Chapter 14
The Ecophos Process: Highest Quality Market Products Out of Low-Grade Phosphate Rock and Sewage Sludge Ash

Mohamed Takhim, Marc Sonveaux, and Rob de Ruiter

Abstract Ecophos s.a. has developed a unique modular process for the valorization of low-grade phosphate rock and/or various alternative P resources such as sewage sludge ash on the basis of soft digestion by hydrochloric acid or phosphoric acid. The process is extremely flexible and is, by the modular setup, capable of using several types of raw materials and producing a variety of products (fertilizer-, feed-, and food-grade phosphoric acid (PA), animal feed (DCP and MCP), and liquid NPK, PK, and NP fertilizers). The process has economic and ecological advantages over conventional industrial processes and those in development for valorization of sewage sludge ash, since it is simple, stable, and easy to control without needing expensive chemicals, raw materials, and equipment. The performance has already been tested in industrial plants at Bulgaria, Syria, and Peru as well as pilot- and lab-scale installations. Uptime longer than 7800 h/a is easily reached and the yield on P_2O_5 is 90% or higher. Furthermore the process can use excess HCl in the manufacture of products such as isocyanate, caustic soda, or SOP (Sulfate of Potassium). The energy balance is more positive than competing processes, since PA of high concentration (>42%) can be obtained without evaporation. The process can generate uranium (U)-free fertilizers, while conventional fertilizers generally contain 300–500 mg U/kg P_2O_5. Main by-products include high-purity $CaCl_2$ (as solution, flakes, or prills), radiation-free gypsum, silicate filter residue, and Fe/Al-chlorides. By applying different modules, most of the by-products can be split into sellable products, thereby minimizing final waste.

Keywords Ecophos process · Low-grade phosphate rock · Sewage sludge ash · Phosphoric acid

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H. Ohtake, S. Tsuneda (eds.), *Phosphorus Recovery and Recycling*,
https://doi.org/10.1007/978-981-10-8031-9_14

14.1 Introduction

Phosphorus (P) is, together with many other elements such as oxygen, hydrogen, carbon, nitrogen, potassium, and various micronutrients, essential for living organisms including microorganisms, plants, animals, and humans on earth. Every cell of a living organism contains P which is irreplaceable with any other element. Phosphate (P_i) found in soil is taken up by plants. Plants are then consumed by animals that use P in biological building blocks and cellular energy metabolism. At the end of a life, P_i is returned back to nature. This natural P cycle has been in balance for many years. However, humans have influenced the P cycle mainly by intensive agriculture. While synthetic fertilizer is inefficiently used in agriculture, P is lost from soil by runoff and erosion on a global scale. This challenge needs to be addressed for feeding the ever-growing world population.

P_i-rich rocks have been found in limited geographical areas on the planet. The industry has come up with a solution by synthesizing fertilizers from these natural resources, thereby returning P_i back to farmland to feed the world population. However, today, this solution is increasingly challenged. High-grade P_i reserves which have been used by the fertilizer industry are in dangerous decline. What is more, the fertilizer-manufacturing processes consume lots of energy and produce tons of waste. Furthermore, approximately 45% of the world's high-quality P_i rock reserves is located in one specific region, North Africa. Europe's food supply is already depending on the P import from this region. Another 45% of the P_i rock reserves can be found in Asia, mainly China and Kazakhstan, but it is not readily available for export. The USA accounts for about 6% but has ceased the export since 1997. According to Fertilizers Europe, Europe imports around 1.75 Million tons of P annually in the form of P_i rock, fertilizers, phosphoric acid (PA), and feed phosphates. The situation for other countries with no substantial P_i rock resources is similar.

Nevertheless, hundreds of thousands of tons of P are lost annually in Europe alone. The main waste streams containing P are animal manure, sewage sludge, and bone meal. However, a large portion of the waste streams are disposed of into the environment without being efficiently recycled. For example, flow analyses from France show that 50% of the total P used there is lost – around 20% in wastewater, the same through erosion and leaching, and about 10% in the form of food waste and other biowastes (Consultative communication on the Sustainable Use of Phosphorus (European Commission) Brussels 2013, COM 2013). Intensive animal production is concentrated in specific areas close to ports and major population centers with available labor and expertise. This concentration has led to an oversupply of manure in these regions with a gradual build-up of P_i in soil and increased risks of water pollution. In addition, urbanization contributes to disrupt the P cycle by aggregating P-containing sewage sludge and food waste, few of which is returned to farmland. "Waste of today will generate food for tomorrow" is the slogan for the cradle-to-cradle concept of chemist Michael Braungart and architect William McDonough. The European Committee also advocates "urban mining" to find ways for valorizing wastes and to make them the mines for the future. Recycling of urban P_i resources is an essential issue for the future of the cycle of P and ultimately for the cycle of life. Once P is dispersed into the natural environment, it is practically difficult to recover for recycling.

14.2 Ecophos Philosophy

The fastest way to expand the global P availability may be to find ways to economically process the low-grade P_i rock. The United States Geological Survey (2017) estimates the world resources of P_i rock are more than 300 billion tons, while the reserves which can be economically extracted with proven technology and current economics are estimated to be about 68 billion tons (USGS 2017). However, P_i rock is generally contaminated with toxic substances such as cadmium (Cd) and radioactive uranium (U). Conventional technologies cannot completely remove these toxic substances in fertilizer-manufacturing processes. Certain plants such as sunflower, colza, and tobacco can accumulate relatively high concentrations of cadmium. In terms of health impact, the EU Risk Assessment Report on cadmium (European Commission Joint Research Center 2007) found that the major risk of cadmium is kidney damage through food consumption and smoking. The radioactive uranium ends up in fertilizers in the range of 300–500 mg U/kg P_2O_5, posing the contamination risk of food. Ecophos believes that fertilizers should be free from such toxic substances as heavy metals, radioactive elements, and other contaminants. It is critical to apply the right technology for valorizing “urban mines” and low-grade P_i rock as high-quality, contaminant-free P_i resources for the manufacture of fertilizer.

Producing high-purity P sources has another advantage. High-purity PA makes it easy to supply tailor-made fertilizers suited for the needs of the specific soil. Ecophos believes that the key concept of the fertilizer industry will shift from a volume-based standard product approach to a quality-based specific composition approach. The specifics of the soil and consumer needs will determine not only what macronutrients are needed but also the requirement for specific micronutrients. Precision agriculture in terms of fertilizer composition and timing of fertilization will become more and more important. Ecophos believes that future fertilizers will be manufactured using high-purity macro- and micronutrients. The Ecophos technology enables this approach for supplying high-quality P-containing building blocks from a variety of resources, regardless of high- or low-grade P_i rock or secondary P resources from “urban mines.”

Regarding “urban mines,” it is logical to valorize waste streams that have the highest P content and are most readily available. In this perspective, bone meal and sewage sludge have the highest potential. Animal manure is also an option, but its use is logistically more difficult. In Europe, more than 10 million tons of sewage sludge (dry mass) arises every year (Table 14.1). One fifth of this quantity is from Germany where about 47% of sewage sludge is used in farming and landscaping, and the remaining 53% is incinerated (45% mono-incinerated (220 kt (kilo tons)

Table 14.1 Estimates for sewage sludge and sewage sludge ash production in Europe, USA, and Japan

Sewage sludge and mono-incineration (%)					
	Sludge (DS)	Ash		Ash (mono)	As P_2O_5
	kt/a	kt/a	% mono-inc.	kt/a	kt/a
Europe	8330	3165	20	633	107
Germany	2450	931	28	260	44
Austria	245	93	31	28	4
Switzerland	203	77	47	36	6
USA	8200	3116	22	685	116
Japan	3000	1140	50	570	96
Total	22,428	8522		2214	376

ash/a) and 55% co-incinerated). In Germany alone, approximately 24 kt of meat and bone meal (MBM) and 55 kt of sewage sludge are generated annually. Germany is one of the leading countries to study valorization of these waste streams. However, according to the conclusion of the PhoBe-Study (Pinnekamp et al. 2011), today no single process to recycle P from waste streams is economically viable. Since the occurrence of BSE crisis MBM is classified into the three categories. The category 2 and 3 materials are allowed to be used as animal feed or fertilizers, whereas the category 1 (high risk) material must be incinerated. Unfortunately this material is mostly incinerated in cement kilns or in power plants as a high calorific substitute. This simply means that proteins and phosphorus are lost forever. If they are mono-incinerated, the ash would be a high-quality P resource (35–40% P_2O_5, no heavy metals and no uranium).

Several processes are known to recover P from waste streams (Sartorius et al. 2011 and see Chap. 1). P can be recovered from (i) sludge liquor, (ii) digested sludge, or (iii) sludge ash. Although chemical precipitation (mostly as calcium phosphate or struvite) from sludge liquor is a relatively easy option. However, the main disadvantage is that the overall potential of P recovery from sewage is low, normally between 50% and 60%. Another issue almost never mentioned is the fact that excess Mg (e.g., via struvite) in the soil could hamper the uptake of Ca, K, and other essential cations by crops (Hammond and White 2005). As the sludge contains organics (e.g., antibiotics, pathogens, and pharmaceuticals), the recovered P products are often contaminated with these organics. Depending on the specific process, heavy metal contamination can also occur. By contrast, sludge incineration has advantages such as energy integration and high mercury removal. Organic pollutants such as PCBs, dioxins, hormones, and POPs are also decomposed.

The Ecophos philosophy is simple and straightforward: any risk concerning organic contaminants in fertilizers, animal feed, and food must be avoided. Therefore, incineration is a must in the Ecophos's view. Furthermore, it is highly prioritized to design a technology that leads to the high-purity P-containing building blocks that are identical to today's market products and that can be easily used as a P source to manufacture specifically designed fertilizers in the new fertilizer economy. The type of P_i-precipitates should be carefully selected with respect to the crop accessibility (the water- and citric acid-solubility). Moreover, the market for P fertilizers in Germany is only 10%, while the majority are NPK fertilizers. It is therefore economically preferable to aim for NPK fertilizer production out of waste materials. This calls for a flexible, economically and ecologically feasible, new technology that is able to produce several types of P compounds that can be used either as such or in an NPK formulation out of low-grade P_i rock, MBM, and sewage sludge ash.

14.3 The Ecophos Process

To understand the advantages of the Ecophos process, it is useful to give a short introduction about the basics of conventional industrial processes for the manufacture of phosphoric acid. Conventionally, calcium apatite ($Ca_{10}(PO_4)_6(OH)_2$) in P_i Rock has been made accessible for crops using a wet acid process. Sulfuric acid is most commonly used for the wet acid process (Fig. 14.1). Drawback of this process is that the acid also solubilizes heavy metals such as Cd and Pb as well as radioactive elements such as radium (Ra) and U, causing their contamination of the end products. Radium is the most problematic radioactive element as it generates Radon which causes lung cancer. Radium is concentrated in the by-product phosphogypsum of the conventional wet processes.

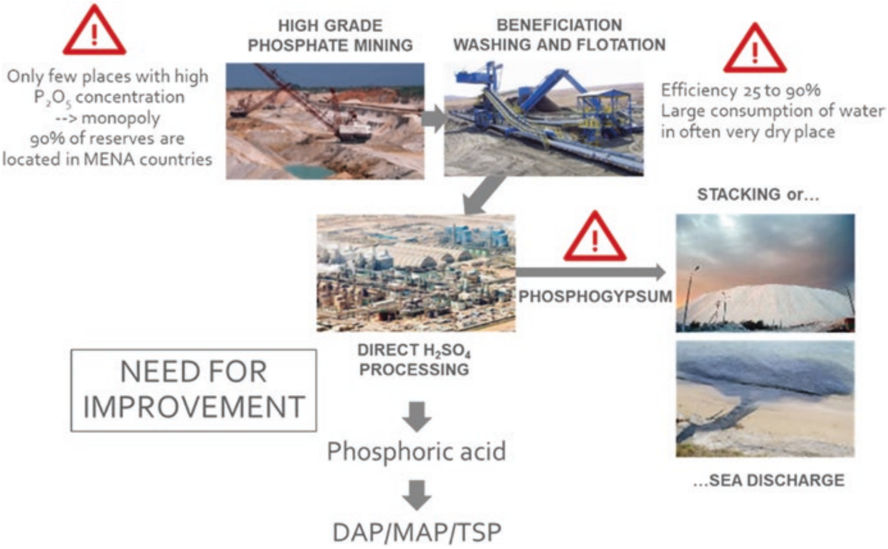

Fig. 14.1 Conventional process for the production of phosphates

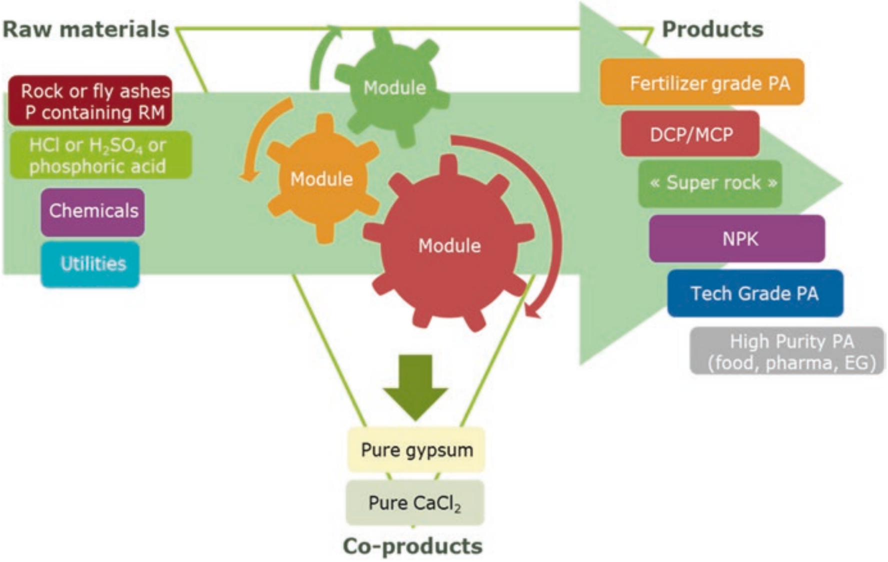

Fig. 14.2 Raw materials, products, and coproduct scheme of the modular Ecophos approach

P_i rock is obtained mostly by open-cast mining. This type of mining requires large areas of land not only for mining itself but also for spoil heaps and clay settling ponds. The quantities of total solid waste produced are so large that about 21.8 tons of mine wastes and 6.5 tons of tailings are produced for each ton of phosphoric acid (PA) produced. The PA-manufacturing plants also generate large quantities of a by-product called phosphogypsum. In some countries phosphogypsum is stored at large stacks due to regulation of radioactivity levels or because the alternative (natural gypsum and flue gas gypsum) are more competitive. In a few countries such as Brazil and China, however, it is increasingly used in the construction and agriculture sectors. It should be noted that natural radioactivity levels in P_i rock can differ widely, depending on the geology of the mine. The conventional mining is also a water- and energy-intensive process.

Taking these into account, Ecophos has developed and patented technologies for:

- The production of dicalcium phosphate (DCP) and/or phosphoric acid using a wide variety of phosphate resources including low-grade P_i rock and sewage sludge ash, regardless of their quality and P content
- The conversion of low-grade phosphoric acid such as green phosphoric acid into high-purity products such as technical-grade, feed-grade, food-grade, and electronical-grade phosphoric acid
- The production of phosphate specialties from a variety of raw materials

Ecophos has developed the processes as modular units that can be combined to generate target products using a variety of raw materials as P sources (Fig. 14.2). The philosophy of the Ecophos processes is basically very simple and therefore

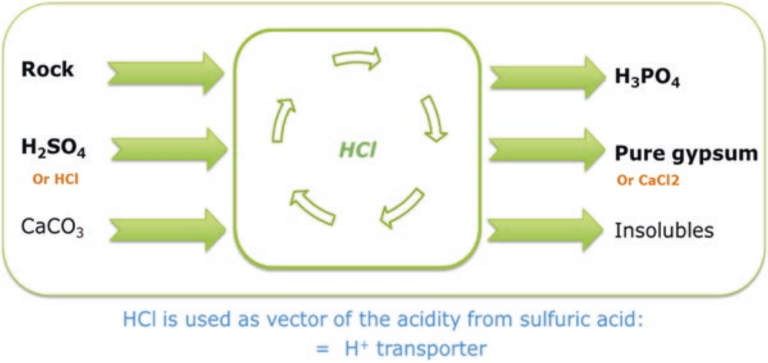

Fig. 14.3 Simple block scheme for the production of DCP and/or phosphoric acid

extremely effective. Firstly, the raw materials are digested in such a way that phosphate is mostly released from the matrix. After this first digestion, insoluble solid residues are separated from the leachate. During the second stage of the process, the phosphate is purified from the leachate either by the chemical precipitation of DCP or by the ion exchange technology, depending on the leaching agent (HCl or H_3PO_4) used in the first step (Fig. 14.3).

14.4 The HCl-Process for the Production of DCP and/or PA

The input P_i-containing raw materials react with dilute HCl in the Module 1A (Fig. 14.4), generating a phosphate solution containing dissolved $Ca(H_2PO_4)_2$, H_3PO_4, and $CaCl_2$. Cd and Mg are dissolved together with the phosphate. A liquid/solid separation step is performed to remove the solid residue that contains most of the impurities – Al, Fe, organics, radioactive elements, and fluorides present in the P_i rock or the sewage sludge ash. The liquor obtained from the Module 1A reacts with a calcium source in the Module 1B. Dicalcium phosphate (DCP) is precipitated. Then, the second liquid/solid separation step is performed. The solid phase consists of DCP, while the liquid phase is a $CaCl_2$ solution containing heavy metals and magnesium. This $CaCl_2$ solution is purified by precipitation of heavy metals and Mg at high pH (not shown in Fig. 14.4). Very pure $CaCl_2$ solution at a concentration of 15–18% is obtained. In the optional Module 4, the purified $CaCl_2$ reacts with sulfuric acid, resulting in the formation of a slurry of dihydrate gypsum in dilute HCl solution. $CaCl_2$ can be generated prior to the Module 4, and a makeup of HCl is recycled to the Module 1A to maintain equilibrium in water and impurity balances. The gypsum is separated from HCl before HCl is returned back to the Module 1A for digestion. Gypsum which is very pure and free of radioactive elements and phosphate is a coproduct of this process. $CaCl_2$ can either be purged to the sea, or sold as a solution, or after vaporization brought to the market as flakes or prills for deicing, dedusting,

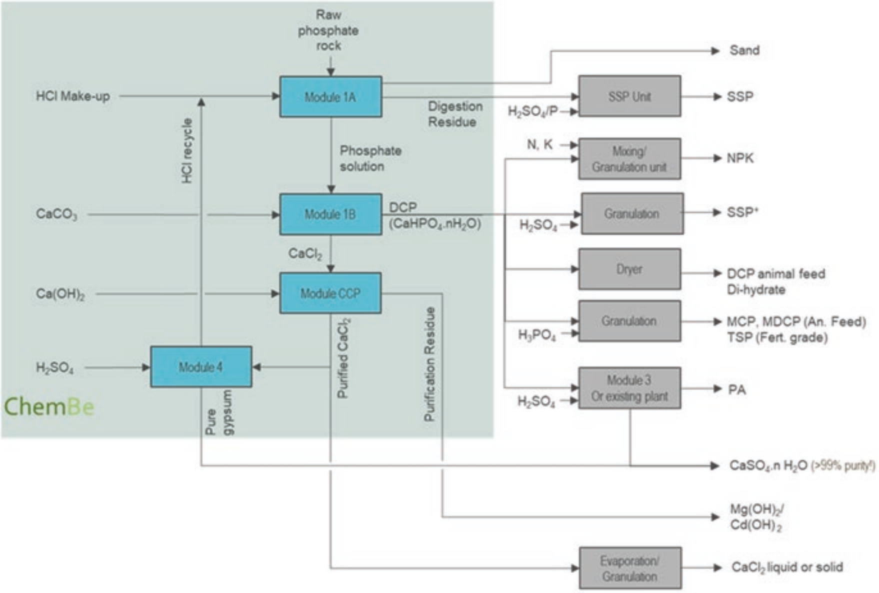

Fig. 14.4 More extended scheme for the production phosphate products by the Ecophos method

or oil-drilling applications. The main input of this process is either sulfuric acid or hydrochloric acid, depending on whether the Module 4 is used.

Similarly, in the Module 3, which is an optional module, the DCP resulting from Module 1B can be sold on the market (animal feed) or digested in sulfuric acid. Phosphoric acid is produced in a rather high concentration (>42% P_2O_5) and pure gypsum is obtained as a coproduct. The phosphoric acid is then concentrated to the merchant-grade (52% or higher). Furthermore Ecophos offers efficient and economical processes to generate NPK fertilizers, MKP, MAP (monoammonium phosphate), DAP (diammonium phosphate), STTP (sodium tripolyphosphate), MCP (monocalcium phosphate), MDCP (monodicalcium phosphate), MgP (magnesium phosphate), SSP (single super phosphate), TSP (triple super phosphate), and many others (Fig. 14.4). Other projects relevant to the HCl process are summarized in Table 14.2.

14.5 The Phosphoric Acid Process for the Production of H_3PO_4

Especially for local applications, Ecophos designed a process based on phosphoric acid digestion and ion exchange. This process (see Fig. 14.5) can be applied to downstream of sewage sludge incineration and is economically feasible from SSA-input volumes of around 10 kt SSA/a or larger.

Table 14.2 Shows reference projects of the HCl approach

			Module and unit							
Project	Country	Year	1A/6	1B	CCP	Dry DCP	3	4	$CaCl_2$ C/G	SSP
Decaphos	Bulgaria	2006	○	○		○				
UCCI	Syria	2010	○	○	○	○		○		
Quimpac	Peru	2014	○	○	○	○	○			
Eurochem	Kazakhstan	2014	○	○	○	○		○	○	
LLNP	Namibia	2015	○	○			○	○	○	
Technophos	Bulgaria	2016	○	○	○		○	○	○	
Aliphos	France	2017	○	○	○	○				
Evergrow	Egypt	2018	○	○	○	○	○		○	○
EGIL	India	2019	○	○	○	○				○
Everphos	Egypt	2020	○	○	○	○		○	○	○

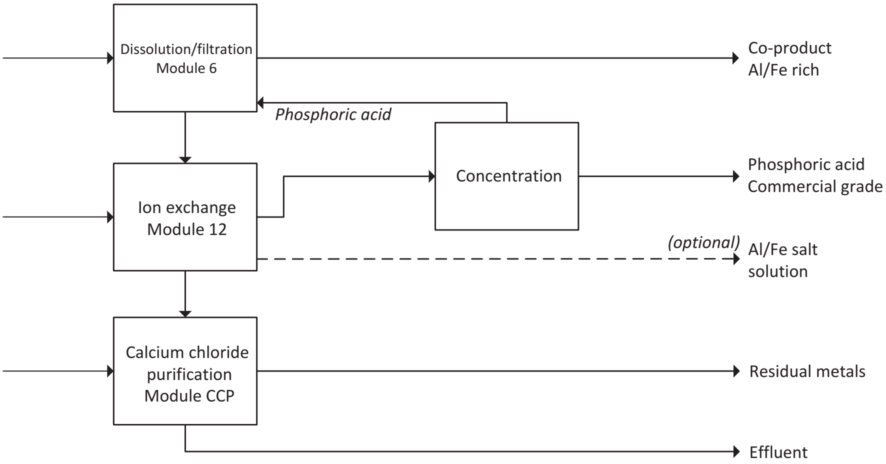

Fig. 14.5 Schematic representation of the Ecophos process based on phosphoric acid digestion

In this approach, the fly ashes are digested by phosphoric acid. The insoluble solid residues are separated by a press filter from the cation-loaded phosphate solution. In the next stage, the cations (Al, Fe, Ca, Mg, and heavy metals) are captured and exchanged with protons by an ion exchange unit to obtain purified phosphoric acid with a concentration of approximately 25% P_2O_5. This solution is partially recycled for digestion in the first stage of this process. The ion exchange resin is regenerated by hydrochloric acid. The final product is concentrated by evaporation to reach the preferred concentration for the market. All products and by-products specifications comply with or exceed market quality requirements.

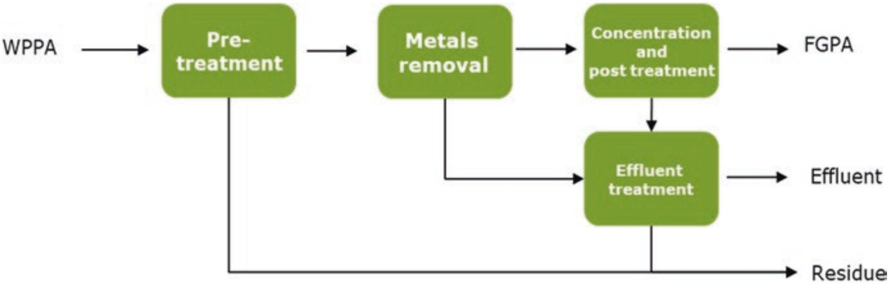

Fig. 14.6 Schematic representation of the process for the purification of phosphoric acid

14.6 Process for the Purification of Phosphoric Acid

The Ecophos process can also convert fertilizer-grade PA from the Module 3 to technical- and food-grade PA in three steps (Fig. 14.6):

Step 1: pre-purification to remove gypsum, arsenic, and cadmium
Step 2: removal of heavy metals, anions, and color by different techniques
Step 3: concentration of PA to 62% P_2O_5 by evaporation

The effluent is treated to remove the metals and impurities as solid cake. All Ecophos processes are stable and easy to control. Uptimes longer than 7800 h/a or longer are easily reached, and the P_2O_5 yields of 90% or higher can be guaranteed. This modular approach is flexible in terms of raw materials, products, and by-products and offers a new insight to fertilizer chemistry to shift from volume-based standards to quality-based dedicated products.

14.7 Conclusion

Ecophos changes one's mind about phosphorus and the circular economy thereof. The several patented processes enlarge the usable amount of phosphorus that is essential for life, in an economically and ecologically feasible way. The Ecophos process can generate the high-quality P products from low-grade P_i rock and untapped secondary P resources, thereby making a great contribution to realizing a circular economy for future generations.

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