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# **Utilization of Apatite Ores**

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http://dx.doi.org/10.5772/62215

## Abstract

Phosphate rock is an important mineral commodity used in the chemical industry and production of food. The first section of ninth chapter of this book introduces utilization of apatite ores for manufacturing of phosphorus. The second part deals with production of phosphoric acid via wet and thermal process and utilization of byproducts such as phosphogypsum, phosphorous slag and ferrophosphorus. The last section of this chapter describes the methods for production of fertilizers, such as supephosphates, Thomas slag, ammonium phosphates, thermophosphates, etc., and the chapter ends with environmental demand of phosphate fertilizers.

**Keywords:** Apatite, Apatite Ore, Phosphorus, Phosphoric Acid, Fertilizers, Superphosphate, Thomas Slag

The group of apatite minerals was studied by the physiologists, biochemists or soil scientists as well as the geologists or mineralogists. Each group of scientists concerned with the apatite minerals see their own problems and make attempts to solve them in their own way. The soil scientists are mainly interested in the availability of  $P_2O_5$  to plants. The physiologists focus on the prevention of dental caries or on the mechanism of various types of metal poisoning. The geologists study the mode of formation of phosphorite deposits, the chemists carry out the equilibrium studies and analytical methods and the mineralogists investigate the crystal chemistry of entire group [1].

# 9.1. Manufacturing of phosphorus

The original procedure for the production of elemental phosphorus, as described by R. BOYLE in 1680, was based on the method of H. BRANDT [2],[3],[4]. The substance glowed in





Fig. 1. Phosphorus retort condensation arrangement (Albricht & Wilson) (a) and a French bone furnace (Four pour la calcination des os) (b) [7].

the dark<sup>1</sup> and burst in flame into  $P_4O_{10}$  when exposed to air [2],[5]. The procedure involved the distillation of large quantity of partly digested urine to the consistency of thick syrup. Fine white sand was added and the mixture was heated in a retort at first gently to remove the volatiles and then very intensely to produce phosphorus, which was distilled over and cooled under water. When the bone ash (M.M. COIGNET) was used as a raw material for the production of phosphorus, the process consisted of the treatment with sulfuric acid to produce phosphoric acid, which was then concentrated and heated with coke in a retort to produce phosphorus according to the following equations [6],[7]:

$$\operatorname{Ca}_{3}(\operatorname{PO}_{4})_{2} + 3 \operatorname{H}_{2}\operatorname{SO}_{4} \rightarrow 3 \operatorname{CaSO}_{4} + 2 \operatorname{H}_{3}\operatorname{PO}_{4}$$
(1)

$$H_{3}PO_{4} \rightarrow HPO_{3} + H_{2}O$$

$$(2)$$

$$4 \text{ HPO}_{3} + 12 \text{ C} \rightarrow P_{4} + 2 \text{ H}_{2} + 12 \text{ CO}$$

$$(3)$$

The drawing of the kiln for the calcination of bones<sup>2</sup> is shown in **Fig. 1(b)**.

<sup>&</sup>lt;sup>1</sup> The name phosphorus (light-bearing) was often used by alchemists to name various light-bearing materials, which were devoid of the element, e.g. the Bologna phosphorus (luminescent barium sulfide), the Baldwin's phosphorus (luminescent calcium nitrate), etc. Probably the earliest prepared phosphorus salt was sodium ammonium hydrogen phosphate, which has been known since the ancient times [2].

<sup>&</sup>lt;sup>2</sup> Bones became the source increasingly difficult to achieve. It is stated that the use of bones was so great in England during the eighties of 19th century that the battlefields on the continent of Europe were plundered to supply Great Britain's demand for phosphates [7].

The discovery of elemental (white) phosphorus<sup>3</sup> was soon followed by the characterization of its combustion products, phosphorus pentaoxide,<sup>4</sup> and in 1694, R. BOYLE prepared phosphoric acid by dissolving  $P_2O_5$  in water. Phosphorus was found in plants by B. ALBINO in 1688, and the element was detected in human brain tissue by J.T. HENSING in 1719. In about 1770, phosphorus was recognized as an essential ingredient of animal bones and teeth by C.W. SHEELE, when he prepared the element from bone ash, carbon and sand. By 1779, the first phosphorus-containing mineral pyromorphyte (**Section 1.6.4**) was identified by J.T. HENSING [2].

The first organic phosphorus compound to be identified was probably lecithin, isolated from barin fat in 1811 by VAUQUELIN and characterized as a phosphorus-containing lipid by GOBLEY in 1850. The earliest laboratory synthesis of an organic phosphorus compound was reported by LASSAIGNE, who in 1820 obtained crude alkyl phosphates by the reaction of alcohols with phosphoric acid. The discovery of the first metal-phosphine complex by Rose in 1847 was followed by CAHORS AND HOFFMANN who prepared the first organic complex with metal-phosphorus bond. It can be considered as the beginning of the metallophosphorus chemistry [2].

The following major classes of phosphorus compounds (Fig. 2) are recognized [2]:





Fig. 2. The major division of oxyphosphorus compounds [2]:

<sup>&</sup>lt;sup>3</sup> Three forms of phosphorus include (a) white phosphorus (the most reactive form) with at least two crystalline forms, (b) red phosphorus (discovered in 1847 by VON SCHROTTER) and (c) black phosphorus (discovered in 1914 by BRIDGEMAN) [5].

<sup>&</sup>lt;sup>4</sup> Three forms of  $P_4O_{10}$  are recognized [5]: (a) **H-form**, (b) **O-form** and (c) **O'-form**. The H-form is rhombohedral (R3c, *a* = 7.43 Å,  $\alpha = 87.0^{\circ}$  and Z = 2). In the hexagonal setting, Z = 6, a = 10.31 and c = 13.3 Å. The O-form is orthorhombic of the space group FDD2 and the cell parameters *a* =13.3, *b* = 8.14 and *c* = 5.26 Å and Z = 8. The O'-form is orthorhombic, the space group PNAM, a = 9.23, b = 7.18 and c = 4.94 Å and Z = 2.

- **2. Carbophosphorus** (**organophosphorus**) **compounds**, which contain the P-C linkages including carbophosphanes (organophosphanes, P-C), carbophosphenes (organophosphenes, P=C) and carbophosphynes (organophosphynes, P≡C).
- **3. Azophosphorus compounds**, which contain the P-N linkages including azophosphanes (phosphazanes, P-N), azophosphenes (phosphazenes, P=M) and azophosphynes (phosphazynes, P=N).
- **4. Metalophosphorus compounds**, which contain the P-metal linkages including metallophosphanes (P-M), metallophosphenes (P=M) and metallophosphynes (P=M).

These compounds vary greatly in their abundance and importance. The compounds with the P-O linkages dominate the phosphorus chemistry. The most important types of oxyphosphorus compounds are phosphates (salts with PO<sub>4</sub><sup>3-</sup> anion), phosphate esters (P-O-C linkage) and phosphoric compounds (P=O linkage) [2].



Fig. 3. Parker's electric furnace (a) [7] and the scheme of phosphorus furnace (b) [11].

The production of phosphorus by heating the mixture of silica, coke and phosphate rock was first proposed by AUBERTON and BOBLIQUE in 1867, and the use of electric furnace for the heating of the mixture was proposed in 1888 by the patents by J.B. READMAN [8] and T. PARKER and A.E. ROBINSON [9]. **Fig. 3**(a) shows Parker's electric furnace from his later patent in 1892 [10].

The basic method for the production of elemental phosphorus today (**Fig. 4**), except for engineering improvements, is essentially that of the method originated by READMAN. Lower-grade phosphate sand contaminated with clay is concentrated by washing to an average

content of  $P_2O_5$  in the range from 28 to 30%. Higher-grade sand with the content of  $P_2O_5$  of 26 – 28% is used directly in the combination with washed sand. These fine phosphatic grains are compacted or "nodulized" and then sintered into fused agglomerates. The nodules are then mixed with silica and coke particles of similar size. Such mixture is called the "furnace burden". A typical furnace burden has the SiO<sub>2</sub>/CaO ratio of 0.8 to 1.2 and the  $P_2O_5/C$  ratio of 2.3 to 2.6 [6].



Fig. 4. The flow sheet for the electrothermal manufacture of elemental phosphorus [12].

Modern reduction plants for the manufacture of elemental phosphorus (**Fig. 4**) has three main units [12]:

- i. The electrothermal reactor (furnace);
- **ii.** The gas purifier (electrostatic precipitator);
- **iii.** The phosphorus condenser.

The electric furnace for the reaction **Fig. 3(b)** is lined on the bottom and sides with thick carbon blocks, while the top is lined with refractory bricks. The furnace is heated by symmetrically positioned carbon electrodes. They go through almost airtight seal in the furnace roof into the reaction zone and are supported in a manner that enables them to move vertically depending on the power requirements of fluctuating furnace conditions. The temperature in the reaction zone ranges from 1400 to 1500°C. Under this condition, phosphorus vaporizes and rises with carbon monoxide and entrained dust through the space between the furnace burden particles. The mixture next passes through an electrostatic precipitator where the most of the dust is removed. The phosphorus vapor is then cooled, condensed and collected under water [6],[11], [12],[13].

The condensation of white phosphorus<sup>5</sup> is carried out in two stages. In the first stage, the condensation tower water of 50 to 60°C is sprayed from the top to meet the phosphorus vapor

<sup>&</sup>lt;sup>5</sup> Red phosphorus is produced in much less quantities than white phosphorus. The conversion of white phosphorus to red phosphorus is an exothermic reaction producing red phosphorus as a solid product. Since the conduction of heat from the reaction is difficult, the conversion is carried out semi-continuously in a ball mill at 350°C. White phosphorus is fed into the mill with such rate that the reaction temperature is kept constant [12].

being transported countercurrently from below, whereupon phosphorus condenses as a liquid. Solid phosphorus is formed in the second condensation tower, which uses water with the temperature of 10 to 25°C. CO gas is recovered for the use as a fuel in the sintering operation. The by-product calcium silicate is drawn off from the bottom of the furnace as molten liquid. Iron phosphide, "ferrophos" or ferrophosphorus (**Section 9.2.7**) formed from the iron impurities present in the phosphate ore is also drawn off as a melt [6],[12].

The mechanism of phosphate reduction is complex and there is no complete agreement among the exact path of each step in the reaction sequence. The overall reaction can be presented by the following equation [6]:

$$\operatorname{Ca}_{3}(\operatorname{PO}_{4})_{2} + 3 \operatorname{SiO}_{2} + 5 \operatorname{C} \to 3 \operatorname{CaSiO}_{3} + 5 \operatorname{CO} + \operatorname{P}_{2}$$

$$\tag{4}$$

Proposed mechanisms for the reactions are:

**1.** Phosphide mechanism [14]:

$$5 \operatorname{Ca}_{3}(\operatorname{PO}_{4})_{2} + 40 \operatorname{C} \to 5 \operatorname{Ca}_{3}P_{2} + 40 \operatorname{CO}$$
 (5)

$$3 \operatorname{Ca}_{3}(\operatorname{PO}_{4})_{2} + 5 \operatorname{Ca}_{3}\operatorname{P}_{2} \to 24 \operatorname{CaO} + 8 \operatorname{P}_{2}$$
 (6)

2. Acid displacement mechanism:

$$2 \text{ Ca}_{3}(\text{PO}_{4})_{2} + 6 \text{ SiO}_{2} \rightarrow 6 \text{ CaSiO}_{3} + P_{4}O_{10}$$

$$P_{4}O_{10} + 10 \text{ C} \rightarrow 2 P_{2} + 10 \text{ CO}$$
(8)

**3.** CO reduction mechanism:

$$\operatorname{Ca}_{3}(\operatorname{PO}_{4})_{2} + 5 \operatorname{CO} \to 3 \operatorname{CaO} + 5 \operatorname{CO}_{2} + \operatorname{P}_{2}$$

$$\tag{9}$$

$$5 \text{ CO}_2 + 5 \text{ C} \rightarrow 10 \text{ CO} \tag{10}$$

The phosphide theory is generally considered as unlikely due to the thermodynamic reasons, but the acid displacement mechanism has considerable experimental support [6].

# 9.2. Properties and manufacturing of phosphoric acids

## 9.2.1. Orthophosphoric acid

Orthophosphoric acid<sup>6</sup> [15] is a colorless polyprotic weak acid with stepwise dissociation that involves three equilibrium reactions described by the following equations [2],[16], [17],[18]:

$$H_{3}PO_{4} \leftrightarrow H^{+} + H_{2}PO_{4}^{-} \qquad K_{1} = 7.52 \cdot 10^{-3}$$

$$H_{2}PO_{4}^{-} \leftrightarrow H^{+} + HPO_{4}^{2-} \qquad K_{2} = 6.23 \cdot 10^{-8}$$

$$7.2 \le pH \le 12.37$$
(11)
(12)

$$HPO_{4}^{2-} \stackrel{k_{3}}{\longleftrightarrow} H^{+} + PO_{4}^{3-} \qquad K_{3} = 2.2 \cdot 10^{-13}$$

$$pH \ge 12.37$$
(13)

However, due to very low values of the equilibrium constants associated with reactions (**Eqs. 12** and **13**), orthophosphoric acid has only one strongly ionizing hydrogen atom and only the first acidic dissociation (**Eq. 11**) has significant effect on the system composition.  $HPO_4^{2-}$  and  $PO_4^{3-}$  ionic species are present at significant concentrations in very highly diluted solutions only [2].

Orthophosphoric acid gives three series of salts (Eqs. 11 – 13):

- **1.** Normal phosphates with trivalent PO<sub>4</sub><sup>3-</sup> anion, e.g. trisodium phosphate dodecahydrate (Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O);
- Hydrogen phosphates with divalent HPO<sub>4</sub><sup>2-</sup> anion, e.g. disodium hydrogen phosphate dedecahydrate (Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O);
- **3.** Dihydrogen phosphates with monovalent  $H_2PO_4^-$  anion, e.g. sodium dihydrogen phosphate monohydrate (Na $H_2PO_4$ · $H_2O$ ).

When heated, orthophosphoric acid condenses to pyrophosphoric acid (250°C) and then to metaphosphoric acid (316°C) [19]:

$$2 H_{3}PO_{4} \xrightarrow{\geq 250^{\circ}C} H_{4}P_{2}O_{7} + H_{2}O$$
(14)

 $<sup>^{6}</sup>$  Orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>, phosphoric(V) acid) is often termed simply as phosphoric acid, but other phosphoric acids exist: metaphosphoric acid (HPO<sub>3</sub>) and pyrophosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) [15].

$$H_4 P_2 O_7 \xrightarrow{\geq 316^{\circ}C} 2 \text{ HPO}_3 + H_2 O$$
(15)

Hence, from the PO<sub>4</sub> building block, a long series of two- and three-dimensional phosphates originates through P-O-P linkages. There is a continuous series of phosphates from orthophosphate (one P atom) to phosphorus pentaoxide (P<sub>2</sub>O<sub>5</sub>) followed by homologous series of straight-chained, branched and cyclic phosphates. The members of the series having one atom of phosphorus are called orthophosphates; the dimers (two P atoms) are pyrophosphates followed by the triphosphates (tripolyphosphates, three P atoms) and by the tetraphosphates (four P atoms). The members of homologous series (H<sub>2</sub>P<sub>n</sub>O<sub>3n+1</sub>) with 5 – 15 P atoms are referred to as oligophosphates. In general, any phosphate having three or more P atoms is considered to be polyphosphate. Metaphosphates are cyclic with general formula (HPO<sub>3</sub>)<sub>n</sub> or (P<sub>n</sub>O<sub>3n</sub>)<sup>-</sup>. The phosphates with three-dimensional structure are termed as ultraphosphates with the composition given by general formula: P<sub>n</sub>O<sub>3n+x</sub>, where  $1 \ge x \le n/2$  [20].

In the crystalline state, phosphoric acid exists as prismatic crystal of  $H_3PO_4$  and as hemihydrate ( $H_3PO_4 \cdot 1/2H_2O$ , **Fig. 5**), but  $10H_3PO_4 \cdot H_2O$  hydrate was also reported. The crystals of  $H_3PO_4$  have layered structure, where each molecule is connected to six others via hydrogen bonds. Heated to temperatures higher than the melting point (42.35°C), phosphoric acid slowly dehydrates according to the equation:

$$2 H_3 PO_4 \leftrightarrow H_4 P_2 O_7 + H_2 O \tag{16}$$



**Fig. 5.** The  $H_2O-H_3PO_4$  phase diagram (a) and the structure of  $H_3PO_4\cdot 1/2H_2O$  (b) viewed along the b-direction: large and small empty cycles represent water and hydrogen atoms, respectively.  $PO_4^{3-}$  tetrahedra are given in polyhedral representation [5].

The crystal structure of H<sub>3</sub>PO<sub>4</sub> (**Fig. 6**) is monoclinic with the space group P2<sub>1</sub>/c and the cell parameters a = 5.80 Å, b = 4.85 Å, c = 11.62 Å,  $\beta = 95.20^{\circ}$  and Z = 4. H<sub>3</sub>PO<sub>4</sub>·1/2H<sub>2</sub>O is monoclinic (space group P2<sub>1</sub>/A) with the cell parameters a = 7.92 Å, b = 12.99 Å, c = 7.47 Å,  $\beta = 109.9^{\circ}$  and Z = 8 [5],[21].



**Fig. 6.** The projection of the structure of  $H_3PO_4$  along the b-axis (a) and c-axis (b). H-bonds are figured by dotted lines. This view induces the feeling that some H-bonds connect two O atoms of the same phosphoric tetrahedron, but they are, in fact, established between two superimposed tetrahedra [5].

Furthermore, polyphosphoric acids and deutronic phosphoric acid are known. Deutrophosphoric acid ( $D_3PO_4$ ) can be prepared by dissolving phosphorus pentaoxide in  $D_2O$  or by the hydrolysis of POCl<sub>3</sub> with  $D_2O$ . This acid has slightly higher melting point, density and viscosity but lower electrical conductivity than the hydrogen analogue [2],[5].

## 9.2.2. Properties of phosphoric acid

The solutions of phosphoric acid show unique phenomena of sonoluminescence (SL) in which the nonlinear oscillations of a single bubble under the influence of sufficiently strong sound field lead to a violent collapse of the bubble and to the production of very brief light pulse with the duration of several picoseconds at the end of the bubble collapse. The standard spectrum of SL radiation is a featureless continuum spectrum, ranging from 200 to 800 nm, which is well fitted by the black-body radiation with the temperature of 6000 – 20,000 K. The temperature inside the bubble has been predicted to be even much higher, as the spectrum of radiation from the regions close to the bubble center is fitted by thermal bremsstrahlung radiation from the plasma with temperature more than 10<sup>6</sup> K. The experiments show that the SL emission from sulfuric acid (**Fig. 7**) is about 2700 times greater than the brightest SL in water. Also, the SL radiation from phosphoric acid can be up to four orders of magnitude brighter than SL from water [22],[23],[24],[25].

Phosphoric acid is a key material for the manufacture of detergents, food products and alimentary supplies for cattle, toothpastes and fertilizers such as monoammonium phosphate (MAP,  $(NH_4)H_2PO_4$ , ammonium dihydrogen phosphate), diammonium phosphate (DAP,  $(NH_4)_2HPO_4$ , diammonium hydrogen phosphate) and triple superphosphate (TSP) [26], [27], which are described in **Section 9.3**.



Fig. 7. Sonoluminescence occurs as the bubble collapse under some specific conditions including very low vapor pressure liquids [25].

Another applications of phosphoric acid include the treatment of surface of metals (**Section 10.8**), the utilization in dentistry [28],[29],[30],[31],[37],[38] (described in **Section 10.1.2**), phosphate binders [32], geopolymers [33], phosphoric acid fuel cells [34],[35],[36], gel-based electrolytes [39] and solid membranes [40],[41],[42] for fuel cells, the activation of carbon adsorbents [43],[44] and catalysts [45],[46], the modification of zeolites [47], catalytic decomposition of  $H_2O_2$  [48] and organic syntheses, e.g. esterification [49],[50]. Direct applications of phosphoric acid are shown in **Fig. 8**.



Fig. 8. Direct applications of orthophosphoric acid [2].

## 9.2.3. Manufacturing of phosphoric acids

Globally, about 81% of phosphate rock is used for the production of phosphoric acid [51],[52]. There are two processes (**Fig. 9**) described below used for the preparation of phosphoric acid [7],[26],[53],[54],[56],[57]:



Fig. 9. The scheme of phosphate processes [57].

Since the concentration and the purity grade of phosphoric acid depend on the purpose, the content of waterless  $H_3PO_4$  in the product is usually expressed as  $P_4O_{10}$ , where waterless  $H_3PO_4$  = 1.38 ×  $P_4O_{10}$ . For example, the product of TPA with the content of 66.33%  $P_4O_{10}$  contains 66.33 × 1.38 = 91.54% of waterless  $H_3PO_4$ . With increasing content of  $P_4O_{10}$  in the system, pyrophosphoric acid (diphosphoric acid,  $H_4P_2O_4$ ) becomes the dominant species.

# 9.2.4. Wet process

Several companies began developing the hemihydrate technologies during the 1960s and fullscale plants began to appear during the 1970s [53]. The wet process (**Fig. 10**) is named as wet because the concentrated solution of sulfuric acid (93%) was used to digest the apatite ore [5], [26],[58]:

$$Ca_{10}(PO_{4})_{6}(OH)_{2} + 10 H_{2}SO_{4} \rightarrow 10 CaSO_{4}(s) +6 H_{3}PO_{4} + 2 H_{2}O$$
(17)

Since the ore is invariably contaminated by fluorapatite  $(Ca_{10}(PO_4)_6F_2)$  and calcium carbonate  $(CaCO_3)$ , hydrofluoric acid is formed during the dissolution process:



**Fig. 10.** The flow sheet for the production of orthophosphoric acid via the fission hemihydrate process (a) and the dihydrate process (b) [12].

$$Ca_{10}(PO_4)_6F_2 + 10 H_2SO_4 \rightarrow 10 CaSO_4(s) + 6 H_3PO_4 + 2 HF$$
 (18)

or  

$$Ca_{10}(PO_{4})_{6}F_{2} + 10 H_{2}SO_{4} + 20 H_{2}O \rightarrow 10 CaSO_{4} \cdot 2H_{2}O(s) \qquad (19)$$

$$+6 H_{3}PO_{4} + 2 HF \qquad (20)$$

The dissolution of silicate minerals in the ore by HF leads to the formation of fluorosilicates, including volatile silicon tetrafluoride (SiF<sub>4</sub>) and hexafluorsilicic acid (H<sub>2</sub>SiF<sub>6</sub>) or its salts (Na<sub>2</sub>SiF<sub>6</sub>).

According to the kind of produced hydrate of calcium sulfate (**Fig. 11**), the wet process is further divided to:



Fig. 11. The influence of reaction conditions on the crystallization of calcium sulfate [53].

- **a.** Hemihydrate wet process in which CaSO<sub>4</sub>·½H<sub>2</sub>O (HH) is formed in the temperature range from 360 to 380 K;
- **b.** Dihydrate wet process in which CaSO<sub>4</sub>·2H<sub>2</sub>O (DH) is formed in the temperature range from 340 to 350 K;
- **c. Hemidihydrate wet process** (HDH) where HH crystals are converted to DH and next filtered out to recover weak phosphoric acid from the filtration cake (**Fig. 12**).

Calcium sulfate and other insoluble impurities such as silica were filtered out and the vacuum distillation process was used to increase the concentration of phosphoric acid<sup>7</sup> to 56%. The major part (about 85%) of phosphorous fertilizers is produced by wet process [26]. Since phosphate ores are a potential resource of rare-earth elements (REE) as well, the recovery of rare earths during the wet processing of phosphoric acid is investigated [59],[60],[61],[62], [63].

The crucial step in the decomposition of apatite is the formation of calcium sulfate. Its properties, in particular, its ability to be filtered, are very important, e.g. for the throughput optimization. The incorporation of phosphate in the crystal lattice of calcium sulfate reduces the phosphate yield and can render the calcium sulfate unusable in the building industry [12].

<sup>&</sup>lt;sup>7</sup> The Karl Fisher titration was used to determine the amount of water in phosphoric acid [64].



Fig. 12. Yara HDH process [53].

Yara, as Fisons Fertilizers, started its research and development to find an alternative to the traditional dihydrate process route (**Fig. 12**) during the late 1950s and early 1960s at its R&D establishment at Levington, UK. The comprehensive laboratory-scale work established that the hemihydrate process route was a feasible alternative. Subsequent pilot plant testing was employed at the Fisons (JAMES FISON) Kings Lynn factory to develop the process on a larger scale and to confirm earlier findings that the hemihydrate process could be adopted successfully [53].

When the Kings Lynn factory closed, all research and development was concentrated at the R&D center in Levington, UK. A new pilot plant facility was constructed, this time using reactors made from high-grade stainless steel. The size of the equipment was somewhat smaller because all raw materials had to be specially delivered and produced acid and the by-product phosphogypsum dispatched to the nearest production unit for disposal. During the 1980s and 1990s, the research facilities were subsequently based in Sweden, the Netherlands and Norway. Currently, all phosphoric acid research and development is carried out at Yara's phosphate R&D center in Siilinjarvi, Finland [53].

However, the organic matter (OM) contained in acid may interact with organic solvents to form stable foams, preventing the phase settling, or simply by forming cross-layers and organic phases and denaturing part of the solvent. Hence, the removal of these organics seems to be an important step for the production of decontaminated phosphoric acid. The utilization of activated bentonite [65],[66], activated carbon and coal [67] for the adsorption of organic matter was investigated.

### 9.2.5. Thermal process

The **thermal (dry) process** or the electric furnace process is based on the oxidation of phosphorus in the furnace heated to temperatures from 1800 to 3000 K (**Eq. 21**). If wet (undried) air is used for the oxidation, the gaseous product of this reaction is led directly through the hydration tower, where  $P_4O_{10}$  gas is adsorbed and hydrated by water to phosphoric acid (**Eq. 22**) [55]:

$$P_4(\ell) + 5 O_2(g) \rightarrow P_4 O_{10}(g)$$

$$(21)$$

$$P_4O_{10}(g) + 6 H_2O(\ell) \rightarrow 4 H_3PO_4(aq)$$
 (22)

The product of phosphorus oxidized by dry air,  $P_2O_5$ , was condensed as white powder and next hydrated to phosphoric acid.



Fig. 13. The scheme of the plant for the production of thermal phosphoric acid [11].

These two operations can be carried out in the apparatus connected in series (**Fig. 13**), but the hydration takes place in large extent directly in the combustion tower. The combustion nozzle is arranged centrally at the head of the tower and directed downwards. It is a nozzle for two components. Phosphorus is atomized by compressed air or vapor into fine particles, which spontaneously ignite immediately upon leaving the nozzle. Phosphorus is fed in the liquid state through pipes by means of pumps or pressure vessels. The combustion aid is either forced through the apparatus by means of suction fan arranged at the outlet of final purification

device. If complete oxidation to  $P_2O_5$  is assured, the waste gases must contain 4 to 5% of oxygen. The nebulous  $P_2O_5$  is conducted from the combustion chamber in a tower like so-called hydrator. The gas entering at the bottom is washed with water or diluted phosphoric acid sprayed in through several rows of nozzles [11].

Small amount of pure phosphoric acid can be prepared by heating white phosphor with diluted nitric acid (using concentrated  $HNO_3$  turns the course of reaction to explosive) or by the oxidation of red phosphor by concentrated nitric acid:

$$P + 3HNO_3 \rightarrow H_3PO_4 + NO + 2 NO_2$$
(23)

The oxidative reaction is catalyzed by the trace of iodine anions ( $I^{-}$ ). The evaporation of solution on platinum dish (thickening) leads to the viscous (syrupy) liquid from which concentrated H<sub>3</sub>PO<sub>4</sub> precipitates [55].

#### 9.2.6. Phosphogypsum

Phosphogypsum (PG) is a by-product produced by phosphate fertilizer industry during the production of phosphoric acid (**Eq. 19**) from phosphate rocks (**Section 9.2.4**). About 4.5 - 5 kg of phosphogypsum are produced for every kilogram of  $P_2O_5$  manufactured [68]. PG is mainly composed of gypsum, but it also contains high level of impurities, which include naturally occurring radionuclides, metals and other trace elements, the quantity varying with element and the production process. Major PG reuse includes the production of cement, china and crystallite glass as well as soil amendments in agriculture (PG appears to be good source of S and Ca for crops [69]) without a consideration of element recovery, but even these latter reuses are limited due to the radioactivity within PG. Presently, PG is mainly stockpiled without any treatment. It can, however, be discharged into aquatic environments and pose a radioactive threat to ecosystems [51],[57],[70],[71],[72],[73],[74],[75], [76],[77].

Potential utilization of phosphogypsum (**Fig. 14**), the by-product from fertilizer industries, as a bitumen modifier for paving industry was reported by CUADRI et al [68]. It was found that when activated with small quantity of sulfuric acid (0.5 wt.%), the addition of 10 wt.% phosphogypsum leads to a notable improvement in the rheological response of resulting material at high temperatures. On the contrary, poor level of modification was noticed when in such formulation phosphogypsum was substituted by the same amount of commercial gypsum.



Fig. 14. Main environmental concerns due to the storage and agricultural use of phosphogypsum [77].

The reduction in the concentration of radionuclides content from PG was based on leaching of <sup>226</sup>Ra, <sup>210</sup>Pb, <sup>238</sup>U and <sup>40</sup>K using tributyl phosphate (TBP) and trioctyl phosphine oxide (TOPO) in kerosene [70].

## 9.2.7. Phosphorus slag and ferrophosphorus

Phosphorus slag<sup>\*</sup> and ferrophosphorus are the by-products of the production of elemental phosphorus. Phosphorus slag has applications similar to those of PG, but more than 80% of phosphorus slag is stored near the factory instead of being recycled. At present, the recycling of phosphorus slag appears not being considered for its element recovery potential. Ferrophosphorus containing roughly 75% Fe and 25% P is usually sold as an additive for the steel industry after being crushed and screened [51],[78]. Ferrophosphorus is used in the steel industry to prevent the steel plates from sticking together during the pack annealing [79]. Ferrophosphorus contains FeP, Fe<sub>2</sub>P and perhaps little amount of Fe<sub>3</sub>P [2]. The utilization of ferrophosphorus as a heavyweight additive for API oil well cements was investigated by BENSTED [80]. Ferrophosphorus is used for steelmaking, providing a convenient source for phosphorus addition to alloy steels [13].

# 9.3. Production of phosphatic fertilizers

Phosphorus is essential to plant and animal life.<sup>°</sup> It provides the matter for the skeletal bone structure in animals and for the cell membranes in both plants and animals. Phosphorus is also

<sup>&</sup>lt;sup>8</sup> The by-product known as Thomas (basic or phosphatic) slag is obtained from the iron industry [78].

<sup>&</sup>lt;sup>9</sup> Three primary (major) plant nutrients are N, P and K. The elements Ca, Mg and S are the secondary nutrients and Fe, Cu, Zn, Mn, B, Mo and Cl are the micronutrients [84]. Primary and secondary nutrients together with C, H and O (available from air and water) are termed as macronutrients [85].

the second most abundant element in the human body after calcium. It is essential for healthy formation of bones and teeth and energy storage system and helps maintain the blood sugar level. The largest and least expensive source of phosphorus is obtained by mining and beneficiation of phosphate rocks from numerous phosphate deposits throughout the world (**Section 7.2**). The principal use of these phosphate rocks is the manufacture of fertilizers (**Fig. 15**) [81],[82]. Phosphorus is important because it is an essential component of energy metabolism of all forms of life. Together with N and K, phosphorus presents the three macronutrients needed by all crops [83].



Fig. 15. The utilization of phosphate ore [82].

Most virgin soils in temperate climates contain enough phosphorus to support good crop production, but many soils in tropical climates are naturally deficient in phosphorus because it is leached out during advanced stages of chemical weathering. Phosphorus can be added to deficient soils in the form of natural or artificial fertilizers,<sup>10</sup> and for sustainably good yields, it must be added to all soils when they are cropped heavily for long periods. Phosphate fertilizers are used extensively now in the developed countries, but in many less developed countries their use must be strongly increased to bring the crop production to acceptable levels [86].

Incidental phosphorus fertilization in the form of manures, such as plant and animal biomass, and other natural materials, such as bones, has probably been practiced since the agriculture began. Although the specific nitrification benefits were unknown, ARTHUR YOUNG described in the *Annals of Agriculture* in the mid-19th century the experiment evaluating a wide range of products including the poultry dung, the gunpowder, the charcoal, ashes and various salts. The results showed positive crop responses to certain materials. Benefiting from the achievements in chemistry by ANTOINE LAVOISIER and others, THEODORE DE SAUSSURE was perhaps the first to develop the concept that plants absorb specific mineral elements from the soil. The science of plant nutrition advanced considerably in the 19th century, owing to the contribu-

<sup>&</sup>lt;sup>10</sup> A fertilizer is any material, organic or inorganic, natural or synthetic, that supplies the plants with one or more chemical elements necessary for normal growth [85].

tion by Carl Sprengel, A.F. Wiegmann, Jean-Baptiste Boussingault and Justus von Liebig. Based on the ubiquitous presence of phosphorus in soil and plant materials and the crop response to phosphorus-containing products, it became apparent that phosphorus is essential for the plant growth [87].

An important concept in the nitrification of plant was developed by J. VON LIEBIG in about 1840. It is known as "The Law of the Minimum" (**Fig. 16**). According to this concept, the plant growth is limited by particular growth factors that are in the shortest supply to the plant. Different factors could potentially control the rate of plant growth at different times during the crop growth. For example, the temperature might limit early spring growth, the moisture affects the growth during a droughty period and nitrogen supply may influence the growth even in cases when the previous factors are inactive [88].



Fig. 16. Illustration of the Liebig's law of the minimum [88].

LIEBIG observed that dissolving bones in sulfuric acid enhanced the phosphorus availability to plants. Familiar with Liebig's work, JOHN LAWES and coworkers evaluated several apatitecontaining products as the phosphorus nutritional source for plants. They performed experiments in which they ultimately became the world's most famous agricultural experiment station — his estate in Rothamsted. Limited supply of bones prompted the developments in the utilization of phosphate rocks where LAWES obtained the first patent concerning the utilization of acid-treated phosphate rock in 1842. The first commercial production of rock phosphate began in Suffolk, England, in 1847. Mining of phosphate in the United States began in 1867. Thus, the phosphorous fertilizer industry began [87].

Non-organic fertilizers contain mainly phosphate, nitrate, ammonium and potassium salts [90]. Phosphorus as an essential element for all life on earth and global food production is highly dependent on the use of fertilizers produced from phosphate rock [91]. Globally, about 150 million tones of phosphate rock are extracted each year for the production of

phosphate fertilizers (**Fig. 17**) and the demand for this finite resource is projected to increase to feed growing global population [92]. Due to higher cost per unit of nutrient and availability the bone meal, guano and other natural organic phosphate sources are of only minor commercial importance [89].



Fig. 17. The relation between phosphate rock and fertilizers [89].

The content of phosphorus in fertilizers (**Table 1**, the grade of fertilizer<sup>11</sup>) is usually expressed as  $P_2O_5$  (or as  $P_4O_{10}$ ) and the phosphate rock grade is often listed in the trade publications as **BPL**, <sup>12</sup> referring to "**bone phosphate of lime**" [93],[94], the common name for tricalcium phosphate (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>). Early workers believed that tricalcium phosphate was the chief constituent of phosphate rock. These commercial terms are widely used and the following conversion factors are included for the reference purposes [51],[85],[88],[89],[95].

- $P_2O_5 = 0.4576 \cdot BLP;$
- BLP =  $2.1852 \cdot P_2 O_5$ ;
- $TPL^{13} = BLP;$
- P = 0.1997·BLP;
- $P_2O_5 = P \cdot 2.2914$  and  $P = P_2O_5 \cdot 0.4364$ .

<sup>&</sup>lt;sup>11</sup> The grade of a fertilizer is the nutrient content expressed in weight percentages [85].

<sup>&</sup>lt;sup>12</sup> 1%  $P_2O_5 = 2.1852\%$  BLP [89]. The peculiar compound occurs in bones after the calcination, which gives a gelatinous precipitate when pouring calcium chloride into a solution of rhombic phosphate of soda or when adding ammonia to the solution of any phosphate of in acids [93].

<sup>&</sup>lt;sup>13</sup> Denotes the triphosphate of lime. This salt is commonly called neutral phosphate and appears as a granular precipitate when rhombic phosphate of soda is added drop by drop to calcium chloride in excess [93].

<sup>&</sup>lt;sup>14</sup> A product made by treating phosphate rock with sulfuric or phosphoric acid or by a mixture of two acids [85].

Name	Chemical composition	Solubility	P <sub>2</sub> O <sub>5</sub> [%]
Superphosphate <sup>14</sup>	$Ca(H_2PO_4)_2 + CaSO_4$	Water sol.	18 – 22
Triple superphosphate	$Ca(H_2PO_4)_2$		46 – 47
Monoammonium phosphate	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>		48 - 50
Diammonium phosphate	$(NH_4)_2HPO_4$		54
Basic (Thomas) slag	$Ca_3P_2O_8$ ·CaO + CaO·SiO <sub>2</sub>	Citric acid sol.	10 – 22
Sinter(Thermo)phosphate	CaNaPO <sub>4</sub> ·Ca <sub>2</sub> SiO <sub>4</sub>	$NH_4^+$ citrate sol.	25 – 29
Ground rock phosphate	Apatite	Soluble in citric acid	29
Fused Mg phosphate	Ca-Mg phosphate		20

 Table 1. Direct phosphate fertilizers [96].

Commercial phosphate rocks vary in grade from about 80 to 60 BLP. Most international trade involves higher-grade phosphate rocks and lower-grade rocks are often used at local processing facilities [88].

Phosphorus is utilized in fully oxidized and hydrated forms as orthophosphate. Plants typically absorb either  $H_2PO_4^-$  or  $HPO_4^{2-}$  depending on the pH of growing medium. However, under certain conditions, plants might absorb soluble organic phosphates, including nucleic acids. A portion of absorbed inorganic phosphorus is quickly combined into organic molecules upon the entry into the roots or after it is transported into the roots. Total phosphorus in plant tissue ranges from 0.1 to 1%. Typical plant might contain approximately 0.004% P as DNA (deoxyribonucleic acid), 0.04% P as RNA (ribonucleic acid), 0.03% as lipid, 0.02% as ester and 0.13% as inorganics [87].

## 9.3.1. Single superphosphate

Single superphosphate (SSP, ordinary termed as normal or ordinary superphosphate) was the main phosphate fertilizer for more than a century and supplied over 60% of the world's phosphate until as late as 1955. Since then, the importance of SSP has been steadily decreasing with time. In 1975, it supplied only 20% of the phosphate fertilizers and this amount fell to 17% in 1988. Recent decline in actual tonnage has been small, the single superphosphate is still an important phosphate fertilizer and is likely to remain so even though its importance will decrease [97].

The advantages of single superphosphate fertilizer are [97]:

- **1.** The process of manufacturing of SSP is simple, requiring only little technical skill and small capital investment.
- **2.** The economies of scale are minor; thus, small plants can be economical.
- **3.** Since the process is not capital intensive, there is little advantage of high percentage utilization of capacity. In fact, many SSP plants operate on a planned seasonal schedule.

- **4.** The fertilizer effectiveness of SSP is unquestioned. In fact, it is a standard for the comparison of other phosphate fertilizers.
- **5.** SSP supplies two secondary elements, sulfur and calcium, which are sometimes deficient in the soil.

Despite many advantages, the disadvantage of low analysis (from 16 to  $22\% P_2O_5$ , i.e. from 35 to 48% BLP) and consequent high distribution costs have caused the declining interest in its production because the delivered cost at the farm level is usually higher per unit of  $P_2O_5$  than that of TSP or ammonium phosphates.

Single superphosphate is an optimal choice in the following situations [97]:

- **a.** Where both P<sub>2</sub>O<sub>5</sub> and sulfur are deficient, SSP can be the most economical product to meet these needs.
- **b.** In small countries or remote regions where the demand is insufficient to justify the economic scale of production of concentrated phosphate fertilizers and where the importation is expensive, SSP can be the most economical means of supplying local needs.
- **c.** In many cases, SSP can be an attractive way to use the by-product of sulfuric acid that cannot be used to produce more concentrated product because the quality or the quantity of acid is unsuitable. Likewise, SSP can use the deposits of phosphate rock, which are too small to supply more extensive plant.

Since the grade of phosphate rock determines the grade of the SSP product, high-grade rocks are desirable. Since less reactive rocks must be ground more finely, the reactivity is also important. It is extremely difficult to produce single superphosphate from some igneous rocks (**Section 7.1.2**). Iron and aluminum compounds can be tolerated up to a certain point, although they decrease the  $P_2O_5$  water solubility. Silica has no other adverse effect than the decrease in grade. An increase of CaO: $P_2O_5$  ratio raises the consumption of sulfuric acid per unit of  $P_2O_5$  and decreases the grade. High chloride rocks (with the content of up to 0.5% Cl and perhaps higher) can be used without serious disadvantage, since the corrosion is not a serious problem in the production of SSP [88].

The preparation of single superphosphate (**Fig. 18**) via the treatment of finely ground phosphate rocks by sulfuric acid is based on the conversion of insoluble fluorapatite or natural tricalcium phosphate to monocalcium phosphate [97]:

$$2 \operatorname{Ca}_{5}(\operatorname{PO}_{4})_{3} \operatorname{F} + 7 \operatorname{H}_{2} \operatorname{SO}_{4} + 3 \operatorname{H}_{2} \operatorname{O} \rightarrow 7 \operatorname{CaSO}_{4} +3 \operatorname{Ca}(\operatorname{H}_{2} \operatorname{PO}_{4})_{2} \cdot \operatorname{H}_{2} \operatorname{O} + 2 \operatorname{HF}$$

$$(24)$$

$$Ca_{3}(PO_{4})_{2} + 2 H_{2}SO_{4} + 5 H_{2}O \rightarrow 2 CaSO_{4} \cdot 2H_{2}O +Ca(H_{2}PO_{4})_{2} \cdot H_{2}O$$
(25)

It has been generally accepted that this process proceeds in two stages [97]:



Fig. 18. Manufacturing of superphosphate [88].

- **i.** Phosphoric acid and calcium sulfate are formed by the reaction of sulfuric acid with part of the phosphate rock.
- **ii.** Phosphoric acid formed in the first step of the process reacts with other portion of phosphate rock to form monocalcium phosphate.

These two reactions proceed concurrently, but the first one is fast, while the second one continues for several days or weeks.

#### 9.3.2. Triple superphosphate

Triple superphosphate (TSP) was prepared by the reaction of phosphoric acid with phosphate rock or bone ash [78]:



Triple phosphate is a concentrated form of single superphosphate and it contains 46 - 48% P<sub>2</sub>O<sub>5</sub>, i.e. the content of P<sub>2</sub>O<sub>5</sub> is three times higher than that of single superphosphate.

#### 9.3.3. Enriched superphosphate

Enriched superphosphate is essentially a mixture of SSP and TSP, usually made by the acidification of phosphate rock with a mixture of sulfuric and phosphoric acid. Theoretically,

any grade between SSP and TSP can be produced, but the usual range is 25 - 35% P<sub>2</sub>O<sub>5</sub>. The processes and used equipment are the same as for SSP. Enriched superphosphate may be useful product for the applications in sulfur-deficient areas where SSP would supply more sulfur than necessary. One advantage is that mixed acid of proper concentration can be obtained by mixing concentrated sulfuric acid (93 – 98% H<sub>2</sub>SO<sub>4</sub>) with diluted phosphoric acid (30% P<sub>2</sub>O<sub>5</sub>), thereby avoiding the need for concentrating the latter [88].

#### 9.3.4. Thomas slag

Thomas, basic or phosphatic slag<sup>15</sup> is actually obtained as a by-product in iron industries. This results from the presence of small amounts of phosphorus in iron ores. When the iron ore is burnt with limestone in the presence of air, calcium phosphate and calcium silicate appear as slag. Thus, the mixture of calcium phosphate and calcium silicate is known as Thomas (basic or phosphatic) slag and contains 14 - 18% of  $P_2O_5$  and 40% of lime. The following reactions accompany the formation of Thomas slag [78],[99],[100]:

$$4 P + 5 O_2 \rightarrow 2 P_2 O_5 \tag{28}$$

$$3 \operatorname{CaO} + \operatorname{P_2O_5} \to \operatorname{Ca_3}(\operatorname{PO_4})_2 \tag{29}$$

$$CaO + SiO_2 \rightarrow CaSiO_3$$
 (30)

The composition of Thomas slag is shown in Fig. 20.

#### 9.3.5. Ammonium phosphate

Ammonium phosphate (ammoniated superphosphate) was prepared from phosphate ore treated by ammonium sulfate and sulfuric acid [78]:

$$Ca_{3}(PO_{4})_{2} + (NH_{4})_{2}SO_{4} + 2H_{2}SO_{4} \rightarrow 2NH_{4}H_{2}PO_{4} + 3CaSO_{4}$$
 (31)

This product contains  $61 - 73\% P_2O_5$ .

Anhydrous ammonia passes through triple superphosphate in a rotary drum ammoniator where **reaction 32** takes place to evolve considerable amount of heat to granulate the ammoniate superphosphate, which is subsequently dried and bagged [101]:

<sup>&</sup>lt;sup>15</sup> Also known as Thomas phosphate powder. The utilization as fertilizer was firstly tried as a manure on fields in Germany, and in November 1883, HERREN HOYRMANN and MEYER were able to report to the German Royal Agricultural Society the most excellent effect of its use [99].

$$NH_{3} + Ca(H_{2}PO_{4})_{2} \rightarrow NH_{4} \cdot H_{2}PO_{4} + CaHPO_{4}$$
(32)

Orthophosphoric acid neutralized by ammonia yields to monoammonium phosphate (MAP):

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$$
(33)

When ammonia passes through phosphoric acid to maintain the pH of the resulting solution in the range from 5.8 to 6, diammonium phosphate (diammonium hydrogen phosphate, DAP) is formed:

$$2 \operatorname{NH}_{3} + \operatorname{H}_{3}\operatorname{PO}_{4} \to (\operatorname{NH}_{4})_{2} \operatorname{HPO}_{4}$$
(34)

Mono- and diammonium phosphates are manufactured by treating orthophosphoric acid in a preneutralizer where the ratio of  $NH_3$ :PO<sub>4</sub> is adjusted to 0.6 in the case of monoammonium phosphate and to 1.4 in the case of diammonium phosphate. The heat of reaction raises the slurry temperature to the boiling point and some moisture evaporates. Further addition of ammonia, so that the  $NH_3$ :PO<sub>4</sub> ratio increases to 1.0 (monoammonium phosphate) and to 2.0 (diammonium phosphate), generates additional heat to evaporate water during the granulation [84],[101].

Diammonium phosphate provides the following additional favorable factors [84]:

- i. Decreases the amount of reactants otherwise required in ammoniators.
- **ii.** Lowers the moisture content in formulation, which decreases the requirement for drying.
- **iii.** May contribute to higher production rates.
- iv. Formulations using DAP are often less expensive than other convectional formulations.
- v. Improves physical stability.
- vi. Less tendency of product caking in storage.

DAP can favorably be used in irrigation systems and in the production of liquid suspension fertilizers, because it is completely soluble in water [84].

### 9.3.6. Nitrophosphate and urea nitrate phosphate

Nitrophosphate (calcium superphosphate nitrate) is prepared by the same way as superphosphate using nitric acid instead of sulfuric acid [78]:



Fig. 19. The scheme of a plant for the production of thermal phosphoric acid [101].

$$\operatorname{Ca}_{3}(\operatorname{PO}_{4})_{2} + 4 \operatorname{HNO}_{3} \to \operatorname{Ca}(\operatorname{H}_{2}\operatorname{PO}_{4})_{2} + 2 \operatorname{Ca}(\operatorname{NO}_{3})_{2}$$
(35)

The amount of nitric acid applied for the treatment of phosphate rock affects the ratio between formed monocalcium phosphate and calcium nitrate, as the following equations reveal [101]:

$$\operatorname{Ca}_{5}(\operatorname{PO}_{4})_{3} \operatorname{F} + 10 \operatorname{HNO}_{3} \to 5 \operatorname{Ca}(\operatorname{NO}_{3})_{2} + 3 \operatorname{H}_{3} \operatorname{PO}_{4} + \operatorname{HF}$$
(36)

$$Ca_{5}(PO_{4})_{3}F + 9 HNO_{3} \rightarrow 0.5 Ca(H_{2}PO_{4})_{2} + 4.5 Ca(NO_{3})_{2} + 2 H_{3}PO_{4} + HF$$
(37)

$$Ca_{5}(PO_{4})_{3}F + 8 HNO_{3} \rightarrow Ca(H_{2}PO_{4})_{2} + 4 Ca(NO_{3})_{2} + H_{3}PO_{4} + HF$$

$$Ca_{5}(PO_{4})_{3}F + 7 HNO_{3} \rightarrow 1.5 Ca(H_{2}PO_{4})_{2} + 3.5 Ca(NO_{3})_{2} + HF$$
(38)
(39)

These fertilizers are also the source of nitrogen.<sup>16</sup> For the preparation of urea nitrate phosphate, nitrophosphate contains the product of **Eqs. 35 – 39** conveyed to the decanter (**Fig. 19**) to get rid of the insoluble impurities. Urea is added to the solution in the mixer [78],[101].

The following reactions accompany the formation of urea nitrate phosphate [101]:

<sup>&</sup>lt;sup>16</sup> Fertilizers containing two or more nutrients are termed as compound nutrients (not in the United States). The names complex fertilizers and chemically mixed fertilizers are used in the same meaning in some countries [84].

$$Ca(NO_3)_2 + H_3PO_4 + 2 CO(NH_2)_2 \rightarrow Ca(H_2PO_4)(NO_3)CO(NH_2)_2 + CO(NH_2)_2 HNO_3$$
(40)

$$\operatorname{Ca}(\operatorname{NO}_{3})_{2} + 4 \operatorname{CO}(\operatorname{NH}_{2})_{2} \to \operatorname{Ca}(\operatorname{NO}_{3})_{2} \cdot 4\operatorname{CO}(\operatorname{NH}_{2})_{2}$$
(41)

$$Ca(NO_{3})_{2} + H_{3}PO_{4} \rightarrow Ca(NO_{3})_{2} \cdot H_{3}PO_{4}$$

$$Ca(H_{2}PO_{4})_{2} + Ca(NO_{3})_{2} + 2 CO(NH_{2})_{2} \rightarrow Ca_{2}(H_{2}PO_{4})_{2}(NO_{3})_{2} CO(NH_{2})_{2}$$

$$(42)$$

$$(42)$$

$$(42)$$

$$2 \text{ HF} + \text{Ca}(\text{NO}_3)_2 + 2 \text{ CO}(\text{NH}_2)_2 \rightarrow \text{CaF}_2 + 2\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$$
(44)

After removing insoluble impurities in the decanter, the reaction product, the slurry is dehydrated and concentrated, granulated and dried.

#### 9.3.7. Dicalcium phosphate

Dicalcium phosphate is a citrate soluble fertilizer. Phosphate rock is first converted to orthophosphoric acid via the treatment by HCl. Orthophosphoric acid reacting with lime gives dicalcium phosphate [78]:

$$H_{3}PO_{4} + CaO \rightarrow CaHPO_{4} + H_{2}O$$
(45)

#### 9.3.8. Thermophosphates

Thermophosphates (rhenania phosphates, thermal phosphate) are manufactured by the reaction of rock phosphates with soda and quartz [96],[102]:

$$Ca_{5}(PO_{4})_{3}F + 2 Na_{2}CO_{3} + SiO_{2} \rightarrow 3 NaCaPO_{4} + +Ca_{2}SiO_{4} + NaF + 2 CO_{2}(g)$$

$$(46)$$

Rhenania phosphate is prepared by the calcination of mixture of phosphate rock, sodium carbonate and silica in a rotary kiln at 1250°C. The fertilizer contains  $28 - 30\% P_2O_5$  and has an alkaline effect and hence is more efficient in acid soils. In neutral or basic soils, it reacts more slowly.

A somewhat similar product, Roechling phosphate uses soda slag, which is a by-product from the steel industry, as the source of sodium. Also, naturally occurring source of minerals such as trona  $(Na_3(HCO_3)(CO_3)\cdot 2H_2O \ [103])$  or natron  $(Na_2CO_3\cdot 10H_2O \ [104])$  can be applied. A

similar product can be also prepared by sintering potassium carbonate with phosphate rocks and silica where the formation of CaKPO<sub>4</sub> is supposed [85]:

$$Ca_{5}(PO_{4})_{3}F + 2 K_{2}CO_{3} + SiO_{2} \rightarrow 3 KCaPO_{4} + Ca_{2}SiO_{4}$$
  
+KF + 2 CO<sub>2</sub>(g) (47)

The origin of thermal phosphate can be derived from Thomas slag (**Fig. 20**). Since Thomas slag became popular, numerous attempts have been made to produce fertilizers by thermal treatment of phosphate rock with additives. The most of these attempts are not successful, except for a few that attained commercial production of fertilizers such as rhenania phosphate, fused magnesium phosphate (FMP) and calcined defluorinated phosphate [84].



**Fig. 20.** Ternary diagram of thermal phosphates: calcined defluorinated phosphate tested in the United States (A), Thomas slag (B), calcined defluorinated phosphates produced in Japan, United States, etc. (C), silicophosphate tested in England (E) and Rhenania phosphate in Germany (F) [84].

The composition of some systems is shown in the ternary diagram in **Fig. 20**. Rhenanite (R, CaNaPO<sub>4</sub>) has two forms ( $\beta$ - and  $\alpha$ -rhenanite) with  $\beta \rightarrow \alpha$  transition temperature of 670°C. Both phases are highly soluble in 2% citric acid and ammonium citrate.  $\beta$ -Rhenanite is the major constituent of Rhenania phosphate [84].

#### 9.3.9. Environmental demand on phosphate fertilizers

Fertilizers are essential to provide adequate nutrients for the crop growth and to ensure successful harvests. Continuing exponential growth in human population and increasing demand for biofuels point to ever-increasing demand for fertilizers. Despite the apparent success of current agricultural production systems, the overuse of fertilizers has caused severe environmental problems and increasing number of health concerns. Overall, environmental and human health concerns associated with the overuse of fertilizer result in two main problems [90],[105],[106],[107],[108]:

- i. Disruption of natural nitrogen and phosphorus nutrient cycles because of massive infusion of nitrogen and phosphorus from fertilizers.
- **ii.** Inadvertent release of heavy metals and radionuclides from mineral fertilizers and pathogens, veterinary pharmaceuticals and endocrine disrupters from organic fertilizers.

Moreover, fertilizers can be adulterated products containing the raw material sometimes from unknown and/or questionable sources. Besides certified nutritional ingredients for plants, they may contain, most notably, the trace element contaminants that can be inadvertently introduced into soils. The fertilizer applications are by far one of the most consistent sources of trace elements to accumulate in cropland soils. Based on the analysis of existing data from literature and of results from model simulations, we have concluded that a long-term use of phosphorus fertilizers and micronutrients could cause the As, Cd and Pb contents of the cropland soils to rise if the products used contained high levels of these elements [92],[105], [106].

Since naturally occurring nuclides <sup>238</sup>U, <sup>232</sup>Th and <sup>40</sup>K have strong association with phosphate ore, which is the major raw material for the production of phosphate fertilizers, radon 222 (<sup>222</sup>Rn) (the most significant natural isotope of radioactive element radon) was formed as a decay product of <sup>238</sup>U. Radon is colorless, odorless poisonous gas, and sustained exposure of humans to its increased level can lead to lung cancer. Radon is a noble gas and does not undergo chemical reaction. When concentrated in enclosed environment, it can only diminish by diffusion, advection and radioactive decay [70],[109],[110],[111],[112].

Phosphate fertilizers are being enriched with <sup>238</sup>U during their production from phosphate rocks. The activity of <sup>238</sup>U is higher in phosphate-rich fertilizers like TSP and SSP. The application of phosphate fertilizer significantly increases the radioactivity level of cultivated soil as compared to soil from barren land [113],[114].

Current waste of phosphorus fertilizers causes a great deal of environmental problems, and it is questionable if it is a good idea to extract all the phosphate rock reserves if it would still end up in lakes, streams and sea. As more and more phosphorus has been added to the ecosystem, many lakes and coasts have seen an increased algae growth, which in some cases have led to serious eutrophication and dead zones due to lack of oxygen [91]. CARPENTER and BENNETT [115] even consider that the planetary limits for the eutrophication of freshwater due to phosphorus have already been exceeded. It is possible to recycle phosphorus from different sources (human excreta, manure, different types of waste products, etc.) and improve the efficiency in the production and usage in order to postpone the potential production peak.

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