PHOSPHORUS

1. Introduction

Phosphorus [7723-14-0] is a nonmetallic element having widespread occurrence in nature as phosphate compounds (see PHOSPHORIC ACIDS AND PHOSPHATES). Fluorapatite [1306-05-4], $Ca_5F(PO_4)_3$, is the primary mineral in phosphate rock ores from which useful phosphorus compounds (qv) are produced. The recovery from the ore into commercial chemicals is accomplished by two routes: the electric furnace process, which yields elemental phosphorus; and the wet acid process, which generates phosphoric acid. The former is discussed herein (see FURNACES, ELECTRIC). Less than 10% of the phosphate rock mined in the world is processed in electric furnaces. Over 90% is processed by the wet process, used primarily to make fertilizers (qv).

Most of the phosphorus produced as the element is later converted to high purity phosphoric acid and phosphate compounds; the remainder is used in direct chemical synthesis to produce high purity products. In contrast, phosphoric acid produced by the wet process is used in lower purity applications, especially in fertilizer and to a lesser degree in animal feed (see FEEDS AND FEED ADDITIVES, NONRUMINANT FEEDS). More recently, a small portion of wet acid is purified in a second process and then also used in high purity acid and phosphate compound applications.

Elemental phosphorus is produced and marketed in the α-form of white or yellow phosphorus, the tetrahedral P_4 allotrope. A small amount of red amorphous phosphorus, P, is produced by conversion from white phosphorus. White phosphorus as the element is characterized by its combustion in air to form phosphorus pentoxide. Consequently, white phosphorus is generally stored and handled under water. Elemental white phosphorus is also highly toxic, and suitable precautions are required by those who manufacture or handle it. The black phosphorus modification prepared under high pressure does not have commercial importance.

The history of elemental phosphorus has been reviewed (1). Discovery is credited to Hennig Brandt in 1669. Early commercial production was by reduction of phosphoric acid using carbon in the 1830s and by the reduction of bones in the 1840s. The main application was in matches (qv), which has been discontinued owing to the toxicity of white phosphorus. In 1888 the electric furnace process was patented by Readman in Britain. This process has been developed over the years. A significant increase in U.S. production occurred beginning in the 1930s in Tennessee and Alabama, driven by the low cost of electric power from the Tennessee Valley Authority and the high purity of phosphoric acid made by the electric furnace route as compared to the wet-acid process. A further expansion took place in the 1940s as a result of the development of detergents based on phosphates, especially sodium tripolyphosphate. North American production of elemental phosphorus reached its zenith in the early 1970s. Production has declined since then because of reformulations of detergent phosphates. References (1–7) contain additional information.

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2. Physical Properties

The dominant commercial form of elemental phosphorus is the α-white allotrope. α-White phosphorus is often designated simply as P_4 because the solid consists of tetrahedral P_4 molecules. In its pure form, it is a white solid that forms a clear liquid when melted. However, the commercial product is generally somewhat yellow, both as a solid and as a liquid, owing to the presence of small amounts of a red phosphorus allotrope. Commercial white phosphorus may also be slightly gray in color because of incomplete separation of coke dusts and other impurities generated in the manufacturing process.

Upon storage, the amount of red phosphorus in solid white or liquid phosphorus may increase if the material is exposed to light or contains contaminants such as iodine, sulfur, selenium, or sodium that catalyze the conversion from white to red. Also, because white phosphorus is generally stored under water, some surface oxidation to form viscous white or colored polymeric oxyacids also occurs, especially if the oxygen content of the water can be replenished by exposure to air.

White phosphorus is a soft waxy solid often compared to paraffin wax. Small samples under water can be cut with a knife with some difficulty. Large samples are always transferred and handled as a liquid under water, which protects the phosphorus from air oxidation.

The solubility of phosphorus in water is about 3 ppm. However, process water used in phosphorus manufacture or handling often carries larger amounts of phosphorus as particulates or small droplets, depending on the water temperature. Phosphorus-contaminated water is commonly called phossy water. Phosphorus has low solubility in most common solvents, but is quite soluble in carbon disulfide and some other special solvents. The solubility in CS_2 and benzene was formerly used in phosphorus analyses, but toxicity and increasing waste disposal costs have led to more use of toluene and xylene, and more recently to the use of nonchemical turbidity measurements.

Other phosphorus allotropes can be made from the α-form. At temperatures below $-76.9°C$ a hexagonal β-white phosphorus having a higher ($1.88\ g/cm^3$) density can be produced reversibly. The difference between the α- and β-forms has been shown by ^{31}P nmr to be that the P_4 tetrahedra are not free to rotate in the β-white modification.

Some of the more common physical properties of α-white phosphorus are given in Table 1. White phosphorus is easily melted at low (44°C) temperatures using hot water, facilitating its transfer and handling. Like solid white phosphorus, the liquid has been shown to consist of P_4 tetrahedra. Upon cooling, the liquid P_4 shows a strong tendency to supercool several degrees and then to solidify with a high freezing rate. Cubic, transparent crystals can be crystallized from the melt or from phosphorus vapor. However, most solid phosphorus does not show crystal faces, but rather freezes into the massive waxy solid. Freezing liquid phosphorus yields α-white phosphorus.

Upon heating, α-white phosphorus first melts, then either vaporizes or converts to amorphous red phosphorus. The conversion to red P proceeds slowly in one to two days at temperatures slightly below the 280°C boiling point of liquid P_4. The product is amorphous to x-ray diffraction.

Besides the amorphous red P which is a commercial product, there are perhaps five other crystalline or poorly crystalline red modifications that are not produced commercially. These include a triclinic, an orthorhombic, a high temperature form, and two poorly crystalline forms. Red phosphorus varieties are rather stable in air and are of lower reactivity than white phosphorus.

Several allotropes of black phosphorus have also been reported (2). These include one amorphous and three crystalline modifications. At increasing pressures and temperatures reaching above 1200 MPa (12 kbar) and several hundred degrees, a series of black phosphorus modifications are formed that are characterized by even higher densities ($2.70\,g/cm^3$). These include orthorhombic, rhombohedral, and cubic varieties. The black forms have lower reactivity and solubility than red phosphorus.

Phosphorus vapor exists as P_4 molecules until dissociation to P_2 begins at 800°C. Essentially all the vapor is P_2 at 1500°C, but further dissociation to monatomic P is less than 0.1% at that temperature.

3. Chemical Properties

Phosphorus shows a range of oxidation states from -3 to $+5$ by virtue of its electronic configuration. Elemental P_4 is oxidized easily by nonmetals such as oxygen, sulfur, and halides to form compounds such as P_2O_5, P_2S_5, and PCl_3. It is also reduced upon reaction with metals to generate phosphides. The phosphides may be quite inert when formed with transition metals, for example, iron(III) phosphide, FeP, or may be chemically reactive when formed with active metals like aluminum or sodium, AlP or Na_3P. In some reactions phosphorus may be both oxidized and reduced, as in reactions with metal salt solutions like copper sulfate, where both phosphoric acid and copper phosphide are generated. Certainly the more useful and common reactions of phosphorus involve oxidation with air, sulfur, or chlorine. The largest volume products are phosphoric acid and phosphate derivatives of phosphoric acid (see PHOSPHORUS COMPOUNDS).

Elemental phosphorus reacts with oxidizing acids such as nitric or strong sulfuric. It also reacts with alkali, forming a combination of phosphine, hypophosphite, and phosphite at increasing rates as the pH increases. In reactions related to electric furnace operation, P_4 is not reactive with carbon monoxide over a wide range of temperatures as shown by its compatibility in furnace gases. However, at high temperatures over 1000°C, P_4 reacts with steam to generate P_2O_5 and hydrogen (8).

4. Manufacture of White Phosphorus

All commercial phosphorus is manufactured at a few sites around the world. Significant production occurs in Idaho the United States, in the Netherlands, in Kazakstan, and in China; smaller production occurs in France, Russia, and India. A large amount of furnace capacity has been shut down worldwide because of cost pressure from electric power costs, phosphate derived from purified wet acid, and detergent phosphate bans legislated in the Western World.

Elemental phosphorus is produced from a phosphorus-rich ore mostly recovered by strip mining. This ore usually contains fluorapatite, plus some silica and silicates. When a carbon source, usually coke, is added to the ore at temperatures greater than 1100°C, the following overall reaction occurs:

$$2\,Ca_5F(PO_4)_3 + 9\,SiO_2 + 15\,C \rightarrow 9\,CaSiO_3 + CaF_2 + 15\,CO(g) + 3\,P_2(g)$$

At the lowest reaction temperatures, P_4 tetrahedra rather than P_2 dimers may be produced, or as the gas cools, dimers combine as:

$$2\,P_2 \rightarrow P_4$$

There are several theories about the course of this reaction, but the actual reaction mechanism in the electric furnace is not proven and may vary depending on the location in the furnace. The reaction is endothermic and does not occur at significant rates except at elevated temperatures. The reaction is facilitated by adding additional silica beyond that contained in the ore, usually as the mineral quartzite. The silica serves a twofold purpose. First, it lowers the slag melting point, and second, it combines with the lime values in the ore to improve the thermodynamics of the reaction. Controlling the melting point of the slag is critical for optimizing phosphorus production. If reaction temperatures are increased over 1700°C, unwanted side reactions such as the reduction of silica become excessive. These reactions unproductively consume energy and can contaminate the phosphorus product. The most productive reaction temperature range appears to be 1400–1600°C.

The most effective phosphorus production technology uses a submerged arc furnace. The submerged arc furnace performs three functions: chemical reactor, heat-exchanger, and gas–solid filter, respectively, each of which requires a significant amount of preparation for the solid furnace feed materials.

The two ore preparation technologies in common use are moving grate calciners and rotary kilns. The primary purposes of this preparation step are to produce strong feed agglomerates, often called nodules; to provide a consistently sized material; and to remove energy-consuming impurities that disrupt furnace operation. Some common preparation steps for the silica include crushing, screening, washing, and drying. The coke may be metallurgical, petroleum, or formed coke, but must be size-controlled and is often dried before use.

Once each of these materials has been prepared for furnace use, a furnace charge (burden) is produced by mixing and proportioning the three components. The mixing process is accomplished using accurate weighing systems. The burden is then transported to the furnace charge bins. As the furnace is operated, feed falls continuously by gravity from the charge bins through a system of vertical chutes into the furnace. Two molten furnace by-products, slag and ferrophos, are tapped (removed) from the furnace using either interval or continuous tapping. The furnace off-gas containing primarily phosphorus and carbon monoxide leaves the furnace by flowing up through the porous burden while exchanging heat and dust. Next, the off-gas is usually cleaned of dust particles, using an electrostatic precipitator. Lastly, P_4 is separated from the CO using a water-spray condenser, and the molten P_4 is pumped to storage tanks. Each of these process steps is discussed in greater detail in the following sections. The general steps in the process are shown schematically in Figure 1.

4.1. Mining. Phosphate rock minerals are the only significant global resources of phosphorus. With the closure of all North American white phosphorus production facilities outside of the western United States, the only remaining mines utilized for U.S. P_4 production are located in Idaho (9). However, some ore mined in Florida is still shipped overseas for use in elemental phosphorus plants.

The western phosphates are sedimentary deposits in adjoining areas of Wyoming, Idaho, and Utah derived from a former inland sea. They consist of layers of limestone, phosphate, and chert, now buckled and faulted so they are rarely horizontal. The phosphate ore is strip-mined using large earth-moving equipment such as shovels, scrappers, dump trucks, and bulldozers to mine the overburden and phosphate ore. Mining ratios of overburden to metric ton of recovered ore are from 1–3 m^3/t (2–4 yd^3/short ton). The typical mining practice is to remove ore and overburden from a pit in discrete layers (lifts) of 10–20 m in depth. Overburden from the pit is back-hauled to a previously mined pit. Extensive land reclamation practices are later carried out to return the mine areas to natural states.

The ore is stockpiled at the mine in several piles based on the particular operating strategy of assay and ore chemistry. Typical assay of the blended grades used in the process is about 23–30% P_2O_5, 35–40% CaO, and 20–30% SiO_2. Owing to the cold winters in Idaho, the ore is usually shipped to the plants only during the warm part of the year, between April and October. This eliminates the need for ore car heating to remove frozen ore from the cars. Transportation methods include both open railcars and large trucks, depending on the mine and plant locations and associated economics.

4.2. Feed Preparation. The burden charged to a phosphorus furnace must be kept porous enough to allow the gases generated in the reaction zone near the bottom of the furnace to escape while losing heat to the feed and being cleaned of entrained dust. To allow sufficient porosity, the diameter of the phosphate ore, quartzite, and coke particles are sized in the range of 0.5–5 cm and must not contain excessive fines that will block the gas flow. The coke is received from suppliers already in the appropriate sizes or is crushed and screened on-site. The quartzite is generally mined locally and is crushed and screened to obtain the desired size distribution. The phosphate ore usually consists of fine particles that must be agglomerated and sintered by some process into a hardened mass that will resist deterioration during subsequent handling. The sintering or calcination step also serves to remove organics and other impurities that contaminate the product and cause bridging of the burden above the reaction zone in the furnace, which again restricts the gas flow and inhibits the heat exchange and dust removal from the off-gas. A number of technologies are therefore utilized in the phosphorus industry to prepare the phosphate ore.

One ore preparation method employs a grate calciner similar to a Dwight-Lloyd Sintering Machine. This machine consists of a continuous belt of connected cast iron grate modules that move through various heating and cooling zones on tracks. In this process the fine phosphate ore is first pressed into green briquettes similar in appearance to charcoal briquettes (Fig. 2). The briquettes are fed onto the grate to form a level bed of material. Combustion of carbon monoxide from the furnace off-gas, supplemented by other fuel, is used to heat an air stream that is pulled down through the briquettes. The temperature of the bed can reach to above 1200°C. This process forms a durable ore nodule which can undergo additional handling without significant deterioration prior to being charged into the furnace.

Another preparation method is a sintering process where phosphate ore, sand, and coal are blended together and ignited on the grates of a sintering machine. Air is pulled through the blend, and the entire mass is allowed to burn. The resulting fused bed of material is then crushed and screened to the appropriate size distribution, and the undersized material is reprocessed.

Still another ore preparation is the nodulizing process where the ore is heated in a rotary kiln to incipient fusion. The tumbling action in the kiln causes the phosphate ore to cohere and form spheroidal agglomerates. Combustion of carbon monoxide from the furnaces is used along with supplemental fuel to supply heat to 1300–1500°C. A boring bar is used near the kiln discharge to aid in breaking up the fused ore. The material is then cooled, crushed, and screened to the appropriate size for furnace feed.

One other method used to size the phosphate ore is disk agglomeration. After preparation, the disk agglomerates are sintered at high temperature in separate process steps, followed by screening to the appropriate size specifications.

Some producers beneficiate the phosphate ore prior to agglomeration to increase the phosphate content and remove undesirable contaminants. One approach uses a water wash to remove fines which are lower in assay and higher in contamination. If too much clay is removed from the ore by the beneficiation, a binder such as bentonite clay must be added back to the ore to facilitate agglomeration.

4.3. Electric Furnace. Two basic types of phosphorus furnaces based on electrode configuration are in use. First, the in-line type having three electrodes lined up in a row allows for a simpler layout and a rectangular furnace design at the expense of electrical energy efficiency. Single-phase transformers incorporating Y or delta electrical connections having power ratings of 15–40 MW are typical of operating in-line furnaces. Second, the delta type of furnace uses a three-electrode, symmetrical triangular configuration with a three-phase Y or delta electrical connection operating in the 45–65 MW range at potentials of 200–650 V. World class phosphorus furnaces are of this type. The delta furnace is circular, polygonal, or of a rounded triangular cross-section type. A typical delta furnace along with accompanying off-gas handling system is shown in Figure 3. The furnaces are basically run continuously, except during repairs, process upsets, power curtailments, or electrode building. Typical operating characteristics for a large (60-MW), phosphorus furnace are shown in Table 2.

The electrodes are cylindrical and hang vertically in the furnace from suspension cables or hydraulic, water-cooled electrode clamps, which allow up-and-down movement of the electrode via an automated amperage control system. Prebaked carbon–graphite electrodes are used exclusively in domestic furnaces, with some foreign facilities utilizing Søderberg electrodes. Electrodes of 110–140 cm diameter and a nominal 2.5-m length are generally used. A tapered male–female thread design is used to build electrodes on top of one another as they are consumed in the furnace at about 15–30 kg per 1000 kg phosphorus. Substantial mechanical and thermal stresses are imposed on the electrodes during operation and can result in electrode breakage which can severely affect furnace operation and on-stream time. Proper attention to assuring electrode quality, joint integrity, and building procedures is essential. Electrodes carry up to 65 kA, which necessitates careful attention to electrical design in order to optimize the furnace power factor, which is about 0.96–0.98. Some producers have developed hollow electrode technology to convey carbon–coke fines directly into the reaction zone at the tip of the electrode, which results in decreased electrode consumption.

The outer shell of the furnace (roof, sides, and bottom) is of welded steel plate construction employing various alloys to meet the electrical, thermal, and corrosion requirements at specific locations. Water and air cooling are used extensively to control refractory and metal temperatures. Large carbon blocks cemented together with carbon paste or ramming material are used to construct a monolithic bottom hearth 1–1.5 m thick. Carbon and graphite bricks, rams, and pastes are used as the primary refractory materials in the sidewall to just above the molten slag zone of the furnace. Fire brick is typically used on the upper sidewalls with castable and gunnite high alumina refractory used on the furnace roof. The electrodes enter the furnace through special refractory lined sleeves that are sometimes water-cooled. A telescopic seal is customarily used to provide a gas seal between the electrode and the furnace, which operates at about ± 23 cm water pressure. Refractory performance is critical in obtaining satisfactory furnace operability, and is key to getting long life between furnace rebuilds, which is a significant cost factor of P_4 manufacturing.

The raw materials, or burden, are fed by gravity from surge bins above the furnace via choke-fed feed chutes that distribute burden evenly around each of the three electrodes. It is important in the design of the feed delivery system to minimize material segregation, feed pluggages, and size degradation in order to maintain optimal furnace operation. It is common practice to inject inert gas into the feed chutes to minimize the chance of air in-leakage into the furnace or furnace off-gas leakage to the feed bins. Hollow electrode technology can also result in improved raw material utilization and furnace control. Control of the burden sizing and chemistry is necessary to control the reaction zone position and burden porosity, which is a key factor in optimizing P_4 recovery efficiency and off-gas temperature, off-gas flow, and dust carryover.

The phosphate reduction occurs in the high (1300–1600°C) temperature reaction zone in the lower portion of the furnace. Slag and ferrophos are two molten by-products produced from the reduction reaction. Ferrophos, which is more dense than slag, is tapped from one or more tapholes about 5–8 cm in diameter near the top of the carbon hearth refractory. The slag is tapped from one or more tapholes about 5–8 cm in diameter nominally 25 cm above the ferrophos taphole. Both tapholes are plugged with clay or other suitable material. The slag taphole is generally water-cooled to extend the life of the surrounding refractory. Slag is tapped almost continuously from the larger furnaces. Three principal slag-handling techniques are (*1*) tapping into pits which are cooled via water sprays, followed by removal with front-end loaders; (*2*) tapping into ladles which allow transport of the molten slag to remote slag dumps; and (*3*) granulating with high volumes of water to rapidly cool the slag into small-sized aggregate. Ferrophos is tapped 1–3 times per day, depending on iron concentrations in the burden. Care must be taken to avoid and protect against contact between molten ferrophos and water because of the likelihood of steam explosions, which can be extremely hazardous. Ferrophos tapping is into pots or molds where it is allowed to cool and is later crushed and sized for sale for metal recovery processing or alloy additives.

4.4. Product Recovery. At standard conditions (25°C, 101.3 kPa (1 atm)) typical off-gas compositions are about 86% CO, 7.5% P_4, 5% H_2, 1% N_2, and traces of PH_3, CO_2, F, and S; large furnaces generate off-gas at a rate of about 120–180 m^3/min. In most installations the off-gas is passed through a series of Cottrell electrostatic precipitators which remove 80–95% of the dust particles. The precipitators are operated at temperatures above the 180°C dew point of the phosphorus. The collected dust is either handled as a water slurry or treated dry. Final disposal is to a landfill or the dust is partially recycled back to the process. The phosphorus is typically condensed in closed spray towers that maintain spray water temperatures between 20 and 60°C. The condensed product along with the accompanying spray water is processed in sumps where the water is separated and recycled to the spray condenser, and the phosphorus and impurities are settled for subsequent purification.

Although most of the particulate in the off-gas from the furnace can be captured by the electrostatic precipitators before condensing the phosphorus, some carryover into the product P_4 is inevitable. This particulate is partly separated into the condenser water. The remainder reports to the phosphorus to yield either dirty product or a stable emulsion called phosphorus mud or sludge. Over many years a variety of approaches have been used to minimize the formation of sludge and to recover phosphorus product from the sludge.

Less stable parts of the sludge can be treated by holding in tanks for extended periods of time to allow the weaker emulsion to break and separate a clean P_4 product. The more stable sludges can be broken by mechanical action in filters or centrifuges, by recycle to the furnace for redistillation, or by redistillation in auxiliary units. Chemical attack via oxidation or complexing agents that break the emulsion has also been employed.

4.5. By-Products. The electric furnace process generates four streams that can be considered by-products: slag, ferrophos, precipitator dust, and carbon monoxide off-gas. The approximate composition of the slag and precipitator dust are given in Table 3. These vary somewhat among different phosphorus manufacturers.

The slag has the primary chemical composition of pseudowollastonite, $CaSiO_3$, having significant contents of calcium fluoride and alumina, and other components depending on the ore source. This slag has been used as railroad ballast and road and building-block aggregate. Application is clouded as of this writing by questions about the low level radioactivity common in western U.S. ores and slags. Most furnace slag has been accumulated at plant sites, where it is considered inert and nonhazardous.

Ferrophos consists primarily of 50–60 wt% iron and 18–28 wt% phosphorus in proportions representing Fe_2P plus smaller amounts of either FeP or Fe_3P. However, varying amounts of chromium (4–5 wt%) and vanadium (5–6 wt%) present in the ore are also included in the ferrophos, and are recovered in some cases. From 0–2 wt% of silicon may also be present. Ferrophos is also sold for use in specialty steels that can accommodate the phosphorus content in their formulation (see STEEL).

Precipitator dust often contains concentrated amounts of minor ore components that make it attractive. The potassium, phosphate, and zinc content have resulted in its use in fertilizer, and the silver and gallium content have been the subject of some recovery efforts (see RECYCLING, INTRODUCTION).

The carbon monoxide off-gas which is saturated with H_2O and P_4 after condensation of the phosphorus is usually used as a fuel for calcination of the ore in the front end of the process. This gas contains 90–93% CO, 1–3% N_2, 1–8% H_2, and 0–1% CO_2.

4.6. Product Quality and Specifications. Most of the elemental phosphorus produced is converted to derivatives by the manufacturer. Some white phosphorus is sold on the open market. Typical manufacturers' phosphorus analyses for a straw yellow product follow:

phosphorus, wt%	>99.90
arsenic, ppm	30–250
toluene insolubles, wt%	0.01–0.05
oils (hydrocarbons), ppm as carbon	30–100

Trace metals are analyzed and kept at levels appropriate to the special needs of the customer.

For analysis, white phosphorus is typically extracted through a fritted thimble with refluxed toluene. Any trace amounts of water are captured in a calibrated sidearm to the apparatus. The solids on the frit are weighed, the water measured, and the phosphorus calculated by difference. For impure samples of phosphorus, the toluene extract may be analyzed with a gas chromatograph (gc) equipped with a phosphorus–nitrogen detector.

Trace contaminants in the phosphorus may be determined by oxidation of the phosphorus by various techniques. The metals are then determined by an inductively coupled plasma spectrophotometer or by atomic absorption. The most important trace metal is arsenic, which must be reduced in concentration for food-grade products. Numerous other trace metals have become important in recent years owing to the specifications for electronic-grade phosphoric acid required by the semiconductor industry (see ELECTRONIC MATERIALS; SEMICONDUCTORS, SILICON-BASED SEMICONDUCTORS). Some trace elements must be reduced to the low ppb range in phosphoric acid to comply.

Analyses of raw materials and by-products from the phosphorus process are generally done by x-ray florescence or other instrumental methods. Statistical process control is utilized to ensure that critical process parameters are maintained in control. Key analytical parameters that are monitored include P_2O_5 and ignition loss in the ore; Fe_2O_3, SiO_2, CaO, and sizing in all raw materials;

fixed carbon in coke; and P_2O_5 and SiO_2/CaO ratio in the slag, to name a few. Very few classical wet methods are employed except for occasional nonroutine samples or for instrument standardization.

5. Manufacture of Red Phosphorus

Red phosphorus is manufactured from white phosphorus for applications such as striking surfaces for matches, fireworks and military pyrotechnics (see PYROTECHNICS), flame retardants in polymers, semiconductors, and PH_3 used to manufacture semiconductors. The batch conversion process requires one to two days and involves heating molten white phosphorus at temperatures somewhat below its boiling point of 280°C. The conversion is exothermic, so the reaction temperature must be controlled to prevent accidents. About half of the added white phosphorus is converted before the accumulation of solid red P in the molten phosphorus drives the viscosity of the melt to a thick slurry. Solidification occurs at about 70% conversion to red phosphorus. After most of the conversion takes place, the reaction may be driven to completion at higher temperatures of 300–600°C, where the remaining white P_4 is converted or vaporized. Alternatively, the remaining P_4 can be reacted with alkali. If the particle size is not controlled during reaction, the final product is then wet-ground or ball-milled and finally dried.

Continuous processes and routes involving added pressure and shorter conversion times have been developed. The process may also be adapted either to add stabilizers to reduce the final reactivity of the red P, or to ensure high reactivity such as for subsequent conversion to PH_3.

6. Shipping and Handling

Phosphorus is stored and handled under a protective layer of water. Production quantities are transferred as a liquid by either water displacement or pumps, with water recycle to maintain the water balance and cover. In earlier times, phosphorus was sometimes stored in underground tanks or pits, but as of the 1990s storage is limited to tanks located inside diked areas that are accessible on the outside for safety and leakage control.

For off-site transportation, the phosphorus is loaded into railcars for transfer to the sites where it is used directly as a raw material or burned and hydrated to phosphoric acid. During shipping, the phosphorus is allowed to solidify in the cars. The railcars are commonly double walled with a jacket that can be heated with steam or hot water so that the phosphorus can be remelted on-site for transloading to local storage tanks. For overseas shipping, tanktainers with reinforced superstructure for safe handling are used. Formerly, full tanker ships were in use.

Smaller amounts of phosphorus, or elemental phosphorus-containing materials, are also shipped in 115-L (30-gal) drums that are DOT regulated (U.S. DOT 1A1 or 1A2 classification) and have thick shells and special gaskets and fittings for protection. Quantities up to 0.5 kg (1 lb) are allowed for shipping in two hermetically sealed (soldered), nested cans inside a wooden box where the empty space is filled with vermiculite (U.S. DOT 4C1, 4C2, 4D, or 4F classification). All air transportation of elemental P_4, both U.S. and international, was prohibited beginning in 1992.

A DOT regulation covers both domestic and international shipping (10). For transportation safety, the DOT has information for first responders to incidents involving elemental phosphorus (11). The phosphorus producers in the United States have established a Phosphorus Emergency Response Team (PERT) to assist in handling P_4 emergencies.

7. Economic Aspects

Beginning in 1969, a movement to restrict and then legally ban the use of phosphates in detergents led to the closing of significant amounts of plant capacity. The movement derived from an unproven belief that eutrophication of lakes and streams could be reduced by eliminating the phosphates contained in home laundry detergents. Phosphorus producers objected that only 3% of the phosphorus in U.S. rivers, lakes, and streams was contributed by detergent phosphates. The remaining 97% of the phosphorus comes mostly from agricultural fertilizer run-off, plus human and animal waste (12). Nevertheless, legal bans on phosphate detergents were instituted in enough locations to effectively eliminate phosphate detergents in most of the United States. Similar legislative bans have been enacted in some European countries.

Phosphate rock minerals are the only global resources of phosphorus. Worldwide, the United States is the leading producer and consumer of phosphate rock and the leading producer, consumer, and supplier of phosphate fertilizers. Phosphate rock consumption rose from 36.4 Mt in 2003 from 34.7 Mt in 2002. Wet-process phosphoric acid manufacturing consumed more that 95% of reported U.S. phosphate rock usage. The remainder was used to produce elemental phosphorus or sold for direct application to soil. Elemental phosphorus is used for the production of phosphorus compounds for a variety of food additives and industrial applications.

Table 4 gives U.S. statistics for phosphate rock (13). Table 5 shows U.S. imports for consumption of phosphate rock and phosphatic materials. Elemental phosphorus is included in this list. U.S. exports of elemental phosphorus are given in Table 6.

8. Health and Safety Factors

At ambient temperatures white phosphorus spontaneously ignites when exposed to air. It has an autoignition temperature of 30°C. As a result, any human exposure to white phosphorus can cause severe thermal burns to the skin and eyes. The vapor from phosphorus can cause severe lung irritation, followed by a buildup of fluid in the lungs. Continuous long-term inhalation of white phosphorus vapor ($>0.1\,\mathrm{mg/m^3}$) can result in bone loss to the jawbone structure causing loosening of teeth and severe pain and swelling of the jaw (14). This condition is commonly referred to as phossy jaw. Some evidence exists that increased infant mortality can result when pregnant women are exposed to P_4 vapor in excess of 0.075 mg/kg/day (15). Ingestion of white phosphorus is potentially fatal. The lowest reported fatal dose is 1 mg/kg for humans (14). Absorption through the skin is also possible but is only considered to be a moderate hazard compared to the other routes of exposure.

When exposed to air, white phosphorus oxidizes to phosphorus pentoxide forming copious quantities of white smoke. This smoke may be irritating but is not considered to be toxic. White phosphorus solid, liquid, or vapor is also extremely reactive with oxidizers such as strong acids, alkaline hydroxides, halogens, and nitrates. Contact of phosphorus with water or oxidizers also generates phosphine [7803-51-2], PH_3, a highly toxic and flammable gas. Phosphine has an 8-h time-weighted average exposure limit of 0.3 ppm (16). Under alkaline conditions the rate of PH_3 formation is high. At neutral or acidic pH, the PH_3 generation is slow but still very hazardous if the PH_3 is allowed to accumulate in a confined vapor space. The safest commercial handling conditions for molten phosphorus are generally considered to be from pH 6 to 8 at 45–65°C.

Red phosphorus is a human poison by an unspecified route. It may have white phosphorus as an impurity. Red phosphorus is generally less reactive than white phosphorus. It is a dangerous fire hazard when exposed to heat or by chemical reaction with oxidizers. It can also react with reducing agents. Water can be used to fight fire. It might explode on impact (17).

Phosphorus production plants and users should ensure that processing of the material is contained and that potential high exposure areas are well ventilated. Workers must wear aluminized fiber glass or Kevlar flame-retardant full protective clothing, face shield with hard hat, rubber boots, and heavy rubber gloves when handling or transferring the product. The phosphorus should always be kept under neutral pH water at temperatures less than 65°C or under an inert atmosphere to avoid oxidation and exposure hazards. High potential exposure areas should also be equipped with well-maintained, water-filled safety tubs, deluge systems, and water-spray extinguishing systems as a precautionary measure. If high exposure levels to phosphorus vapors or phosphine are anticipated, then self-contained breathing apparatus units should be utilized. Individuals exposed to phosphorus through skin or eye contact should have the exposed area flushed immediately with large amounts of water. The affected area should be kept wet until all of the phosphorus is removed or flushed away. Victims of phosphorus inhalation should immediately be removed to an area with fresh air and have artificial respiration administered, if necessary. Workers who have had dental surgery and pregnant women should be kept away from phosphorus exposure areas completely. Anyone who ingests phosphorus should drink a large volume of water and be induced to vomit. Medical assistance should be obtained as soon as possible after any instance of phosphorus exposure.

9. Environmental Concerns

Pollution control has become a primary concern and expense of elemental phosphorus producers since the 1970s. Problem areas include mining dusts, feed preparation and feed-handling dusts, slag dusts and emissions, precipitator dust, off-gas flare emissions, and phossy water and sludge treatment. The specific contaminants include elemental phosphorus, dust particulates, leachable hazardous metals, and low level radioactivity. These problems are being addressed by a variety of technical options which are often unique to each process site. The final discharges from the phosphorus plants are being confined to slag, ferrophos, and precipitator dusts, which are all nonhazardous wastes. Commercial application of the slag and precipitator solids is a point of contention owing to low level radioactivity. Ferrophos is often sold for its iron, vanadium, and chromium content.

U.S. production of phosphate rock is not likely to rise above 40×10^6 t per year because of the gradual depletion of high quality deposits in Florida. New mines are in the development and permitting stages in Florida. The time needed to complete the permitting process has increased significantly because of environmental concern in southwest Florida. Some are concerned that new mines in Desoto and Hardee Counties may adversely affect downstream water resources in the Peace River, which is a major source of drinking water.

Recent U.S. patent literature involves the removal of phosphorus from sludge (18), wastewater (19,20), and a sewage treatment process (21).

10. Uses

About 85% of the elemental P_4 is burned to P_2O_5 and hydrated to phosphoric acid. Part of the acid is used directly, but the biggest part is converted to phosphate compounds. Sodium phosphates account for the largest use; calcium, potassium, and ammonium phosphates are the second largest use. Final applications include home laundry and automatic dishwasher detergents, industrial and institutional cleaners, food and beverages, metal cleaning and treatment, potable water and wastewater treatment, antifreeze, and electronics. The purified wet acid serves the same markets.

The remaining elemental P_4 is used in P_4-dependent applications which require the element as a direct reactant. The principal products include P_2S_5, PCl_3 and $POCl_3$, P_2O_5, and hypophosphite, with much smaller amounts leading to PH_3, red P, phosphonates, and various other phosphorus derivatives. Final applications include flame retardants (qv), lubricant additives, insecticides, herbicides, water treatment, cleaning compounds, plasticizers, semiconductors, and surfactants (6).

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Table 1. **Physical Properties of α-White Phosphorus, P_4[a]**

Parameter	Value
melting point, °C	44.1
boiling point, °C	280.5
heat of fusion, J/(kg·mol)[b]	2.5×10^6
heat of vaporization, J/(kg·mol)[b]	49.8×10^6
density, g/cm^3	
solid	1.83
liquid at 50°C	1.74
liquid viscosity, at 50°C, mPa (=cP)	1.69
solubility of P_4, g/100 g solvent	
carbon disulfide at 10°C	89.8
benzene at 15°C	2.7
water at 15°C	0.00033

[a] See especially Ref. 3.

[b] To convert J to cal, divide by 4.184.

Table 2. **Operating Characteristics of a 60-MW Phosphorus Furnace**

Parameter	Value
average potential between electrodes, V	250–350
power factor	0.96–0.98
raw materials consumed[a]	
power, kWh	13–15
fluorapatite ore, kg	10–13
coke, kg	1.2–1.7
silica, kg	1–2
products formed[a]	
slag	8–9
ferrophos	0.1–0.2
furnace off-gas	2.6–2.9
recovery, based on P_4 charged to the furnace, %	84–90
temperature of off-gas, °C	300–450
temperature of slag at tapping, °C	1400–1500

[a] Per kilogram of elemental P_4 produced.

Table 3. **Composition of Phosphorus Manufacture By-Products, Wt%**

By-product	P_2O_5	CaO	SiO_2	Al_2O_3	F	Fe_2O_3	K_2O	ZnO	C
slag	1.0–2.5	40–50	38–44	3–7	2–3	0.1–0.5			
precipitator dust	20–30	5–15	15–30	2–4	3–5		5–20	5–15	0–10

Table 4. **U.S. Phosphate Rock Statistics**[a]

Salient statistics	2000	2001	2002	2003	2004
production, marketable	38,600	31,900	36,100	35,000	37,000
sold or used by producers	37,400	32,800	34,700	36,400	36,300
imports for consumption	1,930	2,500	2,700	2,400	2,400
exports	299	9	62	64	40
consumption[c]	39,000	35,300	37,400	37,400	38,700
price, average value, dollars per ton, f.o.b. mine	24.14	26.82	27.47	27.01	27.12
stocks, producer, yearend	8,170	7,510	8,860	7,540	7,600
employment, mine and beneficiation plant, number[b]	3,500	3,400	3,200	3,200	3,300
net import reliance[d] as a percentage of apparent consumption	1	9	3	9	6

[a] Ref.13.

[b] Estimated.

[c] Sold or used + imports − exports.

[d] Imports − exports + adjustments for government and industry stock changes.

Table 5. **U.S. Imports for Consumption of Phosphate Rock and Phosphatic Materials**[a]

	2002		2003	
Phosphate materials	Quantity, t	Value[b], $\$ \times 10^3$	Quantity,t	Value[b], $\$ \times 10^3$
phosphate rock				
unground [c]	730	22,300	828	21,200
ground	595	32,700	460	23,900
phosphate rock[d]	2,700	112,000	2,400	84,000
dicalcium phosphate	6	6,400	6	7,090
elemental phosphorus	34	50,900	16	23,600
normal superphosphate	8	1,220	1	175
triple superphosphate	29	3,500	33	4,960
diammonium phosphate	156	32,800	142	30,700
fertilizer containing nitrates and phosphates	3	835	26	5,270
phosphoric acid	18	10,200	51	20,100

[a] From Ref. 9 .

[b] Declared cost, insurance, freight values.

[c] Some phosphate rock tonnages and values were suppressed by the U.S. Census Bureau.

[d] Includes an estimate for data suppressed by the U.S. Census Bureau based on reported Moroccan exports to the United States.

Source: U.S. Census Bureau.

Table 6. **U.S. Exports of Elemental Phosphorus**[a,b]

	2002		2003	
Country	Quantity,t	Value[c], $\$ \times 10^3$	Quantity,t	Value[c], $\$ \times 10^3$
Brazil	7,150	21,100	7,540	16,200
Canada	698	1,580	689	1,490
China	2	10	39	73
Japan	38	81	60	117
Korea	5	15	112	217
Mexico	2,500	5,030	120	236
Malaysia	19	37	113	267
Taiwan	133	253	12	23
other	51[d]	106[d]	52	163
Total	*10,600*	*28,200*	*8,740*	*18,800*

[a] Data are rounded to no more than three significant digits; may not add to totals shown.

[b] Free alongside ship values.

[c] Source: U.S. Census Bureau.

[d] Revised.

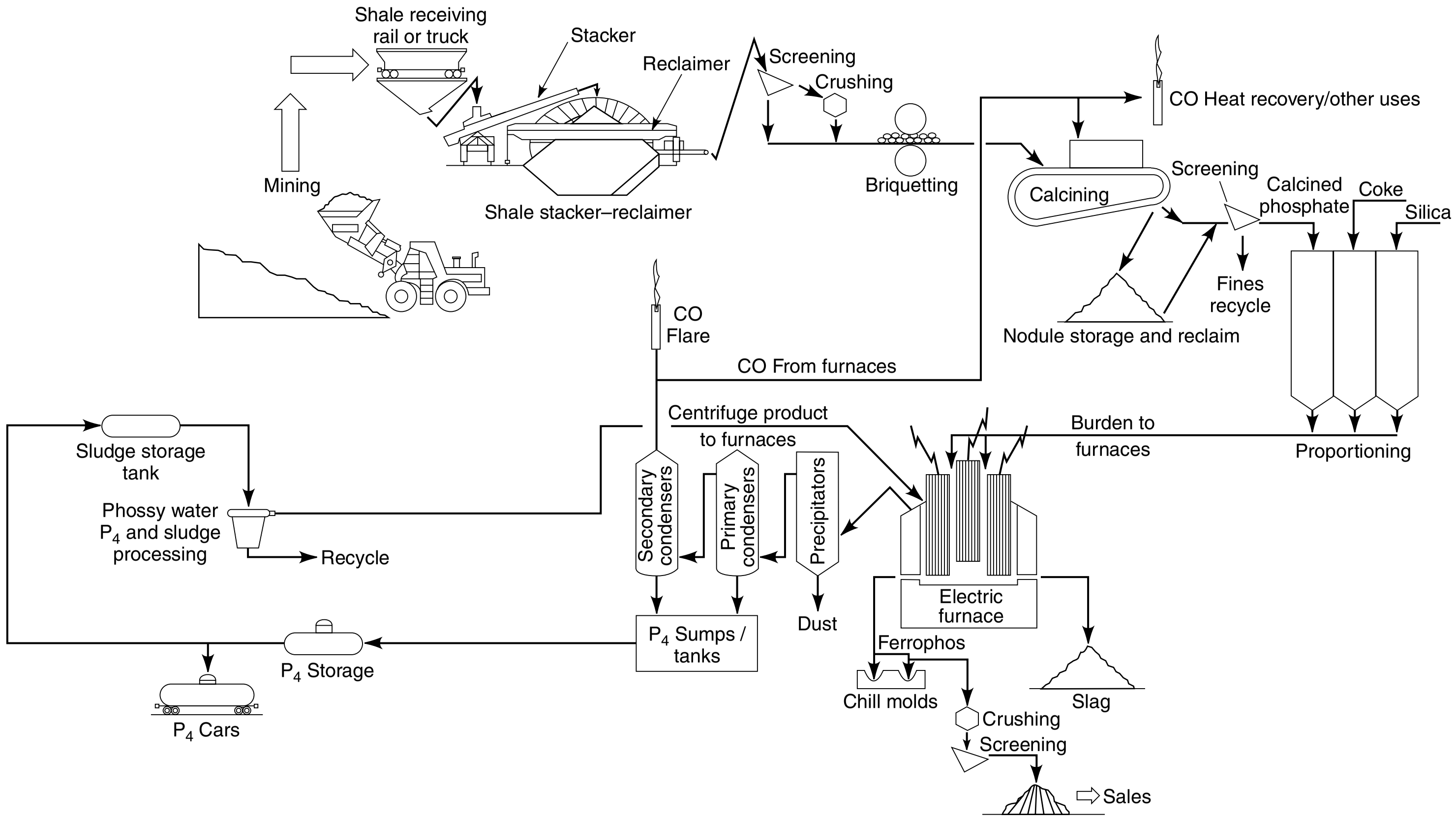

Fig. 1. Schematic of the elemental phosphorus process.

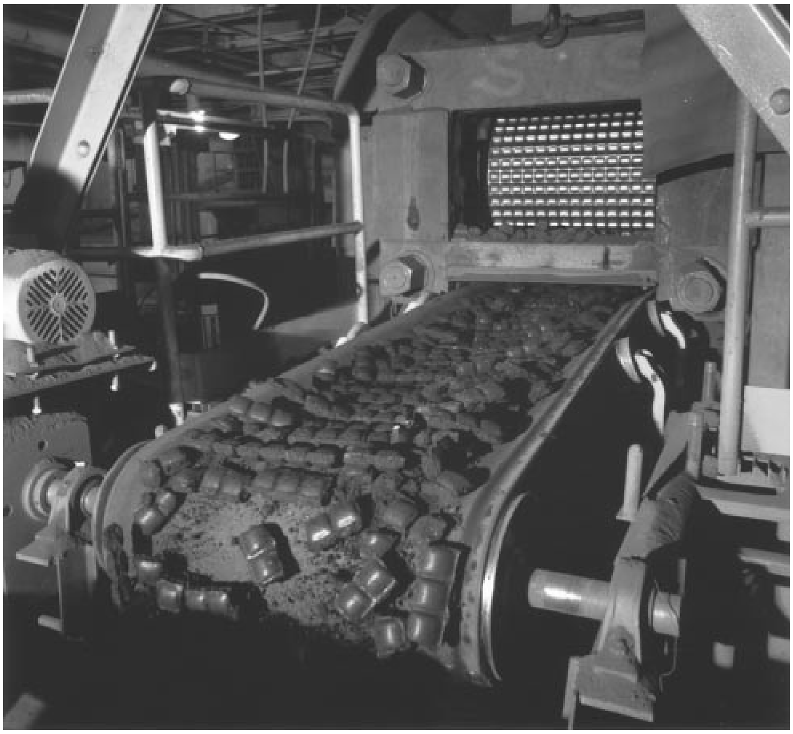

Fig. 2. Phosphate ore briquetting.

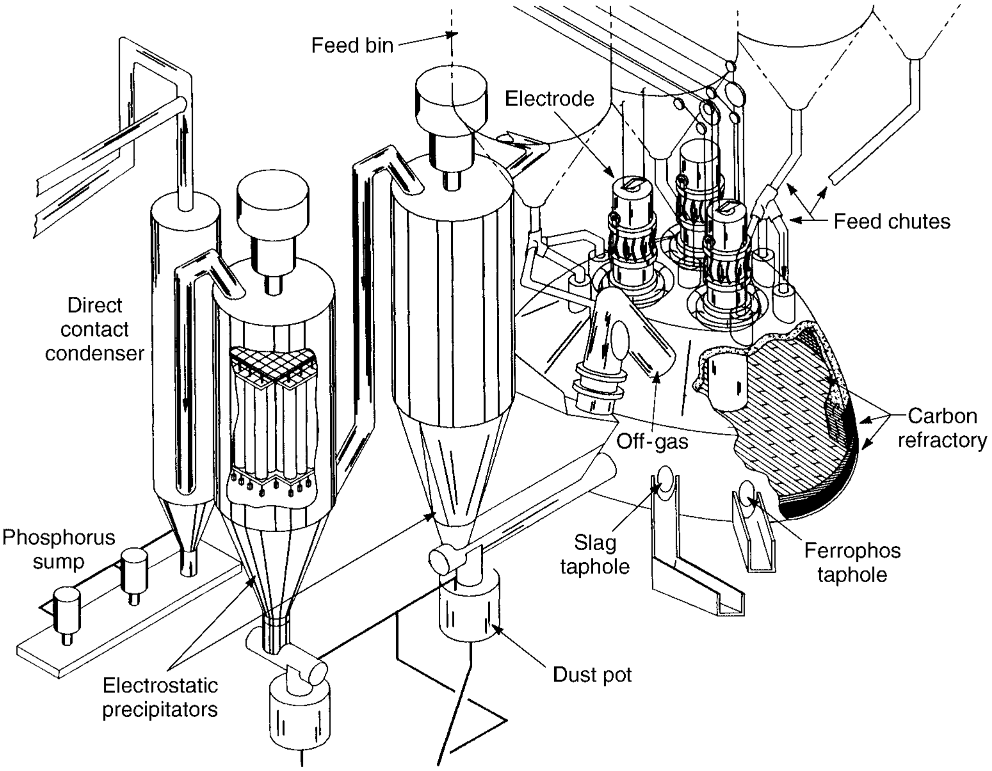

Fig. 3. Elemental phosphorus furnace.