



WORLD PHOSPHATE INDUSTRY

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ABSTRACT

Phosphate rocks are the commercial source used as raw material for manufacturing phosphoric acid, phosphate fertilizers and certain other chemicals. Phosphate rocks can be used directly in some applications, whereas beneficiation is required to upgrade the ore to more than 29% of P_2O_5 when used as a raw material for the production of fertilizers, phosphoric acid and many other phosphate compounds. Phosphatic fertilizers are the most important end-product of phosphoric acid. Production of phosphoric acid is the first step in the manufacture of many phosphatic fertilizers. Phosphoric acid and phosphate compounds can be used directly in chemical industries or as a key ingredient in the production of many other chemicals required in detergents, animal feed, food, beverages, surface treatment (metal cleaning, coating), water treatment, dentistry, tooth pastes, fire extinguishers amongst many others. High purity phosphate compounds are also used in food and pharmaceutical production. Phosphorus as an element and some other phosphoric chemicals derived from phosphate rocks are used in pesticides, matches, fireworks and also in many military applications.

الصناعة الفوسفاتية في العالم

هجران زين العابدين طعمة

المستخلص

تعتبر الصخور الفوسفاتية المصدر الرئيسي لتصنيع حامض الفوسفوريك والأسمدة الفوسفاتية وبعض الكيماويات الأخرى. يمكن استخدام الصخور الفوسفاتية مباشرة في بعض التطبيقات، ولكن معظم الصخور الفوسفاتية يتم تركيزها إلى نسبة لا تقل عن 29% من خامس أكسيد الفوسفور لتستخدم كمادة أولية في إنتاج الأسمدة وحامض الفوسفوريك والعديد من المركبات الفوسفاتية. الأسمدة الفوسفاتية هي المنتج النهائي الأهم لحامض الفوسفوريك، الخطوة الأساسية لتصنيع معظم الأسمدة الفوسفاتية هي إنتاج حامض الفوسفوريك. يمكن أن يستخدم حامض الفوسفوريك، والمركبات الفوسفاتية الأخرى مباشرة في الصناعات الكيماوية، كما يمكن استخدامها كعنصر أساسي أو ثانوي في عمل وتصنيع العديد من المنتجات المستخدمة في المنظفات، الأعلاف الحيوانية، الأغذية، المشروبات، المعالجة السطحية للمعادن (تنظيف المعادن والطلاء)، معالجة المياه، طب الأسنان، معاجين الأسنان، مطافئ الحريق، وغيرها من الاستخدامات. العديد من مركبات الفوسفات عالية النقاوة تدخل في إنتاج الأغذية والأدوية. من جانب آخر، يستخدم عنصر الفوسفور بالإضافة إلى بعض المواد الكيماوية الفوسفورية الأخرى المشتقة من صخور الفوسفات في صنع المبيدات الحشرية، الألعاب النارية، وفي العديد من التطبيقات العسكرية.

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INTRODUCTION

Phosphate rock is a general term for a rock that contains a high percentage of the apatite group of minerals, but in marine sedimentary phosphorites it is usually a carbonate-fluorapatite (francolite) $\{Ca_{10}(PO_4, CO_3)_6F_2\}$. World phosphate rock production was 241 Mt in 2015 and is forecasted to be 250 Mt in 2020 (USGS, 2017; Heffer and Prud'homme, 2016). The world phosphate production by countries in 2016 is shown in Figure (1).

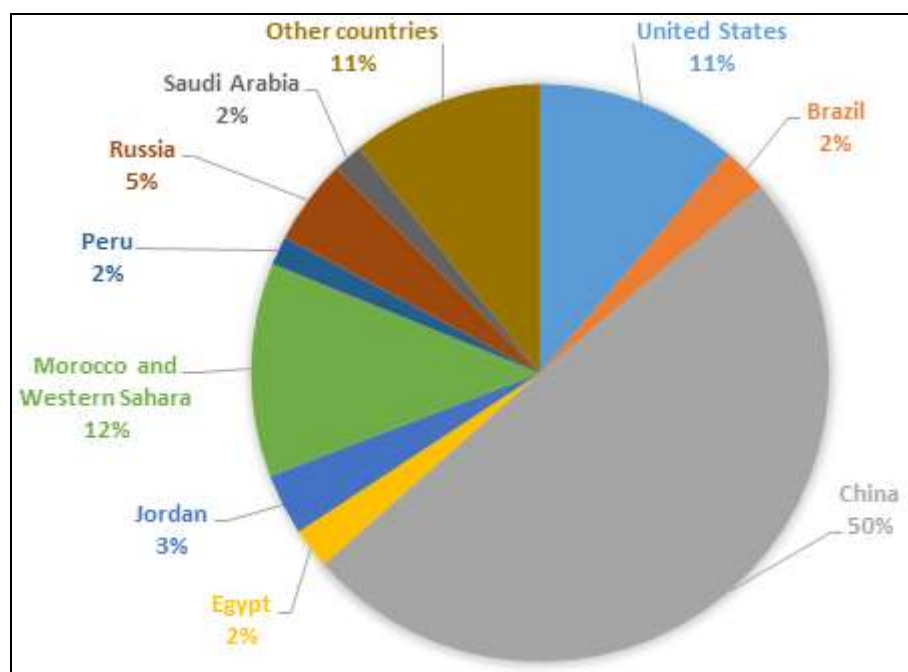


Fig.1: World phosphate rock production capacity in 2015 according to U.S. Geological Survey, Mineral Commodity Summaries, January 2017 (USGS, 2017)

Phosphate rocks of various deposits usually range between low grade and high grade reaching up to 35% P_2O_5 . The beneficiation process increases the phosphate content of the marketable phosphate concentrates (beneficiated phosphate rock) to about 27% – 40% of P_2O_5 (IFA, 2015). Phosphate rocks are the main source of elemental phosphorus used and its compounds are required for the production of commercial phosphatic fertilizers and certain other chemicals. About 88 – 90 % of phosphate rocks are consumed in fertilizer industry and the remaining is used for non-fertilizer applications (Potash Corp, 2014; Jasinski, 2016).

Phosphates can be used directly in some applications, mainly for fertilizers as in a powdered product. However, this represents a very low percent of phosphate use (Rajan and Chien, 2001). For general use, phosphate rock is concentrated by a beneficiation process where the beneficiated concentrate is upgraded to not less than 29% P_2O_5 which is the accepted grade for the phosphate industry. It is the raw material for fertilizers, phosphoric acid and many other phosphate compounds (Bornman, 2012; Kawatra and Carlson, 2014).

Phosphoric acid and phosphate compounds may be used directly by the chemical industry or as the key ingredient for many other chemicals that are essentials in detergents, animal feed, surface treatment (metal cleaning, coating), water treatment, dentistry, tooth pastes, fire extinguishers and other industries.

High purity phosphates are used in food, beverages, and pharmaceutical production. Elemental phosphorus (white and red) and some phosphoric chemicals derived from phosphate rock are used in pesticides, matches, fireworks, and in military applications for generating smoke screens, signaling and incendiary bullets and bombs (IBM, 2013). Phosphoric acid is ultimately used in a wide range of industries in varying concentrations, but it is used mainly in phosphatic fertilizer production. It can also be used further in the production of super-phosphoric acid, technical grade or food grade acid along with many other applications. Figure (2) shows the general production route of mineral phosphates and finished phosphate fertilizers (Roy, 2007).

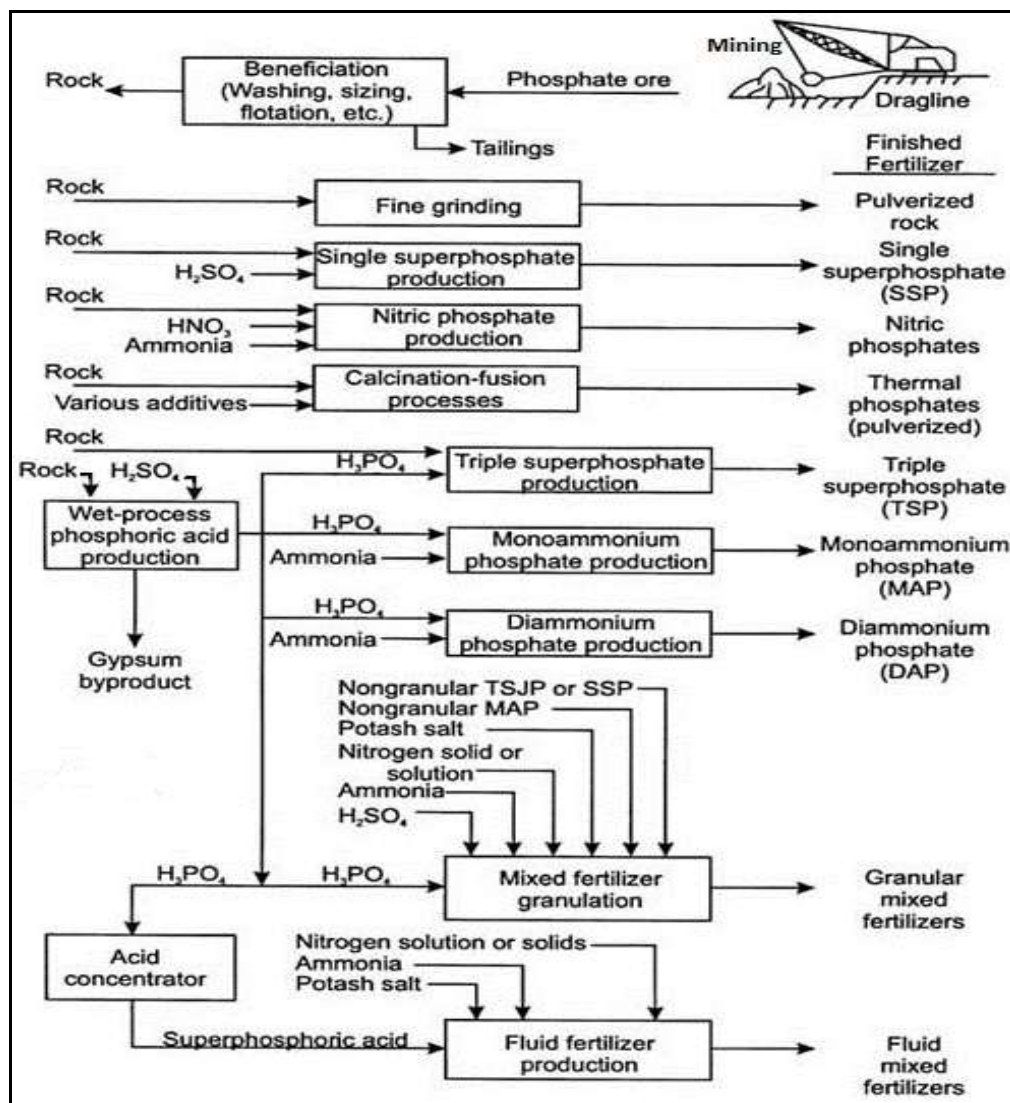


Fig.2: The general production route of mineral phosphates and finished phosphate fertilizers (Roy, 2007)

PHOSPHORIC ACID

One of the largest worldwide applications for phosphate rock is in the production of phosphoric acid. It is the intermediate product between beneficiated phosphate rock and other phosphate compounds where phosphorus is the key ingredient element in the form of a phosphate. The global phosphoric acid (as P_2O_5) production capacity in 2014 was about

55 MT (Heffer and Prud'homme, 2015; FAO, 2015). The concentration of phosphoric acid can be expressed as a percentage of phosphoric acid ($\text{H}_3\text{PO}_4\%$) or a percentage of phosphorus (P%), but normally it is expressed as a percentage of phosphorous pentoxide ($\text{P}_2\text{O}_5\%$) (Potash Corp, 2012). Fertilizer production accounts for about 84 – 90 % of the world market for phosphoric acid and animal feed for about 6%; the rest is used in different industrial applications. The present global phosphoric acid consumption and uses by various sectors is shown in Figure (3) (Potash Corp, 2014).

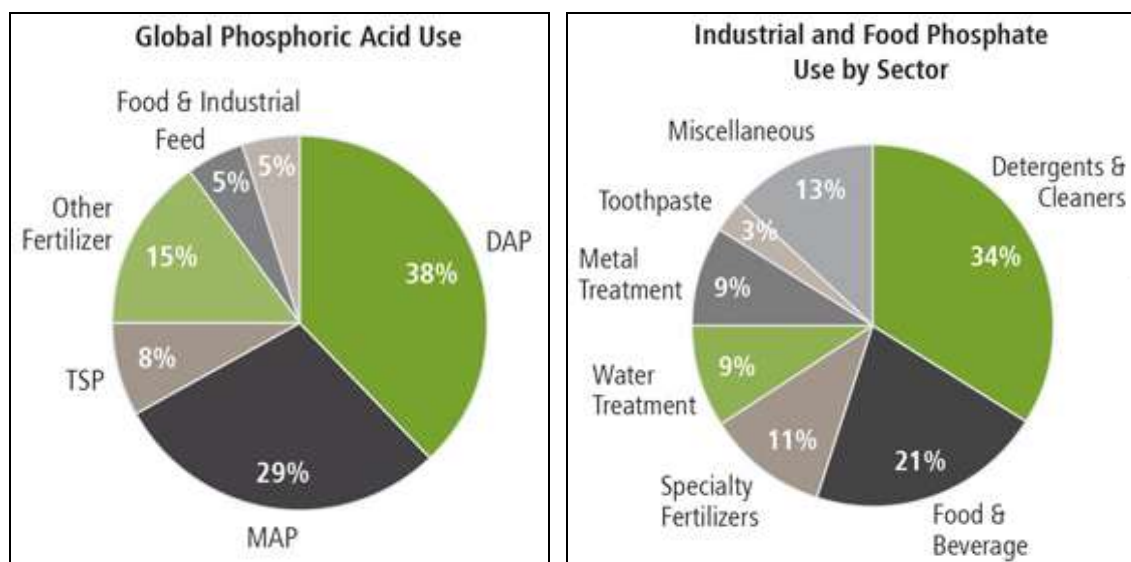


Fig.3: Consumption and uses of phosphoric acid by sectors (Potash Corp, 2014)

There are two main processes used commercially for phosphoric acid production; wet process and dry process (thermal or furnace process). The wet process is the most common and older of the two, where beneficiated phosphate rock is acidulated (digested) by mineral acid. Phosphate acidulation is carried out using either sulphuric acid, nitric or hydrochloric acid. Hydrochloric acid is rarely used in phosphoric acid production, due to its high price, corrosiveness and it is not as available as the other acids. Nitric acid is used with phosphoric acid, particularly in Europe, for the production of multi-nutrient fertilizers. Sulphuric acid is the main mineral acid used in phosphoric acid production. Acid produced by the wet process represents about 90% of the world production of acid (Weterings, 1985; Tunks, 2011).

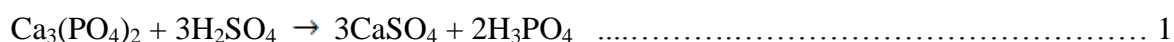
The alternative method of manufacturing phosphoric acid is by dry process (thermal or electric furnace). This method is considered less abundant for production of a purer and more concentrated acid as it requires more energy and involves higher operational costs (UNEP, 1998).

■ Wet Process

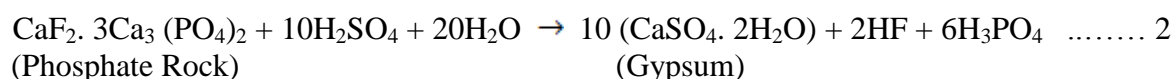
In this most common process, phosphoric acid is produced by acidulation of the beneficiated phosphate rock with a strong mineral acid. Mineral acids being used for the acidification of phosphate rock are; sulphuric, hydrochloric, or nitric acids (Van Der Sluis, 1987; Omri and Batis, 2013). In general, the term “wet process” is mainly used when sulphuric acid is applied. Reaction of sulphuric acid with phosphate rock forms phosphoric acid and an insoluble precipitate of hydrated calcium sulphate, making easy separation of phosphoric acid directly by filtration. In cases where other acids are used, such as

hydrochloric acid or nitric acid, soluble chlorides and nitrates of calcium are formed. As a result, the recovery of phosphoric acid needs special techniques, such as ion exchange, cooling crystallization or solvent extraction (UNEP, 1998).

– **Sulphuric Acid Route:** In the wet process, phosphate rock interacts with the sulphuric acid in a well-stirred reactor. The tricalcium phosphate in phosphate rock is converted to diluted phosphoric acid and insoluble hydrated calcium sulphate according to the following reaction (Becker, 1989; Speight, 2002):



Within the general reaction:



The insoluble gypsum (hydrated calcium sulphate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and other insoluble materials such as silica are separated from the phosphoric acid by filtration (EPA, 1996a). The phosphoric acid produced is called filter acid or weak acid and has a different percentage of P_2O_5 content dependent on the process route used. There are three major types of phosphoric acid production routes when using sulphuric acid, dependent on the route of calcium sulphate production; dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), or anhydrite. In general, five process routes are well-known and available commercially (Roy, 1976; Wing, 2008):

- Dihydrate process
- Hemihydrate process
- Hemi-Dihydrate process (single-stage)
- Di-Hemihydrate process (double-stage)
- Hemi-Dihydrate process (double-stage)

Each process has its own requirements regarding raw materials, utilities, product and byproduct quality and last but not least, overall phosphate concentration efficiency. In the dihydrate process, which is adaptable to a wide-range of phosphate rocks, the filtered acid contains 26 – 30 % P_2O_5 . The filter grade acid is then concentrated up to 50 – 54 % P_2O_5 by vacuum evaporation to meet fertilizer production requirements. In the hemihydrate process route, the filter grade acid produced is about 40 – 50 P_2O_5 % (EFMA, 2000a; CPCB, 2014).

During phosphoric acid production in a reactor, other reactions occur, where the fluoride constituent of the carbonate-fluorapatite reacts with the sulphuric acid to form hydrogen fluoride (HF) (Samrane and Al-Hjouj, 2011). The hydrogen fluoride (HF) produced reacts with the silica to form silicon tetrafluoride (SiF_4), which then hydrolyzes to fluorosilicic acid (H_2SiF_6) (Becker, 1989):



Fluorosilicic acid is an important by-product of the phosphoric acid production process. It can be treated with sodium hydroxide to form sodium hexafluorosilicate. The acid is also used to produce aluminium fluoride that is used in the aluminum industry and some other fluorine compounds such as potassium and/ or sodium fluorosilicates. Fluorosilicic acid and sodium hexafluorosilicate are used as fluoridation agents for drinking water and other applications such as; enamels for china and porcelain, in ceramics and glass, ore flotation,

wood and leather preservatives, electroplating and insecticides (Abbar, 2011; Drevet, 2014).

The acid produced from the wet process is used mainly for fertilizer manufacturing. A further evaporation step is required to form super phosphoric acid with about 70% P_2O_5 , which is used in special chemical industries or used directly in liquid fertilizer. In Figure (4) a flow diagram of one of the commercially available dihydrate processes is shown (EFMA, 2000a).

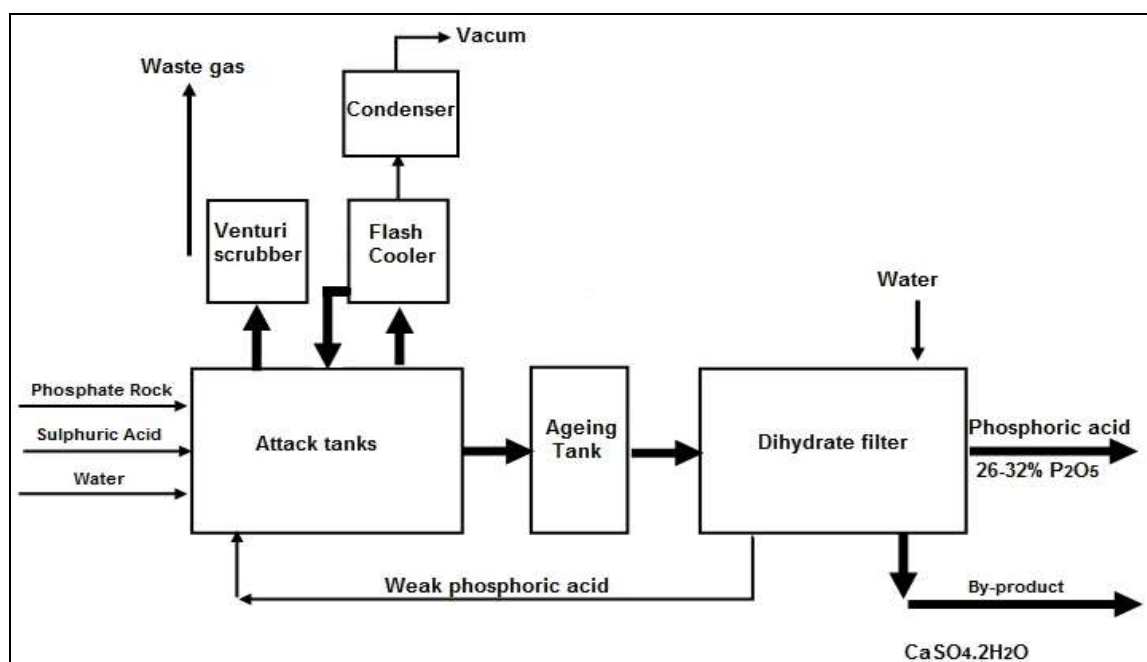
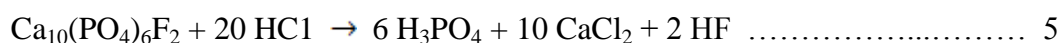


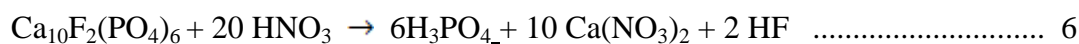
Fig.4: Flow diagram of Dihydrate Process (EFMA, 2000a)

– **Hydrochloric Acid Route:** Phosphoric acid can also be produced by digestion of beneficiated phosphate rock with hydrochloric acid as in following reaction:



The acid produced by solvent extraction has a low level of impurity and higher concentration of phosphoric acid (> 50 wt % P_2O_5). Limitations in this process are the environmental impact of calcium chloride disposal and the severe corrosion of hydrochloric acid solutions. This process can produce super phosphoric acid or food grade phosphoric acid, which is suitable for animal feed phosphate, liquid fertilizers, and detergents. The process produces lower waste when compared with the route of sulphuric acid treatment (Habashi *et al.*, 1987; Wing, 2008).

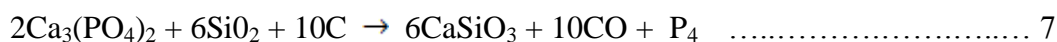
– **Nitric Acid Route:** When crushed phosphate rock is acidulated with nitric acid in a reaction mixture vessel, phosphoric acid and a soluble nitrate of calcium are formed according to the following equation:



The produced phosphoric acid contains 55 – 72 % P_2O_5 . This process is also called the Nitrophosphate process (EFMA, 2000b; El-Zahhar *et al.*, 2013).

▪ Dry Process (Thermal or Electric Furnace Process)

This is the older process and was developed for producing phosphoric acid before being dominated by the wet process of sulphuric acid. High purity acid can be obtained by this method which is suitable for food, medicine and the beverage industry and also in the production of detergents and other inorganic and organic phosphate chemicals. In the dry process, elemental phosphorus is produced by heating phosphate rock with coal (carbon) and silica sand in an electric arc furnace according to the following reaction (Speight, 2002, Hocking, 2006):



The process produces an elemental vapor of phosphorous P_4 which is then directly condensed on leaving the electric arc furnace. In the combustion chamber, the condensed elemental phosphorus is burned (oxidized) to form a vapor of phosphorus oxide (P_4O_{10}). To produce phosphoric acid; phosphorus oxide vapor is hydrated with water at concentrate range from 75 – 85% P_2O_5 as shown in the reaction below (Hocking, 2006):



The phosphoric acid thus produced has very small amounts of impurities. It is nearly pure and more expensive and used mainly in the food industry (food grade acid) and special chemical industries, in the manufacture of phosphate salts for use in detergents and animal feed supplements and in organic and inorganic chemical applications. Fertilizers produced from white phosphoric acid, as the main phosphorus source, are generally more expensive and require high energy consumption for production (Rehm *et al.*, 1997).

FERTILIZERS

The bulk of phosphate rock mined in the world (about 90%) is used in the phosphate fertilizer industry (Jasinski, 2016). Many types of fertilizers are produced using phosphate rock, phosphoric acid, ammonia, sulphuric acid and many other raw materials. The fertilizer industry is an integrated complex, production line of different processes and has been further developed recently for global agricultural needs essential to human life (Kogel *et al.*, 2006).

The three products currently dominating the world phosphate market include normal superphosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$], concentrated superphosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$], and complex fertilizers including monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$); diammonium phosphate [$(\text{NH}_4)_2\text{HPO}_4$]; and nitric phosphates of varying composition. Figure (5) shows the global consumption and the rate of growth of consumption of different types of phosphate fertilizers for the period of 1973 – 2011 (EPA, 1996b; UNEP, 1998; Stewart, 2010; IFA, 2013).

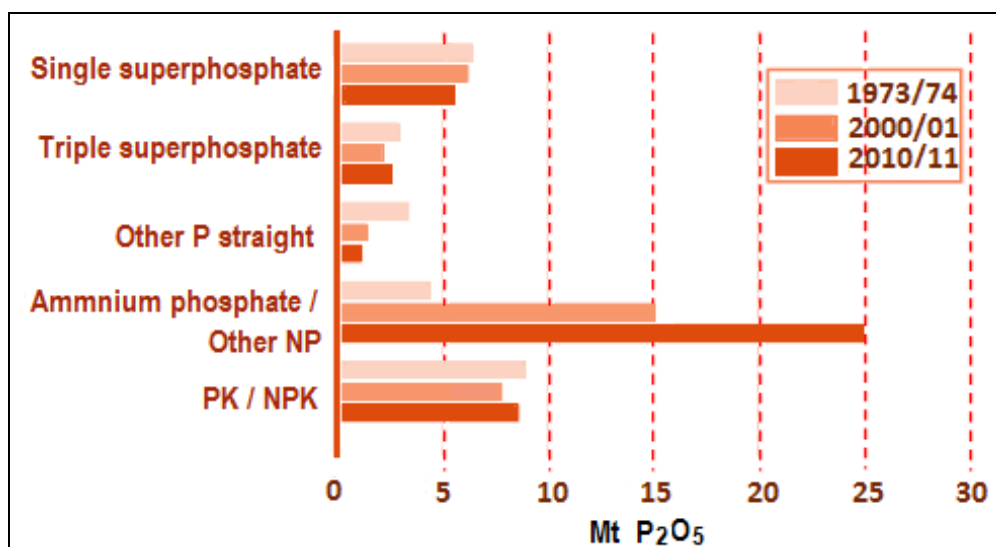
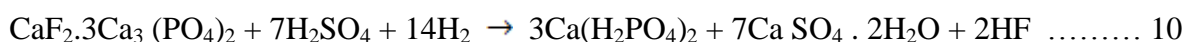


Fig.5: Global consumption and the growth of consumption of different types of phosphate fertilizers (IFA, 2013)

▪ Single Superphosphate Fertilizer

Single superphosphate (SSP) is the earliest type of phosphatic fertilizer produced, also known as normal or simple superphosphate. The manufacturing process of this fertilizer involves the reaction of concentrated sulphuric acid with beneficiated phosphate rock as shown below (Plotegher and Ribeiro, 2015; IPNI, 2016a):



The fertilizer contains about (16 – 20 %) P₂O₅. Calcium phosphate produced by this reaction remains in the fertilizer. The global production of this type of fertilizer is declining due to environmental and economical considerations.

▪ Triple superphosphate

Superphosphate is the most widely used phosphorus fertilizer, produced by treating of ground milled phosphate rock with concentrated phosphoric acid by the basic reaction below:



The product contains 45 – 48 % P₂O₅ (average 46%) and can be produced in two basic forms; granular (GTSP) and non-granular. The granular TSP of uniform particle size gives best storage and handling characteristics. Its P₂O₅ content is equivalent to three times the effective P₂O₅ content of the single super phosphate, thus, it is referred to as “Triple Super Phosphate” or simply “TSP” (UNIDO and IFDC 1998; Taylor, 2004; IPNI, 2016b). Figure (6) shows the simplified block flow diagram for triple superphosphate manufacturing by Jacobs-Dorrco process, formerly known as the Dorr-Oliver type slurry process.

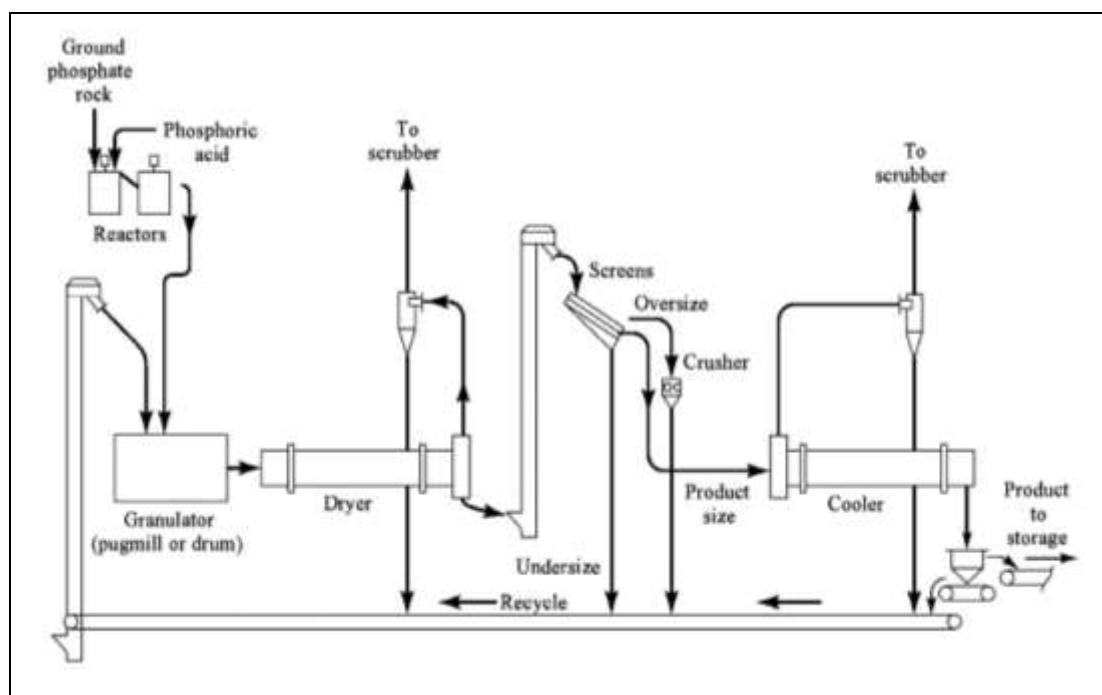


Fig.6: Flow diagram for triple superphosphate manufacturing by slurry-type granulation process (Nielsson, 1987)

▪ Ammonium Phosphate

Mono-ammonium phosphate and di-ammonium phosphate are the common types. In both types ammonium phosphate is made by neutralizing phosphoric acid with ammonia. Monoammonium phosphate is produced at ammonia to phosphoric acid ratio of 0.6 and 1.0 in pre-neutralizer and granulator respectively. In di-ammonium phosphate production, the ratios are 1.4 in the pre-neutralizer and 1.0 in granulator (UNEP, 1998; Gowariker *et al.*, 2009).

– **Mono-Ammonium Phosphate (MAP):** Produced by reacting anhydrous ammonia with phosphoric acid in a neutralizing reactor according to the following reaction:



The slurry produced from the reactor is granulated and then dried. This fertilizer, in its commercial form, contains 11 – 12 % of nitrogen and 48 – 53 % of P_2O_5 . It can be produced as powder or granules. Powder form is used for the production of other types of NPK and blended fertilizers. The granular form can be used directly as a fertilizer (Roy, 2007).

There are other production technologies for powdered MAP using a pipe reactor where phosphoric acid and ammonia reaction takes place in a pipe reactor. The Mono-ammonium phosphate, in its powder form, is also a component of some dry powder fire extinguishers (Gargouri *et al.*, 2012; IPNI, 2016c).

– **Diammonium Phosphate (DAP):** Diammonium phosphate is another type of ammonium phosphate fertilizer. It is produced by the reaction of phosphoric acid with gaseous ammonia:



Diammonium phosphate is the best and most common type of phosphate-nitrogen fertilizer used. It contains 18% nitrogen and 46% phosphorus pentoxide (P_2O_5) in granular form and has good solubility properties. It is also used as an intermediate material for the production of other types of NPK compounds and bulk blends of fertilizers (IPNI, 2016d; Ivella, 2011).

▪ **Other Types of Fertilizers**

– **Nitrophosphate (NP):** NP is a nitrogen-phosphorus compound fertilizer made from treating phosphate rock with nitric acid, sometimes known as the ‘ODDA Process’. Nitrophosphate solution is produced from a reaction neutralized with ammonia to produce NP fertilizer. Potassium chloride can be added to form a liquid or granulated compound fertilizer NPK (Nitrogen, Phosphorous, and Potassium). Industrial plants using this technology have gained popularity in some European countries and also in Pakistan (El-Zahhar *et al.*, 2013; IPNI, 2016e).

– **Fused Calcium Magnesium Phosphate (FCMP):** FCMP is a type of vitreous phosphate fertilizer formed by melting phosphate rock with a fusing agent (containing magnesium and silicon minerals) at temperatures above 1400 °C, followed by rapid hardening with water. The P_2O_5 content of the product is 12 – 20 % (Ranawat *et al.*, 2009).

DIRECT APPLICATION OF PHOSPHATE ROCK IN AGRICULTURE

Finely-ground phosphate rock, mainly of sedimentary origin, can be used for direct application to soils under certain conditions. It is considered as an alternative fertilization option particularly in developing countries. It is cheap in price and takes advantage of the available phosphate resources instead of imports and is well-considered for the purposes of ecological agriculture.

Direct use of finely-ground phosphate rock has some benefits where chemical processing is not accessible or available. It meets with good soil solubility characteristics and climate conditions. It can be applied directly without any chemical process and is soluble in acidic soils. The availability of a phosphate nutrient for crops depends on soil properties, crops grown, agricultural systems, climatic conditions, fertilizer management practices and type of rock. The use of direct application of phosphate rock worldwide has declined and has considerably slowed down and currently it is barely being used (Rajan and Chien, 2001; IBM, 2013; Husnain *et al.*, 2014).

URANIUM EXTRACTION

Phosphate rocks usually contain a trace amount of uranium, the average concentration is found at around 50 – 200 ppm. Some studies have reported that uranium concentration can be more than this figure in some areas (Ragheb, 2008; Ragheb and Khasawneh, 2010; Astley and Stana, 2014). The estimated world uranium resources in phosphate rock deposits is about 13.8×10^6 tons of uranium as was reported by the "International Atomic Energy Agency (IAEA) World Distribution of Uranium Deposits (UDEPO)" in April 2015 (Montaser, 2016). With the ever increasing demand for electricity, uranium extraction processes from phosphate rock makes it economically feasible for use in nuclear electricity generation.

Extraction of uranium from phosphate rocks started in the 1950's in the United States. At the end of the 1970's and beginning of the 1980's, many plants were built around the world for uranium extraction, including one in Iraq. All plants (including the Iraqi plant) used solvent extraction technology (Ragheb, 2008; Zhang, 2012). Uranium extraction requires the

conversion of beneficiated phosphate to phosphoric acid followed by solvent extraction. In general there are three main solvent extraction processes used; (IAEA 1989; Walters *et al.*, 2008):

- OPPA Process (uses Octyl Pyro Phosphoric Acid as extractant).
- 2 Stage DEPA-TOPO Process {uses Di(2-Ethylhexyl) Phosphoric Acid and Trioctyl Phosphine Oxide as extractants}.
- OPAP Process (uses Octyl phenyl Acid Phosphate as extractant).

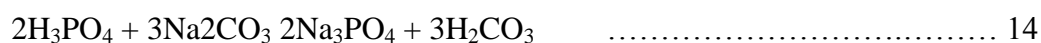
New technologies are now available, which offer some improvement on solvent extraction processes; such as membrane systems and ion exchange (IAEA 1989; Mousa *et al.*, 2013; Astley and Stana, 2014).

PHOSPHATE SALTS

Phosphoric acid, as a normal wet phosphoric acid, technical grade, or food grade is used to produce different phosphate salts of sodium, calcium, potassium and aluminum, with some other elements on lower scale of production. The final specifications depend on the quality of both the phosphoric acid and the metal salt. Sodium and calcium phosphate salt production are more dominant than other salts. The production steps for phosphate salts are generally similar, they include neutralization, crystallization, drying, calcination, milling and sizing. The major uses of phosphate salts are for animal feed, detergents, metal treatments and human food products (Gilmour, 2013).

▪ Sodium Phosphate

Commercially, sodium phosphates are the largest group of phosphate salts. A generic term for a variety of phosphate salts produced from the treatment of phosphoric acid with sodium hydroxide (caustic soda) or sodium carbonate (soda ash), the overall reactions are (EPA, 2000; Speight 2002; Gilmour, 2013):



The production process for different grades of these salts depends on the sodium/phosphate ratio at the reactor stage. In general, wet phosphoric acid is used in the production of industrial phosphate salts, but for food production purposes, a food grade quality of phosphoric acid should be used.

The following main sodium phosphate salts are common:

- Monosodium phosphate (H_2NaPO_4)
- Disodium phosphate or sodium orthophosphate (HNa_2PO_4)
- Trisodium phosphate (Na_3PO_4).

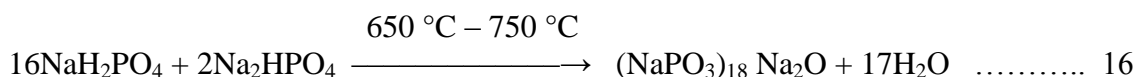
– **Monosodium Phosphate (MSP):** Monosodium Phosphate (H_2NaPO_4) is a white powder crystalline material used in various chemicals and the food industry. In the chemical industry, MSP is used for metal surface treatments and metal finishing by providing an undercoating for paints, such as pH control in boiler water treatment and corrosion control, as a food additive in the food and beverage industry and mainly as a pH buffering agent, emulsification agent, or nourishment agent in the production of baking powders. It is also used in other applications such as livestock feed supplements and toothpaste (EPA, 2000; Gilmour, 2013).

– **Disodium and Trisodium Phosphate Processes (DSP and TSP):** To produce these salts, sodium hydroxide is mixed with phosphoric acid with an appropriate ratio of sodium/phosphate, the resultant sodium phosphate solution is then dried and subsequently heated to the desired temperature.

Disodium phosphate (HNa_2PO_4) is used as a water softening agent for boilers. It is used by the food industry as a buffer agent, emulsifier and to make condensed or evaporated milk and as a supplement for animal feeds. Disodium Phosphate is also used for wood and paper as a flame retardant and in some detergents and cleaning agents including many other chemical processes (EPA, 2000; Corbridge, 2013).

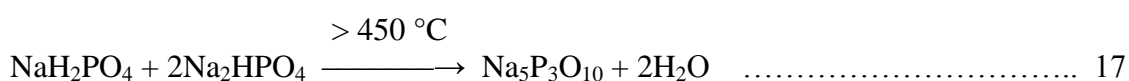
Trisodium phosphate (Na_3PO_4) is incorporated in detergent compositions used in automatic dishwashing appliances, as an alkaline source for metal cleaners and can also be used as a retardant in the setting rate of calcium sulphate plasters. It is also *used* in water treatment to adjust the pH and as a corrosion inhibitor (EPA, 2000; Gilmour, 2013).

– **Sodium Hexametaphosphate SHMP:** In many sodium hexametaphosphate plants, monosodium phosphate/ disodium phosphate solution of the appropriate Na/P ratio is made. The diluted solution is fed to a furnace at a temperature range of $650\text{ }^\circ\text{C} - 750\text{ }^\circ\text{C}$ where free water is removed and the MSP/DSP undergoes a polymerization reaction. The following equation shows the forming reaction of SHMP (Gilmour, 2013):



Sodium Hexametaphosphate is used as a refractory binding agent. It is used in powdered detergents and cleaners, in water treatment formulations as a water softener and also by the food industry, e.g. in the synthetic dairy products and also to improve the water holding capacity of meat (EPA, 2000).

– **Sodium Tripolyphosphate Process (STPP):** Sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) is produced by reacting sodium hydroxide or sodium bicarbonate with phosphoric acid by adjusting the sodium to phosphorus ratio to 5: 3. The resultant sodium phosphate solution, containing a mixture of MSP and DSP, is calcined to the desired temperature as shown in following reaction (Gilmour, 2013; Kowalski and Makara, 2013):

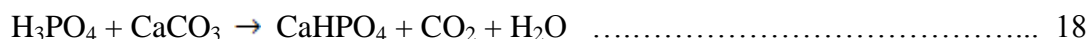


There are different grades of STPP found in various applications. STPP is used in the pulp and paper manufacturing industry to improve brightness and appearance and is used to de-ink recycled paper. It is used also in the food industry as a flavor enhancer for meats and seafood, to improve the water holding capacity of meat and seafood products and in the processing of canned foods as a quality improver. It is also used as an ingredient in detergent manufacturing, a tanning agent for leather making, metal cleaning and water treatment, amongst other uses (Gorazda *et al.*, 2014).

▪ Calcium Phosphate

Three types of calcium phosphate are mainly produced and are found in the manufacturing of animal feeds; monocalcium, dicalcium, and tricalcium phosphates. Monocalcium and dicalcium phosphates are produced by the reaction of defluorinated

phosphoric acid with high quality limestone or other types of calcium salts (oxides and hydroxides) (Speight, 2002; Casacuberta *et al.*, 2010).



These salts can also be produced by the reaction of phosphate rock with hydrochloric acid:



The Mono-dicalcium phosphate, which contains about 15 – 20 % calcium and about 21% phosphorus, is the most commercially known compound that is commonly used for animal feed supplements. Dicalcium phosphate (DCP) contains about 18 – 24 % calcium and about 18.5% phosphorus. Total worldwide production of animal feed of DCP is about 4,000,000 tons per year. Most commercial feed phosphates are the mixtures of monocalcium and dicalcium phosphates (Viljoen, 2001; Hoffmann *et al.*, 2011). Tricalcium phosphate (TCP) is manufactured by mixing phosphate rock with phosphoric acid and sodium hydroxide and calcining the mixture at high temperature. It contains about 30% calcium and about 18% phosphorus. Calcium phosphate is also used in certain prepared foods as the phosphates and calcium work together to promote muscle and bone health, also to assist in the absorption of B vitamins. DCP is also used as a tableting agent in pharmaceutical preparations, as a body odor removal in personal care products and as a tartar control agent in toothpastes (Viljoen, 2001; Hoffmann, 2007).

GENERAL USES OF PHOSPHATES

▪ Use of Phosphate in Detergents

Some phosphate compounds are used as the main ingredient in different detergent formulations; liquids, free-flowing powders or granular. Phosphates are considered as builders or softeners when introduced into cleaning product formulations. The phosphates function in relation to detergency by contributing to the control of the pH, by providing and controlling alkalinity which can assist in the removal of fatty soils, to prevent corrosion, as a water softener which prevents dirt or soil from getting stuck on surfaces being cleaned and to prevent lime-scale build-up in the washing appliances. Sodium tripolyphosphate (STPP) and tetrapotassium pyrophosphate (TKPP) are some important ingredient in detergent manufacture (Glennie *et al.*, 2002; Cimcool, 2016).

▪ Metal Surface Treatments

Phosphoric acid and some phosphate salts are used in metal surface treatments (cleaning and coating) mainly iron, zinc, manganese and aluminum. In electrolysis plating for example, to deposit the desired metal on any surface, sodium hypophosphite is used as a reducing agent (Narayanan, 2005; Debnath, 2013).

Phosphate coating or phosphatizing (sometimes called conversion coating) provides an insoluble and inert coating when the metal is immersed in a phosphate solution. Manganese phosphatizing provides excellent corrosion resistance, high hardness and wear resistance surfaces. Zinc phosphatizing applied to equipment exposed to extreme corrosion in severe environmental conditions. It can improve the appearance of finished goods. Phosphatizing also improves the surface of iron and ferrous metals and is used to increase paint adhesion for subsequent finish paints as well as improving impact resistance (Marikkannu *et al.*, 1999; Hafiz *et al.*, 2008).

▪ Phosphate in the Food Industry

Many phosphate salts, produced from high purity and quality phosphoric acid, are commonly used in the food industry and as ingredients provide many important functions (Molins, 1990; Branen *et al.*, 2001; Potash Corp, 2012). In Pastry industry (bakery industry); phosphate salts used in the fermentation and leavening agents of chemical pulp operations, baking powder, antibacterial effects of polyphosphates have also been observed. Phosphate compounds are also used to make dough soft, pastries and to balance the alkalinity of the bicarbonate (Molins, 1990; Branen *et al.*, 2001).

In Meat, poultry and fish industry; phosphate salts are used for improving the water-holding capacity (to improve water retention) of meat, stabilizing the texture, emulsification of fat, slowing down oxidation reactions, reduce shrinkage (moisture loss) during cooking and to enhance flavor, color and appearance. Also used for pH value adjustment, to protect meat during storage and extend shelf-life (Son Long *et al.*, 2011). In the dairy industry; phosphate salts are used to stabilize milk products such as cheeses, yoghurt and milk desserts due to the calcium-binding properties of phosphates. In processed cheese for example; to prevent undesirable changes such as preventing the separation of fat butter, enabling a smooth mixing of fats, proteins and moisture during cooking and storage also the development of beneficial bacteria in cheese (Munchbach and Gerstner, 2010; Gaucheron, 2012; Ritz *et al.*, 2012).

Phosphate salts are also used in the soft drinks, energy drinks in yeasts and fermentation as nutrients in alcohol production. Phosphate is also used to improve the texture of some types of canned vegetables (peeled tomatoes), to whiten and clarify sugar, as an anti-caking or fluxing agent, to modifying starches, flavorings, gelatin and also drinking water (Branen *et al.*, 2001; Molins, 1990; Son Long *et al.*, 2011).

▪ Toothpaste

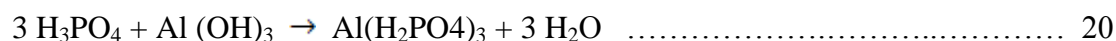
Phosphate compounds such as sodium hexametaphosphate and sodium monofluorophosphates are used as fluoride sources and in the formulations of dental care products such as toothpastes. These compounds used to provide protection against dental erosion, to protect human enamel against the initiation and progression of damage due to dietary acid and bacterial attacks, it form protective barrier on teeth to reduce and prevent stains and tartar from forming, in addition to reducing the incidence of dental caries (Al-Sanabani *et al.*, 2013; Davies *et al.*, 2010; Faller *et al.*, 2011).

▪ Fire-Fighting Materials

Monoammonium phosphate is used as one of the basic materials in the manufacture of fire-fighting materials (powders) as well as some organic phosphate compounds are used in the tissue industry and for fire-resistant clothing (Voelkert, 2009). Ammonium polyphosphate is used as a flame-retardant and is very useful for many flammable materials like synthetic polymers, polyamide, paints and wood protective coatings (Dittrich *et al.*, 2014).

▪ Phosphates for Refractory Industries

Aluminium phosphates types have many extensive uses within ceramics industry and refractories. Monoaluminium phosphate is the most well-known type and it is produced by the exothermic reaction between phosphoric acid and aluminium hydroxide according the following reaction;



It is used as a bonding agent for refractories, dental cements and other applications. Monoaluminium phosphate is also used as base for the production of many aluminum phosphate compounds such as aluminium tripolyphosphate ($\text{AlH}_2\text{P}_3\text{O}_{10}$), Trialuminium phosphate (AlPO_4), aluminium metaphosphate and aluminium polyphosphate (Kingery, 1950; Giskow *et al.*, 2004).

WASTE AND ENVIRONMENTAL IMPACT

All industrial phosphate related activities cover wide and varied industrial processes and production methods and have a high risk potential to cause a significant and negative impact on the environment. These impacts can take different forms; Air quality (Air emissions/ air pollution); Water quality/ quantity (Wastewater/ water contamination, excessive water consumption), changes to the landscape (Land impacts, Acid mine drainage), Hazardous materials, and waste (UNEP, 2001; WBG, 2007).

Gaseous and particulate emissions represent a significant source of air pollution which contributes to the majority of air quality problems. These emissions from various activities of the phosphate industry also include many gaseous pollutants such as; dust, sulphur oxides, nitrogen oxides, carbon oxides, hydrocarbons and other particulate matter emissions that contain a variety of chemical constituents. Water quality and quantity are adversely affected from phosphate industries; high water consumption, effluents that may contaminate water resources (surface and groundwater).

To reduce water impact, it is important to understand how specific phosphate industries processing techniques contribute to the negative impact on surface and groundwater and to highlight the associated environmental implications. Phosphate industry operations have a significant impact on the land. These impacts include removal of topsoil and vegetation, soil contamination, excavation and overburden and disposal of processed wastes (UNEP, 2001; Wang *et al.*, 2004).

Solid and liquid wastes in the phosphate industry are generated during various procedures and processing plants; mining, beneficiation, production of phosphoric acid, production of fertilizers, and other chemical compound production plants. The huge volume of waste clay from beneficiation plants and phosphogypsum generated from phosphoric acid causes massive environmental impact on land and water quality. Therefore, it is imperative to seek methods that ensure safe waste disposal. For example, more than 4 – 5 tons of phosphogypsum is generated for each ton of phosphoric acid, which translates to tens of millions of tons per year. There is great difficulty in the use of such large amounts of phosphogypsum because they contain compounds of different chemical elements. Some researchers have shown the possibility of waste use in agriculture as it contains essential elements for plant growth, in construction as replacements in the cement and materials industry and as a chemical raw material to produce other chemical compounds such as sulphuric acid and ammonium sulphate. To reduce the environmental impact of the phosphate industry, it is necessary to focus on increasing P_2O_5 recovery, developing more efficient technologies and to utilize waste to produce other materials (Wang *et al.*, 2004; Mishra *et al.*, 2010; Zhang, 2014; CPCB, 2014).

CONCLUSION

In this review, the importance and impact of phosphate rocks and phosphorus compounds in industry is demonstrated. It includes a range of production processes and many of the

primaries, intermediate and final products that play an important and key role not only in industry but also in our daily life.

Industrial uses of phosphate, especially phosphoric acid and phosphate salts cannot be confined; they are involved in many important areas and large chemical industries. The importance of phosphate remains as the backbone of the fertilizer industry and in supplying the most important elements needed to increase agricultural yields and in helping to solve the problem of producing enough food to feed the growing number of the world's population.

The global phosphate production rate is increasing as well as its environmental impact, so to boost and further develop this industry, whilst achieving a balance between agricultural production and resources on one hand and protecting the environment on the other, it is of great importance that we achieve a fully managed and sustainable development plan. The phosphate industry has many opportunities but faces many pressures. Increased production and increased demand for phosphate products means the need to further develop modern methods and introduce new technologies to combat the significant related environmental challenges.

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