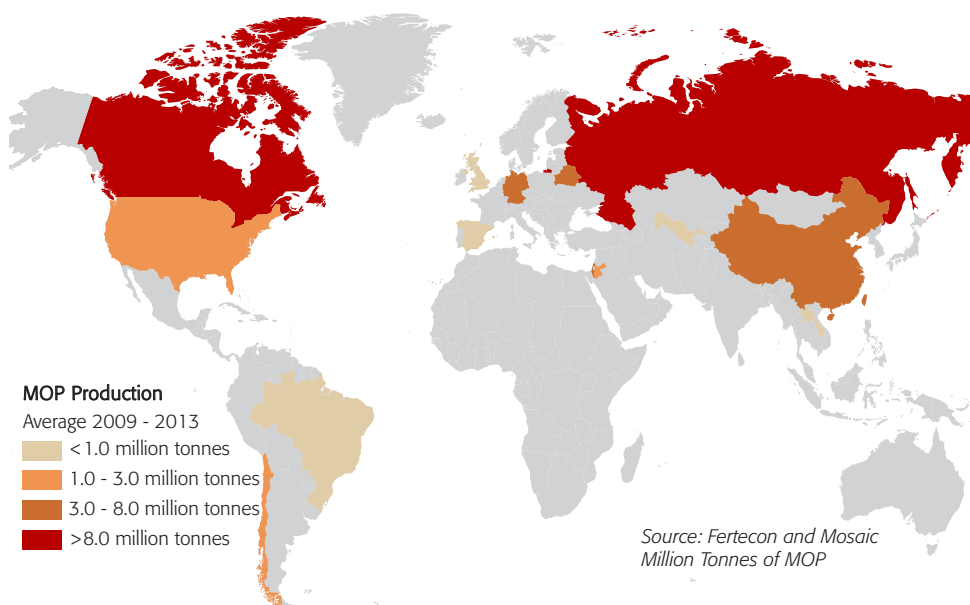
Potassium Nitrate (13-0-44) Potassium nitrate, commonly known as saltpeter, typically contains 13% nitrogen and 44% K_2O . Large quantities of primary potassium nitrate were mined more than a century ago mostly from the Atacama Desert in Chile, but nearly all of the potassium nitrate today is produced by reacting potassium chloride with nitric acid.

NPK Compounds (several analyses such as 15-15-15) NPK compounds are products that have the primary nutrients chemically bonded in each granule, while NPK blends are simply physical mixtures of products such as urea, DAP and MOP. There are several ways to make NPK compounds ranging from large scale nitric acid operations in Russia to small scale pan granulation in China. NPK compounds deliver significant amounts of potassium in some countries. For example, about 60% of the potash applied in China is in the form of NPK compounds, and standard grade MOP is the main potash product used in these pan granulation operations.

Feed-Grade Potassium Feed-grade potassium products are similar in chemical composition to potassium chloride and potassium magnesium sulphate. Mosaic produces Dyna-K, a feed-grade potassium chloride product, as well as Dynamate, a feed-grade mineral consisting of the sulphate form of potassium and magnesium.

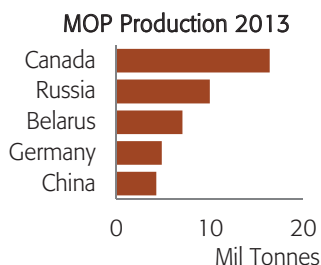


Global Potassium Chloride Production



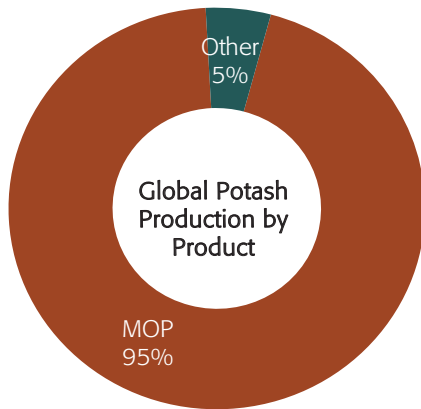
Economically recoverable deposits of potassium are not found everywhere. According to U.S. Geological Survey, the largest reserves are located in Canada, Russia, and Belarus. Today, potassium chloride is produced in just 14 countries, and global production totaled 53 million tonnes in 2013, according to statistics published by Fertecon.

The top five countries accounted for 80% of global potassium chloride output in 2013. Canada ranked as the largest producer, accounting for 31% of world production. Russia (19%), Belarus (13%) and Germany (9%) were the next largest producers. China has developed significant production capacity during the last 10 years primarily from the brines of Qinghai Salt Lake. China moved into the top five producing countries in 2009 and accounted for 8% of global output in 2013.

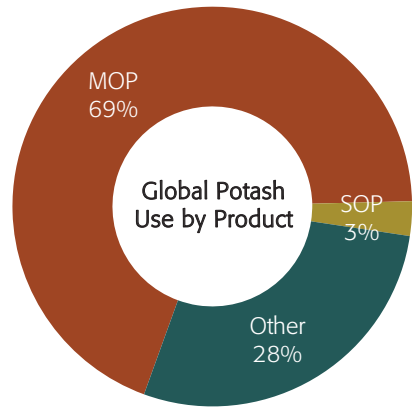


Source: Fertecon and Mosaic

The Leading Potash Products



Source: Fertecon and Mosaic
Average 2009-2013

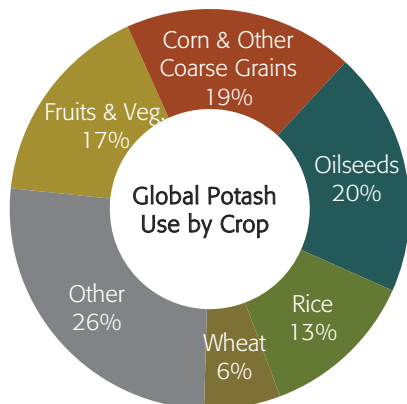


Source: IFA and Mosaic
Average 2009-2013

Potassium chloride (KCl) is the most widely used potash product in the world by a gaping margin. Potassium chloride accounts for 95% of global potash production. However, a significant amount of potassium chloride is used to produce, and therefore gets applied as, other products such as NPK compounds, secondary potassium sulphate and secondary potassium nitrate.

Other primary products such as potassium sulphate and potassium magnesium sulphate account for the remaining 5% of global output. These products are refined from scarce ores found in a limited number of brines or mineral deposits. For example, primary potassium sulphate is produced from kainite in the brines of the Great Salt Lake and potassium magnesium sulphate is refined from langbeinite ore in New Mexico. China by far is the largest producer of other primary products, but Germany, the United States and Chile also produce significant amounts of these products. The charts show global production of primary potash products as well as consumption of the leading potash products from both primary and secondary production.

Potash Use by Crop



Source: IFA
Use in 2010/11

Soybeans and other oilseeds are the largest consumers of potash and account for 20% of global potash use, according to estimates by the International Fertilizer Industry Association (IFA). Brazil and the United States make up the lion's share of use on soybeans. In Indonesia and Malaysia, palm oil accounts for 62% and 86% of total potash use, respectively.

Field crops are heavy potassium users by virtue of their large area under cultivation. Corn and other coarse grains account for 19% of global potash use, and rice and wheat combined capture an equivalent share. In the United States, corn accounts for almost one-half of domestic use. In India, one out of every three tonnes of potash goes down on rice.

Fruits and vegetables account for 17% of global potash use. These crops are farmed intensively over vast areas especially in large and rapidly growing countries such as China and India. In China, 40% of potash consumed is applied to fruits and vegetables. Fruits and vegetables are potassium intensive crops and bananas are, well, the top banana. According to the International Plant Nutrition Institute (IPNI), bananas require more potassium per unit of production than any other crop – as much as 1,000 kilograms per hectare.

Page Intentionally Left Blank