WORLD FERTILIZER®

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ChemBe : Refining Phosphate

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Introduction

Fluoroapatite is mined and processed mainly for the phosphorus it contains. Very seldom however, phosphate ore is considered as a resource for other elements such as calcium, fluorine, magnesium, uranium and rare earths which are most of the time discarded as waste. The most visible by-product of phosphoric acid production is calcium sulfate, a useful construction material often discharged to the sea or stockpiled because it is too contaminated to be valorized. Not only this practice destroys value but also impairs the environment.

For economical purpose, extractive industries have built refineries and always tried to utilize and recycle by-products so nearly all process inputs leave as products. Crude Oil contains many different organic molecules that are separated in different fractions and converted into other chemicals, with virtually zero waste. This concept is similarly applied to salt leading to chlor-alkali industry and then PVC, food oil, sugar, metals, etc. But in the phosphates industry, which public image is often linked to pollution, such concept is not yet applied sufficiently and in the meantime, producers are compelled to solve their environmental issues.

Some effort shall be acknowledged to reduce carbon footprint, optimize water usage and remediate mines. But from our experience, it is largely accepted and allowed to stockpile phosphogypsum and discharge waste to the environment. No or too little credit is considered for more capital intensive yet more sustainable processes: it is clear that such process shall also be economical.

EcoPhos, a Belgian firm owned by Mohamed Takhim (Process Engineer and inventor of the EcoPhos Process), has developed a set of processes that allows to produce high quality phosphates and add value to most of the constituents of phosphate ore regardless of its grade, without traditional beneficiation. This vision, called ChemBe process, enables the phosphate refinery configuration using a chemical beneficiation with virtually zero waste and high P recovery. In this article we would like to change your mind about phosphate production and present what we believe is the future for a sustainable phosphate industry.

But first, let's examine the current situation.

Wet Process Phosphoric acid production

Phosphate contained in phosphate ore is generally not directly available without processing. The main relevant method developed to extract P is the wet process to convert commercial phosphate rock into phosphoric acid.

First phosphate rock is mined and beneficiated (crushing, milling, washing, flotation, sometimes calcination) to produce commercial phosphate rock. The P_2O_5 recovery from this step varies from 25 to 90%, with average in the 70-80%, which results in large water consumption and loss of P_2O_5.

Commercial phosphate rock is then digested with sulfuric acid. If P recovery varies from 90 to 95%, on average about 5.3 tons of phosphogypsum per ton of P_2O_5 is produced and largely discarded as its purification is generally uneconomical and its agricultural use limited. Fluoride is recovered as fluosilicic acid H_2SiF_6 which also has limited use, and which conversion to more valuable product like Anhydrous HF requires additional investment.

Phosphoric acid is the major intermediate to produce fertilizers. In 2016, nearly 74% of the world phosphoric acid was used to make three major phosphate fertilizers : DAP, MAP and TSP, and its production generated about 300 Millions tons of phosphogypsum in one year.

Product	Production P_2O_5 100%	Note
H_3PO_4	58.3	
DAP	29.1	50% of phosphoric acid production
MAP	12.7	about 22% of phosphoric acid production
TSP	3.8	of which about 1.3MTPA from Phosphoric acid

Table 1 : 2016 Production figures in millions metric tons per annum (1)

Limitation of the traditional wet process

The wet process route has been implemented for several decades. Over that period of time it has evolved with hemihydrate, dihydrate, hemi-dihydrate,…but its principle has not changed since its introduction. One of its great contributors, Mr. Pierre Becker, starts his renowned handbook by admitting some of its flaws : “By its nature, wet process technology conserves most of the impurities found in the original phosphate ore, which are then included in the phosphoric acid”(2). Wet process route is generally very sensitive to impurities as shown in table 2 below :

Impurity	Acceptable level	Effect
MgO	<1%	Decreases filtration rate (blinding filter cloth and high viscosity) May create insoluble magnesium ammonium phosphate
Fe_2O_3 / Al_2O_3	2-3% and <5% can be tolerated	Decreases P recovery, post-precipitation, Reduces corrosiveness
SiO_2	<2%	Erosion and abrasion Active silica avoids HF
Organics	Depends on nature/can be reduced by calcination of ore	Foaming/increased viscosity
Cl	<0.1%	Increases corrosion rate on stainless steel
Na, K	0.1 to 0.8% Na_2O in typical phosphate	Increased scaling, corrosion, precipitation
Cd		Hazardous to human

Table 2 : Effect of impurities in phosphate rock on the traditional wet process (3)

It is particularly true for heavy metals, for which the European Union proposes more control of Cd in fertilizers which is only possible with costly purification or a new way of producing.

Another author, Rodney Gilmour (4) starts his book on phosphoric acid purification by introducing need for change to adapt to future situation “The end of the Twentieth century saw the consolidation of [the phosphate] industry with fewer corporations and larger plants taking their raw materials from fewer sources. It is quite possible that during the next 50 years that situation will reverse with small local plants utilizing locally recycled sources.”

A vital element

Why change is needed? The matter is not only a concern for pollution and smart use of natural resources.

Phosphorus is a vital and unreplaceable nutrient for living species (DNA, bones, teeth…). As proven centuries ago, agriculture depletes nutrients in the soil, and for an efficient food production, fertilizers shall be applied to supplement what is consumed by plants. What is not absorbed or rejected is diluted to the sea : this cycle is an open loop.

Earth crust contains 0.12% of P, making it the 11th most abundant element. Yet, with an annual phosphate rock consumption of 191M t/y[(5)], and phosphate rock resources estimated by Jasinsky (2012)[(6)] of 71 Billions tons, only of which 16 Billion tons are usable, respectively 370 years or max 80 years of reserves are left. The decline of phosphorus is well-known with a production peak estimated in 2040[(7)], yet industry still thinks as if resources are infinite, mostly because change is difficult to accept.

If the phosphorus peak is generally true for commercial grade ore, it does not account for the use of lower grade reserves and phosphorus recycling. Several scientists and engineers work passionately to introduce new processes to ensure a more sustainable use of phosphorus with objective to close the loop of the phosphate cycle, thus opening the way for greenfield projects to make a respectful use of this resource.

A noble ressource

The most important minerals for the production of phosphates belong to the apatite group, which contain up to 39%P_2O_5, but also up to 4% of F, 55% of CaO, 15% of SiO_2, 0.6% of REE, 0.02% of U_3O_8, in the form of the following minerals :

- Apatite $Ca_5(PO_4)_3(OH,Cl,F)$, fluoroapatite being most sought after $Ca_5(PO_4)_3F$,
- Calcite ($CaCO_3$)
- Dolomite ($CaMg(CO_3)_2$)
- Quartz (SiO_2)
- Iron and Aluminium Oxides
- Clay Minerals
- Organic matter
- Calcium Sulfate
- Pyrite

As known for long :"Most phosphates ores, whatever their origin, have to be concentrated or beneficiated before they can be consumed or sold on the international phosphate market"[(2)]. The table 3 below provides composition of some commercial and low grade phosphate rocks. Low grade rock are phosphate rocks with low P_2O_5 content or with average P_2O_5 content but high amount of impurities. Some other phosphate rock of lower grade, can contain more elements.

	Unit	Commercial Grade[(3)]		Low grade rocks (Source : EcoPhos lab)						
		Range	Average	Egypt A	Egypt B	Egypt C	Marine phosphate	FSU	Brazil	Algeria
P_2O_5	%	29-38	33	22	20	28	25.1	27	13.4	27
CaO	%	46-54	51	34 to 40	36	42	49.2	45.1	15.9	47.6
SiO_2	%	0.2-8.7	2	12	6	5	7.9	7.1	-	2.36
Al_2O_3	%	0.4-3.4	1.4	0.9	1.5	1	1.3	0.62	15.3	0.6
Fe_2O_3	%			2.4	4	3.3	3.29	0.28	9.8	1.27
MgO	%	0.1-0.8	0.2	0.8	2 - 4	0.7	0.98	3.9	0.57	1.45
K_2O	%	-	-	0.3	0.3	0.2	1.21	0.37	0.66	0.27
Na_2O	%	0.1-0.8	0.5	0.3	0.7	0.7	1.48	0.47	0.08	1.54
F	%	2.2-4.0	3.7	3.5	1.8	2.3	3	2.6	0.78	3.2
Cl	%	0.0-0.5	0.02	-	-	-	0.15	0.51	-	0.05
Organics	%	-	-	0.3	-	-	5.1	<0.1	-	3.4
CO_2	%	0.2-7.5	4.5	-	-	-	5.6	12.3	-	4.4
SO_4	%	0-3.5	1.2	2.40%	10-14%	-	3	1.62	-	2.7

Table 3 : Graph composition phosphate rock

EcoPhos phosphate refinery concept applied to phosphate valorisation

There are many initiatives to apply sustainable engineering practice in the fertilizer industry and throughout the food chain : for exemple mine remediation, recovery of struvite from sewage sludge water, controlled use of fertilizer and water by using soluble fertilizers in drip irrigation systems, use of organic fertilizers, use of biopesticides, improvement of habits to avoid wasting food,…

At EcoPhos we believe in making right high quality product first time. EcoPhos implements several solutions to improve the situation by implementing processes which are more tolerant to impurities in the phosphate ore and generate cleaner products and co-products, allowing to increase reserves and overall value while being more careful for the environment.

EcoPhos process was designed to tolerate up to 15% SiO_2, 10% MgO, 5% Fe_2O_3 and 5% Al_2O_3, higher level of Cd, Cl or organics. Ashes from sewage sludge incineration can also be processed, allowing to recycle phosphorus. It produces higher quality phosphates suitable for drip irrigation, and high quality Dicalcium Phosphate (DCP) Dihydrate which has a higher biodigestibility in livestock than anhydrous DCP, and are overall more economically.

The modular approach of the EcoPhos process allows to adapt to local constraints but also to separate all constituents of phosphate rock. it thus allows to take advantage of all the ingredients of phosphate rock and to refine this noble ressource. This refining is, as a matter of fact, a chemical beneficiation (ChemBe) that prevents needs for most of the other beneficiation steps (Flotation, crushing, calcination,…), see diagrams 1 and 2.

This process is possible thanks to hydrochloric acid, which use to process phosphate ore was first introduced eighty years ago. Such process was applied mainly to get rid of HCl either by making DCP : Tessenderlo (Ham, Belgium), Ercros (Flix, Spain), and later Technical phosphoric acid when solvent extraction technics improved : Haifa in Israel, GACL and Aditya Birla in India, …The size of those plants was governed by the amount of HCl available.

Advance in material of construction like fiberglass reinforced plastics or other polymers allows to reasonably apply hydrochloric acid based process on large scale. The second barrier is the psychological acceptance of a chloride based process. What distinguish EcoPhos process to the previous one? By working on the digestion process, low grade phosphate rock can be utilized while removing impurities in the residue, and significantly reducing production costs. The second advantage is the greater concentration of the calcium chloride making it economical to concentrate and valorize. The third major advance is the regeneration of hydrochloric acid allowing to scale-up large phosphate plants. And last, but not least, a significant strength of EcoPhos is not scientific but managerial: entrepreneurship and risk taking approach.

Most of the other technology providers utilise sulfuric acid digestion with a different concept and different chemistry.

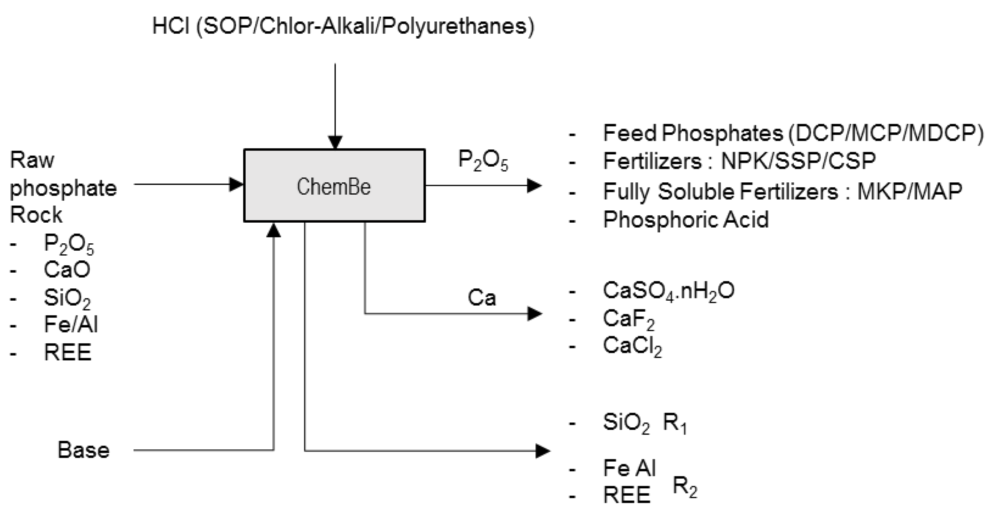


Diagram 1 : Phosphate refinery concept

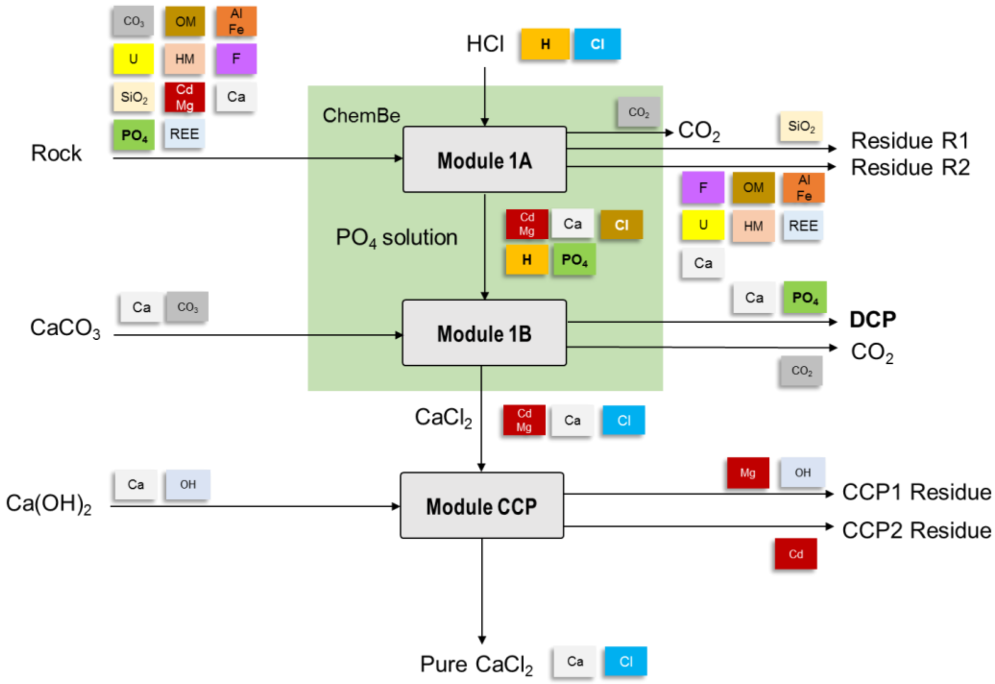


Diagram 2 : Fate of impurities in the EcoPhos process

Dicalcium Phosphate (DCP) is a key product of the EcoPhos process. It is a pure and stable salt of phosphate that contains 41% P_2O_5 and up to 48% if anhydrous (theoretical content is 52%). It is produced at a cheaper cost than phosphoric acid and can be transported in small bags, big bag and bulk. The ChemBe concept introduces the use of DCP as an intermediate to other phosphates :

- Animal Feed Phosphates : DCP, MCP, MDCP
- Cadmium Free Fertilizers : NPK, CSP (Concentrated Super Phosphate 31-33% P_2O_5, containing 7 to 10% S)
- Water soluble fertilizers : MKP, MAP
- Phosphoric acids : Soluble Fertilizer (table 4), Technical or Food grade

	Unit	EcoPhos Soluble Fertiliser Grade Acid
P_2O_5	%	>62
SO_4	ppm	100
NO_3	ppm	-
Volatile	ppm	-
Fe	ppm	<850
Cl	ppm	10 to 50
F	ppm	10 to 50
Ca+Mg	ppm	<600
As	ppm	<0.1
Pb	ppm	<0.1
Cd	ppm	<0.1

Table 4 ; typical analysis of Soluble Fertilizer Grade Phosphoric acid produced using Ecophos process

This process generates three clean co-products : gypsum, calcium chloride and carbon dioxide.

- Calcium sulfate produced is not made from phosphate rock and sulfuric acid, but from calcium chloride and sulfuric acid. It is therefore very pure (See typical analysis in table 5) and can be utilized in cement industry, plaster board, soil amendment, but also as a whitening agent for paper, and other high quality applications. For 2015, USGS expects 258 Millions Tons mined gypsum worldwide [(8)], so the demand for such material is tremendous. In the US only about 50% of the gypsum is synthetic, mainly originating from flue gas desulfurisation.

	Unit	DH Gypsum (dry) >99,8%
CaO	%	32.48
SO_4	%	55.9
P_2O_5	ppm	Below test limits
Cl	ppm	<300
Al_2O_3	ppm	<2
F	ppm	<100
Fe_2O_3	ppm	<2
MgO	ppm	<20
Na_2O	ppm	<20
K_2O	ppm	<2
SIO_2	ppm	<20
As	ppm	<2
Cd	ppm	<2
Hg	ppm	<0.5
Pb	ppm	<0.5

Table 5 : Typical analysis of gypsum produced in module 4

- Calcium Chloride after purification is also of substantial quality (see typical analysis in Table 6). Depending of the location, seasons and nearby markets it is sold as a liquid solution or concentrated and granulated or flaked.
  The three major markets for this product are nearly of the same size : deicing, dedusting and oil drilling.

	Unit	Calcium Chloride after CCP
$CaCl_2$	%w/w	≥15.0 – 18.0
P_2O_5	ppm	Below test limits
SO_3	ppm	≤40
Si	ppm	≤0.2
Mg	ppm	≤7
K	ppm	≤100
Na	ppm	≤700
As	ppm	≤0.6
Ba	ppm	≤15
Cd	ppm	≤0.01
Pb	ppm	≤0.01

Table 6 : Typical analysis of calcium chloride after CCP unit

- Carbon dioxide is produced in a concentrated form by the neutralization of the phosphate solution with calcium carbonate.

The residues from phosphate rock leaching and calcium chloride purification can also be valorised:

- After potential desanding, the solid residue is already soluble in citrate. It can contain up to 5% P_2O_5 that can be adjusted to higher concentration in order to produce low grade fertilizer or SSP.
- The residue from CCP unit could also be also valorised depending on the metal present : rocks rich in magnesium could be a source for magnesia.

EcoPhos Process Modules

How does the EcoPhos process work? In this section the key modules are explained in further details.

<u>Module 1A - Digestion of Phosphate rock : first refining step</u>

Phosphate rock is digested by dilute hydrochloric acid (5-15% HCl) at moderate temperature (25 to 75°C) to adequately digest the rock : maximization of P_2O_5 dissolved vs. minimization of impurity, following the simplified chemical reactions below:

$$Ca_3(PO_4)_2\ (s) + 4HCl \rightarrow Ca(H_2PO_4)_2 + 2\ CaCl_2$$
$$Ca(H_2PO_4)_2 + 2HCl \rightarrow 2H_3PO_4 + CaCl_2$$

The slurry obtained is composed of rock residue and a liquor that consists of a mixture of H_3PO_4, $Ca(H_2PO_4)_2$ (MCP), and $CaCl_2$. 70 to 80% of the Al and Fe remain in the solid residue, furthermore no HF nor H_2SiF_6 is emitted at this stage. A purification step is performed to reduce the fluoride that will mostly end up in the solid residue. The residue, composed mainly of Silica, clays, fluoride compounds, insoluble heavy metals and gypsum, is separated from the phosphate solution by filtration. The P_2O_5 remaining in the cake is mainly unreacted P_2O_5 fixed by the rock matrix as insoluble complex component.

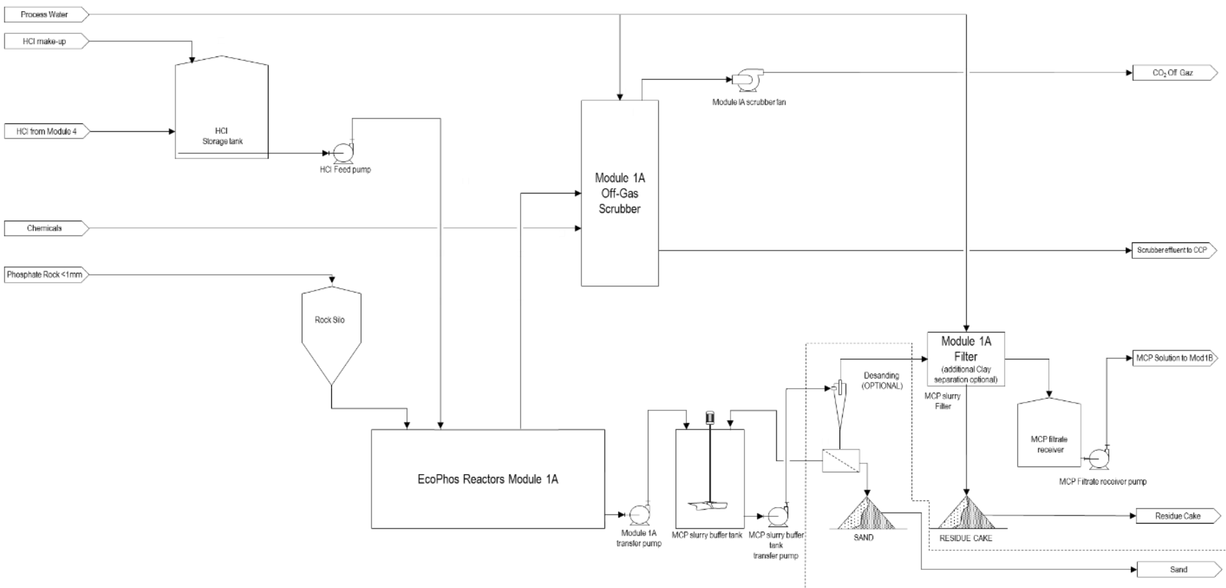


Diagram 3 : Simplified Process Flow Diagram for module 1A

Module 1B - Crystallization of DCP : the second refining step

In Module 1B, the P_2O_5 content of the phosphate solution obtained from Module 1A is separated from calcium chloride by crystallization. It is precipitated as dihydrate or anhydrous dicalcium phosphate (depending on temperature), with addition of a base ($CaCO_3$, $Ca(OH)_2$, CaO, NaOH, $Mg(OH)_2$,…) that is added in several steps to control by pH increase and optimise the product crystallisation. The CO_2 emitted is almost pure and can be valorised as co-product.

$$H_3PO_4 + CaCO_3 + H_2O \rightarrow CaHPO_4.2H_2O\ (s)\downarrow + CO_2\uparrow$$
$$Ca(H_2PO_4)_2 + CaCO_3 + 3H_2O \rightarrow 2\ CaHPO_4.2H_2O\ (s)\downarrow + CO_2\uparrow$$

At the end of the crystallisation step and after solid/liquid separation DCP is washed.

The soluble impurities present in the phosphate/$CaCl_2$ solution, such as $MgCl_2$, but also Cadmuim and Arsenic remain soluble in the $CaCl_2$ solution. As solubility of DCP in $CaCl_2$ media is extremely low, there is virtually no P_2O_5 lost in the $CaCl_2$ solution, making the process yield very high at this stage of the process. The filtrate is a solution of $CaCl_2$ with a concentration between 15% and 18%.

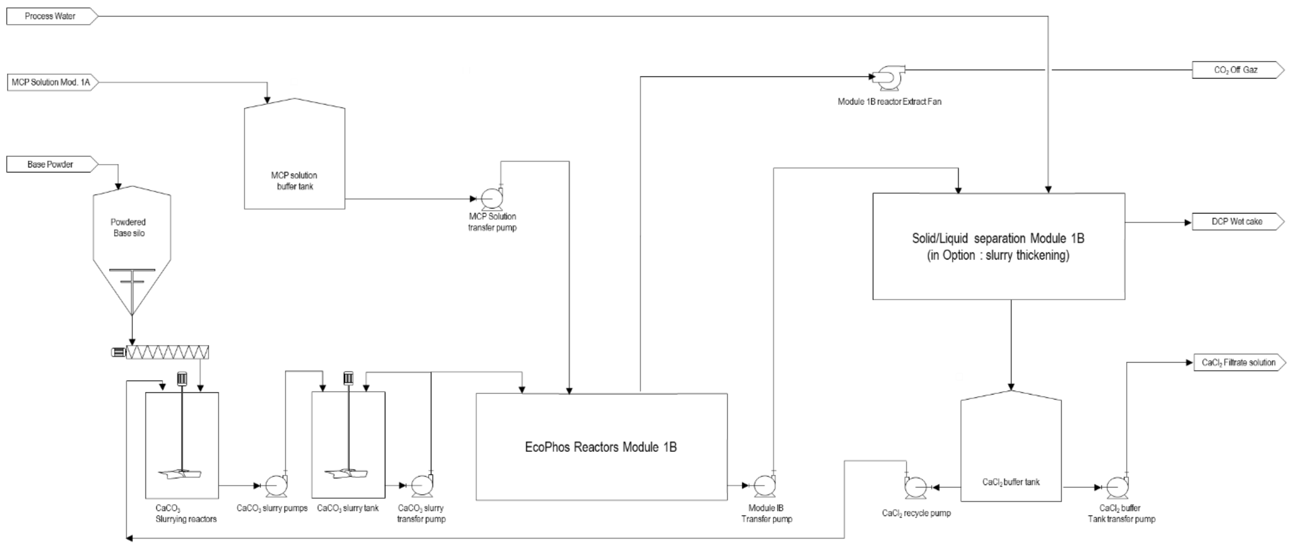


Diagram 4 : Simplified Process Flow Diagram for module 1B

Module 3 - Production of Phosphoric acid

To produce phosphoric acid, DCP produced in Module 1B is mixed with Sulfuric acid 98%. This reaction is the same as for traditional processes except that it uses rock with a low Ca/P_2O_5 ratio at 41-42% P2O5 and 22% Ca but without organics, without CO_3 and Silica! The phosphate from the DCP is converted into a concentrated solution of H_3PO_4 (about 40% P_2O_5) while the calcium from the DCP is converted into gypsum. The slurry obtained is transferred to other reactors for maturation of the gypsum crystals.

$$CaHPO_4.2H_2O + H_2SO_4 \rightarrow H_3PO_4 + CaSO_4.nH_2O\ (s)\downarrow + (2\text{-}n)\ H_2O$$

After the crystallization step, the gypsum is separated from the phosphoric acid by filtration. The gypsum cake is washed to recover a maximum of P_2O_5. The phosphoric acid is then concentrated to 62% which removes fluorine, chlorine and any traces of Silica. If required, further post treatment can be done to remove color, sulfate and remaining heavy metals.

The acid produced is suitable for production of water soluble fertilizers. For purification to Technical or Food grade phosphoric acid, additional ion exchange or/and solvent extraction is required.

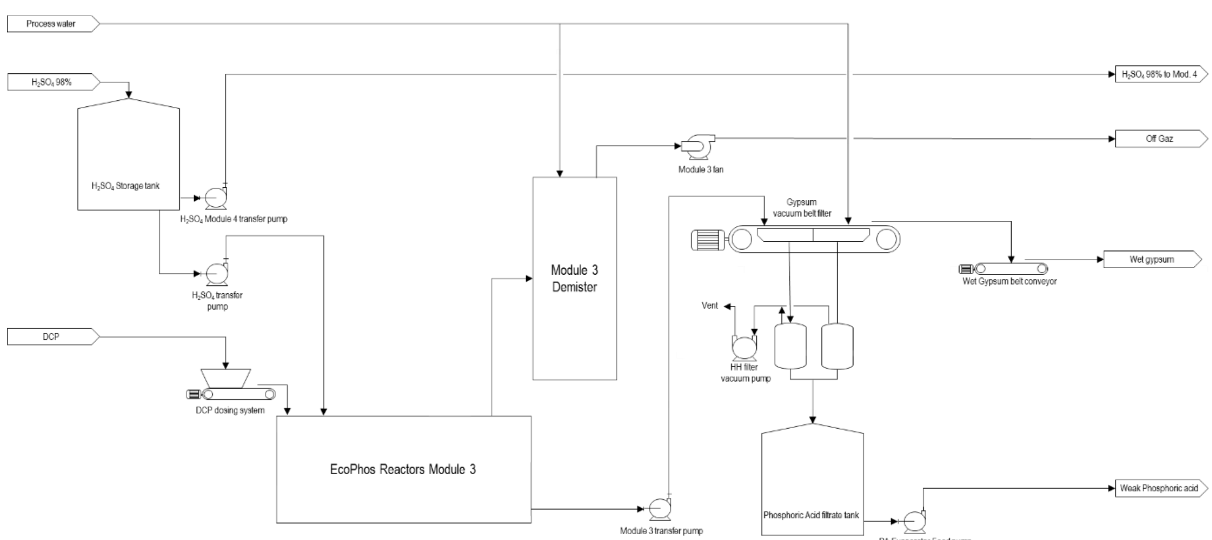


Diagram 5 : Simplified Process Flow Diagram for module 3

Module 4 - regeneration of hydrochloric acid : path for large capacities

The purpose of module 4 is to regenerate HCl. This module was introduced in order to target larger capacities when hydrochloric acid is not available in sufficient quantities. The minimum requirement for HCl make-up is about 10% of the total loop, and depends on the impurity spectrum. All chloride entering the system will leave as Calcium chloride either as bleed or as impurities in the products or residues.

$CaCl_2$ from Module 1B is treated with concentrated sulfuric acid that yields calcium sulfate dihydrate and hydrochloric acid. A slurry of gypsum in diluted HCl is obtained. The reaction, which is exothermic, is as follows :

$$CaCl_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4.2H_2O + 2HCl$$

Dihydrate gypsum is separated from HCl liquor by filtration. Diluted HCl is then mixed with concentrated HCl make-up prior to be recycled in Module 1A.

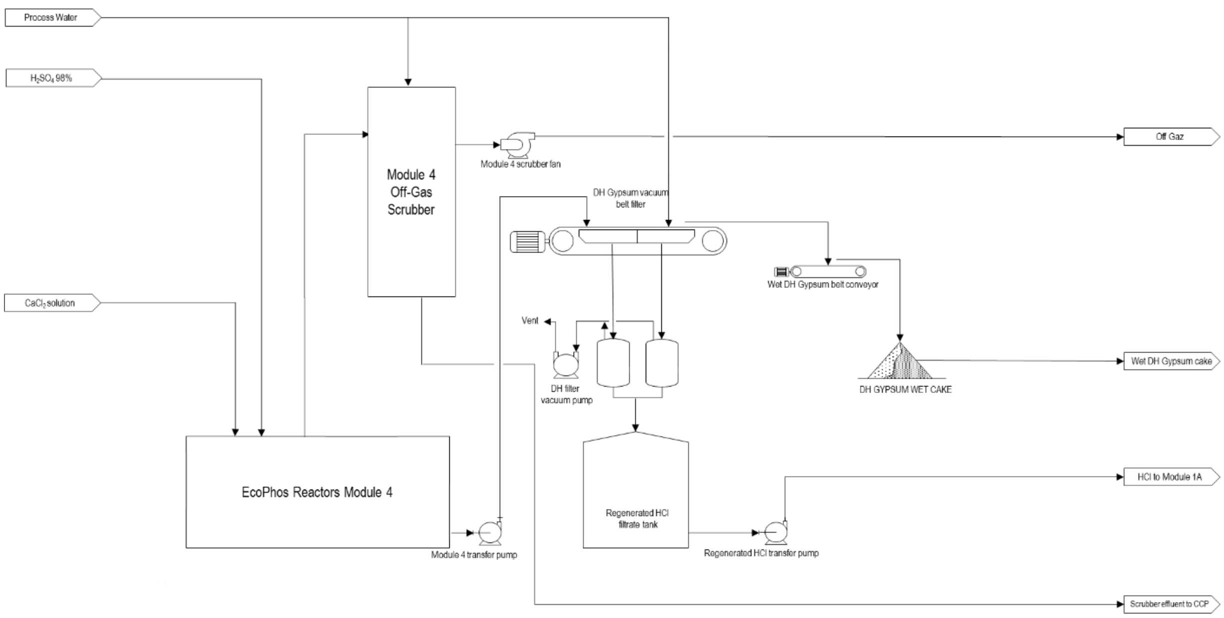


Diagram 6 : Simplified Process Flow Diagram for module 4

Module CCP - Calcium Chloride Purification

The calcium chloride filtrate from module 1B, is purified by pH increase with addition of lime of milk. This allows metal to precipitate as hydroxides or other insoluble salts at higher pH.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2$$

The impurities are then filtered in a press filter and discarded. The calcium chloride solution gathered is of high purity, and after pH adjustement it is sent to the $CaCl_2$ evaporation and granulation unit or although not preferred, discarded safely to the sea.

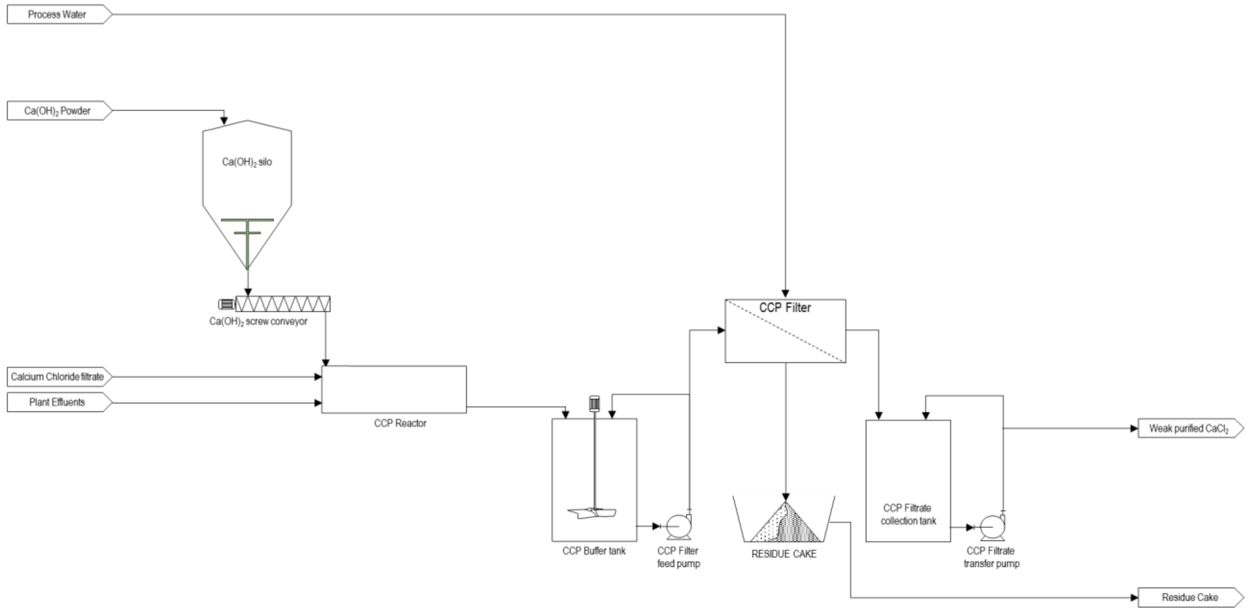


Diagram 7 : Simplified Process Flow Diagram for module CCP

Process design considerations

Modules are a succession of reaction and filtration steps. For all modules, design of reactors, (type, geometry, residence time, material of construction,…), mixing, solid liquid separation (type, surface area, cycle time, Filter media, material of construction,…), process control, is critical :

- To control foaming and emission of contaminants
- Ensure transfer, suspension while avoiding settling, fouling
- To get the most adequate crystal shape and size allowing a good liquid/solid separation and control of residual impurities content, and to some extent amount of wash water added to the system.
- Achieve an efficient solid recovery and clean product

Reactors, agitators, filters and control system are EcoPhos proprietary equipment developed with the most popular brands in the chemical process industry.

As several plants are being built using EcoPhos process, the technology will become more mature and optimized. This feedback will allow to build and operate larger size plants, which will drive down capital expenditure.

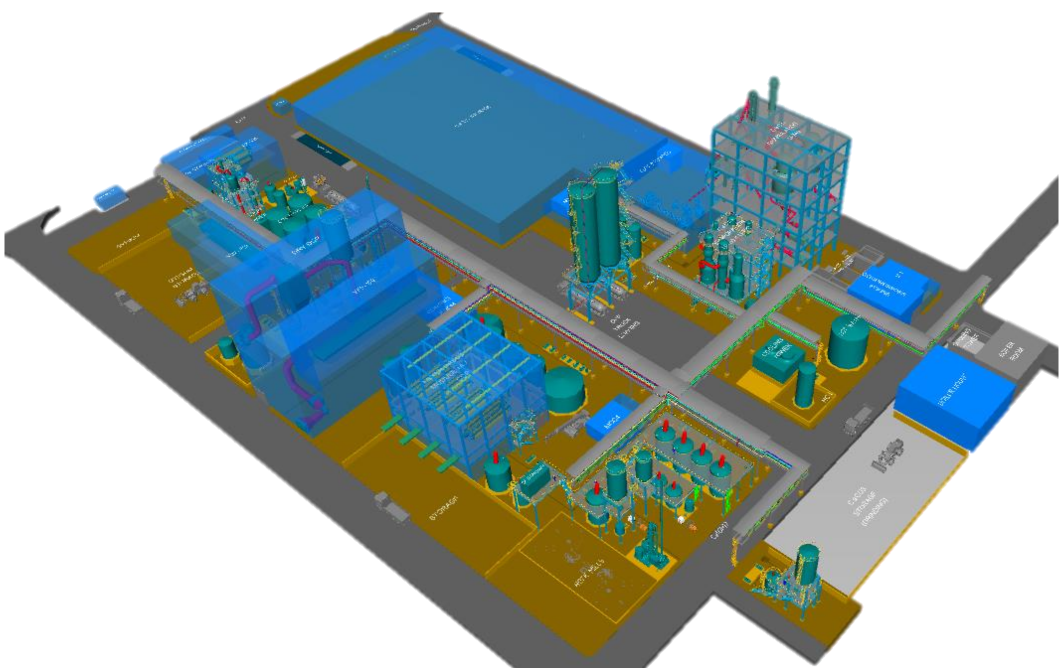
Ongoing projects

Dunkerque : Ecophos is currently building a 220 000 TPA Animal Feed Grade DCP Dihydrate Plant in France for Aliphos (Ph. 1), 100% fully, start-up expected in Q4 2017. Ph.2 project is for the valorization of 100 000 TPA of Sewage Sludge Ashes.

Picture 1 : Aliphos Dunkerque Site under construction

India : in JV with Gujarat Narmanda Fertilizer Company (85% EcoPhos – 15% GNFC), a 200 000 TPA Animal Feed Grade DCP Dihydrate in Dahej, Gujarat. Under execution, expected start-up in 2019.

Egypt : EcoPhos engineers and supplies a 110 000 TPA DCP Plant in Sadat City for Evergrow. 60 000 TPA DCP Animal Feed Grade will be offtaken by Aliphos and 50 000 will be converted to purified phosphoric acid. Calcium Chloride in concentrated and granulated to 96% $CaCl_2$. Start-up expected mid 2018.



Picture 2 : 3D Model of Evergrow project

In October 2016, EcoPhos and Evergrow decided to enter into a partnership agreement to establish a JV 50-50 to build a second 110 000 TPA DCP Plant, and consider future development in the NPK. Expected start-up end 2019.

Technophos a semi-industrial demonstration plant

In order to attract new clients and their engineers, as well as to validate new processes for the group, EcoPhos has invested 10 million euros to build its new technology centre TechnoPhos in Bulgaria, inaugurated in September 2016. All the semi-industrial units of the different EcoPhos processes are present in this technology centre, operating between 0.2 to 1T/h of phosphate ore in shifts if needed. A DCS allows to control precisely the process and to gather useful process data for the scale-up.

Technophos is a training plateform for the operators of our clients, as well as a marketing tool allowing to produce first batch of produced material.

Picture 3 : Technophos building in Devnya (Bulgaria)

Picture 4 : Demonstration plant of Technophos

Conclusion

EcoPhos has developed and patented several processes to produce phosphates from low grade and high grade phosphate rock as well as urban phosphate sources. This latest source allows at some point to close the phosphate loop, but more importantly the use of low grade rock :

- Allows to utilise phosphate ore that could not be processed with conventional sulfuric acid technology because of too high levels of contaminants: organics, Silica, Mg, Al and Fe.
- Allows to utilise raw rock without beneficiation : saving tremendous amount of water, which is not negligible considering 90% of worldwide phosphate resources lay in arid if not desertic regions. This also means no tailings, no slimes,…
- Allows to even use mine rejects and old tailings accumulated for decades
- Ensures nearly 100% of P_2O_5 recovery because the digestion residue containing some citrate soluble P_2O_5 can be used to produce SSP or as a filler for NPK.
- Increases phosphate reserves

The EcoPhos process is modular, adjustable to the raw material available and end-products required.

Aknowledgement

All EcoPhos team

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